Facets and Sharp Edges in Metal Nanostructures for Plasmonics and Electrocatalysis

Author: Nathan Taylor Nesbitt

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Boston College

The Graduate School of Arts and Sciences

Department of Physics

Facets and Sharp Edges in Metal Nanostructures for Plasmonics and Electrocatalysis

A dissertation by

Nathan Taylor Nesbitt

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Nathan Taylor Nesbitt

Advisor: Prof. Michael J. Naughton

Abstract: The nanoscale morphology of metals can enable special functionality in plasmonic and electrochemical devices, with applications in energy conversion and storage, sensors, and computers. In particular, sharp edges on metal nano and microstructures are understood to affect the density of electrons on the metal surface. The associated concentration of electric field can concentrate surface plasmon polaritons (SPPs) and enable waveguiding of the SPPs, as we show in this thesis for sharp ridges along aluminum nanowires. Also important is the presence of facets on the metal structures, which determines the orbitals that electrons occupy on the metal surface. Changes in both the electron density and orbitals can affect the binding of molecules to the metal, which can improve reaction kinetics in catalysis. We demonstrate this on gold dendrite and plate electrocatalysts for CO₂ electrolysis.

Regarding metal nanostructure fabrication, electrochemical deposition and corrosion have demonstrated promising control over the morphology, including the topography, crystallinity, grain boundaries, and crystal faceting. This is important, because existing methods for metal nanostructure fabrication can only produce a circumscribed assortment of morphologies. In contrast, semiconductors and insulators have many new deposition techniques that produce a wide range of controlled morphologies. Of further appeal, electrochemical techniques are solution-based and typically operate at room temperature and pressure, allowing facile scale-up to industrial production. Here we demonstrate and discuss the mechanisms of two new techniques, which produce the aluminum nanowires and gold dendrites and plates discussed above. (This page is intentionally left blank.)

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Symbol definitions

TABLE 1. Roman symbols A–N.

Symbol	Definition
A	surface area
a	index to specify a thermodynamic phase
a	index to specify a thermodynamic phase
CE	counter electrode
$C_{\rm O}(0,t)$	surface concentration of oxidized species at the cathode
C_0^*	bulk concentration of oxidized species
$\widetilde{C_{\mathrm{R}}(0,t)}$	surface concentration of reduced species at the cathode
C_{R}^{*}	bulk concentration of the reduced species
$C_{\rm i}({f r})$	concentration of species i at position \mathbf{r}
D_{i}	diffusion constant of species i
E	the electric potential of the WE relative to a standard RE
E^0	the equilibrium electric potential of the WE relative to a standard RE
F	Faraday's constant
G	Gibbs free energy in a thermodynamic system
h	Planck's constant
i	index for a chemical species
J	net current density through the WE
J_{i}	net current density of species i
$\mathbf{J}_{\mathrm{i}}(\mathbf{r})$	current density of species i at position \mathbf{r}
$J_{ m L}$	diffusion limited current density
j_0	exchange current density
K_1, K_2	cubic harmonics
\mathcal{K}_1	equilibrium constant of a reaction's first step
k_1	forward reaction rate constant of a reaction's first step
k_{-1}	reverse reaction rate constant of a reaction's first step
k^o	standard heterogeneous rate constant
$k_{ m B}$	Boltzmann constant
k_{x}	wavenumber in the direction along a metal surface
L	length
$m_{ m i}$	mobility of species i
N	number of particles in a thermodynamic system
N_{a}	number of adatom sites on a crystal surface
$N_{ m a,o}$	number of sites on a crystal surface occupied by adatoms
n	number of electrons transferred during a reaction
\hat{n}	unit vector along a coordinate axis
\hat{n}_{dend}	unit vector along dendrite growth direction

TABLE 2. 1	Roman	symbols	O-	-Z.
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Symbol	Definition
Р	pressure in a thermodynamic system
${\cal P}$	Péclet number
R	gas constant
\mathcal{R}	radius of dendrite tip
RE	reference electrode
Re_x	Reynolds number of the electrolyte
r	position in the cell relative to the electrode of interest
S	entropy in a thermodynamic system
T	temperature
T^0	equilibrium temperature
$\mathbf{u}(\mathbf{r})$	velocity of the electrolyte as a result of stirring
V	volume in a thermodynamic system
$\mathbf{v}(t)$	dendrite tip growth velocity
WE	working electrode
$Y_{\rm lm}(heta,\phi)$	spherical harmonics
7	the total number of nearest neighbors that atom would have in the bulk
L	of the crystal
z_{i}	electric charge of species i

TABLE 3. Greek symbols.

Symbol	Definition
α	reaction charge transfer coefficient
β	reaction symmetry factor
Δ_1	the bulk salt concentration
$\Delta \varphi$	electric potential difference between an electrode and a solution
$\delta_{ m laminar}$	boundary layer thickness for laminar fluid flow
$\delta_{\mathrm{turbulent}}$	boundary layer thickness for turbulent fluid flow
ϵ_0	dielectric constant in free space
ϵ_1, ϵ_2	anisotropy factors for cubic harmonic expansion of surface energy
$\epsilon_{ m edge}$	energy of an atom at the edge of a terrace on a crystal surface
$\epsilon_{\rm r}$	real component of dielectric constant
$\epsilon_{ m r,Al}$	real component of dielectric constant of Al
ε	anisotropy factor for crystal with four-fold symmetry
η	overpotential on the cathode
$\eta_{\rm p.c.}$	parabolic coordinate
θ	fractional surface coverage of the catalytic sites on the cathode
κ	transmission coefficient
λ	the deviation between a parabolic fit and the actual profile of a faceto
	dendrite tip
$\lambda_{ m D}$	constant in Poisson's equation
μ	electrochemical potential
$\mu_{\rm in}$	internal chemical potential
$\xi_{\rm p.c.}$	parabolic coordinate
$\rho_{\rm m}$	number density of a metallic crystal
$\varphi(\mathbf{r})$	electric potential at position \mathbf{r} relative to the working electrode
$\varphi_{\rm p}$	electric potential in phase p (e.g. in a crystal or solution)
$\varphi^{\hat{0}}$	equilibrium electric potential
$\bar{\varphi}$	reduced electric potential, $\bar{\varphi} \equiv \frac{zq}{k_{\pi}T}\varphi$
$\phi_{\rm nc}$	parabolic coordinate
$\phi_{ m lat}$	energy to break lateral bonds between a surface atom and its neighboring
	surface atoms
$\phi_{ m nor}$	energy to break bonds between a surface atom and its neighboring bu
	atoms
χ_1	the number of nearest neighbor sites within the surface layer
ω	angular frequency
∇	gradient operator

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1. INTRODUCTION AND MOTIVATION

1.1. The renewable energy transition. Our society has depended on fossil fuels to power our machines for the past century, causing anthropogenic climate change by emitting fossilized carbon into the atmosphere as CO_2 [1]. These fossil fuels are hydrocarbons, molecules made of carbon and hydrogen, and they store energy captured from the sun millions of years ago. A brief history of our use of fossil fuels begins with the invention of a steam locomotive for cargo transport in 1803 by Richard Trevithick and the internal combustion engine in 1826 by Samuel Morey. Subsequent development and adoption of fossil fuel technologies included the release of the Ford Model T in 1908, generally regarded as the first affordable automobile. 110 years later, our economy is dependent upon an enormous amount of fossil fuel consumption. In 2014, for example, the world's primary energy consumption was over 11,000 million tonnes oil equivalent (Mtoe)—or 127,930 terawatt hours (TWhr). Averaged over the 8,760 hours of the year, that was 14.6 TW of steady power consumption. The rest of the energy that year was from renewables, nuclear, and hydroelectricity, which together generated 2,000 Mtoe—23,260 TWhr—of primary energy; 2.7 TW on average [2].

When hydrocarbons are burned, the carbon and hydrogen atoms are oxidized into CO_2 and H_2O and energy is released. These molecules are gasses at atmospheric temperature and pressure, and they trap heat in the atmosphere through the greenhouse effect. This greenhouse effect that causes global warming was initially proposed in 1824 by Jean-Baptiste Joseph Fourier [3]. In 1856, Eunice Foote published experimental measurements in which she showed CO_2 and H_2O absorb sunlight stronger than dry air, hydrogen, or oxygen gas, thereby identifying gasses that could cause the greenhouse effect Fourier suggested [4] (this discovery is often attributed to John Tyndall, who independently published a similar observation in 1861 [5, 6]). In 1895, Svante August Arrhenius published calculations predicting the temperature rise of

the earth's surface as a result of increasing the atmospheric CO_2 concentration [7]. In 1960, Charles David Keeling published experimental measurements of atmospheric CO_2 concentration from Mauna Loa Observatory, Hawaii; La Jolla, California; Little America, Antartica; South Pole, Antartica; and various cruises and flights. He observed "at the South Pole the observed rate of increase is nearly that to be expected from the combustion of fossil fuel (1.4p.p.m.)..." [8]. In 1988, James E. Hansen, the head of the NASA Goddard Institute for Space Studies, testified to congress that [9]:

"...My principal conclusions are: (1) the earth is warmer in 1988 than at any time in the history of instrumental measurements, (2) the global warming is now sufficiently large that we can ascribe with a high degree of confidence a cause and effect relationship to the greenhouse effect, and (3) in our computer climate simulations the greenhouse effect now is already large enough to begin to affect the probability of occurrence of extreme events such as summer heat waves; the model results imply that heat wave/drought occurrences in the Southeast and Midwest United States may be more frequent in the next decade than in climatological (1950–1980) statistics."

The environmental consequences of climate change and pollution from fossil fuel extraction are an existential threat to society, and impact most those who are least responsible for the crisis [10, 11]. Business as usual requires an increasing number of sacrifice zones; places where the land and people are poisoned by fossil fuel mining and threatened by extreme weather events [12]. With the world's population increasing in number and prosperity, our energy demands are also increasing. Energy consumption is expected to double by mid century, reaching approximately 50 TW. Meeting these energy demands while mitigating environmental impacts will require technological advances in energy efficiency and renewable energy sources, with a full transition away from fossil fuels. This is often called the *terawatt challenge*, a phrase coined by

Richard Errett Smalley in his 2005 article on this issue [13]. Development of metal nanostructured electrodes for plasmonics and electrocatalysis has made important contributions to these technological advances, and promises more. Contributing to these advances is the motivation of this thesis. The work herein includes fabrication of several new metal nanostructures, their application to plasmonics and electrocatalysis, and attempts to understand the physics of the nanostructure fabrication processes.

1.2. Metal nanostructures' applications.

1.2.1. Nanostructures for plasmonics. Plasmonics is the study of waves in the free electrons of a metal. Much of the research is focussed on waves in the free electrons at the surface of a metal, which very much resemble water waves on the surface of the ocean. These waves are called surface plasmon polaritons (SPPs). They are often excited on a metal surface by incident photons. When SPPs are supported on nanostructures with sharp points they produce very strong electric fields for certain colors of light, a phenomenon called localized surface plasmon resonance (LSPR). This typically requires points with radius of curvature below ~ 10 nm. When embedded in photovoltaic materials, this electric field enhancement can increase light absorption to improve the performance of solar cells [14].

Nanostructuring of metal surfaces has also been used to guide propagating SPPs as a means of information transfer [15]. With sufficient advances, this could allow plasmonic circuits of electron surface waves on metals to replace electronic circuits of electric currents [16]. The substitution may reduce waste heat generation. In this thesis, we show a novel fabrication mechanism for aluminum (Al) nanowires with sharp ridges along their length, and demonstrate guiding of SPPs along the ridges.

1.2.2. Nanostructures for electrocatalysis. Electrocatalysis enables direct energy conversion between electricity and chemical fuels. Many renewable energy sources, primarily wind and solar, are intermittent and vary significantly by season. As such, to reach their full deployment potential, utility scale energy storage will be necessary on time scales ranging from seconds to months. Li-ion batteries are a rapidly maturing technology that is well suited for residential and industrial storage from seconds to hours, and is becoming the industry standard for new energy storage installations. One of the appealing attributes of batteries is $\sim 90-94\%$ round-trip energy efficiency (energy received from battery discharge / energy used to charge battery) [17]. However, this technology will likely remain too expensive per unit energy to power the

grid for time scales longer than several hours. That's because the storage capacity scales with the mass of the Li, the anode material, and the cathode material. These materials must be mined, carrying with them the associated burden of environmental impact, energy cost, and limited supply of rare elements (such as cobalt).

 CO_2 electrolysis uses renewable energy to convert CO_2 into a C-based fuel similar to the fossil fuel hydrocarbons our society is currently designed around. The chemical reaction is called the CO_2 reduction reaction (CO_2RR). Here, the energy storage capacity scales with the mass of the C and the material for a storage vessel. A major downside is that the round-trip energy efficiency is lower than batteries. For example, mature hydrogen gas technology, which is similar to the electrolysis and burning of hydrocarbon fuels, typically has 69% efficient electricity to fuel, and 48% efficient fuel back to electricity, for a roundtrip energy efficiency of 33% [18]. Fortunately, the $\rm CO_2$ feedstock can be sourced from the tail pipes of fossil fuel infrastructure, where it is presently vented to atmosphere (at great cost if the destruction from global warming is considered). Technology for CO_2 capture from the atmosphere is under development, and could be adopted when fossil fuel infrastructure is retired [19, 20]. Also, much of the world already has sufficient hydrocarbon fuel storage capacity to power their infrastructure for several months, avoiding the need to build fuel storage vessels [21]. Renewable energy storage on long time scales could allow seasonal energy storage: converting it into fuel when it is abundant (during the summer), and burning the fuel when the renewable energy is scarce (in the winter). Since the hydrocarbons could be compatible with existing fossil fuel infrastructure, this renewable fuel may also provide a drop-in replacement to fossil fuels. Not needing to prematurely retire cars, home heating systems, manufacturing plants, and other equipment in order to transition off fossil fuels would save society substantial energy, raw materials, and money. It would likely also make for a faster transition. Finally, the renewable Cbased fuel could provide a feedstock for C-based materials, such as plastics [22]. When made from atmospheric CO_2 , this sequesters the C to mitigate global warming.

The challenge to implementing this technology is catalyzing the reaction. Without good room temperature catalysts, the fuel must be generated by operating at high temperatures. Approaches to this include combining C and CO₂ to produce CO, referred to as the Boudouard reaction, combining H₂ and CO₂ gas, referred to as the reverse water-gas shift reaction, or reducing CO₂ in solid oxide electrolysis cells. The drawback to high temperatures is the energy cost from lost heat, and the financial cost of materials that resist thermal degradation (although recent research on microwave heating could reduce these challenges for the Boudouard reaction [23]). A major appeal of CO₂ electrolysis is the ability to operate at room temperature and pressure. Metal plates, foils, and films are the simplest electrodes for this purpose, and have been extensively tested as catalysts. However, these simple electrodes exhibit a slow fuel production rate, low energy efficiency, low product selectivity, and poor stability [24]. Nanostructured catalysts have demonstrated improved stability, activity, and selectivity, necessary for the commercial viability of electrochemical CO₂ reduction [25, 26].

In electrochemical cells, the good conductivity of metal electrodes facilitates the transport of charge through the electrodes into chemical species in the electrolyte. The reaction kinetics are dependent on (1) the exposed crystal facets of the electrode, (2) the packing density of the nanostructure (*i.e.* the distance between adjacent metal surfaces), and (3) the sharpness of points on the metal surface (for radius of curvature below ~ 10 nm). (1) The exposed facet of the metal surface, or lack of a well-defined facet, affects the arrangement of metal atoms on the surface, the dangling bonds of these atoms, and thus their binding energy to reactants, intermediates, and products of chemical reactions. (2) The packing of the nanostructure affects the

local concentration of reactants and products at the metal surface, such as the pH. If the reactant concentration for a particular reaction is locally decreased more than another, this can change the relative speed of competing reactions. (3) The sharp points on a metal surface with a net charge enhances the local electric field. For a negative net charge, this increases the free electron density at the surface, providing more electrons for filling bonding orbitals with adsorbed reactants and intermediates. The enhanced electric field also attracts cations from the electrolyte, whose image charge further increases the free electron density at the metal surface, and whose presence in the ionic double layer displaces protons.

The CO_2RR at a Au surface is a well studied example of these phenomena. (1) Nanostructures with different dangling bonds at the surface show different binding energy to CO_2 , H⁺ (reactants), COOH, H (intermediates), H₂, and CO (products). Such dangling bond variation is the result of different facets, proportions of edgeto-corner atoms, or grain boundaries at the Au surface [27, 28]. (2) Au foams have shown the production of OH⁻ from the CO_2RR to change the local pH for different thicknesses of foam and thereby favor CO_2RR over H⁺ reduction in thicker foams [29]. Finally, (3) on Au needles with tip radius below ~10 nm, electrons have been shown to collect at the tip, and the CO_2RR to occur more rapidly with higher Faradaic efficiency for CO production than for Au rods with ~100 nm tip radius [30].

In summary, the CO_2RR is driven by electrical energy to produce C-based fuels and O_2 , providing a path towards large scale seasonal energy storage and renewable gas or liquid fuels compatible with conventional infrastructure. Au nanostructured electrodes have demonstrated the best catalytic performance—high current density at low overpotential, good selectivity of products, and stable operation for many hours. In this thesis we demonstrate a novel Au nanostructure and electrodeposition process and measure the catalytic performance for the CO_2RR . We also provide an explanation for the underlying physics of the solution-based crystal growth, drawing connections between electrocrystallization and crystallization from melts.

1.3. Experimental techniques.

1.3.1. Optical microscopy. Optical microscopy measures the intensity and color of light in an image. This is often simply a photograph recorded by a CCD camera. For high magnification of small samples the camera can be integrated into a microscope, or for macroscopic images, camera phones were often used. Microscope images in this thesis were taken by a Leica DM6000 M. Low-pass filtered light was passed through a Thorlabs FEL0500 Longpass Filter, Cut-On Wavelength: 500 nm, Diameter: 1 inch.

1.3.2. Scanning electron microscopy (SEM). SEM scans a columnated beam of electrons in a raster pattern to create an image of a sample surface. The electrons are produced by either thermal emission from a hot tungsten filament, or by field emission from two electrodes with a large voltage between them. The electrons are then accelerated towards the sample by a voltage of approximately 5 to 30 kV. When they hit the sample surface, the inelastic collision releases a cloud of electrons within a few nanometers of the surface, called secondary electrons. These are collected by a detector, which is composed of a metal mesh with a positive voltage relative to the sample surface. The secondary electrons accelerate towards this mesh, pass through it, and hit a phosphor or scintillator, producing light via cathodoluminescence, which is detected by a photomultiplier. Due to the short de Broglie wavelength of the electrons in the beam, $\lambda = h/p$, where h is planck's constant and p is the electron momentum, and the close vicinity of secondary electrons to the sample surface, SEM can produce images with sub-nanometer resolution. For electrons to travel unimpeded through space, the sample chamber must be under vacuum. To avoid build up of charge on the sample surface, the sample must be conducting. The SEMs used in this work are: JEOL JCM-6000, JEOL 6340F, JEOL 6010LA, Tescan Mira 3 LMU, and a JEOL JSM-7001F, which is integrated with the NPGS systems for EBL, as described in the fabrication section.

1.3.3. Transmission electron microscopy (TEM). TEM shines a stationary columnated beam of electrons through a thin sample to produce either an image of the sample, or an electron diffraction pattern. The electrons in the beam are accelerated to much higher velocities than in SEM, by a voltage of approximately 30 to 1000 kV. These high energy electrons travel through the sample, and are detected below the sample by a phosphorescent screen and a CCD camera. The de Broglie wavelength of these electrons is even smaller than in SEM, allowing sub Angstrom resolution and thus imaging of atoms and crystal lattice planes. For images of electron diffraction patterns, the electron beam is focussed to a very small spot on the sample. The diffraction pattern produced provides information about the crystallinity and crystal orientation of a material. The TEM used in this work was a JEOL 2010F.

Samples were prepared for TEM by scratching the sample surface with a knife, sonicating the sample in isopropanol to suspend small pieces of dendrites or plates, and dropcasting the suspension onto a Ted Pella 01890-F grid (Lacey Carbon Type-A, 300 mesh, Copper approx. grid hole size: $63 \ \mu m$). Images were taken with a JEOL 2010F TEM.

1.3.4. Cathodoluminescence (CL). CL measures light produced by interactions between the electron beam and the sample in a SEM. Even though the diffraction limit of light is several hundred nanometers, this technique has approximately nanometer resolution because of the spot size of the electron beam, and the accuracy of the spot location. One mechanism that can produce this light is the excitation of surface plasmon polaritons (SPPs) on a metal surface by the electron beam, and the coupling of these SPPs into far-field radiation by roughness or sharp points on the metal surface. The CL system used in this work was integrated in a Tescan Mira 3 LMU SEM.

1.3.5. Energy dispersive X-ray spectroscopy (EDS). EDS measures X-rays produced by interactions between the electron beam and the sample in a SEM. These X-rays are produced when incident electrons from the beam have enough energy to knock core level electrons out of their orbital, allowing electrons from higher energy orbitals drop into the vacant state. By measuring the energy and number of these X-rays, the atomic composition of a sample can be determined. The EDS system used in this work is a JEOL EX-37001 on a JEOL JCM-6000, and an Oxford on a JSM-7001F.

1.3.6. X-ray diffraction (XRD). XRD has an X-ray source and detector arranged so that the angle of incidence of X-rays from the source can be controlled, and the detector can measure the intensity of X-rays that are spectrally reflected from the surface, *i.e.* X-rays emitted at the same angle as their angle of incidence. For powder samples, this provides information on the crystallinity and crystal structure of the material; for single crystals the crystal orientation can also be determined. The XRD used in this work is a Bruker D8 ECO.

X-ray Diffraction (XRD) analysis of dendritic structures, via comparison to a gold powder, can provide information on the exposed facets on Au crystals [31, 32].

XRD was performed using a Bruker D8 ECO in the Bragg-Brentano geometry with a copper X-ray source (Cu-K α), a nickel filter to absorb the K β radiation, a 2.5° Soller slit after the source, and a 2.5° Soller slit before the LYNXEYE XE 1-D energy dispersive detector. Intensity data were collected in the 2θ range between 5° and 70° with sample rotation.

1.3.7. X-ray photoelectron spectroscopy (XPS). XPS shines X-rays onto a sample and measures the energy of electrons ejected from it. It has better energy resolution than an EDS, but worse spatial resolution. The energy resolution gives it sensitivity to the presence of small atomic concentrations, and can also provide information on the oxidation state of the atoms. Its sensitivity to the presence of low concentrations of elements on the surface of an electrode makes it a useful technique for detecting the presence of contaminants on a catalyst following a CO_2RR experiment, which could come from the electrolyte or the electrochemical cell. The XPS used in this work is a Thermo Scientific K-alpha apparatus equipped with an Al K-alpha X-ray Source and a Flood Gun.

XPS was performed using the Thermo Scientific K-alpha apparatus equipped with an Al K-alpha X-ray Source and a Flood Gun. Parameters used for the measurements were: spot size of 400 μ m, pass energy of 50 eV, energy step size of 0.1 eV, dwell time of 50 ms, 20 scans in the vicinity of Au 4f and O 1s orbitals binding energies.

1.3.8. Atomic force microscopy (AFM). AFM measures the topography of a sample's surface with a cantilever containing a sharp point. This point is approximately 10-100 nm in diameter. The cantilever is rastered across the sample via a piezoelectric material, with sub-nanometer position accuracy. A laser is reflected off the back of the cantilever at an angle, onto a photodetector that is broken into four quadrants. By measuring the relative intensity of the laser spot on each of these quadrants, the tilt of the cantilever can be measured. This tilt changes as the tip is dragged along the surface of a sample with changing height, providing sub-nanometer accuracy of the height of the sample. The system can be operated in contact mode, with the tip in constant contact with the sample; in tapping mode, where the tip is oscillated at kHz frequencies and repeatedly whacks the sample; or in non-contact mode, where the tip is oscillated and kept far enough away from the sample that contact is never made, but van der Walas interactions between the tip and sample cause a shift in the resonant frequency of the tip. The AFM used in this work was the Digital Instruments Veeco Dimension 3100.

1.3.9. Near-field scanning optical microscopy (NSOM). NSOM measures the nearfield intensity of the electric field from visible light excitations on the surface of a sample. The instrument is essentially an AFM in which the cantilever tip has been modified to include an optical fiber that runs from the tip, along the cantilever, ultimately to a photodetector. It is useful for measuring standing wave patterns of SPPs on metal surfaces. The NSOM used in this work is a Nanonics Imaging Ltd. MultiView 4000.

1.3.10. Chronoamperometry. Chronoamperometry measures the current produced in an electrochemical cell for a given voltage between two electrodes. Typically, a three electrode setup is used; the sample is called the working electrode (WE), a Pt wire or mesh the counter electrode (CE), and a glass tube containing an electrode and electrolyte with a well-defined reduction potential the reference electrode (RE). The glass tube of the RE typically has an opening filled by a frit; a porous material that allows slow migration of ions between the electrolyte inside and outside of the glass tube. An instrument called a potentiostat is used to apply voltages and measure currents. In the typical setup, a desired voltage set-point between the WE and RE is entered to the potentiostat, and the instrument applies a voltage between the WE and CE that results in the desired WE/RE potential. The current between the WE and CE is measured. The assumption in this arrangement is that the voltage drop between the WE and RE from electrical resistance is negligible, so that all the voltage drops happen due to differences in reduction potential between electrodes, and due to overpotentials that drive reaction kinetics; the RE is often positioned close to the WE in the electrochemical cell to minimize this resistance. The current between the WE and RE is kept very low, so that the overpotential at the RE is negligible, and it can be assumed to be pinned to the reduction potential of its electrode-electrolyte system. As such, the potential of the WE relative to the known potential of the RE can be measured. The voltage between the WE and CE is not typically measured, as it contains the overpotential of both the WE and the CE and the voltage drop from electrical resistance, making it difficult to distinguish the source of the voltage difference. The details of the reaction at the CE is usually not of particular interest anyway. For chronoamperometry, a constant potential is held between the WE and RE, and the change in current over time is measured. This provides information on how the reaction at the WE changes over time. In our experiments, this is used to measure the temporal stability of the Au catalysts during the CO_2RR . The potentiostat used in this work is the Gamry Reference 600, the Gamry Interface 1000, and the Princeton Applied Research VersaSTAT 3.

1.3.11. Cyclic voltammetry (CV). CV measures the current produced in an electrochemical cell for a given voltage between the WE and RE. The setup is the same as described above for chronoamperometry. For CV, the voltage is swept between two electric potentials, cycling back and forth between two limit potentials to determine the reproducibility of the current-voltage relationship. The relationship between the current and voltage provides information on the reaction kinetics, mass transfer of reactants and products, and the reduction potential of the WE.

1.3.12. Cyclic voltammetry surface area measurement. A typical three electrode setup was used with a Gamry Interface 1000 potentiostat. The working electrode was the Au sample, the reference electrode Ag/AgCl in saturated KCl solution, and the counter electrode a Pt or Au wire spiral. All three electrodes were immersed into a 80 ml crystallization dish containing either 500 or 375 mM H_2SO_4 . Electrolytes were prepared from pure sulfuric acid and deionized water.

1.3.13. Electrochemical Impedance Spectroscopy (EIS). Potentiostatic EIS measures the impedance (Z) and phase-offset (ϕ), as a function of angular frequency (ω), between an applied electric potential and an electrode in a solution. Typically, a three electrode setup is used, as described above for CV's.

A typical three electrode setup was used with a Gamry Interface 1000 potentiostat. The working electrode was the Au sample, the reference electrode Ag/AgCl in saturated KCl solution, and the counter electrode a Au wire spiral. All three electrodes were immersed into a 25 ml beaker containing the electrolyte under study. All electrolytes were prepared with deionized water. 1.3.14. Au crystal synthesis. To grow the Au dendrites and plates, a two electrode setup was used. The counter electrode was a Pt wire spiral. The working electrode was a 2 x 2 x 0.1 cm Ti foil chip, sputter coated on the front with 100 nm of Au. The back of the Ti foil was covered by scotch tape, and for samples tested for CO_2RR , the front was covered by teflon tape with a 1 cm diameter hole for the electrodeposition. Scotch tape was used on the back for easy removal for subsequent experiments. The electrodes were immersed into a small beaker with 20 ml of 2 to 20 mM HAuCl₄ in deionized water. A function generator was used to apply a 20 MHz square wave electric potential between the electrodes, with $\varphi_{offset} = -0.625$ to -2 V and $\varphi_{pp} =$ $8\varphi_{offset}$. An oscilloscope was attached in parallel to the electrodes to measure the waveform of the applied potential. Measurements of the current passing through the circuit were not made to avoid modifying the waveform of the high frequency applied potential.

1.3.15. Gas chromatography (GC). GC measures the concentration of chemicals in gas samples. It has a loop of pipe that a gas sample flows through from an experimental apparatus, such as from a CO_2RR cell. Separately, there is a column of a porous material, which a carrier gas flows through—typically He, H₂, N₂, or Ar. To take a measurement, a small volume of the sample gas is injected from the loop into the column. The column is designed for detecting a particular set of gasses, and by selecting an appropriate porous material for the column, the rate at which each gas passes through the column is different. For example, in the work on nanostructured Nafion membranes, the carrier gas was He, and H₂ took 3.15 minutes to pass through the column, while CO took 6.75 minutes. At the end of the column there is a detector for measuring the concentration of each gas as it leaves the column. The detectors and GC's used in this work were a mass spectrometer on a Shimadzu GCMS-QP2010, a flame ionization detector (FID) with methanizer and a thermal conductivity detector (TCD) on a SRI Multiple Gas Analyzer 5, and a Thermo Scientific TRACE 1310.
Calibration of the instrument is done by flowing samples of known concentration into the system.

1.3.16. CO_2 reduction. A typical three electrode setup was used with a Princeton Applied Research VersaSTAT 3. The metal catalyst was the working electrode, the reference electrode Ag/AgCl in saturated KCl solution, and the counter electrode a platinum mesh. A Nafion membrane separated the counter electrode from the working and reference electrodes. The electrolyte was deionized water with 0.25 M Na₂CO₃, which after CO₂ was bubbled through it for 30 minutes was considered 0.5 M NaHCO₃. CO₂ was continuously bubbled through the catholyte at 6 sccm and the anolyte at 20 sccm. The gas stream from the catholyte was passed through the gas chromatograph (Thermo Scientific TRACE 1310) to measure the product gas concentration. Both electrolytes were stirred by magnetic stir bars.

1.3.17. Hard-NIL Al nanowire fabrication procedure. Here, Ni posts were used to imprint the Al surface with an array of indents. Ni was chosen because of its hardness and compatibility with an electron-beam lithography (EBL) technique for fabricating post arrays. The use of EBL allowed Ni posts to be left out of certain lattice sites in the array, such that after imprinting the Al there would be missing indents at certain lattice sites of the indent array. This prevented the Al from anodizing at the sites of the missing indents. As shown in Fig. 35, there is apparently a maximum indent diameter for which pores selectively nucleate at indented sites and not sites missing an indent. Fig. 1 shows photographs of the experimental setup used in the fabrication of Ni posts and Al nanowires.

Stamp preparation: To produce the stamp in Fig. 34a, glass slides 16 mm x 15 mm were piranha cleaned and then coated with 50 nm of Ni with a Sharon electron beam deposition system. HMDS (VLSI grade 0.1 μ m filtered from Ultra Pure Solutions, Inc.) was spun on (step 1: 5 sec, 500 rpm, 100 rpm/sec; step 2: 45 s, 4000 rpm, 550 rpm/s) to remove moisture from the sample surface, followed by electron

beam resist (950 PMMA A4 from MicroChem) spun on (step 1: 5 s, 500 rpm, 100 rpm/s; step 2: 45 s, 4000 rpm, 550 rpm/s) to create a nominally 200 nm thick PMMA film. A 120 s delay between applying the PMMA and initiating the spin steps was included to allow bubbles in the PMMA to dissipate. The PMMA was then pre-expose baked at 180 °C for 25 min on a hotplate. Arrays of nominally 100 nm diameter holes were written into the PMMA with a JEOL SEM using a dosage of ~ 1300 μ C/cm². The PMMA was then developed with 1:3 MicroChem MIBK:IPA (MIBK/IPA 1:3 Developer from MicroChem) for 40 s, IPA for 20 s, and finally deionized water (DI) for 20 s. Ni was then electroplated into the holes using Ni plating solution (SN-10 Ni Plating Solution from Transene, Inc.), a counter electrode (47 mm² of exposed surface area of coil of Pt wire, 0.1 mm diameter, Premion 99.997% Pt from Alfa Aesar), and a potentiostat (Gamry Interface 1000 running a chronopotentiometry scan) to produce nominally 100 nm tall Ni posts. The PMMA was subsequently dissolved by placing the stamp in a bath of acetone for a few minutes.

Electropolish Al: High purity Al foil (annealed, Puratronic, 99.9995%, Alfa Aesar) of thickness 200 μ m and surface roughness of 30 nm (measured by AFM), was cut into 5 mm x 10 mm strips using scissors. The strips were flattened between two glass slides using a custom-made vice composed of two flat Al plates (one plate could move vertically by turning a 5 mm diameter screw, the other comprised the base of the vice). The Al foil was then rinsed with ethanol to remove moisture from the surface (moisture causes degradation of the Al surface during electropolishing—specifically the appearance of a rough off-white film) and immersed in a bath of 1 perchloric acid : 3 ethanol (70% perchloric acid Reagent ACS Grade from GFS Chemicals, 90% ethanol (5.5% Isopropanol, 4.5% Methanol) HPLC Grade from Fisher), which was stirred at 120 rpm with a 10 mm magnetic Teflon coated stirring rod and held at 5 °C via a jacketed beaker and circulating bath (Polystat 1212202 from Cole Parmer). A 5 mm diameter 80 mm length carbon rod (Fisher Scientific, cat. no. S43501) was simultaneously immersed in the solution as a counter electrode. Electrical contact was made to the Al foil and C rod via flat-tipped alligator clips (Micro 1-1/8" Smooth Clips from RadioShack). 10-20 V was applied with a high current voltage source (Kepco model: KS36-10Mcurrent regulated power supply) for 5-10 min (voltage and time were fine-tuned each day electropolishing took place). The polished Al had a mirror finish with surface roughness 3.9 nm as determined by AFM.

Imprint Al: The polished Al foil was placed polished-side-down on top of the Ni stamp (with Ni posts facing up) and a small piece (2 mm x 2 mm) of Teflon plumbing tape was placed on top of the Al at the region to be imprinted. This stack was sandwiched between two glass slides, and the sandwich was placed into the custom vice. The vice was carefully closed to compress the Al against the Ni stamp and imprint the Al. The imprinted Al developed iridescence in the region imprinted by Ni posts, and had a surface roughness of 2.8 nm.

Anodize Al: A 2.5-3.5 mm diameter circular window was cut into adhesive Teflon tape (Tape with PTFE Film, Beige 5498, Silicon-free, 4 mil, part #5498-10 from All-Spec Industries), and the tape was used to mask the imprinted Al foil. The tape was arranged such that the window exposed the imprinted region of the Al. The Al foil was placed in a beaker of:

- 50 ml ethylene glycol (E178-4 Ethylene Glycol Certified from Fisher),
- 50 ml 2% wt citric acid (anhydrous, reagent ACS, 99.5% from Acros),
- 2.9 ml 0.1% wt phosphoric acid (85% solution in water from Acros Organics),

which was held at 10 °C via a jacketed beaker and circulating bath (Polystat 1212202 from Cole Parmer). For Al nanowires with a minimum pitch of 2.4 μ m (*i.e.* an AAO template of pitch 1.2 μ m), 480 V was applied with a DC voltage source (Fluke 412B) between the Al foil and a carbon counter electrode for a duration appropriate for the desired height of the Al nanowires.

Etch Al_2O_3 : The anodized Al foil was rinsed with DI and placed for 50 minutes in a beaker containing 50 ml of 6% wt Phosphoric Acid (85% Phosphoric acid from Acros Organics) and 1.8% wt Chromic Acid (10% w/v Chromic Acid from Ricca Chemical Company) in DI held at 63 °C.

Final Rinse: The Al foil was rinsed with DI and dried by flowing a nitrogen stream across it. This exposed the Al nanowires allowing them to be imaged via SEM. Iridescence was visible to the eye where there were Al nanowires.



FIGURE 1. Photos of fabrication process and setup: (a) Ni-coated glass with PMMA film for EBL, (b) after development of the nanopores in the PMMA film, (c-e) electrodeposition of Ni into the PMMA pores, (f) stack of electropolished Al lying polished side-down on Ni posts, with PTFE tape over region to be stamped, (g) stack sandwiched between two glass slides, (h) custom-made vice for indenting the Al, (i) Ni stamp and the indented Al, (j) Al masked with adhesive PTFE tape, with a window exposing the indented region of the Al, (k) anodization setup including the jacketed beaker for temperature control, (l) carbon rod counter electrode, PTFE coated magnetic stirring rode, and masked Al during anodization, (m) Al after anodization, (n) Al and PTFE tape after removal of the tape. Reprinted with permission from ref [33]. Copyright 2015 American Chemical Society.

1.3.18. Soft-NIL Al nanowire fabrication procedure. Nanoimprint lithography (NIL) is a powerful method for fabrication of nanostructures. Intricate structures can be fabricated on a stamp using expensive and slow processes, such as electron beam lithography (EBL). Then they can be transferred from the stamp to a large quantity of samples. Done properly, the fidelity of the transferred structures can be very good on nm length scales, especially for pattern transfer between soft polymers. The stamping process can be fast and low-cost compared to other lithography options, which allows the expense of stamp fabrication to be amortized across many samples.

This process allowed for the fabrication of nanowire diameter, height, shape and array pitch previously unavailable to metals. However, the hard stamp required expensive and time-consuming EBL processing, and was easily damaged when directly imprinting Al. Here, we report a process to mask the Al with Al_2O_3 and a polymer, and to imprint the polymer using a soft stamp. This results in less damage to the stamp. Also, the expensive EBL procedure is used to make a hard master mold from which the soft stamp is drop-cast. As such, the expensive procedure is amortized across many samples per stamp, and many stamps per master.

Master stamp fabrication: A Si chip with a $\langle 100 \rangle$ surface orientation was patterned to produce a master from which the PDMS mold was made. The Si chip was sputter coated by 50 nm of Cr (AJA International sputtering system). Before spin-coating with PMMA, the chip was rinsed in an acetone bath for 5 min, an isopropanol stream for ~10 s, a deionized water stream for ~10 s, and dried in a N₂ stream for ~10 s, and on a hotplate at 200 °C for \geq 5 min. From the hotplate, the chip was moved to the spinner (Laurell WS-400E) and a 180 nm PMMA film was spun on (acceleration step: 5 s, 550 rpm/s, 500 rpm; spin step: 45 s, 550 rpm/s, 4000 rpm). Before spinning, the solution of PMMA solids (Mircochem 495 PMMA A4) was filtered through a 0.45 um Nylon Acrodisk (PALL) using a disposable 6 ml syringe. The PMMA was immediately soft baked on a hotplate at 180 °C for 90

s. Arrays of 300 nm circles were written in the PMMA with an JEOL SEM (probe current ~ 10 pA, working distance 10 mm, acceleration voltage 30 kV). Arrays were hexagonal with pitch of 1 μ m, 1.2 μ m, and 1.4 μ m. They each contained a super-array of missing circles with twice the pitch of the circles. The PMMA was developed for 60 s in (1:3) MIBK:IPA (MIBK/IPA 1:3 Developer from MicroChem) and 20 s in IPA (Microchem). The Cr film was etched through the openings in the PMMA for 15 s in Transene Cr Etchant 1020 at 40 °C. The etch was quenched by immersing the chip in a bath of 40 °C deionized water. The chip was rinsed in a deionized water stream for ~ 10 s and dried in a N₂ stream for ~ 10 s. The PMMA mask was removed by immersing the chip in acetone for 5 min. The chip was rinsed briefly in a stream of deionized water, and dried in a stream of N_2 . For the next step, an aqueous solution of 40% wt KOH was prepared. KOH pellets were added to a beaker of deionized water, and the solution was raised to 80 $^{\circ}$ C to facilitate dissolution of the pellets. The solution temperature was then lowered to 40 °C. The solution was stirred at 300 rpm with a 1 inch magnetic stir bar. To etch the exposed Si through the openings in the patterned Cr film, the Si native oxide was removed by immersing the chip in a room temperature buffered oxide etch (BOE from J. T. Baker, 7:1 NH₄F:HF) for ~ 100 s. The chip was rinsed by immersion into two separate baths of deionized water, and then was immersed in the 40 °C, 40 %wt, aqueous solution of KOH for ~ 300 s. The etch was quenched by immersion in deionized water. The Cr mask was removed by immersing the chip in the Transene Cr Etchant 1020 for ~ 4 min. The resulting Si chip master had an array of pyramid shaped depressions where circles were written in the PMMA by the electron beam.

Slave stamp fabrication: PDMS stamps were prepared in the following process. To dropcast the PDMS mold from the Si chip master, the Si was placed face-up in a petri dish (50 mm diameter, 10 mm deep). 4.76 g of Sylgard 184 Silicone Elastomer Base and 0.49 g of Sylgard 184 Silicone Elastomer Curing Agent were mixed and then poured into the petri dish. The solution was degassed in a vacuum chamber for 10–15 min until bubbles stopped forming. The PDMS was then cured at 75 °C for 2 hrs. The cured PDMS was peeled away from the Si master, and cut to a convenient size with a scalpel. This PDMS mold had hexagonal arrays of pyramids on it, each with a super-array of missing pyramids at twice the pyramid pitch.

Fig. 47 in Chapter 3 shows cartoons and representative SEMs of the following fabrication steps.

Electropolish Al: Al foil (Alfa Aesar, $\geq 99.99\%$ Al) was flattened in a clamp between two glass microscope slides, rinsed in 3:1 acetone:IPA for 30 s, and then electropolished in 180 ml ethanol + 30 ml 70% perchloric acid (Acros Organics) for 10 min at 10-12 V vs. a graphite bar counter electrode. The electrolyte was contained in a 50 x 90 mm crystallization dish, and the dish submerged in water in a jacketed beaker, which was cooled to 3 °C by a circulating chiller (Cole-Parmer Polystat 1212202). The electrolyte was stirred at 200 rpm by a 1" magnetic stir bar.

Coat Al with patterned mask: A 400 nm thick alumina film was deposited by ALD, followed by a 300 nm thick film of SU8 negative photoresist. The SU8 was spun on (acceleration step: 7 s, 110 rpm/s, 500 rpm; spin step: 30 s, 550 rpm/s, 3000 rpm), soft baked on a hotplate at 65 °C for 5 min, followed by 95 °C for 90 s. A PDMS stamp was pressed into the SU8 with a homemade clamp. The clamp assembly was pre-expose baked at 95 °C for 5 min, the SU8 was exposed to UV light for 75 s through a window in the clamp assembly, the assembly was post-expose baked at 95 °C for 5 min, and left to cool on a lab bench for 40 min. The sample was removed from the clamp and stamp, the SU8 exposed again for 75 s, and hard baked (the hotplate was set to 2 min long temperature steps of 65 °C, 95 °C, 120 °C, 150 °C, 180 °C, held at 210 °C for 42 min, stepped back in the reverse order of the up-ramp, turned off, and left to cool to 50 °C before sample removal). Fig. 47b-i shows the patterned SU8 surface. Selectively expose Al_2O_3 through SU8 mask: Fig. 47b-ii shows alumina exposed through holes in the SU8 after etching the SU8 in a plasma barrel etcher (PVATepla PS-210) for ~30 s with 150 sccm $O_2 + 20$ sccm CF_4 , 250 W, and the sample on a glass plate inside a faraday cage.

Selectively expose Al through Al_2O_3 mask: Fig. 47b-iii shows bowls etched into the alumina film by immersion in ~20 ml of 1.8 %wt chromic acid + 6 %wt phosphoric acid on a hotplate at 65 °C for 100 min.

Anodize Al: Fig. 47b-iv shows the AAO membrane formed after ~ 40 hours of anodization at 480 V vs. a carbon rod counter electrode in 100 ml of 50.5 mM citric acid, 0.287 mM phosphoric acid, 8.71 M (*i.e.* 50%) ethylene glycol in a beaker immersed in water in a jacketed beaker cooled to 10 °C by a circulating chiller (Cole Parmer Polystat 1212202). To begin anodization, the aluminum electric potential was stepped in 30 s and 10 V intervals from 10 to 80 V and 2 min and 100 V intervals from 180 to 480 V.

Etch anodic Al_2P_3 : Fig. 47b-v shows the partially etched AAO membrane and the underlying Al surface, exposed by SU8 removal in the plasma barrel etcher and immersion of the sample into the chromic acid etch described above. Fig. 47-vi shows the exposed Al surface after full removal of alumina.

1.4. Organization of this thesis. In Chapter II, we will discuss the fundamentals of electrochemistry and plasmonics and review the relevant literature on metal nanostructure fabrication, nanostructures in plasmonics applications, and nanostructures in electrocatalysis of the CO_2RR . In this literature review, we will highlight the need to expand metal nanostructure fabrication techniques. In Chapter III, we will focus on our development of a fabrication method for Al nanowires, and measurements of SPPs guided by sharp ridges running along the nanowire's length. In Chapter IV, we will discuss the results of our investigation into the electrodeposition mechanism of Au dendrites, and the implication of our findings on controlling the exposed facet of Au crystals. We then report the performance of different Au nanostructures for the CO_2RR . In Chapter V, we discuss conclusions of the thesis and suggest future work that could explored to build upon these results.

2. Fundamentals and literature review

2.1. Electrochemical cell configurations. There are several cell configurations typically used in electrochemical studies. The simplest has a single electrolyte providing electrical connection between two electrodes, referred to as the working electrode (WE) and counter electrode (CE). These studies focus on reactions at the WE. A potentiostat sets the electric potential between the electrodes, and measures the current that passes between them. Advanced software programs have been developed to regulate this potential in either a pre-determined manner, or actively in response the current measurements.

The three electrode configuration adds a reference electrode (RE) to the cell. The RE is typically immersed in a standardized electrolyte, which is separated by a porous glass frit from the cell's electrolyte. The RE is an ideally non-polarizable electrode, meaning that the reaction kinetics occur so easily that the potential difference between the electrode and its electrolyte is negligible. The RE and its electrolyte are designed to have a well-defined reduction potential, to provide a reference point from which the potential of the WE can be measured. To ensure that the RE doesn't develop any polarization from the overpotential of charge transfer, the potentiostat in a three electrode configuration measures the potential between the WE and RE, and increases the potential between the WE and CE until enough current passes through the cell that a user-defined potential between the WE and RE is reached. This provides detailed information about the WE. Typically the potential and reaction kinetics at the CE are ignored. To provide insight into the reaction kinetics at the WE, the RE is typically located as close as possible to the WE, so that the potential drop from mass transport is negligible.

Common REs used in experiments are the Ag/AgCl electrode and the saturated calomel electrode (SCE). The former is a Ag wire coated with a layer of AgCl, and immersed into an aqueous solution of KCl or NaCl with a known concentration of the

salt. The later is a liquid mercury electrode, in contact with calomel (solid Hg_2Cl_2), which is immersed in saturated KCl. These electrodes have well established equilibrium potentials, which are typically reported relative to the standard hydrogen electrode (SHE) or the reversible hydrogen electrode (RHE). The former is an experimentally inconvenient RE which would be immersed in water saturated by hydrogen gas, with its potential fixed to the equilibrium potential between H⁺ ions in solution and the dissolved H_2 gas. The potential of a SHE RE depends on the pH of the solution. By definition, the RHE RE accounts for the variation of the potential with pH. Thus, if the equilibrium potential of a reaction taking place at a WE is reported relative to the RHE, this potential will depend on the pH of the solution. If one were to report the equilibrium potential of the same reaction relative to the SHE, then the pH of the solution used in the experiment would also need to be specified. A useful property of the SHE is that it is defined relative to the potential of a charge in a vacuum, which allows for comparison of electrochemical potentials with the valence band and conduction band potentials of materials. The potential of SHE vs. vacuum is 4.44 ± 0.02 V at 25 °C.

It is common to separate the electrolytes for the WE and CE. A salt bridge, porous glass membrane, solid oxide, or polymer membrane are common separators. They allow sufficient transfer of ions for electrical conduction but otherwise keep the electrolytes from mixing. 2.2. Mass transport. Facile transport of reactants and products to and from an electrode is important for efficient cell operation. These transport phenomena are described by the Nernst-Planck equation [34],

(1)
$$\mathbf{J}_{i}(\mathbf{r}) = z_{i}FD_{i}\nabla C_{i}(\mathbf{r}) + z_{i}n_{i}F^{2}m_{i}C_{i}(\mathbf{r})\nabla\varphi(\mathbf{r}) - z_{i}FC_{i}(\mathbf{r})\mathbf{u}(\mathbf{r})$$

where \mathbf{r} is the position in the cell relative to the electrode of interest, F is Faraday's constant, z_i is the valence of chemical species i, n the number electrons it transfers during the reaction, D_i its diffusion constant, $C_i(\mathbf{r})$ its concentration, m_i its mobility, $\varphi(\mathbf{r})$ the electric potential relative to the electrode, and $\mathbf{u}(\mathbf{r})$ the velocity vector of the solution (typically as a result of stirring). We limit ourselves to the common case that any given reaction considered only consumes one species i, and drop the subscript for this case. The net current density due to mass transport of species i is often referred to as the limiting current, J_L , because when the reaction kinetics are faster than J_L , the current through the electrochemical cell becomes limited by mass transport. That is to say, J_L is the largest current that can be produced by the electrochemical cell, and is determined by the parameters in Eq. 1.

