Understanding and Controlling Photoelectrode Surface for Solar Fuel Production and Beyond

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UNDERSTANDING AND CONTROLLING PHOTOELECTRODE SURFACE FOR SOLAR FUEL PRODUCTION AND BEYOND

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Wei Li

Advisor: Dunwei Wang, Ph.D.

Among the existing strategies to direct solar energy harvesting and storage, solar fuel production by photoelectrocatalysis promises a comparatively simple, low-cost route. The science behind this process is straightforward: stable semiconductors absorb sunlight and use the energy to excite charges, which then drive redox reactions at the surface. Careful studies of the photoelectrode surface provide important considerations in building a highperformance photoelectrode. Specifically, I focused on controlling the surface band alignment of Cu₂O photocathode|water for hydrogen evolution reaction. A ZnS buried heterojunction is formed to improve the photovoltage. Then I focused on understanding the influence of chemical species on surface kinetics and energetics for water oxidation reaction. Two hematite photoanodes with preferably exposed $\{001\}$ and $\{012\}$ facets were examined. Further, I systematically studied three different types of surfaces, bare hematite, hematite with a heterogenized Ir water oxidation catalyst (WOC), and a heterogeneous IrO_x WOC. While both WOCs improve the performance of hematite by a large margin, their working mechanisms are found to be fundamentally different. I also focused on utilizing surface photoexcited species to control product selectivity. Selective CO production by photoelectrochemical methane oxidation is successfully demonstrated. Detailed experimental investigations revealed that a synergistic effect by adjacent Ti³⁺ sites is the key to CO formation.

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TABLE OF ABBREVIATIONS

- **PEC:** photoelectrochemical
- SCLJ: semiconductor/liquid junction
- **TE:** transfer efficiency
- **HER:** hydrogen evolution reaction
- **OER:** oxygen evolution reaction
- **RHE:** reversible hydrogen electrode
- **STH:** solar to hydrogen
- **ABPE:** applied bias photon to current conversion efficiency
- **IPCE:** incident photon to current conversion efficiency
- EQE: external quantum efficiency
- ALD: atomic layer deposition
- **SEM:** scanning electron microscopy
- STEM: scanning transmission electron microscopy
- **OCP:** open circuit potential
- **IMPS:** intensity modulated photocurrent spectroscopy
- **TEM:** transmission electron microscopy
- **XPS:** x-ray photoelectron spectroscopy
- **DFT:** Density functional theory
- **FTO:** fluorine doped tin oxide
- **WOC:** water oxidation catalyst

Het-WOC: heterogenized water oxidation catalyst

EIS: electrochemical Impedance Spectroscopy

KIE: kinetic Isotope Effect Measurements

SRM: steam reforming of methane

FTIR: Fourier-transform infrared spectroscopy

EPR: Electron paramagnetic resonance spectroscopy

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Chapter 1: Introduction

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1.1 Photoelectrochemical (PEC) solar fuel production

In the consideration of energy potentials and state-of-art technologies, solar energy is the only renewable energy source which meets human being's increasing energy demand. Photovoltaic solar cell is one of the most successfully commercial solar energy conversion techniques, and its research & development process still attracts broad interests. Despite that much progress has been achieved, the intermit nature of sunlight requires solar cell to combine with scalable energy storage techniques, which greatly undermines the costeffectiveness of solar electricity. Alternatively, sunlight could be directly converted to solar fuels, which promises a scalable storage technology. For instance, H₂ is one of the most promising candidates, owing to it is carbon-neutral, high in energy density and easily portable. Extracting H₂ from solar water splitting enables recycle of H₂O, and allows to collect and store solar energy in the simplest chemical bond H_2 , as nature accomplishes through photosynthesis.

Among existing strategies for solar fuel production, PEC water splitting promises a simple, low-cost and durable route. The typical configurations are illustrated in Chapter 1.3. Water is reduced to hydrogen on photocathode; and oxidized to oxygen on photoanode for the completeness of whole chemical cycle. A PEC cell is based on a semiconductor/liquid junction, and n-type (p-type) semiconductor serves as photoanode (photocathode), where electrons (holes) are free majority carriers. Upon illumination, charges (electrons and holes) are generated. Meanwhile, a built-in field near the surface is developed due to the differences in Fermi level in the bulk and band edges at the surface. This field separates electrons and holes by driving them toward opposite directions. Once the photogenerated-holes reach the reactive sites at the surface, they participate in water oxidation. The photoelectrodes also generally have electrocatalysts to facilitate desired multielectron reactions. To evaluate overall performance, it is helpful to study half reaction.

1.2 Semiconductor photoelectrochemistry

Semiconductor photoelectrochemistry deserves special attention because the system features a highly unique interface – the semiconductor/liquid junction (SCLJ). For a typical system where the Fermi level of the semiconductor is not at the same level as the electrochemical potential of the electrolyte prior to contact, the formation of the junction suggests that one or both of the energy levels should move to reach equilibrium. As the

charge density of the electrolyte is typically several orders of magnitude higher than that of the semiconductor, typically it is the Fermi level of the semiconductor which moves to align with the electrochemical potential of the electrolyte. While the same description would be true for a metal/liquid junction as well, the semiconductor is unique because it can form a relatively wide depletion region (up to µm's, depending on the dielectric constant, the carrier density, and the energy difference).^{1, 2} As is seen in Figure 1.1, a SCLJ with a bent band is effectively a Schottky-type diode that can separate photogenerated charges. This junction is the fundamental reason why semiconductor photoelectrochemistry is interesting.

For the ease of discussions, we choose to use a photoanode system as shown in Figure 1.1 as a prototypical platform to lay out the details. Upon contact, the SCLJ results in the formation of a space charge region (depletion region of electrons), whose width (W_{sc}) depends on the difference between the Fermi level of the semiconductor in vacuum and the electrochemical potential of the electrolyte ($\Delta \phi_{sc}$), the relative permittivity (ε) and the doping density (N_{d}):

$$W_{sc} = \left(\frac{2\Delta\phi_{sc}\varepsilon\varepsilon_0}{qN_d}\right)^{1/2} \tag{1.1}$$

The capacitance of the space charge region can be derived from the variation of the space charge (C_{sc}) with the potential drop $(\Delta\phi_{sc})$, $C_{sc} = dQ_{sc}/d\Delta\phi_{sc}$, as described by the *Mott–Schottky equation*:

$$\frac{1}{C_{sc}^2} = \frac{2}{qN_d\varepsilon\varepsilon_0} \left(\Delta\phi_{sc} - \frac{k_BT}{q}\right)$$
(1.2)

Because the electrical field generated within the space charge region varies linearly from distance $x = W_{sc}$ to the surface (x = 0), the variation of electrical potential will be proportional to x^2 and can be represented as band bending (Figure 1.1b). The degree of band bending is

governed by the Fermi level difference between the semiconductor and the redox pair. This is analogous to a Schottky junction formed between a semiconductor and a high work function metal.³ Under reverse bias conditions (positive potentials), the Schottky barrier is increased, which makes it more difficult for electrons to transfer from the semiconductor to the electrolyte. For an anode system, such charge transfer would be considered back electron transfer and should be minimized. In the meanwhile, the enhanced band bending under reverse bias make it easy for holes to transfer into the electrolyte to drive oxidation reactions. Conversely, under forward bias (more negative potential applied on semiconductor), the band bending will be reduced and it becomes easier for electrons transferred from conduction band to oxidized redox species (a reduction reaction). Similar to a Schottky diode of an n-type semiconductor, however, holes are minority carriers, meaning that the current under reverse bias is limited. As such, we expect a photoanode to exhibit low reverse bias current. That is, negligible oxidation reactions would take place on a photoanode without illumination.

Upon illumination (hv > E_{gap}), electron-hole pairs are generated within the semiconductor as a result of electrons excitation from the valance band to the conduction band (process 1 in Figure 1.1c). At thermal equilibrium, the generation of electron-hole pairs from photon excitation is balanced by the recombination on a timescale > 10^{-9} s. Because these photogenerated electrons and holes can equilibrate with the lattice vibration (phonons) on a timescale < 10^{-12} s, the populations can be described by Fermi-Dirac statistics.¹ A quasi-Fermi level can then be derived by simply interpreting the steady-state carrier concentration of holes as representing a quasi-equilibrium situation ($E_{F,p}$ in Figure 1.1c), but

since the electron concentration is expected to be similar to the equilibrium value, $E_{F,n}$ is typically close to that under equilibrium. From a thermodynamics perspective, the driving force for water oxidation on a photoanode originates from the free energy difference between electrons and holes quasi-Fermi levels. The physical model of band bending near surface is still valid under such a circumstance. The magnitude of the quasi Fermi levels splitting determines the maximum photovoltage (V_{ph}) one photoanode can provide. Under the likely assumption that one can probe the $E_{F,n}$ through back contact under equilibrium conditions (e.g., through the measurement of the open circuit voltage, V_{oc}), the difference between the E_F (under dark, Figure 1.1b) and the $E_{F,n}$ (under illumination, Figure 1.1c) represents the V_{ph} .⁴⁻⁷



Figure 1.1 Schematic illustration of the band diagrams under different conditions. (a) prior to contact between the semiconductor and the electrolyte. (b) upon contact under equilibrium conditions without light. (c) quasi-equilibrium with illumination. The various processes are labelled as follows. (1) charge excitation by light; (2) electron extraction through back contact; (3) hole transfer to surface states; (4) hole transfer to the electrolyte; (i) bulk recombination; (ii) surface recombination; (iii) electron trap by surface states.

The recombination of photogenerated electron-hole pairs can take place either in bulk (process i in Figure 1.1c) or near surface (process ii and iii in Figure 1.1c), which may involve processes such as Shockley-Read-Hall recombination (through defects or impurities), radiation (band to band) recombination or Auger recombination.⁸ The recombination in bulk follows a pseudo first order rate law due to the excess of majority carriers (electrons in n-type semiconductor), and is characterized by the minority carrier lifetime τ_{min} . This value ranges from nanoseconds in many compound semiconductors to milliseconds in ultrapure silicon.⁹ Since the electrical field in bulk is limited, the minority carriers (holes in n-type semiconductor) generated in this region can only diffuse a certain distance before they are recombined, trapped or transferred to the electrolyte to drive oxidation reaction. This is one important bulk property of a semiconductor and characterized as minority carrier diffusion length L_{min} , which is determined by the diffusion coefficient D_{min} , the mobility of minority carriers μ_{min} and τ_{min} :

$$L_{min} = \sqrt{D_{min}\tau_{min}} = \sqrt{\frac{k_B T}{q}\mu_{min}\tau_{min}}$$
(1.3)

Ideally, a photoanode should have long L_{min} , comparable or greater than the characteristic thickness of the material, so that most photogenerated holes could diffuse to the surface to drive the desired oxidation reactions. By assuming hole-electron recombination in the space charge region is negligible, and that the recombination on the surface is minimum due to rapid interfacial holes transfer, we can calculate the hole flux J_h to the surface, and the *incident photon to current conversion efficiency (IPCE)* or *external quantum efficiency (EQE)*, as follows,

$$J_h = I_0 \left(1 - \frac{exp(-\alpha W_{SC})}{1 + \alpha L_{min}} \right)$$
(1.4)

$$IPCE = \frac{J_h}{I_0} = 1 - \frac{exp(-\alpha W_{SC})}{1 + \alpha L_{min}}$$
(1.5)

where α is the absorption coefficient at a given wavelength. Of course, as an oversimplified description for an idealized situation, the Gartner equation would be inadequate to describe actual systems. It nonetheless defines the upper limit of the achievable quantum efficiencies based on the measureable photophysical constants of a material. The current voltage characteristics as predicted by *Gärtner equation* is shown in Figure 1.2. The current voltage relationship for a realistic system is different primarily due to the loss of photogenerated holes. Specifically, the onset-potential (where the photocurrent starts) will be shifted toward the more positive direction (as depicted in Figure 1.2). In addition, recombination in the space charge region (process ii in Figure 1.1c) can proceed through defects close to mid-band gap. The analytical expressions with these considerations were previously discussed by Reichman and El Guibaly et al.¹⁰⁻¹³ Surface recombination (process iii in Figure 1.1c) is yet another important factor to consider. The situation is particularly important when surface hole concentrations are high due to reasons such as slow interfacial hole transfer. Surface states can also arise from crystal defects, surface dangling bonds and/or chemisorbed species. Further, the photogenerated holes trapped by surface states can be annihilated through recombination with electrons. It is important to note here that the definition of surface states used here is rather broad. They may refer to electronic states within the band gap caused by a number of reasons, including surface chemisorbed species as a result of chemical reactions.



Figure 1.2 Idealized photocurrent-voltage relationship of a photoelectrode (broken line) and the one for a realistic system (solid line).

In a way, the Gartner equation and the Reichman correction consider the photophysical properties of the semiconductor, both in the bulk and near/on the surface, and predict the rate at which photogenerated charges that can *potentially* drive the chemical reactions in the electrolyte. The charges that are actually transferred to the electrolyte may be calculated by the charge transfer efficiency. Assuming the likely scenario that surface processes are first order relative to charge concentrations, we have

$$TE = \frac{k_{tran}}{k_{tran} + k_{rec}}$$
(1.6)

where, *TE* is the transfer efficiency, k_{tran} is the forward charge transfer rate constant, and k_{rec} is the charge recombination rate constant. The measured photocurrent densities can then be calculated as:

$$J_{meas} = J_h \times TE \tag{1.7}$$

1.3 PEC cell configurations

Typically, a PEC cell can be constructed either from a single p-type semiconductor as photocathode (or n-type semiconductor as photoanode), or two semiconductors connected separately (or in series).

For a single semiconductor PEC cell where only half-reaction occurs on the working electrode, a counter electrode is required for the other half-reaction to complete the electrical circuit. Often, a reference electrode is connected to the working electrode to characterize external applied voltage. If necessary, to avoid product crossover, two compartments or ion exchange membrane will be present to separate working and counter electrode. This three-electrode configuration is depicted in Figure 1.3. To overcome the thermodynamics barrier of water splitting and the potential loss caused by recombination processes, the working electrode should have a band gap of at least 1.6 eV.¹⁴ Nevertheless, if the band gap is too broad, the visible light absorption efficiency will be low. The common photoelectrode material candidates which have suitable band edge positions include p-Si (1.1 eV), p-InP (1.3 eV), p-Cu₂O (2.1 eV), n-Fe₂O₃ (2.2 eV), n-BiVO₄ (2.4 eV), n-Ta₃N₅ (2.0 eV).¹⁵ Other potential loss mechanisms include back contact and overpotential induced by poor catalytic activity. To address this issue, the semiconductor material should be deposited on highly conductive substrate to form excellent Ohmic contact, which allows rapid injection of majority carriers from working electrode to counter electrode. Additionally, hydrogen evolution reaction (HER) or oxygen evolution reaction (OER) catalyst is required to facilitate surface kinetics accordingly.