Electrolytes are typically chosen to have a high ionic conductivity, which removes any potential drop across the electrolyte and neglects the migration term (2nd term in Eq. 1). If the solution is well mixed, then we can also neglect the convection term (3rd term in Eq. 1), assuming that outside the boundary layer of the electrode the species are all present in their bulk concentration. This boundary layer is the consequence of assuming a no-slip boundary condition at the electrode surface when modeling the fluid dynamics of the cell. Its thickness is given by the Blasius solution to fluid flow over a flat plate,

(2a)
$$\delta_{\text{laminar}} = \frac{0.5x}{Re_x^{1/2}}$$

(2b)
$$\delta_{\text{turbulent}} = \frac{0.37x}{Re_x^{1/5}}$$

where x is the distance along the electrode surface from its edge, and Re_x is the Reynolds number of the electrolyte. We now need only consider diffusion of the reactant through the boundary layer. Assuming the electrode surface is much wider and longer than the boundary layer thickness, edge-effects can be neglected. If the electrode is also flat on the length scales of the boundary layer thickness, and the boundary layer thickness doesn't change significantly along the length of the electrode, then diffusion of species through the boundary layer can be assumed 1-dimensional; $\nabla C(\mathbf{r}) \approx \partial C(y)/\partial y$, where y is the distance from the electrode surface. In a mass transport limited reaction, the reactant will be immediately consumed at the electrode surface, and its concentration there can be assumed zero. This allows us the approximation $\partial C(y)/\partial y \approx C^*/\delta$, where C^* is the concentration in the electrolyte bulk. This produces a simplified form of the Nernst equation for the limiting current density,

(3)
$$J_{\rm L} = \frac{zFDC^*}{\delta}$$

2.3. Reaction kinetics.

2.3.1. Single step reaction. When the current density is much less than $J_{\rm L}$, then the current-potential relationship is determined by the reaction kinetics. This is described by the Butler-Volmer equation [35, 36],

(4)
$$J = j_0 \left(\frac{C_{\rm O}(0,t)}{C_{\rm O}^*} e^{\frac{-nF\alpha}{RT}\eta} - \frac{C_{\rm R}(0,t)}{C_{\rm R}^*} e^{\frac{nF(1-\alpha)}{RT}\eta} \right)$$

where j_0 is the exchange current density, α is the reaction charge transfer coefficient, $C_{\rm O}(0,t)$ is the surface concentration of oxidized species at the cathode, $C_{\rm O}^*$ is the bulk concentration of oxidized species, $C_{\rm R}(0,t)$ is the surface concentration of reduced species at the cathode, $C_{\rm R}^*$ is the bulk concentration of the reduced species, η the overpotential on the cathode, R the gas constant, and T the temperature.

The overpotential is defined as $\eta = E - E^0$, where E is WE potential, and E^0 the equilibrium potential of the particular electrode/electrolyte combination, both measured relative to a standardized potential, such as the RHE. The first term in Eq. 4 is for the cathodic current at the electrode, and the second term for the anodic current. Figure 2 shows the flow of charge for positive cathodic current, by the common convention that we have adopted in this thesis. In the potential range where η is negative, and the cathodic current is much larger than the anodic current, the later can be approximated as zero. The equation then simplifies to,

(5)
$$J = j_0 \left(\frac{C_{\rm O}(0,t)}{C_{\rm O}^*} e^{\frac{-nF\alpha}{RT}\eta} \right)$$

which can be written as,

(6a)
$$\eta = \left(\frac{2.3 \ RT}{-nF\alpha}\right) \log \left(\frac{J}{j_0 \frac{C_{\rm O}(0,t)}{C_{\rm O}^*}}\right)$$

(6b)
$$\eta = \left(\frac{2.3 \ RT}{-nF\alpha}\right) \left(\log(J) - \log(j_0 \frac{C_{\rm O}(0,t)}{C_{\rm O}^*})\right)$$

(6c)
$$\eta = a - b \cdot \log(J)$$

(6d)
$$\implies a = \left(\frac{2.3 \ RT}{nF\alpha}\right) \log\left(j_0 \frac{C_{\rm O}(0,t)}{C_{\rm O}^*}\right)$$

(6e)
$$\implies b = \left(\frac{2.3 \ RT}{-nF\alpha}\right) \ .$$

Eq. 6c is known as the Tafel equation. Note, the approximation has been made that $\log_{10}(e) \approx 1/2.3$. By plotting the overpotential η against the log of the current, J, the charge transfer coefficient, α , can be determined from the slope b. If the current is small compared to the limiting current $J_{\rm L}$, then $C_{\rm O}(0,t) \approx C_{\rm O}^*$ and the exchange current density can be determined from the y-intercept, a.



FIGURE 2. Schematic diagram of electron flow for positive cathodic current. The oxidized species, O, is reduced by electrons that leave the cathode, to produce the reduced species, R. The reaction happens at the catalytic site on the cathode surface, represented by the asterisk symbol, *.

2.3.2. Multistep reaction. In the case of multi-electron transfer reactions, a current $J_{\rm i}$ can be derived from the Butler-Volmer equation for each of the reaction steps. The current for each step can be summed via an inverse law [37],

(7)
$$\frac{1}{J} = \sum_{i} \frac{1}{J_{i}}$$

to determine the total current density, J. If one reaction step is much slower than the others, it will limit the reaction, and the total current will be approximately equal to the current for this rate limiting step (RLS), $J \approx J_{\text{RLS}}$. The slope b in the Tafel equation (Eq. 6e) indicates which step is the RLS of a multi-electron process. It is calculated by comparing the expression for the total reaction current to that of the RLS. For the RLS as the initial electron transfer in a cathodic reaction we have,

(8a)
$$J = nFk_1C_0 \ e^{\frac{-nF\alpha E}{RT}}$$

(8b)
$$J_{\text{RLS}=1} = Fk_1 C_0 \ e^{\frac{-F\beta E}{RT}}$$

where we have used that $j_0 = nFk_1C_0e^{\left(\frac{-F\alpha E_{\text{rev}}}{RT}\right)}$, with k_1 the forward rate constant of the initial electron transfer. β is the symmetry factor relating the shape of the anodic and cathodic currents of the reaction step. The two directions of current are typically assumed symmetrical; $\beta = 0.5$. For one electron transferred in the initial step, n = 1is substituted into Eq. 8b. Comparing 8a and 8b we thus find that $n\alpha = 1\beta$, which allows us to calculate the Tafel slope *b* for a reaction limited by an initial electron transfer,

(9a)
$$b = \left(\frac{2.3 \ RT}{-F\alpha}\right)$$

(9b)
$$b_{\text{RLS}=1} = \left(\frac{2.3 \ RT}{-F\beta}\right)$$

(9c)
$$b_{\text{RLS}=1} = \left(\frac{2.3 \cdot 8.314 \cdot 298}{-96485 \cdot 0.5}\right)$$

(9d)
$$b_{\text{RLS}=1} = -118 \text{ mV/decade}$$

For the case of the second reaction step as the RLS, the situation is slightly more complicated. In this circumstance the first reaction will be in quasi-equilibrium, and we make the following relation,

(10a)
$$k_1 C_{\rm O}(1-\theta) e^{\left(\frac{-\beta EF}{RT}\right)} = k_{-1} \theta e^{\left(\frac{(1-\beta)EF}{RT}\right)}$$

(10b)
$$\frac{\theta}{1-\theta} = \mathcal{K}_1 C_0 e^{\left(\frac{EF}{RT}\right)}$$

(10c)
$$\mathcal{K}_1 = \frac{k_1}{k_{-1}}$$

where θ is the fractional surface coverage of the catalytic sites on the cathode, *i.e.* the ratio of occupied sites to the total number of sites, and for reaction step 1: k_1 is the forward reaction rate constant, k_{-1} is the reverse reaction rate constant, and \mathcal{K}_1 is the equilibrium constant. To obtain an explicit expression for θ , we can consider the case where surface coverage is very low ($\theta \ll 1$). In this limit $(1 - \theta) \approx 1$, and we find,

(11)
$$\theta = \mathcal{K}_1 C_0 e^{\left(\frac{EF}{RT}\right)}$$

This gives the concentration of the reactant, θ , of the second reaction. From this we can write the expression for the current of the second reaction step, compare it to

the expression for the total current, and find $n\alpha$ for the case that the second reaction step is the RLS,

(12a)
$$J = nFk_2C_0 \ e^{\frac{-nF\alpha E}{RT}}$$

(12b)
$$J_{\text{RLS}=2} = Fk_2 C_0 \theta \ e^{\frac{-F\beta E}{RT}}$$

(12c)
$$= Fk_2C_0\mathcal{K}_1C_0 \ e^{\frac{-F(1+\beta)E}{RT}}$$

(12d)
$$\implies n\alpha = (1+\beta) = (1+0.5) = 1.5$$
.

We can then calculate the Tafel slope to be,

(13a)
$$b = \left(\frac{2.3 \ RT}{-F\alpha_c}\right)$$

(13b)
$$b_{\text{RLS}=2} = \left(\frac{2.3 \cdot 8.314 \cdot 298}{-96485 \cdot 1.5}\right)$$

(13c)
$$b_{\text{RLS}=2} = -40 \text{ mV/decade}$$
.

Continuing along the same lines, it can be found that for a RLS at the m^{th} electron transfer, $n\alpha_c = (m - 1 + \beta)$. For m = 3, a Tafel slope of $b_{\text{RLS}=3} = -23 \text{ mV/decade}$ would be expected. For a more detailed discussion of this derivation, see *Electrode kinetics for chemists, chemical engineers, and materials scientists* by Gileadi [35]. The goal of catalysis is to increase the current density J for a given overpotential η . The result above shows that for multistep reactions this can be accomplished by stabilizing reaction intermediates to increase the value of α .

2.3.3. *Exchange current density*. The exchange current density is a critical value for determining the rate of a reaction. Its derivation follows from thermodynamics, and is given as [36],

(14)
$$j_0 = Fk^o C_{\rm O}^{*^{1-\alpha}} C_{\rm R}^{*^c}$$

where k^{o} is the standard heterogeneous rate constant. This rate constant is equal to,

(15)
$$k^o = \kappa \frac{k_{\rm B}T}{h} e^{\frac{-\Delta G^{\#}}{RT}}$$

where κ is the transmission coefficient, $k_{\rm B}$ the Boltzmann constant, h Planck's constant, and $\Delta G^{\#}$ the standard Gibbs free energy of activation. The conventional understanding is that this k^{o} is independent of reactant or product concentration. κ has a value between 0 and 1, representing the fraction of reactant that transitions to product from the intermediate complex, rather than back to reactant [34]. From this expression we see that the exchange current density is proportional to the concentration of the oxidized species, reduced species, and the $\Delta G^{\#}$.

Combining Eqs. 4 and 14 we can see directly the influence of species' concentration on the current density,

(16)
$$J = Fk^{o} \left(\frac{C_{\rm R}^{*^{\alpha}} C_{\rm O}(0,t)}{C_{\rm O}^{*^{\alpha}}} e^{\frac{-nF\alpha}{RT}\eta} - \frac{C_{\rm O}^{*^{1-\alpha}} C_{\rm R}(0,t)}{C_{\rm R}^{*^{1-\alpha}}} e^{\frac{nF(1-\alpha)}{RT}\eta} \right).$$

If we consider $O + ne \rightarrow R$, the cathodic reduction reaction of species O to R at negative values of η , and assume the reverse reaction is negligible, we get,

(17)
$$J = Fk^{o} \left(\frac{C_{\mathbf{R}}^{*^{\alpha}} C_{\mathbf{O}}(0,t)}{C_{\mathbf{O}}^{*^{\alpha}}} e^{\frac{-nF\alpha}{RT}\eta} \right).$$

This shows an interesting and often neglected result—that the current density is proportional to the concentration of the product raised to the positive power α . From Eq. 17 we see that additional approaches to increasing J for a given η are to increase $C_{\rm O}(0,t)$, $C_{\rm R}^{\alpha}$, or k^{o} ; the last is increased by lowering $\Delta G^{\#}$.

2.4. Anodized aluminum oxide (AAO) template formation.

2.4.1. Self-assembled pore formation. AAO templates form as the result of a positive feedback process, as discussed in detail in a thorough review in 2014 by Lee and Park [38]. Before the anodization begins, any Al exposed to standard atmosphere and pressure will have a 3–5 nm native oxide on its surface. When this is immersed into an electrolyte, and an anodic potential is applied, the oxide layer grows. This growth occurs via migration of Al^{3+} cations from the Al/Al_2O_3 surface towards the Al_2O_3 /electrolyte surface, and O^{2-} anions in the reverse direction. As these ions reach the opposite surface from which they originated, they combine to form new oxide. This process continues until the oxide layer reaches a thickness for which the electric field through the oxide is not strong enough to drive the ion migration. This flat oxide layer is called a barrier oxide. There is typically not significant stress in this film, so it tends to be very stable and well adhered to the underlying Al.

However, the applied potential does cause electrostriction, applying a compressive force on this film. For certain electrolytes, anions besides O^{2-} can migrate through the oxide layer. These can compromise the mechanical stability of the film. Provided there is also sufficient roughness to the original Al surface, the combination of ion doping and electrostriction can cause the Al₂O₃ layer to buckle with a periodicity of approximately triple the thickness of the oxide layer. This buckling of the oxide concentrates the potential drop to the spots where the oxide layer remained flat, as the buckled portions are thicker. As such, a steady-state is reached where oxide continues to form in flat spots, but this oxide flows sideways towards the buckling points, pushing that oxide upwards to form walls surrounding the oxidation point. These walls form the AAO template, with the oxidation sites located at the base of each pore.

The lowest energy packing arrangement of the pores is hexagonal close-pack (hcp). As such, as the oxide layer grows, pores will gradually merge or diverge to self-order themselves into a hcp arrangement. Well-ordered hcp pore arrays can be produced by anodizing an Al surface in the above manner, then selectively etching away the oxide, and finally restarting the anodization. However, there tend to be 'grain boundaries' that separate adjacent ordered regions. These regions typically have a diameter of about 10–100 μ m.

2.4.2. Directed pore formation via NIL. NIL can be used to pattern an Al surface with an array of indents that direct the position of pore nucleation. This allows for perfect hcp pore arrays over arbitrarily large areas. Additionally, for AAO templates of pitch greater than $\sim 1 \ \mu$ m, the barrier oxide is too mechanically stable to auto-nucleate pores. In this regime, the use of NIL to direct the formation of pore nucleation is necessary for AAO templates to form. 2.5. Surface plasmon polaritons. SPPs are charge density waves present at the surface of a metal; essentially ripples in the sea of free electrons. They obey very similar physics to waves at the boundary between a liquid and gas, such as those observed on an ocean or lake, except for the restoring force being Coulomb, rather than gravity. They are quasiparticles that results from interactions between plasmons and photons, which is reflected in their energy-momentum dispersion—at low energies, the dispersion is essentially identical to that of free-space photons, diverging as energy increases into a plasmon regime. At energies in the photon regime, the SPPs can couple to photons and propagate away from the metal surface (provided the surface has some roughness); at energies in the plasmon regime, the SPPs are spatially-localized at the surface of the metal.

Plasmonics is the study of waves in the free electrons of a metal. This includes longitudinal density waves, like sound in air, and transverse surface waves, like water waves in the ocean. Much of the research focusses on surface plasmon polaritons (SPPs), which are transverse surface waves in the free electrons at the surface of a metal. SPPs were first proposed in 1957 by Ritchie [39], and experimentally observed in 1959 by Powell and Swan [40]. Significant interest in studying plasmonics developed in 1977 when electric field enhancement at sharp metal edges was found to enhance the signal strength in Raman spectroscopy, a technique used to study the structure of molecules [41, 42]. The new technique was called surface enhanced Raman spectroscopy (SERS). The phenomenon that enabled this electric field enhancement is called localized surface plasmon resonance (LSPR), a topic that has received significant investigation in its own right. Interest in studying plasmonics was raised again in 1998 by the discovery of extraordinary optical transmission [43], where light was observed to be transmitted through subwavelength holes. These holes were too small to allow transmission based on conventional physics, thus demonstrating the plasmonic effect discovered. For a detailed discussion of the physics of plasmonics, a review of the intersection of the relatively new field of plasmonics and the more established field of plasma physics was compiled in 2011 by Wang *et al.* [44].

Figure 3 shows the dispersion of SPPs on Al. The dispersion is plotted for both the Drude model for Al, and for experimental measurements of the dielectric constants of Al. The light line is overlaid on the plot to show the dispersion of freely propagating photons. The expressions for each dispersion are:

(18a)
$$k_{\rm x} = \frac{\omega}{c} \sqrt{\frac{\omega^2 - \omega_{\rm p}^2}{2\omega^2 - \omega_{\rm p}^2}}$$
 (Drude model)
(18b) $k_{\rm x} = \frac{\omega}{c} \sqrt{\frac{\epsilon_{\rm r,Al}}{\epsilon_{\rm r,Al} + 1}}$ (Experimental $\epsilon_{\rm r}$ data)

(18c) $k_{\rm x} = \frac{\omega}{c}$ (light line)

where $k_{\rm x}$ is the wavenumber in the direction along the metal surface, and ω the angular frequency.



FIGURE 3. SPP dispersion of visible and near infrared light on the surface of Al in a vacuum. The solid line shows the dispersion calculated with a dielectric constant of Al from experimental data for epsilon reported in 1998 by Rakic [45]. The dotted line shows the dispersion calculated with a dielectric constant of Al predicted by the Drude model. The dashed line is the light line. Wavelengths of different colored light, and the technologically relevant 1550 nm near infrared light used for telecommunications, are highlighted along the experimental data line.

Although Al was the first metal whose plasmonic properties were studied in depth [46], it has only recently been investigated for applications in nanostructured plasmonic devices [47, 48, 49]. This is a result of fabrication challenges for Al nanostructures [48, 49] and the location of the Al surface plasma resonant frequency in the deep UV [50]; most plasmonics research has focused on visible light manipulation. Noble metals such as Au and Ag have surface plasma resonances in the visible and near-UV [47, 51, 52], respectively, which has made them materials of choice for plasmonic device development. Recent studies, however, have demonstrated resonant modes on Al disks and rectangles [48, 53], as well as improved performance in sensors and photovoltaics using arrays of these structures [54, 55]. Thus, the Al nanowires reported herein may offer a means to further explore such applications, along with a scalable route to manufacturing.

2.6. Methods to fabricate vertically-oriented metal nanowire arrays. Nanowires can be described as one-dimensional-like structures: elongated solids with two dimensions thinner than about a micrometer (μ m). They allow the study of novel physical phenomena and have many technological applications including capture and storage of energy, thermal transport, and sensing. These applications often use arrays of nanowires on flat surfaces, and sometimes specifically require the nanowires to be vertically-oriented rather than randomly-oriented, arranged in lithographically-ordered arrays rather than randomly distributed, or both. Additionally, the nanowires' height, diameter, cross-sectional shape, and the array pitch often must be controlled. Methods exist to exercise much of this control over insulating and semiconducting nanowires, but less control has been demonstrated for metal nanowires, and highlight areas in need of further development. Microwire fabrication is discussed in the context of methods that show promise for adaptation to nanowires.

2.6.1. Introduction. The number of methods to fabricate vertically-oriented metal nanowire arrays is limited, as are the physical dimensions that cannot be produced in a diversity of elements. Most notably, this includes arrays of high aspect ratio, vertically-oriented wires with pitch of a few to tens of micrometers. This contrasts strongly with the numerous techniques for production of non-metal nanowire arrays of nearly any size and shape and made of many different materials. Additionally, to our knowledge, the metal nanowire fabrication methods that do exist have not been recently amassed and critically reviewed. In the review below, we discuss existing state-of-the-art metal nanowire array fabrication techniques and the applications that would benefit from such arrays, and highlight promising routes to expand metal nanowire fabrication capabilities.

Arrays of nanowires, and microwires with diameters several micrometers or less, have been demonstrated as useful nanoarchitectures for tuning many surface properties of materials. For example, the chemical surface energy [56] of a Si substrate was tuned with a randomly-oriented, disordered-array of nanowires by increasing the effective surface area for contact to water, which enhanced the hydrophobic or hydrophillic nature of the surface. For heterogeneous chemical reactions at electrode surfaces, the reaction rate [57] was tuned by adjusting the height of vertically-oriented, lithographically-ordered Si microwire arrays coated by metal hydrogen evolution catalysts, which tuned the catalysts' effective surface area. In another case, the product selectivity [58] was tuned by adjusting the height of randomly-oriented Cu nanowires in disordered arrays, which tuned the local concentration of reactants at the Cu surface during electrochemical CO_2 reduction. In a Li ion battery, the mechanical stability [59] of an Al anode was improved by the presence of space between verticallyoriented Al nanowires in a disordered array. By giving the Al space to expand during Li ion intercalation, grinding between adjacent crystallites, which would pulverize a flat Al film anode, was mitigated. Furthermore, optical properties of a metal surface [60] were tuned with vertically-oriented C nanotubes in a disordered array—the nanotubes, said to act as antennas, specularly reflected only light polarized parallel to them, and scattered only light with a half-wavelength equal to an integer multiple of their length. Finally, thin Ag nanowires have been shown to guide light in the form of propagating surface plasmons [61]; arrays of such wires arranged in the proper manner could provide a means for a sub-diffraction limited optical microscope [15].

In addition to tuning surface properties, the three dimensionality of nanowire arrays has allowed the fabrication of nanocoax devices, made by coating the metal nanowires with a thin insulating or semiconducting film, and then a metal film. With this middle layer as amorphous silicon, a high efficiency solar cell was made—the effective path length of light determined by the nanowire height, and the electron path length by the thickness of the amorphous silicon film [62]. With the middle layer as Al_2O_3 , and the nanowire top polished to expose both the inner nanowire and outer metal film, a high sensitivity biochemical sensor was made [63]. By coating an array of vertical pores with a metal-insulator-metal film, electrical capacitance was increased by the large surface area to create a high energy and high power density energy storage device [64]. Many of these applications, and others [65], require the nanowires to be metallic, but are limited by the geometries accessible with existing fabrication processes. In particular, they are limited by the height, diameter, and cross-section of the nanowires and the pitch and lattice configuration of the array.

The presence of sharp edges on nanostructures can drastically change the physical interactions between them and their environment due to confinement of free electrons at the low radius of curvature. We refer to this phenomenon as sharpedgeonics. In the field of plasmonics, this has been observed in the strong electric field caused by surface plasmon resonance at the tips of metal points, which can be useful for sensing via surface enhanced Raman spectroscopy. For example, Au nanostars with the radius of curvature at their points less than 5 nm showed a 10,000x increase in electric field intensity at these points compared to elsewhere on the stars, when illuminated by 753 nm wavelength light [52]. In another case, surface plasmons excited by 660 nm wavelength light were observed to propagate along ridges of an Al nanowire with approximately 10 nm radius of curvature [33]. In electrochemical catalysis, it has been observed that reduction of CO_2 to higher energy molecules at a high current density occurs at a much lower overpotential, a higher faradaic efficiency, and with more stable operation over time at electrodes containing sharp metal points than at any previously reported catalyst [30, 66]. This is proposed to result from fieldinduced reagent concentration, in which the high local electric field influences the concentration of species in the electrolyte adjacent to the metal tip. For example, forests of Au needles with radius of curvature approximately 5 nm have demonstrated CO_2 reduction to CO at 38 mA/cm² at -0.4 V vs. renewable hydrogen electrode (RHE) for tens of hours [67]. Since the small radius is crucial to these phenomena, and only select fabrication processes can produce such features, devices utilizing such phenomena have few options for fabrication.

The various processes to fabricate metal nanowire arrays can be categorized as coating metal onto non-metal nanowire arrays (Fig. 4a), depositing metal into pores of a template (Fig. 4b), directly growing metal nanowires (Fig. 4c), and etching them out of a bulk metal substrate (Fig. 4d). Each of these approaches has its own merits and limitations, which are discussed below. Suggestions of future research that could expand these capabilities of metal nanowire fabrication are also provided.



FIGURE 4. Cartoon of metal nanowire array fabrication processes that are representative of (a) metal-coating, (b) template, (c) bottom-up growth, and (d) top-down etch methods. Reprinted with permission from ref [33]. Copyright 2015 American Chemical Society.

2.6.2. Metal-coated nanowire arrays. Non-metallic nanowires can be made by several methods, including: mechanical deformation and UV curing of a polymer via NIL with a template (Fig. 5a,b) [68, 63, 26]; bottom-up growth via vapor-liquid-solid deposition (Fig. 5c,d) [69, 70, 71]; and top-down etch via metal-assisted wet etching (Fig. 5e,f) [72, 73, 74, 75] or deep reactive ion etching into bulk material [76]. Local curing of a polymer film via photolithography can produce microwires (Fig. 5g,h) [77, 78, 79], but due to the diffraction limit of light and divergence of the light beam outside the focal plane, high aspect-ratio structures with sub-micrometer diameter cannot be made. These various fabrication methods provide a high degree of control over array geometries—as seen in Fig. 5, lithographically-ordered arrays of vertically-oriented nanowires and microwires have been made with smooth surfaces and consistent cross-sections, with wire diameter, height, and array pitch spanning up to 2 orders of magnitude for each fabrication method. This flexibility of nonmetal nanowire fabrication can be leveraged for metal nanowire arrays by coating them with metal films, but with certain compromises. The "dead-space" created by the non-metal core of the nanowire imposes a minimum diameter on the final metal-coated wire. This creates a trade-off between the metal film conductance and nanowire diameter. The nanowire surface topography is also modified by the metal deposition process. Atomic layer deposition (ALD) is highly conformal, providing the best preservation of underlying topography, but will still round out sharp edges. Historically, ALD has also been restricted to a few of the most noble metals, such as Pt and Ru, but recent work has expanded this to include less expensive metals, such as W [80, 81] and TiN [64]. Electro- and electroless-deposition can conformally coat nanowires, but these methods can accumulate material faster at sharp edges [82] and parts of the nanowires that are more exposed to the electrolyte, resulting in roundedout edges and deformed nanowire topography. Physical vapor deposition (PVD) and chemical vapor deposition (CVD), which spray material up onto a downward-facing

nanowire array, accumulate material at the pillar tops (Fig. 6) [62] and cannot coat the undersides of off-vertical nanowires.



FIGURE 5. Non-metal nanowire and microwire arrays, demonstrating the excellent control over nanowire diameter and height, and array pitch, that is possible for non-metal nanowires. Arrays are fabricated via (a,b) NIL, (c,d) vapor-liquid-solid deposition, (e,f) metal-assisted wet etching, and (g,h) photolithography; imaged via SEM. Panel (a) is reprinted with permission from ref [63]. Copyright 2013 American Chemical Society. Panels (b,c) are reprinted with permission from refs [26] and [70], respectively. Copyright 2016 and 2012 Royal Society of Chemistry. Panel (d) is reprinted with permission from ref [71]. Copyright 2014 The Optical Society. Panels (e,h) are reprinted with permission from ref [75] and [79], respectively. Copyright 2012 and 2007 Institute of Physics. Panel (f) is reprinted with permission from ref [74]. Copyright 2010 John Wiley and Sons. Panel (g) is reprinted with permission from ref [78]. Copyright 2017 MicroChem.



FIGURE 6. Accumulation of material at the top of non-metal nanowires when the material is deposited via PVD and CVD; imaged via SEM. Reprinted with permission from ref [62]. Copyright 2010 John Wiley and Sons.
2.6.3. Solid metal nanowire arrays. Solid-metal nanowire arrays can avoid the compromises associated with metallization of non-metal nanowires, but are restricted to certain geometries and materials that can be accessed by the limited fabrication methods available. Most notably, template-based methods (Fig. 4b) have a limited pitch for nanowires with a high aspect ratio; bottom-up methods (Fig. 4c) have not produced lithographically-ordered arrays; and top-down methods (Fig. 4d) also have pitch constraints. Controlled fabrication of anodized Al oxide (AAO) membranes provides the only mechanism, of which we are aware, to produce nanowires with smooth surfaces, consistent cross-section, high aspect ratio, and arranged in lithographically-ordered arrays, vertically-oriented on a flat surface. For pitch less than 2 μ m, the resulting membrane is used as a template; for pitch greater than 2 μ m, the anodization is a top-down etch.

2.6.4. *Template-based fabrication*. Template-based methods utilize insulator or semiconductor templates with vertical pores. Typically, the template is grown from or adhered to a substrate, its pores filled with metal, and is then dissolved away to yield nanowires on the substrate. Following dissolution of the template, subsequent deposition or etching can adjust the nanowire diameter. As such, the pitch, height, initial diameter, and array lattice-configuration are determined by the template's geometry and its compatibility with metal deposition processes for pore filling. This is a significant restriction, because the several template technologies that have been explored for fabrication of metal nanowire arrays, delineated below, have a quite limited selection of these parameters.



FIGURE 7. Solid metal nanowire arrays fabricated via template-based processes, using an (a,b) AAO template, (c) electron-beam-resist polymer template, and (d) photoresist polymer template; imaged via SEM. Panels (a,b) and (c) are reprinted with permission from refs [83] and [33], respectively. Copyright 2003 and 2015 American Chemical Society. Panel (d) is reprinted with permission from ref [84]. Copyright 2013 Massachusetts Institute of Technology.

Lithographically-ordered AAO template fabrication [85] and subsequent templatebased metal nanowire fabrication [86] have been thoroughly documented [38, 87]. Template thickness as much as 100 μ m [83, 88], pitch from 30 to 2000 nm [89, 90], and pore height-to-diameter aspect ratio as high as 500 have been demonstrated [91]. Metals have been deposited into many of these templates, with subsequent nanowire heights as much as 30 μ m reported (Fig. 7a,b) [83]. One should note that lithographically-ordered templates have only been reported above 150 nm pitch [91, 92]; templates with smaller pitches are only quasi-ordered. Due to a clustering phenomenon (see end of section), the maximum array pitch of 2 μ m translates into a limited height of freestanding nanowires. Track-etch membranes have disordered arrays of pores over a similar range of thickness and pitch to AAO templates, and have been used to make metal nanowire arrays similar to those produced via AAO templates [93, 94].

Electron beam lithography (EBL) has been used to create templates with very precise pore size and placement, but is typically used to make in-plane structures at most a few micrometers thick; the thickest e-beam resist being ~ 5 μ m [95]. Due to the top-down exposure process used to create pores via EBL, scattering of electrons within the dielectric during exposure limits the aspect ratio of the pores. As such, the largest pore or subsequent metal nanopillar aspect ratio is approximately 2 (Fig. 7c) [33]. However, lines of resist have been reported with height-to-separation ratio as high as 5 [96], suggesting the same could likely be accomplished for pores. Of note for EBL is the serial nature of writing patterns, making it time consuming and costly for applications that require larger than square-mm-scale patterned areas.

Photolithography has also been used to create templates with precise pore placement and size. However, as described above, this method is only practical for fabricating high-aspect ratio features with diameters greater than a micrometer. The smallest diameter metal nanowire array we found in the literature was 26 μ m, for 60 μ m pitch and 80 μ m tall microwires (Fig. 7d) [84]. With subsequent etching of metal microwires, though, nanowire arrays with very large pitch (tens-of-micrometers) could in principle be made.

Regarding metal filling of the template, restrictions arise on the nanowire height, material, and deposition process. Top-down deposition processes, such as PVD and CVD, are typically only used to deposit films a micrometer or less thick. Also, accumulation of material at the pore opening can clog it, preventing fabrication of high aspect ratio nanowires. Electrodeposition on conductive substrates and ALD on arbitrary substrates can, in principle, fill pores of any height and diameter. This restricts metal nanowires taller than a micrometer to materials that can be deposited by these methods; some metals such as Ti require specialized procedures for electrodeposition [97], and as mentioned above, ALD is not available for all materials.

The template material used in these processes is typically removed with a liquid solvent or etchant. This can be an issue when the liquid evaporates, because if the nanowire height is too large relative to the pitch and diameter, then the nanowires will cluster due to local attractive forces and lose their freestanding nature [98, 99]. This is demonstrated in the scanning electron microscope (SEM) image in Fig. 8. This clustering prevents application of the nanowire array to many core-shell and nanocoaxial architectures, since common top-down processes, including PVD and CVD, cannot coat the underside of the nanowires. Clustering also impacts applications sensitive to the nanowire geometry, such as the nano-antenna array mentioned above, which requires the nanowires to be vertical and freestanding. The clustering may be circumvented via a critical point dryer, but this extra step may not always be compatible with fabrication processes.



FIGURE 8. Clustering of Si nanowires as a function of separation distance, imaged via SEM. For diameter 160 nm and height 4 μ m, nanowires begin to adhere to each other when brought within 450 nm. Reprinted with permission from ref [99]. Copyright 2014 American Chemical Society.

2.6.5. *Bottom-up growth*. A number of bottom-up growth processes have been developed for solid-metal nanowire arrays. However, it so happens that lithographicallyordered arrays, and nanowires that have smooth surfaces, consistent cross-section, and good conductivity, are presently mutually exclusive for bottom-up growth.

CVD of Ni on Si with a thermal oxide (Fig. 9a–c) [100, 101] and Co on sapphire (Fig. 9d,e) [102] have been shown to produce rectangular cross-section, single-crystal, vertically-oriented nanowires arranged in disordered arrays. Electron diffraction in a transmission electron microscope (TEM) demonstrates the single crystal nature of these nanowires. They are notable for their atomically smooth surfaces composed exclusively of $\{100\}$ facets. It is proposed that they grow at their base, with their morphology controlled by the solubility of Ni (Co) in SiO₂ (Al₂O₃) and the exposed facet of the substrate.

CVD of C (Fig. 9f,g) [103, 104, 105, 106, 107] has produced vertically-oriented carbon nanofibers at Ni nanoparticles distributed on a Si surface. The Ni particles could, in principle, be arranged to produce lithographically-ordered nanowire arrays. However, the fibers have a disordered surface and poor electrical conductivity compared with true metals (where true metals have bulk conductivity at room temperature over 1 MS/m) [108]. The fibers are proposed to grow at their top, where the Ni particle is located, lifting the particle up as they grow [105].

Simultaneous magnetron sputtering of Al_2O_3 and Ag (Fig. 9h,i) [109] has produced disordered arrays of Ag nanowires embedded in Al_2O_3 , vertically-oriented with a smooth surface and consistent cross-section. These nanowires are notable for their small diameter and pitch of 2–3 nm and 6–8 nm, respectively. The Ag nanowires form due to phase separation driven by the low solubility of Ag in Al_2O_3 ; during the initial deposition Ag particles form in an Al_2O_3 matrix, and grow into nanowires during continued deposition. Glancing angle deposition (GLAD) (Fig. 9j,k) [59], has produced vertically-oriented and disordered arrays of Al nanowires with a narrow base, wide top, and rough surface. It uses a traditional PVD chamber, except with the substrate tilted a few degrees offparallel to the deposition beam. When particles randomly nucleate on the surface, they cast shadows on the substrate that prevent deposition adjacent to them. This causes further deposition to be confined to the particles, creating nanowires with their length pointed towards the deposition target. Rotation of the substrate produces the nominally vertically-oriented nanowire arrays, albeit highly disordered.

Thermal stress-induced growth (Fig. 9l,m) [110] of Al nanowires from an Al film sputtered on glass has produced disordered arrays of nanowires with very high aspect ratio, smooth surface, consistent cross-section, and a wide variety of cross-sectional geometries. The nanowires were formed when a 100 nm Al film on glass, heated to 250 °C, had hydroflouric acid (HF) dripped onto it with a concentration of HF:H₂O between 1:100 and 1:200. It was proposed that the heating produces stress in the Al, which is sandwiched between the glass and a native oxide on the Al surface, because Al has a higher thermal expansion coefficient than SiO₂ and Al₂O₃. The HF then etches away small surface contaminants that originated from the glass, opening weak points on the Al₂O₃ surface through which the Al extrudes to relieve the thermal stress (sufficient cleaning of the glass ceased Al nanowire growth). The Al nanowire cross-section is thus likely determined by the geometry of the pore through which it extrudes.

Electrochemical reduction of CuO nanowires (Fig. 9o) [58] has produced disordered arrays of oxide-derived Cu nanowires with a smooth surface and consistent crosssection. The nanowires were formed by immersing a Cu foil into $0.133 \text{ M} (\text{NH}_3)_2\text{S}_2\text{O}_8$ and 2.667 M NaOH to spontaneously grow Cu(OH)₂ nanowires (Fig. 9p,q) [111]. Longer immersion time produced longer nanowires. These Cu(OH)₂ nanowires were annealed at 150 °C in air for 2 hours to create CuO nanowires, which were then electrochemically reduced into Cu nanowires in 0.1 M $\rm KHCO_3$ at -0.7 to -1.1 V vs. RHE.



FIGURE 9. Solid metal nanowires grown via bottom-up processes: (a–c) CVD of Ni on Si with a native oxide, (d,e) CVD of Co on sapphire, (f,g) CVD of C on Ni nanoparticles, (h,i) co-sputtering of Ag and Al_2O_3 , (j,k) glancing angle PVD of Al, (l–n) thermal stress-induced extrusion of Al on glass, (o) electrochemical reduction of CuO nanowires, (p,q) spontaneous growth of Cu(OH)₂ nanowires from immersion of Cu in $(NH_3)_2S_2O_8$ and NaOH; imaged via SEM, except (c,h,i) via TEM. Panels (a–c) are reprinted with permission from ref [100]. Copyright 2010 American Chemical Society. Panels (d,e) are reprinted with permission from ref [102]. Copyright 2015 Royal Society of Chemistry. Panels (f,g) are reprinted with permission from ref [105]. Copyright 1998 American Association for the Advancement of Science. Panels (h,i) are reprinted with permission from ref [109]. Copyright 2016 Institute of Physics—Journals. Panels (j,k) are reprinted with permission from ref [59]. Copyright 2009 Elsevier. Panels (l–n), (o), and (p,q) are reprinted with permission from refs [110], [58], and [111], respectively. Copyright 2014, 2016, and 2003 John Wiley and Sons.

2.6.6. Top-down etching. Top-down processes that etch into metal substrates have produced nanowires via anodization of Al and microwires via reactive ion etching (RIE) of Ti. These wires are vertically-oriented with a smooth surface and consistent cross-section. They are positioned within the array using standard lithography techniques, limited primarily by a minimum demonstrated pitch of 2.4 μ m. Thus, these processes provide the greatest degree of control over array pitch and lattice configuration of any of the solid metal nanowire fabrication processes.



FIGURE 10. Solid metal nanowires etched from metal substrates via top-down processes: (a–c) Anodization of Al and etching away the AAO, (d,e) RIE of Ti with Cl and F gasses; imaged via SEM. Panels (a–c) are reprinted with permission from ref [33]. Copyright 2015 American Chemical Society. Panel (d) is reprinted with permission from ref [112]. Copyright 2010 Institute of Electrical and Electronics Engineers. Panel (e) is reprinted with permission from ref [113]. Copyright 2012 Elsevier.

Anodization of Al and subsequent etching of the Al_2O_3 to produce arrays of Al nanowires (Fig. 10a–c) [33] was demonstrated by our group in 2015 by modifying a recently reported Al anodization procedure [92]. To direct the formation of Al nanowires, NIL was used to pattern a flat Al surface with a hexagonal array of indents of pitch 1.2 μ m: by pressing the Al surface into a glass slide coated by an array of Ni posts, indents were made in the Al at the Ni post positions. At a site in this array where a nanowire was desired, the Ni post was omitted from the stamp so no indent was formed. The Al was then anodized at 480 V relative to a C counter electrode in a solution of ethylene glycol and dilute phosphoric and citric acid, which produced an oxide film on the Al surface. Pores nucleated in the oxide at the indents and etched down vertically into the Al substrate, forming an AAO template with Al nanowires embedded at the sites without indents. As such, an indent array of 1.2 μm pitch containing a super-lattice of missing indents of 2.4 μm pitch produced Al nanowires with 700 nm diameter in an array of 2.4 μ m pitch. A notable property of these nanowires is their very smooth surface and consistent hexagonal cross-section, with sharp edges of ~ 10 nm radius of curvature.

Reactive ion etching (RIE) of Ti, with a mask that blocks etching to create Ti microwires, was first demonstrated in 2009 using toxic Cl gas (Fig. 10d) [114, 115, 116, 112] and more recently using non-toxic F gases (Fig. 10e) [113]. For Cl gas, the Ti substrate was covered by an SU8, TiO₂, or SiO₂ mask, and an Ar/Cl₂ mixture was fed into an inductively coupled plasma (ICP) RIE system. The authors proposed that the mask was etched only by physical bombardment, and produced residues that passivated etching on the Ti surface. The Ti was etched by a combination of physical bombardment and chemical reactions: physical bombardment etched native TiO₂ and residues from the surface to expose Ti; Cl radicals reacted with Ti to produce volatile TiCl₁-TiCl₄ compounds. Due to a more direct line-of-sight from the plasma to the array floor than to the microwire sidewalls, the physical bombardment preferentially

exposed the floor to etching, providing an anisotropic etch rate. As such, high aspect ratio features were made by tuning gas flows, chamber pressure, platen power, and ICP power to maximize the etch rate of Ti relative to the mask. With a SiO₂ mask, this produced microwires with 5 μ m diameter and 50 μ m height in arrays with 10 μ m pitch.

For RIE with the F gases, the Ti substrate was masked by SiO₂ and Al. The authors proposed that the Al blocked chemical etching, and the SiO_2 provided mechanical support to the Al film and adhesion between the Al and Ti. To etch the Ti, a mixture of SF_6 , CHF_3 , and O_2 was fed into a conventional parallel plate reactor system. The SF_6 was the primary etchant of Ti, producing F radicals that reacted with Ti to generate the volatile TiF_4 compound. The CHF_3 produced a flourocarbon polymer that coated the Ti to passivate this chemical etching. The O_2 etched this residue from the Ti surface via physical bombardment, preferentially at the array floor for the reasons explained above. This left the microwire sidewall protected, providing an anisotropic etch rate. Not perfectly anisotropic, though, so the concentration ratio of gasses, total flow rate, and chamber pressure were tuned to maximize the floorto-sidewall etch rate. This produced 5 μ m tall pillars with a square cross-section 5 μ m wide and 5 μ m thick, in an array of 10 μ m pitch. While both the Cl- and F-based processes were used to produce microwire arrays, they were included in this review because there is no reason evident to us they could not be applied to nanowire fabrication; masking the Ti surface with sub-micrometer diameter features would likely produce high aspect ratio metal nanowires with smooth surfaces and consistent cross-section in lithographically-ordered arrays.

2.6.7. *Metal nanowire array fabrication summary*. Arrays of metal nanowires have many technological uses, some of which require vertically-oriented nanowires with smooth surfaces, consistent cross-sections, lithographic control of nanowire placement, and particular nanowire height, diameter, and array pitch. While non-metal nanowire arrays can be produced on length scales from tens to thousands of nanometers with excellent control of their geometry, metal nanowire arrays have significant restrictions on the sizes and shapes that can be made. For some applications, non-metal nanowire arrays can be coated by metal to achieve the desired geometry and function, but not all materials and geometries are compatible with this approach. Fortunately, the past decade has seen significant progress on metal nanowire array fabrication, as demonstrated by the literature cited herein. Based on these developments, promising routes to expand such fabrication capabilities include: increasing the range of AAO template pitch; adding lithographic control over the placement of Ni and Co nanowires grown via CVD; developing chemistries for CVD nanowire growth of a wider variety of elements; developing anodization processes for etching nanowires from a wider variety of elements; refining RIE lithography to produce smaller diameter and pitch; and developing RIE chemistries for etching nanowires from a wider variety of elements. 2.7. Electrocrystallization of metal nanodendrites. Dendrites are branched structures. The mechanics of dendrite growth have been well developed to describe metal solidification from the metal's melt. The growth speed and branch thickness are determined by the balance of the Mullins-Sekerka and the Gibbs-Thompson effects. The former states that sharp protrusions of the solid at the growth front can grow faster due to faster diffusion of heat from the surface; the later that sharp protrusions of the solid will melt more easily than more rounded ones. This has been adapted to dendrite electrodeposition from aqueous solutions [117] via analogy of heat diffusion in melt solidification to metal ion diffusion in electrodeposition.

Experimental, theoretical, and simulation work have produced a series of theories to describe whether crystals will have atomically smooth faceted surfaces or rounded atomically rough surfaces when grown from a solution, vapor, or melt [118]. These studies found the surface stiffness, γ^* , to be the determining characteristic. In 2D, this is defined as $\gamma^* = \gamma + \frac{d^2\gamma}{d\theta^2}$, where γ is the surface energy and θ is the angle along which the curved surface traces an arc-length. In 3D, $\gamma^* = 2\gamma + \frac{\partial^2\gamma}{\partial\theta^2} + \frac{1}{\sin^2(\theta)}\frac{\partial^2\gamma}{\partial\phi^2} + \cot(\theta)\frac{\partial\gamma}{\partial\theta}$, where ϕ is the azimuth and θ the zenith (Eqn. 50). The surface stiffness represents the energy necessary to bend the crystal surface, *i.e.*, the energy to make it rough by having incomplete monolayers of atoms. A large stiffness relative to the deposition temperature resulted in a smooth faceted surface for a given crystal orientation, material, and ambient growth phase.

Studies have found the surface stiffness, in particular its minimum, to also determine the crystal orientation along which dendrites grow. For metals, this is typically $\langle 110 \rangle$ or $\langle 100 \rangle$ [119, 120, 121]. The particular morphology of the growth correlated to the anisotropy factors, ϵ_1 and ϵ_2 , of the surface energy γ . Studies of dendritic solidification from supersaturation of a salt solution demonstrated the faceting of the tips of dendrites [122]. The size of the facets was found to be a function of the dendrite growth velocity. Finally, studies on electrocrystallization since the 1920s [123], and recently of Au electrodeposition [124], have established the reaction energetics (kinetics and thermodynamics) of electrodeposition. This has allowed properties such as the surface energy of Au crystals in aqueous solutions to be determined. A survey of Au electrodeposition using different solutions and applied potentials will reveal both smooth faceted surfaces and rough rounded surfaces on the deposited crystals.

2.7.1. Basic thermodynamics of crystal growth. Substantial experimental and theoretical work has been devoted to describing the mechanisms of crystal growth over the last century. A detailed summary of this work, with thorough explanations of fundamental concepts and few presumptions of previous knowledge about crystal growth, is contained in *Crystal Growth for Beginners* by Markov [118]. The relevant fundamentals needed to describe the crystal growth reported in this thesis are summarized in the sections below.

Crystal growth takes place from the transport of the fundamental components of the crystal, typically atoms or molecules, from an ambient phase surrounding a solid crystalline surface. This ambient phase can be a vapor, solution, or melt containing the material to be crystallized. Crystallization results from changing thermodynamic parameters of the system—such as temperature, pressure, or an applied electric potential—to move in the phase diagram from a phase boundary to the solid phase. As such, the first step to describing crystallization is to derive the phase diagram of the system. In this analysis we notate the internal chemical potential as μ_{in} , defined as $\mu_{in} = (\partial G/\partial N)_{S,V}$, where G is the Gibbs free energy, N the number of particles, S the entropy, and V the volume. We define the electrochemical potential as $\mu = \mu_{in} + zF\varphi$. To start, we consider the simple case of a single component system composed of two infinitely large phases, a and b. At equilibrium, in which the pressure and temperature are located on the phase boundary, the internal chemical potential of the phases are equal,

(19)
$$\mu_{\mathrm{in},\mathrm{a}}(P,T) = \mu_{\mathrm{in},\mathrm{b}}(P,T)$$

Changing the pressure and temperature by an infinitesimal amount, that maintains the equilibrium, gives,

(20)
$$\mu_{\rm in,a}(P,T) + d\mu_{\rm in,a}(P,T) = \mu_{\rm in,b}(P,T) + d\mu_{\rm in,b}(P,T) ,$$

and therefore,

(21)
$$d\mu_{in,a}(P,T) = d\mu_{in,b}(P,T).$$

From the properties of Gibbs free energy (dG = VdP - SdT) we can rewrite (Eq. 21) as,

(22)
$$-s_a dT + v_a dP = -s_b dT + v_b dP$$

where s_{a} and s_{b} are the molar entropies, and v_{a} and v_{b} are the molar volumes of the two phases that are in equilibrium with each other. Rearrangement gives,

(23)
$$\frac{\mathrm{d}P}{\mathrm{d}T} = \frac{\Delta s}{\Delta v} = \frac{\Delta h}{T\Delta v}$$

where $\Delta s = s_{\rm a} - s_{\rm b}$, $\Delta v = v_{\rm a} - v_{\rm b}$, and $\Delta h = h_{\rm a} - h_{\rm b}$ is the enthalpy of the phase transition. For the case of crystallization from vapor to crystal, the subscripts become $a \rightarrow$ vapor and $b \rightarrow$ crystal, and the enthalpy of sublimation, $\Delta h = \Delta h_{\rm sub}$. The molar volume of the crystal is negligible compared to that of the gas, giving $v_{\rm crystal} \approx 0$ and $\Delta v \approx v_{\text{vapor}}$. Assuming the vapor behaves as an ideal gas, $1/v_{\text{vapor}} = P/RT$, we have,

(24a)
$$\frac{\mathrm{d}P}{\mathrm{d}T} = \frac{\Delta h_{\mathrm{sub}}}{T\Delta v} = \frac{\Delta h_{\mathrm{sub}}P}{RT^2}$$

(24b)
$$\frac{\mathrm{d}P}{P\mathrm{d}T} = \frac{\Delta h_{\mathrm{sub}}}{RT^2}$$

(24c)
$$\frac{\mathrm{d}\ln P}{\mathrm{d}T} = \frac{\Delta h_{\mathrm{sub}}}{RT^2}$$

known as the equation of *Clapeyron–Clausius*. For $\Delta h_{\rm sub}$ independent of temperature, Eq. 24c can be integrated to produce,

(25)
$$\frac{P}{P^0} = \exp\left[-\frac{\Delta h_{\rm sub}}{R}\left(\frac{1}{T} - \frac{1}{T^0}\right)\right]$$

where P^0 is the equilibrium pressure at some temperature T^0 . For evaporation from the liquid phase, *i.e.* the material's melt, Eq. 25 would have $\Delta h_{\rm sub}$ replaced by $\Delta h_{\rm evap}$. For melting from the crystal to the liquid phase, the change in enthalpy $\Delta h_{\rm melt}$ would be used. From this result we can construct the phase diagram between the crystal, liquid, and vapor phases. The enthalpy of sublimation is greater than that of evaporation, so the slope of the crystal-vapor phase boundary will be greater than that of the liquid-vapor phase boundary. The molar volume $v_{\rm liquid}$ of the liquid-phase is usually greater than that of the crystal phase $v_{\rm crystal}$, but by a small difference, which causes the crystal-liquid phase boundary slope, dP/dT, from in Eq. 23, to be much larger than the other two boundaries. This allows us to draw the pressure– temperature phase diagram in Fig. 11.