As seen here, it is challenging for a single photoelectrode to achieve obtainable photovoltage for solar water splitting, the combination of dual semiconductors will be more advantageous. A second photoelectrode can replace the counter electrode where the other half-reaction occurs, and compensate the insufficient photovoltage (shown in Figure 1.3b). The illumination should be directed from larger band gap photoelectrode (transparent substrate) to smaller band photoelectrode for a better light utilization. Alternatively, these two semiconductors can form a wireless back-to-back Ohmic contact, sharing one transparent conductive substrate.¹⁶ By doing this, potential loss in electrolyte and pH gradient between two photoelectrodes can be reduced.¹⁷ Similarly, the illumination should

pass through larger band gap material to smaller one. This tandem cell configuration is shown in Figure 1.3c, promising a relative cost-effective device structure.



Figure 1.3 Schematic illustration of basic components of PEC cell for (a) a single band gap photoanode with metal cathode. (b) a photoanode and a photocathode connected separately in a tandem configuration. (c) a photoanode and a photocathode electrically connected in series in a back-to-back configuration.

1.4 Calculation of efficiencies

To evaluate performance of solar water splitting, it is well acknowledged to compare onset potentials and photocurrent density (normalized to projected surface area of photoelectrode) at 1.23 V vs. RHE (reversible hydrogen electrode) for photoanode, 0 V vs. RHE for photocathode respectively. Normalized metrics based on energy input, product conversion, *et al.* are of equal significance. Since the value-added product of water splitting is hydrogen, *solar-to-hydrogen (STH) efficiency* is the most critical figure of merit for measuring the performance and efficiency of solar water splitting on practical device level. It is defined as the ratio of output chemical/electric energy to input solar energy via the following equation:

$$\eta_{STH} = \left[\frac{\phi_{H_2}(mol.s^{-1}.m^{-2}) \times G^0_{f,H_2}(kJ.mol^{-1})}{P_{light}(W.m^{-2})} \right]_{AM\ 1.5G}$$
(1.9)

Where Φ_{H_2} is the hydrogen gas production rate, G^{0}_{f,H_2} is the Gibbs free energy of hydrogen gas (237 kJ/mol at 25 °C) and P_{light} is the total solar irradiation input. The light source should match simulated solar irradiation spectra of air mass global (AM) 1.5. As mentioned, a STH efficiency over 20% is desired for large scale application in the future, and a maximum 27% STH efficiency has been predicted for a 1.7 eV/1.1 eV tandem cell configuration with optimal light absorption.¹⁸ Alternatively, output chemical energy can be substituted by electric energy that multiplies short-circuit current density j_{sc} and the redox potential of interest (1.23 V for water oxidation). Note that possibly not 100% current will contribute to redox reaction, Faradaic efficiency must be considered in the equation. Faradaic efficiency (η_F) describes efficiency of passing charges contributing to desired

electrochemical reaction, which is defined as the ratio of the measured product quantity and the theoretical value derived by passing charges.

$$\eta_{STH} = \left[\frac{j_{SC}(mA.cm^{-2}) \times 1.23V \times \eta_F}{P_{light}(mW.m^{-2})} \right]_{AM\ 1.5G}$$
(1.10)

In general, the value of j_{sc} can be replaced by the externally measured current density at zero applied potential under steady-state condition which is analogous to short circuit condition.

The STH efficiency is of particularly interest to evaluate the performance of unassisted overall solar water splitting system, STH efficiencies are modelled using some of the most active catalysts for the HER (Pt) and the OER (NiFeO_x).¹⁸ Extensively, to evaluate the performance of a single photoelectrode independently, where extra applied potential is often required from a second photoelectrode or external power supply, another concept of conversion efficiency can be introduced. At a certain j_{sc} and η_F , applied bias photon to current conversion efficiency (ABPE) can be written as follows, where V_{app} is the applied potential between photoelectrode and counter electrode;

$$ABPE = \left[\frac{j_{SC}(mA.cm^{-2}) \times (1.23V - V_{app}) \times \eta_F}{P_{light}(mW.m^{-2})}\right]_{AM\ 1.5G}$$
(1.11)

In addition with conversion efficiencies characterized by entire solar spectrum on device level, it is important to understand efficiency of holes/electrons converted from photons at individual wavelengths of light on single photoelectrode material level. To serve this purpose, *incident photon to current conversion efficiency (IPCE)* or *external quantum efficiency (EQE)* mentioned above can be written in an alternative format as follows;

$$IPCE(\lambda) = EQE(\lambda) = \frac{electron flux (mol.s^{-1})}{photon flux (mol.s^{-1})} = \frac{|j_{ph}(mA.cm^{-2}| \times hc(V.m))}{P_{\lambda}(mW.cm^{-2}) \times \lambda(nm)}$$
(1.12)

in which λ is the single wavelength light source, P_{λ} is the power of irradiation, *h* is Plank's constant, *c* is the speed of light, and j_{ph} is the photocurrent density. To acquire IPCE, a monochromator (single wavelength light source) and a three-electrode configuration are essential, that j_{ph} at the identical applied potential with individual wavelengths of light can be obtained accurately. Apparently, the cavity of IPCE is that 100 % Faradaic efficiency is assumed. In other words, IPCE can barely provide information on efficiency of photogenerated holes/electrons contributing to water oxidation/reduction. With respect to this consideration, a maximum photogenerated current density can be estimated by using IPCE;

$$J_{AM \ 1.5} = \int (IPCE_{\lambda} \times \phi_{\lambda} \times e) d\lambda \tag{1.13}$$

in which *e* is the elementary electron (*C*), ϕ_{λ} is photon flux of irradiation (m²s), and $J_{AM I.5}$ is the total photocurrent density (mA.cm⁻²). This integrated photocurrent derived from IPCE excludes the possible competing recombination processes.

1.5 The importance of understanding and controlling photoelectrode surface

On a practical level, semiconductor photoelectrochemistry also represents a powerful tool to understand the detailed processes that govern the operation of a photocatalytic system. Consider solar water splitting as an example. In order to achieve high efficiencies, we desire to have a system that is efficient in all three processes: absorbing light, separating charges, and driving hydrogen and oxygen evolution reactions. Careful studies of the SCLJ can help us understand which parts of the system are responsible if a system fails to deliver expected performance. For instance, the performance of a photoanode may be limited by any of the following reasons. First, the recombination of electrons and holes in the bulk is too severe. Second, poor surface band alignment between photoelectrode|water limits the photovoltage. Third, surface mediated electron and hole recombination contributes significantly to the annihilation of photogenerated charges. Fourth, the charge transfer from the semiconductor to the electrolyte is too sluggish to compete with charge recombination processes as outlined above. Fifth, the measured photocurrent might not contribute to the desired chemical reaction. Surface processes are vital to determine the PEC performance. Being able to accurately describe the various processes is critical to the understanding and, ultimately, solving the various issues for high-efficiency solar fuel production.

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Chapter 2: Controlling the surface band alignment to improve the photovoltage

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2.1 Cu₂O photocathode as prototypical platform

Based on cost and stability considerations, metal oxides are attractive photoelectrode candidates for solar water splitting. While significant research efforts have been devoted to studying oxides as photoanodes,¹⁻⁸ comparably little has been done on using metal oxides as photocathodes. This is in part because p-type metal oxides are relatively rare compared to n-type ones. The lack of research on oxide photocathodes is also a result of band gap matching considerations for dual absorber systems.⁹ Because metal oxides are often of wide band gaps (>2 eV), studies on oxide photocathodes would be of practical value only when stable narrow bandgap (~1 eV) photoanodes are available. Previously, this has been a challenge. Recent developments in stabilizing narrow band gap photoanodes such as Si changed the situation.^{10, 11} It is within this context that Cu₂O, a non-toxic, low-

cost p-type semiconductor with a band gap of 2 eV, stands out as a photocathode choice.^{12,} ¹³ Indeed, Cu₂O has received sustained interest for over a decade, and prior research has been primarily focused on increasing the photocurrent and stabilizing it in water under reducing conditions.¹³⁻¹⁵ An important question concerning how to increase its photovoltage has not been addressed. Limited by the difference between the Fermi level of Cu₂O (-5.19eV)^{13, 16} and the hydrogen evolution potential (-4.50 eV at pH 0), the highest photovoltage measured on Cu₂O in H₂O was 0.6 V,^{15, 17} lower than what is needed to match the relatively low photovoltage by a narrow band gap photoanode. When characterized in a non-aqueous system, up to 0.8 V photovoltage has been measured on Cu₂O,¹⁸ suggesting that there is still much room for improvement in terms of photovoltage generation by Cu_2O in H₂O. Here we show a strategy to address this issue. By substituting the Cu₂O/H₂O interface with a Cu₂O/ZnS junction, we were able to readily increase the photovoltages by up to 20%. Importantly, our approach is compatible with treatments aimed at stabilizing Cu₂O such as that by atomic layer deposition (ALD)-grown TiO₂.¹³⁻¹⁵ The system is shown to perform well in conjunction with earth-abundant elements-based catalysts (e.g., NiMo and CoMo^{19, 20}).

2.2 Materials and methods

Preparation of Cu₂O film: Cu₂O film was synthesized by a thermal oxidation method. In a typical experiment, a Cu foil (0.1 mm in thickness) was cleaned in acetone, methanol, isopropanol and deionized (DI) water with sonication, sequentially. Afterward,

it was preheated at 1010 °C for 60 min in N₂ and then oxidized in air (N₂ and O₂ at a ratio of ~4:1) at 1010 °C for 120 min to fully convert to Cu₂O. The film was then annealed for another 120 min in N₂ for better crystallinity. After cooling down to room temperature, the Cu₂O film was etched in 8 M HNO₃ for 2 sec to remove CuO formed on the surfaces. ²¹ The preparation process was concluded by Au sputtering (200 nm) in a AJA International Orion 8 sputter system.

Deposition of ZnS thin film: ZnS film was prepared by thermal evaporation deposition (Kurt J. Lesker PVD-75) with 5nm for 34s. The rate of deposition was 1.5 Å/s as monitored by resonant quartz microbalance.

Deposition of TiO₂ protection film: The TiO₂ thin film was deposited following procedures described elsewhere in a Cambridge nanotech (Savannah 100) ALD system. The reaction was performed at 275 °C chamber temperature with a constant flow of N₂ at 20 sccm (standard cubic centimetre per minute; chamber base pressure ~500 mTorr). Ti(i-PrO)₄ (heated to 75 °C) served as the Ti precursor, and DI water at room temperature was used as the oxygen precursor. The pulse and purge time for Ti(i-PrO)₄ and H₂O was 0.1s & 5s, and 0.01s & 10s, respectively. A growth of 3000 cycles was found to produce a film of 100 nm.

Electrodeposition of NiMo/CoMo catalyst: NiMo catalyst was potentiostatically electrodeposited on the electrode under illumination from a solution containing 0.2M NiSO₄·6H₂O, 0.3M Na₂MoO₄·2H₂O, 0.3M Na₃C₆H₅O₇·2H₂O, whose pH was adjusted to 10.5 by NH₄OH. The potential was fixed at -1.0V vs. Ag/AgCl for 270s to obtain a loading density of 6.1 ± 0.2 mg/cm².

CoMo catalyst was potentiostatically electrodeposited on the electrode under illumination from a solution containing $0.2M \text{ Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $0.3M \text{ Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$, $0.3M \text{ Na}_3\text{C}_6\text{H}_5\text{O}_7 \cdot 2\text{H}_2\text{O}$, whose pH was adjusted to 10.5 by NH₄OH. The potential was fixed at -1.0V vs. Ag/AgCl for 120s to obtain a loading density of $6.7\pm0.3 \text{ mg/cm}^2$.

For NiMo/CoMo bi-catalyst, Cu₂O based photocathodes were fixed at -1.0V vs. Ag/AgCl in NiMo solution for 270s, then in CoMo solution for 120s.

Photoelectrochemical characterizations: PEC characterizations were carried out using a potentiostat/galvanostat (CH Instruments CHI604C) in a three-electrode configuration. Cu₂O-based photoelectrode served as the working electrode, with an Ag/AgCl electrode (CH Instrument) soaked in saturated KCl aqueous solution as the reference, and a Pt wire as the counter electrode. The electrolyte was a 0.2M K₂HPO₄ solution whose pH was adjusted to 7. The light source for data presented in this work was an AM 1.5 solar simulator (100 mW cm⁻², Newport Oriel 96000). In a typical J-V experiment, the voltage was swept linearly from negative to positive at a rate of 10 mV.s⁻ ¹. For open circuit potential measurement under various light intensities, the light source was a solar simulator (Newport Oriel, Model 6297NS) equipped with AM 1.5 filter with the illumination intensity adjusted by a thermopile optical detector (Newport, Model 818P-010-12), and H₂ was continuously bubbled through the electrolyte to maintain reversible HER at or near standard conditions. For the monochromatic illumination shown in Figure 2.4b, a 375nm laser (Advanced Laser Diode Systems, GmbH Model PiL037SPS) was coupled with control unit EIG1000G.

Material Characterizations: Raman spectra were acquired using a micro-Raman system (XploRA, Horiba) with a 532nm laser excitation. The cross section sample was freshly cut and characterized by a Scanning Electron Microscope (SEM, JSM6340F). The cross section sample was prepared by a focused ion beam (FIB, JOEL 4500 multibeam system). A W film (~0.5 μ m) was deposited sequentially to minimize ion beam damage during the preparation process. A thin slice (~15 × 15 μ m span; 1 μ m thick) was cut from the planar substrate and transferred to a Cu support with a nano-manipulator (Kleindiek Nanotechnik MM3A). The slice was further thinned to e-beam transparent by low-energy ion beam (5 kV). The sample was imaged by transmission electron microscope (JEOL 2010F) operating at an acceleration voltage of 200kV. Energy-dispersive X-ray spectroscopy in chemistry mapping modes was used in conjunction with the TEM (JEOL 2010 FEG) to determine material compositions at Center for Nanoscale Systems in Harvard University.

H₂ detection by mass-spectrometry: H₂ was analyzed using a mass spectroscope (MKS special V2000P).