FIGURE 11. Schematic diagram a typical pressure-temperature phase diagram. Reprinted with permission from ref [118]. Copyright 2017 World Scientific.

This phase diagram shows paths for driving crystallization: AA' increasing pressure for crystallization from vapor; AA" lowering temperature for crystallization from vapor; and BB" lowering temperature for crystallization from liquid. Such a shift from the equilibrium point causes an excess concentration of the material in the vapor or liquid phase, termed supersaturation. For the uncharged species considered here, the strength of the driving force can be quantified by the difference in internal chemical potential between constituents of the crystal and those of the ambient phase. As the internal chemical potential of an ideal gas has a logarithmic relationship to pressure $\mu_{in,v} \sim \ln P$, and a crystal has a linear relationship $\mu_{in,c} \sim P$, at pressures below the equilibrium pressure P^0 a crystal will sublimate into a vapor, while at pressures above P^0 the vapor will crystallize, as sketched in Fig. 12.



FIGURE 12. Schematic diagram of internal chemical potential vs. pressure. At P^0 the crystal and vapor phases are in equilibrium with each other. At lower pressures the vapor has a lower potential, and the crystal will sublimate. At higher pressures the crystal has a lower potential and the vapor will crystallize. Reprinted with permission from ref [118]. Copyright 2017 World Scientific.

This difference in internal chemical potential between the vapor and crystal as a function of pressure, for constant temperature, we write as,

(26)
$$\Delta \mu_{\rm in} = \mu_{\rm in,vapor}(P) - \mu_{\rm in,crystal}(P)$$

Since $\mu_{in,vapor}(P^0) = \mu_{in,crystal}(P^0)$, we can rewrite this as,

(27)
$$\Delta \mu_{\rm in} = \left[\mu_{\rm in,vapor}(P) - \mu_{\rm in,vapor}(P^0)\right] - \left[\mu_{\rm in,crystal}(P) - \mu_{\rm in,crystal}(P^0)\right]$$

which for small deviations from equilibrium can be written,

(28)
$$\Delta\mu_{\rm in} \approx \int_{P^0}^{P} \frac{\partial\mu_{\rm in,vapor}}{\partial P} \mathrm{d}P - \int_{P^0}^{P} \frac{\partial\mu_{\rm in,vapor}}{\partial P} \mathrm{d}P = \int_{P^0}^{P} (v_{\rm vapor} - v_{\rm crystal}) \mathrm{d}P \approx \int_{P^0}^{P} v_{\rm vapor} \mathrm{d}P$$

Treating the vapor as an ideal gas, such that $v_{\text{vapor}} = kT/P$, integration provides the relation,

(29)
$$\Delta \mu_{\rm in} = kT \ln \frac{P}{P^0}.$$

Likewise, for crystallization from a solution, in the ideal case, it can be shown that,

(30)
$$\Delta \mu_{\rm in} = kT \ln \frac{C}{C^0} \,.$$

Finally, in the case of electrocrystallization, also referred to as electrodeposition, we add an electric potential to the system and substitute the internal chemical potential $\mu_{\rm in}$ with the electrochemical potential, $\mu = \mu_{\rm in} + zF\varphi$. At the equilibrium potential

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 $\varphi = \varphi^0$, the electrochemical potential of atoms in the crystal and ions in the solution is the same,

(31a)
$$\Delta \mu = \mu_{\rm soln} - \mu_{\rm crystal} = 0 \,,$$

(31b)
$$\mu_{\rm soln} = \mu_{\rm crystal} \,,$$

(31c)
$$\mu_{\rm in,soln} + zF\varphi_{\rm soln}^0 = \mu_{\rm in,crystal} + zF\varphi_{\rm crystal}^0,$$

(31d)
$$\mu_{\rm in,soln} = \mu_{\rm in,crystal} + zF(\varphi^0_{\rm crystal} - \varphi^0_{\rm soln}),$$

(31e)
$$\mu_{\rm in, soln} = \mu_{\rm in, crystal} - zF(\Delta\varphi^0).$$

For an arbitrary potential $\varphi,$ the supersaturation is given by,

(32a) $\Delta \mu = \mu_{\rm soln} - \mu_{\rm crystal} \,,$

(32b)
$$\Delta \mu = (\mu_{\text{in,soln}} + zF\varphi_{\text{in,soln}}) - (\mu_{\text{in,crystal}} + zF\varphi_{\text{crystal}}),$$

(32c)
$$\Delta \mu = \mu_{\text{in,soln}} - \mu_{\text{in,crystal}} + zF\Delta\varphi,$$

(32d)
$$\Delta \mu = (\mu_{\rm in,crystal} - zF\Delta\varphi^0) - (\mu_{\rm in,crystal} - zF\Delta\varphi),$$

(32e)
$$\Delta \mu = zF(\Delta \varphi - \Delta \varphi^0),$$

(32f)
$$\Delta \mu = z F \eta \,.$$

Here, $\eta = \Delta \varphi - \Delta \varphi^0$ is the overpotential, *i.e.* the difference between the applied potential difference $\Delta \varphi$ and the equilibrium potential difference $\Delta \varphi^0$ of the particular metal-solution system.

2.7.2. *Crystal shape*. Considering the variation of Gibbs free energy in a closed system in equilibrium at constant pressure and temperature, and in which surface energy is

isotropic (*e.g.* a liquid droplet in a vapor, or a very small crystallite in vapor, liquid, or solution), we have, for the example of a small crystallite in vapor,

(33)
$$\Delta G = \mu_{\text{in,vapor}} dn_{\text{vapor}} + \mu_{\text{in,crystal}} dn_{\text{crystal}} + \gamma dA = 0.$$

where n_{vapor} and n_{crystal} are the number of moles in the vapor and crystal phases, respectively. Here γ is "the work spent to create reversibly and isothermally a unit area of a new surface, called *specific surface free energy*." [118] We assign the bulk values to the crystal and vapor phase chemical potentials in this equation, and assume the surface energy γA accounts for the finite dimensions of the phases. The system is closed, so $n_{\text{vapor}} + n_{\text{crystal}} = \text{constant}$, $dn_{\text{vapor}} + dn_{\text{crystal}} = 0$, and $dn_{\text{vapor}} = -dn_{\text{crystal}}$. We thus arrive at the expression,

(34)
$$\mu_{\rm in,vapor} - \mu_{\rm in,crystal} = \gamma \frac{\mathrm{d}A}{\mathrm{d}n_{\rm crystal}} \,.$$

Using the relation $n_{\rm crystal} = 4\pi r^3/3v_{\rm crystal}$ provides the Thomson-Gibbs equation,

(35)
$$\mu_{\rm in,vapor} - \mu_{\rm in,crystal} = \frac{2\gamma v_{\rm crystal}}{r} \,.$$

The difference in chemical potential between the two phases is the supersaturation defined above, $\mu_{in,vapor} - \mu_{in,crystal} = \Delta \mu_{in}$, giving,

(36)
$$\Delta \mu_{\rm in} = \frac{2\gamma v_{\rm crystal}}{r} \,.$$

Finally, to consider an electrochemical system with a rounded crystal surface in equilibrium with a solution, we replace the internal chemical potential with the change in electrochemical potential,

(37a)
$$\Delta \mu = z F \eta = \frac{2\gamma v_{\text{crystal}}}{r} \,,$$

(37b)
$$\Delta \varphi^{0,\mathrm{r}} - \Delta \varphi^{0,\infty} = \frac{2\gamma v_{\mathrm{crystal}}}{zFr},$$

(37c)
$$\Delta \varphi^{0,\mathbf{r}} = \frac{2\gamma v_{\text{crystal}}}{zFr} + \Delta \varphi^{0,\infty} \,.$$

Eq. 37a describes the required overpotential η for a crystal of finite radius r to be at equilibrium with the surrounding solution. With the equilibrium electric potential difference of a flat surface $(r \to \infty)$ represented by $\Delta \varphi^{0,\infty}$, Eq. 37c defines the equilibrium electric potential difference of a rounded surface of finite radius r, $\Delta \varphi^{0,r}$. Its a more positive potential by the term $2\gamma v_{\text{crystal}}/zFr$.

The result above shows that the overpotential required to keep a crystal in equilibrium with its surroundings depends on the curvature of its surface. Also, the result shows that the overpotential depends on the surface energy γ , which was assumed to be isotropic for very small crystallites. However, real crystals have anisotropic surface energy, which depends on the crystallographic orientation. Herring's equation [125] relates the difference in electrochemical potential, $\Delta \mu$, to the equilibrium crystal surface radii of curvature R_1 and R_2 , with associated orthogonal polar angles θ_1 and θ_2 ,

(38a)
$$\Delta \mu = \frac{v_{\text{crystal}}}{R_1} \left(\gamma + \frac{\mathrm{d}^2 \gamma}{\mathrm{d}\theta_1^2}\right) + \frac{v_{\text{crystal}}}{R_2} \left(\gamma + \frac{\mathrm{d}^2 \gamma}{\mathrm{d}\theta_2^2}\right)$$

(38b)
$$\Delta \mu = \frac{v_{\text{crystal}}}{R_1} \gamma^* + \frac{v_{\text{crystal}}}{R_2} \gamma^*$$

From this relation, we see that $\Delta \mu$ not only depends on the surface energy γ , but also on the second order rate of change of γ with respect to crystal orientation. We define these combined terms as $\gamma^* = \gamma + d^2 \gamma / d\theta^2$, the surface stiffness. It is a measure of the resistance of the surface to bending—the larger the surface stiffness, the larger the radii of curvature for a given $\Delta \mu$. Thus, for a cusp in the surface energy γ , the surface stiffness γ^* would be infinite. Since $\Delta \mu$ is finite, this would require R_1 and R_2 to be infinite as well. Flat faceted surfaces at crystal orientations with surface energy cusps would be observed for the equilibrium shape of a crystal.

2.7.3. Atomistic description of crystallization. For the sake of clarity and relevance to crystals in this work, we consider the case of a crystal whose components are individual atoms. The surface of such a crystal is composed of a monolayer of atoms whose packing arrangement corresponds to a particular Miller index. If such a monolayer is finite then the underlying layer of atoms will be exposed at its edge, each layer will be called a terrace, and the edge between them a step. The step is thus composed of a row of atoms, and if a particular row of atoms is incomplete, the end of the row is called a kink [118, 126]. Fig. 13 shows a schematic of the surface of a crystal with a cubic lattice, in which atom 1 is part of the lower terrace, atom 2 part of a step, atom 3 at a kink, atom 4 adsorbed to a step, and atom 5 adsorbed to the upper terrace. Atoms in positions 1-3 are considered part of the crystal, and thus denoted surface atoms. Atoms in positions 4 and 5 are simply adsorbed to the crystal surface, and thus denoted adatoms. The terraces have the atomic packing arrangement of one of the close-packed faces of the crystal, which for face-centered-cubic (fcc) crystals corresponds to the low Miller index faces (111) or (100). Crystal faces with a higher index, and a surface normal close to that of one of the densely packed faces, are called vicinal faces. These are composed of a periodic arrangement of steps separating terraces of the close-packed orientation, as shown in Fig. 14.



FIGURE 13. Schematic diagram of terraces, steps, and kinks on a crystal surface. Reprinted with permission from ref [118]. Copyright 2017 World Scientific.



FIGURE 14. Schematic diagram of terraces and steps on a vicinal face. Reprinted with permission from ref [118]. Copyright 2017 World Scientific.

In the models describing crystal growth, an atom joining the crystal is imagined to diffuse from the ambient phase to the crystal surface, adsorb to the crystal surface (atom positions 4 and 5), randomly move about the crystal surface following Brownian motion, and finally bond with the surface atoms at a kink site to become part of the crystal (atom position 3). The kink position is also regarded as the half-crystal position because an atom there has as many saturated as unsaturated bonds. As such, for an infinite crystal surface (*i.e.* large enough that size effects can be neglected), the crystal's surface energy is unchanged by the addition or removal of an atom from the kink site, and a crystal can be constructed or disintegrated one atom at a time. Since the internal chemical potential of a system is defined by the energy to add or subtract one constituent particle, the change in energy of an atom moving from the ambient phase to a kink site defines the internal chemical potential of the crystal. This energy, denoted $\phi_{1/2}$, is equal to the work necessary to break half the bonds of an atom in the crystal bulk, and is thus determined by the crystal lattice symmetry. For a crystal in its vapor, $\phi_{1/2}$ may be taken as approximately equal to the enthalpy of evaporation, $\Delta h_{\rm evap}$, and the internal chemical potential of a crystal with monoatomic vapors can be shown to be,

(39a)
$$\Delta \mu_{\rm in} = kT \ln \frac{P_{\infty}}{P^0}$$

(39b)
$$= \mu_{\text{int},0} + kT \ln P_{\infty}$$

$$(39c) \qquad \qquad = -\phi_{1/2} + kT \ln P_{\infty}$$

(39d)
$$= -\phi_{1/2} + kT \ln\left[\frac{(2\pi m)^{3/2} (kT)^{5/2}}{h^3}\right].$$

where m is the atomic mass and h is Planck's constant.

This energy $\phi_{1/2}$ can be broken into the sum of two parts, $\phi_{1/2} = \phi_{\text{lat}} + \phi_{\text{nor}}$, where the terms are the energy of breaking lateral bonds with surface atoms, and breaking surface-normal bonds with bulk atoms, respectively. Restricting ourselves to nearest neighbor interactions, and considering the fcc close-packed faces (111) and (100), we observe that on the (111) face three lateral bonds and three normal bonds are broken to remove a kink atom, while on the (100) face two lateral bonds and four normal bonds are broken. Thus, while both require breaking six bonds, the adsorption potential $\phi_{1/2}$ is greater on the (100) face than the (111) face. The enthalpy of evaporation or melting, along with the associated activation energy needed to transfer atoms between the ambient phase and crystal, are shown schematically in Fig. 15.

Crystal surfaces that are atomically smooth have no steps, and thus no kink sites. As such, a description of their growth requires details of step formation, which can occur either through nucleation of terraces, or formation of screw dislocation growth fronts. Once one of these is formed, then the growth will proceed via addition of atoms at kink sites, as occurs on a rough surface (in the case of terrace nucleation, repeated nucleation of new monolayers will be necessary). To start, we describe the growth rate of crystals from solution for rough surfaces.



FIGURE 15. Schematic diagram of the free energy of atoms transferred from crystal to ambient phase. The energy difference between the crystal and the ambient phase, Δh , is the change in enthalpy. The energy barrier between the phases, ΔU , is the activation energy needed for crystallization. Reprinted with permission from ref [118]. Copyright 2017 World Scientific.

As described in chapter 3.2.1.2 of Markov's text [118], for growth of crystals from solution, the rate of advancement of steps on a crystal surface can be compared to the rate of diffusion of ions to the crystal surface to determine whether the growth is limited by the kinetics or by the mass diffusion. The kinetics of step advancement depend on the geometry of the particular vicinal surface considered.

Interestingly, a key difference in crystal growth from vapor, solution, and melt is how the atoms transport to the kink site. In vapor the primary flux of atoms to a step is from surface diffusion along a terrace, the flux of atoms directly to a step is negligible compared to the flux to terraces and then along terraces to steps. In solution, the primary flux is of atoms directly to the step site, the flux of atoms from surface diffusion along terraces is negligible [118].

This atomistic description of crystal growth has been reported for electrocrystallization of lead, silver, tin, and cadmium in various electrolytes [127]. Using micrographs and x-ray measurements, the study showed the layer by layer growth of metal crystals during electrodeposition, as well as the different morphologies and growth directions obtained. It was found that a primary determining factor of growth direction was the current density. Dendrites grown at high current densities were found to have similar morphologies to dendrites grown from a melt, a typically rapid process.

2.7.4. Equilibrium shape of crystals. For a crystal at equilibrium with its surroundings, such as a crystal in a vapor, melt, or saturated solution, the crystal's shape will minimize its surface energy. Depending on the material and the deposition environment, this can produce either rounded (atomically rough) surfaces, or faceted (atomically smooth) surfaces. Faceted crystals get enclosed primarily by low energy facets, with higher energy facets cutting off corners of the crystal to reduce the total surface area. This shape can be determined by the Wulff-construction [128, 129]. For crystals in non-equilibrium, such as a growing crystal, the shape is determined by the rate-limiting growth process. This will be either the attachment kinetics or the mass transport of atoms to the crystal surface.

Metal crystals in equilibrium with their vapor have been observed to maintain faceted surfaces up to their melting temperature. However, metal crystals in their melt demonstrate a roughening temperature, above which facets are no longer observed, replaced by rounded atomically rough surfaces.

2.7.5. Jackson α factor for crystal faceting. Whether facets form on a crystal, or the crystal simply has an atomically rough and macroscopically rounded surface, has been described for the case of crystallization from a material's melt, dictated by what is commonly referred to as the Jackon α -factor. Crystal growth from a solution has complexity added by the presence of solvent molecules and other dissolved species, which has hindered a complete description of the formation of faceted surfaces [130]. Several studies specifically discussing the faceting of dendrites have been done over the past two decades [122, 131, 132, 133].

In the formalism for solidification from a melt developed by Jackson, adsorbed atoms will bind to the surface most easily at a step, as this provides a higher coordination environment, and thus a lower energy state. If the atom creates a new terrace, rather than find a step, it will be at a higher energy level, this energy difference defining the barrier to the formation of a step on the surface. The packing arrangement of atoms for a given Miller index determines this barrier energy. Indices with a large barrier energy will tend to form atomically smooth facets, while those with low barrier energy will tend to be atomically rough.

In several publications by Kenneth A. Jackson [134, 130, 135], the relative free energy of a solid surface, $\Delta G_{\text{solid}}/NkT_{\text{melt}}$, effectively the above mentioned barrier energy, is plotted against the surface coverage, $\theta = N_{\text{a,o}}/N_{\text{a}}$, for different values of the α -factor, which is defined below (Fig. 16). The total number of adatom sites on the surface is N_{a} , and the number of sites occupied by adatoms is $N_{\text{a,o}}$. The plot shows that for $\alpha < 2$ there is a minimum in the free energy at half coverage, $\theta = 1/2$, while for $\alpha > 2$ the minimum shifts to the degenerate cases of nearly full or nearly no coverage, $\theta \approx 0$, or 1; thus, a smooth faceted surface would be expected when $\alpha > 2$. (The $\alpha > 2$ case is degenerate because each layer of atoms is identical to the layer above and below it.)



FIGURE 16. Jackson α -factor profiles for relative free energy vs. surface coverage. This plot shows that for $\alpha \leq 2$ the relative free energy of the surface is minimized for half coverage by adatoms (atomically rough surfaces), while for $\alpha > 2$ it is minimized for low surface coverage (atomically smooth, faceted, surfaces). Reprinted with permission from ref [135]. Copyright 2004 John Wiley and Sons.

This α -factor is defined as,

(40)
$$\alpha = \frac{|\Delta S|}{R} \frac{\chi_1}{Z}$$

where ΔS is the change in entropy of an atom upon solidification, R the gas constant, χ_1 the number of nearest neighbor sites within the surface layer, and Z the total number of nearest neighbors that atom would have in the bulk of the crystal. χ_1 can be determined by projecting a lattice plane with a given Miller index through the origin of a crystal structure and counting the bonds-per-atom contained in that plane, as shown for several indices of a face-center-cubic (fcc) crystal in Fig. 17. Table 4 shows values of the χ_1/Z geometric factor for the most typical Miller indices; values for (111), (100), and (110) are consistent with those reported by Jackson [135], values for (211) and (210) are our extrapolation of this method to these higher Miller index facets.




FIGURE 17. Schematic diagrams of fcc surface atom bonding for given Miller indices. The integers (hkl) specify the Miller index of the facet shown in each panel, χ is the number of bonds each surface atom has to adjacent surface atoms, Z is the number of bonds each atom would have in the bulk material.

TABLE 4. χ_1/Z and Jackson α values for several fcc Miller indices. The geometric factor χ_1/Z for each Miller index is multiplied by the change in entropy, $\Delta S/R$, for electrodeposition of Au from an aqueous solution of HAuCl₄, to produce the listed α values.

Miller Index	χ_1/Z	α
(111)	1/2 = 0.5	131
(100)	1/3 = 0.33	87
(110)	1/6 = 0.17	47
(211)	1/6 = 0.17	47
(210)	0 = 0	0

To calculate the α factor for electrodeposition of Au from an aqueous solution of HAuCl₄, we begin by writing the helmholtz energy for each species present in the reduction of Au³⁺(aq) to Au(s),

$$(41a) \qquad \qquad \mathrm{AuCl}_4^{-}(\mathrm{aq}) + 3\mathrm{e}^- \to \mathrm{Au}(\mathrm{s}) + 4\,\mathrm{Cl}^-(\mathrm{aq})\,,$$

(41b)
$$\Delta A_{\rm f}^0: -322.17 \,\frac{\rm kJ}{\rm mol} + 0 \to 0 + 4(-167.15 \,\frac{\rm kJ}{\rm mol}).$$

This results in the change in Helmholtz energy of the system,

(42a)
$$\Delta A^0 = \Delta A_f^0$$
 (products) $-\Delta A_f^0$ (reactants)

(42b) =
$$(\Delta A_{\rm f}^0[{\rm Au}({\rm s})] + \Delta A_{\rm f}^0[4\,{\rm Cl}^-({\rm aq})]) - (\Delta A_{\rm f}^0[{\rm Au}{\rm Cl}_4^-({\rm aq})] + \Delta A_{\rm f}^0[3\,{\rm e}^-])$$

(42c) =
$$\left(0\frac{kJ}{mol} + 4*(-167.15\frac{kJ}{mol})\right) - \left(-322.17\frac{kJ}{mol} + 0\frac{kJ}{mol}\right)$$

(42d) =
$$(-668.60 \frac{\text{kJ}}{\text{mol}}) - (-322.17 \frac{\text{kJ}}{\text{mol}})$$

(42e)
$$= -346.43 \frac{\text{kJ}}{\text{mol}}.$$

The change in Gibbs free energy of the system is,

(43a)
$$\Delta G = -nFE_{\rm rxn}$$

(43b)
$$= -(3)(96485 \frac{\mathrm{C}}{\mathrm{mol}})(-1.002 \mathrm{V})$$

(43c)
$$= 290.03 \frac{\text{kJ}}{\text{mol}},$$

which gives a change in entropy of,

90

(44a)
$$\Delta S = \frac{\Delta A - \Delta G}{T}$$

(44b)
$$= \frac{(-347.43 \frac{\text{kJ}}{\text{mol}}) - (290.03 \frac{\text{kJ}}{\text{mol}})}{293 \text{ K}}$$

(44c)
$$= \frac{-637.46 \frac{\text{kJ}}{\text{mol}}}{293 \text{ K}}$$

(44d)
$$= -2176 \frac{J}{\text{mol} \cdot \text{K}}$$

and an entropy factor in α of,

(45a)
$$\alpha = \frac{|\Delta S|}{R} \frac{\chi_1}{Z}$$

(45b)
$$= \frac{|-2176 \frac{J}{\text{mol·K}}|}{8.3145 \frac{J}{\text{mol·K}}} \frac{\chi_1}{Z}$$

$$(45c) \qquad \qquad = 262\frac{\chi_1}{Z} \,.$$

This entropy change of 262, in units of the gas constant R, for the solidification of Au atoms from a solution, is much larger than values for solidification of a metal from a melt (typically of order 1), and is comparable to the entropy change of polymers solidifying from their melt (typically > 100) [135]. Table 4 combines this with the geometric factor χ_1/Z of several Miller indices to produce the corresponding α values. These values are much larger than 2. Thus, based on the formalism for solidification from a melt, one would expect electrodeposited Au crystals to have atomically smooth faceted surfaces composed of any of the above Miller indices, except for (210). The behavior of (210) can be understood by studying Fig. 17, where one can observe that an atom forming a new terrace would have the same number of bonds as one joining the existing terrace, since none of the surface atoms are bound to each other.

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2.7.6. Criterion of Fisher and Weeks for crystal faceting. The analysis by Jackson is based on the assumption that roughness on a surface is only composed of two monolayers, and that atoms don't leave the crystal, *i.e.* a mean-field approximation. Temkin improved on Jackon's model by allowing for an arbitrary number of incomplete monolayers, but maintained the mean-field approximation. Fisher and Weeks developed a theoretical treatment without the mean-field approximation, which resulted in an expression for the roughening temperature in terms of the surface stiffness of a given crystal face,

(46)
$$kT_{\rm r} = \frac{2}{\pi} \gamma^*(T_{\rm r}) d_{\rm hkl}^2$$

where $d_{\rm hkl}$ is the interplanar distance parallel to the crystal face. The more closely packed a given crystal face is, the larger the interplanar distance, and the higher the roughening temperature will be. For example, on a fcc lattice, $d_{111} = a_0/\sqrt{3} \approx$ $0.6a_0$ and $d_{100} = a_0/2 = 0.5a_0$. Thus, in equilibrium at some $T_{\rm r,low-packing} < T <$ $T_{\rm r,close-packed}$ the most closely packed faces may be atomically smooth, while others will be rough. Slight deviation from equilibrium will lead to growth of the rough regions and their subsequent disappearance, to confine the crystal to only close-packed faces. If the equilibrium is returned, the rough regions should reappear.

To calculate the roughening temperature at different crystal faces, we thus need to calculate the surface stiffness, γ^* , as a function of a orientation relative to the crystal lattice. This has been studied extensively [119], and it has been shown that the surface energy γ can be accurately approximated by expansion into a series of cubic harmonics that includes two anisotropy terms, ϵ_1 and ϵ_2 ,

(47)
$$\gamma(\theta,\phi) = \gamma_0 [1 + \epsilon_1 K_1(\theta,\phi) + \epsilon_2 K_2(\theta,\phi) + \ldots],$$

where the cubic harmonics are combinations of the standard spherical harmonics $Y_{\text{lm}}(\theta, \phi)$ with cubic symmetry [121]. The particular K_1 and K_2 referenced above are,

(48a)
$$K_1(\theta, \phi) = \sum_{i=1}^3 n_i^4 - \frac{3}{5}$$

(48b)
$$K_2(\theta, \phi) = 3\sum_{i=1}^3 n_i^4 + 66n_1^2n_2^2n_3^2 - \frac{17}{7},$$

where $\hat{n} = (n_1, n_2, n_3)$ is the interface normal [120]. In spherical coordinates these have their typical definition,

(49a)
$$n_1 = \cos(\phi)\sin(\theta)$$

(49b)
$$n_2 = \sin(\phi)\sin(\theta)$$

(49c)
$$n_3 = \cos(\theta)$$

From the above calculation of the angular dependence of the surface energy γ relative to the crystal lattice, the surface stiffness tensor can be calculated by the expression,

(50)
$$\gamma^* = 2\gamma + \frac{\partial^2 \gamma}{\partial \theta^2} + \frac{1}{\sin^2(\theta)} \frac{\partial^2 \gamma}{\partial \phi^2} + \cot(\theta) \frac{\partial \gamma}{\partial \theta}.$$

This expression for surface stiffness allows for prediction of the growth direction of crystals. Depending on the relative values of the anisotropy parameters ϵ_1 and ϵ_2 , the orientation of the minimum surface stiffness is shifted, determining the direction of growth. Fig. 18 shows 3D plots of the inverse of the surface stiffness for various values of ϵ_1 and ϵ_2 . The maxima of these 3D plots correspond the to preferential

crystal growth direction. From these plots it is apparent that values near the ϵ_1 axis correspond to $\langle 100 \rangle$ growth, values near the ϵ_2 -axis correspond to $\langle 110 \rangle$ growth, and values between have a more isotropic inverse surface stiffness, allowing for more arbitrary growth directions. Fig. 19 shows phase-field simulation results of dendritic crystal growth for $\epsilon_1 = 0$ to 0.15 at constant $\epsilon_2 = -0.02$. The misorientation angle ϕ is the angle from $\langle 100 \rangle$ to the direction of growth of simulated crystals at the highlighted ϵ_1 values; $\phi = 45^{\circ}$ corresponds to growth in the $\langle 110 \rangle$ direction. Fig. 20 shows the anistropy values for various metal crystals in their melt, and the anticipated growth direction. Dendritic Au crystals, with the values $\epsilon_{1,\text{Au-melt}} = 0.064 \pm 0.011$ and $\epsilon_{2,\text{Au-melt}} = -0.003 \pm 0.002$ calculated by molecular dynamics simulations of Au crystals in their melt [120, 121], should thus have a morphology similar to Fig. 19c. The anisotropy factors for a variety of metals crystallizing from their melt are shown in Fig. 20.



FIGURE 18. Growth direction dependence on anisotropy parameters, ϵ_1 and ϵ_2 . Reprinted with permission from ref [121]. Copyright 2006 Springer Nature.



FIGURE 19. Phase-field simulations for anisotropy parameters, ϵ_1 and ϵ_2 . Reprinted with permission from ref [121]. Copyright 2006 Springer Nature.



FIGURE 20. Anisotropy parameters, ϵ_1 and ϵ_2 , for metal crystals in their melt. Reprinted with permission from ref [121]. Copyright 2006 Springer Nature.

With an expression for surface stiffness in hand, it can be calculated using the mean value of the surface energy, $\gamma_{0,\text{melt}} = 0.786 \text{ eV/nm}^2$ [119] and the anisotropy parameters listed above. The polar and azimuthal angles for evaluating the surface stiffness at given Miller indices can be calculated from the expressions,

(51a)
$$\theta = \arccos\left(\frac{z}{\sqrt{x^2 + y^2 + z^2}}\right)$$

(51b)
$$\phi = \frac{\pi}{2} - \arctan\left(\frac{y}{x}\right)$$

where x = 1/h, y = 1/k, and z = 1/l.

Using this result for surface stiffness γ^* , the measured values of the interplanar separation distance of Au $d_{\rm hkl}$ [136], and making the approximation that they are independent of temperature, we can calculate the angular dependence of the roughening temperature, T_r , with Eq. 84. Table 5 shows these results, and compares the thermal energy for facet roughening to the thermal energy at the melting temperature of Au, 1337 K. From the table it can be seen that many facets should be present on a Au crystal grown from its melt. Fig. 21 and 22 show the calculated inverse surface stiffness for Au in its melt for the values of $\gamma^*_{0,\rm Au-melt}$, $\epsilon_{1,\rm Au-melt}$, and $\epsilon_{2,\rm Au-melt}$ defined above.

Miller Index	$d_{\rm hkl}$	θ	ϕ	γ^*	$k_{\rm B}T_r$
	(nm)	(rad)	(rad)	(eV/nm)	(eV)
(111)	0.235	0.304π	$\pi/4$	1.70	0.400
(100)	0.203	$\pi/2$	0	1.16	0.236
(110)	0.1436	$\pi/2$	$\pi/4$	1.75	0.251
(311)	0.1225	0.403π	0.398π	1.43	0.176
(111)(2)	0.1173	0.304π	$\pi/4$	1.70	0.200
(100)(2)	0.1016	$\pi/2$	0	1.16	0.118
(331)	0.0933	0.426π	$\pi/4$	1.73	0.161
(210)	0.0909	$\pi/2$	0.352π	1.50	0.137
(211)	0.0830	0.366π	0.352π	1.59	0.132
(511)	0.0783	0.438π	0.437π	1.27	0.100
(111)(3)	0.0783	0.304π	$\pi/4$	1.70	0.133
$k_{\rm B}T_{\rm melt}$					0.12

TABLE 5. Interplanar separation distances, $d_{\rm hkl},$ for several fcc Miller indices of Au. Values measured Ref. [136].



FIGURE 21. Inverse surface stiffness of Au crystal in a Au melt. The maxima in the plot of the inverse surface stiffness show the direction of growth of Au crystals in their melt.



FIGURE 22. Inverse surface stiffness of Au crystal in a Au melt—polar plot. The maxima in the plot of the inverse surface stiffness show the direction of growth of Au crystals in their melt.

The same process can be carried out for a Au crystal in its vapor. Here $\gamma_{0,\text{vapor}} = 6.16 \text{ eV/nm}^2 [137].$

To determine the growth direction and faceting of Au crystals grown via electrodeposition from HAuCl₄, we must determine specific surface energy $\gamma_{0,Au-HAuCl_4}$ and the anisotropy parameters $\epsilon_{1,Au-HAuCl_4}$ and $\epsilon_{2,Au-HAuCl_4}$. $\gamma_{0,Au-HAuCl_4}$ is the difference in the chemical potential between the crystal surface and the solution. For electrochemical deposition, this difference is,

(52)
$$\Delta \mu = kT \ln\left(\frac{C}{C^0}\right) + zq\Delta\varphi,$$

where C is the bulk concentration, C^0 is the saturation concentration, and $\Delta \varphi$ is the electric potential between the solution bulk and the crystal.

To determine the anisotropy parameters, we can consider the polar plots of the first two cubic harmonics, K_1 and K_2 , shown in Fig. 23 and 24. It is clear from these plots that the 1st harmonic represents higher than average surface energy in the $\langle 100 \rangle$ directions, and lower than average surface energy in the $\langle 111 \rangle$ directions. Likewise, the second harmonic represents surface energy maxima in the $\langle 111 \rangle$ directions, and minima in the $\langle 110 \rangle$ directions. Thus, a rough estimate of the relative magnitude of $\epsilon_{1,Au-HAuCl_4}$ and $\epsilon_{2,Au-HAuCl_4}$ should be attainable by calculating $\gamma_{100,Au-HAuCl_4}$, $\gamma_{110,Au-HAuCl_4}$, and $\gamma_{111,Au-HAuCl_4}$. Comparison of the experimental observation of crystal growth direction and morphology with the calculated growth directions in Fig. 18 and calculated morphologies in Fig. 19 can also provide a measure of the anisotropy parameters. From these and the average surface energy, the surface stiffness can be calculated, and predictions made of the expected crystal faceting.



FIGURE 23. Polar plot of the first cubic harmonic, K_1 . This harmonic accounts for higher than average surface energy on crystal faces with surface normal in the $\langle 100 \rangle$ orientations, and lower than average in $\langle 111 \rangle$ orientiations.



FIGURE 24. Polar plot of the first cubic harmonic, K_2 . This harmonic accounts for higher than average surface energy on crystal faces with surface normal in the $\langle 111 \rangle$ orientations, and lower than average in $\langle 110 \rangle$ orientiations.

Regarding the dendritic crystal growth directions, plotted in Fig. 18, the angle between adjacent maxima for $\langle 100 \rangle$ growth is 90° and for $\langle 110 \rangle$ growth is 60°. The case for the $\langle 110 \rangle$ is somewhat more difficult to visualize, which Fig. 25 of an offset (111) plane bisecting 6 $\langle 110 \rangle$ directions may help with.



FIGURE 25. Angle between adjacent $\langle 110 \rangle$ directions. An offset (111) plane bisects six $\langle 110 \rangle$ directions, clearly showing that the angle between these adjacent directions is 60°.

As described above, for an fcc crystal, a kink atom has a different number of lateral bonds to surface atoms and normal bonds to bulk atoms on different faces: the {111} face has three lateral bonds and three normal bonds; the {100} face has two lateral bonds and four normal bonds; the {110} face has one lateral bond and five lateral bonds. This makes the adsorption potentials have the relative values of $\phi_{110} > \phi_{100} > \phi_{111}$, and thus the surface energy γ_{hkl} have the same order. As such, the {110} face has the largest surface energy (is the most energetically stable, involving the greatest change in chemical potential for atoms transitioning from between the crystal and ambient phase). $\gamma_{100} > \gamma_{111}$ corresponds to a positive ϵ_1 factor in front of K_1 ; $\gamma_{110} > \gamma_{111}$ corresponds to a negative ϵ_2 factor in front of the K_2 cubic harmonic. This is consistent with the reported molecular dynamics simulations of metal fcc crystals in their melt [120, 121]. The relative magnitudes of these anisotropy factors for the case of electrodeposition is then most easily determined by comparison of the observed growth direction and morphology with simulation results [121].

Application of this formalism to electrodeposition is challenging, as the exchange of atoms between the crystal and solution requires the flow of charge between electrodes, which is externally controlled by a power supply, and which is hindered by large activation energy barriers.

Nucleation experiments have been conducted to measure the specific surface energy γ of different crystal faces in either a melt or vapor environment. For example, the surface energy of the {111} face on Ge was measured as 251 erg/cm² in its melt, and 1100 erg/cm² in its vapor. For the interplanar distance $d_{111} = 0.326$ nm, this gives the roughening temperatures $T_{\rm r,melt} = 1150$ K, and $T_{\rm r,vapor} = 5000$ K. As the melting temperature of Ge is 1210 K, crystals in their melt will be rounded, while those in their vapor will be faceted up to high temperatures [118]. Nucleation experiments for Au crystals in HAuCl₄ have not been done. They are difficult to do, since it is difficult to prepare an atomically smooth electrode surface of a single Miller index.

2.7.7. Single crystal Au bead electrode fabrication. Monocrystalline microelectrodes for electrochemical measurements can be fabricated by heating the end of a metal wire, causing it to melt and form a bead [138]. {111} facets are visible via optical microscopy or SEM, allowing the control of the crystal orientation relative to a capillary tube or polisher. Between the {111} facets is a rounded atomically rough surface.

2.7.8. Voltammetric profiles of Au electrodeposition. Voltammetric profiles of Au electrodeposition provides information on the nucleation and growth of Au crystals [118, 139. Specifically, it provides information on the energetics of the deposition—the rate of nucleation and deposition at different applied potentials. This provides information on the energy barriers to nucleation and growth, the growth mechanism, the surface energy of the crystal, and the crystallographic orientations of the growth direction and faceted surfaces. Special electrolytic cells have been designed, in which a seed particle is placed in a capillary, oriented with a desired Miller index facing the capillary opening, as shown in Fig. 26. Electrodeposition onto the particle fills the capillary with a metal surface that grows towards the capillary opening. With the proper metal, electrolyte, and deposition potentials this surface can be made atomically smooth with few to no defects. This allow for measurement of the energy necessary to deposit a new atomic layer [118]. More simply, if one has a crystal with a flat and atomically smooth surface, it can be dipped onto the surface of an electrolyte to wet only the flat crystal surface [139]. Lifting the crystal back up slightly ensures only contact with the flat surface, as shown in Fig. 27.



FIGURE 26. Schematic of seed growth in capillary method for electrocrystallization experiments. Reprinted with permission from ref [140]. Copyright 1964 Elsevier.



Abb. 1. Prinzip der Messanordnung: S: Spannfutter aus. Teflon mit Überwurf U; K: Kontaktblech, leitend verbunden mit Kontaktring R; G: Gewindestab; BE: Luggin-Kapillare der Bezugselektrode.

FIGURE 27. Schematic of dipping method for electrocrystallization experiments. Reprinted with permission from ref [139]. Copyright 1976 Elsevier.

Another approach often used for electrocrystallization experiments is deposition of a metal onto a different material. This provides information about the interface energy between the two materials, as seeds form. Also, as the seeds grow, information about the metal deposition onto itself can be observed. Fig. 28 shows a CV measurement of Au deposition onto glassy carbon [124]. Insight into the reaction mechanism of Au deposition from HAuCl₄ was reported in a recent study comparing aqueous and ionic liquid electrolytes for Au electrodeposition from the gold complexes tetrachloroaurate (III) (AuCl₄⁻) and dicyanoaurate (I) (Au(CN)₂⁻) [141]. Specifically, in aqueous solutions, the reduction of AuCl₄⁻ to metallic gold was reported to take place via a three-electron process,

(53)
$$\operatorname{AuCl}_{4}^{-}(\operatorname{aq}) + 3e^{-} \rightarrow \operatorname{Au}(s) + 4\operatorname{Cl}^{-} E^{0} = 1.002 \,\mathrm{V} \,\mathrm{vs.} \,\mathrm{NHE}.$$



FIGURE 28. CV of electrodeposition of Au onto a glassy carbon electrode from 1 mM $AuCl_4^-$ + 100 mM $HClO_4$. Reprinted with permission from ref [124]. Copyright 2008 Elsevier.

2.7.9. Kinetically limited crystal growth. Literature on the homogeneous growth of Ag nanoparticles from solution (24 mM AgNO₃ in the reducing agent ethylene glycol, with polyacrylamide to slow the reduction of Ag⁺) [142, 143] has shown that in kinetically controlled growth, plates with {111} facets can be produced. Stacking faults and/or twin defects at the particle edges provide favorable growth sites over the {111} facets, provided the concentration is low enough that nuclei will not be able to grow autocatalytically into lower-energy polyhedral structures. Plates with the same exposed facet and hexagonal shape were also observed from electrodeposition with a 3 mM AgNO₃ solution [144]. Similarly, Au plates with {111} facets have been produced from solution (14.7 mM HAuCl₄ and ortho-phenylenediamine in aqueous solution, the later a reducing agent) [145]. In our work, Au plates were produced via electrodeposition with a 20 mM HAuCl₄ solution. As discussed in more detail in chapter 4, we believe it is reasonable to expect that a similar kinetically limited growth mechanism is responsible for their morphology.

2.7.10. Microscopic solvability theory of dendritic growth. Significant research has been conducted on the phenomenon of dendritic growth. Original work focussed on crystal growth driven by super-cooling a molten material—that is, dropping the temperature of the melt below the freezing point to cause rapid solidification of the material. If a surface of the melt is dropped below the freezing point, then solidification begins on that surface and propagates through the melt. At the solidification front, heat is released by the phase change from liquid to solid. This locally raises the temperature, hindering further solidification until the heat is conducted away. As such, the velocity of the solidification front is determined by the material's thermal conductivity. To first order, the morphology of this surface is determined by two competing effects: the Mullins-Sekerka instability and the Gibbs-Thompson effect. The Mullins-Sekerka instability is the observation that if a protrusion forms on the solid at the solidification front, it will extend into the heat-diffusion field towards cooler material, and heat released from the phase-change can be dissipated approximately spherically into this surrounding volume, rather than linearly as would occur at a flat solidification front. The enhanced heat dissipation favors growth of the protrusion over growth on the surrounding flat surface; taken to its logical extreme, this suggests that a solidification front should be composed of many infinitely thin spikes. The Gibbs-Thompson effect is the observation that if a protrusion forms, the surface energy is increased by the increased surface area—the sharper the point, the greater the surface area, and thus the greater the surface energy. This favors growth of a flat solidification front over protrusions. The balance of these two effects selects a diameter and density of protrusions that will propagate into the melt, forming dendrites. Additionally, materials with anisotropic surface energy, such as crystals, have crystallographic directions in which dendrites tend to grow, as described in the discussion above about surface stiffness γ^* .

This formalism, originally developed for crystallization from melts and vapors, has been adapted to solidification of metal ions from a liquid electrolyte onto an electrode by an electric potential, *i.e.* electrodeposition [117]. Here, the solidification front velocity is determined by the diffusion of ions through the liquid. The Mullins-Sekerka instability applies as before; if a protrusion forms, it extends into the diffusion field and gains access to a higher concentration of ions in solution, which will cause more rapid growth. Likewise for the Gibbs-Thompson effect, surface energy is still minimized for a flat surface, opposing the formation of protrusions. Anisotropy in the surface energy, with regard to the crystallographic orientation, will cause growth in particular directions.

Flanders [117] detailed in a recent review how dendritic growth in electrodeposition can be described mathematically. The following is a summary of those results, as to lay a foundation for discussion of the dendrite growth observed in our study. We discuss the particular case of Au deposition from an aqueous solution of HAuCl₄, but the approach is general for electrodeposition of a number of other metals. Flanders took as a starting point the electrochemical potential μ of the metallic cation in solution, the diffusion equation, Fick's law of mass transport, and Poisson's equation for the electric potential,

(54)
$$\mu(r,t) = k_{\rm B}T \ln C(r,t) + zq\varphi(r,t)$$

(55)
$$\dot{C}(r,t) = -\nabla \cdot \boldsymbol{j}(r,t)$$

(56)
$$\boldsymbol{j}(r,t) = -\frac{DC(r,t)}{k_{\rm B}T}\nabla\mu(r,t)$$

(57)
$$\nabla^2 \varphi = -\frac{1}{\epsilon \epsilon_0} \sum_{\mathbf{k}} q z_{\mathbf{k}} C_{\mathbf{k}} \,.$$

Here μ is the electrochemical potential, $k_{\rm B}$ boltzmann constant, T temperature, CAu ion concentration in the electrolyte, z valence of the cation, q elementary charge, φ electric potential, r distance from the solidification front, t time, j current density, D diffusion constant, ϵ dielectric constant of the solution, ϵ_0 free space permittivity, and k an index for all the ionic species. C, μ , φ , and j are all dependent on position r and time t, which we subsequently assume as implicit. It is common to see Eq. 54 substituted into Eq. 56, and Eq. 56 into Eq. 55 to produce the Nernst-Planck equation,

(58)
$$\dot{C} = D\nabla^2 C + \frac{Dzq}{k_{\rm B}T}\nabla C\nabla\varphi + \frac{Dzq}{k_{\rm B}T}C\nabla^2\varphi.$$

Several boundary conditions are assumed in the following derivation: conservation of mass (Eq. 59), infinitely fast surface attachment kinetics (*i.e.* local thermal equilibrium) (Eq. 60), and the far field boundary condition which says that many microns from the working electrode, labeled $r = \infty$, the electrochemical potential μ is equal to that of the grounded electrode (Eq. 61):

(59)
$$\hat{n} \cdot \boldsymbol{j}_{\text{int}} = -\hat{n} \cdot \boldsymbol{v}(t) [\rho_{\text{m}} - c_{\text{int}}], \mu(r, t)$$

(60)
$$u_1 = \Delta(t) - \tilde{\gamma} \kappa \rho_{\rm m}^{-1}$$

(61)
$$\mu(r=\infty,t) = \mu(L,t)$$

where $\boldsymbol{v}(t)$ is the growth velocity, $\rho_{\rm m}$ number density of the metallic crystal, and "int" specifies the interface.

Making the assumptions that there is no electric potential drop in solution (*e.g.* if a supporting electrolyte is added), that the surface stiffness is zero (*i.e.* the surface energy is isotropic), and that the system is quasi-static (with a slow solidification front velocity relative to Au ion diffusion), allows the Nernst-Planck equation (Eq. 58) to be reduced to,

(62)
$$(\nabla^2 C + C \nabla^2 \bar{\varphi}) = 0$$

where $\bar{\varphi} \equiv \frac{2q}{k_{\rm B}T} \varphi$. The Debye-Hückel approximation simplifies Poisson's equation (Eq. 57) to $\nabla^2 \bar{\varphi} \approx \lambda_D^{-2} \bar{\varphi}$, where $\lambda_D = (\frac{2c_{\infty}q^2}{\epsilon\epsilon_0 k_{\rm B}T})^{-1/2}$.

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Au dendrites have been observed to grow approximately as paraboloids-of-revolution at their solidification front; thus, a parabolic coordinate system was used, with coordinates $\eta_{\text{p.c.}}$, $\xi_{\text{p.c.}}$, and $\phi_{\text{p.c.}}$ related to the cartesian coordinates by,

(63a)
$$\xi_{\text{p.c.}} = r + z$$

(63b)
$$\eta_{\rm p.c.} = r - z \,,$$

(63c)
$$\phi_{\text{p.c.}} = \arctan(\frac{g}{x})$$

where $r^2 = x^2 + y^2 + z^2$.

Assuming that near the solidification front the concentration of Au ions is approximately equal to the saturation concentration, the simplified Nernst-Planck equation (Eq. 62) and the conservation of mass boundary condition (Eq. 59) yield an expression for the growth velocity at a dendrite tip,

(64)
$$v = \frac{2D}{R\ln\left(\frac{\xi_{\text{p.c.},\infty}}{R}\right)} \frac{C_{\text{sat}}}{\rho_{\text{m}} - C_{\text{sat}}} (\Delta_1 - \bar{\varphi^0})$$

where \mathcal{R} is the radius of the dendrite tip, $\xi_{\text{p.c.},\infty}$ the parabolic surface where $\mu = \mu_{\infty}$, C_{sat} the saturation concentration of Au ions in solution, Δ_1 the bulk salt concentration, and $\bar{\varphi}_0$ the electric potential applied between the electrodes. Setting $\xi_{\text{p.c.},\infty} \to \frac{2D}{v}$ and defining what's known as the Péclet number to be $\mathcal{P} \equiv \frac{v\mathcal{R}}{2D}$ produces,

(65)
$$(\Delta_1 - \bar{\varphi^0}) = \frac{\rho_{\rm m}}{c_{\rm sat}} \mathcal{P} \ln \mathcal{P} \,.$$

The expression above shows that the bulk ion concentration (Δ_1) and applied potential $(\bar{\varphi^0})$ determine a unique \mathcal{P} value, and thereby the product $v\mathcal{R}$, but not specific dendrite tip growth velocity v or radius \mathcal{R} . This result is called the Ivantsov relation, and was originally developed for the supercooled melts.

To determine the specific v and \mathcal{R} values, a relation known as the solubility criteria was developed for thermal melts,

(66)
$$\gamma = \frac{2d_0D}{v\mathcal{R}^2}$$

where γ is the stability parameter, and d_0 is the capillary length. The stability parameter is defined as $\gamma = \gamma_0 \varepsilon^{7/4}$, where γ_0 is approximately unity, and ε characterizes the anisotropy of the surface energy of the dendrite. For example, a crystal with four-fold symmetry may have its surface energy approximated as $\gamma = \gamma_0(1 + \varepsilon \cos 4\theta)$, where γ_0 is a constant that, in this case, equals the average surface energy of a cubic crystal. Notably, it follows from the derivative in the definition of the surface stiffness γ^* that anisotropy in the surface energy has a pronounced effect on the anisotropy of γ^* . For example, in the cubic crystal with $\varepsilon = 1$, $\gamma = \gamma_0(1 + \cos 4\theta)$, $\gamma^* = \gamma + d^2\gamma/d^2\theta = \gamma_0(1 - 15\cos 4\theta)$. Flanders adopts the above solubility criteria for the electrodeposition without derivation, on the assumption that a similar relation of $\gamma \approx 1/v\mathcal{R}^2$ exists. With both Δ_1 and γ , the growth velocity v and dendrite radius \mathcal{R} are uniquely determined.

2.7.11. Dendrite growth via MHz oscillation. The above derivation is for an applied potential constant in time, *i.e.* deposition under direct current (DC) conditions. By applying an oscillating potential, the values Δ_1 and γ vary with time, requiring a non-stationary theory of dendritic solidification to describe their growth and resulting morphology. The expression for the dendrite growth velocity v derived above (Eq. 64) shows that it is directly proportional to the applied potential $\overline{\varphi^0}$. The Ivantsov relation (Eq. 65) shows that v and \mathcal{R} are anti-correlated. For a high frequency oscillating potential, in which the time of one period is less than the time for deposition of a monolayer of Au, a time-averaged frequency-dependent growth velocity v and dendrite radius \mathcal{R} can be expected to result. This has indeed been observed in experiments [146]. To describe this, Flanders assumed spherical symmetry, and the electrochemical potential μ (Eq. 54) was plugged into Fick's law of mass transport (Eq. 56) to produce,

(67)
$$\boldsymbol{j}(r,t) = -D\nabla C - \frac{DzqC}{k_{\rm B}T}\nabla\varphi.$$

The approximation that $\nabla \varphi \approx 0$ was made to simplify the above expression, based on the assumption that the potential had little spatial variability across the thickness of the Au ion diffusion layer. The diffusion equation (Eq. 55) was used to substitute for \boldsymbol{j} and produce the expression,

(68)
$$\frac{\partial C}{\partial t} = D\nabla^2 C \,.$$

Defining the deviation of the Au ion concentration at a given position, C, from the bulk ion concentration, C_{bulk} , we have $C_{\delta} = C_{\text{bulk}} - C$. Using this, we can define the following boundary conditions:

(69a)
$$C_{\delta}(r \to \infty, t) = 0$$
,

(69b)
$$C_{\delta}(r,0) = 0,$$

(69c)
$$C_{\delta}(\mathcal{R}, 0) = C_{\text{bulk}} - C_{\text{int}},$$

where $r = \mathcal{R}$ denotes the solution-sphere interface and $r = \infty$ denotes the bulk of the solution. C_{int} is the Au ion concentration at the sphere-solution interface. Applying

these boundary conditions to the mass transport equation (Eq. 68) gives the general solution,

(70)
$$C = C_{\text{bulk}} - (C_{\text{bulk}} - C_{\text{int}}) \frac{\mathcal{R}}{r} \operatorname{erfc}\left(\frac{r - \mathcal{R}}{\sqrt{rDt}}\right)$$

where erfc is the complementary error function. This is the main result produced by Flanders. Plotting the ion concentration against the radial position, with the solutionsphere interface at $r = 0.10 \,\mu$ m, for the deposition half-cycle times, t, of 0.14, 0.2, 0.33, 0.5 and 1 μ s produced Fig. 29. These half-cycle deposition times correspond to 0.5– 3.5 MHz voltage waveform frequencies, used in several experiments [146]. From this plot, it is evident that the time-averaged Au ion concentration near the solidification front is higher for higher frequency oscillations. Faster oscillations allow less time for this layer to grow, maintaining a higher average AuCl₄⁻⁻ concentration at the Au surface; the concentration is assumed to replenish during the off half period. This causes a faster solidification front velocity, v, and thus a smaller tip radius \mathcal{R} . As the deposition half period of a 20 MHz oscillation provides a sub-monolayer of deposition, the time averaged concentration likely acts as an effective deposition concentration for crystal growth. Varying the solution concentration, applied potential, and frequency has produced dendrites of different morphologies, such as thin wires whose diameter decreased and growth velocity increased with increasing concentration and frequency.



FIGURE 29. Ion concentration profile. Au ion concentration profile plotted against the radial position, using spherical coordinates centered on the dendrite tip. Reprinted with permission from ref [146]. Copyright 2007 IOP Publishing.

In this work, by using a square wave oscillation with $\varphi_{\rm pp} = 8\varphi_{\rm offset}$, and $\varphi_{\rm offset}$ between -0.5 and -2 V, the average concentration of AuCl₄⁻ at the surface of a growing crystal can be controlled. Note, the counter electrode is a Pt wire, at which the water splitting reaction is likely taking place to produce O₂, pinning it at +1.23 V vs. RHE; the reduction potential of AuCl₄⁻ is 1.002 V vs. RHE, so the $\varphi_{\rm offset} = -2$ V vs. the counter electrode provides an overpotential of magnitude 1.77 V minus the approximately 0.3–0.5 V of overpotential needed to drive the oxygen evolution, and the $\varphi_{\rm offset} = -0.5$ V vs. the counter electrode an overpotential of magnitude 0.27 V.

2.7.12. Dendrite growth with faceted tips. The above model draws strongly on the literature that describes dendritic growth during solidification of materials from their melts [147]. In many of these studies, the melt is confined between two barriers, often glass plates $\approx 10 \text{ x} 10 \text{ cm}$ separated by $\approx 1 \text{ mm}$, to confine the solidification to a 2D plane and allow observation of the growth front. These experiments have shown preference for growth along certain crystallographic directions. For example, when the seed for crystal growth has its $\{100\}$ direction tilted by θ_0 from the growth direction of the crystal, \hat{n}_{dend} , the dendrites will grow at an angle $\theta < \theta_0$ from the growth direction. If the seed is oriented with the $\{111\}$ along the growth direction, then "seaweed" structures were observed rather than dendritic ones. Thus, the anisotropy of the surface tension of the crystal plays an important role in the growth of the dendrites. These cannot result from anisotropy in the electrodeposition reaction kinetics, because they can be assumed instantaneous at all Miller indices relative to the diffusion-limited growth rate. When the attachment kinetics are rapid relative to the rate of mass transport of solute to the crystal surface, the solid-liquid interface can be considered to be locally in thermodynamic equilibrium [121]. Attachment kinetics thus being isotropic, the growth direction of the crystal is determined by anisotropy in the solidliquid interfacial energy, $\gamma(\hat{n}_{dend})$. To first approximation, the growth is assumed to progress in the direction of lowest "capillary forces", i.e. lowest surface stiffness, for which additional layers of atoms can most easily be added. In thermal dendrite growth, the capillary length, $d_0 = \gamma^*/L$, where L is the latent heat per unit volume. For clarity, attachment kinetics refers to the desolvation and charge transfer process of integrating a Au ion from solution onto the metal electrode surface. Capillary forces then determine where on the crystal surface these atoms are integrated into the crystal.

The results of molecular dynamics simulations of Au solidifying from its melt show that it should have dendritic growth in the {100} direction [121]. Crystal growth on facets occurs by propagation of steps along the surface, adding monolayers of material. This depends critically on the density of active step sources, such as crystal lattice defects (dislocations) intersecting the interface. These slow, nonlinear kinetics often leads to very unsteady growth regimes [148, 147]. In weakly faceted systems, macroscopic facets present a high mobility even at small undercooling, and grow in a similar way to atomically rough regions of the solid-liquid interface.

"If a given macroscopic surface of a crystal does not coincide in orientation with some portion of the boundary of the equilibrium shape, there will always exist a hilland-valley structure which has a lower free energy than a flat surface, while if the given surface does occur in the equilibrium shape, no hill-and-valley structure can be more stable." [128]

Literature on the growth of NH₄Br faceted dendrites from super saturated aqueous solutions of ammonium bromide showed the formation of {110} facets at the dendrites tips, for growth in the {100} direction [122]. A power law, $\lambda \approx v^{-0.5+0.1}$, was observed between λ , a measure of the facet size relative to the tip's radius of curvature, and v, the velocity of the dendrite growth. This is amongst a small body of literature on dendrites with faceted tips.
2.8. Electrochemical CO₂ reduction reaction.

2.8.1. CO_2 reduction reaction cell design. Electrochemical cells for CO_2 reduction strongly resemble electrolyzer cells used to split water into oxygen and hydrogen gas. There are typically two compartments separated by a proton exchange membrane (PEM). Nafion, a fluoropolymer composed of a teflon backbone with perfluorovinyl ether groups terminated in sulfonate groups, is commonly used for the PEM. It has good mechanical and thermal stability, is not porous to water or anions, can conduct protons via hopping between sulfonate groups, and can be tuned to have different pore sizes that allow conduction of cations.

The two compartments are typically filled with the same electrolyte, such as potassium or sodium bicarbonate, and CO_2 gas is bubbled through the electrolyte in both compartments to saturate it with dissolved CO_2 . Stir rods are typically included to keep the solution well mixed. In each compartment an electrode is immersed in the electrolyte; the electrode at which electrons leave the solution is designated the anode, and the opposing electrode where electrons enter solution the cathode. A positive potential is applied to the anode, which is coated in an oxygen evolution catalyst and thus splits water into protons and oxygen gas. The oxygen is purged from the cell, as it has little commercial value. The protons travel through the electrolyte and PEM to the cathode, where they combine with CO_2 and electrons. Depending on the catalyst on the cathode this creates different products: on Au catalysts, CO gas and OH⁻ are the primary products. Via a competing side reaction, the protons can also combine directly with electrons in the cathode to produce H_2 gas. Such H_2 gas could be produced much more efficiently on a hydrogen evolution catalyst, so at the higher voltages of a CO_2 reduction cell, it is desirable to produce only the target carbon-based products. A summary of the products of different catalysts can be seen in Table 1.

М	СО	HCOO ⁻	CH_4	C_2H_4	EtOH	PrOH	H_2
Au	87%	0.7%	-%	-%	-%	-%	10%
Ag	82%	0.8%	-%	-%	-%	-%	12%
Zn	79%	6.1%	-%	-%	-%	-%	10%
Cu	1%	9.4%	33%	26%	5.7%	3.0%	21%

TABLE 6. $\rm CO_2$ reduction products for several metal films. Table of values from Ref. [24].

2.8.2. CO_2 reduction reaction mass transfer. In the case of CO_2 reduction at a Au, Ag, or Zn surface, several reaction mechanisms have been proposed. One mechanism has the steps,

(71a)
$$\operatorname{CO}_2(\operatorname{aq}) + \operatorname{e}_M +^* \to \operatorname{CO}_2^{*-}$$

(71b)
$$\operatorname{CO}_2^{*-} + \operatorname{HCO}_3^{-}(\operatorname{aq}) \to \operatorname{COOH}^* + \operatorname{CO}_3^{2-}(\operatorname{aq})$$

(71c) $COOH^* + e_M \rightarrow COOH^{*-}$

(71d)
$$\operatorname{COOH}^{*-} \to \operatorname{CO}(g) + \operatorname{OH}^{-}(\operatorname{aq}) +^{*}$$

where the * represents an active reaction site on the catalyst, (aq) designates species dissolved in the electrolyte, (g) species in a gaseous state, and e_M electrons present in the electrode.

We can calculate J_i for each species *i* that requires transport to the electrode, namely CO₂ in step 71a and HCO₃⁻ in step 71b. For a typical electrolyte concentration of 0.5 M_{KHCO3} in a well stirred solution, to first order we can assume the solution is sufficiently conductive that we can neglect migration of the species; also, since CO₂ has no charge, to first order it will not experience migration.

We now need only consider diffusion of the CO₂ and HCO₃⁻ through the boundary layer. In a mass transport limited situation, the reactants will be immediately consumed at the electrode surface, and their concentration there can be assumed zero. This allows us to re-write the $\vec{\nabla}C_i(y)$ factor as C_i^*/δ , where y is the distance away from the electrode surface. For CO₂ the bulk concentration is a function of the pH of the electrolyte, which for 0.5 M KHCO₃ (pH 7.5) is approximately 30 mM. The HCO₃⁻ concentration is set by the electrolyte concentration to 0.5 M. If we enter values from literature for the diffusion constants, $D_{\rm CO_2} = 1.9 \times 10^{-9}$ m²/s and $D_{\rm HCO_3^-} = 1.2 \times 10^{-9}$ m²/s, we find,

(72a)
$$J_{\rm CO_2} = \frac{z_{\rm CO_2} F D_{\rm CO_2} C_{\rm CO_2}}{\delta} = \frac{11 \times 10^{-6}}{\delta}$$

(72b)
$$J_{\text{HCO}_{3}^{-}} = \frac{z_{\text{HCO}_{3}} - FD_{\text{HCO}_{3}} - C_{\text{HCO}_{3}^{-}}}{\delta} = \frac{58 \times 10^{-6}}{\delta}$$

from which it is clear that the mass transport of CO_2 will determine the limiting current J_L . Direct measurement of this boundary layer thickness, to calculate an expected J_L of the system, is nontrivial; however, by applying a large overpotential to a given electrochemical cell, the J_L can be measured directly, and itself used to calculate what the boundary layer thickness is. So, in summary, the limiting current due to mass transport will be approximately,

(73)
$$J_{\rm L} = \frac{z_{\rm CO_2} F D_{\rm CO_2} c_{\rm CO_2}}{\delta} = \frac{11 \times 10^{-6}}{\delta} \,.$$

2.8.3. CO_2 reduction reaction kinetics. Au is the 79th atom on the periodic table, with core electrons the same as Xe, and valence electrons: 4f¹⁴, 5d¹⁰, 6s¹. It is the 7th least abundant element in the earth's crust, causing its high cost and limited supply for industry. The crystal structure is face-center-cubic (fcc), alternatively termed cubic close-packed (it is a packing structure obtainable by stacking canon balls in an ABC fashion). The space group for this crystal structure is O_h , which leads to the band structure shown on presentation slide 7.

For the CO₂RR, a two electron transfer process, a Tafel slope of ~40 mV/decade was first obtained experimentally in 2016; to date only a Au nanoneedles [30, 67] and the Au dendrites reported here have produced it. Future work will need to develop catalysts that maintain high stability and selectivity, while increasing the activity by increasing the exchange current density j_0 . This will be accomplished by lowering the free energy ΔG of the intermediate species bound to the catalyst surface.

In principle, the band structure of the surface of Au can be calculated from the crystal structure and surface faceting. However, a simpler analysis, which can illuminate general trends, is counting the number of bonds broken when a crystal is cleaved along a certain Miller index. The more bonds broken per adatom, the higher the surface energy (also often called surface tension). By this analysis, the higher the Miller index of a facet, the higher the surface energy. These high index facets will also have more electrons available for binding to molecules adsorbed to the surface. Thus, higher index facets typically bind more strongly with adsorbed molecules. This is demonstrated in Fig. 30 for Au and Ag binding to H, COOH, and CO. In this plot, the scaling relation between the binding energy of COOH, CO, and H is shown; whenever the binding energy is increased for one species, it is also increased for the other two. This poses a challenge to CO_2 reduction, that to stabilize the intermediate COOH and thereby improve CO_2 reduction activity, the binding strength is also increased for CO (a catalyst poison when its adsorption is energetically favored over desorption) and for H (the intermediate for the competing reaction: H_2 evolution). In addition to different facets, different metals also have different binding energies to certain molecules, which is shown in the volcano plot in Fig. 31. This plot shows CO_2 reduction activity plotted against CO binding strength. Here it is clear that Au has the strongest binding strength to CO, while still having it energetically favorable for the CO to be a gas rather than adsorbed to the Au surface. As stated before, this binding strength means the intermediate COOH is stabilized on the Au surface as well as possible, due to the scaling relation between CO and COOH. The other elements in the volcano plot have worse activity as a consequence of either less stabilized COOH, or poisoning from too-strong binding to CO.



FIGURE 30. Scaling relation between COOH, CO, and H adsorption to catalysts. The linearly increasing binding energy of both COOH and H with increased binding energy of CO demonstrates a "scaling relation." More negative binding energy corresponds to stronger binding. The vertical dotted line indicates the energy of CO adsorption; to the left CO will not release from the Au or Ag surface, to the right it will. Regions within the dashed red circles indicate the optimal conditions for CO_2 and H_2O reduction; here the intermediates COOH and H are most stable while still allowing CO to release from the catalyst surface [28].



FIGURE 31. Volcano plot for CO_2RR (a) current density and (b) onset potential for several different metals. Reprinted with permission from ref [149]. Copyright 2014 American Chemical Society.

The free energy of each intermediate in CO_2 electrochemical reduction on Au is plotted in Fig. 32 for each of four crystal facets. This plot demonstrates how the binding strength of the Au to an intermediate affects the catalytic activity: if the free energy of an intermediate is higher than that of the reactant and product, then it creates an activation energy barrier, reducing the reaction current density for a given applied voltage. This plot clearly shows that the higher index (211) facet has a lower free energy for COOH than the low index facet (111), which will cause the (211) to have higher catalytic activity.



FIGURE 32. Free energy diagram of the CO_2RR on different Au facets. Reprinted with permission from ref [30]. Copyright 2016 Springer Nature.

Group theory calculations of CO_2 and CO allow for the calculation of the molecular orbitals of the molecules, and the identification of which orbitals correspond to vibrational modes that can be excited by IR radiation. By depositing a Ag film, which has similar CO_2 reduction performance to Au, onto a Ge attenuated total-internal refection (ATR) crystal, Firet and Smith recently showed the detection of CO_2 reduction intermediates in-situ using fourier transform infrared (FTIR) spectroscopy [150]. The results of the study showed that at low overpotentials the intermediate COO- is present, while at higher overpotentials it is not. This indicates that at low overpotentials, there are sequential reaction steps, in which CO_2 is first adsorbed to the Ag surface by an electron transfer, followed by protonation; at high overpotentials, these two steps are combined into a single proton coupled electron transfer (PCET).

The phenomenon of field-induced reagent concentration (FIRC) was reported in 2016 by Liu, et al. [30]. The report demonstrated that Au needles with radius of curvature of approximately 50 nm or less have much higher catalytic activity than needles with a radius of curvature much larger. Simulations and control experiments make the case that the high activity is the result of high electron density at the Au needle tip. This is due to the high electric field at the tip, a result of the high radius of curvature on a charged metal surface, and to the high concentration of adsorbed K⁺ cations on the Au surface, whose mirror charges draw electrons to the Au surface. Density functional theory calculations show that the presence of a K⁺ cation near a COOH molecule adsorbed to the Au surface causes a higher electron charge density between the carbon and the Au atoms, thus facilitating a stronger adsorption bond.

3. Aluminum nanowire arrays for plasmonic waveguides

3.1. Aluminum nanowire arrays via directed assembly. Freestanding and vertically oriented metal nanowire arrays have potential utility in a number of applications, but presently lack a route to fabrication. Template-based techniques, such as electrodeposition into lithographically-defined nanopore arrays, have produced wellordered nanowire arrays with a maximum pitch of about 2 μ m; such nanowires, however, tend to cluster due to local attractive forces. Here, we modify this template fabrication method to produce well-ordered, vertically oriented, freestanding Al nanowire arrays, etched from an underlying Al substrate, with highly tunable pitch.

Vertically-oriented, lithographically-ordered, metal nanowire arrays have potential utility as capacitors [64], high surface area electrodes [57], electrochemical biosensors [63], optical nanoscopes [15, 151], rectennas [152, 60, 84], and solar cells [153, 62, 54]. In many of these applications, the nanowires are coated with materials to produce core-shell or nanocoax structures, [65] which, for many deposition processes, requires the nanowires to be freestanding to accomplish a homogeneous coating.

Currently, only a limited range of nanowire heights and array pitches can be produced in ordered arrays using metallic materials. Chemical vapor deposition (CVD), a method of nanowire fabrication with tunable height and pitch, produces metal nanowires in only disordered arrays (Fig. 33a) [100, 102] or carbon nanofibers having low electrical conductivity (~ 10⁴ S/m [107, 106]), three decades lower than good metals [108]) (Fig. 33b). Electroplating metals in anodized aluminum oxide (AAO) template nanopores produces highly conductive and ordered arrays (Fig. 33c) [91, 92, 153, 87, 83], but a maximum pitch of 2 μ m [92, 153] typically causes the nanowires to cluster together due to local attractive forces [98, 99]. As greater tunability of nanowire height and pitch could be advantageous for the aforementioned applications, we have modified the preparation of AAO templates to produce highly ordered and freestanding aluminum nanowire arrays (Fig. 33d). This process etches the nanowires from the underlying substrate at lithographically-defined locations, providing high tunability of the array geometry. Additionally, the process is amenable to low-cost, large-scale production because it is solution based, roll-to-roll compatible [154, 153], operates at atmospheric pressure with temperatures between 0 °C and 60 °C, and uses Al, an earth abundant [155] and inexpensive metal.



FIGURE 33. Methods of fabricating metal nanowire arrays. (a) CVD of Ni or Co [100, 102]: a bottom-up process that produces vertically oriented nanowires with irregular spacing between them. (b) CVD of carbon nanofibers: a bottom-up process that produces disordered nanowires with poor conductivity relative to good metals [107, 106, 108]; orange rectangles represent particles the nanofibers nucleate on. (c) Electrodeposition of metal nanowires in templates [153, 91, 92, 87, 83]: a template-based method that produces metal nanowires in an ordered array. Existing templates, such as porous AAO, have limited pitch, which causes these wires to bundle; orange rectangles represent a porous template. (d) Al nanowire arrays via directed assembly: a top-down process that produces lithographically ordered, vertically oriented, freestanding metal nanowire arrays—possibly the first top-down method of metal nanowire fabrication; orange layer represents AAO. Reprinted with permission from ref [33]. Copyright 2015 American Chemical Society.

An AAO template consists of an array of pores passing through the thickness of an oxidized aluminum film. The oxide is developed by anodizing the Al, with pores formed during anodization due to a positive-feedback process. Well-ordered arrays can be obtained by pre-patterning the Al surface with an ordered array of indents, steering pore nucleation at the indent sites [85], as discussed in a recent review article [38].

In our approach, fabrication of an Al nanowire requires a defect in the form of an intentional lack of an indent in the Al surface, which blocks the formation of a pore when anodizing the Al to produce an AAO template. Scanning electron microscope (SEM) images and associated schematics in Fig. 34 demonstrate this process. A stamp composed of an array of Ni posts, with some posts missing from the array to produce directed defects (Fig. 34a), is pressed against an Al film to create indents in the Al (Fig. 34b). When the film is subsequently anodized, pores preferentially form at the indents, while the Al below the missing indents is protected from oxidation. This process yields Al nanowires embedded in the AAO template at the missing indent sites (Fig. 34c). Selective etching of the aluminum oxide leaves freestanding Al nanowires (Fig. 34d). The locations of such nanowires can be lithographically controlled by the placement of the missing posts in the stamp. As such, the nanowires can be as far from each other as desired, or as close to each other as separated by one anodized pore (e.g. 2.4 μ m center-to-center in Fig. 39a). We found that for stamps with Ni posts of variable diameter, from 200 nm to 700 nm, there was a maximum Ni post diameter of approximately 400 nm that would produce an AAO template with embedded Al nanowires (Fig. 35). The percent yield of nanowires was much less than desired, and in need of improvement. Typical experiments patterned areas of 200 x 200 um, corresponding to about 7,000 nanowires, but results varied from only a few nanowires to about 30% of the desired nanowires actually forming, as shown in Fig. 36.



FIGURE 34. Fabrication process of Al nanowires, with representative SEM data of neighboring regions on the sample showing each step on top, and corresponding cartoons on bottom. (a) SEM of Ni stamp used to indent the Al, (b) SEM of indented Al surface, (c) SEM of AAO template surface, (d) SEM of Al nanowires, (e) cartoon of Ni stamp, (f) cartoon of the imprinted Al surface, (g) cartoon of the AAO template with missing pores with a cross-section of the template where Al nanowires are embedded, (h) the Al nanowires after etching away the AAO. For a-d, above the dashed green line there is a periodic array of missing Ni posts in the stamp, translating into Al nanowires on the sample; below this line depicts a conventional AAO process with no posts missing from the stamp. Scale bars 2 μ m. Reprinted with permission from ref [33]. Copyright 2015 American Chemical Society.



FIGURE 35. Dependence of Al nanowire growth on imprint post diameter, shown in SEM images. Images show fabrication steps: (a) imprinted Al, (b) anodized Al, (c) Al surface after etching away anodized aluminum oxide. These images, along with the results in Fig. 37, show that: (i) pores did not nucleate in the area on the left with no indents, (ii) indents of diameter ≤ 400 nm produced pores at indent sites and Al nanowires at missing indent sites, (iii-v) indents of diameter > 450 nm did not cause pores to nucleate. At areas where no pores nucleated, the anodized aluminum oxide was approximately conformal to the Al surface; after etching this oxide away a rough and planar Al surface was revealed. Thus, for an indent array pitch of 1.2 μ m, this sample suggests imprint post diameter must be ≤ 400 nm for an AAO template and embedded Al nanowires to form. SEMs (a.i) and (a.ii) are representative images from areas of the sample neighboring (b.i), (c.i) and (b.ii), (c.ii), respectively. Scale bars 2 μ m. Reprinted with permission from ref [33]. Copyright 2015 American Chemical Society.





FIGURE 36. Percent yield of Al nanowires, shown in SEM images. Images show successive decreases in magnification from top left to bottom. Red boxes show the magnified areas. In bottom image, the top-left area did not get stamped due to a defect in the stamp. The stamp should have produced Al nanowire arrays in a square lattice of 2.4 x 2 μ m in all 5 recessed regions shown in the bottom image. The proportion of nanowires that was actually produced here is typical for the process.

To fabricate the Al nanowire arrays in Fig. 37 and 39, we used a hexagonal array of Ni posts (~400 nm diameter and height, 1.2 μ m pitch), fabricated via electron beam lithography on a Ni-coated-glass surface, to imprint the aluminum. From this underlying hexagonal matrix, we fabricated both hexagonal (Fig. 37a-c) and square (Fig. 37d-f) arrays of nanowires by proper placement of missing posts in the stamp. Geometrically, an aluminum nanowire is the result of subtracting a cylinder with a hemispherical base (*i.e.* the pore and surrounding oxide) from the bulk aluminum at the site of each indent. For a hexagonal array of indents, each missing indent is surrounded by six indents, which ultimately produces Al nanowires with a hexagonal cross-section (Fig. 37b & 3e). Other lattice configurations of indents have been demonstrated to produce AAO templates, such as a square array [153], and may also produce Al nanowires; we expect a square array of indents would produce Al nanowires with square cross-section.



FIGURE 37. Different Al nanowire array lattice geometries. Diagram and SEMs demonstrating how the same underlying matrix (a hexagonal array of pores) can produce different lattice geometries of nanowires (hexagonal and square arrays). (a, d) Blue circles and yellow dots represent sites of nanowires and pores, respectively; circled yellow dots emphasize that all the nearest neighbors of a nanowire are pores, which causes the nanowires to have a hexagonal cross-section. (b, e) SEMs of resulting Al nanowire arrays in a (left) hexagonal lattice and (right) square lattice, tilt 0°. (c, f) SEMs of same region with tilt 30°. Scale bars 2 μ m. Reprinted with permission from ref [33]. Copyright 2015 American Chemical Society.

To explain the growth mechanism of the nanowires, we compare our results to previous reports of imprinting a hexagonal array of indents into Al and leaving out indents at certain sites in the hexagonal lattice. In a study using an aqueous oxalic acid solution [156], the lack of an indent had little impact on the pore formation and subsequent AAO template—pores formed at the sites of missing indents nearly as well as at sites with indents. In a study using an aqueous phosphoric acid solution [157], a site with a missing indent produced a pore with a relatively small radius and caused adjacent pores to have diamond shaped cross-sections, rather than the typical circular shape. In our study, using citric acid with very dilute phosphoric acid in a solution of half deionized water and half ethylene glycol, a missing indent successfully prevented the formation of a pore.

The variations in the reports above, from minor impact on pore formation, to producing only a small pore, to fully blocking pore formation, track with several other trends in AAO fabrication. For example, a missing indent becomes less likely to form a pore as anodization voltage or pitch is increased [156, 157]. Also, different electrolyte anions penetrate different percentages of the barrier layer oxide at the pore base [158], and missing indents are less likely to form pores as this penetration depth decreases (see Table 7 for details). To explain how these trends impact pore formation we consider the flow model for AAO growth, in which mechanical instabilities in the oxide cause pore nucleation. Reports supporting this model [159, 160, 161, 162, 163, 38] have found pore nucleation to result from buckling of the oxide film, forming walls around pores [163], initiated during anodization when the applied potential was high enough for electrostriction of the oxide to overcome the oxide surface tension. Since anions contaminating the oxide near the electrolyte/oxide interface modify the oxide's mechanical properties, such as its surface tension [160, 163] and elasticity [164], the type and concentration of anions in the oxide determines the voltage at which pores nucleate. Such contamination by phosphorous anions into the oxide is depicted in Fig. 38a. We propose that the low oxide contamination during anodization in phosphoric acid, compared to oxalic acid [158] may be what limits the formation of a pore at a missing indent; the thick layer of relatively pure alumina may resist mechanical deformation into a pore during anodization (Fig. 38b). Due to limited studies on citric acid anodization, the role of these anions is unclear; however, the model we propose would suggest that citric acid anions have limited penetration into the oxide.

TABLE 7. Trends in AAO fabrication procedures, organized by anodization solu-
tion, including the impact that a missing indent has on pore formation. Reprinted
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Anodization solution:	Oxalic acid	Phosphoric acid	Citric + phosphoric + ethylene glycol	
Anodization voltage:	80 V (ref [156])	120 V (ref [157])	480 V (this work)	
Pitch of pores in AAO template:	$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	1200 nm (this work)	
Percent of barrier ox- ide at pore base pene- trated by anions:	90% (ref [158])	66% (ref [158])	No data	
Pore formation at missing indent:	Nearly normal pore (ref [156])	Small pore with diamond shaped adjacent pores (ref [157])	Pore formation blocked to produce Al nanowire (this work)	

This flow model also offers an explanation for why the Al nanowires do not anodize through the sidewall of the AAO pores. In a recent study of the distribution of elements within the alumina of a pore grown in phosphoric acid [163], the pore wall was found to have less penetration of phosphorous anions than the pore base (Fig. 38c). A separate study, using a tungsten tracer layer in the Al substrate to track the flow of oxide in the pore during anodization [161], elucidates this result; they found that oxide was generated at the metal/oxide interface at the pore bottom, and then flowed up and out into the sidewalls of the pore, as depicted in Fig. 38d. The expected high resistance to electronic and ionic flow [158] of the relatively pure oxide in the pore sidewalls and above the nanowires is highlighted in Fig. 38e.



FIGURE 38. Mechanism of Al nanowire growth. (a) Studies have shown phosphorous from the electrolyte to penetrate into the alumina, (b) with a layer of relatively pure alumina adjacent to the oxide/metal interface (barrier oxide) [158]; we propose this pure layer may resist deformation into a pore at sites where the Al surface was not indented. (c) Studies have shown the phosphorous to penetrate deeper into the oxide at the pore base than along the pore walls [163]. (d) Based on a separate study, this may result from plastic flow of relatively pure alumina from the metal/oxide interface at the pore bottom up into the pore walls [161]. (e) This relatively pure alumina is thought to resist ion flow [158], which may protect the Al nanowires from anodization through the pore wall. (f) Sites on the Al surface that are not indented, but surrounded by indents, produce Al nanowires, as demonstrated in this study. Reprinted with permission from ref [33]. Copyright 2015 American Chemical Society.

The Al nanowires were observed to have attributes desirable for technological applications. For example, the process that produces the nanowires yields a hexagonal cross-section with sharp edges and smooth, concave surfaces, including a 6-pointed crown shape. These features are evident in the SEM images in Fig. 39. The smoothness of the surface is quantified in AFM images shown in Fig. 40, where variation in surface height is approximately 1 nm along a 150 nm line on the top of a nanowire. The crown points (Fig. 39b) have radii of curvature ~ 10 nm (Fig. 39c). In addition to such small pitch arrays, we can also fabricate arrays with pitch over 10 μ m, and with wire height to e.g. 20 μ m (Fig. 39d). Such sharp edges and smooth surfaces may be of relevance for photonic and plasmonic applications [165, 61], such as electric field enhancement. The strong secondary electron signal at the nanowire edges, relative to that at the faces, in Fig. 39a, is more probable than not evidence of such enhancement—the alternative explanation being charging due to an anomalously thick native oxide at the edges. Likewise, in the NSOM measurement shown in Fig. 41, bright spots located near the corners of vertical Al nanowires suggest electric field enhancement. Additionally, as the nanowires' purity is determined by that of the starting Al foil/substrate, these wires are 99.9995% Al. Due to a low bulk oxide content, surface plasmon resonances (SPRs) on the nanowires should have high light scattering efficiency—advantageous for certain plasmonic devices [47]. Panchromatic cathodoluminescence images of the nanowires (Fig. 42) show these edges to be dark for measurements at normal incidence, but not for measurements with sample tilt of 30°—potential evidence of strong light scattering at the edges.



FIGURE 39. SEMs demonstrating attributes of the Al nanowires. (a) High contrast SEM of Al nanowires demonstrates electric field enhancement at the nanowire edges and corners. (b, c) SEMs show the radius of curvature of the nanowire corner to be ~ 10 nm. (d) SEM of Al nanowires with large height and pitch demonstrates tunability of Al nanowire array geometry. Tilt 30°. Reprinted with permission from ref [33]. Copyright 2015 American Chemical Society.



FIGURE 40. AFMs demonstrating smoothness of the Al nanowires. Images show surface topography of an array of Al nanowires. (a) Large area AFM, (b) magnification of Al nanowire top, (c) magnification of center of nanowire top, (d) further magnification of nanowire top to show nanoscopic region. (e) Line-cut of the nanoscopic region to show surface roughness.



FIGURE 41. NSOM measurement demonstrating bright spots near corners of vertical Al nanowires. Color represents electric field intensity. Image topography represents the convolution of the height of the surface of the Al nanowire array with the NSOM probe. Inset shows four wires in the array. White arrows highlight bright spots where high electric field was detected. Black hexagon highlights where a small feature on the NSOM probe tip convolved with the corners of the Al nanowire top.



FIGURE 42. SEM, panchromatic cathodoluminescence, and simulations of Al nanowire arrays. (a) Secondary electron (SE) image of an Al nanowire array (sample tilt 0°). (b) Panchromatic cathodoluminescence (CL) image (350-650 nm) of an Al nanowire array (sample tilt 0°) showing dark highlights at the sharp edges of the nanowires. (d) CL image of an Al nanowire array (sample tilt 30°) showing light highlights at sharp edges of the nanowires. (c) Simulations of the radiation pattern for two cases: electric dipole (with vertical moment) excitation at the center (left) and at the corner (right) of the nanowire top, represented by a red dot. The radiation pattern is expected to represent the cathodoluminescent response of the nanowire to excitation by the electron beam. For the dipole at the nanowire topcenter, the radiation pattern has maxima directed upwards away from the nanowire, with a broad minima in the plane perpendicular to the nanowire. For the dipole at the corner, the radiation pattern shows maxima in the plane perpendicular to the wire axis, and a broad minima upwards away from the nanowire. This is consistent with the dark and bright highlights observed by CL at the sharps edges relative to the top face of the nanowires for 0° and 30° sample tilts. Reprinted with permission from ref [33]. Copyright 2015 American Chemical Society.

3.2. Al nanowire plasmonics. Although Al was the first metal whose plasmonic properties were studied in depth [46], it has only recently been investigated for applications in nanostructured plasmonic devices [48, 47, 49]. This is a result of fabrication challenges for Al nanostructures [48, 49] and the location of the Al SPR cutoff frequency in the deep UV [50]; most plasmonics research has focused on visible light manipulation. Noble metals such as Au and Ag have SPR cutoff frequencies in the visible and near-UV [47, 51],[52] respectively, which have made them materials of choice for plasmonic device development. Recent studies, however, have demonstrated SPR modes on Al disks and rectangles,[48, 53] as well as improved performance in sensors and photovoltaics using arrays of such structures [54, 55].

To elucidate the plasmonic properties of the Al nanowires, measurements with a NSOM, an AFM, and a conventional optical microscope (imaged onto a CCD) were taken of an isolated nanowire lying flat on glass and illuminated by a laser spot with 660 nm wavelength (Fig. 43). The nanowire height (AFM signal), encoded as the color scale in Fig. 44a, shows lengthwise ridges running along the nanowire; the electric field intensity (NSOM signal), encoded as the topography of Fig. 44a, shows evidence of surface plasmon polaritons (SPPs) propagating from the laser spot along the nanowire length at the ridges. The apparent AFM signal modulations along the nanowire length are the artifact of the shading effect from the overlying NSOM pattern. A line-cut of the NSOM signal along a ridge (Fig. 44b) shows the SPP standing wave pattern with wavelength of ~ 550 nm. Simulations (not shown) predict the SPP wavelength to be 600 nm for an Al nanowire coated by 3-5 nm of aluminum oxide and illuminated by 660 nm radiation. Images taken with the conventional optical microscope (Fig. 44c) show light scattering from the nanowire tip with increasing intensity as the tip is moved closer to the laser spot, providing evidence that light is coupled from the laser spot to SPPs on the nanowire, and scattered into photons at the nanowire tip.



FIGURE 43. Schematic of experimental setup for NSOM measurements of an Al nanowire. A Nanonics Imaging Ltd. MultiView 4000 NSOM was used to illuminate the nanowire with a 660 nm wavelength laser source. A single-mode optical fiber, diameter 4 μ m, coupled light from the laser into a 63 numerical aperture (NA) = 1.40 objective below the Al nanowire. Laser light passed from this objective, through immersion oil and a glass slide to form a spot in a focal plane containing the Al nanowire. Far-field radiation from the laser spot was observed by a charge-coupled device (CCD) camera through a 50 NA=0.45 objective above the nanowire. Near-field radiation at the nanowire and glass surfaces was measured by an NSOM probe (500 nm aperture, 150 nm Cr-Au coating, multimode fiber). Reprinted with permission from ref [33]. Copyright 2015 American Chemical Society.

The large wavelength of the standing wave pattern in Fig. 44b (approaching the SPP wavelength) results from the large (compared to SPP wavelength) circumference of the wire. This causes the back-scattered SPP waves to have small axial components of their wave vectors, and therefore the resulting standing wave along the wire has its wave vector dominated by the incoming wave. This also explains the rapid decay of the standing wave pattern (with exponential decay range of $\sim 1 \mu m$), as shown in Fig. 44b; due to the large wire circumference, only a small fraction of the SPP back-scatters into the original (along the wire ridge) propagation channel, to produce the scattering wave pattern. This, with increasing distance away from the excitation point, effectively depletes the ridge propagation channel of back-scattered plasmon waves. This evidence of SPPs supported on and guided along an Al nanowire demonstrates the potential efficacy of these Al nanowires for plasmonic device applications, such as a waveguide for light.



FIGURE 44. Optical and AFM measurements of an Al nanowire on a glass slide and illuminated by a laser spot of wavelength 660 nm; laser polarization is along the wire axis to excite longitudinal SPP modes. (a) A composite NSOM and AFM signal [166]: figure topography shows NSOM signal, *i.e.* near-field optical intensity; color scale shows height of Al nanowire (red & yellow) and glass surface (blue), as measured by AFM. A yellow streak running lengthwise along the wire in the red region shows evidence of a ridge along the nanowire. White arrows highlight antinodes of standing waves on this ridge, formed by forward and backward propagating SPPs, which are created by the laser spot and reflection off the nanowire tip, respectively. (b, top) Black solid line shows line-cut of near-field optical intensity (NSOM) along dashed line in (a), demonstrating a standing wave of 550 nm wavelength in superposition with an exponentially decreasing intensity with increasing distance from the laser spot; red dashed line shows exponential fit that measures the standing-SPP decay length to be $\sim 1 \ \mu m$. (b, bottom) ΔI , the near-field optical intensity minus the exponential fit, shows the standing wave with greater clarity; grey arrows spaced by 550 nm highlight antinodes. (c) Far-field images of the Al nanowire under the laser spot show increasing light scattering from the Al nanowire tip with decreasing distance between the laser spot and the tip, likely due to SPPs propagating from the laser spot and scattering off the nanowire tip into photons; scale bar 2 μ m. Reprinted with permission from ref [33]. Copyright 2015 American Chemical Society.

3.3. Al nanowire dark-lobe polarization effect. Interesting polarization effects were observed from the arrays of vertical Al nanowires, when observed from above at normal incidence. Fig. 45 shows the experimental setup, which includes a polarizer for the light incident on the Al nanowires and an analyzer for the light reflected. White light from a halogen lamp was passed through a low-pass filter to remove wavelengths shorter than 500 nm, and thereby exclude wavelengths that would excite surface plasmons; all wavelengths incident on the Al nanowires should interact with the Al as though its a perfect electrical conductor. Images of the Al nanowire array are shown in Fig. 46 under a variety of orientations of the polarizer and analyzer. In these images the focal plane of the microscope is positioned at the top of the nanowires. The first observation to note is that light reflected from the top of the nanowires does not seem to have its polarization modified; when the polarizer and analyzer are perpendicular the nanowire tops are dark (Fig. 46 top-left and bottom-middle)—when parallel these tops are bright (Fig. 46 top-middle and bottom-left). The interesting observation is the presence of two dark lobes on opposite sides of the Al nanowires, which track in their orientation with the analyzer orientation. This indicates that light propagating along the length of the Al nanowire was polarized perpendicular to the surface normal of the side of the nanowire. As such, light with polarization parallel to this surface normal seems to be either scattered away or absorbed, since we do not observe it in the microscope. As shown by the presence of lobes when illuminated by light of different linear polarization angles, and by unpolarized light (Fig. 46 right column), this effect is present independent of the polarization of the incident light.



FIGURE 45. Setup for optical far-field images of dark lobes on Al nanowires. Grey bar indicates the path of white light. Yellow bars indicate the path of light with wavelengths longer than 500 nm.



FIGURE 46. Optical far-field images of Al nanowires for different analyzer angles and polarizations of incident light. Black arrows show polarizer orientation. White arrows show analyzer orientation. Right column has unpolarized light. Al nanowires are arranged in a rectangular array with pitch of 2.4 x 2 μ m. Al nanowire diameter is ~ 700 nm, with a hexagonal cross-section.
3.4. Mechanism of slow pore formation. Anodized aluminum oxide (AAO) membranes have been necessary for fabrication of vertically-oriented and well-ordered arrays of high aspect-ratio metal nanowires, which have broad utility in plasmonic devices and high surface area electrodes for electrochemistry, as we recently reviewed [N. T. Nesbitt, M. J. Naughton, Ind. Eng. Chem. Res. **56**, 10949–10957 (2017)]. Todate, AAO pore nucleation has been directed by a periodic pattern in the aluminum surface topography. Here, we report directed-nucleation by patterning an oxide mask to selectively expose a flat aluminum surface to electrolyte where pores were desired. Aluminum nanowires embedded in the AAO were produced. Two distinct tops to aluminum nanowires were observed, smooth bowls and flat rough surfaces. We deduce that aluminum nanowires with bowl-tops result not from blocking pore nucleation, as previously suggested, but from slow pore development relative to pattern-nucleated pores. We suggest that the large pitch allows Joule's heating to locally accelerate pattern-nucleated pores, while pores over nanowires remain below a critical current density threshold and develop slowly.

Anodized aluminum oxide (AAO) membranes are currently necessary for the fabrication processes of vertically-oriented and well-ordered arrays of high aspect-ratio metal nanowires over large areas [167]. For these processes, an aluminum surface is imprinted with a periodic pattern to direct pore formation during anodization of the aluminum. For nanowire array pitches above a few micrometers, anodization etches away aluminum to create aluminum nanowires [33]; for pitches below a few micrometers, the pores in the AAO membrane provide a template that is filled with metal [38]. Such metal nanowire arrays have broad utility, including in plasmonic devices, super-capacitors, and high surface area electrodes for electrochemistry.

Here, we report the first directed-nucleation of AAO pores by patterning an oxide mask on flat aluminum. The mask was made of alumina, and applied to an electropolished Al surface via atomic layer deposition (ALD). Previous to this work, directed nucleation of AAO pores had been achieved by patterning the Al surface via etching the Al through a mask, or, more often, indenting the Al with a hard mask.

Our development is technologically important because it enables large-pitch aluminum nanowire arrays to be made by relatively inexpensive and scalable soft nanoimprint lithography (NIL) instead of the expensive and easily damaged hard stamps that are conventionally used. Scientifically, the result provides insight into the physics of pore formation in AAO membranes. It confirms our expectation that a patterned Al surface isn't necessary to direct pore nucleation—deposition and patterning of an oxide on flat Al also works. Additionally, two distinct nanowire types were observed: (i) some with smooth bowl tops, and (ii) some with rough flat tops. These were understood to result from (i) slowly developing pores relative to pattern-nucleated pores, and (ii) full blockage of pore nucleation. In our previous work on this Al nanowire fabrication process [33], we only observed bowl-tops and suggested that the lack of an indent in the Al blocked pore nucleation to some ambiguous extent. The new observation emphasizes an interesting result—that a pore can be engineered to develop more slowly than other pores surrounding it. We propose that the fast propagation velocity results from electric field enhanced alumina dissolution confined to pattern-nucleated pores; unpatterned sites, on the other hand, may only have slow incipient pore formation.

Fig. 47a shows a cartoon of the soft-NIL stamping process and the subsequent pattern transfer, Al anodization, and Al exposure steps for fabrication of Al nanowire arrays. The detailed experimental procedures, including stamp fabrication via electron beam lithography, are provided below in the soft-NIL Al nanowire fabrication procedure section. Fig. 47b shows representative SEMs of the Al surface following several fabrication steps. These images focus on an area with short nanowires so the surrounding pores and anodized alumina can also be viewed. Fig. 47b-v shows the Al surface after partial etching of the alumina. The nanowire in the center appears to be below a pore (type i); it has a bowl-shaped top with an alumina film that resembles the alumina at the base of the adjacent pattern-nucleated pores. The nanowire in the bottom-right shows no evidence of pore formation at that site (type ii); it has a rough flat surface with no alumina covering it. Since all the alumina present in this image is in the shape of a pore, we assume the alumina from ALD etched faster and has been completely removed. Fig. 47c shows an SEM of higher aspect ratio nanowires; the nanowire on center-left (shown enlarged with high contrast in the inset) appears to have multiple bowl-shapes, suggesting multiple small pores forming at this unpatterned site.



FIGURE 47. Soft-NIL process for Al nanowire fabrication. (a) Cartoon of the process for patterning an SU8 film with a soft PDMS stamp, transferring the pattern into an alumina mask, anodizing the Al, and etching everything beside Al to expose metal nanowires. Hatched lines indicate anodized alumina that would result in the case that a pore forms over a nanowire, at an unpatterned site. (b) Representative SEMs showing the result of the indicated fabrication steps; very short nanowires allow comparison of nanowire tops, the scalloped bottom, and the anodized alumina layer. (c) SEM of higher aspect ratio nanowires.

Fig. 48 shows a closer look at Al nanowires embedded in anodized alumina after partial alumina etching. In Fig. 48a there is clear contrast between smooth-topped (type i) nanowires and rough-topped (type ii) nanowires. There is also an interesting pattern in the topography of the anodized alumina; notches dipping down exist where three pores intersect and where the alumina borders Al nanowires. Fig. 48b shows a high contrast magnified image of the alumina adjacent to an Al nanowire, in which the layers of different alumina can be seen. These layers have been previously shown to form during anodization, with the layer closer to the Al pure Al_2O_3 and the layer further from the Al doped by ions from the electrolyte. Fig. 48c shows a cartoon of the anodization process we imagine may have produced the alumina topography observed along the dotted white line in Fig. 48a. Interstitial Al nanowires, present where three AAO pores intersect, can be seen in Fig. 49. The presence of these interstitial Al nanowires offers an explanation for the location of notches observed in the partially etched alumina; the height of the partially etched alumina is lower wherever the alumina abuts an Al nanowire.



FIGURE 48. Partially etched alumina showing unusual topography. (a) Nanowires with either a smooth bowl top or a flat rough top can be seen, along with trenches along the alumina pore walls where either three pores intersect or where Al nanowires are present. (b) Different layers of the oxide are visible. (c) Cartoon depiction of the likely anodization process that would produce the cross-section observed along the white dotted line in (a).



FIGURE 49. Interstitial Al nanowires.

Fig. 50 shows the current density j vs. time for the anodization process. Fig. 50a shows j while the potential φ is stepped from 0 to 480 V first in increments of 10 V and then increments of 100 V. The saw-tooth current peaks correlate with the expected capacitive charging of the ionic double layer. The offset of the baseline of this sawtooth pattern correlates with the expected oxidation of Al and dissolution of Al₂O₃.