PEC cell including Cu₂O based photocathodes as the working electrode, Pt disk as the counter electrode and Ag/AgCl as the reference electrode was built for H₂ detection. The reaction was carried out under illumination, with the potential fixed at 0V vs. RHE. The generated H₂ was tested every 10min or 15min, which gas sample (fixed volume of 100 μ L) was injected and data were collected.

Pt disk was used as the working electrode to serve as a calibration standard. Afterward, the amount of H_2 produced by the Cu₂O based photocathode was calculated based on the Pt calibration curve.

2.3 Addressing the challenges of Cu₂O photocathode

The governing principle of metal oxide-based PEC water splitting is the effect known as band edge pinning, in which the band edge positions are pinned relative to H₂O redox potentials. The degree of band bending and, hence, the maximum achievable photovoltage is defined by the difference of flatband potential (V_{fb}) and the chemical potential of the targeted reaction in H₂O (hydrogen evolution reactions, or HER, in the present study).^{22, 23} In the case of Cu₂O, the value is ~0.6 based on Fermi level data in vacuum. To break the barrier, we would need to shift band edge positions by means such as introducing surface dipoles. Although organic dipole molecules have been shown to work well for this purpose in dye-sensitized solar cells^{24, 25}, their utility in solar water splitting devices is limited due to poor stabilities under harsh conditions. An alternative approach would be forming buried solid-solid junctions. For this purpose, we need n-type semiconductors whose valence and conduction band edges are sufficiently negative. With a valence band maximum of -7.58 eV and a conduction band minimum of -3.90 eV,²⁶ ZnS stands out. The understanding is depicted schematically in Figure 2.1a. The approach is similar to decorating p-type Si with n^+ players carried out Lewis *et al.*²⁷ It also aligns with our approach to form homojunctions on hematite for water oxidation.⁴ The key to its success is to keep the top layer thin because the primary role of the n-type layer is to increase band bending within the p-type photocathode. Opposite band bending may develop in a thicker n-type layer, trapping electrons to negatively influence the functionality of the device (see Figure 2.1b).



Figure 2.1 Replacing Cu_2O/H_2O interface with Cu_2O/ZnS readily improves photovoltage generation by Cu_2O . (a) Schematic band structures shown how ZnS moves the band edge position positively for a more substantial built-in field. (b) Due to band edge pining, a thicker n-type ZnS will result in an opposite band bending, and photoexcited electrons will be trapped at the interface of photocathode/electrolyte. The band edge positions of Cu_2O is depicted as pale green color, as pale blue color for ZnS before contacted with electrolyte.
One particular weakness of Cu₂O that has received significant research attention is its instability in H₂O. Often, Cu₂O undergoes reduction to yield Cu instead of H₂ when used as photocathode. To address this issue, we employed the proven strategy of using ALD-grown TiO₂ (~100 nm) as a protection layer.^{13, 14, 28} Catalysts were used to promote HER. The overall material structure is shown schematically in Figure 2.2a. The structural details are presented in Figure 2.2b with scanning electron microscopy (SEM) data. We see from Figure 2.2b that a conformal coverage of Cu₂O by TiO₂ overlayer is afforded by the ALD growth. The ZnS decoration, due to its thinness, is not pronounced at the magnification shown in Figure 2.2b. Scanning transmission electron microscopy (STEM) was therefore carried out to probe the elemental composition (Figure 2.2c).

In principle, the design as shown in Figure 2.1a and 2.2a should work for any HER catalysts. In practice, the performance of the photoelectrode is sensitive to the nature of the catalyst/semiconductor interface. To focus the discussions on the effect of ZnS decoration on Cu₂O, we next present results obtained on the best performing HER catalyst, Pt nanoparticles, for the next section. Afterward, we will show that similar results can be obtained on more earth abundant catalysts such as NiMo and CoMo alloys.



Figure 2.2 (a) Three-dimensional perspective view of the material structure, where the TiO_2 protective layer and surface hydrogen evolution reaction catalysts are shown. Microstructures of $Cu_2O/ZnS/TiO_2$ photocathode. (b) Scanning electron micrograph showing a conformal overlayer of TiO_2 on Cu_2O . (c) Scanning transmission electron micrographs with selected filters revealing the elemental composition of different layers across the top image. From top: overall view; Cu distribution; Zn distribution; S distribution, Ti distribution, and W distribution. W was deposited as a protection layer during focused ion-beam milling process.

2.4 ZnS heterojunction improves the photovoltage

Our first task was to prove that the application of ZnS indeed increases the degree of band bending within Cu₂O. Steady-state current-voltage characteristics are the most popularly used technique to evaluate the performance of photoelectrodes. As shown in Figure 2.3, the difference between Cu₂O with and without ZnS decoration was obvious. If we define the turn-on voltage as the potential where we first observed photocurrent under chopped light, a Von of 0.6 V was obtained on Cu₂O photoelectrode. When ZnS was present, a Von of 0.72 V was measured. Nevertheless, the steady-state current measurements are not suitable for quantitative analysis because the change of V_{on} may be influenced either by thermodynamic (increase of band bending) or kinetic (reduction in kinetic overpotentials) factors or both.^{29, 30} To tease out information specific to band bending, we previously developed an open-circuit potential (OCP) measurement technique that permits us to probe the resting potentials at zero net exchange current densities, under which conditions kinetic factors do not play a role.^{3, 30} As shown in Figure 2.4a, in the absence of illumination, the resting potential should equal to that of HER, 0 V vs. RHE. We caution that it is critical to establish reversible HER at or near standard conditions to measure 0 V vs. RHE. It means that the solution should be saturated with H₂ gas, and the presence of HER catalyst is necessary. Otherwise erroneous OCP values in dark were obtained. Once the conditions outlined above are met, the results as presented in Figure 2.4a are highly reproducible. Under illumination, photoexcited electrons populate the conduction band on or near the surface, splitting the quasi-Fermi levels of electrons and holes. The effect leads to the flattening of the band. The measured OCP tracks that of the Fermi level of majority carriers (holes in the case of p-type Cu₂O). It is expected to move to the positive direction, and the OCP difference in dark and light reports on the photovoltage generated by the semiconductor/water interface. Indeed, Cu₂O without ZnS records a photovoltage of 0.58 \pm 0.04 V, consistent with literature reports. The presence of ZnS modifies the Cu₂O/H₂O interface and increases the degree of band bending. A greater photovoltage (0.73 \pm 0.03 V) was correspondingly measured (Figure 2.4a). It is noted that Al-doped ZnO (AZO) has been previously used to form p-n⁺ junctions on Cu₂O. While the charge collection has been improved, no obvious effect on photovoltage has been reported.¹⁸ The degenerate doping and the positions of the Fermi level relative to the band edges may be a reason for the apparent differences.

The degree of quasi-Fermi level splitting and, hence, the measured photovotlage, are expected to depend on light intensities.³¹ Under relatively weak illuminations, the band is partially flattened; the degree of band flattening tracks the light intensity following an exponential relationship and reaches saturation under strong illumination due to saturation of states available for minority carrier densities. The trend was indeed observed by us, as shown in Figure 2.4b. The results offer us confidence that the OCP measurement as discussed above is a reliable technique to probe the degree of band bending without the influence of kinetic factors. In addition, it is noted that the OCP results are not sensitive to pH, further highlighting the validity of the technique.

Because the surface of both photoelectrodes (with and without ZnS decorations) are decorated by the same HER catalysts (Pt nanoparticles), the charge transfer kinetics across the photoelectrode/water interface may be regarded as comparable. Under such limiting conditions, we may quantify V_{on} 's by steady-state measurements more precisely following the Butler method.³² To do so, we need monochromic illumination so that light absorption coefficient by the photoelectrode is better defined. A V_{on} for Cu₂O of 0.59 V was measured; with ZnS, the value increased to 0.71 V (Figure 2.5a). An anodic shift of 0.12 V was obtained.

Collectively, the OCP measurements, steady-state characterizations under white light, and the Butler quantification under monochromic light support that the application of ZnS increases the degree of band bending within Cu₂O from 0.59 V to 0.71 V. While the absolute increase (0.12 V) may seem modest, it is the first time that a photovoltage greater than 0.6 V, the theoretical value based on the difference between the Fermi level of Cu₂O and HER, is measured and reported. The result highlights that there is indeed much to gain from Cu₂O, opening up the possibilities of integrating it with narrow band-gap anodes stabilized by metal oxide protections. Lastly, we emphasize the steady-state measurements as presented in Figures 2.3 and 2.5a are indeed corresponding to HER. By detecting the reaction product, H₂, and compare its quantity with the number of charges passed through, we obtained a Faradaic efficiency close to 100% (Figure 2.5b).



Figure 2.3 Polarization curves of bare Cu_2O ($Cu_2O/TiO_2/Pt$) and Cu_2O/ZnS ($Cu_2O/ZnS/TiO_2/Pt$) in 0.2M KH₂PO₄ pH=7 buffer solution, under chopped AM 1.5 light illumination.



Figure 2.4 OCP measurements of Cu₂O/ZnS/TiO₂/Pt photocathode. (a) Compared with bare Cu₂O, Cu₂O/ZnS shows more positive open circuit potential in light, indicating a positive shift of its V_{fb} , as shown in Figure 2.1a. (b) The true V_{fb} 's of both bare Cu₂O (blue) and Cu₂O/Zn (orange) are probed by increasing the illumination intensities.



Figure 2.5 Characterization of Cu₂O/ZnS performance. (a) Butler plot demonstrating more positive V_{fb} for Cu₂O/ZnS. (b) Hydrogen evolved by Cu₂O based photocathodes as detected by MS matching the amount of charge measured. The theoretical line are calculated according to Faraday's law of electrolysis (N_{H₂} = $\frac{1}{2}$ N_{Charge}).

2.5 Atomic layer deposition (ALD) TiO₂ as protective layer

Before the system as shown in Figure 2.1 can be put into practical applications, there are still two issues that deserve further discussions. The first issue concerns the ALD TiO₂ layer. Despite its thickness, the presence of this layer does not seem to alter the nature of the Cu₂O/H₂O interface in any significant fashion. Similar results have been independently observed by Gratzel *et al.* on ALD-grown TiO₂ and Chorkendorff *et al.*^{14, 28} on thermally-grown TiO₂. It has been suggested that the result may be enabled by the coincidental alignment of the TiO₂ Fermi level with HER. The understanding of the true electronic nature of the TiO₂ protection layer, however, requires additional research. It is noted that the TiO₂ layer employed in our studies is without any intentional doping. Films thinner than 20 nm failed to provide adequate protection, and those thicker than 200 nm resulted in dramatically low photocurrent densities. Films of 100 nm offered the best combination in terms of stability and photocurrent densities.

2.6 NiMo/CoMo dual-layer as earth-abundant hydrogen evolution reaction (HER) catalyst

The second issue concerns the usage of Pt. There is a rapidly growing interest in replacing Pt with earth abundant HER catalysts. New classes of compounds based on chacolgenides or phosphides have proven effective,³³ some of which have been employed in combination with Cu₂O for photoelectrode reduction of H₂O.^{15, 34} As a proof-of-concept,

we show the strategy presented here is compatible with earth abundant HER catalysts. For this purpose, we studied two Mo-based alloy systems, NiMo and CoMo nanoparticles, which have been shown to enable HER in neutral and basic solutions, with Ni_{8.6}Mo exhibiting n=200 mV and Co₃₇Mo n=170 mV at J=100 mA/cm².²⁰ Interestingly, we found in the present study that while CoMo exhibits better HER activity as measured by D. L. Piron, NiMo enables greater photovoltages as measured by the more positive V_{on} . It is understood that CoMo produced in our studies is catalytically more active while NiMo affords a higher quality interface with TiO₂. Inspired by Choi et al. approach to decorating BiVO₄ surfaces with FeOOH and NiOOH,³⁵ we applied dual-layer catalysts with NiMo as the underlayer and CoMo as the outer layer. In the absence of ZnS, a V_{on} of 0.61 V was measured, the corresponding J at HER was 0.47 mA/cm². When ZnS was present, the V_{on} was increased to 0.73 V, and the J at HER was also increased to 0.71 mA/cm². Clearly, optimization is still needed to bring the performance comparable to that with Pt. Higher current densities have been achieved when nanoscale features are introduced to the Cu₂O substrate.^{18,20} The turn-on characteristics, nonetheless, represent the highest in the literature, to the best of our knowledge.



Figure 2.6 Polarization curves of NiMo/CoMo dual-layer catalyst modified bare Cu_2O (black) and Cu_2O/ZnS (grey) in 0.2M KH₂PO₄ pH=7 buffer solution, under chopped AM 1.5 light illumination.

2.7 Summary

In conclusion, we have shown that a simple ZnS modification strategy can readily increase the photovoltage generated by Cu₂O in H₂O. The work addresses an important issue in photoelectrochemical water splitting. While a dual-absorber system is widely recognized as a promising configuration, how to achieve large photovoltage from the wide bandgap top layer constitutes a significant challenge. Often the achievable photovoltage is limited by the difference between the flatband potential and the electrochemical potential of the solution, compounded by partial or complete band edge unpinning effects. Our results suggest that modifying the semiconductor/H₂O interface is a strategy that can change the situation to enable the construction of photoelectrode materials for desired performance. While there is still much more needed in terms of photovoltage and photocurrent from promising materials such as Cu₂O, new doors are opened up to practical solar water splitting devices based on earth abundant, stable metal oxide semiconductors.

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Chapter 3: Understanding the influence of surface chemical species on surface kinetics and energetics

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3.1 Hematite with predominately facet as prototypical platform

The study on Cu_2O photocathode highlights the importance of controlling the degree of the band bending, which defines the photo-to-charge conversion efficiencies. Another critical characteristic of the interface is the efficiency of charge transfer for desired chemical reactions.¹ Together, the electronic properties within the semiconducting photoelectrode and the chemical kinetics at the surface determine the overall performance of a PEC system. It is well known that the electronic properties of a semiconductor, such as the Fermi level and band edge energetics, are sensitive to the crystal field. The relationship between the facets and the electronic properties of a semiconductor has been extensively studied previously. For instance, Liu *et al.* demonstrated that the conduction

band edge of anatase TiO₂ crystals with 82% $\{101\}$ is more negative than that with 72% {001}.² Similarly, it is also well accepted that the detailed chemical reactions are dependent on the surface species, which in turn is sensitive to the atomic structures of the substrate. For example, Li et al. found that anatase TiO₂ nanoparticles with predominantly exposed {001} facets have higher photodegradation activity relative to {101} facets, owing to a greater number of five-fold coordinated Ti⁴⁺ sites.³ Taken as a whole, we see that the detailed surface crystal structure of the photoelectrode at the photoelectrode |H₂O interface is of critical importance. To date, how the PEC performance depends on this interface is poorly studied. We aim to address this issue in this chapter. Using hematite nanocrystals as a material platform, we show that $\{001\}$ facets feature lower surface OH concentrations than {012} facets. The difference in OH concentration is directly correlated to the kinetics at the interface, where the {012} facets exhibit higher rate constants for both charge transfer and recombination. The high surface OH concentrations also imply a higher density of surface states that would pin the Fermi level for the {012} facets to undermine the overall performance, which was directly observed in our experiments.