FIGURE 50. Anodization current density vs. time. (a) Stepwise ramp of anodization potential from 0 to 80 V in increments of 30 seconds and 10 V, and from 80 to 480 V in increments of 2 minutes and 100 V. (b) Potentiostatic hold at 480 V for 24 hours.

To understand these results, we consider previous work on the topic. It has been shown there are two types of anodization: mild anodization at potentials below the dielectric breakdown potential ($\varphi < \varphi_B$), and hard anodization at potentials above it ($\varphi > \varphi_B$) [38]. Work has also revealed a relationship between applied potential, φ , and the interpore separation, D_{int} ,

(74)
$$D_{\rm int} = k\varphi$$

where $k \approx 2.5$ nm/V for mild anodization, and $k \approx 2.0$ nm/V for hard anodization [168, 38]. Fig. 51 shows the distance D_{int} in a schematic of AAO pores. The current density varies significantly between the anodization types: mild anodization approximately 1–10 mA/cm² and hard anodization approximately 30–250 mA/cm² [168, 38].



FIGURE 51. Schematic of alumina geometry in an AAO template, showing two pores between Al nanowires. Left pore is labeled with the thickness of each component of the pore: $D_{\rm film}$ the flat alumina above an Al nanowire, $D_{\rm W}$ the thickness of the pore wall, $D_{\rm B}$ the thickness of the alumina between the electrolyte/alumina interface and alumina/aluminum interface at the pore bottom, $D_{\rm int}$ the diameter spanning the outer edge of the poor wall (also equal to the AAO template pitch), $r_{\rm Al}$ the radius from pore center to the outer edge of the poor wall, and $r_{\rm p}$ the radius of the pore. Right pore shows converging field lines at the pore base.

For self-ordered AAO membranes, a given electrolyte has a potential φ that optimizes how well the pores match an ideal hexagonal array. For these optimally-ordered pores, the interpore distance is twice the barrier oxide thickness $D_{\rm B}$ that is at the pore bottom; $D_{\rm int} \approx 2D_{\rm B}$. The oxide layer is dissolved into the electrolyte as it slides laterally from the pore bottom to become the pore wall, with thickness $D_{\rm W}$. This defines the pore radius as $r_{\rm p} = D_{\rm B} - D_{\rm W}$. The pore radius thus depends on the rate of alumina dissolution into electrolyte.

A 10% porosity rule has been empirically shown for optimally-ordered pores produced by mild anodization, meaning pores compose 10% of the area in a cross-section normal to the pore-axis [169]. Hard anodization, on the other hand, has shown porosity of 3.3–3.4% in oxalic acid [169]. Using this definition for porosity, we can re-write eq. 74 as,

(75)
$$\varphi = \sqrt{\frac{2\pi}{\sqrt{3}P}} \frac{r_{\rm p}}{k}$$

where P is the porosity fraction.

It has been suggested that the dissolution rate of alumina into the electrolyte is enhanced by the electric field [170]. This field-enhanced dissolution begins after a threshold potential is passed; the threshold is lower for lower pH electrolytes [171]. This means optimally-ordered AAO membranes with larger pitch, requiring a higher potential φ , are made in higher pH electrolytes. From the pore geometry shown in Fig. 51, it can be seen there is an increase in electric field from the alumina/aluminum interface to the electrolyte/alumina interface of the pore bottom. This is a function of porosity. If we assume the electrolyte/alumina interface and the alumina/aluminum interface to be concentric sphere segments of respective radii r_p and r_{Al} then the electric field E_p at the electrolyte/alumina interface of the pore base is related to the field $E_{\rm Al}$ at the Al surface by,

(76)
$$E_{\rm p} = \left(\frac{r_{\rm p}}{r_{\rm Al}}\right)^2 E_{\rm Al} \,.$$

where $r_{\rm Al} = D_{\rm int}/2$. Defining the porosity P in terms of these radii leads to the field dependence on P,

(77a)
$$P = \frac{\pi r_{\rm p}^2}{(2r_{\rm Al})^2}$$

(77b)
$$E_{\rm p} = \frac{\pi}{4P} E_{\rm Al}$$

This shows that a decrease in porosity increases the electric field $E_{\rm p}$, driving stronger dissolution of alumina.

Pattern-directed nucleation of pores can cause pore nucleation at adjacent unpatterned sites. Mild anodization in 56 mM oxalic acid (pH ≈ 1.5 , T = 17 °C, $\varphi = 80$ V, $D_{\text{int}} = 200 \text{ nm}, k = 2.5 \text{ nm/V}, \text{ porosity} = 7\%$) showed a "self-healing" effect, in which unpatterned sites had pores similar to adjacent pattern-nucleated pores, except with $\sim 40\%$ the cross-sectional area [156]. Mild anodization in 300 mM phosphoric acid (pH \approx 1.4, T = 5 °C, φ = 120 V, $D_{\rm int}$ = 300 nm, k = 2.5 nm/V, porosity = 16%) showed a greater impact on pore formation; unpatterned sites had pores with ${\sim}15\%$ the cross-sectional area of pattern-nucleated pores, and the pattern-nucleated pores were distorted into diamond shapes [157]. Mild anodization in a solution of 50.5 mM citric acid, 0.287 mM phosphoric acid, 8.71 M (*i.e.* 50%) ethylene glycol (pH \approx 2.2, T = 10 °C, j \approx 10 mA/cm², φ = 480 V, $D_{\rm int}$ = 1200 nm, k = 2.5 nm/V, porosity = 2%) showed the greatest impact on pore formation; unpatterned sites showed pores with openings that were difficult to resolve in SEM images. These pores were incorrectly claimed to have not even formed; instead it was suggested that the lack of an indent in the Al blocked pore nucleation. Upon etching away the oxide, pores at these unpatterned sites were found to have negligible depth compared to the

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adjacent pattern-nucleated pores, which resulted in the formation of Al nanowires below the unpatterned sites.

The above summary highlights an interesting inconsistency between normal AAO templates, and those reported in this thesis, which produce Al nanowires: the current density of 10 mA/cm² and the pitch-to-voltage ratio of k = 2.5 nm/V are that of mild anodization, while the porosity of 2% is that of hard anodization.

The pore formation at unpatterned sites suggests coupling between adjacent pore sites for pore nucleation. It means that local variations in physical properties that are required to create a pore get induced on an unpatterned site by the adjacent patterned sites. There is a trend of diminishing unpatterned pore size, relative to pattern-nucleated pore size, with increasing pitch. This suggests that these local property variations may not be transferred as easily in larger pitch anodization.

Pore nucleation will take place differently at pattern-nucleated and unpatterned sites. Patterned sites should progress in the typical way. Unpatterned sites, however, have an alumina film that is thicker than the barrier oxide of the anodization potential used. As such, this oxide should be stable, with an electric field too weak to drive O^{2-} or Al³⁺ through it. The oxide will be slowly etched by solution and deformed by adjacent pore deveopment. This could eventually thin the film enough to support ion migration.

Incipient pore formation, and subsequent pore propagation, are affected by several local properties. A mechanical stress model provides the following description of incipient pore formation. At a given applied electric potential, an alumina film will grow until its thickness is enough that the potential drop across the film no longer creates sufficient electric field to drive Al^{3+} and O^{2-} ions through it. When the applied potential is ramped up, the alumina film increases in thickness until it reaches this stable state. Electrostriction due to the potential drop across the alumina applies a compressive force on the film. This can be relieved by roughening the surface.

However, the surface tension of the film resists this. At a certain potential, the electrostriction will be strong enough to overcome the surface tension, and the film will buckle with a periodicity proportional to the film thickness. This creates the incipient pore geometry, which leads to electric field enhancement at the pore base, due to the radially converging electric field lines through the film. These field lines are shown schematically in Fig. 51.

One may imagine that in an electrolyte with pH slightly too high for the applied potential, that pores nucleated by imprinting or masking the surface may have a locally lowered pH that would initiate field-enhanced dissolution. Adjacent sites without imprinting may stay at too high a pH, preventing full pore formation. Very gradual pore development may take place due to mechanical stress from adjacent pores. Increased viscosity from partial replacement of water with ethylene glycol could lower diffusion constants and aid the localization of pH. Nucleation of two pores with spacing less than $D_{\rm int}$, such as that observed in the inset of Fig. 47c, could impede full pore formation through merging of the pores, preventing the narrow pore from forming needed for enhanced field dissolution. Increased conductivity of the solution as the alumina is dissolved into it could lead to increased current density, and a decreased local pH at incipient pores, causing full pores to grow at nanowire sites. In hard anodization, where the current density is much higher, it has been shown that stable hard anodization is determined by the initial limiting current density [172]. Increasing current density corresponded to a decrease in D_{int} and k. Thus, the high resistivity of the solution used to make AAO with a large $D_{\rm int}$ and Al nanowires, unique from the other electrolytes considered above due to the presence of the ethylene glycol, may explain the mixture of mild anodization current density and k-ratio with hard anodization porosity. To this effect, it is worth noting that, to avoid burning of the Al and a corresponding rapidly increasing current density, the glassware must be carefully cleaned and the solution uncontaminated.

3.5. Conclusions. In conclusion, we have demonstrated a tunable process for templatefree fabrication of vertically-oriented, spatially-ordered, freestanding aluminum nanowire arrays with lateral spacing unobtainable by existing metal nanowire fabrication processes. The arrays' high conductivity and unique spatial dimensions have potential utility in electrical, electrochemical, photonic and photovoltaic applications. Additionally, the nanowire topography has sharp edges and smooth surfaces that may be favorable for electric field enhancement and plasmonic applications. Finally, the process shows promise to be scalable for low-cost manufacturing of large surface area (m^2) devices.

4. Au dendrite electrocatalysts for CO_2 electrolysis

4.1. Introduction. Rapidly falling electricity prices from renewable sources, such as wind and solar, show promise to provide society with cheap domestic energy, while also mitigating the adverse human health impacts of anthropogenic climate change and pollution from fossil fuel extraction and utilization. These energy sources are generally intermittent, and thus require energy storage technology for full deployment. Electrochemical CO_2 reduction may provide a means for large-scale storage of renewable electrical energy in hydrocarbon fuels, which are relatively inexpensive to store and are compatible with much of the world's existing infrastructure.

In this study, the CO_2 reduction reaction (CO_2RR) takes place at a metal catalyst immersed in an aqueous electrolyte: 0.5 M NaHCO₃ saturated with CO_2 . The desired product is CO, produced in the reaction,

(78)
$$CO_2 + 2H^+ + 2e^- \rightarrow CO + H_2O$$
 (-0.11 V vs. RHE).

Thorough studies have been reported on the electrocatalytic performance of flat films of various metals that are selective for the formation of CO [24, 173]. These results showed Au to have the best catalytic performance as it demonstrated the highest values for three important parameters of electrocatalysts: activity (reaction rate per given overpotential (η)), selectivity (percent of the total products generated that were the desired chemical), and stability (constant performance over time). The potential (φ) of -0.35 V vs. reversible hydrogen electrode (V_{RHE}) is convenient for comparing the performance of Au catalysts; it is slightly more cathodic than the onset of cathodic current on Au films, and it has a reasonable energy efficiency of 85% for the partial current directed to CO production (energy efficiency = $E^0/(E^0 + \eta) =$ (1.34 V) / (1.34 V + 0.24 V) = 0.85). This only considers energy losses at the cathode, ignoring losses present at the anode, which can be separately mitigated via

reactor engineering and using specialty membranes [174]. At this low overpotential of 0.24 V, polycrystalline Au films have been shown to produce only $\sim 10 \ \mu A/cm^2$ total current density (j_{total}) at nearly 0% Faradaic efficiency for CO (H₂ was the primary product) [25]. However, recent studies have found nanostructuring Au significantly improves its performance. Specifically, in 2012, a Au nanoparticle film was produced by repeated electrochemical oxidation and reduction of a polycrystalline Au film [25]. The nanoparticle film showed improved performance over both a planar film and a film of commercially available nanoparticles. It produced about $j_{\rm total} = 2~{\rm mA/cm^2}$ at over 96% Faradaic efficiency for CO [25]. This suggested there was a special quality of the electrochemically-reduced surface that improved catalytic performance. In 2016, direct current (DC) electrodeposition of Au nanoneedles was shown to produce about $j_{\text{total}} = 15 \text{ mA/cm}^2$ at over 95% Faradaic efficiency for CO at the same applied potential [30, 67]. It was suggested that the high performance was a result of enhanced electric fields at the needles' sharp tips. This was the first and only report to date of a 40 mV/dec Tafel slope for the CO_2RR on Au, which corresponds to stabilizing all the reaction intermediates in several proposed reaction schemes [173].

In light of the positive results of electrochemically-produced nanostructures of Au, here we tested a technique for the growth of nanoscale Au dendrites and Au plates from an aqueous HAuCl₄ solution with a megahertz (MHz) square-wave potential oscillation and a DC offset potential [175, 176, 177, 146, 117]. Different electrodeposition conditions were found to produce different proportions of exposed facets on Au dendrites and plates. Scanning electron microscopy (SEM), transmission electron microscopy (TEM), and X-ray diffraction spectroscopy (XRD) were used to determine the crystallographic orientation of the Au surfaces. X-ray photoelectron spectroscopy (XPS) was used to determine the composition. Electrochemical impedance spectroscopy (EIS) was used to measure the change in surface energy (γ) vs. φ in various aqueous solutions. An electrochemical cell, potentiostat, and gas chromatograph (GC) were used to measure the performance of the nanostructures as electrocatalysts for CO_2 reduction. The purpose of this study was to understand the nanostructure growth mechanism and thereby provide a platform for rational design of future nanostructures. Our results were compared to existing models for crystallization from aqueous solutions and metal melts to identify common trends. Correlations between nanostructure morphology and catalytic performance offer a pathway for improved structure functionality relationships for nanostructured electrocatalysts used in CO_2 reduction.

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4.2. Morphology and catalytic performance of Au dendrites and plates. Electrochemical CO_2 reduction can convert CO_2 into fuels and valuable chemicals using renewable electricity, which provides a prospective path toward large-scale energy storage. Au nanostructured electrodes have demonstrated the best catalytic performance for CO_2 conversion: high catalytic selectivity for CO formation at low overpotentials, high current density, and long-term durability. Here, we report selective electrocatalytic CO_2 reduction to CO on nanostructured Au with various morphologies, prepared via electrocrystallization with a megahertz potential oscillation. X-ray diffraction showed that the proportion of $\{100\}$ and $\{110\}$ to $\{111\}$ surfaces increased at more negative deposition potentials. Cyclic voltammetry showed the potential of zero charge on a Au film was approximately 0.35 V vs. standard hydrogen electrode (SHE), and that the surface energy decreased by $\sim 1 \text{ eV/nm}^2$ at -0.5 V vs. SHE, tending to 0 within several volts in either direction. Scanning electron micrograms showed that the Au crystals grow primarily in the $\langle 110 \rangle$ directions. From these data, a model for crystallization from melts was adapted to calculate the roughening temperature of the $\{111\}$, $\{100\}$, and $\{110\}$ Miller indices as 7000, 4000, and 1000 K, decreasing for more negative deposition potentials. This offers a framework for exposed facet control in electrocrystallization. In CO_2 electrocatalysis, -0.35 V vs. reversible hydrogen electrode was observed to be a turn-on potential for improved CO_2 reduction activity; dendrites showed 50% Faradaic efficiency for CO production at more cathodic potentials. The Tafel slope was measured to be 40 mV/decade for $\{100\}$ and $\{110\}$ -rich Au dendrites and 110 mV/decade for $\{111\}$ -dominated Au plates, suggesting the higher surface energy crystal facets may stabilize all the CO_2 reduction reaction intermediates.

4.2.1. Au dendrite growth and morphology. To survey the crystal morphologies produced by this deposition process, the following parameters were varied across a number of samples: offset potential (φ_{offset}), peak-to-peak amplitude (φ_{pp}), HAuCl₄ concentration, and Coulombs of deposition per unit area. Figure 52a-d shows the effect of different φ_{offset} , with the ratio $\varphi_{\text{pp}} = 8\varphi_{\text{offset}}$ held constant. For a concentration of 20 mM HAuCl₄, deposition time 40 min, and deposition area 3.60 cm², the lowest applied potential, $\varphi_{\text{offset}} = -0.625$ V, showed no deposition. When the potential was increased to $\varphi_{\text{offset}} = -0.8125$ V, rounded plates formed slowly. At $\varphi_{\text{offset}} = -1$ V the plates grew faster and acquired a well-defined geometry with roughly parallel flat faces and edges tracing a regular hexagon shape. At $\varphi_{\text{offset}} = -2$ V dendrites began to grow; Figure 52d shows a typical crystal covering the Au surface around the base of the dendrites, which had roughly μ m-scale faces and a triangular bipyramid shape with periodic ridges. Figure 52l shows the tips of dendrites grown under the same conditions. Figure 52s shows another variety of the dendrite tip found on the same sample.



FIGURE 52. Representative SEMs of Au crystals grown in various conditions. In all cases, a 20 MHz square wave was applied between the sample and a Pt wire spiral CE, separated by approximated 20 mm and immersed in 20 ml of solution. For (a–p) $\varphi_{\rm pp} = 8\varphi_{offest}$. (a–d) For the electric potential study, there were 40 min of deposition to a geometric surface area of 3.6 cm² from approximately 20 mM HAuCl₄; φ_{offset} was varied from -0.625 to -2 V. (e–l) For the concentration study, $\varphi_{offset} = -2$ V was applied for 40 min to a geometric surface area of 0.8 cm² and the molarity of HAuCl₄ was varied from 2 to 20 mM. (m–p) For the time and surface area study, $\varphi_{offset} = -1$ V was applied with approximately 20 mM HAuCl₄, while the time was varied from 20 to 40 min and the geometric surface area from 7.2 cm² to 0.8 cm². (q–t) For the $\varphi_{\rm pp}$ study, $\varphi_{offset} = -2$ V was applied for 40 min to a geometric surface area from 40 min to a geometric surface area of 0.8 cm². (q–t) For the $\varphi_{\rm pp}$ study, $\varphi_{offset} = -2$ V was applied for 40 min to a geometric surface area from 40 min to a geometric surface area of 0.8 cm². (q–t) For the $\varphi_{\rm pp}$ study, $\varphi_{offset} = -2$ V was applied for 40 min to a geometric surface area of 0.8 cm² with approximately 20 mM HAuCl₄, and $\varphi_{\rm pp}$ was varied between 8, 12 and 16 V. Scale bars are 1 μ m unless otherwise indicated. Reprinted with permission from ref [178]. Copyright 2018 American Chemical Society.

The HAuCl₄ concentration also influenced the growth of the nanostructures. For deposition time 40 min, area 3.6 cm², and $\varphi_{\text{offset}} = -2$ V, 2 mM of HAuCl₄ produced spherical granules a few hundred nanometers in diameter (Figure 52e). 8 mM produced dendrites with approximately half- μ m rounded dendrite tips, and many small granules covering the dendrite stalk (Figure 52f). From 12 to 20 mM the dendrite surface became smoother, with fewer small granules on the surface, developing the appearance of a single crystal containing periodic ridges running approximately 60° from the direction of growth (Figure 52g–1).

Variation of the time and exposed electrode surface area showed no "loading effect" apparent under SEM inspection—increasing the Coulombs per surface area only increased plate size, and the deposition rate appeared to be constant with time and surface area. Specifically, for the plates grown in 20 mM HAuCl₄ at $\varphi_{\text{offset}} = -1$ V, 20 min of deposition onto 7.2 cm² showed plates of 0.5 μ m or less (Figure 52m). 20 min of deposition onto 3.6 cm² showed larger plates, approaching a μ m in width (Figure 52n). 40 min of deposition onto 7.2 cm² showed similar results (Figure 52o). 40 min of deposition onto 0.8 cm² showed approximately 2 μ m width plates (Figure 52p).

Changing the ratio $\varphi_{\text{offset}}/\varphi_{\text{pp}}$ had little influence on the Au dendrite topography (Figure 52q-t). As such, the ratio $\varphi_{\text{pp}} = 8\varphi_{\text{offset}}$ was typically held constant.

The shape of Au crystals can provide information on the crystal orientation of the surfaces, and can be quantified by measuring the angle between adjacent edges, corners, and branches. For Au plates deposited in 20 mM HAuCl₄ at $\varphi_{\text{offset}} = -1$ V, the angle between adjacent corners is approximately 60°, producing approximately regular hexagons (Figure 53a). Each corner is the nexus of four edges, two connecting to adjacent corners and two running from the corner to the center of the crystal. The plates are quite flat, with an approximately 100–110° angle between edges connecting corners (Figure 53a), and acute angles between edges that run from the corner to center, such as 23° (Figure 53b). The large plate in Figure 53b shows small recesses between the corners, suggesting growth is primarily at the corners, followed by filling in along the edge between corners. For Au dendrites deposited in 20 mM HAuCl₄ at $\varphi_{\text{offset}} = -2$ V, the angle between the dendrite branches is 60° (Figure 53c). The angles between adjacent edges is acute, covering a wide range of values from 35° to 80° (Figure 53c,d). The common 60° angle between plate corners and dendrite branches suggests there's a similar deposition process of preferred growth at corners, in which a dendrite forms when a corner grows faster than the adjacent edges can fill in. The corner then evolves into a branch from which new corners can nucleate. As Au has a fcc crystal lattice, the 60° angle between corners indicates a preferred crystallographic growth direction of $\langle 110 \rangle$.



FIGURE 53. Representative SEMs showing the angle between primary growth directions, and the angles between adjacent edges of the Au crystals in (a,b) plates, and (c,d) dendrites. (e) Cartoons of the plate growth (left and center) and the dendrite growth (right). Arrows represent the growth velocity of corners and edges. These show how increasing corner growth more than edge growth can give rise to the crystal shapes observed via SEM. Scale bars 1 μ m. Reprinted with permission from ref [178]. Copyright 2018 American Chemical Society.

In XRD measurements, the relative intensity of peaks associated with different orientations indicates the relative prevalence of each crystal orientation on the sample surface [31, 32]. Figure 54 shows representative patterns for Au dendrite, plate, and sputtered film samples, normalized so that the intensity of the $\{111\}$ peak equals one. The data for these Au dendrite and plate samples was recorded following 18 hours of CO_2 reduction. These data show that all the samples were dominated by $\{111\}$ surfaces, the dendrites had more surface with $\{100\}$ and $\{110\}$ orientations than the plates, and the sputtered film nearly no $\{100\}$ or $\{110\}$ surface. Note, the peaks for the (200) and (220) orientations were considered representative of the $\{100\}$ and {110} orientations, respectively. The double-peak structure for the curves from Au dendrites and plates indicates they have high crystallinity, and the single broad {111} peak for the sputtered film that it has lower crystallinity. The two peaks are produced because the copper source emits two very nearby wavelengths, $K_{\alpha 1}$ and $K_{\alpha 2}$ at 0.1540 and 0.1544 nm, respectively, which are both reflected by the crystal Bragg planes. Figure 62 shows the XRD patterns for dendrites grown at $\varphi_{\text{offset}} = -2$ V for several different φ_{pp} , indicating a slight tendency for more {100} and {110} surface orientation with increasing amplitude.



FIGURE 54. XRD spectrum of Au dendrite, plate, and polycrystalline film samples, normalized so the Au (111) peak height is 1. (a) full spectrum, (b) (111) peak, (c) (200) peak, (d) (220) peak. Reprinted with permission from ref [178]. Copyright 2018 American Chemical Society.

TEM images allow for spot analysis of surface crystal orientation over small sample areas. Figure 55a shows a dendrite crystal, and 55b the crystal orientation at a corner of the crystal. The the image plane is along the {100} orientation, and the edge appears to terminate in small {100} and {110} faces. Figure 55c shows a plate crystal, and 55d the crystal orientation of the flat crystal face. The image plane is also along the {100} orientation, and the edge appears to terminate in a {100} face. No μ m-scale facets were observed via TEM for either dendrites or plates.



FIGURE 55. TEM of Au dendrites and plates: dendrites under (a) low magnification (b) high magnification; Au plates under (c) low magnification, (d) high magnification. Both scale bars in (c) are 50 nm. Insets in (b) and (d) show the Fourier transform of areas highlighted by dashed line. Reprinted with permission from ref [178]. Copyright 2018 American Chemical Society.

With potentiostatic EIS, we measured the impedance (Z) and phase (ϕ) vs. frequency (f), for Au nanostructures made at different φ and in different electrolyte compositions. From this, we calculated the differential capacitance per unit area $(C_{\rm d}/A)$ of Au electrodes, shown in Figure 56a. From the shape of $C_{\rm d}/A$ vs. φ we determined the potential of zero charge (PZC) for each electrolyte. Specifically, the curve has a minimum at the PZC in the case of non-specific binding and dilute electrolyte [179], as demonstrated for mercury in numerous electrolytes of concentration ~ 10 mM or less [180]. The PZC of Au in vacuum is 0.55 V vs. standard hydrogen electrode (V_{SHE}), and should be similar in solutions with low binding energy to the metal surface [137]. We thus considered the local minimum of $C_{\rm d}/A$ located near 0.55 V_{SHE} to indicate the PZC. For pure HAuCl₄ solutions, we modeled our electrode-solution interface with a Randles circuit, shown in Figure 63 [34]. From this we calculated C_d/A of a sputtered Au surface in our standard dendrite growth solution, 20 mM HAuCl₄. However, this could only probe φ near the reduction potential of $AuCl_4^-$, 0.9 V_{SHE} at pH=1.7, where the reaction kinetics are slow. The over potential for ${\rm AuCl_4^-}$ reduction at 0.55 $\rm V_{SHE}$ drives the reaction kinetics faster than $AuCl_4^-$ can diffuse to the electrode surface. This creates a non-negligible Warburg impedance (Z_W) that is convoluted with the capacitive double layer impedance, evidenced by the deviation from a semi-circle in the Nyquist plots in Figure 64 for potentials negative of $0.8 V_{\rm SHE}$. The convolution prevents standard analysis of the Randles circuit, which would normally yield $C_{\rm d}$ and the charge transfer resistance $R_{\rm ct}$.



FIGURE 56. Potentiostatic EIS of a sputtered Au surface with geometric surface area 0.8 cm² in 100 mM H₂SO₄ with various concentrations of HAuCl₄. (a–c) Left of gray dashed line is extrapolation of C_d/A as a constant vs. φ , right of the gray dashed line is measured data. (a) C_d/A vs. φ ; electrode area A was measured by CV of the Au in H₂SO₄. (b) σ vs. φ calculated from (a). (c) $\Delta\gamma$ vs. φ calculated from (b). (d–g) Nyquist plots of the EIS measurements at each φ , for each of the HAuCl₄ concentrations. Reprinted with permission from ref [178]. Copyright 2018 American Chemical Society.

Aqueous solutions of pure H_2SO_4 provide a simpler measurement because no charge transfer reactions should occur in the electrochemical window for water, 0 to 1.23 V_{RHE} (-0.06 to 1.17 V_{SHE} at pH=1). This allows the system to be modeled as only R_{Ω} in series with $C_{\rm d}$. Figure 65a shows $C_{\rm d}/A$ vs. φ for aqueous solutions of H₂SO₄ of concentration 1, 10, 100, and 500 mM. It demonstrates that the minimum in $C_{\rm d}/A$ near 0.55 V_{SHE} changes little between 1, 10, and 100 mM H_2SO_4 , confirming that for this system 100 mM falls within the "non-specific binding and dilute electrolyte" case for identifying the PZC. It also shows the PZC to be approximately independent of pH. Nyquist plots in Figure 65d–g show a partial semicircle negative of 0.35 V_{SHE}, which we attribute to a slow transfer of Au from the counter to working electrode. Figures 66–73 show the individual Nyquist plots. However, for $\omega \gg 1/(C_{\rm d}R_{\rm ct})$, the imaginary component of the impedance (Z_i) of the Randles circuit reduces from $Z_{\rm i} = \omega C_{\rm d} R_{\rm ct}^2 / (1 + \omega^2 C_{\rm d}^2 R_{\rm ct}^2)$ to that of R_{Ω} and $C_{\rm d}$ in series, $Z_{\rm i} = 1 / (\omega C_{\rm d})$. Figure 74 shows that the measurements of $C_{\rm d}$ are approximately 50 $\mu {\rm F}$ or greater, and the semicircle radii in these plots, representative of $R_{\rm ct}$, are 200 Ω or greater. As such, the simpler circuit model is valid for $f \gg 100$ Hz, where $f = \omega/2\pi$. Reported $C_{\rm d}$ values are an average of measurements with 1,000 < f < 10,000 Hz.

 $Z_{\rm W}$ and $R_{\rm ct}$ are both inversely proportional to the concentration of the species responsible for the Faradaic current [34]. As we are only interested in $C_{\rm d}$ and not $R_{\rm ct}$, we used 100 mM H₂SO₄ as a supporting electrolyte and made measurements for 0, 0.01, 0.1, and 1 mM HAuCl₄, shown in Figure 56a. With the low HAuCl₄ concentrations, $R_{\rm ct}$ in series with $Z_{\rm W}$ was 200 Ω or greater, as shown by the Nyquist plots in Figure 56d–g. Figures 75–80 show the individual Nyquist plots. The high total concentration kept the capacitance at 50 μ F or greater. As such, for 1,000 < f < 10,000 Hz, we could again model the system as only R_{Ω} in series with $C_{\rm d}$. This allowed measurement of $C_{\rm d}/A$ from 1 to $-0.2 V_{\rm SHE}$ in the presence of different HAuCl₄ concentrations. Water splitting and significant Au deposition at more negative potentials obscured measurements.

The Lippman, or electrocapillary equation, shows that $\gamma(\varphi)$ equals the integral of the surface charge density (σ) on the metal half of the metal-electrolyte interface [181],

(79)
$$\gamma(\varphi) = \gamma_{\rm PZC} - \int_{\rm PZC}^{\varphi} \sigma(\varphi') d\varphi' = \gamma_{\rm PZC} - \Delta \gamma(\varphi),$$

where γ_{PZC} is the surface energy at the PZC. To solve this for $\gamma(\varphi)$ we need to know $\gamma_{\text{PZC}}, \sigma(\varphi)$, and the PZC. Per the electrocapillary equation, $\sigma(\varphi)$ can be determined by integrating $C_{\rm d}/A$ from the PZC to φ ,

(80)
$$\sigma(\varphi) = \int_{\text{PZC}}^{\varphi} C_{\rm d}(\varphi') d\varphi'.$$

By definition, $\sigma(\text{PZC}) = 0$, which allows evaluation of the integral in eq 80. Figure 56b shows the resulting $\sigma(\varphi)$. From this, the integral in eq 79 can be evaluated for $\Delta\gamma(\varphi)$, shown in Figure 56c. $C_{\rm d}/A$ was extrapolated as a constant from -0.2 to -1 V_{SHE} to make an approximation of γ down to -1 V_{SHE}. For the two-electrode plate and dendrite depositions, we assumed the Pt counter electrode was at ~ 1.5 V_{SHE}; the water oxidation potential of 1.13 V_{SHE} at pH=1.7 plus several hundred mV of overpotential and ohmic drop. As such, the plate growth would have occurred at $\varphi_{\text{offset}} \approx 0.5$ V_{SHE} and dendrite growth at $\varphi_{\text{offset}} \approx -0.5$ V_{SHE}. These correspond to decreases in γ of $\Delta\gamma(0.5) \approx 0$ eV/nm² and $\Delta\gamma(-0.5) \approx 1$ eV/nm². During the deposition half-cycles for plates and dendrites, where $\varphi \approx -3.5$ V_{SHE} and $\varphi \approx -8.5$ V_{SHE}, respectively, our data suggests $\Delta\gamma$ would be many eV/nm².

Cyclic voltammetry allowed for measurements of the sample surface area. These were made by sweeping across the oxidation and reduction potentials of Au in H_2SO_4 , and integrating the total charge passed during the reduction peak. Assuming a uniform and repeatable Au oxide layer, the relative surface area of the electrode could be measured [182]. Figure 57a shows the reduction peak of dendrite, plate, and flat Au film samples. Figure 57b shows the actual surface area and the roughness factor of each of these samples, normalized to the flat film. Figure 81 shows data taken between EIS measurements that had different electrolytes. Linear interpolation between these surface area measurements of EIS samples was used to approximate the C_d/A shown in Figure 56a.



FIGURE 57. Cyclic voltammetry of a dendrites, plates, and a flat film of Au on Si with geometric area 0.8 cm² in 500 mM sulfuric acid. (a) Overlayed cyclic voltammograms of each nanostructure. (b) Real surface area of the electrode, calculated by integrating the total charge of the Au reduction peak for each curve. The roughness factor was calculated by normalizing relative to the flat film. Reprinted with permission from ref [178]. Copyright 2018 American Chemical Society.

4.2.2. Electrochemical CO_2 reduction. XPS measurements before and after CO_2 reduction experiments were used to quantify the surface atomic composition and the Au oxidation state. Figure 82 shows that the XPS spectrum for the Au4f and O1s peaks are very similar before and after CO_2 reduction, suggesting no change is made to the Au oxidation state.

The performance of the Au dendrites, plates, and sputtered film as electrocatalysts for CO_2 reduction was assessed by measuring j_{total} and product gas composition at a variety of applied potentials. Figure 58a shows the geometric j_{total} of the dendrites, plates, and sputtered film; φ was started at $-0.2 \text{ V}_{\text{RHE}}$ for 4 hours, and then stepped in -50 mV increments every two hours to $-0.5 \text{ V}_{\text{RHE}}$. Finally, φ was returned to -0.25 V_{RHE} to test the sample's stability over time. j_{total} at the end of the experiment decreased substantially for the dendrites, but actually increased for the plates and sputtered film. Figure 58b shows the performance of dendrite and plate samples starting at $-0.2 V_{\text{RHE}}$ and stepping in -25 mV increments every 2 hours to -0.475 V_{RHE} , followed by 6 hour holds at -0.25, -0.35, and $-0.4 V_{RHE}$. With a smaller step size, more time will have passed before each electric potential is reached. The two different potential step sizes were compared to ensure this did not affect catalytic performance, a confirmation that the catalysts didn't degrade significantly with time. For both dendrites and plates, this hold to test stability showed much lower j_{total} at -0.25 V_{RHE} than the start of the experiment, but -0.35 V_{RHE} and -0.4 V_{RHE} showed only slight degradation. Comparing the -50 mV steps to the -25 mV steps, $j_{\rm total}$ was found to match very well at -0.35 and -0.4 V_{RHE}. The -0.25 V_{RHE} current densities matched for the end-of-experiment holds. For both step increments, the dendrite samples showed a decreasing j_{total} at each applied potential until -0.35 $V_{\rm RHE}$ was applied, after which $j_{\rm total}$ was stable with time for increasingly negative φ . The plates showed a similar response for the -50 mV steps, but continued to show decreasing j_{total} at all applied potentials throughout the -25 mV steps.


FIGURE 58. Current density and Faradaic efficiency of Au dendrites, Au sputtered film, and Au plates. (a) Total current density of a sample with (blue) Au dendrites, (black) Au sputtered film, and (red) Au plates under the potentials -0.2 to -0.5 V_{RHE}, stepped by -50 mV every 2 hrs, except for an initial 4 hr hold at -0.2 V_{RHE} for the current to stabilize. (b) Total current density of a sample with Au dendrites and plates under the potentials -0.2 to -0.475 V_{RHE}, stepped by -25 mV every 2 hrs, and followed by 6 hour holds at -0.25, -0.35, and -0.4 V_{RHE} to test stability. (c, d) Faradaic efficiencies for CO vs. φ . Reprinted with permission from ref [178]. Copyright 2018 American Chemical Society.

The Faradaic efficiency for production of CO by the dendrites, plates, and sputtered films are shown in Figure 58c for the -50 mV steps, and 58d for the -25 mV steps. The data show dendrites have approximately 50–60% Faradaic efficiency for CO for $\varphi \leq -0.35 \text{ V}_{\text{RHE}}$. The plates and film have CO Faradaic efficiency of approximately 20–40% and 5–10%, respectively, during the -50 mV steps; plates showed nearly 0% CO Faradaic efficiency during -25 mV steps. Notably, the dendrites seemed to show a slight increase in the CO Faradaic efficiency during the 6 hour holds at -0.35 and $-0.4 \text{ V}_{\text{RHE}}$, compared to the values measured during the 2 hour -25 mV steps; the CO Faradaic efficiency for the 6 hour hold at $-0.25 \text{ V}_{\text{RHE}}$ was too noisy to produce a reliable average. Figure 59 shows Tafel plots for the dendrites, plates, and sputtered film. The data show the kinetically limited reaction regimes to have a slope of 40 mV/dec for dendrites and 110 mV/dec for the plates and film.



FIGURE 59. Tafel slopes of Au dendrite and Au plate samples from -25 mV steps, and Au sputtered film from -50 mV steps. Reprinted with permission from ref [178]. Copyright 2018 American Chemical Society.

4.3. Comparison of dendrites and plates with literature. During electrocrystallization, the solute near the crystal surface gets added to the crystal surface via an electrochemical reaction. This depletes the solute concentration, establishing a diffusion boundary layer. In continued crystallization, the solute must diffuse across the diffusion boundary layer from the solution bulk to the crystal surface. The slower of these serial steps, diffusion or electrochemical reaction, will determine the rate of deposition and control the morphology of the crystals grown. Equivalent steps occur for crystallization from melts and vapors.

When crystallization is diffusion limited, three dimensional structures can be formed, such as dendrites. This occurs because protrusions on the crystal surface extend into the diffusion field, receiving faster diffusion of solute than the surrounding flat surface. The phenomenon is known as the Mullins-Sekerka effect [183]. The sharper the protrusions, the faster solute diffusion will be. This effect is balanced by the Gibbs-Thompson effect [184], in which the local surface energy of a crystal increases with decreasing radius of curvature; for a given deposition condition, protrusions with radius of curvature below a certain value will be thermodynamically unstable and dissolve/melt/sublimate.

To provide a model that describes the morphology of the crystals, we draw comparisons between the electrocrystallization and crystallization from melts and vapors. For crystallization upon a polycrystalline film, where a random assortment of crystal orientations are present for nucleation, growth will proceed along the orientation of lowest surface stiffness, γ^* [121]. This is a measure of the energy per unit area necessary to create curvature on a surface; adding atoms onto an atomically flat surface requires creating such a curvature. γ^* is derived from the surface energy, γ , via Herring's Equation [125, 118]; γ is defined as the energy it takes to create a unit area of interface between the crystal and solution. Figure 60a shows the predicted values of γ for several ambient phases and crystal orientations. Comparison of molecular dynamics simulations and experiments [121, 119, 120] has developed a theory to describe the dendrite morphology of different metals solidified from their melts. These calculations approximate the surface energy of crystals with underlying cubic symmetry by expansion into a series of cubic harmonics with two anisotropy factors, ϵ_1 and ϵ_2 ,

(81)
$$\gamma(\theta,\phi) = \gamma_0 [1 + \epsilon_1 K_1(\theta,\phi) + \epsilon_2 K_2(\theta,\phi) + \dots],$$

where the cubic harmonics are combinations of the standard spherical harmonics with cubic symmetry. The particular K_1 and K_2 referenced above are,

(82a)
$$K_1(\theta, \phi) = \sum_{i=1}^3 n_i^4 - \frac{3}{5},$$

(82b)
$$K_2(\theta, \phi) = 3\sum_{i=1}^3 n_i^4 + 66n_1^2 n_2^2 n_3^2 - \frac{17}{7},$$

where $\hat{n} = (n_1, n_2, n_3)$ is the interface normal. In spherical coordinates these have their standard definition, $n_1 = \cos(\phi) \sin(\theta)$, $n_2 = \sin(\phi) \sin(\theta)$, $n_3 = \cos(\theta)$. Equation 81 shows that the shape of γ is dictated by the value of ϵ_1 and ϵ_2 , scaled in magnitude by the surface energy prefactor, γ_0 . ϵ_1 and ϵ_2 thus determine the shape of γ^* , and the direction of growth of dendritic crystals. This angular dependence of the surface stiffness tensor can be calculated by,

(83)
$$\gamma^* = 2\gamma + \frac{\partial^2 \gamma}{\partial \theta^2} + \frac{1}{\sin^2(\theta)} \frac{\partial^2 \gamma}{\partial \phi^2} + \cot(\theta) \frac{\partial \gamma}{\partial \theta}.$$



FIGURE 60. Comparison of the tendency of Au to form facets at various Miller indices, in several ambient phases. Experimental d_{hkl} values from Ref. [136]. To calculate T_r , γ^* was assumed constant with temperature. For a Au vapor ambient phase, we used $\gamma_0 \approx 6.16$ (eV/nm²), the value for Au in a non-interacting atmosphere [137]. For a Au-melt ambient phase, $\gamma_{0,melt} = 0.786$ (eV/nm²) Ref. [119]. For the Au vapor and Au melt, we used $\epsilon_1 = 0.064 \pm 0.011$, $\epsilon_2 = 0.003 \pm 0.002$ Ref. [120]. For the HAuCl₄(aq) ambient phase, we used $\gamma_0 \approx 6.16$ (eV/nm²) for the PZC and $\gamma_0 \approx 5.16$ (eV/nm²) for the dendrite φ_{offset} , consistent with $\Delta\gamma$ measurements in 1 mM HAuCl₄(aq) + 100 mM H₂SO₄(aq). (a) γ ; the inset shows a rounded Au sphere with {111} facets formed by melting a Au wire. (b) γ^* . (c) T_r . (d) Cartoon of facets present at different deposition temperatures, relative to T_r for each Miller index. Reprinted with permission from ref [178]. Copyright 2018 American Chemical Society.

Values of ϵ_1 and ϵ_2 for various metals solidifying from their melt have been calculated by these molecular dynamics simulations, with plots generated of the inverse of γ^* and the expected dendrite morphology [121]. Comparing these with the dendrite morphology shown in Figure 53, the single branch in each $\langle 110 \rangle$ direction suggests the anisotropy factors for Au electrocrystallization from HAuCl₄(aq) are approximately $\epsilon_1 = 0.02$ and $\epsilon_2 = -0.02$. Interestingly, this differs significantly from the values reported for Au dendrites grown from their melt, where $\epsilon_1 = 0.064 \pm 0.011$ and $\epsilon_2 = -0.003 \pm 0.002$ [120], corresponding to dendrite growth in the $\langle 100 \rangle$ directions. As such, electrocrystallization allows for a unique dendritic Au structure than crystallization from melts allows. Figure 60b shows γ^* for several ambient phases. Electrocrystallization of Au dendrites with different growth directions would require tuning the anisotropy parameters, potentially possible with chemicals that would selectively interact with certain Au crystallographic orientations.

It has been shown through comparison of experiment and density functional theory calculations that γ of the Au {111} surface in vacuum is approximately 6 eV/nm² [137]. Using the ϵ_1 and ϵ_2 values determined above for electrocrystallization, this corresponds to $\gamma_0 = 6.16 \text{ eV/nm}^2$. This is a rough estimate; other work has reported $\gamma_0 = 4.3 \text{ (eV/nm}^2)$ [185]. Using a model that considers only polarization due to the ionic double layer, calculations showed γ to be unchanged by immersion in 500 mM H₂SO₄(aq). This model calculated the PZC to be 0.55 V_{SHE}.

Our measurements show the PZC of Au in 1, 10, and 100 mM $H_2SO_4(aq)$ to be ~0.35 V_{SHE} —and closer to ~0.4 V_{SHE} for 500 mM. This suggests there is some interaction between the Au and $H_2SO_4(aq)$ besides polarization. The negative shift indicates a negative species in the $H_2SO_4(aq)$ with an affinity to the Au, which at 0.55 V_{SHE} would draw a net positive charge onto the Au. The PZC of Au in 0.01, 0.1, and 1 mM HAuCl₄(aq) + 100 mM $H_2SO_4(aq)$ is also 0.35 V_{SHE} . If we assume $\Delta\gamma(0.55) = 0.1 \text{ eV/nm}^2$ equals the change in γ from the interactions with solution, then the change is negligible compared to $\gamma_0(\text{PZC}) \approx 6 \text{ eV/nm}^2$. Figure 56c does show a significant change of 1 eV/nm² at $\varphi = -0.5 \text{ V}_{\text{SHE}}$, though. This roughly corresponds to $\varphi_{\text{offset}} = -2 \text{ V}$ for dendrite deposition. Under our approximations, γ would reach 0 eV/nm² before the deposition half-cycle potentials for plate and dendrite growth, -3.5 and $-8.5 \text{ V}_{\text{SHE}}$, respectively. A negative γ would correspond to a dissolving electrode, so our approximation that C_{d}/A is constant at potentials negative of $-0.2 \text{ V}_{\text{SHE}}$ is evidently an overestimate. γ is likely quite low at these very negative potentials, though.

Regarding the structure of the crystal's surface, the surface of a crystal is either a flat atomically smooth facet with a particular crystallographic orientation, or a rounded atomically rough surface with a gradually changing orientation along its surface. If the deposition temperature is above the roughening temperature (T_r) for a particular crystallographic orientation, then the surface will be rough. T_r is a function of γ^* for a given ambient growth phase [186],

(84)
$$kT_{r,hkl} = \frac{2}{\pi}\gamma^*(T_r)d_{hkl}^2$$

where d_{hkl} is the interplanar distance parallel to the crystal face. "The more closely packed a given crystal face is, the larger the interplanar distance, and the higher T_r will be" [118]. For example, on a fcc lattice, the most closely packed face has $d_{111} = a_0/\sqrt{3} \approx 0.6a_0$, followed by $d_{100} = a_0/2 = 0.5a_0$; deposition at a temperature $T_{r,100} < T < T_{r,111}$ should produce crystals with rough rounded surfaces except for flat {111} facets. Figure 60c shows T_r for several ambient phases. Figure 60d demonstrates the meaning of T_r via a cartoon. The Au surface should be completely rough for room temperature deposition at φ for which $\gamma_0 \leq 0.25 \text{ eV/nm}^2$.

For context, we first consider T_r in Figure 60c for a Au surface in a Au melt and Au vapor. The plot indicates that solidification from a Au melt should not produce faceted Au crystals, as $T_r = 700$ K for the most densely packed faces, {111}, is below the melting point of 1300 K [120]. This is approximately confirmed by the SEM in the Figure 60a inset, showing the result of melting the tip of a Au wire with a butane flame and letting it crystalize in room temperature atmosphere; all the surfaces appear rounded except for small facets in the {111} directions. For the Au vapor, lacking a better option, ϵ_1 and ϵ_2 were somewhat arbitrarily set to the same values as for a Au melt. $T_r = 5400$ K for growth from a Au vapor, much higher than for the melt. However, Au must be raised over 900 K just to reach the minute vapor pressure of 10^{-11} Torr, and over 1500 K to reach 10^{-3} Torr [187]. As such, Au vapor should produce faceted Au crystals, but would require low pressure and high temperature equipment.

Per Figure 60c, T_r for HAuCl₄(aq) at the PZC and the dendrite φ_{offset} is slightly larger than for a Au vapor, and has a different shape than the melt and vapor due to the different ϵ_1 and ϵ_2 values. The large T_r means that, for deposition at room temperature and near the PZC, many crystallographic orientations should have faceted surfaces rather than rough. Since the {111} facet has the lowest surface energy, this would be expected to dominate, assuming local thermodynamic equilibrium during crystal growth. This is consistent with our XRD analysis of plates, which shows {111} to dominate. T_r for the dendrite φ_{offset} potential is slightly lower, but still over 500 K for all Miller indices considered. XRD does show {111} to continue to dominate the dendrites, but the peaks for {100} and {110} increase significantly compared to the plates. Growth of these crystals is diffusion limited, which could prevent full formation of {111} facets, and explain these increased peaks. Observations in TEM show nanometer-scale {100} and {110} facets along rounded surfaces; no {111} were observed. The prevalence of rough surfaces with scattered small facets, as observed via TEM, suggests that T_r for a Au surface may depend on the instantaneous potential. For our deposition process, this would sweep T_r widely between 0 and over 500 K during the MHz potential oscillation.

The structure of the Au plates is very similar to several Au [31, 188, 145] and Ag [142, 143, 144] plates recently reported. In these reports, it is proposed that sufficiently low ion concentration ensures nuclei cannot grow autocatalytically into lower-energy polyhedral structures. Instead, stacking faults and/or twin defects at the particle edges provide favorable sites for nucleation of new atomic layers on the {111} facets. The similarity in structure and dilute electrolyte suggests a similar kinetically limited growth mechanism is responsible for the morphology of the Au plates we produced.

The formation of dendrites at more cathodic φ is consistent with the mechanism discussed above. The higher overpotential could be sufficient to drive the kinetics of deposition faster than solute diffusion, establishing the diffusion limited growth condition. Separately, this overpotential may also drive nucleation of new atomic layers without the aid of twin defects, and thereby change the crystal morphology.

The effect of a MHz potential oscillation on dendrite growth has been described in detail [175, 176, 177, 146, 117]. The primary result of the oscillation is to increase the effective solute concentration at the dendrite surface, since the solute can replenish during the anodic half of the oscillation. The solute concentration has a significant impact on the dendrite morphology; as the concentration increases we have shown the dendrite crystals have fewer small granules on them (Figure 52e–1), and literature has shown the tip gets sharper [30, 146]. However, increasing the concentration of $HAuCl_4$ has the simultaneous impact of lowering the pH. Lower solution pH is understood to produce rounded surfaces instead of faceted ones [189].

Regarding CO_2 reduction electrocatalyst efficacy, the dendrites had the highest current density, while that of the plates and sputtered film was similar. Dendrites also showed the highest selectivity for CO, followed by the plates, and finally the sputtered film. This selectivity is consistent with the literature. Calculations and experiments have demonstrated the binding energy of the intermediate COOH to have the relative magnitudes of $\{110\} > \{100\} > \{111\}[28]$. This intermediate should thus be most stable on the dendrites, which have the greatest proportion of $\{110\}$ and $\{100\}$ facets, followed by plates, and finally the sputtered film.

The mechanism of the conversion of CO_2 to CO at a gold catalyst in an aqueous bicarbonate solution involves two electron transfers and two proton transfers to a $\mathrm{CO}_2.$ Different mechanisms for this process have been proposed, as summarized recently [173]. In all mechanisms, if the first reaction step produces an intermediate that is not stable on the Au surface, then it will be the rate limiting step (RLS). If the intermediate is stable, then the RLS will be the last step that produces an unstable (*i.e.* poorly bound) species. We assume the symmetry factor $\beta = 0.5$ for the electron transfers. As such, the 40 mV/dec slope measured for the dendrites suggests the RLS is an electron transfer to the intermediate COOH, producing CO and H_2O . This step completes the reaction, and is thus the lowest possible Tafel slope for mechanisms that are consistent with the appearance of a 40 mV/dec slope. The 110 mV/dec slope measured for the plates and film matches the first or second reaction step of the mechanisms reported in the above mentioned article. Fig. 61 shows two example schemes, in which the first step involves an electron transfer with a predicted Tafel slope of 118 mV/dec, and the last step is an electron transfer with a predicted Tafel slope of 40 mV/dec. Fig. 61a depicts an electron transfer to bind the CO_2 to Au, followed by protonation, and finally a proton-coupled-electron transfer (PCET). Fig. 61b depicts a PCET step to bind the CO_2 to Au, followed by another proton-coupled-electron transfer (PCET) to finish the reaction. The H^+ in the scheme cartoon represents a generic proton source—further studies of the reaction orders of different chemical species would be necessary to determine the proton source. The $40~{\rm mV/dec}$ slope has only been produced by one other structure we are aware of, Au nanoneedles [30, 67].



FIGURE 61. Two possible reaction schemes for the CO_2RR on Au plates and dendrites. (a) An electron transfer, followed by protonation, and finally a PCET. (b) Two sequential PCET reactions. The H⁺ represents any proton source. The predicted Tafel slope for the first electron transfer matches measurements of {111} dominated plates; the predicted Tafel slope for the second electron transfer matches measurements of {110} and {100}-rich dendrites. Reprinted with permission from ref [178]. Copyright 2018 American Chemical Society.

The dendrites clearly have much higher specific surface area than the film or plates, which can in part explain their higher current density. However, other characteristics are independent of the specific surface area. The lower Tafel slope of the dendrites is evidence of higher CO_2RR activity, which can result from stronger binding to the intermediate COOH. This reaffirms the expectation that nanostructures with a greater proportion of {110} and {100} relative to {111} facets provide faster reaction kinetics.

The potential -0.35 V_{RHE} stands out as a turning point where catalytic performance significantly increases as the potential becomes more negative. This was true for the dendrites, plates, and film. At the more negative potentials, $j_{total}(t)$ is stable during 42 hours of CO₂RR and shows a stark decrease in noise. The dendrites show a somewhat abrupt increase in the CO Faradaic efficiency from ~0 to ~50% with increasing overpotentials. Finally, the Tafel slopes change: for both the dendrites and the film there is an increase in the mV/dec of partial current density, typically understood to signify the point at which the reaction kinetics outpace the rate of mass transport to make the reaction mass transport limited. For plates, the slope decreases from ∞ to 110 mV/dec at this potential. Notably, a slight increase in the CO Faradaic efficiency is observed during the 6 hour potential holds, as shown in Figure 58d.

The plate samples demonstrated inconsistent results between -25 mV steps and -50 mV steps. This may be a result of poor stability of the plates during the long experiment time of the -25 mV steps, resulting in degradation. We excluded the CO Faradaic efficiency at -0.2 and $-0.25 \text{ V}_{\text{RHE}}$ during -50 mV steps because it was produced at very low and unstable current density, giving the data questionable accuracy.

4.4. **Conclusions.** In summary, electrocrystallization with a MHz oscillation of the potential φ allows for the fabrication of various Au nanostructures, namely plates and dendrites. According to XRD analysis, the surface of dendrites contains a larger proportion of $\{100\}$ and $\{110\}$ than the plates; the other major surface orientation on both nanostructures is {111}. EIS measurements of C_d/A vs. φ for polycrystalline Au in aqueous solutions show the PZC \approx 0.35 $V_{\rm SHE},$ with γ decreasing as φ moves away from the PZC. Adaption of a model for crystallization from melts and vapors suggests that, in this electrocrystallization, more crystal orientations should be faceted at φ with large γ . No facets should be present for room temperature deposition at φ with $\gamma_0 \leq 0.25 \text{ eV/nm}^2$. Comparison with literature on crystallization from aqueous solutions suggests that plate growth is kinetically limited, growing via stacking faults and/or twin defects at the plate edges to produce predominantly $\{111\}$ surfaces. Dendrite growth is likely mass transport limited, creating hierarchical nanostructures that are $\sim 10 \ \mu m$ tall. SEMs of plate corners and dendrite tips look similar, suggesting the kinetic process for the growth at these sites may be the same. Due to the hierarchical nature of these nanostructures, with nm-scale features on μ m-scale plates and dendrites, there is a certain degree of randomness and variation of Au surface within each sample. As such, precise control of exposed facets proves to be challenging. The averaging effect of XRD over cm^2 areas made it a powerful tool for analyzing the surface's distribution of crystal orientation. The different nanostructures were found to have significantly different performance as $\rm CO_2 RR$ electrocatalysts, supporting previous findings that $\{100\}$ and $\{110\}$ orientations are more active for CO_2RR than the {111} orientation. Stable performance was observed for 42 hours on the dendrites. $\varphi = -0.35 V_{\rm RHE}$ was observed to be the turn-on potential for the CO_2RR ; cathodic of this potential $j_{total}(t)$ was more stable, and the dendrite's Faradaic efficiency for CO was ~ 50 %. For future studies, higher HAuCl₄ concentrations may be considered to change the kinetic process, which for plates was likely dependent on low ion concentration. To avoid $\{111\}$ surfaces, which our data suggests has the highest roughening temperature, two approaches could be taken. First, more cathodic φ could be considered as a means to avoid the formation of any facets. Second, φ near the PZC could be focussed on, as a means to maximize the formation of facets besides $\{111\}$. 4.5. Supporting information. Below are circuit model schematics for electrochemical impedance spectroscopy (EIS) measurements; Nyquist plots used to calculate the differential capacitance of a Au surface; XRD spectra that show little change of facet preference between Au nanostructures deposited using different voltage amplitudes; differential capacitance, surface charge, and change in surface energy of a Au surface in different concentrations of sulfuric acid to establish an understanding of how a Au surface interacts with sulfuric acid—the supporting electrolyte used to study the interactions between a Au surface and chloroauric acid; electrochemical surface area measurements of the Au surface during EIS measurements; XPS spectra of the Au nanostructured surface before and after CO_2 reduction experiments.



FIGURE 62. XRD spectrum of Au dendrites grown at $\varphi_{\text{offset}} = -2$ V with different potential amplitudes, normalized so the Au (111) peak height is 1. (a) full spectrum, (b) (111) peak, (c) (200) peak, (d) (220) peak. Reprinted with permission from ref [178]. Copyright 2018 American Chemical Society.



FIGURE 63. Randles circuit model with ideal EIS response, used to interpret EIS data [34].



FIGURE 64. Nyquist plots showing electrochemical impedance spectroscopy measurements for a Au electrode in 20 mM HAuCl₄ at different DC potential biasses. The measurements were made starting at $\varphi = 1$ V_{SHE} and stepping in 100 mV increments to 0 V_{SHE}. The bottom right plot is a repeat of $\varphi = 1$ V_{SHE} after the other measurements to confirm the electrode did not significantly change during the measurements. Reprinted with permission from ref [178]. Copyright 2018 American Chemical Society.



FIGURE 65. Potentiostatic EIS of a sputtered Au surface with geometric area 0.8 cm² in various concentrations of H_2SO_4 . (a–c) Left of gray dashed line is extrapolation of C_d as a constant vs. φ , right of the gray dashed line is measured data. (a) C_d per unit area vs. φ ; electrode area A was measured by CV of the Au in H_2SO_4 . (b) σ vs. φ calculated from (a). (c) $\Delta \gamma$ vs. φ calculated from (b). (d–g) Nyquist plots of the EIS measurements at each φ , for each of the H_2SO_4 concentrations. Red solid lines are positive of 0.35 V_{SHE}, the black solid lines are at 0.35 V_{SHE}, and the dashed red lines are negative of 0.35 V_{SHE}. Reprinted with permission from ref [178]. Copyright 2018 American Chemical Society.



FIGURE 66. Nyquist plots of potentiostatic EIS measurements made in 1 mM $H_2SO_4(aq)$ from 1 V_{SHE} to 0.4 V_{SHE} . Reprinted with permission from ref [178]. Copyright 2018 American Chemical Society.



FIGURE 67. Nyquist plots of potentiostatic EIS measurements made in 1 mM $H_2SO_4(aq)$ from 0.375 V_{SHE} to $-0.2 V_{SHE}$. Reprinted with permission from ref [178]. Copyright 2018 American Chemical Society.



FIGURE 68. Nyquist plots of potentiostatic EIS measurements made in 10 mM $H_2SO_4(aq)$ from 1 V_{SHE} to 0.4 V_{SHE} . Reprinted with permission from ref [178]. Copyright 2018 American Chemical Society.



FIGURE 69. Nyquist plots of potentiostatic EIS measurements made in 10 mM $H_2SO_4(aq)$ from 0.375 V_{SHE} to $-0.2 V_{SHE}$. Reprinted with permission from ref [178]. Copyright 2018 American Chemical Society.



FIGURE 70. Nyquist plots of potentiostatic EIS measurements made in 100 mM $H_2SO_4(aq)$ from 1 V_{SHE} to 0.4 V_{SHE} . Reprinted with permission from ref [178]. Copyright 2018 American Chemical Society.



FIGURE 71. Nyquist plots of potentiostatic EIS measurements made in 100 mM $H_2SO_4(aq)$ from 0.375 V_{SHE} to $-0.2 V_{SHE}$. Reprinted with permission from ref [178]. Copyright 2018 American Chemical Society.



FIGURE 72. Nyquist plots of potentiostatic EIS measurements made in 500 mM $H_2SO_4(aq)$ from 1 V_{SHE} to 0.4 V_{SHE} . Reprinted with permission from ref [178]. Copyright 2018 American Chemical Society.



FIGURE 73. Nyquist plots of potentiostatic EIS measurements made in 500 mM $H_2SO_4(aq)$ from 0.375 V_{SHE} to $-0.2 V_{SHE}$. Reprinted with permission from ref [178]. Copyright 2018 American Chemical Society.



FIGURE 74. Net $C_{\rm d}$ vs. φ for potentiostatic EIS of a sputtered Au surface with geometric area 0.8 cm² in various concentrations of H₂SO₄. (left) All EIS measurements. (right) Magnified view of the pure H₂SO₄ electrolytes. Left of gray dashed line is extrapolation of $C_{\rm d}$ as a constant vs. φ , right of the gray dashed line is measured data. Reprinted with permission from ref [178]. Copyright 2018 American Chemical Society.



FIGURE 75. Nyquist plots of potentiostatic EIS measurements made in 0.01 mM $HAuCl_4(aq) + 100 \text{ mM } H_2SO_4(aq)$ from 1 V_{SHE} to 0.4 V_{SHE}. Reprinted with permission from ref [178]. Copyright 2018 American Chemical Society.



FIGURE 76. Nyquist plots of potentiostatic EIS measurements made in 0.01 mM $HAuCl_4(aq) + 100 \text{ mM } H_2SO_4(aq)$ from 0.375 V_{SHE} to $-0.2 V_{SHE}$. Reprinted with permission from ref [178]. Copyright 2018 American Chemical Society.



FIGURE 77. Nyquist plots of potentiostatic EIS measurements made in 0.1 mM $HAuCl_4(aq) + 100 \text{ mM } H_2SO_4(aq)$ from 1 V_{SHE} to 0.4 V_{SHE}. Reprinted with permission from ref [178]. Copyright 2018 American Chemical Society.



FIGURE 78. Nyquist plots of potentiostatic EIS measurements made in 0.1 mM $HAuCl_4(aq) + 100 \text{ mM } H_2SO_4(aq)$ from 0.375 V_{SHE} to $-0.2 V_{SHE}$. Reprinted with permission from ref [178]. Copyright 2018 American Chemical Society.



FIGURE 79. Nyquist plots of potentiostatic EIS measurements made in 1 mM $HAuCl_4(aq) + 100 \text{ mM } H_2SO_4(aq)$ from 1 V_{SHE} to 0.4 V_{SHE}. Reprinted with permission from ref [178]. Copyright 2018 American Chemical Society.



FIGURE 80. Nyquist plots of potentiostatic EIS measurements made in 1 mM $HAuCl_4(aq) + 100 \text{ mM } H_2SO_4(aq)$ from 0.375 V_{SHE} to $-0.2 V_{SHE}$. Reprinted with permission from ref [178]. Copyright 2018 American Chemical Society.


FIGURE 81. Cyclic voltammetry of a Au-coated Ti foil with geometric area 0.8 cm^2 in 500 mM sulfuric acid for variable concentration of H_2SO_4 and 375 mM sulfuric acid for variable concentration of HAuCl₄. (left) Overlayed cyclic voltammograms taken before or after EIS measurements for indicated electrolytes. (right) Real surface area of the electrode, calculated by integrating the total charge of the Au reduction peak for each curve and normalizing relative to reduction peaks of sputtered Au on a flat silicon wafer. Reprinted with permission from ref [178]. Copyright 2018 American Chemical Society.



FIGURE 82. XPS spectrum of Au dendrites before and after the CO_2 reduction experiment with -25 mV steps. (a) The Au4f peak, (b) the O1s peak. Reprinted with permission from ref [178]. Copyright 2018 American Chemical Society.

5. Conclusions

5.1. Concluding remarks. Metal nano and microstructures have many technological applications, including devices for electronics and renewable energy conversion and storage. Facets and sharp edges on the nanoscale can enable improved functionality in these devices in ways that are only recently being understood. Towards this end, an improved understanding of the physics behind the fabrication of these structures could allow better control of the nanostructures' morphology. As we have argued, it behooves the research community to place a greater emphasis on this research field, since metals have broad application but have somewhat fallen by the wayside as the community has focussed intently on semiconductors. In this thesis, we have summarized some of the literature that exists on the physics of metal nanostructure fabrication, and investigated two new methods for electrochemically forming such structures. We tested these new structures in plasmonic and electrochemical devices to draw connections between different morphologies and device functionality.

Aluminum nanowire arrays can be fabricated with nanoimprint lithography and electrochemical anodization, which was shown for the first time in this thesis work. These arrays have a pitch, diameter, and height that is unique amongst metal nanostructures. Also unique to these nanowires are sharp uniform ridges and corners surrounded by an otherwise smooth surface. We showed that these ridges are a waveguide for surface plasmon polaritons (SPPs), which may provide insight for the realization of SPP-based computer circuits.

Computer hardware currently depends on the translation of charge via electric currents to make calculations and store information. While gains in computational power and data storage density have long been made through miniaturization of circuitry, technology is reaching a roadblock from the limitation on heat dissipation during fast computations. If the electric currents used today could be replaced by beams of light, the heat generation could be mitigated. However, the diffraction limit of light propagating in free space is too large to allow for today's compact computer circuits. But, if the light could be confined as SPPs to narrow metal ridges [16], such as those on the Al nanowires we reported, then we may have the makings of a viable alternative to electronic circuits.

Gold nanodendrite films can be fabricated by electrodeposition, as we have discussed to great length above. Literature has shown that, with the addition of a MHz oscillation, the dendrite-tip growth velocity and the dendrite diameter can be controlled with the oscillation frequency when growing dendritic wires between closely spaced microelectrodes. Encouraged by the additional tunability this oscillation provides, in this thesis we used this method to grow dendrite films on macroscopic areas. We showed that the dendrite morphology depends on the electric potential frequency, offset and amplitude, as well as the electrolyte's HAuCl₄ concentration and the duration of the deposition. One important aspect of the morphology affected by these parameters is the crystal orientation of the exposed Au surface, which is known to determine the catalytic performance of Au in electrochemical CO_2 reduction. We tested this, and as one would expect, the nanodendrites that contained a greater proportion of $\{100\}$ and $\{110\}$ facets relative to $\{111\}$ facets had better electrocatalytic performance. Indeed, the best nanodendrites actually matched the lowest reported Tafel slope for CO_2 reduction on Au. This was only otherwise demonstrated on Au nanoneedles, which were suggested to gain their functionality from their sharp tips of sub 10 nm radius of curvature [30].

Electrochemical CO_2 reduction may play an important role in transitioning away from fossil fuels for energy and for materials synthesis. Amongst many attributes, it may offer a commercially viable method for seasonal energy storage, which few if any other technologies can reasonably project to accomplish. It has a rather simple mechanical design, closely resembling the already commercialized PEM electrolyzer cell used to split water and generate H₂ gas. The performance of CO_2 electrolysis systems is a function of the mass transport of reactants between electrodes, and the reaction kinetics at these electrodes. The underlying physics have been described in detail above, but are still not fully understood. Future work to move towards commercial systems will require substantial improvements in the catalyst on the cathode. Fortunately, this field has been receiving substantial and rapidly increasing attention in the academic and industrial research community.

5.2. Suggested future work.

5.2.1. Applications of Al nanowire arrays. With the Al nanowire arrays' unique diameter, height, and pitch, they may find application in numerous technologies, as discussed in chapter 2. In particular, devices that require large specific surface area on electrically or thermally conducting materials are likely to, at least in certain circumstances, find use for the Al nanowires. Such devices would include electrodes in electrolyzers. For example, it has been shown that Ni–Al films on glassy carbon electrodes produce hydrocarbon products with up to three carbon atoms bonded together [190]. It has also been shown that the sharpness of Au nanoneedles is an enabling attribute for their record setting CO_2RR catalytic performance [30]. Given these recent findings, it may be interesting to alloy the surface of the Al nanowire arrays with Ni to create an array of sharp electrocatalytic sites made of earth abundant materials.

Electrodes for batteries may also find use for Al nanowire arrays. There have been two recent reports of tri-valent secondary (rechargeable) Al-ion batteries [191, 192], the more recent of which used an Al metal anode and a high surface area carbon cathode. Very high charging rates, compared to typical Li-ion batteries, were obtained due to the high surface area cathode. Because of this, one might imagine that the integration of an Al nanowire array as the anode may further increase the charging rate. Separately, Al has been demonstrated as a desirable cathode for intercalation in secondary Li-ion batteries. Unfortunately, large volume expansion of the Al during intercalation can degrade this cathode after repeated charge/discharge cycles, due to grinding between adjacent Al crystallites. Various disorganized 3D Al nanostructures have been tested for this application, in anticipation that the empty space within the nanostructures could allow for non-destructive Al expansion [193, 194, 59, 195]. These studies indeed showed improved performance over flat films, but it is unlikely that the size and fill factor of these structures are optimized, since the randomness precludes a careful study of the optimal size of the Al and voids. This optimization may be possible with the uniform and well-ordered Al nanowire arrays reported in this thesis.

High thermal conduction in heat sinks is an increasingly important topic for high performance electronic circuits. Especially rapid modes of heat transfer are convection and phase change cycles of a working fluid in a heat tube connecting a heat source with a heat sink. A recent report showed that a titanium heat tube coated on the inside with a Ti microwire array allowed for good thermal conduction [112]. The Al nanowire arrays reported here are an order of magnitude smaller in pitch and diameter, which may allow for improved thermal conduction due to better thermal contact with the working fluid as a result of higher specific surface area. Optimizing the array pitch and the nanowire diameter and height would be an interesting study that may result in improved heat tubes featuring Al nanowire array coatings.

5.2.2. Direct measurement of Au surface energy, γ . Direct measurement of the Miller index-dependent surface energy of solid metal electrodes is difficult. However, it has been done for select metals, and may be possible for Au via the process outlined here, which is based on techniques discussed in chapter 2. The Volmer Weber model for the nucleation rate of 2D monolayers of metal during electrocrystallization is,

(85)
$$J = A_{2D} \exp\left(-\frac{b\Omega\epsilon^2}{ze|\eta|kT}\right)$$

where the pre-exponential factor A_{2D} can be considered roughly a constant, b is the number of sides of the nucleus, and Ω is the area of one atom on the surface.

To determine the maximum surface energy of the crystal, γ_{pzc} , nucleation experiments could be conducted on pristine Au(111) to measure the nucleation overpotential. The Au(111) surface could be obtained by flame annealing a thin Au wire to produce a particle faceted by {111} surfaces. Coating this wire with photoresist could expose just the particle via direct write lithography. From the derivation by Budevski (pg. 211) [189], the nucleation rate, J, can be calculated from the measured time lapse $\tau_{0.5}$,

$$(86) J = \frac{\ln 2}{\tau_{0.5}A}$$

where A is the electrode area. $\tau_{0.5}$ would be measured at different amplitudes of the overpotential pulse, η , by periodically pulsing the potential to η for different durations, to find the duration at which nucleation happens during half the pulses. Nucleation occurs when a deposition current is measured in the growth time following the nucleation pulse. This would provide the $J - \eta$ dependence. The slope of the plot of $\ln(J)$ vs. $1/|\eta|$ would determine the specific edge energy ϵ and the y-intercept the exponential pre-factor A_{2D} from the relation,

(87)
$$\ln J = \ln A_{2\mathrm{D}} - \frac{b\epsilon^2}{q_{\mathrm{mon}}kT} \frac{1}{|\eta|}$$

so that $\epsilon = \sqrt{(\text{slope})(q_{\text{mon}}kT)/b}$ and $A_{2\text{D}} = J(\eta^{-1} = 0)$. This information would be useful for understanding the physics of electrocrystallization of the Au, and determining the optimal morphology of the Au for electrocatalysis of the CO₂RR.

5.2.3. Faceting of dendrite tips. As described in chapter 2, limited work has been done to understand the faceting of dendrite tips. In the work that was done, NH_4Br crystals were grown from supersaturation of an aqueous solution. I am not aware of an analogous study of the faceting of dendrite tips from electrodeposition. Such a study could be conducted by adjusting the frequency of dendrite growth, which has been shown to control the tip growth velocity. SEM, TEM, and XRD analysis could then quantify the size and orientation of facets on the dendrite tips. One could imagine that this may offer a method to grow Au crystals that favor facets besides the energetically favorable {111}. This would be beneficial for electrochemical CO_2RR catalysis, which occurs better at non-{111} facets. 5.2.4. Role of sharp edges and grain boundaries in dendrite electrocatalytic activity. While XRD and electrolysis data show a clear correlation between an increased proportion of {100} and {110} and improved catalytic performance reflected in Tafel slopes, it doesn't rule out the possibility that sharp edges or grain boundaries on Au dendrites could instead be responsible for lower Tafel slopes than Au plates. Recent work on Au nanoneedles has shown that sharp points, with radius of curvature below 10 nm, can be very active [30]. It was suggested field-induced reagent concentration may be responsible for this. Other work on oxide-derived Au nanoparticles has shown that grain boundaries can be very active [25]. The Au dendrites have a complex morphology, which contains sharp points and likely many different grain boundaries. Fig. 83 shows SEMs of dendrites and plates that include such features. While the 20 nm radius of curvature of sharp points on the dendrites appears too large for field-induced reagent concentration, the tips are indeed sharper than the 40 nm radius of curvature of the plates. Likewise, the crystallites in the dendrites appear smaller and to intersect with a different geometry than the plates do, which would create different grain boundaries on the two structures. Further work would be required to rule out these mechanisms. This could include adjustments in the dendrite fabrication to produce less diverse structures and hone in on their enabling feature. A good first step in this process may be to reduce the deposition time, so that the dendrites have less time to develop diverse features. Other experiments could include detailed TEM to more accurately determine the sharpness of points on dendrites and plates. Finally, back-scatter SEM images and recently developed scanning probe techniques could be utilized to carefully measure the catalytic performance of different parts of the dendrites and plates to discern if certain boundaries or sharp edges are responsible for the catalytic performance [196].



FIGURE 83. Comparison of sharp edges and grain boundaries on Au dendrites (left) and plates (right). Left inset shows magnified view of sharp points on dendrites. Sharpest dendrite tips had 20 nm radius of curvature, while plates had 40 nm.

6. Appendix I: Microstructured Nation membranes

Reducing CO_2 to CO through electrolysis, for the eventual conversion to hydrocarbons, provides a path towards utility-scale, seasonal storage of renewable energy. It has previously used a two chamber cell, separated by a Nafion membrane, with a liquid electrolyte at the anode and cathode. Here we replace the liquid catholyte with CO_2 gas to increase its concentration and diffusion rate. With a liquid anolyte and gas catholyte, electrolysis is performed by integrating the cathode onto the Nafion membrane. This membrane electrode assembly (MEA) is fabricated via nanoimprint lithography (NIL), simultaneously achieving high active surface area and permeability.

6.1. Introduction. The typical cell for electrochemical CO_2 reduction is shown in Figure 84a. It consists of two chambers separated by a proton exchange membrane (PEM), which are filled with aqueous electrolytes that are saturated by dissolved CO_2 . The electrolyte facilitates ion conduction between the electrodes without simultaneous electron conduction [197]. Provided the electrode is reasonably hydrophilic, the electrolyte will conform to the electrode surface to create an interface for electrons in the electrode to react with CO_2 and protons in the electrolyte. This reaction site is called the triple point. Nation, a perfluorosulfonic acid, or a polymer with sulfate groups on a Teflon backbone, is used for the PEM [198]. This membrane allows proton conduction between the electrodes, while separating the O_2 produced at the anode from the CO and H_2 produced at the cathode. This cell design has some limitations. The concentration of CO_2 in the aqueous electrolyte is limited by its solubility, about 30 mM at room temperature and pressure [199]. Also, the diffusion rate of CO₂ from the electrolyte bulk to the electrode surface, and of product gases away from the electrode surface, are relatively slow in aqueous solutions $(2 \times 10^{-9} \text{ m}^2 \text{s}^{-1})$ [200]; in $\rm CO_2$ gas, the diffusion rate is about 10,000 times faster (1.5 $\times 10^{-5} \ m^2 s^{-1})$ [201].

To improve upon this cell design, here we report a membrane electrode assembly (MEA) that allows the liquid catholyte to be replaced by CO_2 gas. The MEA is composed of a Nafion membrane with a micropillar array on one side. This surface is coated by a Au film such that a $\sim 3 \mu$ m diameter hole in the film is present next to each pillar. This allows CO_2 gas in the cathode chamber to react with protons passing through the membrane and electrons in the Au film. By filling the cathode chamber with CO_2 , the concentration increases to about 50 mM and the diffusion rate of gasses is increased. A drawback is the small surface area for the reaction triple-point. However, trace amounts of electrolyte from the anode chamber leaking onto the Au film could make a liquid film on the Au surface to allow protons to access

the entire Au surface, while potentially only somewhat limiting gas diffusion to and from the Au.

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FIGURE 84. Schematic of CO_2 electrolysis cell. a) Conventional cell design, b) our new cell design with a Nafion micropillar-based MEA and CO_2 gas in the cathode chamber.

6.2. Device fabrication. The Nafion membrane was dropcast via a nanoimprint lithography (NIL) process [202]. For this, electron beam lithography was used to create a Si master chip. In this process a hexagonal array of 3 μ m circles was written in a film of PMMA on a Si chip. The chip dimensions were 30 x 30 x 0.5 mm. Sputtering 120 nm of Al, followed by etching the PMMA with acetone, produced a hexagonal array of Al circles on the Si. The Si chip was then etched in a reactive ion etch system to create Si pillars of 3 μ m diameter, 10 μ m pitch, and 2 μ m height. The Al film was removed by immersion in an Al wet etchant (Transene aluminum etchant type A). The Si chip was cleaned via rinsing in acetone, DI, and isopropyl alcohol.

This Si chip master was used to make a PDMS mold with the negative of the micropillar array. For this, the Si chip was placed on an acrylic block (30 x 30 x 3 mm), and both were placed inside a small plastic petri dish (50 mm diameter, 9 mm deep). Dow Corning polydimethylsiloxane (PDMS), Sylgard 184 Silicone Elastomer Base and the corresponding Sylgard 184 Silicone Elastomer Curing Agent were mixed and then poured into the petri dish. The base and curing agent were used at a 10:1 ratio, 8 g and 0.8 g, respectively. This elastomer base was used because PDMS in its vicious liquid form will form around the silicon micropillar master and will hold this shape as a flexible solid after it is dried and removed from the sample. The PDMS mixture was degassed for 20–30 minutes in a vacuum chamber attached to a rough pump; a vent valve was used to prevent bubbles from overflowing out of the petri dish. Removal of bubbles is important for reproduction of nano-scale features. After de-gassing, the PDMS was cured at room temperature and pressure for 48 hours. When the mold was fully hardened, it was carefully removed from the plastic petri dish, and the chip and block were peeled from the PDMS. This created a well in the PDMS with the negative of the micropillar array at the well bottom. The PDMS mold was rinsed with deionized water and isopropanol, and placed well-side-up in a large plastic petri dish (100 mm diameter, 15 mm deep). No release layer was needed on the PDMS for good reproduction of the micropillar structure in Nafion membranes. Figure 85a shows a schematic of this mold fabrication process.

Nafion membranes were dropcast from the PDMS mold. For this, 1.5 ml of a solution of Nafion solids and alcohol solvent (Dupont D2021 Nafion Solution from Ion Power) was poured into the PDMS mold. Membranes made with 1 ml of solution were not mechanically robust enough, and would tear during handling. Pouring was done slowly to avoid bubbles, which would produce holes in the cured membrane. During the Nafion cure, management of solvent evaporation was of prime importance to minimize mechanical stress in the membrane. Flat films were important for a good seal to the electrochemical cell in CO_2 reduction studies. To allow controlled solvent evaporation, the lid of the large petri dish had nine 1.5 mm diameter holes drilled into it, to create a porous $35 \ge 35$ mm square area in the center of the lid; trial and error showed this number and arrangement of holes in the lid to work well. A $45 \ge 45$ mm square piece of paper towel (VWR Spec-Wipe 5) was taped at its corners to the inside of the petri dish lid, and a scalpel was used to punch holes through the paper towel inline with the lid holes. This towel caught condensation before it dripped from the lid onto the curing Nafion. Curing the Nafion for 2.5 hours at 60° in an oven preheated for 2 hours produced the flattest films; other heating methods produced stress in the membrane that caused it to curl. Figure 85b shows a schematic of this membrane fabrication process.

The membrane was coated by a Au film with electron beam (e-beam) deposition. The membrane was tilted to 60° from the surface of the deposition stage. As such, the 2 μ m tall pillars cast a 3.5 μ m long shadow during Au deposition. This produced a regular array of openings in the Au film, to allow protons to pass from the Nafion membrane and interact with CO₂ on the Au surface. Figure 85c shows a schematic of this deposition process. Figure 85d shows an SEM of the Au-coated Nafion micropillar array membrane.



FIGURE 85. Schematic diagrams of the fabrication process for (a) PDMS mold, (b) Nafion membrane, and (c) Au-coated Nafion membrane. (d) SEM of Au-coated Nafion micropillar array membrane. *(SEM and membrane made by Brittany Carter.)*

6.3. Device characterization. The catalytic performance of the MEA for the CO_2RR will be tested in a custom electrochemical cell with a potentiostat and gas chromatograph. As a control, 0.5 M KHCO₃(aq) saturated by CO_2 will be used as the catholyte and anolyte, with CO_2 bubbling through the electrolyte. The aqueous catholyte will then be replaced by gaseous CO_2 ; the anolyte unchanged.

In this configuration, preliminary experiments showed salt deposits on the surface of the Au film. Electron diffraction spectroscopy (EDS) of the deposit's composition showed it to come from the analyte, presumably due to diffusion of ions through the Nafion. To mitigate this issue, one could use a more acidic analyte to provide a higher ratio of proton to K^+ concentration. This should decrease the proportion of K^+ in the cations diffusing through the Nafion, slowing the formation of deposits on the Au surface. It should also increase the supply of protons available at the Au surface for reactions with CO_2 .

7. Appendix II: Au dendrites for biosensing

7.1. **Introduction.** Point-of-care (PoC) medical diagnostic instruments, especially if low-cost, are valuable for controlling disease outbreaks. This is especially true for populations that don't have easy access to hospitals or other appropriate medical facilities. Here we report a lab-on-chip biosensor that is based on biofunctionalization of gold nanodendrites as a means to detect the infectious disease biomarker cholera toxin. This PoC-compatible technology could be useful for rapid diagnosis of cholera.

The nanodendrites used in this study were fabricated by electrodeposition with a MHz electric potential oscillation, similar to the dendrites reported earlier in this thesis. The high surface area of the dendrites improves the detection limit of the sensor, in comparison to a flat Au surface. To biofunctionalize the Au surface and enable electrochemical detection of cholera toxin, the surface was coated with a conductive polypyrrole polymer. Following previous work [203], this layer was an N substituted polypyrrole with terminal cyano groups able to electrostatically tether antibodies to the surface. In that work, the cyano group of the polymer could bind to antibodies via hydroxyl groups in the Fc region, which left the recognition element available for sensing. 7.2. Device fabrication. Si chips for detector devices were diced to $30 \ge 30 \ge 0.5$ mm and coated by Ti/Au via physical vapor deposition. Before metal deposition, the chips were sonicated in acetone for 10 min, rinsed with isopropanol, rinsed with DI, and finally dried with an N₂ stream. E-beam deposition in a Sharron system was used to deposit a 10 nm Ti adhesion layer, followed by 125 nm of Au.

Au electrodeposition onto the Ti/Au coated chips was carried out with a waveform generator (Agilent 33600A Series) using a two-electrode setup. The waveform was monitored with an oscilloscope (Agilent MSO-X 3024A) during electrochemical deposition, using a 10:1 passive probe (Agilent N2863B) to minimize the oscilloscope's disturbance of the waveform. The Au film served as the working electrode, and a platinum wire as the counter electrode. A square waveform with frequency of 30 MHz, peak-to-peak amplitude of 8 V, offset of -1.25 V, and duty cycle of 50% was applied for 20 min in a solution of 30 mM HAuCl₄.

Biofunctionalization was conducted in an electrochemical cell with a three-electrode setup. The gold chip surface was the working electrode, an Ag/AgCl wire the reference electrode, and a platinum wire the counter electrode. To deposit a Poly-(2cyano-ethyl)pyrrole (PCEPy) film, 10 mM 2-cyano-ethylpyrrole was dissolved in a supporting electrolyte of 0.1 M NaClO₄. The pyrrole monomer was electrooxidized at 0.8 V for 100 s. Electrodes were rinsed with DI. Differential pulse voltammetry (DPV) in an aqueous NaClO₄ electrolyte containing no monomer was used to confirm electrogeneration of the PCEPy film. A sample measurement of such confirmation is shown in Fig. 86.



FIGURE 86. DPV to confirm electrogeneration of PCEPy film on the Au surface.

PCEPy coated electrodes were incubated for 48 hours at $4 \,^{\circ}\text{C}$ in 0.1 M NaHCO₃, pH 9.6, with 1 mg/ml of the ELISA capture antibody. After incubation, the electrodes were rinsed three times with TBST (0.05% Tween-20, 50 mM Tris, 150 mM NaCl, pH 7.4). To avoid nonspecific binding to any remaining free cyano sites, the electrodes were blocked for 1 hour at room temperature in 5% BSA + 5% glycerol in TBST.

7.3. Device characterization. The lab-on-chip protocol for electrochemical cholera toxin detection was developed by modifying a standard ELISA protocol. Rather than electrostatically tether the capture antibody (anti-cholera toxin PAb) to a 96 well plate, it was tethered to the chip surface. The following ELISA steps (cholera toxin, secondary and tertiary antibodies, and enzyme substrate) were conducted in the standard way, except that all reagents were applied directly to the chip, so all elements became tethered to the dendrite surface. DPV measurements with a potentiostat (Gamry Interface 1000) in a three electrode setup were then made, with the chip as working electrode, Ag/AgCl wire as reference electrode, and Pt wire as counter electrode. DPV settings were: potential range of -0.3 V to 0.2 V, potential step of 2 mV, pulse amplitude of 50 mV, pulse width of 50 ms, pulse sample period of 100 ms, and an equilibrium time of 10 s.

The results of the electrochemical ELISA measurements are shown in Fig. 87. The current produced by a planar electrode during the DPV potential sweep, at different concentrations of CTX in the electrolyte, is in Fig. 87a. The peak current magnitude vs. CTX concentration, averaged over several repeated measurements, is shown in Fig. 87b. The same for a dendrite electrode is in Fig. 87c and Fig. 87d. These currents are normalized by geometric surface area of the working electrode, and the current density for the planar and dendrite electrodes plotted vs. CTX concentration in Fig. 87e. For the range of CTX concentrations tested, 50–500 ng/ml, this clearly shows the dendrite electrode to have a higher signal strength than the planar electrode, as well as a greater sensitivity of the current density to changes in CTX concentration. As such, the addition of dendrites to the working electrode offers a simple method to improve the performance of lab-on-chip electrochemical ELISA measurements devices.



FIGURE 87. DPV on planar and dendrite electrodes for electrochemical ELISA. (a) Planar electrode on-chip ELISA titration. (b) Average peak current of three planar electrode lab-on-chip ELISA devices plotted against cholera toxin subunit B concentration. (c) Dendrite electrode on-chip ELISA titration. (d) Average peak current of five dendrite electrode lab-on-chip ELISA devices plotted against cholera toxin subunit B concentration. (e) Comparison of the average peak current density of dendrite electrode and planar electrode devices at two cholera toxin subunit B concentrations.

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8. Appendix III: Aluminum nanowire arrays via directed assembly

Nathan T. Nesbitt, Juan M. Merlo, Aaron H. Rose, Yitzi M. Calm,

Krzysztof Kempa, Michael J. Burns, and Michael J. Naughton

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Aluminum Nanowire Arrays via Directed Assembly

Nathan T. Nesbitt,* Juan M. Merlo, Aaron H. Rose, Yitzi M. Calm, Krzysztof Kempa, Michael J. Burns, and Michael J. Naughton*

Department of Physics, Boston College, 140 Commonwealth Avenue, Chestnut Hill, Massachusetts 02467, United States

Supporting Information

ABSTRACT: Freestanding and vertically-oriented metal nanowire arrays have potential utility in a number of applications, but presently lack a route to fabrication. Template-based techniques, such as electrodeposition into lithographically defined nanopore arrays, have produced well-ordered nanowire arrays with a maximum pitch of about 2 μ m; such nanowires, however, tend to cluster due to local attractive forces. Here, we modify this template fabrication method to produce well-ordered, vertically-oriented, freestanding Al nanowire arrays, etched from an underlying Al substrate, with highly tunable pitch. In addition, optical measurements demonstrated that the nanowires support the propagation of surface plasmon polaritons.



KEYWORDS: Metal nanowires, anodized aluminum oxide (AAO), plasmonics

Vertically-oriented, lithographically-ordered, metal nanowire arrays have potential utility as capacitors,¹ high surface area electrodes,² electrochemical biosensors,³ optical nanoscopes,^{4,5} rectennas,^{6,7} and solar cells.^{8–12} In many of these applications, the nanowires are coated with materials to produce core–shell or nanocoax structures,¹³ which, for many deposition processes, requires the nanowires to be freestanding to accomplish a homogeneous coating.

Currently, only a limited range of nanowire heights and array pitches can be produced in ordered arrays using metallic materials. Chemical vapor deposition, a method of nanowire fabrication with tunable height and pitch, produces metal nanowires in only disordered arrays (Figure 1a)^{14,15} or carbon nanofibers having low electrical conductivity ($\sim 10^4$ S/m,^{16,17} three decades lower than good metals¹⁸) (Figure 1b). Electroplating metals in anodized aluminum oxide (AAO) template nanopores produces highly conductive and ordered arrays (Figure 1c),^{9,19–22} but a maximum pitch of 2 μ m^{9,20} typically causes the nanowires to cluster together due to local attractive forces.^{23,24} As greater tunability of nanowire height and pitch could be advantageous for the aforementioned applications, we have modified the preparation of AAO templates to produce highly ordered and freestanding aluminum nanowire arrays (Figure 1d). This process etches the nanowires from the underlying substrate at lithographically defined locations, providing high tunability of the array geometry. Additionally, the process is amenable to low-cost, large-scale production because it is solution based, roll-to-roll compatible,^{9,25} operates at atmospheric pressure with temperatures between 0 and 60 °C, and uses Al, an earth abundant²⁶ and inexpensive metal.

An AAO template consists of an array of pores passing through the thickness of an oxidized aluminum film. The oxide is developed by anodizing the Al, with pores formed during anodization due to a positive-feedback process. Well-ordered arrays can be obtained by prepatterning the Al surface with an



Figure 1. Methods of fabricating metal nanowire arrays. (a) Chemical vapor deposition (CVD) of Ni:^{14,15} a bottom-up process that produces vertically-oriented nanowires with irregular spacing between them. (b) CVD of carbon nanofibers: a bottom-up process that produces disordered nanowires with poor conductivity relative to good metals;^{16–18} orange rectangles represent particles the nanofibers nucleate on. (c) Electrodeposition of metal nanowires in templates:^{9,19–22} a template-based method that produces metal nanowires in an ordered array. Existing templates, such as porous AAO, have limited pitch, which causes these wires to bundle; orange rectangles represent a porous template. (d) Al nanowire arrays via directed assembly: a top-down process that produces lithographically-ordered, vertically-oriented, freestanding metal nanowire fabrication; orange layer represents AAO.

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Figure 2. Fabrication process of Al nanowires, with representative SEM data of neighboring regions on the sample showing each step on top, and corresponding cartoons on bottom. (a) SEM of Ni stamp used to indent the Al, (b) SEM of indented Al surface, (c) SEM of AAO template surface, (d) SEM of Al nanowires, (e) cartoon of Ni stamp, (f) cartoon of the imprinted Al surface, (g) cartoon of the AAO template with missing pores with a cross-section of the template where Al nanowires are embedded, and (h) the Al nanowires after etching away the AAO. For parts a–d, above the dashed green line there is a periodic array of missing Ni posts in the stamp, translating into Al nanowires on the sample; below this line depicts a conventional AAO process with no posts missing from the stamp. Scale bars 2 μ m.

ordered array of indents, steering pore nucleation at the indent sites,²⁷ as discussed in a recent review article.²⁸

In our approach, fabrication of an Al nanowire requires a defect in the form of an intentional lack of an indent in the Al surface, which blocks the formation of a pore when anodizing the Al to produce an AAO template. Scanning electron microscope (SEM) images and associated schematics in Figure 2 demonstrate this process. A stamp composed of an array of Ni posts, with some posts missing from the array to produce directed defects (Figure 2a), is pressed against an Al film to create indents in the Al (Figure 2b). When the film is subsequently anodized, pores preferentially form at the indents, while the Al below the missing indents is protected from oxidation. This process yields Al nanowires embedded in the AAO template at the missing indent sites (Figure 2c). Selective postetching of the aluminum oxide leaves freestanding Al nanowires (Figure 2d). The locations of such nanowires can be lithographically controlled by the placement of the missing posts in the stamp. As such, the nanowires can be as far from each other as desired, or as close to each other as separated by one anodized pore (e.g., 2.4 μ m center-to-center in Figure 5a). We found that for stamps with Ni posts of variable diameter, from 200 to 700 nm, there was a maximum Ni post diameter of approximately 400 nm that would produce an AAO template with embedded Al nanowires (Figure S1). Further details are provided in the Supporting Information.

To fabricate the Al nanowire arrays in Figures 3 and 5, we used a hexagonal array of Ni posts (~400 nm diameter and height, 1.2 μ m pitch), fabricated via electron beam lithography on a Ni-coated-glass surface, to imprint the aluminum. From this underlying hexagonal matrix, we fabricated both hexagonal (Figures 3a-c) and square (Figures 3d-f) arrays of nanowires by proper placement of missing posts in the stamp. Geometrically, an aluminum nanowire is the result of subtracting a cylinder with a hemispherical base (i.e., the pore and surrounding oxide) from the bulk aluminum at the site of each indent. For a hexagonal array of indents, each missing indent is surrounded by six indents, which ultimately produces Al nanowires with a hexagonal cross-section (Figure 3, parts b and e). Other lattice configurations of indents have been demonstrated to produce AAO templates, such as a square



Figure 3. Diagram and SEMs demonstrating how the same underlying matrix (a hexagonal array of pores) can produce different lattice geometries of nanowires (hexagonal and square arrays). (a, d) Blue circles and yellow dots represent sites of nanowires and pores, respectively; circled yellow dots emphasize that all the nearest neighbors of a nanowire are pores, which causes the nanowires to have a hexagonal cross-section. (b, e) SEMs of resulting Al nanowire arrays in a (left) hexagonal lattice and (right) square lattice, tilt 0°. (c, f) SEMs of same region with tilt 30°. Scale bars 2 μ m.

array,⁹ and may also produce Al nanowires; we expect a square array of indents would produce Al nanowires with square cross-section.

To explain the growth mechanism of the nanowires, we compare our results to previous reports of imprinting a hexagonal array of indents into Al and leaving out indents at certain sites in the hexagonal lattice. In a study using an aqueous oxalic acid solution,²⁹ the lack of an indent had little impact on the pore formation and subsequent AAO template—pores formed at the sites of missing indents nearly as well as at

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Figure 4. Mechanism of Al nanowire growth. (a) Studies have shown phosphorus from the electrolyte to penetrate into the alumina, (b) with a layer of relatively pure alumina adjacent to the oxide/metal interface (barrier oxide);³¹ we propose this pure layer may resist deformation into a pore at sites where the Al surface was not indented. (c) Studies have shown the phosphorus to penetrate deeper into the oxide at the pore base than along the pore walls.³⁶ (d) On the basis of a separate study, this may result from plastic flow of relatively pure alumina from the metal/oxide interface at the pore bottom up into the pore walls.³⁴ (e) This relatively pure alumina is thought to resist ion flow,³¹ which may protect the Al nanowires from anodization through the pore wall. (f) Sites on the Al surface that are not indented, but surrounded by indents, produce Al nanowires, as demonstrated in this study.

sites with indents. In a study using an aqueous phosphoric acid solution,³⁰ a site with a missing indent produced a pore with a relatively small radius and caused adjacent pores to have diamond shaped cross sections, rather than the typical circular shape. In our study, using citric acid with very dilute phosphoric acid in a solution of half deionized water and half ethylene glycol (EG), a missing indent successfully prevented the formation of a pore.

The variations in the reports above, from minor impact on pore formation, to producing only a small pore, to fully blocking pore formation, track with several other trends in AAO fabrication. For example, a missing indent becomes less likely to form a pore as anodization voltage or pitch is increased.^{29,30} Also, different electrolyte anions penetrate different percentages of the barrier layer oxide at the pore base,³¹ and missing indents are less likely to form pores as this penetration depth decreases (see Supporting Information, Table S1, for details).

To explain how these trends impact pore formation we consider the flow model for AAO growth, in which mechanical instabilities in the oxide cause pore nucleation. Reports supporting this $model^{28,32-36}$ have found pore nucleation to result from buckling of the oxide film, forming walls around pores,³⁶ initiated during anodization when the applied potential was high enough for electrostriction of the oxide to overcome the oxide surface tension. Since anions contaminating the oxide near the electrolyte/oxide interface modify the oxide's mechanical properties, such as its surface tension^{33,36} and elasticity,³⁷ the type and concentration of anions in the oxide determines the voltage at which pores nucleate. Such contamination by phosphorus anions into the oxide is depicted in Figure 4a. We propose that the low oxide contamination during anodization in phosphoric acid, compared to oxalic acid,³¹ may be what limits the formation of a pore at a missing indent; the thick layer of relatively pure alumina may resist mechanical deformation into a pore during anodization (Figure 4b). Because of limited studies on citric acid anodization, the role of these anions is unclear; however, the model we propose would suggest that citric acid anions have limited penetration into the oxide.

This flow model also offers an explanation for why the Al nanowires do not anodize through the sidewall of the AAO pores. In a recent study of the distribution of elements within the alumina of a pore grown in phosphoric acid,³⁶ the pore wall was found to have less penetration of phosphorus anions than the pore base (Figure 4c). A separate study, using a tungsten tracer layer in the Al substrate to track the flow of oxide in the pore during anodization,³⁴ elucidates this result; they found that oxide was generated at the metal/oxide interface at the pore bottom, and then flowed up and out into the sidewalls of the pore, as depicted in Figure 4d. The expected high resistance to electronic and ionic flow³¹ of the relatively pure oxide in the pore sidewalls and above the nanowires is highlighted in Figure 4e.

The Al nanowires were observed to have attributes desirable for technological applications. For example, the process that produces the nanowires yields a hexagonal cross-section with sharp edges and smooth, concave surfaces, including a 6pointed crown shape. These features are evident in the SEM images in Figure 5. The crown points (Figure 5b) have radii of curvature ~ 10 nm (Figure 5c). In addition to such small pitch arrays, we can also fabricate arrays with pitch over 10 μ m, and with wire height to, e.g., 20 μ m (Figure 5d). Such sharp edges and smooth surfaces may be of relevance for photonic and plasmonic applications,^{38,39} such as electric field enhancement. The strong secondary electron signal at the nanowire edges, relative to that at the faces, in Figure 5a, is more probable than not evidence of such enhancement—the alternative explanation being charging due to an anomalously thick native oxide at the edges. Additionally, as the nanowires' purity is determined by that of the starting Al foil/substrate, these wires are 99.9995% Al. Because of a low bulk oxide content, surface plasmon resonances (SPRs) on the nanowires should have high light scattering efficiency-advantageous for certain plasmonic devices.⁴⁰ Panchromatic cathodoluminescence images of the nanowires (see Supporting Information, Figure S3) show these edges to be dark for measurements at normal incidence, but not for measurements with sample tilt of 30°-potential evidence of strong light scattering at the edges.