We chose hematite as a prototypical material platform for this study because a broad knowledge base on this material exists thanks to decades of research by a large number of groups.⁴⁻⁶ For instance, we have learned that the relatively late turn-on potential of a hematite-based PEC was mainly due to poor charge separation as a result of surface Fermi level pinning.⁷ Slow charge transfer kinetics play a relatively smaller role in this regard.⁸ We also learned that the surface OH groups play important roles in water oxidation, as well as in co-catalyst deposition.^{1, 9, 10} Notwithstanding, these previous studies have not

specifically addressed the dependence of these results on the crystal facets. To address this issue, we built our current study on successes in synthesizing hematite with preferred surfaces by Cha *et al.* and Chen *et al.*, respectively.^{11, 12} The materials permitted us to carry out detailed kinetic and thermodynamic studies by intensity modulated photocurrent spectroscopy (IMPS) and open circuit potential (OCP) measurements, which generated quantitative information to support the conclusion that hematite {012} surfaces are more active for charge transfer and recombination than hematite {001} surfaces.

3.2 Materials and methods

Hematite {012}: Pseudo-cube hematite nanoparticles with predominately exposed {012} facets were prepared by a hydrothermal method as reported previously.¹¹ Briefly, FeCl₃•6H₂O (Sigma Aldrich, ACS reagent, 97%) was dissolved into a 0.4 M NaOH (Sigma Aldrich, ACS reagent, \geq 97.0%, pellets) solution to make a 0.2 M Fe³⁺ gel solution, with continuous stirring for 10 min at room temperature. Then the 20 mL gel solution was transferred into a 25 mL Teflon lined autoclave and heated at 150 °C for 5 h. The assynthesized hematite nanoparticles were washed with ethanol and deionized (DI) water, and dried at 60 °C in an oven. For convenience of discussions, these samples will be referred as hematite {012} henceforth.

Hematite {001}: The synthesis of hexagonal-disc hematite nanoparticles with predominately exposed {001} facets followed the reported method in the literature.¹² Briefly, FeCl₃•6H₂O (Sigma Aldrich, ACS reagent, 97%) was dissolved into a solution of

10 mL ethanol and 0.7 mL DI water to make a 1 mM Fe^{3+} gel solution. After the $FeCl_3$ was almost dissolved, 2 g of sodium acetate (Alfa Aesar, anhydrous, ACS, 99.0% min) was added. Then, the gel solution was transferred into a 25 mL Teflon lined autoclave and heated at 180 °C for 12 h. The as-synthesized hematite nanoparticles were washed with ethanol and DI water, and dried at 60 °C in an oven. For convenience of discussions, these samples will be referred to as **hematite {001}** henceforth.

Characterization of hematite: Transmission electron micrographs (TEM) showing the exposed facets were taken on a JEOL (model: 2010F) microscope operating at a 200 kV acceleration voltage. Scanning electron micrographs (SEM) showing the morphology were taken on a field-emission JEOL (model: 6340F) operating at a 10 kV acceleration voltage. X-ray photoelectron spectra (XPS) were obtained on a K-Alpha⁺ instrument (Thermo Scientific) equipped with a micro-focused, monochromated Al K α source (1486.7) eV). All experiments utilized a 50.00 eV pass energy and the acquired spectra were calibrated to the binding energy of C1s peak at 284.8 eV. The X-ray diffraction (XRD) measurements were carried out on a Bruker D2 PHASER with a Cu Ka radiation source. Raman spectra were obtained on a Micro-Raman system (XploRA, Horiba) with a 532 nm laser excitation. Light absorption of hematite collected using was а reflectance/transmittance integrating sphere (SphereOptics) and recorded using a spectrometer (Ocean Optics USB 4000).

Electrode Fabrication: A 2.2 mm thick glass slide coated with fluorine-doped tin oxide conductive film (Sigma Aldrich, 7 Ω /sq surface resistivity) was cleaned in acetone, methanol, isopropanol and DI water. The dried hematite powders were mixed with a 0.3

wt% polyethyleneimine (PEI) aqueous ethanol solution (1:1 v/v) to make a 0.5 wt% hematite solution. Hematite nanoparticles were dispersed in an ultrasonic bath for 30 min. Then 30 µL of the hematite solution was dropcasted on a 1×1 cm² FTO glass substrate and dried naturally in ambient air at room temperature. The application of PEI was reported to orient the preferably exposed facet of the hematite nanoparticle parallel to the substrate, due to the tension of the polymer during the drying process.^{11, 13} The FTO glass substrate with monodispersed hematite was then annealed in air at 500 °C to fully convert β-FeOOH to α-Fe₂O₃, removing organic solvents in the hematite solution and improving the adhesion between the hematite nanoparticles and the substrate. To make an photoelectrode, the resulting hematite sample was connected to a Cu wire using Ag paste (MG Chemicals, 8331 Silver Conductive Epoxy Adhesive) and protected with non-conductive epoxy (Loctite[®] 615 Hysol Epoxy Adhesive) to expose an active electrode surface area of ca. 0.16 cm².

PEC Characterization: PEC characterization was carried out using a Solartron ModuLab[®] XM potentiostat. A three-electrode configuration was employed, with hematite as the working electrode, a saturated calomel electrode (SCE, CH instruments, model number: CHI150) as the reference electrode and a Pt wire as the counter electrode. The electrolyte was a 1 M NaOH (Sigma Aldrich, ACS reagent, \geq 97.0%, pellets) solution. The light source for all data presented in this work was an AM 1.5 solar simulator (100 mW/cm², Solarlight, Model 16S-300-M). In a typical *J*–*V* plot, the voltage was swept linearly from negative to positive at a rate of 20 mV•s⁻¹ with front illumination.

Intensity Modulated Photocurrent Spectroscopy (IMPS): IMPS spectra were recorded using a Solartron ModuLab[®] XM potentiostat coupled with a Frequency Response Analyzer (FRA, Solartron ModuLab[®]) and a 405 nm LED (ThorLab) with 1000 mA max power and controlled by the ModuLab[®] XM DSSC software. IMPS data were measured using a 10% light intensity modulation (centered at ca. 134 mW/cm²) varying between 10 kHz and 0.01 Hz. The same three-electrode configuration and electrolyte were employed as given in the PEC Characterization section. Structural differences between hematite {012} and hematite {001}.

3.3 Structural differences between hematite {012} and hematite {001}

We first show experimental evidence that we have successfully synthesized hematite {012} and hematite {001}. For this purpose, we used SEM and high-resolution TEM (HRTEM) to study as-synthesized samples, and the representative data are shown in Figure 3.1. We see in Figure 3.1b that hematite {012} is pseudo-cubic with a typical size of 200-250 nm. The HRTEM micrograph (Figure 3.1a) clearly shows two sets of lattice fringes on hematite {012}, both evenly spaced at a distance of 3.7 Å. An intersection angle of 86° was measured between the two sets of lattice fringes. The observation is in excellent agreement with expectations for the hematite (012) and ($\overline{102}$) planes (see the corresponding FFT pattern in Figure 3.1a inset). The zone axis of Figure 3.1a was identified as [$2\overline{21}$]. As such, the front, side and top surfaces of the pseudo-cube are (012), ($\overline{102}$) and ($1\overline{12}$) plane, respectively. The relationships between these facets are illustrated

schematically in Figure 3.1c. The hidden planes of the pseudo-cube as shown in Figure 3.1c are $(0\overline{12})$, $(10\overline{2})$ and $(\overline{112})$. Importantly, all six exposed planes are equivalent and belong to the $\{012\}$ group. We, therefore, concluded that the pseudo-cubic hematite preferably exposes the $\{012\}$ facet. Similarly, as shown in Figure 3.1e, hematite $\{001\}$ exhibits a hexagonal disc morphology with a typical size of 150–200 nm and a thickness of 10–15 nm. HRTEM data of **hematite \{001\}** revealed two sets of lattice fringes, each separated by 2.5 Å. Combining this with the intersection angle of 60°, we assigned these lattice fringes to the $\{110\}$, $\{210\}$ and $\{120\}$ planes. Consequently, the basal top and bottom surfaces were unambiguously confirmed to be the $\{001\}$ planes.



Figure 3.1 Structural characterization of **hematite {012}** and **hematite {001}**. (a) HRTEM image and (b) SEM image of **hematite {012}**; inset in (a): corresponding FFT pattern of the viewing field. (c) Schematic showing the relationships of the front, side and top surfaces of the pseudo-cube. (d) HRTEM image and (e) SEM image of **hematite {001}**; inset in (d): corresponding FFT pattern of the viewing field. (f) Schematic showing the relationship of the side surfaces and the top surface of the hexagonal-plate.

For the study on how the PEC characteristics depend on the facets, it is important to know how the surface chemical species differ for different facets. More specifically, for water oxidation reactions, surface OH species play an important role.^{10, 14} Previous impedance spectroscopic studies suggested that M-OH_x intermediates is key to building up surface-states capacitance and influences surface charge recombination; on the other hand, OH species has been demonstrated to actively participate in PEC water oxidation on hematite by IR spectroscopic measurements. We, therefore, chose the abundance of surface OH species as a descriptor to quasi-quantitatively compare **hematite {012}** and **hematite {001}**. Density functional theory (DFT) was employed to optimize the geometry of bulk hematite and constructed slab models for these two hematite samples. The hydroxyl terminated {012} and {001} facets were then fully relaxed with DFT and their structures, as well as the lattice vector lengths and angles. Our DFT calculations predict the hematite {012} features higher OH density, the OH densities of {012} and {001} facets being 14.5 and 13.5 nm⁻², respectively.

The DFT results are consistent with the characterization by XPS. The O 1s spectra of hematite {012} and hematite {001} are shown in Figure 3.2. As reported in the literature, the broad O 1s peak may be deconvoluted into 3 distinct peaks that correspond to surface OH species, lattice OH species and lattice O^{2-} species.¹⁵ The peaks at 529.4 eV for hematite {012} and 529.8 eV for hematite {001} were assigned to lattice O. The peaks at 530.4 eV for hematite {012} and 530.5 eV for hematite {001} were assigned to hydroxyl groups due to H binding to lattice O. The peaks at 531.0 eV for hematite {012} and 531.2 eV for hematite {001} were assigned to Since Si

the deconvoluted peaks, we were able to quantify the relative abundance of these different species. The results are summarized in Table 3.1. From this set of data, we clearly see a stark difference in the abundance of chemisorbed surface OH species (ca. 63% for **hematite {012}**; 18% for **hematite {001}**). The crystallinity and preferable facet exposure were further confirmed by XRD patterns. It is important to note that these two samples feature similar optical absorption properties, making them an ideal platform to study how the different facets influence the PEC performance to be discussed next.



Figure 3.2 XPS O 1s spectra of: (a) hematite $\{012\}$ and (b) hematite $\{001\}$ showing 3 distinct peaks that correspond to surface OH species, lattice OH species and lattice O²-species.

Table 3.1 Summary of XPS peak position and relative abundance of surface OH species, lattice OH species and lattice O^{2-} species.

	lattice O ²⁻ (abundance %)	lattice OH (abundance %)	chemisorbed OH (abundance %)
{012}	529.4 eV (12%)	530.4 eV (25%)	531.0 eV (63%)
{001}	529.8 eV (55%)	530.5 eV (27%)	531.2 eV (18%)

3.4 Comparison of PEC performance

Next, we measured the PEC performance of monodispersed hematite {012} or hematite {001} for water oxidation. The method of electrode fabrication was detailed in the Chapter 3.3. It is noted here that for this body of research, we employed a relatively sparse distribution of hematite nanoparticles (estimated density: 5-7 particles per µm²). Further increase of the density would lead to bundling of hematite {001} discs, hiding the {001} basal planes, which would be dentrimental to our study. The density of hematite **{012}** was kept at a similarly low level for easy direct comparisons. Although there is a direct contact between FTO and the electrolyte, there was no measurable current within the potential window used for this study when bare FTO substrate was used (Figure 3.4). As such, the shunt current between FTO and the electrolyte contributes little to the measured photocurrents. Moreover, we note that it is beneficial to keep the density of hematite nanoparticles low for this study because higher density would lead to stacking of nanoparticles, in which case the charge transport between different layers of nanoparticles would become another limiting factor, greatly complicating data interpretation.^{11, 16, 17} We thus establish that the photoelectrodes with relatively sparse hematite particles are indeed valid study platforms for the present work.

Figure 3.4 shows the photocurrent density-potential (*J-V*) plot of hematite {012} and hematite {001} under under AM 1.5G (100 mW•cm⁻²) illumination in 1 M NaOH (pH 13.6). Both samples exhibited anodic photocurrents due to photooxidation of water. Two obvious differences were observed in this set of data. First, hematite {012} exhibited an earlier turn-on voltage (0.74 V vs. 0.88 V for hematite {001}). Second, hematite {001} featured a higher photocurrent density at more positive potentials (*e.g.*, at 1.4 V vs. RHE, or reversible hydrogen electrode). We are mindful that due to the relative sparseness of the hematite nanoparticles, the photocurrent density should be treated quasi-quantitatively. Given that both hematite samples featured similar crystallinity with similar light absorption, we concluded that the difference should originate from the difference in their exposed facets. Guided by this hypothesis, we next present experimental efforts aimed at measuring how the charge transfer (kinetics) and surface band bending (thermodynamics) depend on the different facets of hematite.⁸



Figure 3.4 Photocurrent density-potential (J-V) plots of hematite {012} and hematite {001} under AM 1.5G (100 mW•cm⁻²) illumination in 1 M NaOH (pH 13.6).

3.5 Comparison of charge transfer kinetics

For the comparison, our first task was to measure the kinetics of various charge processes at the surface of hematite. Following earlier studies by us,^{1, 18, 19} we show in Figure 3.5a a kinetic model used for this work, where the competing charge transfer and recombination kinetics under PEC water oxidation conditions are illustrated. An important assumption for the current study was that water oxidation by hematite is mediated by surface chemisorbed OH species.¹⁰ These species introduce electronic states on the surface. We also assume that hole transfer from the valence band to these surface states is fast and is not rate limiting. Hence, only hole transfer from the surface states to the electrolyte and electron/hole recombination via surface states are considered in our kinetic model. Such a simplification has proven effective in understanding the important characteristics of hematite|electrolyte interfaces previously.^{1, 18-20} Higher order processes such as charge transfer to and from the surfaces, as well as the detailed chemical processes, would need to be taken into account for a more detailed kinetic understanding of the system, which is beyond the scope of the current work.

Following our previous reports, we focused our present study on 3 key kinetic parameters, forward charge transfer (k_{tran}) , backward charge recombination (k_{rec}) and the overall charge transfer efficiency $TE = (\frac{k_{tran}}{k_{tran} + k_{rec}})$. Representative datasets of normalized IMPS response as a function of frequency are shown in Figure 3.6, in which the normalized interception in the low frequency region reports on the charge transfer efficiency; the radial frequency at the maximum of the semicircle corresponds with the

sum of $(k_{tran} + k_{rec})$. The data as measured by IMPS are presented in Figure 3.5. Given the relatively sparse hematite density and the relatively low current densities, we chose to interpret the data quasi-quantitatively. That is, we emphasize the trend but do not wish to discuss the significance of the quantitative differences. Following this guiding principle, we clearly see the following trend in this set of data. First, hematite {012} featured higher rate constants for both charge transfer (Figure 3.5b) and charge recombination (Figure 3.5c) across the entire potential window. The observation is consistent with our hypothesis that a higher surface OH density would favor water oxidation reactions and, hence, faster charge transfer. The faster charge recombination can be easily understood by a higher density of surface states that would promote charge recombination. Second, within this trend, however, we clearly see the difference of k_{tran} 's between hematite {012} and hematite {001} becomes much smaller at more positive potentials. This is consistent with the understanding that water oxidation at high applied bias is dominated by the bias, but less sensitive to the chemical nature of the surface. Third, we see that the relative difference of k_{rec} 's between hematite {001} and hematite {012} remains unchanged, while both are smaller at higher applied bias. The observation is consistent with previous reports that higher applied bias would suppress recombination. It also supports the conclusion that the recombination is indeed mediated by surface states, and faster recombination would be expected on surfaces with a higher density of surface states (e.g., hematite {012}). Lastly, we note that the trends of TE as shown in Figure 3.5d are consistent with the JV data as shown in Figure 3.4, further supporting the suitableness of using IMPS to study this system.



Figure 3.5 Kinetic comparisons of hematite {012} and hematite {001}. (a) A kinetic model describing the competing charge transfer and recombination processes under PEC water oxidation conditions. It is assumed that water oxidation by hematite is mediated by surface chemisorbed OH species. Comparisons of: (b) rate constant for charge transfer, (c) rate constant for charge recombination and (d) charge transfer efficiency for hematite {012} and hematite {001}, respectively.



Figure 3.6 Representative normalized IMPS response of: a) hematite {012} and b) hematite {001}.

Our understanding of the kinetic differences between hematite {012} and hematite {001} is summarized in Figure 3.7. A higher k_{tran} was observed for hematite {012} because it features a higher density of reactive sites. These active sites also serve as charge recombination centers, resulting in higher k_{rec} . This model explains why we observed an earlier turn-on voltage in Figure 3.4. It also implies that for future improvement of photoelectrode performance, it is critical to increase the active sites to benefit forward charge transfer without simultaneously increasing charge recombination. How to do so remains a critical challenge that deserves additional research. Our recent research of using NiFeO_x catalysts on hematite shed some light on possible solutions to this challenge.^{8, 18} In addition to the influence of different facets on surface holes transfer, it is also expected to influence electron transport within hematite. As reported by Kerisit *et al.*, electron transport within layers of (001) hydroxyl-terminated surface is faster than (012) surface, but is slower between adjacent layers. The complex model is beyond the scope of this work but worth further research and discussions.



Figure 3.7 Schematics illustrating the kinetic differences between: (a) hematite {012} and (b) hematite {001}.

3.6 Comparison of surface energetics

With the kinetics of the surface established, we next measured the surface energetics of hematite {012} and hematite {001} by the OCP technique. Our expectations are as follows. A higher density of surface OH species would lead to a higher density of surface states, which in turn results in a greater extent of Fermi level pinning. We, therefore, would expect less band bending in hematite {012} than hematite {001} under illumination. To test this hypothesis, we measured the OCP under dark and light for three different samples, hematite {012}, hematite {001} and bare FTO as a control. The data are shown in Figure 3.8a. We emphasize the difference between OCP in dark and in light (\triangle OCP), which was 0.21 V for hematite {012}, 0.37 V for hematite {001} and 0 V for FTO, consistent with our expectations. Within this data set, we note that the dark OCPs for all three samples were comparable, at ca. 0.9 V vs. RHE, similar to what we have observed previously on hematite thin films.^{7, 21} The most striking difference in the OCP was observed under illumination, 0.65 V for hematite {012} and 0.53 V for hematite {001}. The difference may be attributed to the different natures of the exposed facets. A similar shift was observed on the pseudo flat-band potentials as measured by the Mott-Schottky technique. Our understanding of this set of data is summarized schematically in Figure 3.8b and 3.8c. In essence, hematite {001} features a lower number of surface OH species than hematite **{012**}. While it is a less active surface for water oxidation, it is also less active for charge recombination. In addition, a larger degree of band bending promises better charge separation. Combining these two facts, hematite {001} enables a higher photocurrent at high applied bias.


Figure 3.8 OCP measurements of **hematite {012}** and **hematite {001}**. (a) Comparisons of OCP in dark and in light for **hematite {012}**, **hematite {001}** and FTO. Schematic illustrating the energetic differences between: (b) **hematite {012}** and (c) **hematite {001}**.

3.7 Summary

In summary, we successfully synthesized hematite nanoparticles with predominately exposed {012} or {001} facets. DFT calculations predicted that the surface crystal structure of these two hematite samples feature different OH concentrations, which is critical to water oxidation under PEC conditions. Indeed, surface characterization using XPS confirmed that **hematite {012**} features higher surface OH concentrations than hematite {001}. IMPS analysis revealed that {012} facets exhibit higher rate constants for both charge transfer and recombination. OCP measurements uncovered a more obvious Fermi level pinning effect on {012} facets, due to a higher density of surface states induced by OH species. Together, the detailed kinetic and thermodynamic studies explained the different PEC performance of hematite {012} and hematite {001}, and highlight the importance of surface structure on determining charge transfer at the photoelectrode|H₂O interface. The different k_{tran} observed on different facets would enlighten studies on understanding catalytic mechanism on the basis of exposed facet, or tuning catalytic activity by hierarchical crystalline domains. This work also sheds lights on how to further improve the PEC performance for hematite photoelectrodes. High-performance photoelectrodes will likely feature surface chemical species that improve charge transfer kinetics but do not promote recombination (e.g., heterogenized molecular catalysts).^{1,9,22}

3.8 Reference

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Chapter 4: Distinguishing the effects of water oxidation catalysts (WOCs) on photoelectrode surface/water interface

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4.1 Functionalizing heterogenized and heterogeneous Ir WOCs

4.1.1 The needs of mono-layer WOC in acidic solutions

To further improve the PEC performance of hematite photoelectrode, introducing WOC is a promising approach to facilitate water oxidation kinetics. However, the rapid developments are hindered by poor integration of catalysts with photoelectrodes. On a system level, its operation needs to be matched with a photocathode. Because the only commercially successful membranes to separate the photoanode and photocathode are proton exchange ones, PEC H₂O oxidation in acidic solutions deserves particular attention.¹ While catalysts for H₂O reduction in acidic solutions are readily available, those for H₂O oxidation at low pHs are rare,^{2, 3} with Ir-based ones being the only functionally stable examples.⁴⁻⁶ One criticism that Ir-based catalysts have to address is the cost associated with the scarcity of the element in the earth's crust; a solution to this problem is made possible by a recently developed strategy that utilizes monolayers of a molecular heterogenized catalyst that can be derived from its homogeneous analogue.⁷⁻¹¹ Here we show that the same strategy can be readily applied to enable the first example of hematite-based complete water splitting in acidic solutions.

4.1.2 Materials and methods

Hematite fabrication: Briefly, a FTO substrate was soaked in a solution of 0.15 M iron(III) chloride hexahydrate and 1 M sodium nitrate at 100 °C for 1 h. The backside of the FTO substrate was protected by Kapton tape to prevent growth during the synthesis. Afterwards, the tape was removed and the substrate was rinsed with deionized (DI) water and dried with N_2 gas. It was then annealed at 800 °C for 5 min to convert the resulting FeOOH to hematite. All hematite photoelectrodes labeled as hematite in this manuscript refer to samples subjected to the growth-annealing cycles three times. The repeated procedures were found to fix surface structural defects and permit the measurement of low turn-on potentials.

Hematite/het-WOC preparation: To prepare a fresh 2.5 mM hom-WOC solution ($[Ir(pyalc)(H_2O)_2(\mu-O)]_2^{2+}$), 5mM precatalyst solution ([Cp*Ir(pyalc)OH]) was used and oxidized by NaIO₄ solution (at least 1:100 Cp*Ir(pyalc)OH:NaIO₄ molar

ratio), and the pH was adjusted to ca. 3 by nitric acid. A hematite electrode was soaked in this homogeneous solution overnight and rinsed with DI water. Afterward, the electrode was connected a Cu wire using Ag paste (MG Chemicals, 8331 Silver Conductive Epoxy Adhesive) and protected with non-conductive epoxy (Loctite® 615 Hysol Epoxy Adhesive) to leave an electrode surface area around 0.05 cm².

Het-WOC loading: UV-Vis absorbance spectra of as-prepared homogeneous Ir WOC solution before and after dozens of heterogenization usage was compared. The absorption peak is at λ =608 nm. The relative decrease in absorbance was used to determine the amount of catalyst loading on a given electrode. Because the decrease in absorption due to the decrease on concentration of the Ir het-WOC for a single anode is too low to be quantified, we used the average change for a multiple (12) loading procedure, with the accumulated geometry area of 82 cm². The Ir loading was estimated to be 61 nmol/cm². Nevertheless, since the attachment of Ir WOC onto the other parts of the electrode other than hematite surface is not excluded, the estimated loading should represent the upper bound of the active catalyst loading.

Hematite/IrO_x preparation: IrO_x was potentiostatically deposited (@ 2.5 V vs. SCE for 10 s) in a three-electrode configuration under illumination from a solution containing 2.1 mM [Cp*Ir(H₂O)]SO₄ and 0.1 M KNO₃ (pH was adjusted to 2.9 by nitric acid) for a loading density 0.5 ± 0.02 mg/cm². It was then transferred to a KNO₃ solution (0.1 M; pH 1.01) for a brief (30 s) high potential (2.5 V vs. SCE) treatment, which was found to help stabilize the catalyst. A saturated calomel electrode (SCE) was used as the reference electrode, and a platinum wire was used as the counter electrode.

PEC characterizations: PEC characterizations were carried out using a potentiostat/galvanostat (CH Instruments CHI604C) in a three-electrode configuration.

Bare hematite, hematite/het-WOC or hematite/IrO_x acted as the working electrode, with an SCE electrode (CH Instruments) soaked in saturated KCl aqueous solution as the reference, and a Pt wire as the counter electrode. The electrolyte was a 0.1M KNO₃ solution whose pH was adjusted to 1.01 by nitric acid. The light source for all data presented in this work was an AM 1.5 solar simulator (100 mW cm⁻², Solarlight Model 16S-300-M Air Mass Solar Simulator). In a typical J-V plot, the voltage was swept linearly from positive to negative at a rate of 20 mV.s⁻¹.

Transmission electron microscopic characterizations: All transmission electron micrographs were taken on a JEOL 2010F microscope operating at an acceleration voltage of 200 kV.

 O_2 detection using a Clark-type oxygen sensor: The evolved O_2 by hematite/het-WOC and hematite/IrO_x was detected in situ using a Clark-type BOD oxygen electrode (Thermo Scientific 9708 DOP). Similar to a typical PEC measurement, a three-electrode configuration was employed, except that the surface area of the photoelectrode was increased to ca. 2 cm² for increased O_2 production. For a typical experiment, the working electrode, the reference electrode, the counter electrode and the oxygen sensor were sealed in a three-neck flask by rubber stoppers (with all possible leaking parts covered by parafilm and high vacuum grease). Ar gas was used to purge dissolved O_2 in the electrolyte for at least 30 min and the headspace was protected by Ar gas to ensure an O_2 free environment. Once we removed the needle purging Ar gas into the electrolyte, and the oxygen sensor had been stabilized close to 0 ppm for a period time (5 min), the O_2 yield could be read on a pH meter connected to the oxygen sensor. **Calculation on O**₂ **saturation in aqueous solution:** At 25°C and 1 standard atmosphere (101.3 kPa), fresh water contains ca. 6.04 mL of oxygen per liter. Based on ideal gas equation (PV = nRT), we get 0.247 mmol O₂ dissolved in 1 L water under this condition. The volume of the solution used in our test system was 45 mL. Therefore, the saturated amount of oxygen would be 11.12 µmol.

 H_2 detection by mass-spectrometry: H_2 was analyzed using a mass spectrometer (MKS special V2000P). A hematite/IrO_x photoanode and a photocathode of a-Si were constructed for H_2 production. The reaction was carried out under illumination without external bias. The generated H_2 was tested every 20 min. The gas sample (fixed volume of 100 µL) was injected manually. Two Pt wires established internal calibration standards by passing the same charges for the hematite/IrO_x and for the a-Si system. Afterward, the amount of H_2 produced by the hematite/IrO_x and a-Si was calculated based on the Pt calibration curve.