Although Al was the first metal whose plasmonic properties were studied in depth,⁴¹ it has only recently been investigated for applications in nanostructured plasmonic devices.^{40,42,43} This is a result of fabrication challenges for Al nanostructures^{42,43} and the location of the Al SPR cutoff frequency in the deep UV;⁴⁴ most plasmonics research has focused on visible light manipulation. Noble metals such as Au and Ag have SPR



Figure 5. SEMs demonstrating attributes of the Al nanowires. (a) High contrast SEM of Al nanowires demonstrates electric field enhancement at the nanowire edges and corners. (b, c) SEMs show the radius of curvature of the nanowire corner to be ~ 10 nm. (d) SEM of Al nanowires with large height and pitch demonstrates tunability of Al nanowire array geometry. Tilt 30°.

cutoff frequencies in the visible and near-UV,^{40,45,46} respectively, which have made them materials of choice for plasmonic device development. Recent studies, however, have demonstrated SPR modes on Al disks and rectangles,^{42,47} as well as improved performance in sensors and photovoltaics using arrays of such structures.^{11,48}

To elucidate the plasmonic properties of the Al nanowires, measurements with a near-field scanning optical microscope (NSOM), an atomic force microscope (AFM), and a conventional optical microscope (imaged onto a CCD) were taken of an isolated nanowire lying flat on glass and illuminated by a laser spot with 660 nm wavelength (see Supporting Information, Figure S4). The nanowire height (AFM signal), encoded as the color scale in Figure 6a, shows lengthwise ridges running along the nanowire; the electric field intensity (NSOM signal), encoded as the topography of Figure 6a, shows evidence of surface plasmon polaritons (SPPs) propagating from the laser spot along the nanowire length at the ridges. The apparent AFM signal modulations along the nanowire length are the artifact of the shading effect from the overlying NSOM pattern. A line-cut of the NSOM signal along a ridge (Figure 6b) shows the SPP standing wave pattern with wavelength of ~550 nm. Simulations (not shown) predict the SPP wavelength to be 600 nm for an Al nanowire coated by 3-5 nm of aluminum oxide and illuminated by 660 nm radiation. Images taken with the conventional optical microscope (Figure 6c) show light scattering from the nanowire tip with increasing intensity as the tip is moved closer to the laser spot, providing evidence that light is coupled from the laser spot to SPPs on the nanowire, and scattered into photons at the nanowire tip.



Figure 6. Optical and AFM measurements of an Al nanowire on a glass slide and illuminated by a laser spot of wavelength 660 nm; laser polarization is along the wire axis to excite longitudinal SPP modes. (a) Composite NSOM and AFM signal:⁴⁹ figure topography shows NSOM signal, i.e., near-field optical intensity; color scale shows height of Al nanowire (red and yellow) and glass surface (blue), as measured by AFM. A yellow streak running lengthwise along the wire in the red region shows evidence of a ridge along the nanowire. White arrows highlight antinodes of standing waves on this ridge, formed by forward and backward propagating SPPs, which are created by the laser spot and reflection off the nanowire tip, respectively. (b, top) Black solid line shows line-cut of near-field optical intensity (NSOM) along dashed line in part a, demonstrating a standing wave of 550 nm wavelength in superposition with an exponentially decreasing intensity with increasing distance from the laser spot; red dashed line shows exponential fit that measures the standing-SPP decay length to be ~ 1 μ m. (b, bottom) ΔI , the near-field optical intensity minus the exponential fit, shows the standing wave with greater clarity; gray arrows spaced by 550 nm highlight antinodes. (c) Far-field images of the Al nanowire under the laser spot show increasing light scattering from the Al nanowire tip with decreasing distance between the laser spot and the tip, likely due to SPPs propagating from the laser spot and scattering off the nanowire tip into photons; scale bar 2 μ m.

The large wavelength of the standing wave pattern in Figure 6b (approaching the SPP wavelength) results from the large (compared to SPP wavelength) circumference of the wire. This causes the backscattered SPP waves to have small axial components of their wave vectors, and therefore the resulting standing wave along the wire has its wave vector dominated by the incoming wave. This also explains the rapid decay of the standing wave pattern (with exponential decay range of ~ 1 μ m), as shown in Figure 6b; due to the large wire circumference, a significant fraction of the SPP scatters away from the propagation channel along the wire ridge. This, with increasing distance away from the excitation point, effectively depletes the ridge propagation channel of plasmon waves. This evidence of SPPs supported on and guided along an Al nanowire demonstrates the potential efficacy of these Al nanowires for plasmonic device applications, such as a waveguide for light.

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In conclusion, we have demonstrated a tunable process for template-free fabrication of vertically-oriented, spatially-ordered, freestanding aluminum nanowire arrays with lateral spacing unobtainable by existing metal nanowire fabrication processes. The arrays' high conductivity and unique spatial dimensions have potential utility in electrical, electrochemical, photonic and photovoltaic applications. Additionally, the nanowire topography has sharp edges and smooth surfaces that may be favorable for electric field enhancement and plasmonic applications. Finally, the process shows promise to be scalable for low-cost manufacturing of large surface area (m^2) devices.

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.nano-lett.5b02408.

Further details on fabrication procedures, the influence of indent diameter on pore formation, cathodolumines-cence measurements, and the NSOM setup (PDF)

AUTHOR INFORMATION

Corresponding Authors

*(N.T.N.) E-mail: nathan.nesbitt@gmail.com. *(M.J.N.) E-mail: naughton@bc.edu.

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Notes

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Supporting Information for nl-2015-02408w

Aluminum Nanowire Arrays via Directed Assembly

Nathan T. Nesbitt, * Juan M. Merlo, Aaron H. Rose, Yitzi M. Calm, Krzysztof Kempa, Michael J. Burns, and Michael J. Naughton*

Department of Physics, Boston College, 140 Commonwealth Avenue, Chestnut Hill, MA 02467

Experimental methods for Al nanowire array fabrication

Here, Ni posts were used to imprint the Al surface with an array of indents. Ni was chosen because of its hardness and compatibility with an electron-beam lithography (EBL) technique for fabricating post arrays. The use of EBL allowed Ni posts to be left out of certain lattice sites in the array, such that after imprinting the Al there would be missing indents at certain lattice sites of the indent array. This prevented the Al from anodizing at the sites of the missing indents. As shown in Figure S1, there is apparently a maximum indent diameter for which pores selectively nucleate at indented sites and not sites missing an indent. Figure S2 shows photographs of the experimental setup used in the fabrication of Ni posts and Al nanowires.

Stamp preparation: To produce the stamp in Figure 2a, glass slides 16 mm x 15 mm were piranha cleaned and then coated with 50 nm of Ni with a Sharon electron beam deposition

system. HMDS (VLSI grade 0.1 um filtered from Ultra Pure Solutions, Inc.) was spun on (step 1: 5 sec, 500 rpm, 100 rpm/sec; step 2: 45 s, 4000 rpm, 550 rpm/s) to remove moisture from the sample surface, followed by electron beam resist (950 PMMA A4 from MicroChem) spun on (step 1: 5 s, 500 rpm, 100 rpm/s; step 2: 45 s, 4000 rpm, 550 rpm/s) to create a nominally 200 nm thick PMMA film. A 120 s delay between applying the PMMA and initiating the spin steps was included to allow bubbles in the PMMA to dissipate. The PMMA was then pre-expose baked at 180 °C for 25 min on a hotplate. Arrays of nominally 100 nm diameter holes were written into the PMMA with a JEOL SEM using a dosage of ~ 1300 μ C/cm². The PMMA was then developed with 1:3 MicroChem MIBK: IPA (MIBK/IPA 1:3 Developer from MicroChem) for 40 s, IPA for 20 s, and finally de-ionized water (DI) for 20 s. Ni was then electroplated into the holes using Ni plating solution (SN-10 Ni Plating Solution from Transene, Inc.), a counter electrode (47 mm² of exposed surface area of coil of Pt wire, 0.1 mm diameter, Premion 99.997% Pt from Alfa Aesar), and a potentiostat (Gamry Interface 1000 running a chronopotentiometry scan) to produce nominally 100 nm tall Ni posts. The PMMA was subsequently dissolved by placing the stamp in a bath of acetone for a few minutes.

Electropolish Al: High purity Al foil (annealed, Puratronic, 99.9995%, Alfa Aesar) of thickness 200 μ m and surface roughness of 30 nm (measured by AFM), was cut into 5 mm x 10 mm strips using scissors. The strips were flattened between two glass slides using a custom-made vice composed of two flat Al plates (one plate could move vertically by turning a 5 mm diameter screw, the other comprised the base of the vice). The Al foil was then rinsed with ethanol to remove moisture from the surface (moisture causes degradation of the Al surface during electropolishing – specifically the appearance of a rough off-white film) and immersed in a bath of 1 perchloric acid : 3 ethanol (70% perchloric acid Reagent ACS Grade from GFS)

Chemicals, 90% ethanol (5.5% Isopropanol, 4.5% Methanol) HPLC Grade from Fisher), which was stirred at 120 rpm with a 10 mm magnetic Teflon coated stirring rod and held at 5 °C via a jacketed beaker and circulating bath (Polystat 1212202 from Cole Parmer). A 5 mm diameter 80 mm length carbon rod (Fisher Scientific, cat. no. S43501) was simultaneously immersed in the solution as a counter electrode. Electrical contact was made to the Al foil and C rod via flat-tipped alligator clips (Micro 1-1/8" Smooth Clips from RadioShack). 10-20 V was applied with a high current voltage source (Kepco model: KS36-10M current regulated power supply) for 5-10 min (voltage and time were fine-tuned each day electropolishing took place). The polished Al had a mirror finish with surface roughness 3.9 nm as determined by AFM.

Imprint Al: The polished Al foil was placed polished-side-down on top of the Ni stamp (with Ni posts facing up) and a small piece (2 mm x 2 mm) of Teflon plumbing tape was placed on top of the Al at the region to be imprinted. This stack was sandwiched between two glass slides, and the sandwich was placed into the custom vice. The vice was carefully closed to compress the Al against the Ni stamp and imprint the Al. The imprinted Al developed iridescence in the region imprinted by Ni posts, and had a surface roughness of 2.8 nm.

Anodize Al: A 2.5-3.5 mm diameter circular window was cut into adhesive Teflon tape (Tape with PTFE Film, Beige 5498, Silicon-free, 4 mil, part #5498-10 from All-Spec Industries), and the tape was used to mask the imprinted Al foil. The tape was arranged such that the window exposed the imprinted region of the Al. The Al foil was placed in a beaker of:

50 ml Ethylene Glycol (E178-4 Ethylene Glycol Certified from Fisher)
50 ml 2%wt Citric acid (anhydrous, reagent ACS, 99.5% from Acros in DI)
2.9 ml 0.1%wt Phosphoric acid (85% solution from Acros Organics in DI)

which was held at 10 °C via a jacketed beaker and circulating bath (Polystat 1212202 from Cole Parmer). For Al nanowires with a minimum pitch of 2.4 μ m (*i.e.* an AAO template of pitch 1.2 μ m), 480 V was applied with a DC voltage source (Fluke 412B) between the Al foil and a carbon counter electrode for a duration appropriate for the desired height of the Al nanowires.

Etch Al₂O₃: The anodized Al foil was rinsed with DI and placed for 50 minutes in a beaker containing 50 ml of 6%wt Phosphoric Acid (85% Phosphoric acid from Acros Organics) and 1.8%wt Chromic Acid (10% w/v Chromic Acid from Ricca Chemical Company) in DI held at 63 °C.

Final Rinse: The Al foil was rinsed with DI and dried by flowing a nitrogen stream across it. This exposed the Al nanowires allowing them to be imaged via SEM. Iridescence was visible to the eye where there were Al nanowires. **Table S1.** Trends in AAO fabrication procedures, organized by anodization solution, includingthe impact that a missing indent has on pore formation.

Anodization solution:	Oxalic acid	Phosphoric acid	Citric + phosphoric + EG
Anodization voltage:	80 V (ref 1)	120 V (ref 2)	480 V (this work)
Pitch of pores in AAO template:	200 nm (ref 1)	300 nm (ref 2)	1200 nm (this work)
Percent of barrier oxide at pore base penetrated by anions:	90% (ref 3)	66% (ref 3)	No data
Pore formation at missing indent:	Nearly normal pore (ref 1)	Small pore with diamond shaped adjacent pores (ref 2)	Pore formation blocked to produce Al nanowire (this work)



Figure S1. SEM images showing the dependence of Al nanowire growth on imprint post diameter. Images show fabrication steps: (a) imprinted Al, (b) anodized Al, (c) Al surface after etching away anodized aluminum oxide. These images, along with the results in Figure 3, show that: (i) pores did not nucleate in the area on the left with no indents, (ii) indents of diameter \leq 400 nm produced pores at indent sites and Al nanowires at missing indent sites, (iii-v) indents of diameter > 450 nm did not cause pores to nucleate. At areas where no pores nucleated, the anodized aluminum oxide was approximately conformal to the Al surface; after etching this oxide away a rough and planar Al surface was revealed. Thus, for an indent array pitch of 1.2 µm, this sample suggests imprint post diameter must be \leq 400 nm for an AAO template and

embedded Al nanowires to form. SEMs (a.i) and (a.ii) are representative images from areas of the sample neighboring (b.i), (c.i) and (b.ii), (c.ii), respectively. Scale bars 2 μ m.



Figure S2. Photos of fabrication process and setup: (a) Ni-coated glass with PMMA film for EBL, (b) after development of the nanopores in the PMMA film, (c-e) electrodeposition of Ni into the PMMA pores, (f) stack of electropolished Al lying polished side-down on Ni posts, with PTFE tape over region to be stamped, (g) stack sandwiched between two glass slides, (h) custom-made vice for indenting the Al, (i) Ni stamp and the indented Al, (j) Al masked with adhesive PTFE tape, with a window exposing the indented region of the Al, (k) anodization setup including the jacketed beaker for temperature control, (l) carbon rod counter electrode, PTFE coated magnetic stirring rod, and masked Al during anodization, (m) Al after anodization, (n) Al and PTFE tape after removal of the tape.



Figure S3. SEM, panchromatic cathodoluminescence, and simulations of Al nanowire arrays. (a) Secondary electron (SE) image of an Al nanowire array (sample tilt 0°). (b) Panchromatic cathodoluminescence (CL) image (350-650 nm) of an Al nanowire array (sample tilt 0°) showing dark highlights at the sharp edges of the nanowires. (d) CL image of an Al nanowire array (sample tilt 30°) showing light highlights at sharp edges of the nanowires. (c) Simulations of the radiation pattern for two cases: electric dipole (with vertical moment) excitation at the center (left) and at the corner (right) of the nanowire top, represented by a red dot. The radiation pattern is expected to represent the cathodoluminescent response of the nanowire to excitation by the electron beam. For the dipole at the nanowire top-center, the radiation pattern has maxima directed upwards away from the nanowire, with a broad minima in the plane perpendicular to the nanowire. For the dipole at the corner, the radiation pattern shows maxima in the plane perpendicular to the wire axis, and a broad minima upwards away from the nanowire. This is consistent with the dark and bright highlights observed by CL at the sharps edges relative to the top face of the nanowires for 0° and 30° sample tilts.



Figure S4. Schematic of experimental setup for NSOM measurements of an Al nanowire. A Nanonics Imaging Ltd. MultiView 4000 NSOM was used to illuminate the nanowire with a 660 nm wavelength laser source. A single-mode optical fiber, diameter 4 μ m, coupled light from the laser into a 63× numerical aperture (NA) = 1.40 objective below the Al nanowire. Laser light passed from this objective, through immersion oil and a glass slide to form a spot in a focal plane containing the Al nanowire. Far-field radiation from the laser spot was observed by a charge-coupled device (CCD) camera through a 50× NA=0.45 objective above the nanowire. Near-field radiation at the nanowire and glass surfaces was measured by an NSOM probe (100 nm aperture, 150 nm Cr-Au coating, multimode fiber).

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9. Appendix IV: A review: Methods to fabricate vertically oriented metal nanowire arrays

Nathan T. Nesbitt and Michael J. Naughton

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A Review: Methods To Fabricate Vertically Oriented Metal Nanowire Arrays

Nathan T. Nesbitt^{*©} and Michael J. Naughton^{*}

Department of Physics, Boston College, 140 Commonwealth Ave., Chestnut Hill, Massachusetts 02467, United States



ABSTRACT: Nanowires can be described as one-dimensional-like structures: elongated solids with two dimensions thinner than about a micrometer. They allow the study of novel physical phenomena and have many technological applications, including capture and storage of energy, thermal transport, and sensing. These applications often use arrays of nanowires on flat surfaces, and sometimes specifically require the nanowires to be vertically oriented rather than randomly oriented, arranged in lithographically ordered arrays rather than randomly distributed, or both. In addition, the nanowires' height, diameter, cross-sectional shape, and the array pitch often must be controlled. Methods exist to exercise much of this control over insulating and semiconducting nanowires, but less control has been demonstrated for metal nanowire fabrication. Here, we review methods published for the fabrication of metal nanowires, and highlight areas in need of further development. Microwire fabrication is discussed in the context of methods that show promise for adaptation to nanowires.

INTRODUCTION

The number of methods to fabricate vertically oriented metal nanowire arrays is limited, as are the physical dimensions that can be produced in a diversity of elements. Most notably, this includes arrays of high aspect ratio, vertically oriented wires with pitch of a few to tens of micrometers. This contrasts strongly with the numerous techniques for production of nonmetal nanowire arrays of nearly any size and shape and made of many different materials. In addition, to our knowledge, the metal nanowire fabrication methods that do exist have not been recently amassed and critically reviewed. In this review, we discuss existing state-ofthe-art metal nanowire array fabrication techniques and the applications that would benefit from such arrays, and we highlight promising routes to expand metal nanowire fabrication capabilities.

Arrays of nanowires, and microwires with diameters of several micrometers or less, have been demonstrated as useful nanoarchitectures for tuning many surface properties of materials. For example, the chemical surface energy¹ of a Si substrate was tuned with a randomly oriented, disordered-array of nanowires by increasing the effective surface area for contact to water, which enhanced the hydrophobic or hydrophilic nature of the surface. For heterogeneous chemical reactions at electrode surfaces, the reaction rate² was tuned by adjusting the height of vertically oriented, lithographically ordered Si microwire arrays coated by metal hydrogen evolution catalysts, which tuned the effective surface area of the catalysts. In another case, the product selectivity³ was tuned by adjusting the height of randomly oriented Cu nanowires in disordered arrays, which tuned the local concentration of reactants at the Cu surface during electrochemical CO₂ reduction. In a Li ion battery, the mechanical stability⁴ of an Al anode was improved by the presence of space between vertically oriented Al nanowires in a disordered array. By giving the Al space to expand during Li ion intercalation, grinding between adjacent crystallites, which would pulverize a flat Al film anode, was mitigated. Furthermore, optical properties of a metal surface⁵ were tuned with vertically oriented C nanotubes in a disordered array-the nanotubes, said to act as antennas, specularly reflected only light polarized parallel to them, and scattered only light with a half-wavelength equal to an integer multiple of their length. Finally, thin Ag nanowires have been shown to guide light in the form of propagating surface plasmons;⁶ arrays of such wires arranged in the proper manner could provide a means for subdiffraction-limited optical microscopy.

In addition to tuning surface properties, the three-dimensionality of nanowire arrays has allowed the fabrication of nanocoax devices, made by coating the metal nanowires with a thin

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insulating or semiconducting film, and then a metal film. With this middle layer being amorphous silicon, a high efficiency solar cell was made-the effective path length of light determined by the nanowire height, and the electron path length by the thickness of the amorphous silicon film.⁸ With the middle layer being Al_2O_{31} and the nanowire top polished to expose both the inner nanowire and outer metal film, a high sensitivity biochemical sensor was made.⁹ By coating an array of vertical pores with a metal-insulator-metal film, electrical capacitance was increased by the large surface area to create a high energy and high power density energy storage device.¹⁰ Many of these applications, and others.¹¹ require the nanowires to be metallic, but are limited by the geometries accessible with existing fabrication processes. In particular, they are limited by the height, diameter, and crosssection of the nanowires and the pitch and lattice configuration of the array.

The presence of sharp edges on nanostructures can drastically change the physical interactions between them and their environment, because of the confinement of free electrons at the low radius of curvature. We refer to this phenomenon as sharpedgeonics. In the field of plasmonics, this has been observed in the strong electric field caused by surface plasmon resonance at the tips of metal points, which can be useful for sensing via surface-enhanced Raman spectroscopy. For example, Au nanostars with the radius of curvature at their points <5 nm showed a 10 000× increase in electric field intensity at these points, compared to elsewhere on the stars, when illuminated by light at a wavelength of 753 nm.¹² In another case, surface plasmons excited by light at a wavelength of 660 nm were observed to propagate along ridges of an Al nanowire with an ~ 10 nm radius of curvature.¹³ In electrochemical catalysis, it has been observed that reduction of CO₂ to higher energy molecules at a high current density occurs at a much lower overpotential, a higher faradaic efficiency, and with more stable operation over time at electrodes containing sharp metal points than at any previously reported catalyst.^{14,15} This is proposed to result from fieldinduced reagent concentration, in which the high local electric field influences the concentration of species in the electrolyte adjacent to the metal tip. For example, forests of Au needles with a radius of curvature of ~5 nm have demonstrated CO₂ reduction to CO at 38 mA/cm^2 at -0.4 V vs renewable hydrogen electrode (RHE) for tens of hours.¹⁶ Since the small radius is crucial to these phenomena, and only select fabrication processes can produce such features, devices utilizing such phenomena have few options for fabrication.

The various processes to fabricate metal nanowire arrays can be categorized as coating metal onto nonmetal nanowire arrays (Figure 1a), depositing metal into pores of a template (Figure 1b), directly growing metal nanowires (Figure 1c), and etching them out of a bulk metal substrate (Figure 1d). Each of these approaches has its own merits and limitations, which are discussed below. Suggestions of future research that could expand these capabilities of metal nanowire fabrication are also provided.

METAL-COATED NANOWIRE ARRAYS

Nonmetallic nanowires can be made by several methods, including mechanical deformation and UV curing of a polymer via nanoimprint lithography (NIL) with a template (Figures 2a and 2b);^{9,17,18} bottom-up growth via vapor–liquid–solid deposition (Figures 2c and 2d);^{19–21} and top-down etch via metalassisted wet etching (Figures 2e and 2f)^{22–25} or deep reactive ion etching into bulk material.²⁶ Local curing of a polymer film via



Figure 1. Cartoon of metal nanowire array fabrication processes that are representative of (a) metal coating, (b) template, (c) bottom-up growth, and (d) top-down etch methods. Reprinted with permission from ref 13. (Copyright 2015, American Chemical Society, Washington, DC.)

photolithography can produce microwires (Figures 2g and 2h);²⁷⁻²⁹ however, because of the diffraction limit of light and divergence of the light beam outside the focal plane, high aspect ratio structures with submicrometer diameter cannot be made. These various fabrication methods provide a high degree of control over array geometries-as seen in Figure 2, lithographically ordered arrays of vertically oriented nanowires and microwires have been made with smooth surfaces and consistent cross-sections, with wire diameter, height, and array pitch spanning up to 2 orders of magnitude for each fabrication method. This flexibility of nonmetal nanowire fabrication can be leveraged for metal nanowire arrays by coating them with metal films, but with certain compromises. The "dead space" created by the nonmetal core of the nanowire imposes a minimum diameter on the final metal-coated wire. This creates a tradeoff between the metal film conductance and nanowire diameter. The nanowire surface topography is also modified by the metal deposition process. Atomic layer deposition (ALD) is highly conformal, providing the best preservation of underlying topography, but will still round out sharp edges. Historically, ALD has also been restricted to a few of the most noble metals, such as Pt and Ru, but recent work has expanded this to include less expensive metals, such as W^{30,31} and TiN.¹⁰ Electrodeposition and electroless deposition can conformally coat nanowires, but these methods can accumulate material faster at sharp edges³² and parts of the nanowires that are more exposed to the electrolyte, resulting in rounded-out edges and deformed nanowire topography. Physical vapor deposition (PVD) and chemical vapor deposition (CVD), which spray material up onto a downward-facing nanowire array, accumulate material at the pillar tops (Figure 3)⁸ and cannot coat the undersides of offvertical nanowires.



Figure 2. Nonmetal nanowire and microwire arrays, demonstrating the excellent control over nanowire diameter and height, and array pitch, that is possible for nonmetal nanowires. Arrays are fabricated via (a,b) NIL, (c,d) vapor–liquid–solid deposition, (e,f) metal-assisted wet etching, and (g,h) photolithography; imaged via SEM. Panel (a) is reprinted with permission from ref 9. (Copyright 2013, American Chemical Society, Washington, DC.) Panels (b,c) are reprinted with permission from refs 18 (Copyright 2016, Royal Society of Chemistry, London) and 20 (Copyright 2012, Royal Society of Chemistry, London), respectively. Panel (d) is reprinted with permission from ref 21. (Copyright 2014, The Optical Society, Washington, DC.) Panels (e,h) are reprinted with permission from ref 25 (Copyright 2012, Institute of Physics, London) and 29 (Copyright 2007, Institute of Physics, London), respectively. Panel (f) is reprinted with permission from ref 24. (Copyright 2010, John Wiley and Sons, Weinheim, Germany.) Panel (g) is reprinted with permission from ref 28. (Copyright 2017, MicroChem, Newton, MA.)

SOLID-METAL NANOWIRE ARRAYS

Solid-metal nanowire arrays can avoid the compromises associated with metallization of nonmetal nanowires, but are restricted to certain geometries and materials that can be accessed by the limited fabrication methods available. Most notably, templatebased methods (Figure 1b) have a limited pitch for nanowires with a high aspect ratio; bottom-up methods (Figure 1c) have not produced lithographically ordered arrays; and top-down



Figure 3. Accumulation of material at the top of nonmetal nanowires when the material is deposited via PVD and CVD; imaged via SEM. Reprinted with permission from ref 8. (Copyright 2010, John Wiley and Sons, Berlin.)

methods (Figure 1d) also have pitch constraints. Controlled fabrication of anodized aluminum oxide (AAO) membranes provides the only mechanism, of which we are aware, to produce nanowires with smooth surfaces, consistent cross-section, high aspect ratio, and arranged in lithographically ordered arrays, vertically oriented on a flat surface. For pitch of <2 μ m, the resulting membrane is used as a template; for pitch of >2 μ m, the anodization is a top-down etch.

Template-Based Fabrication. Template-based methods utilize insulator or semiconductor templates with vertical pores. Typically, the template is grown from or adhered to a substrate, its pores filled with metal, and is then dissolved away to yield nanowires on the substrate. Following dissolution of the template, subsequent deposition or etching can adjust the nanowire diameter. As such, the pitch, height, initial diameter, and array lattice configuration are determined by the template's geometry and its compatibility with metal deposition processes for pore filling. This is a significant restriction, because the several template technologies that have been explored for fabrication of metal nanowire arrays, delineated below, have a very limited selection of these parameters.

Lithographically ordered AAO template fabrication³³ and subsequent template-based metal nanowire fabrication³⁴ have been thoroughly documented.^{35,36} Template thickness as much as 100 μ m,^{37,38} pitch from 30 nm to 2000 nm,^{39,40} and pore height-to-diameter aspect ratio as high as 500 have been demonstrated.⁴¹ Metals have been deposited into many of these templates, with subsequent nanowire heights as much as 30 μ m reported (Figures 4a and 4b).³⁷ One should note that lithographically ordered templates have only been reported above 150 nm pitch;^{41,42} templates with smaller pitches are only quasiordered. Because of a clustering phenomenon (see the end of this section), the maximum array pitch of 2 μ m translates into a limited height of freestanding nanowires. Track-etch membranes have disordered arrays of pores over a similar range of thickness and pitch to AAO templates, and have been used to make metal nanowire arrays similar to those produced via AAO templates.43,44

Electron beam lithography (EBL) has been used to create templates with very precise pore size and placement, but it is typically used to make in-plane structures that are, at most, a few micrometers thick, with the thickest EBL resist being ~5 μ m.⁴⁵ Because of the top-down exposure process used to create pores via EBL, scattering of electrons within the dielectric during exposure limits the aspect ratio of the pores. As such, the largest pore or subsequent metal nanopillar aspect ratio is ~2 (Figure 4c).¹³ However, lines of resist have been reported with



Figure 4. Solid metal nanowire arrays fabricated via template-based processes, using an (a,b) AAO template, (c) EBL resist polymer template, and (d) photoresist polymer template; imaged via SEM. Panels (a,b) and (c) are reprinted with permission from refs 37 (Copyright 2003, American Chemical Society, Washington, DC) and 13 (Copyright 2015, American Chemical Society, Washington, DC), respectively. Panel (d) is reprinted with permission from ref 47. (Copyright 2013, Massachusetts Institute of Technology, Cambridge, MA.)

height-to-separation ratio as high as 5,⁴⁶ suggesting that the same could likely be accomplished for pores. Of note for EBL is the serial nature of writing patterns, making it time-consuming and costly for applications that require larger than square-millimeter-scale patterned areas.

Photolithography has also been used to create templates with precise pore placement and size. However, as described above, this method is only practical for fabricating high aspect ratio features with diameters greater than a micrometer. The smallest diameter metal nanowire array that we found in the literature was $26 \,\mu$ m, for $60 \,\mu$ m pitch and $80 \,\mu$ m tall microwires (Figure 4d).⁴⁷ However, with subsequent etching of metal microwires, nanowire arrays with very large pitch (tens of micrometers) could, in principle, be made.

Regarding metal filling of the template, restrictions arise on the nanowire height, material, and deposition process. Top-down deposition processes, such as PVD and CVD, are typically only used to deposit films a micrometer or less thick. Also, accumulation of material at the pore opening can clog it, preventing the fabrication of high aspect ratio nanowires. Electrodeposition on conductive substrates and ALD on arbitrary substrates can, in principle, fill pores of any height and diameter. This restricts metal nanowires taller than a micrometer to materials that can be deposited by these methods; some metals such as Ti require specialized procedures for electrodeposition,⁴⁸ and, as mentioned above, ALD is not available for all materials.

The template material used in these processes is typically removed with a liquid solvent or etchant. This can be an issue when the liquid evaporates, because if the nanowire height is too large, relative to the pitch and diameter, then the nanowires will cluster due to local attractive forces and lose their freestanding nature.^{49,50} This is demonstrated in the scanning electron microscopy (SEM) image in Figure 5. This clustering prevents



Figure 5. Clustering of Si nanowires, as a function of separation distance, imaged via SEM. For a diameter of 160 nm and a height of 4 μ m, nanowires begin to adhere to each other when brought within 450 nm. Reprinted with permission from ref 50. (Copyright 2014, American Chemical Society, Washington, DC.)

application of the nanowire array to many core—shell and nanocoaxial architectures, since common top-down processes, including PVD and CVD, cannot coat the underside of the nanowires. Clustering also impacts applications sensitive to the nanowire geometry, such as the nanoantenna array mentioned above, which requires the nanowires to be vertical and freestanding. The clustering may be circumvented via a critical point dryer, but this extra step may not always be compatible with fabrication processes.

Bottom-Up Growth. Many bottom-up growth processes have been developed for solid metal nanowire arrays. However, it so happens that lithographically ordered arrays, and nanowires that have smooth surfaces, consistent cross-section, and good conductivity, are presently mutually exclusive for bottomup growth.

Chemical vapor deposition (CVD) of Ni on Si with a thermal oxide (Figures 6a-c)^{51,52} and Co on sapphire (Figures 6d and 6e)⁵³ have been shown to produce rectangular cross-section, single crystal, vertically oriented nanowires arranged in disordered arrays. Electron diffraction in a transmission electron microscopy (TEM) system demonstrates the single crystal nature of these nanowires. They are notable for their atomically smooth surfaces composed exclusively of {100} facets. It is proposed that they grow at their base, with their morphology controlled by the solubility of Ni (Co) in SiO₂ (Al₂O₃) and the exposed facet of the substrate.

CVD of C (Figures 6f and 6g)^{54–58} has produced vertically oriented carbon nanofibers at Ni nanoparticles distributed on a Si surface. The Ni particles could, in principle, be arranged to produce lithographically ordered nanowire arrays. However, the fibers have a disordered surface and poor electrical conductivity, compared with true metals (where true metals have bulk conductivity at room temperature over 1 MS/m).⁵⁹ The fibers are proposed to grow at their top, where the Ni particle is located, lifting the particle up as they grow. 56

Simultaneous magnetron sputtering of Al_2O_3 and Ag (Figures 6h and 6i)⁶⁰ has produced disordered arrays of Ag nanowires embedded in Al_2O_3 , vertically oriented with a smooth surface and consistent cross-section. These nanowires are notable for their small diameter (2–3 nm) and pitch (6–8 nm). The Ag nanowires form due to phase separation driven by the low solubility of Ag in Al_2O_3 ; during the initial deposition, Ag particles form in an Al_2O_3 matrix, and grow into nanowires during continued deposition.

Glancing angle deposition (GLAD) (Figures 6j and 6k),⁴ has produced vertically oriented and disordered arrays of Al nanowires with a narrow base, wide top, and rough surface. It uses a traditional PVD chamber, except with the substrate tilted a few degrees off parallel to the deposition beam. When particles randomly nucleate on the surface, they cast shadows on the substrate that prevent deposition adjacent to them. This causes further deposition to be confined to the particles, creating nanowires with their length pointed toward the deposition target. Rotation of the substrate produces the nominally vertically oriented nanowire arrays, albeit highly disordered.

Thermal stress-induced growth (Figure 6l and 6m)⁶¹ of Al nanowires from an Al film sputtered on glass has produced disordered arrays of nanowires with very high aspect ratio, smooth surface, consistent cross-section, and a wide variety of crosssectional geometries. The nanowires were formed when a 100 nm Al film on glass, heated to 250 °C, had hydrofluoric acid (HF) dripped onto it with an HF:H₂O concentration ratio between 1:100 and 1:200. It was proposed that the heating produces stress in the Al, which is sandwiched between the glass and a native oxide on the Al surface, because Al has a higher thermal expansion coefficient than SiO₂ and Al₂O₃. The HF then etches away small surface contaminants that originated from the glass, opening weak points on the Al₂O₃ surface through which the Al extrudes to relieve the thermal stress (sufficient cleaning of the glass ceased Al nanowire growth). Therefore, the Al nanowire cross-section is likely determined by the geometry of the pore through which it extrudes.

Electrochemical reduction of CuO nanowires (Figure 6o)³ has produced disordered arrays of oxide-derived Cu nanowires with a smooth surface and consistent cross-section. The nanowires were formed by immersing a Cu foil into 0.133 M $(NH_3)_2S_2O_8$ and 2.667 M NaOH to spontaneously grow Cu– $(OH)_2$ nanowires (Figure 6p and 6q).⁶² Longer immersion time produced longer nanowires. These Cu– $(OH)_2$ nanowires were annealed at 150 °C in air for 2 h to create CuO nanowires, which were then electrochemically reduced to Cu nanowires in 0.1 M KHCO₃ at -0.7 V to -1.1 V (vs RHE).

Top-Down Etching. Top-down processes that etch into metal substrates have produced nanowires via anodization of Al and microwires via reactive ion etching (RIE) of Ti. These wires are vertically oriented with a smooth surface and consistent cross-section. They are positioned within the array using standard lithography techniques, limited primarily by a minimum demonstrated pitch of 2.4 μ m. Thus, these processes provide the greatest degree of control over array pitch and lattice configuration of any of the solid metal nanowire fabrication processes.

Anodization of Al and subsequent etching of the Al_2O_3 to produce arrays of Al nanowires (Figures 7a-c)¹³ was demonstrated by our group in 2015 by modifying a recently reported Al anodization procedure.⁴² To direct the formation of Al nanowires, NIL was used to pattern a flat Al surface with a hexagonal

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Figure 6. Solid metal nanowires grown via bottom-up processes: (a-c) CVD of Ni on Si with a native oxide, (d,e) CVD of Co on sapphire, (f,g) CVD of C on Ni nanoparticles, (h,i) co-sputtering of Ag and Al₂O₃, (j,k) glancing angle PVD of Al, (l-n) thermal stress-induced extrusion of Al on glass, (o) electrochemical reduction of CuO nanowires, (p,q) spontaneous growth of Cu– $(OH)_2$ nanowires from immersion of Cu in $(NH_3)_2S_2O_8$ and NaOH; imaged via SEM, except (c,h,i), which were examined via TEM. Panels (a-c) are reprinted with permission from ref 51. (Copyright 2010, American Chemical Society, Washington, DC.) Panels (d,e) are reprinted with permission from ref 53. (Copyright 2015, Royal Society of Chemistry, London.) Panels (f,g) are reprinted with permission from ref 56. (Copyright 1998, American Association for the Advancement of Science, Washington, DC.) Panels (h,i) are reprinted with permission from ref 60. (Copyright 2016, Institute of Physics, London.) Panels (j,k) are reprinted with permission from ref 4. (Copyright 2009, Elsevier, Amsterdam.) Panels (l-n), (o), and (p,q) are reprinted with permission from refs 61 (Copyright 2014, John Wiley and Sons, New York), 3 (Copyright 2016, John Wiley and Sons, New York), 3 (Copyright 2016, John Wiley and Sons, New York), and 62 (Copyright 2003, John Wiley and Sons), respectively.

array of indents of pitch 1.2 μ m: by pressing the Al surface into a glass slide coated by an array of Ni posts, indents were made in the Al at the Ni post positions. At a site in this array where a nanowire was desired, the Ni post was omitted from the stamp so no indent was formed. The Al was then anodized at 480 V relative

to a C counter electrode in a solution of ethylene glycol and dilute phosphoric and citric acid, which produced an oxide film on the Al surface. Pores nucleated in the oxide at the indents and etched down vertically into the Al substrate, forming an AAO template with Al nanowires embedded at the sites without



Figure 7. Solid metal nanowires etched from metal substrates via topdown processes: (a-c) anodization of Al and etching away the AAO, (d,e) RIE of Ti with Cl and F gases (imaged via SEM). Panels (a-c) are reprinted with permission from ref 13. (Copyright 2015, American Chemical Society, Washington, DC.) Panel (d) is reprinted with permission from ref 63. (Copyright 2010, Institute of Electrical and Electronics Engineers, New York.) Panel (e) is reprinted with permission from ref 64. (Copyright 2012, Elsevier, Amsterdam.)

indents. As such, an indent array of 1.2 μ m pitch containing a superlattice of missing indents of 2.4 μ m pitch produced Al nanowires with 700 nm diameter in an array of 2.4 μ m pitch. A notable property of these nanowires is their very smooth surface and consistent hexagonal cross-section, with sharp edges of ~10 nm radius of curvature.

Reactive ion etching (RIE) of Ti, with a mask that blocks etching to create Ti microwires, was first demonstrated in 2009 using toxic Cl gas (Figure 7d)^{63,65-67} and, more recently, using nontoxic F gases (Figure 7e).⁶⁴ For Cl gas, the Ti substrate was covered by an SU8, TiO₂, or SiO₂ mask, and an Ar/Cl₂ mixture was fed into an inductively coupled plasma (ICP) RIE system. The authors proposed that the mask was etched only by physical bombardment and produced residues that passivated etching on the Ti surface. The Ti was etched by a combination of physical bombardment and chemical reactions: physical bombardment etched native TiO₂ and residues from the surface to expose Ti; Cl radicals reacted with Ti to produce volatile TiCl1-TiCl4 compounds. Because of a more direct line of sight from the plasma to the array floor than to the microwire sidewalls, the physical bombardment preferentially exposed the floor to etching, providing an anisotropic etch rate. As such, high aspect ratio features were made by tuning gas flows, chamber pressure, platen power, and ICP power to maximize the etch rate of Ti, relative to the mask. With a SiO₂ mask, this produced microwires with diameters of 5 μ m and heights of 50 μ m, in arrays with 10 μ m pitch.

For RIE with F gases, the Ti substrate was masked by SiO₂ and Al. The authors proposed that the Al blocked chemical etching, and the SiO₂ provided mechanical support to the Al film and adhesion between the Al and Ti. To etch the Ti, a mixture of SF₆, CHF₃, and O₂ was fed into a conventional parallel plate reactor system. The SF₆ was the primary etchant of Ti, producing F radicals that reacted with Ti to generate the volatile TiF₄ compound. The CHF₃ produced a fluorocarbon polymer that coated the Ti to passivate this chemical etching. The O₂ etched this residue from the Ti surface via physical bombardment, preferentially at the array floor for the reasons explained above. This left the microwire sidewall protected, providing an anisotropic etch rate, though not perfectly so. As a result, the concentration ratio of gases, total flow rate, and chamber pressure were tuned to maximize the floor-to-sidewall etch rate. This produced 5 μ m tall pillars with a square cross-section 5 μ m wide and 5 μ m thick, in an array of 10 μ m pitch. While both the Cl- and F-based processes were used to produce microwire arrays, they were included in this review because there is no reason evident to us they could not be applied to nanowire fabrication; masking the Ti surface with submicrometer diameter features would likely produce high aspect ratio metal nanowires with smooth surfaces and consistent cross-section in lithographically ordered arrays.

CONCLUSION

Arrays of metal nanowires have many technological uses, some of which require vertically oriented nanowires with smooth surfaces, consistent cross-sections, lithographic control of nanowire placement, and particular nanowire height, diameter, and array pitch. While nonmetal nanowire arrays can be produced on length scales from tens to thousands of nanometers with excellent control of their geometry, metal nanowire arrays have significant restrictions on the sizes and shapes that can be made. For some applications, nonmetal nanowire arrays can be coated by metal to achieve the desired geometry and function, but not all materials and geometries are compatible with this approach. Fortunately, the past decade has seen significant progress on metal nanowire array fabrication, as demonstrated by the literature cited herein. Based on these developments, promising routes to expand such fabrication capabilities include increasing the range of AAO template pitch, adding lithographic control over the placement of Ni and Co nanowires grown via CVD, developing chemistries for CVD nanowire growth of a wider variety of elements, developing anodization processes for etching nanowires from a wider variety of elements, refining RIE lithography to produce smaller diameter and pitch, and developing RIE chemistries for etching nanowires from a wider variety of elements.

AUTHOR INFORMATION

Corresponding Authors

*E-mail: nathan.nesbitt@gmail.com (N. T. Nesbitt). *E-mail: naughton@bc.edu (M. J. Naughton).

ORCID 🔍

Nathan T. Nesbitt: 0000-0002-1806-1077

Notes

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10. Appendix V: Au dendrite electrocatalysts for CO_2 electrolysis

Nathan T. Nesbitt, Ming Ma, Bartek J. Trześniewski, Samantha Jaszewski, Fazel Tafti, Michael J. Burns, Wilson A. Smith, and Michael J. Naughton

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Au Dendrite Electrocatalysts for CO₂ Electrolysis

Nathan T. Nesbitt,^{*,†®} Ming Ma,[‡] Bartek J. Trześniewski,[‡] Samantha Jaszewski,^{†®} Fazel Tafti,^{†®} Michael J. Burns,^{†®} Wilson A. Smith,^{*,‡®} and Michael J. Naughton^{*,†®}

[†]Department of Physics, Boston College, Chestnut Hill, Massachusetts 02467, United States

[‡]Materials for Energy Conversion and Storage (MECS), Department of Chemical Engineering, Faculty of Applied Sciences, Delft University of Technology, 2629 HZ Delft, The Netherlands

S Supporting Information

ABSTRACT: Electrochemical CO₂ reduction can convert CO₂ into fuels and valuable chemicals using renewable electricity, which provides a prospective path toward large-scale energy storage. Au nanostructured electrodes have demonstrated the best catalytic performance for CO₂ conversion: high catalytic selectivity for CO formation at low overpotentials, high current density, and long-term durability. Here, we report selective electrocatalytic CO₂ reduction to CO on nanostructured Au with various morphologies, prepared via electrocrystallization with a megahertz potential oscillation. X-ray diffraction showed that the proportion of {100} and {110} to {111} surfaces increased at more negative deposition potentials. Cyclic voltammetry showed the potential of zero charge on an Au film was approximately 0.35 V vs standard hydrogen electrode (SHE) and that the surface energy decreased by ~1 eV/nm² at -0.5 V vs SHE, tending to 0 within several volts in either direction. Scanning electron micrograms showed that the Au crystals grow primarily in the $\langle 110 \rangle$ directions. From



these data, a model for crystallization from melts was adapted to calculate the roughening temperature of the {111}, {100}, and {110} Miller indices as 7000, 4000, and 1000 K, decreasing for more negative deposition potentials. This offers a framework for exposed facet control in electrocrystallization. In CO₂ electrocatalysis, -0.35 V vs reversible hydrogen electrode was observed to be a turn-on potential for improved CO₂ reduction activity; dendrites showed 50% Faradaic efficiency for CO production at more cathodic potentials. The Tafel slope was measured to be 40 mV/decade for {100} and {110}-rich Au dendrites and 110 mV/decade for {111}-dominated Au plates, suggesting the higher surface energy crystal facets may stabilize all of the CO₂ reduction reaction intermediates.

INTRODUCTION

Rapidly falling electricity prices from renewable sources, such as wind and solar, show promise to provide society with cheap domestic energy, while also mitigating the adverse human health impacts of anthropogenic climate change and pollution from fossil fuel extraction and utilization. These energy sources are generally intermittent and thus require energy storage technology for full deployment. Electrochemical CO_2 reduction may provide a means for large-scale storage of renewable electrical energy in hydrocarbon fuels, which are relatively inexpensive to store and are compatible with much of the world's existing infrastructure.

In this study, the CO_2 reduction reaction (CO_2RR) takes place at a metal catalyst immersed in an aqueous electrolyte: 0.5 M NaHCO₃ saturated with CO₂. The desired product is CO, produced in the reaction

$$CO_2 + 2H^+ + 2e^- \rightarrow CO + H_2O (-0.11V \text{ vs. RHE})$$
(1)

Thorough studies have been reported on the electrocatalytic performance of flat films of various metals that are selective for the formation of CO.^{1,2} These results showed Au to have the best catalytic performance, as it demonstrated the highest

values for three important parameters of electrocatalysts: activity (reaction rate per given overpotential (η)), selectivity (percent of the total products generated that were the desired chemical), and stability (constant performance over time). The potential (φ) of -0.35 V vs reversible hydrogen electrode (V_{RHE}) is convenient for comparing the performance of Au catalysts; it is slightly more cathodic than the onset of cathodic current on Au films, and it has a reasonable energy efficiency of 85% for the partial current directed to CO production (energy efficiency = $E^0/(E^0 + \eta) = (1.34 \text{ V})/(1.34 \text{ V} + 0.24 \text{ V}) = 0.85).$ This only considers energy losses at the cathode, ignoring losses present at the anode, which can be separately mitigated via reactor engineering and using specialty membranes.³ At this low overpotential of 0.24 V, polycrystalline Au films have been shown to produce only ~10 μ A/cm² total current density (j_{total}) at nearly 0% Faradaic efficiency for CO (H₂ was the primary product).⁴ However, recent studies have found nanostructuring Au significantly improves its performance. Specifically, in 2012, an Au nanoparticle film was produced by

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Figure 1. Representative SEMs of Au crystals grown in various conditions. In all cases, a 20 MHz square wave was applied between the sample and a Pt wire spiral CE, separated by approximately 20 mm and immersed in 20 mL of solution. For (a-p), $\varphi_{pp} = 8 \varphi_{offset}$. (a-d) For the electric potential study, there were 40 min of deposition to a geometric surface area of 3.6 cm² from approximately 20 mM HAuCl₄; φ_{offset} was varied from -0.625 to -2 V. (e-1) For the concentration study, $\varphi_{offset} = -2$ V was applied for 40 min to a geometric surface area of 0.8 cm², and the molarity of HAuCl₄ was varied from 2 to 20 mM. (m-p) For the time and surface area from 7.2 to 0.8 cm². (q-t) For the φ_{pp} study, $\varphi_{offset} = -2$ V was applied for 40 min to a geometric surface area of 0.8 cm² with approximately 20 mM HAuCl₄, and φ_{pp} was varied between 8, 12, and 16 V. Scale bars are 1 μ m unless otherwise indicated.

repeated electrochemical oxidation and reduction of a polycrystalline Au film.⁴ The nanoparticle film showed improved performance over both a planar film and a film of commercially available nanoparticles. It produced about $j_{total} = 2 \text{ mA/cm}^2$ at over 96% Faradaic efficiency for CO.⁴ This suggested there was a special quality of the electrochemically reduced surface that improved catalytic performance. In 2016, direct current (DC) electrodeposition of Au nanoneedles was shown to produce about $j_{total} = 15 \text{ mA/cm}^2$ at over 95% Faradaic efficiency for CO at the same applied potential.^{5,6} It was suggested that the high performance was a result of enhanced electric fields at the needles' sharp tips. This was the first and only report to date of a 40 mV/dec Tafel slope for the CO₂RR on Au, which corresponds to stabilizing all the reaction intermediates in several proposed reaction schemes.²

In light of the positive results of electrochemically produced nanostructures of Au, here we tested a technique for the growth of nanoscale Au dendrites and Au plates from an aqueous HAuCl₄ solution with a megahertz (MHz) square-wave potential oscillation and a DC offset potential.^{7–11} Different electrodeposition conditions were found to produce different proportions of exposed facets on Au dendrites and plates. Scanning electron microscopy (SEM), transmission electron microscopy (TEM), and X-ray diffraction spectroscopy (XRD) were used to determine the crystallographic orientation of the Au surfaces. X-ray photoelectron spectroscopy (XPS) was used to determine the composition. Electrochemical impedance spectroscopy (EIS) was used to measure the change in surface

energy (γ) vs φ in various aqueous solutions. An electrochemical cell, potentiostat, and gas chromatograph (GC) were used to measure the performance of the nanostructures as electrocatalysts for CO₂ reduction. The purpose of this study was to understand the nanostructure growth mechanism and thereby provide a platform for rational design of future nanostructures. Our results were compared to existing models for crystallization from aqueous solutions and metal melts to identify common trends. Correlations between nanostructure morphology and catalytic performance offer a pathway for improved structure functionality relationships for nanostructured electrocatalysts used in CO₂ reduction.