4.1.3 Applying heterogenized Ir WOC

As has been reported by Sheehan *et al.*⁸ and schematically shown in Figure 4.1a, the molecular identity of our heterogenized Ir water oxidation catalyst (het-WOC) is preserved by its bidentate ligands, whereas strong direct binding of the Ir centers to the photoelectrode corrects the drawback of poor stability often found with molecular catalysts. The molecular nature of the Ir het-WOC distinguishes itself from the more widely studied IrO₂ nanoparticles that have been previously integrated with hematite.¹² The effect of the het-WOC on hematite¹³ PEC performance is evident in Figure 4.1b, where the turn-on voltages (V_{on}) are cathodically shifted by 0.25 V (from 0.85 V to 0.60

V using the Butler method) at pH 1.01. To prove that the observed performance enhancement was indeed a result of Ir het-WOC decoration, we examined the photoelectrode using X-ray photoelectron spectroscopy (XPS). Survey scans revealed that the only elements present are Fe, O, C, Ir and N. The peaks at 65 eV and 62 eV correspond to Ir $4f_{5/2}$ and Ir $4f_{7/2}$, respectively (Figure 4.2a). The binding energies agree well with those for Ir(IV) in the surface-bound species, as supported by previous studies on this system.⁸ The inset in Figure 4.2a confirms the existence of N 1s, likely due to the pyalc ligand, which is critical to maintaining the molecular identity of the Ir WOC. The ratio of Ir(IV) to pyalc was calculated as ca. 1:1, in good agreement with what is expected from the het-WOC structure shown in Figure 2.1a.



Figure 4.1 Application of a monolayer of the molecular Ir WOC on hematite. (a) Schematic demonstration of the proposed WOC molecular structure on hematite surface. The surface binding is made possible by Ir-O-Fe bonding. (b) Polarization curves of hematite photoanodes with (dotted line) and without Ir WOC (black). The electrolyte was 0.1 M KNO₃ (pH 1.01, adjusted by HNO₃), and lighting was AM 1.5 at 100 mW/cm². The polarization curve measured in the presence of H₂O₂ is included (grey; under chopped lighting conditions) for comparison. The scan directions for all curves are from positive to negative.



Figure 4.2 Surface studies of the het-WOC-decorated hematite photoelectrode. (a) Xray photoelectron spectroscopy analysis confirming the attachment of Ir and bidentate pyalc ligand. Inset: the spectrum and its fitting corresponding to N 1s binding energies. (b) Detection of evolved O_2 by het-WOC-decorated hematite. Electrolyte: 0.1 M KNO₃ (pH adjusted to 1.01); lighting condition: AM 1.5 illumination at 100 mW/cm²; applied potential: 1.23 V vs. RHE. Black trace: theoretical amount based on passed charge. (c) Polarization curves of various photoelectrodes. Test conditions were identical to those in panel (b). (d) XPS spectra after a 10 h stability test. Inset: the spectrum of N 1s binding energies.

It is noted that, although corrosion of hematite in acidic solutions is known, the reactions are non-redox in nature and, hence, are not expected to contribute to photocurrents. In addition, the reactions are slow enough to permit PEC characterization of bare hematite photoelectrodes. Important to our discussions, the steady-state current voltage curves of het-WOC-decorated hematite without sacrificial hole scavengers are comparable to those with hole scavengers (grey curve in Figure 4.1b, where H_2O_2 is present) in terms of V_{on} and saturation current densities, strongly supporting that the excellent water-oxidation catalytic activities are due to the Ir het-WOC.⁸ To experimentally verify that the measured photocurrents are indeed a result of water oxidation, we measured the evolved O2 using a Clark-type oxygen sensor (Figure 4.2b), where 1.23 V vs. RHE was applied to the hematite/het-WOC photoelectrode.¹⁴ The calculated Faradaic efficiency was 94% during the first 50 min. The efficiency started to decrease after 60 min, however, and the amount of O2 leveled off after 80 min. Several reasons may help explain the observation. First, the detection is based on dissolved O₂. Saturation of O₂ in the solution could lead to apparent deviations of the charge/O₂ linear dependence as shown in Figure 4.2b. Because of the large volume of solutions used here, our calculations show that this cause is unlikely. Second, the Ir het-WOC may be stripped off the photoelectrode during measurements by oxidation of its ligands or simple corrosion of the underlying hematite in highly acidic solutions. To test the latter case, we found that, by simply soaking the het-WOC decorated hematite in testing solutions without passing through any charge, a dramatic degradation of the PEC performance in the form of an anodic shift (Figure 4.2c) was observed. XPS studies showed that, although peaks corresponding to the Ir het-WOC are still observable after 10 h of electrolysis, the intensities are obviously decreased (Figure

4.2d). Given that the monolayer catalyst does not provide a compact, high-density coverage of the hematite surface, it is reasonable that acids corrode hematite to undermine the attachment of het-WOC to hematite. It is, therefore, concluded that significant loss of surface-attached Ir het-WOC during electrolysis indeed took place. When het-WOC dissolves in H₂O, it may serve as a redox shuttle between the anode and cathode, contributing to the photocurrent but not O_2 evolution. To further verify this hypothesis, we reloaded het-WOC on hematite after 10 h of stability testing, replaced the test solution, and observed full recovery of the PEC performance. The results support that the photoelectrode degradation is due to the detachment of the het-WOC from the hematite photoelectrode. It is noted that because the excellent stability of the Ir het-WOC under oxidations condition has been demonstrated previously,⁸ the catalyst's detachment is most likely caused by corrosion of hematite rather than ligand loss, as supported by XPS (Figure 4.2).

Several important advantages are offered by the ultra-thin, monolayer of het-WOC. For example, it significantly reduces the amount of catalyst needed to achieve desired performance, and imparts limited corrosion resistance. That a single-layer catalyst readily shifts V_{on} by as much as 250 mV speaks of the paramount importance of controlling the photoelectrode/electrolyte interface of a PEC.^{6, 14-18} Moreover, the thin layer absorbs little light, making it highly versatile in integration with various types of photoelectrode materials. By comparison, the more extensively studied WOCs such as Co-P_i or amorphous NiFeO_x compete with the photoelectrode for light absorption to a certain extent;^{19, 20} aside from that, they do not function in acidic solutions. These benefits notwithstanding, the instability of the het-WOC-decorated hematite over the course of hours presents a critical challenge. We envision that replacing the

hematite/het-WOC interface with an acid-stable material such as WO₃ should help improve the stability. Approaches toward this direction are under development.

4.1.4 Applying heterogeneous Ir WOC

To further study what is enabled by an acid-active WOC, we next pursued complete solar water splitting with a bulk heterogeneous derivative of a Cp*Ir precatalyst, the "blue-layer" IrO_x WOC.^{5, 21, 22} Our rationale was that this amorphous IrO_x WOC resulting from anodic photo-electrodeposition provides a more dense coverage on the hematite surface to prevent solution penetration. The expectation was confirmed by transmission electron microscopy (TEM, Figure 4.3a), which was obtained by a brief (10 s) deposition at 2.5 V (vs. SCE, saturated calomel electrode).

As far as PEC performance is concerned, the IrO_x WOC yielded comparable results on the surface of hematite as the Ir het-WOC (Figure 4.3b). A similarly low V_{on} of 0.6 V was obtained. Comparing the steady-state current-voltage curve with that in the presence of the hole scavenger H₂O₂ (Figure 4.3c), we see that the photocurrent is limited by the light-harvesting and charge-separation capabilities of hematite, but not the charge transfer through the catalyst. The result further highlights the outstanding H₂O-oxidation activity of the IrO_x WOC. Open circuit voltage measurements in dark and light for bare hematite, with het-WOC, and with IrO_x WOC revealed that the IrO_x clearly shifts the dark equilibrium potential (1.1 V) close to the water oxidation potential of 1.23 V. In the absence of surface states, the dark equilibrium potential is expected to align with the water oxidation potential; any mismatch is perceived as an undesired potential drop in the Helmholtz layer that does not contribute to charge separation in the photoelectrode.¹⁴ The result suggests that the IrO_x improves the PEC performance by changing the interface energetics. Its application increases the degree of band bending within the photoelectrode, affording better charge separation. The effect of het-WOC, however, is less clear. The dark equilibrium potential (0.9 V) only represents a modest shift of 0.1 V when compared with bare hematite (0.8 V). Although it is reasonable to expect the shift to be modest because the het-WOC provides less complete coverage of the hematite surface than IrO_x and, hence, does not modify the surface energetics as significantly as IrO_x , the magnitude fails to explain the observed PEC performance improvement. We suspect that much improved kinetics may play an important role here, as the het-WOC has been shown to outperform IrO_x under certain electrocatalytic conditions.⁸ Further studies are thus needed to better understand this system.



Figure 4.3 Structural and photoelectrochemical studies of IrO_x "blue layer" decorated hematite photoanode. (a) Transmission electron micrographs showing the morphologies of bare hematite (left), with het-WOC (middle) and with a thin IrO_x "blue layer" (right). Scale bar: 2 nm. (b) Polarization curves showing the PEC behavior of IrO_x -decorated hematite tested in 0.1 M KNO₃ (pH 1.01) under AM 1.5 illumination. The polarization curve of a matching amorphous Si (a-Si) photocathode is shown as a gray trace. (c) Polarization curves measured in the presence of H_2O_2 under chopped illumination. (d) Chronoamperometry showing the stability of hematite/IrO_x over 5 h with only a 5% decrease.

4.1.5 Realizing unassisted water splitting

Most important to our next discussions, the stability of the photoelectrode in acids is now greatly improved, with only a 5% decay over 5 h of electrolysis run at 1.23 V vs. RHE (Figure 4.3d; 0.66 mA/cm² at t = 0 and 0.61 mA/cm² at t = 5 h). The outstanding stability opens up new doors to constructing devices for unassisted water splitting, with amorphous Si (a-Si) as a photocathode.^{13, 23} The typical current-voltage performance of the a-Si photocathode is shown in Figure 4.3b as a gray trace. It overlaps with the photoanode curve with IrO_x present, and the current density at the cross-point is 0.36 mA/cm². With simulated sunlight passing through the photoanode (including the IrO_x), a significant reduction in the light intensity is expected, even beyond the absorption of hematite, due to IrO_x absorption and light scattering. As such, the measured photocurrents represent the lower bound of what can be achieved by the hematite/a-Si system. Even with these constraints, it is highly encouraging to measure meaningful photocurrents without applying an external bias in highly acidic solutions. The production of O₂ and H₂ was detected using a Clark-type electrode and mass spectrometry, respectively. Within the first 90 min, near 100% Faradaic efficiency was measured for O₂ production, beyond which the solution would be saturated and further detection is not possible. Similarly, the Faradaic efficiency for H₂ generation was close to 100% during the first 3 h of testing. It is noted that the a-Si photocathode stability in highly acidic solutions requires further optimization because its TiO₂ protection layer is etched relatively rapidly. To the best of our knowledge, this represents the first time unassisted solar water splitting with a meaningful efficiency (estimated efficiency 0.44 %) has been obtained under acidic conditions.

To realize the full potential of solar water splitting as a large-scale energy storage solution, we need a photoanode and a photocathode with complementary light absorption and matching performance under the same operation conditions (e.g., pH). With this consideration in mind, we see that the lack of functional H₂O-oxidation catalysts at low pH presents a conspicuous challenge. Ir-free WOCs that work for extended period of time in acid solutions have not been reported. As such, our strategy of utilizing an ultra-thin, monolayer Ir WOC derived from a molecular analogue is particularly meaningful as it provides a temporary solution to the issues connected to the high cost of Ir by minimizing the amount catalyst used. That the catalyst enables high performance of hematite at low pH is encouraging. Although significant work is still needed to further stabilize the het-WOC/hematite combination, we show that in principle the design should work by employing a heterogeneous coverage of IrO_x derived from an organometallic Ir species. To the best of our knowledge, this is the first time complete solar water splitting in acidic solutions by hematite, or any other photoanode, is achieved.



Figure 4.4 Product detection for photoanode (IrO_x -decorated hematite) and photocathode (a-Si) in acidic solutions (pH 1.01). (a) Amount of evolved O_2 by detected by a Clark-type oxygen sensor. Black line: theoretical O_2 amount calculated from charges. (b) H₂ generated in unassisted overall water splitting system detected by Mass Spectroscopy without external bias. The tandem device configuration is schematically shown in the inset.

4.2 Distinguishing the effects of heterogenized and heterogeneous Ir WOCs

4.2.1 The importance of understanding the mechanism of WOC

The successful implementation of solar water splitting depends on effective combination of efficient light absorbers and catalysts.^{12-14, 24-28} In an integrated system, the light absorber and the catalyst strongly influence each other. Understanding in detail the mechanisms of these effects is of paramount importance to improving the performance of a photochemical system, but is often lacking. Photoanode performance has been shown to improve with the application of WOCs.^{29, 30} This enhancement can be attributed to two factors at the semiconductor|electrolyte interface: better charge transfer and reduced charge recombination.³¹ A growing body of studies focused on hematite and heterogeneous WOCs (mostly oxide-based) supports that the latter, i.e., reduced surface charge recombination and Fermi level un-pinning by the formation of an adaptive junction (and hence better charge separation within hematite), have been the most common reasons for the observed performance improvement.^{6, 14, 32-37} In essence, the application of heterogeneous WOCs slows down surface recombination and improves the efficiency at which photogenerated charges are transferred into the solution for water oxidation. To date, there has been only one report that ascribes the PEC performance enhancement to improved charge transfer kinetics, to the best of our knowledge, where an ultra-thin cobalt oxide WOC was used.³⁸ Such an understanding is reasonable, given that most heterogeneous WOCs provide a complete (sometimes thick) coverage of photoelectrode surfaces. The same complete coverage is not expected when ultra-thin WOCs, such as heterogenized monolayer homogeneous (molecular) WOCs, are applied. It raises an important question, as to whether the same

mechanism (i.e. reduction in surface recombination rates) holds when a molecular WOC is involved in a PEC system.

Compared with heterogeneous systems, molecular-based catalysts feature welldefined catalytic moieties that are advantageous to elucidate mechanistic information. Their high turn-over characteristics also make it possible to achieve high catalytic activities at low loading densities. They have been widely studied for a number of reactions, including water oxidation, CO₂ reduction and hydrogen evolution.^{3, 29, 39-41} Their integration with photoelectrodes has been reported, and performance enhancement has been observed.⁴²⁻⁵³ However, the mechanisms by which molecular catalysts enhance PEC performance remain poorly understood. Moreover, given that reduced surface recombination has been increasingly recognized as the primary reason for improvement of heterogeneous WOC-coated PEC water-oxidation systems, a direct comparison between heterogeneous and molecular-based systems would be of great value, yet is currently missing. Building upon our recent success combining hematite with a heterogenized-molecular system,^{8, 42} here we report a detailed study to correct this deficiency. We show that the het-WOC enhances PEC performance by providing additional charge-transfer pathways that speed up forward reaction kinetics, whereas the heterogeneous IrO_x WOC^{5, 21} improves PEC performance by replacing existing reaction pathways altogether, for simultaneous reduction of surface recombination and improved charge transfer.

4.2.2 Materials and methods

Electrochemical Impedance Spectroscopy (EIS): Impedance spectra were recorded by using a ModuLab[®] XM potentiostat that includes a Frequency Response

Analyzer (FRA) and coupled with the ModuLab[®] XM ECS software. The EIS data were measured by a 10 mV perturbation between 100 kHz to 0.01 Hz, in the dark or under illumination. The same three-electrode configuration, illumination source/intensity, and electrolyte as described in the PEC Characterization section were employed. The EIS data were fit to the equivalent circuits described in the text by using the Zview software.

Kinetic Isotope Effect (KIE) Measurements: The H/D KIE measurements were conducted by comparing the steady-state current density at different applied potentials for samples in either H₂O or 99.9% D₂O (Sigma Aldrich) with 0.1 M KNO₃ for 5 min under illumination. The same three-electrode configuration and illumination source/intensity as described in the PEC Characterization section were employed. The pH of both electrolytes was adjusted to 1.03 by using nitric acid (the pD was calculated by adding 0.4 to the pH meter reading⁸ measured by Orion Star pH meter from Thermo Scientific).

4.2.3 The kinetics models

The kinetic models used in this work are summarized in Figure 4.5a. The following assumptions are made. (i) Water oxidation by hematite is mediated by surface states.⁵⁴⁻⁵⁷ In accordance with literature reports, here "surface states" refer to electronic states induced by surface chemisorption.^{15, 58, 59} (ii) Hole transfer from the valence band of hematite to the surface states is fast.⁶⁰ This step is not considered for the kinetic model, as it is not rate limiting. The rate constant of hole transfer from the surface to the solution is denoted as k_{trans} . A pseudo-first- order dependence of hole transfer on the hole concentration is assumed. Given that all data presented in this work were collected

at low applied potentials (<1.5 V vs. RHE), the assumption is reasonable and supported by recent spectroscopic measurements.⁶¹ (iii) The rate at which electrons recombine with holes on the surface is assumed to be first order with respect to the hole concentration, and the rate constant is denoted as k_{rec} . (iv) k_{trans} and k_{rec} are the key parameters used in this work to compare three different types of electrodes: (a) bare hematite; (b) hematite with het-WOC; and (c) hematite with IrO_x. Together, these variables are used to calculate the overall hole transfer efficiency by using the following relation: $TE = k_{trans}/(k_{trans}+k_{rec})$. We first compare k_{trans} and k_{rec} as measured by IMPS for different substrates. *TE* is then calculated and compared with the measured PEC data. To independently test the validity of the results, we also compare *TE* as computed by EIS. Lastly, KIE data are presented to further improve our understanding.



Figure 4.5 Schematic illustrations of the kinetic models for (a) bare hematite (b) hematite with het-WOC and (c) hematite with IrO_x . Assumptions and explanations of k_{rec} and k_{trans} are detailed in the main text

4.2.4 Intensity modulated photocurrent spectroscopy (IMPS) results

When used to analyze a photoanode, the IMPS technique assumes the followings.^{62,} ⁶³ (i) The surface hole concentration changes with the light intensity linearly. This assumption is expected to hold for hematite as the hole diffusion distance within hematite is negligible, and holes generated away from the depletion region are not expected to contribute to the photocurrent.⁶⁴ Note that this assumption does not necessitate unity-efficiency charge separation within the depletion region, as long as the width of the depletion region is not altered by the light modulation layer. (ii) The light intensity modulation is sufficiently low, so that the changes to the degree of band bending, the space charge capacitance and the density of majority carriers (electrons) are insignificant.⁶⁵ This assumption is also expected to hold as the modulation we used (10% of an overall intensity of 134 mA/cm² at $\lambda = 405$ nm) is mild. Based on these assumptions, the low frequency end, at which the imaginary part of the complex plane photocurrent equals 0 $(Im(j_{photo}/j_h) = 0)$, reports on the charge transfer efficiency $k_{trans}/(k_{trans} + k_{rec})$. The frequency at the apex of the semicircle, where the maximum imaginary part is measured from the complex plane photocurrent, reports on the combination of charge transfer and recombination $(k_{trans} + k_{rec})$. k_{trans} and k_{rec} can be obtained from the experimental data at these two key points. This technique has been previously applied to study hematite-based photoanodes by others and us.^{35, 63, 66, 67} In all previous reports, the improvement of charge transfer efficiency has been explained by the reduction of k_{rec} rather than an increase of k_{trans} . In other words, the WOCs applied onto hematite as studied by IMPS have primarily played the role of surface passivation.^{35, 63} The results we obtained here are different. The extracted k_{trans} and k_{rec}

are summarized in Figure 4.6. Significantly higher values of k_{trans} were measured on hematite modified by both het-WOC and IrO_x. For instance, the highest k_{trans} measured on bare hematite is 57.09 ± 21.27 s⁻¹ at $V_{app} = 1.3$ V. It is 140.65 ± 1.26 s⁻¹ at $V_{app} = 1.2$ V for hematite with het-WOC, and 146.44 ± 16.08 s⁻¹ at $V_{app} = 0.8$ V for hematite with IrO_x. The results support that both het-WOC and IrO_x are high-performance WOCs, yet they operate via distinct mechanisms.

The key difference between the het-WOC and IrO_x is observed when comparing the recombination rate constants (Figure 4.6b). Across the entire measured potential range, the values of k_{rec} are comparable for bare hematite and hematite with het-WOC, but are significantly lower for hematite with IrO_x. For instance, at $V_{app} = 0.8$ V, k_{rec} for bare hematite is $187.56 \pm 32.61 \text{ s}^{-1}$, comparable to $208.60 \pm 10.70 \text{ s}^{-1}$ for hematite with het-WOC, but much higher than that for hematite with IrO_x (65.45 ± 0.40 s⁻¹). These results suggest that while the het-WOC improves charge transfer kinetics (k_{trans}), it does little to reduce the surface recombination. Note that here k_{rec} is the effective rate constant for hole annihilation that involves electrons from the conduction band. For bare hematite, the process is mediated by surface states due to chemisorption. That similar values of k_{rec} were measured on bare hematite and hematite with het-WOC suggests the application of het-WOC does not change these surface states significantly. Given the relatively light loading of the het-WOC species compared to IrO_x (vide infra), this conclusion is reasonable. The presence of het-WOC, nevertheless, opens up new charge transfer pathways via the Ir complex, through which holes are more effectively used for water oxidation than by the surface states inherent to bare hematite in H₂O. It is noted that solution-phase studies on similar molecular Ir compounds have suggested that the mechanism by which these species oxidize water is through nucleophilic attack from

water on a high-valent Ir^{V} -oxo species.⁶⁸ The electron donicity of the pyalc ligand stabilizes the Ir^{IV} oxidation state but de-stabilizes Ir^{V} which would in turn promote decomposition of the high-valent Ir^{V} -oxo species into O_2 .⁶⁹⁻⁷¹

By comparison, a heterogeneous deposit of IrO_x as a WOC forms a dense film on hematite. The surface states that are characteristic of the Fe₂O₃|H₂O interface, through which water oxidation and recombination on bare hematite take place, are replaced. As a result, higher values of k_{trans} and lower values of k_{rec} were measured. It is noted that while reduced values of k_{rec} have been observed on hematite coated with other heterogeneous WOCs such as Co^{2+} , NiFeO_x, Ga₂O₃ and TiO₂, higher values of k_{trans} have not been reported previously.^{13-15, 35, 36, 63} Our results reported here highlight the effectiveness of IrO_x as a WOC. It not only speeds up the rate of water oxidation, but also reduces the rate of surface recombination. Thus, collectively higher charge transfer efficiencies are obtained (Figure 4.6c). This effect is especially obvious at low values of V_{app} (between 0.5 and 1.0 V). The calculated TE values also agree well with the steady-state current-voltage relationship. Our understanding of the mechanistic differences between bare hematite, hematite with het-WOC and hematite with IrO_x is summarized in Figure 4.7. In essence, although the application of het-WOC provides additional hole transfer pathways (green arrows), it does not eliminate the hole transfer pathways inherent to the Fe₂O₃|H₂O interface (orange arrows). In both cases (bare hematite and hematite with het-WOC), significant surface recombination is expected (red arrows). Thus, the het-WOC on hematite's surface improves the overall PEC performance primarily by accelerating hole transfer. IrO_x, on the other hand, replaces the Fe₂O₃|H₂O interface, suppressing both the direct hole transfer through hematite to H₂O and the surface recombination.

One additional feature worth noting in Figure 4.6 is that the values of k_{trans} for IrO_x are higher than those for het-WOC between 0.6 and 1.0 V. For instance, at 0.8 V, k_{trans} for het-WOC is $91.76 \pm 5.53 \text{ s}^{-1}$; it is $145.36 \pm 12.53 \text{ s}^{-1}$ for IrO_x. At high values of V_{app} (>1.1 V), the values of k_{trans} for het-WOC are higher than those for IrO_x. The variation of k_{trans} as a function of V, particularly the decrease at high V, is an artifact of the IMPS that has been observed by others.^{35, 67, 72} Deviation from a first-order reaction and periodic changes in band bending due to light modulation are possible reasons of this artifact. The maximum value of k_{trans} (1.2 V for the het-WOC and 0.8 V for IrO_x) is expected to coincide with the maximum of the AC component of the intermediate concentrations on the surface.⁷² As shown in Figure 4.6a, the k_{trans} - V plot for the het-WOC appears to be shifted by ca. 400 mV when compared with that for IrO_x. As the binding of het-WOC to the surface of hematite does not suppress surface recombination due to surface states inherent to the Fe₂O₃|H₂O interface, significant surface Fermi level pinning is expected to persist when het-WOC is present on a hematite surface. The effective water oxidation driving force as measured by the applied potential (V_{app}) plus the photovoltage (total energy obtained from solar light and applied bias) is reduced by the potential drop in the Helmholtz layer. Such an effect has been previously reported by us,⁴² and the potential drop was measured at ca. 400 mV, in excellent agreement with the shift as shown in Figure 4.6a. Additionally, the higher surface area and loading of IrO_x compared to the het-WOC may also contribute to the higher apparent values of k_{trans} at low applied potentials.



Figure 4.6 Summary of IMPS data for three different photoelectrodes: bare hematite, hematite with het-WOC, and hematite with IrO_x . (a) charge transfer rate constants (k_{trans}); (b) charge recombination rate constants (k_{rec}); and (c) charge transfer efficiencies. Error bars are included in the data set, but in some cases are smaller than the symbols.



Figure 4.7 Mechanistic perspective of bare hematite (a), hematite with het-WOC (b) and hematite with IrO_x (c).

4.2.5 The dependence on WOC loading

The understanding on the difference between the het-WOC and heterogeneous IrO_x as summarized in Figure 4.7 leads to two important predictions. First, the values of k_{trans} should increase with the increase of het-WOC or IrO_x loading before a maximum is reached. This is because the increase of WOC loading provides more reactive sites for enhanced water-oxidation reactions. Indeed, the prediction was confirmed for both het-WOC (Figure 4.8a) and IrO_x (Figure 4.9a). At $V_{app} = 1.2$ V, the highest value of k_{trans} (140.65 ± 10.26 s⁻¹) was obtained with overnight (>12 h) soaking of hematite in hom-WOC solution. As the adsorption and heterogenization of the WOC is self-limiting due to maximal formation of a monolayer, no changes were observed for treatments longer than 12 h. The loading amount of Ir was confirmed to increase monotonically with the treatment time by inductively coupled plasma optoelectronic spectroscopy (ICP-OES). Similarly, at $V_{app} = 0.9$ V, the highest value of k_{trans} (146.44 ± 16.08 s⁻¹) was obtained with 90 s anodic deposition of IrO_x. The increase of IrO_x as a function of deposition time was observed by cross-sectional TEM.

Second, as the het-WOC is not expected to replace surface states due to $Fe_2O_3|H_2O$ interactions and the pyalc ligands on the molecule that prevent coverage as compact as a metal oxide layer, the recombination rate constants for hematite with the het-WOC are not expected to change. However, since IrO_x replaces the hematite|H₂O interface, the recombination rate constants for IrO_x are expected to decrease with an increased loading of IrO_x owing to more complete coverage of the hematite surface. The prediction was also confirmed by the experimental observations (Figure 4.8b & Figure 4.9b), where the values of k_{rec} remain largely unchanged for hematite with different hetWOC loadings but decrease monotonically with increased IrO_x loading. It is noted that an excess amount of IrO_x was found to be detrimental to the overall performance, likely due to light absorption by the catalyst.²⁴



Figure 4.8 Dependence of kinetic constants on the amount of loading of het-WOC. (a) Charge transfer rate constants (k_{trans}) increase monotonically as more het-WOC is deposited. (b) Charge recombination rate constants (k_{rec}) remain unchanged. Inset: magnified view of the same dataset between 0.4 and 0.7 V. Y axis: k_{rec} (s⁻¹); X axis: V (vs. RHE).



Figure 4.9 Dependence of kinetic constants on the amount of loading of IrO_x . (a) Charge transfer rate constants (k_{trans}) increase monotonically, and (b) charge recombination rate constants (k_{rec}) decrease monotonically as more IrO_x is deposited. Inset: magnified view of the same dataset between 0.4 and 0.7 V. Y axis: k_{rec} (s⁻¹); X axis: V (vs. RHE).

4.2.6 Photoelectrochemical impedance spectroscopy (PEIS) results

It is important to be mindful that as a transient technique, IMPS faces several potential drawbacks. For instance, data analysis is based on the premise that the studied processes are either a single-step chemical reaction or are dominated by a single step kinetically.⁷² The surface hole concentration derived from these phenomenological first-order reaction rate constants still falls into the first-order reaction region proposed by Le Formal et al.^{35,} ^{61, 72} Such an assumption might oversimplify the complex processes involved in water oxidation. In addition, the charge transfer efficiencies calculated by IMPS near turn-on potentials tend to predict higher steady-state photocurrents than can be measured.⁷³ These shortcomings notwithstanding, the complex plane impedance data agree well with the mathematical model, which gives us confidence in the data analysis as presented above. Nevertheless, we note that the studies do not identify with which step of the wateroxidation reaction the charge transfer rate constant is associated. As such, the rate constants should be treated quasi-quantitatively. The comparison of the values of k_{trans} and k_{rec} between bare hematite, hematite with het-WOCs and hematite with IrO_x provides a reliable qualitative understanding of the complex systems. To further support our hypothesis as presented in Figure 4.5 & 4.7, we next employed a complementary technique, PEIS, on the systems, wherein the light intensity was held constant and the potential was modulated.⁶, 34, 38, 60, 74

The proposed equivalent circuit^{34, 55, 57, 75} for bare hematite is based on our kinetic model consisting of the series resistance (R_s) from the back contact with the transparent 98
conductive oxide, $R_{trapping}$ (resistance for charge transfer to surface states), $R_{ct,trap}$ (resistance of charge transfer via surface states) in parallel with a capacitance of surface states (C_{traps}). The space charge region capacitance is shown as C_{bulk} . The equivalent circuit for hematite with IrO_x is shown in Figure 4.10a. To reflect our hypothesis that the IrO_x film replaces the existing charge transfer pathway inherent to the Fe₂O₃|H₂O interface, a new set of R_{IrOx} (charge transfer resistance from valance band to IrO_x), $R_{ct,IrOx}$ (charge transfer resistance to the solution via IrO_x), and C_{IrOx} (capacitance of IrO_x) is introduced. The original set of electrical elements ($R_{trapping}$, $R_{ct,trap}$ and C_{trap}) is shown as gray because they are omitted in fitting the PEIS data. A similar equivalent circuit is proposed for hematite with het-WOC (Figure 4.10b), where charge transfer through surface states is considered slow and is, therefore, ignored (shown as gray).