EXPERIMENTAL METHODS

Au Crystal Synthesis. To grow the Au dendrites and plates, a two-electrode setup was used. The counter electrode was a Pt wire spiral. The working electrode was a $2 \times 2 \times 0.1$ cm Ti foil chip, sputter coated on the front with 100 nm of Au. The back of the Ti foil was covered by scotch tape, and for samples tested for CO₂RR, the front was covered by Teflon tape with a 1 cm diameter hole for the electrodeposition. Scotch tape was used on the back for easy removal for subsequent experiments. The electrodes were immersed into a small beaker with 20 mL of 2 to 20 mM HAuCl₄ in deionized water. A function generator was used to apply a 20 MHz square-wave electric potential between the electrodes, with $\varphi_{offset} = -0.625$ to -2 V and $\varphi_{pp} = 8\varphi_{offset}$. An oscilloscope was attached in parallel to the electrodes to measure the waveform

of the applied potential. Measurements of the current passing through the circuit were not made to avoid modifying the waveform of the high frequency applied potential.

XRD. XRD was performed using a Bruker D8 ECO in the Bragg–Brentano geometry with a copper X-ray source (Cu $K\alpha$), a nickel filter to absorb the $K\beta$ radiation, a 2.5° Soller slit after the source, and a 2.5° Soller slit before the LYNXEYE XE 1-D energy dispersive detector. Intensity data were collected in the 2θ range between 5 and 70° with sample rotation.

TEM. Samples were prepared for TEM by scratching the sample surface with a knife, sonicating the sample in isopropanol to suspend small pieces of dendrites or plates, and drop-casting the suspension onto a Ted Pella 01890-F grid (Lacey Carbon Type-A, 300 mesh, copper with an approximate grid hole size of $63 \ \mu\text{m}$). Images were taken with a JEOL 2010F TEM.

EIS. A typical three electrode setup was used with a Gamry Interface 1000 potentiostat. The working electrode was the Au sample, the reference electrode was Ag/AgCl in saturated KCl solution, and the counter electrode was an Au wire spiral. All three electrodes were immersed into a 25 mL beaker containing the electrolyte under study. All electrolytes were prepared with deionized water.

Cyclic Voltammetry Surface Area Measurement. A typical three electrode setup was used with a Gamry Interface 1000 potentiostat. The working electrode was the Au sample, the reference electrode was Ag/AgCl in saturated KCl solution, and the counter electrode was a Pt or Au wire spiral. All three electrodes were immersed into a 80 mL crystallization dish containing either 500 or 375 mM H_2SO_4 . Electrolytes were prepared from pure sulfuric acid and deionized water.

XPS. XPS was performed using the Thermo Scientific Kalpha apparatus equipped with an Al K α X-ray source and a flood gun. Parameters used for the measurements were a spot size of 400 μ m, pass energy of 50 eV, energy step size of 0.1 eV, dwell time of 50 ms, and 20 scans in the vicinity of Au 4f and O 1s orbitals' binding energies.

CO₂ Reduction. A typical three electrode setup was used with a Princeton Applied Research VersaSTAT 3. The metal catalyst was the working electrode, the reference electrode was Ag/AgCl in saturated KCl solution, and the counter electrode was a platinum mesh. A Nafion membrane separated the counter electrode from the working and reference electrodes. The electrolyte was deionized water with 0.25 M Na₂CO₃, which after CO₂ was bubbled through it for 30 min was considered 0.5 M NaHCO₃. CO₂ was continuously bubbled through the catholyte at 6 sccm and the anolyte at 20 sccm. The gas stream from the catholyte was passed through the gas chromatograph (Thermo Scientific TRACE 1310) to measure the product gas concentration. Both electrolytes were stirred by magnetic stir bars.

RESULTS

Crystal Growth and Morphology. To survey the crystal morphologies produced by this deposition process, the following parameters were varied across a number of samples: offset potential (φ_{offset}), peak-to-peak amplitude (φ_{pp}), HAuCl₄ concentration, and Coulombs of deposition per unit area. Figure 1a–d shows the effect of a different φ_{offset} with the ratio of $\varphi_{pp} = 8\varphi_{offset}$ held constant. For a concentration of 20 mM HAuCl₄, deposition time of 40 min, and deposition area of 3.60 cm², the lowest applied potential, $\varphi_{offset} = -0.625$ V, showed no deposition. When the potential was increased to $\varphi_{offset} =$

-0.8125 V, rounded plates formed slowly. At $\varphi_{\text{offset}} = -1$ V, the plates grew faster and acquired a well-defined geometry with roughly parallel flat faces and edges tracing a regular hexagon shape. At $\varphi_{\text{offset}} = -2$ V, dendrites began to grow; Figure 1d shows a typical crystal covering the Au surface around the base of the dendrites, which had roughly μ m scale faces and a triangular bipyramid shape with periodic ridges. Figure 1l shows the tips of dendrites grown under the same conditions. Figure 1s shows another variety of the dendrite tip found on the same sample.

The HAuCl₄ concentration also influenced the growth of the nanostructures. For a deposition time of 40 min, an area of 3.6 cm², and a $\varphi_{\text{offset}} = -2$ V, 2 mM HAuCl₄ produced spherical granules a few hundred nanometers in diameter (Figure 1e). A concentration of 8 mM produced dendrites with approximately 0.5 μ m rounded dendrite tips, and many small granules covering the dendrite stalk (Figure 1f). From 12 to 20 mM, the dendrite surface became smoother, with fewer small granules on the surface, developing the appearance of a single crystal containing periodic ridges running approximately 60° from the direction of growth (Figure 1g–1).

Variation of the time and exposed electrode surface area showed no "loading effect" apparent under SEM inspection increasing the Coulombs per surface area only increased plate size, and the deposition rate appeared to be constant with time and surface area. Specifically, for the plates grown in 20 mM HAuCl₄ at $\varphi_{\text{offset}} = -1$ V, 20 min of deposition onto 7.2 cm² showed plates of 0.5 μ m or less (Figure 1m). A deposition of 20 min onto 3.6 cm² showed larger plates, approaching 1 μ m in width (Figure 1n). A deposition of 40 min onto 7.2 cm² showed similar results (Figure 1o). A deposition of 40 min onto 0.8 cm² showed approximately 2 μ m width plates (Figure 1p).

Changing the ratio $\varphi_{\text{offset}}/\varphi_{\text{pp}}$ had little influence on the Au dendrite topography (Figure 1q-t). As such, the ratio $\varphi_{\text{pp}} = 8\varphi_{\text{offset}}$ was typically held constant.

The shape of Au crystals can provide information on the crystal orientation of the surfaces and can be quantified by measuring the angle between adjacent edges, corners, and branches. For Au plates deposited in 20 mM HAuCl₄ at φ_{offset} = -1 V, the angle between adjacent corners is approximately 60°, producing approximately regular hexagons (Figure 2a). Each corner is the nexus of four edges, two connecting to adjacent corners and two running from the corner to the center of the crystal. The plates are quite flat, with an approximately 100-110° angle between edges connecting corners (Figure 2a) and acute angles between edges that run from the corner to center, such as 23° (Figure 2b). The large plate in Figure 2b shows small recesses between the corners, suggesting growth is primarily at the corners, followed by filling in along the edge between corners. For Au dendrites deposited in 20 mM HAuCl₄ at $\varphi_{\text{offset}} = -2$ V, the angle between the dendrite branches is 60° (Figure 2c). The angles between adjacent edges is acute, covering a wide range of values from 35 to 80° (Figure 2c,d). The common 60° angle between plate corners and dendrite branches suggests that there is a similar deposition process of preferred growth at the corners, in which a dendrite forms when a corner grows faster than the adjacent edges can fill in. The corner then evolves into a branch, from which new corners can nucleate. As Au has an fcc crystal lattice, the 60° angle between corners indicates a preferred crystallographic growth direction of $\langle 110 \rangle$.


Figure 2. Representative SEMs showing the angle between primary growth directions and the angles between adjacent edges of the Au crystals in (a,b) plates and (c,d) dendrites. (e) Cartoons of the plate growth (left and center) and the dendrite growth (right). Arrows represent the growth velocity of corners and edges. These show how increasing corner growth more than edge growth can give rise to the crystal shapes observed via SEM. Scale bars = 1 μ m.

In XRD measurements, the relative intensity of peaks associated with different orientations indicates the relative prevalence of each crystal orientation on the sample surface.^{12,13} Figure 3 shows representative patterns for Au



Figure 3. XRD spectrum of Au dendrite, plate, and polycrystalline film samples, normalized so that the Au (111) peak height is 1. (a) Full spectrum, (b) (111) peak, (c) (200) peak, (d) (220) peak.

dendrite, plate, and sputtered film samples, normalized so that the intensity of the {111} peak equals 1. The data for these Au dendrite and plate samples was recorded following 18 h of CO_2 reduction. These data show that all the samples were dominated by {111} surfaces, the dendrites had more surface with {100} and {110} orientations than the plates, and the sputtered film had nearly no {100} or {110} surface. Note, the

Article

peaks for the (200) and (220) orientations were considered representative of the {100} and {110} orientations, respectively. The double-peak structure for the curves from Au dendrites and plates indicates that they have high crystallinity, and the single broad {111} peak for the sputtered film indicates that it has lower crystallinity. The two peaks are produced, because the copper source emits two very nearby wavelengths, $K_{\alpha 1}$ and $K_{\alpha 2}$ at 0.1540 and 0.1544 nm, respectively, which are both reflected by the crystal Bragg planes. Figure S1 shows the XRD patterns for dendrites grown at $\varphi_{\text{offset}} = -2$ V for several different φ_{pp} , indicating a slight tendency for more {100} and {110} surface orientation with increasing amplitude.

TEM images allow for spot analysis of surface crystal orientation over small sample areas. Figure 4a shows a dendrite



Figure 4. TEM of Au dendrites under (a) low magnification and (b) high magnification; Au plates under (c) low magnification, (d) high magnification. Both scale bars in (c) are 50 nm. Insets in (b) and (d) show the Fourier transform of areas highlighted by dashed line.

crystal, and 4b shows the crystal orientation at a corner of the crystal. The image plane is along the {100} orientation, and the edge appears to terminate in small {100} and {110} faces. Figure 4c shows a plate crystal, and 4d shows the crystal orientation of the flat crystal face. The image plane is also along the {100} orientation, and the edge appears to terminate in a {100} face. No μ m scale facets were observed via TEM for either dendrites or plates.

With potentiostatic EIS, we measured the impedance (Z)and phase (ϕ) vs frequency (f) for Au nanostructures made at different φ and in different electrolyte compositions. From this, we calculated the differential capacitance per unit area (C_d/A) of Au electrodes, shown in Figure 5a. From the shape of C_d/A vs φ , we determined the potential of zero charge (PZC) for each electrolyte. Specifically, the curve has a minimum at the PZC in the case of nonspecific binding and dilute electrolyte,¹⁴ as demonstrated for mercury in numerous electrolytes of a concentration of ~10 mM or less. 15 The PZC of Au in vacuum is 0.55 V vs standard hydrogen electrode (V_{SHE}) and should be similar in solutions with low binding energy to the metal surface.¹⁶ We thus considered the local minimum of $C_{\rm d}/A$ located near 0.55 V_{SHE} to indicate the PZC. For pure HAuCl₄ solutions, we modeled our electrode–solution interface with a Randles circuit, shown in Figure S2.¹⁷ From this, we calculated $C_{\rm d}/A$ of a sputtered Au surface in our standard dendrite growth solution, 20 mM HAuCl₄. However, this could only probe φ



Figure 5. Potentiostatic EIS of a sputtered Au surface with a geometric surface area of 0.8 cm² in 100 mM H₂SO₄ with various concentrations of HAuCl₄. (a–c) Left of gray dashed line is extrapolation of C_d/A as a constant vs φ , and right of the gray dashed line is measured data. (a) C_d/A vs φ ; electrode area, *A*, was measured by CV of the Au in H₂SO₄. (b) σ vs φ calculated from (a). (c) $\Delta \gamma$ vs φ calculated from (b). (d–g) Nyquist plots of the EIS measurements at each φ , for each of the HAuCl₄ concentrations.

near the reduction potential of AuCl₄⁻, 0.9 V_{SHE} at pH = 1.7, where the reaction kinetics are slow. The overpotential for AuCl₄⁻ reduction at 0.55 V_{SHE} drives the reaction kinetics faster than AuCl₄⁻ can diffuse to the electrode surface. This creates a non-negligible Warburg impedance (Z_W) that is convoluted with the capacitive double-layer impedance, evidenced by the deviation from a semicircle in the Nyquist plots in Figure S3 for potentials negative of 0.8 V_{SHE}. The convolution prevents standard analysis of the Randles circuit, which would normally yield C_d and the charge transfer resistance R_{ct} .

Aqueous solutions of pure H₂SO₄ provide a simpler measurement, because no charge transfer reactions should occur in the electrochemical window for water, 0 to 1.23 V_{RHE} $(-0.06 \text{ to } 1.17 \text{ V}_{\text{SHE}} \text{ at } \text{pH} = 1)$. This allows the system to be modeled as only R_{Ω} in series with C_d . Figure S4a shows C_d/A vs φ for aqueous solutions of H₂SO₄ of concentrations of 1, 10, 100, and 500 mM. It demonstrates that the minimum in C_d/A near 0.55 V_{SHE} changes little between 1, 10, and 100 mM H_2SO_4 , confirming that for this system, 100 mM falls within the "nonspecific binding and dilute electrolyte" case for identifying the PZC. It also shows the PZC to be approximately independent of pH. Nyquist plots in Figure S4d-g show a partial semicircle negative of 0.35 V_{SHE} , which we attribute to a slow transfer of Au from the counter to working electrode. Figures S5–S12 show the individual Nyquist plots. However, for $\omega \gg 1/(C_d R_{ct})$, the imaginary component of the impedance (Z_i) of the Randles circuit reduces from $Z_i = \omega C_d R_{ct}^2 / (1 + \omega C_d R_{ct}^2) /$ $\omega^2 C_d^2 R_{ct}^2$ to that of R_{Ω} and C_d in series, $Z_i = 1/(\omega C_d)$. Figure S13 shows that the measurements of C_d are approximately 50 μ F or greater, and the semicircle radii in these plots, representative of R_{ct} are 200 Ω or greater. As such, the simpler circuit model is valid for $f \gg 100$ Hz, where $f = \omega/2\pi$. Reported $C_{\rm d}$ values are an average of measurements with 1000 < f < 10 000 Hz.

 $Z_{\rm W}$ and $R_{\rm ct}$ are both inversely proportional to the concentration of the species responsible for the Faradaic current.¹⁷ As we are only interested in $C_{\rm d}$ and not $R_{\rm ct}$, we used 100 mM H₂SO₄ as a supporting electrolyte and made measurements for 0, 0.01, 0.1, and 1 mM HAuCl₄, shown in Figure 5a. With the low HAuCl₄ concentrations, $R_{\rm ct}$ in series with $Z_{\rm W}$ was 200 Ω or greater, as shown by the Nyquist plots in

Figure 5d–g. Figures S14–S19 show the individual Nyquist plots. The high total concentration kept the capacitance at 50 μ F or greater. As such, for 1000 < f < 10 000 Hz, we could again model the system as only R_{Ω} in series with C_d . This allowed measurement of C_d/A from 1 to –0.2 V_{SHE} in the presence of different HAuCl₄ concentrations. Water splitting and significant Au deposition at more negative potentials obscured measurements.

The Lippman, or electrocapillary, equation, shows that $\gamma(\varphi)$ equals the integral of the surface charge density (σ) on the metal half of the metal-electrolyte interface¹⁸

$$\gamma(\varphi) = \gamma_{\rm PZC} - \int_{\rm PZC}^{\varphi} \sigma(\varphi') d\varphi' = \gamma_{\rm PZC} - \Delta \gamma(\varphi)$$
(2)

where $\gamma_{\rm PZC}$ is the surface energy at the PZC. To solve this for $\gamma(\varphi)$, we need to know $\gamma_{\rm PZC}$, $\sigma(\varphi)$, and the PZC. Per the electrocapillary equation, $\sigma(\varphi)$ can be determined by integrating $C_{\rm d}/A$ from the PZC to φ

$$\sigma(\varphi) = \int_{\text{PZC}}^{\varphi} C_{d}(\varphi') d\varphi'$$
(3)

By definition, $\sigma(\text{PZC}) = 0$, which allows evaluation of the integral in eq 3. Figure 5b shows the resulting $\sigma(\varphi)$. From this, the integral in eq 2 can be evaluated for $\Delta\gamma(\varphi)$, shown in Figure 5c. C_d/A was extrapolated as a constant from -0.2 to -1 V_{SHE} to make an approximation of γ down to -1 V_{SHE}. For the two-electrode plate and dendrite depositions, we assumed the Pt counter electrode was at ~1.5 V_{SHE}: the water oxidation potential of 1.13 V_{SHE} at pH = 1.7 plus several hundred mV of overpotential and ohmic drop. As such, the plate growth would have occurred at $\varphi_{\text{offset}} \approx 0.5$ V_{SHE} and dendrite growth at $\varphi_{\text{offset}} \approx -0.5$ V_{SHE}. These correspond to decreases in γ of $\Delta\gamma(0.5) \approx 0$ eV/nm² and $\Delta\gamma(-0.5) \approx 1$ eV/nm². During the deposition half-cycles for plates and dendrites, where $\varphi \approx -3.5$ V_{SHE} and $\varphi \approx -8.5$ V_{SHE}, respectively, our data suggests $\Delta\gamma$ would be many eV/nm².

Cyclic voltammetry allowed for measurements of the sample surface area. These were made by sweeping across the oxidation and reduction potentials of Au in H_2SO_4 and integrating the total charge passed during the reduction peak. Assuming a uniform and repeatable Au oxide layer, the relative surface area



Figure 6. Cyclic voltammetry of dendrites, plates, and a flat film of Au on Si with a geometric area of 0.8 cm^2 in 500 mM sulfuric acid. (a) Overlayed cyclic voltammograms of each nanostructure. (b) Real surface area of the electrode, calculated by integrating the total charge of the Au reduction peak for each curve. The roughness factor was calculated by normalizing relative to the flat film.



Figure 7. (a) Total current density of a sample with (blue) Au dendrites, (black) Au sputtered film, and (red) Au plates under the potentials of -0.2 to $-0.5 V_{RHE}$, stepped by -50 mV every 2 h, except for an initial 4 h hold at $-0.2 V_{RHE}$ for the current to stabilize. (b) Total current density of a sample with Au dendrites and plates under the potentials of -0.2 to $-0.475 V_{RHE}$, stepped by -25 mV every 2 h, and followed by 6 h holds at -0.25, -0.35, and $-0.4 V_{RHE}$ to test stability. (c,d) Faradaic efficiencies for CO vs φ .

of the electrode could be measured.¹⁹ Figure 6a shows the reduction peak of dendrite, plate, and flat Au film samples. Figure 6b shows the actual surface area and the roughness factor of each of these samples, normalized to the flat film. Figure S20 shows data taken between EIS measurements that had different electrolytes. Linear interpolation between these surface area measurements of EIS samples was used to approximate the C_d/A shown in Figure 5a.

CO₂ Electrolysis. XPS measurements before and after CO_2 reduction experiments were used to quantify the surface atomic composition and the Au oxidation state. Figure S21 shows that the XPS spectrum for the Au 4f and O 1s peaks are very similar before and after CO_2 reduction, suggesting that no change is made to the Au oxidation state.

The performance of the Au dendrites, plates, and sputtered film as electrocatalysts for CO₂ reduction was assessed by measuring j_{total} and product gas composition at a variety of applied potentials. Figure 7a shows the geometric j_{total} of the dendrites, plates, and sputtered film; φ was started at $-0.2 \text{ V}_{\text{RHE}}$ for 4 h and then stepped in -50 mV increments every 2 h to $-0.5 \text{ V}_{\text{RHE}}$. Finally, φ was returned to $-0.25 \text{ V}_{\text{RHE}}$ to test the sample's stability over time. j_{total} at the end of the experiment decreased substantially for the dendrites, but actually increased for the plates and sputtered film. Figure 7b shows the performance of dendrite and plate samples starting at $-0.2 \text{ V}_{\text{RHE}}$ and stepping in -25 mV increments every 2 h to -0.475

 V_{RHE} , followed by 6 h holds at -0.25, - 0.35, and -0.4 V_{RHE} . With a smaller step size, more time will have passed before each electric potential is reached. The two different potential step sizes were compared to ensure that this did not affect catalytic performance, a confirmation that the catalysts did not degrade significantly with time. For both dendrites and plates, this hold to test stability showed a much lower j_{total} at -0.25 V_{RHE} than the start of the experiment, but -0.35 and -0.4 V_{RHE} showed only slight degradation. Comparing the -50 mV steps to the -25 mV steps, j_{total} was found to match very well at -0.35 and -0.4 V_{RHE}. The -0.25 V_{RHE} current densities matched for the end-of-experiment holds. For both step increments, the dendrite samples showed a decreasing j_{total} at each applied potential until -0.35 V_{RHE} was applied, after which j_{total} was stable with time for increasingly negative φ . The plates showed a similar response for the -50 mV step but continued to show decreasing j_{total} at all applied potentials throughout the -25 mVsteps.

The Faradaic efficiencies for production of CO by the dendrites, plates, and sputtered films are shown in Figure 7c for the -50 mV steps and in 7d for the -25 mV steps. The data show dendrites have approximately 50–60% Faradaic efficiency for CO for $\varphi \leq -0.35$ V_{RHE}. The plates and film have a CO Faradaic efficiency of approximately 20–40% and 5–10%, respectively, during the -50 mV steps; plates showed a nearly 0% CO Faradaic efficiency during -25 mV steps. Notably, the

dendrites seemed to show a slight increase in the CO Faradaic efficiency during the 6 h holds at -0.35 and -0.4 V_{RHE}, compared to the values measured during the 2 h 25 mV steps; the CO Faradaic efficiency for the 6 h hold at -0.25 V_{RHE} was too noisy to produce a reliable average. Figure 8 shows Tafel



Figure 8. Tafel slopes of Au dendrite and Au plate samples from -25 mV steps, and Au sputtered film from -50 mV steps.

plots for the dendrites, plates, and sputtered film. The data show the kinetically limited reaction regimes to have a slope of 40 mV/dec for dendrites and 110 mV/dec for the plates and film.

DISCUSSION

During electrocrystallization, the solute near the crystal surface gets added to the crystal surface via an electrochemical reaction. This depletes the solute concentration, establishing a diffusion boundary layer. In continued crystallization, the solute must diffuse across the diffusion boundary layer from the solution bulk to the crystal surface. The slower of these serial steps, diffusion or electrochemical reaction, will determine the rate of deposition and control the morphology of the crystals grown. Equivalent steps occur for crystallization from melts and vapors.

When crystallization is diffusion limited, three-dimensional structures can be formed, such as dendrites. This occurs,

because protrusions on the crystal surface extend into the diffusion field, receiving faster diffusion of solute than the surrounding flat surface. The phenomenon is known as the Mullins–Sekerka effect.²⁰ The sharper the protrusions, the faster solute diffusion will be. This effect is balanced by the Gibbs–Thomson effect,²¹ in which the local surface energy of a crystal increases with decreasing radius of curvature; for a given deposition condition, protrusions with radius of curvature below a certain value will be thermodynamically unstable and dissolve/melt/sublimate.

To provide a model that describes the morphology of the crystals, we draw comparisons between the electrocrystallization and crystallization from melts and vapors. For crystallization upon a polycrystalline film, where a random assortment of crystal orientations are present for nucleation, growth will proceed along the orientation of lowest surface stiffness, $\gamma^{*,22}$ This is a measure of the energy per unit area necessary to create curvature on a surface; adding atoms onto an atomically flat surface requires creating such a curvature. γ^* is derived from the surface energy, γ , via Herring's Equation;^{23,24} γ is defined as the energy it takes to create a unit area of interface between the crystal and solution. Figure 9a shows the predicted values of γ for several ambient phases and crystal orientations. Comparison of molecular dynamics simulations and experiments^{22,25,26} has developed a theory to describe the dendrite morphology of different metals solidified from their melts. These calculations approximate the surface energy of crystals with underlying cubic symmetry by expansion into a series of cubic harmonics with two anisotropy factors, ϵ_1 and ϵ_2

$$\gamma(\theta, \phi) = \gamma_0 [1 + \epsilon_1 K_1(\theta, \phi) + \epsilon_2 K_2(\theta, \phi) + \dots]$$
⁽⁴⁾

where the cubic harmonics are combinations of the standard spherical harmonics with cubic symmetry. The particular K_1 and K_2 referenced above are

$$K_{1}(\theta, \phi) = \sum_{i=1}^{3} n_{i}^{4} - \frac{3}{5}$$
(5a)

$$K_2(\theta, \phi) = 3\sum_{i=1}^{3} n_i^4 + 66n_1^2 n_2^2 n_3^2 - \frac{17}{7}$$
(5b)



Figure 9. Comparison of the tendency of Au to form facets at various Miller indices, in several ambient phases. Experimental d_{hld} values from [ref 27]. To calculate T_v , γ^* was assumed constant with temperature. For an Au vapor ambient phase, we used $\gamma_0 \approx 6.16$ (eV/nm²), the value for Au in a noninteracting atmosphere.¹⁶ For an Au-melt ambient phase, $\gamma_{0,melt} = 0.786$ (eV/nm²) [ref 25]. For the Au vapor and Au melt, we used $\epsilon_1 = 0.064 \pm 0.011$ and $\epsilon_2 = 0.003 \pm 0.002$ [ref 26]. For the HAuCl₄(aq) ambient phase, we used $\gamma_0 \approx 6.16$ (eV/nm²) for the PZC and $\gamma_0 \approx 5.16$ (eV/nm²) for the dendrite $\varphi_{offsetv}$ consistent with $\Delta \gamma$ measurements in 1 mM HAuCl₄(aq) + 100 mM H₂SO₄(aq). (a) γ ; the inset shows a rounded Au sphere with {111} facets formed by melting an Au wire. (b) γ^* . (c) T_r . (d) Cartoon of facets present at different deposition temperatures, relative to T_r for each Miller index.

where $\hat{n} = (n_1, n_2, n_3)$ is the interface normal. In spherical coordinates, these have their standard definition, $n_1 = \cos(\phi)\sin(\theta)$, $n_2 = \sin(\phi)\sin(\theta)$, $n_3 = \cos(\theta)$. Eq 4 shows that the shape of γ is dictated by the value of ϵ_1 and ϵ_2 , scaled in magnitude by the surface energy prefactor, γ_0 . ϵ_1 and ϵ_2 thus determine the shape of γ^* and the direction of growth of dendritic crystals. This angular dependence of the surface stiffness tensor can be calculated by

$$\gamma^* = 2\gamma + \frac{\partial^2 \gamma}{\partial \theta^2} + \frac{1}{\sin^2(\theta)} \frac{\partial^2 \gamma}{\partial \phi^2} + \cot(\theta) \frac{\partial \gamma}{\partial \theta}$$
(6)

Values of ϵ_1 and ϵ_2 for various metals solidifying from their melt have been calculated by these molecular dynamics simulations, with plots generated of the inverse of γ^* and the expected dendrite morphology.²² Through comparison of these with the dendrite morphology shown in Figure 2, the single branch in each $\langle 110 \rangle$ direction suggests that the anisotropy factors for Au electrocrystallization from HAuCl₄(aq) are approximately $\epsilon_1 = 0.02$ and $\epsilon_2 = -0.02$. Interestingly, this differs significantly from the values reported for Au dendrites grown from their melt, where $\epsilon_1 = 0.064 \pm 0.011$ and $\epsilon_2 =$ -0.003 ± 0.002 ²⁶ corresponding to dendrite growth in the $\langle 100 \rangle$ directions. As such, electrocrystallization allows for a unique dendritic Au structure than crystallization from melts allows. Figure 9b shows γ^* for several ambient phases. Electrocrystallization of Au dendrites with different growth directions would require tuning the anisotropy parameters, potentially possible with chemicals that would selectively interact with certain Au crystallographic orientations.

It has been shown through comparison of experiment and density functional theory calculations that γ of the Au {111} surface in vacuum is approximately 6 eV/nm².¹⁶ With use of the ϵ_1 and ϵ_2 values determined above for electrocrystallization, this corresponds to $\gamma_0 = 6.16 \text{ eV/nm}^2$. This is a rough estimate; other work has reported $\gamma_0 = 4.3 \text{ (eV/nm}^2)$.²⁸ Using a model that considers only polarization due to the ionic double layer, calculations showed γ to be unchanged by immersion in 500 mM H₂SO₄(aq). This model calculated the PZC to be 0.55 V_{SHE}.

Our measurements show the PZC of Au in 1, 10, and 100 mM $H_2SO_4(aq)$ to be ~0.35 $V_{SHE}{-\!\!\!-}and$ closer to ~0.4 V_{SHE} for 500 mM. This suggests that there is some interaction between the Au and H₂SO₄(aq) besides polarization. The negative shift indicates a negative species in the $H_2SO_4(aq)$ with an affinity to the Au, which at 0.55 V_{SHE} would draw a net positive charge onto the Au. The PZC of Au in 0.01, 0.1, and 1 mM HAuCl₄(aq) + 100 mM H₂SO₄(aq) is also 0.35 V_{SHE}. If we assume $\Delta \gamma(0.55) = 0.1 \text{ eV/nm}^2$ equals the change in γ from the interactions with solution, then the change is negligible compared to $\gamma_0(PZC) \approx 6 \text{ eV/nm}^2$. Figure 5c does show a significant change of 1 eV/nm² at $\varphi = -0.5$ V_{SHE}, though. This roughly corresponds to $\varphi_{\text{offset}} = -2$ V for dendrite deposition. Under our approximations, γ would reach 0 eV/nm² before the deposition half-cycle potentials for plate and dendrite growth, -3.5 and -8.5 V_{SHE}, respectively. A negative γ would correspond to a dissolving electrode, so our approximation that \bar{C}_d/A is constant at potentials negative of $-0.2 \text{ V}_{\text{SHE}}$ is evidently an overestimate. γ is likely quite low at these very negative potentials, though.

Regarding the structure of the crystal's surface, the surface of a crystal is either a flat atomically smooth facet with a particular crystallographic orientation or a rounded atomically rough surface with a gradually changing orientation along its surface. If the deposition temperature is above the roughening temperature (T_r) for a particular crystallographic orientation, then the surface will be rough. T_r is a function of γ^* for a given ambient growth phase²⁹

$$kT_{\mathrm{r},hkl} = \frac{2}{\pi} \gamma^*(T_{\mathrm{r}}) d_{hkl}^2 \tag{7}$$

where d_{hkl} is the interplanar distance parallel to the crystal face. "The more closely packed a given crystal face is, the larger the interplanar distance, and the higher T_r will be."²⁴ For example, on an fcc lattice, the most closely packed face has $d_{111} = a_0/\sqrt{3}$ $\approx 0.6a_0$, followed by $d_{100} = a_0/2 = 0.5a_0$; deposition at a temperature of $T_{r,100} < T < T_{r,111}$ should produce crystals with rough rounded surfaces except for flat {111} facets. Figure 9c shows T_r for several ambient phases. Figure 9d demonstrates the meaning of T_r via a cartoon. The Au surface should be completely rough for room temperature deposition at φ , for which $\gamma_0 \leq 0.25 \text{ eV/nm}^2$.

For context, we first consider T_r in Figure 9c for an Au surface in an Au melt and Au vapor. The plot indicates that solidification from an Au melt should not produce faceted Au crystals, as $T_r = 700$ K for the most densely packed faces, {111}, is below the melting point of 1300 K.²⁶ This is approximately confirmed by the SEM in the Figure 9a inset, showing the result of melting the tip of an Au wire with a butane flame and letting it crystallize in room temperature atmosphere; all of the surfaces appear rounded except for small facets in the $\{111\}$ directions. For the Au vapor, lacking a better option, ϵ_1 and ϵ_2 were somewhat arbitrarily set to the same values as for an Au melt. $T_r = 5400$ K for growth from an Au vapor, much higher than for the melt. However, Au must be raised over 900 K just to reach the minute vapor pressure of 10^{-11} Torr and over 1500 K to reach 10⁻³ Torr.³⁰ As such, Au vapor should produce faceted Au crystals but would require low pressure and high temperature equipment.

Per Figure 9c, T_r for HAuCl₄(aq) at the PZC and the dendrite φ_{offset} is slightly larger than for an Au vapor and has a different shape than the melt and vapor due to the different ϵ_1 and ϵ_2 values. The large T_r means that, for deposition at room temperature and near the PZC, many crystallographic orientations should have faceted surfaces rather than rough. Since the $\{111\}$ facet has the lowest surface energy, this would be expected to dominate, assuming local thermodynamic equilibrium during crystal growth. This is consistent with our XRD analysis of plates, which shows $\{111\}$ to dominate. T_r for the dendrite φ_{offset} potential is slightly lower but still over 500 K for all Miller indices considered. XRD does show {111} to continue to dominate the dendrites, but the peaks for $\{100\}$ and {110} increase significantly compared to the plates. Growth of these crystals is diffusion limited, which could prevent full formation of {111} facets and explain these increased peaks. Observations in TEM show nm scale {100} and {110} facets along rounded surfaces; no {111} were observed. The prevalence of rough surfaces with scattered small facets, as observed via TEM, suggests that T_r for an Au surface may depend on the instantaneous potential. For our deposition process, this would sweep T_r widely between 0 and over 500 K during the MHz potential oscillation.

The structure of the Au plates is very similar to several Au^{12,31,32} and Ag^{33–35} plates recently reported. In these reports, it is proposed that sufficiently low ion concentration ensures that nuclei cannot grow autocatalytically into lower-energy

polyhedral structures. Instead, stacking faults and/or twin defects at the particle edges provide favorable sites for nucleation of new atomic layers on the {111} facets. The similarity in structure and dilute electrolyte suggests that a similar kinetically limited growth mechanism is responsible for the morphology of the Au plates we produced.

The formation of dendrites at more cathodic φ is consistent with the mechanism discussed above. The higher overpotential could be sufficient to drive the kinetics of deposition faster than solute diffusion, establishing the diffusion limited growth condition. Separately, this overpotential may also drive nucleation of new atomic layers without the aid of twin defects and thereby change the crystal morphology.

The effect of an MHz potential oscillation on dendrite growth has been described in detail.^{7–11} The primary result of the oscillation is to increase the effective solute concentration at the dendrite surface, since the solute can replenish during the anodic half of the oscillation. The solute concentration has a significant impact on the dendrite morphology; as the concentration increases, we have shown the dendrite crystals have fewer small granules on them (Figure 1e–1), and literature has shown that the tip gets sharper.^{5,10} However, increasing the concentration of HAuCl₄ has the simultaneous impact of lowering the pH. Lower solution pH is understood to produce rounded surfaces instead of faceted ones.³⁶

Regarding CO_2 reduction electrocatalyst efficacy, the dendrites had the highest current density, while that of the plates and sputtered film was similar. Dendrites also showed the highest selectivity for CO, followed by the plates, and finally the sputtered film. This selectivity is consistent with the literature. Calculations and experiments have demonstrated the binding energy of the intermediate COOH to have the relative magnitudes of $\{110\} > \{100\} > \{111\}$.³⁷ This intermediate should thus be most stable on the dendrites, which have the greatest proportion of $\{110\}$ and $\{100\}$ facets, followed by plates, and finally the sputtered film.

The mechanism of the conversion of CO₂ to CO at a gold catalyst in an aqueous bicarbonate solution involves two electron transfers and two proton transfers to a CO₂. Different mechanisms for this process have been proposed, as summarized recently.² In all mechanisms, if the first reaction step produces an intermediate that is not stable on the Au surface, then it will be the rate limiting step (RLS). If the intermediate is stable, then the RLS will be the last step that produces an unstable (i.e., poorly bound) species. We assume the symmetry factor $\beta = 0.5$ for the electron transfers. As such, the 40 mV/dec slope measured for the dendrites suggests the RLS is an electron transfer to the intermediate COOH, producing CO and H₂O. This step completes the reaction and is thus the lowest possible Tafel slope for mechanisms that are consistent with the appearance of a 40 mV/dec slope. The 110 mV/dec slope measured for the plates and film matches the first or second reaction step of the mechanisms reported in the above-mentioned article. Scheme 1 shows two example schemes, in which the first step involves an electron transfer with a predicted Tafel slope of 118 mV/dec, and the last step is an electron transfer with a predicted Tafel slope of 40 mV/dec Scheme 1a depicts an electron transfer to bind the CO₂ to Au, followed by protonation, and finally a proton-coupled electron transfer (PCET). Scheme 1b depicts a PCET step to bind the CO₂ to Au, followed by another PCET to finish the reaction. The H⁺ in the scheme cartoon represents a generic proton source-further studies of the reaction orders of different





^{*a*}(a) An electron transfer, followed by protonation, and finally a PCET. (b) Two sequential PCET reactions. The H⁺ represents any proton source. The predicted Tafel slope for the first electron transfer matches measurements of $\{111\}$ dominated plates; the predicted Tafel slope for the second electron transfer matches measurements of $\{110\}$ and $\{100\}$ -rich dendrites.

chemical species would be necessary to determine the proton source. The 40 mV/dec slope has only been produced by one other structure of which we were aware, Au nanoneedles.^{5,6}

The dendrites clearly have a much higher specific surface area than the film or plates, which can in part explain their higher current density. However, other characteristics are independent of the specific surface area. The lower Tafel slope of the dendrites is evidence of higher CO_2RR activity, which can result from stronger binding to the intermediate COOH. This reaffirms the expectation that nanostructures with a greater proportion of {110} and {100} relative to {111} facets provide faster reaction kinetics.

The potential -0.35 V_{RHE} stands out as a turning point where catalytic performance significantly increases as the potential becomes more negative. This was true for the dendrites, plates, and film. At the more negative potentials, $j_{\text{total}}(t)$ is stable during 42 h of CO₂RR and shows a stark decrease in noise. The dendrites show a somewhat abrupt increase in the CO Faradaic efficiency from ~0 to ~50% with increasing overpotentials. Finally, the Tafel slopes change: for both of the dendrites and the film there is an increase in the mV/dec of partial current density, typically understood to signify the point at which the reaction kinetics outpace the rate of mass transport to make the reaction mass transport limited. For plates, the slope decreases from ∞ to 110 mV/dec at this potential. Notably, a slight increase in the CO Faradaic efficiency is observed during the 6 h potential holds, as shown in Figure 7d.

The plate samples demonstrated inconsistent results between -25 mV steps and -50 mV steps. This may be a result of poor stability of the plates during the long experiment time of the -25 mV steps, resulting in degradation. We excluded the CO Faradaic efficiency at $-0.2 \text{ and } -0.25 \text{ V}_{\text{RHE}}$ during -50 mV steps, because it was produced at very low and unstable current density, giving the data questionable accuracy.

CONCLUSIONS

In summary, electrocrystallization with an MHz oscillation of the potential φ allows for the fabrication of various Au nanostructures, namely, plates and dendrites. According to XRD analysis, the surface of dendrites contains a larger proportion of {100} and {110} than the plates; the other major surface orientation on both nanostructures is {111}. EIS

measurements of C_d/A vs φ for polycrystalline Au in aqueous solutions show the PZC \approx 0.35 V_{SHE}, with γ decreasing as φ moves away from the PZC. Adaptation of a model for crystallization from melts and vapors suggests that, in this electrocrystallization, more crystal orientations should be faceted at φ with large γ . No facets should be present for room temperature deposition at φ with $\gamma_0 \leq 0.25 \text{ eV/nm}^2$. Comparison with literature on crystallization from aqueous solutions suggests that plate growth is kinetically limited, growing via stacking faults and/or twin defects at the plate edges to produce predominantly {111} surfaces. Dendrite growth is likely mass transport limited, creating hierarchical nanostructures that are $\sim 10 \ \mu m$ tall. SEMs of plate corners and dendrite tips look similar, suggesting that the kinetic process for the growth at these sites may be the same. Due to the hierarchical nature of these nanostructures, with nm scale features on μm scale plates and dendrites, there is a certain degree of randomness and variation of Au surface within each sample. As such, precise control of exposed facets proves to be challenging. The averaging effect of XRD over cm² areas made it a powerful tool for analyzing the surface's distribution of crystal orientation. The different nanostructures were found to have significantly different performance as CO2RR electrocatalysts, supporting previous findings that $\{100\}$ and $\{110\}$ orientations are more active for CO_2RR than the {111} orientation. Stable performance was observed for 42 h on the dendrites. $\varphi = -0.35 V_{RHE}$ was observed to be the turn-on potential for the CO₂RR; cathodic of this potential $j_{total}(t)$ was more stable, and the dendrite's Faradaic efficiency for CO was ~50%. For future studies, higher HAuCl₄ concentrations may be considered to change the kinetic process, which for plates was likely dependent on low ion concentration. To avoid $\{111\}$ surfaces, which our data suggests have the highest roughening temperature, two approaches could be taken. First, more cathodic φ could be considered as a means to avoid the formation of any facets. Second, φ near the PZC could be focused on, as a means to maximize the formation of facets besides {111}.

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpcc.8b01831.

Circuit model schematics for electrochemical impedance spectroscopy (EIS) measurements; Nyquist plots used to calculate the differential capacitance of an Au surface; XRD spectra that show little change of facet preference between Au nanostructures deposited using different voltage amplitudes; differential capacitance, surface charge, and change in surface energy of an Au surface in different concentrations of sulfuric acid to establish an understanding of how an Au surface interacts with sulfuric acid—the supporting electrolyte used to study the interactions between an Au surface and chloroauric acid; electrochemical surface area measurements of the Au surface during EIS measurements; XPS spectra of the Au nanostructured surface before and after CO_2 reduction experiments (PDF)

AUTHOR INFORMATION

Corresponding Authors

*E-mail: nathan.nesbitt@gmail.com; Phone: +1-617-552-3595 (N.T.N.)

*E-mail: w.smith@tudelft.nl; Phone: +31-15-27-82659 (W.A.S.)

*E-mail: naughton@bc.edu; Phone: +1-617-552-3575 (M.J.N.) ORCID ©

Nathan T. Nesbitt: 0000-0002-1806-1077 Samantha Jaszewski: 0000-0002-4958-1219 Fazel Tafti: 0000-0002-5723-4604 Michael J. Burns: 0000-0001-9804-405X Wilson A. Smith: 0000-0001-7757-5281 Michael J. Naughton: 0000-0002-6733-2398

Notes

The authors declare no competing financial interest.

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Au Dendrite Electrocatalysts for CO₂ Electrolysis

Nathan T. Nesbitt,^{*,†} Ming Ma,[‡] Bartek J. Trześniewski,[‡] Samantha Jaszewski,[†]

Fazel Tafti,[†] Michael J. Burns,[†] Wilson A. Smith,^{*,‡} and Michael J. Naughton^{*,†}

†Department of Physics, Boston College, Chestnut Hill, Massachusetts 02467, United States
 ‡Materials for Energy Conversion and Storage (MECS), Department of Chemical
 Engineering, Faculty of Applied Sciences, Delft University of Technology, 2629 HZ Delft,
 The Netherlands

E-mail: nathan.nesbitt@gmail.com; w.smith@tudelft.nl; naughton@bc.edu Phone: +1-617-552-3595; +31-15-27-82659; +1-617-552-3575

Supporting Information



Figure S1: XRD spectrum of Au dendrites grown at $\varphi_{\text{offset}} = -2$ V with different potential amplitudes, normalized so the Au (111) peak height is 1. (a) full spectrum, (b) (111) peak, (c) (200) peak, (d) (220) peak.



Figure S2: Randles circuit model with ideal EIS response, used to interpret EIS data.¹



Figure S3: Nyquist plots showing electrochemical impedance spectroscopy measurements for a Au electrode in 20 mM HAuCl₄ at different DC potential biasses. The measurements were made starting at $\varphi = 1$ V_{SHE} and stepping in 100 mV increments to 0 V_{SHE}. The bottom right plot is a repeat of $\varphi = 1$ V_{SHE} after the other measurements to confirm the electrode did not significantly change during the measurements.



Figure S4: Potentiostatic EIS of a sputtered Au surface with geometric area 0.8 cm² in various concentrations of H₂SO₄. (a–c) Left of gray dashed line is extrapolation of C_d as a constant vs. φ , right of the gray dashed line is measured data. (a) C_d per unit area vs. φ ; electrode area A was measured by CV of the Au in H₂SO₄. (b) σ vs. φ calculated from (a). (c) $\Delta \gamma$ vs. φ calculated from (b). (d–g) Nyquist plots of the EIS measurements at each φ , for each of the H₂SO₄ concentrations. Red solid lines are positive of 0.35 V_{SHE}, the black solid lines are at 0.35 V_{SHE}, and the dashed red lines are negative of 0.35 V_{SHE}.



Figure S5: Nyquist plots of potentiostatic EIS measurements made in 1 mM $\rm H_2SO_4(aq)$ from 1 $\rm V_{SHE}$ to 0.4 $\rm V_{SHE}.$



Figure S6: Nyquist plots of potentiostatic EIS measurements made in 1 mM $\rm H_2SO_4(aq)$ from 0.375 $\rm V_{SHE}$ to $-0.2~\rm V_{SHE}.$



Figure S7: Nyquist plots of potentiostatic EIS measurements made in 10 mM $\rm H_2SO_4(aq)$ from 1 $\rm V_{SHE}$ to 0.4 $\rm V_{SHE}.$



Figure S8: Nyquist plots of potentiostatic EIS measurements made in 10 mM $\rm H_2SO_4(aq)$ from 0.375 $\rm V_{SHE}$ to $-0.2~\rm V_{SHE}.$



Figure S9: Nyquist plots of potentiostatic EIS measurements made in 100 mM $\rm H_2SO_4(aq)$ from 1 $\rm V_{SHE}$ to 0.4 $\rm V_{SHE}.$



Figure S10: Nyquist plots of potentiostatic EIS measurements made in 100 mM $H_2SO_4(aq)$ from 0.375 V_{SHE} to $-0.2 V_{SHE}$.



Figure S11: Nyquist plots of potentio
static EIS measurements made in 500 mM $\rm H_2SO_4(aq)$ from 1
 $\rm V_{SHE}$ to 0.4 $\rm V_{SHE}.$



Figure S12: Nyquist plots of potentiostatic EIS measurements made in 500 mM $\rm H_2SO_4(aq)$ from 0.375 $\rm V_{SHE}$ to $-0.2~\rm V_{SHE}.$



Figure S13: Net C_d vs. φ for potentiostatic EIS of a sputtered Au surface with geometric area 0.8 cm² in various concentrations of H₂SO₄. (left) All EIS measurements. (right) Magnified view of the pure H₂SO₄ electrolytes. Left of gray dashed line is extrapolation of C_d as a constant vs. φ , right of the gray dashed line is measured data.



Figure S14: Nyquist plots of potentiostatic EIS measurements made in 0.01 mM HAuCl₄(aq) + 100 mM H₂SO₄(aq) from 1 V_{SHE} to 0.4 V_{SHE}.



Figure S15: Nyquist plots of potentiostatic EIS measurements made in 0.01 mM HAuCl₄(aq) + 100 mM H₂SO₄(aq) from 0.375 V_{SHE} to -0.2 V_{SHE}.



Figure S16: Nyquist plots of potentiostatic EIS measurements made in 0.1 mM $HAuCl_4(aq)$ + 100 mM $H_2SO_4(aq)$ from 1 V_{SHE} to 0.4 V_{SHE} .



Figure S17: Nyquist plots of potentiostatic EIS measurements made in 0.1 mM $HAuCl_4(aq)$ + 100 mM $H_2SO_4(aq)$ from 0.375 V_{SHE} to -0.2 V_{SHE} .



Figure S18: Nyquist plots of potentio
static EIS measurements made in 1 mM $\rm HAuCl_4(aq)$ + 100 m
M $\rm H_2SO_4(aq)$ from 1 $\rm V_{SHE}$ to 0.4 $\rm V_{SHE}.$



Figure S19: Nyquist plots of potentiostatic EIS measurements made in 1 mM $HAuCl_4(aq)$ + 100 mM $H_2SO_4(aq)$ from 0.375 V_{SHE} to -0.2 V_{SHE} .



Figure S20: Cyclic voltammetry of a Au-coated Ti foil with geometric area 0.8 cm² in 500 mM sulfuric acid for variable concentration of H_2SO_4 and 375 mM sulfuric acid for variable concentration of HAuCl₄. (left) Overlayed cyclic voltammograms taken before or after EIS measurements for indicated electrolytes. (right) Real surface area of the electrode, calculated by integrating the total charge of the Au reduction peak for each curve and normalizing relative to reduction peaks of sputtered Au on a flat silicon wafer.



Figure S21: XPS spectrum of Au dendrites before and after the CO_2 reduction experiment with -25 mV steps. (a) The Au4f peak, (b) the O1s peak.

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