It is noted that for PEIS analyses of hematite with IrO_x , a short (i.e., 10 s) deposition time was employed. This is because the spectra would be dominated by the redox behaviors of the Ir species for samples with longer deposition (e.g., 90 s) times. The following features are observed in the PEIS fitting. First, much higher values of C_{IrOx} were measured than those of C_{traps} at low potentials (<0.8 V). This is indicative of better charge separation at low potentials when IrO_x is present.^{6, 34} This conclusion is consistent with the reduction in k_{rec} as shown in Figure 4.6b. Second, in the same potential region, the values of $C_{het-WOC}$ were also greater than those of C_{traps} , albeit only by a small margin. The result is again consistent with the observation by IMPS that the het-WOC does not reduce surface recombination significantly. Furthermore, the maximum value of C_{IrOx} is much greater than that of C_{traps} , which in turn is greater than that of $C_{het-WOC}$. The results suggest that IrO_x, as a relatively thick heterogeneous film, is effective in storing photogenerated holes.^{6, 34} The het-WOC, as an ultra-thin molecular catalyst layer, is effective toward utilizing photogenerated holes for water oxidation without storing them.³⁸ This conclusion is consistent with the schematics shown in Figure 4.7. Third, the values of $R_{ct,IrOx}$ and $R_{ct,het}$ -*WOC* are both significantly lower than those of $R_{ct,trap}$ in the low potential region (<1.2 V). These results are consistent with the higher values of k_{trans} extracted from the IMPS data (Figure 4.6a). Lastly, using the model developed by Peter *et al.*, $^{60, 74}$ we calculated charge transfer efficiencies using the PEIS data, and the results are shown in Figure 4.10c. The trend is in good agreement with that obtained by IMPS data (Figure 4.6c). The decrease of TE in the high applied potential region (>1.3 V vs. RHE) might be due to deviations of the charge transfer kinetic models under a large degree of band bending. To further study the band edge position of these three systems, C_{bulk} and Mott-Schottky plots are carried out. The flatband potential of hematite with IrO_x is 0.35 V vs. RHE, which is more negative than bare hematite (0.50 V vs. RHE) and hematite with het-WOC (0.48 V vs. RHE), indicating that a heterojunction forms after IrO_x deposition due to its oxidizing nature.³⁷ Fermi level pinning is eliminated and band bending in hematite increases due to the suppression of surface states by IrO_x while severe Fermi level pinning still remains after het-WOC decoration,^{24, 32} which is consistent with the IMPS and EIS results. Taken as a whole, the PEIS data provide strong additional support for the kinetic models presented in Figure 4.7. They highlight the differences in the mechanisms by which the het-WOC and IrO_x improve hematite-based PEC water oxidation.



Figure 4.10 PEIS studies. Equivalent circuits for (a) hematite with IrO_x and (b) hematite with het-WOC. (c) Charge transfer efficiencies of bare hematite, hematite with het-WOC, and hematite with IrO_x derived from PEIS (100 mW/cm², Solarlight Model 16S-300-M Air Mass Solar Simulator).

4.2.7 Kinetic isotope effects (KIE) measurements

Critical to the conclusions drawn in this study is the experimental evidence that the mechanisms by which water oxidation occurs on the het-WOC and IrO_x are distinct, or at a minimum possess unique rate-limiting steps. In order to further support this understanding, H/D KIE measurements were employed by comparing steady-state current densities at different potentials in H₂O and D₂O (Figure 4.11). H/D KIE studies serve to probe the rate-determining step (RDS) in chemical reactions that involve proton transfer or proton-coupled electron transfer (PCET). In the case of a reaction such as water oxidation, where four successive proton- and electron-transfer steps must be successfully completed to generate O₂, the KIE can be used as an analytical tool to identify which step is ratelimiting.⁷⁶ A KIE of unity shows that PCET is not involved in the RDS; instead, it reveals that hole transfer into the catalyst (rather than into water) is rate-limiting, indicative of very fast subsequent transfer of holes into water.⁷⁷ This is the case for hematite with het-WOC, for which the measured KIE is close to 1.0. The system's turnover frequency is thus limited by hole transfer into the catalyst. This shows that the RDS, with rate equal to the measured value of k_{trans} , is charge transfer from hematite to the het-WOC, rather than water oxidation itself which occurs more rapidly via het-WOC. In contrast, the KIE measured for hematite with IrO_x is ca. 2.0, consistent with prior studies on IrO_x which show that water oxidation is the RDS.²¹ This implies that RDS of water oxidation by the IrO_x-coated hematite system is the charge transfer from IrO_x to water, instead of charge transfer from hematite to IrO_x . These studies show that the RDS for water oxidation by the het-WOC and IrO_x are distinct, consistent with differing interfacial charge transfer mechanisms for each.



Figure 4.11 Steady-state current of (a) hematite coated with het-WOC after overnight soaking and (b) hematite coated with IrO_x , with 10 s deposition time, in H_2O/D_2O at different potentials.

4.3 Summary

We systematically compared how two Ir-based, chemically distinct, WOCs improve the performance of hematite-based photoelectrochemical water splitting. When an ultra-thin heterogenized molecular catalyst was applied, it readily sped up the hole transfer rate for a faster overall oxygen-evolution reaction. Due to its thinness, however, the electronic states inherent to the Fe₂O₃|H₂O interface remained unchanged. The detrimental effects such as surface recombination by these states persisted. When a relatively thick heterogeneous oxide catalyst was applied, it replaced the Fe₂O₃|H₂O interface with a new Fe₂O₃|IrO_x|H₂O one. Not only was faster charge transfer measured, but reduced surface recombination was also obtained. The latter case, nevertheless, required the application of a significant amount of material, which would be impractical for large-scale use when the catalyst consists of a scarce element, such as Ir. Furthermore, the newly introduced semiconductor|catalyst interface may require individualized optimization for each system, the process of which could be onerous. By comparison, the application of molecular (or molecular-based) catalysts is much more straightforward, provided that the catalyst improves charge transfer without significantly accelerating surface recombination with new surface states.

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Chapter 5: Utilizing surface photoexcited species to control product selectivity

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5.1 The challenges of selective methane oxidation

Steam reforming of methane (SRM) is an important process that produces H_2 and syngas, which are key feedstocks for downstream chemical processes such as Fischer– Tropsch synthesis.^{1, 2} Despite the scale, SRM faces critical challenges, including catalyst deactivation and high energy consumption, most of which are associated with the high temperatures needed to activate the C-H bond. To solve these issues, one may meet the energy needs for CH₄ activation by electrochemical or photochemical instead of thermochemical activation.³⁻¹¹ Indeed, promising results have already been obtained. For instance, Surendranath *et al.* recently reported selective CH₄ conversion toward methanol derivatives by electrochemically turning over a Pd-based molecular catalyst in concentrated H₂SO₄.¹⁰ By comparison, photochemical CH₄ oxidation is less developed. The pioneering work by Yoshida *et al.* succeeded in oxidizing CH₄ by photocatalysts, but mostly produced CO₂ instead of CO or other valuable products.¹²⁻¹⁷ An important reason is the lack of understanding of the reaction mechanisms by these photocatalytic processes.

More broadly, poor understanding of reaction mechanisms, especially at the molecular level, is a critical weakness of researches on heterogeneous catalysis.^{18, 19} In recognition of this deficiency, great research efforts have been made to unravel the mechanisms that govern the selectivity of heterogeneous catalytic reactions.^{20, 21} Within the context of CH₄ oxidation, the demonstrations of colloidal PdAu nanoparticles catalysts with >98% selectivity toward CH₃OH formation highlight the importance of initial activation of CH₄ by \cdot OH.²² *In situ* XANES (X-ray absorption near edge spectroscopy) and Fourier-transform infrared (FTIR) spectroscopic studies of copper-exchanged mordenite zeolite (CuMOR) have revealed that the bridging O in Cu-O-Cu is key to CH₃OH production.²³ Notably, these examples were all thermochemical transformations. Recent advances in a parallel field of CO₂ reduction studies also exemplify the importance of mechanistic understanding to heterogeneous catalysis.²⁴⁻³⁰

Inspired by these previous efforts and the importance of CH₄ oxidation, we studied this reaction under photoelectrochemical (PEC) conditions, wherein the chemical

reaction proceeds at the semiconductor photoelectrode/electrolyte interface under light with an applied bias. The externally applied potential creates an extra electric field to facilitate charge separation between photogenerated electrons and holes. Our goal was to enable the reaction at room temperature so as to address the critical challenges faced by conventional SRM. It was found that the product selectivity is highly sensitive to the applied potentials, and photoexcitation is critical to the selective formation of CO. Detailed mechanistic studies by spectroscopic and computational methods revealed that surface O· radical formation is key to the observed results, and that the synergistic effect between adjacent Ti sites plays a critical role. Our results shed new light on the interactions of C species with metal centers of heterogeneous catalyst substrates.³¹⁻³³ They highlight the importance of synergistic effects in defining the reaction routes.³⁴⁻³⁶ The insights may find applications in CO₂ reduction, as well.^{24, 26, 27, 37}

5.2 Materials and methods

ALD TiO₂: TiO₂ was deposited on a 2.2 mm thick glass slide coated with fluorinedoped tin oxide conductive film (7 Ω /sq surface resistivity, Sigma-Aldrich) in a Cambridge nanotech (Savannah 100) system. FTO coated glass substrate was cleaned in acetone, methanol, and deionized (DI) water. The reaction was performed at 275°C with a constant flow of N₂ (UHP, 99.999%, Airgas) at 20 sccm (background pressure ~1000 mTorr). Ti(i-PrO)₄ (99.999% trace metals basis, Sigma-Aldrich) served as the Ti precursor, and was heated to 75°C. DI H₂O at room temperature was used as the oxygen precursor. The pulse and purge time for Ti(i-PrO)₄ and H₂O was 0.1s & 5s, and 0.01s & 10s, respectively. The dependence of photocurrent density on TiO₂ thickness was discussed in the application of solar water splitting, the optimum TiO₂ thickness was ~50 nm for planar devices corresponding with 3000 cycles growth. The ALD TiO₂ featured anatase (101) surface. Raman spectra confirmed the anatase phase of ALD TiO₂, using an XploRA micro-Raman system (Horiba) with an excitation laser of 638 nm.

Commercial anatase TiO₂ and P25 TiO₂: Commercial anatase TiO₂ powder (Sigma Aldrich, 99.8% trace metal basis) or P25 TiO₂ powder (Evonik Industries, Aeroxide TiO₂ P25) was dispersed in ethanol to make a TiO₂ suspension solution with a concentration of 0.1 g/mL. The resulted solution was drop-casted on FTO substrate and followed a spin coating procedure at a rate of 2500 rpm. Then, the TiO₂ coated FTO substrate was annealed at 475°C in air for 3 h to remove the solvents and improve the adhesion between FTO substrate and TiO₂.

CO detection: Similar to a typical PEC measurement, a three-electrode configuration was employed, except that CH₄ (UHP, 99.99%, Airgas) or N₂ (UHP, 99.999%, Airgas) gas was encapsulated during bulk electrolysis with coulometry. The evolved CO in the headspace was sampled with a gastight syringe (100 μ L) for product analysis using GC-MS (Shimadzu QP2010 Ultra, with Carboxen 1010 PLOT column). CO (UHP, 99.9%, Airgas) was used to calibrate the GC-MS.

Carbonate detection: Measuring the weight increase of carbonate precipitation after bulk electrolysis was used to quantify the carbonate formed in electrolyte. Prior to experiments, DI water was boiled to remove dissolved CO₂. After bulk electrolysis of ALD TiO₂ photoelectrode in the presence of CH₄ was finished, 10.0 mL of 1.0 M Ba(NO₃)₂ (ACS, > 99%, Alfa Aesar) was added to the electrolyte (also to fresh electrolyte as controlled experiment). No significant difference was obtained, suggesting the amount of carbonate product in the electrolyte was beyond the detection limit by this method.

Carbonate adsorbed on the TiO₂ surface was characterized by XPS and attenuated total reflection-Fourier transformed infrared spectroscopy (ATR-FTIR). XPS spectra in were obtained using K-alpha⁺ XPS (Thermo Scientific, Al K α = 1486.7 eV), showing the carbonate formation on ALD TiO₂ surface only after PEC bulk electrolysis in the presence of CH₄. ATR spectra were obtained using a Brüker ATR model Alpha spectrometer with diamond as the ATR crystal. ALD TiO₂ with different electrolysis history was placed on ATR plate with elastic pressing to improve the contact between the sample and the crystal. Acetone was used to clean the ATR substrates between each measurement. Air spectrum was measured as background. Data were collected using the Omnic software package. Each spectrum was collected with 32 scans at a 2 cm⁻¹ spectral resolution.

 H_2O_2 detection: After PEC electrolysis, 1 M HCl was used to adjust the pH of electrolyte to 2~2.5. Then 50 µL of the Mo catalyst was added into the solution and

incubated for 3 min. Finally, 0.5 mL starch solution with concentration of 2 wt% was added to the solution. If there was H_2O_2 , the solution would turn blue.

EPR spectroscopy: A Bruker ELEXSYS E500 spectrometer equipped with a SHQ resonator was used for the EPR experiments. An Oxford ESR-900 continuous flow cryostat was used to measure spectra at 7.5 K. The EPR parameters used for recording the spectra are as follows: microwave frequency, 9.38 GHz; modulation frequency, 100 kHz; modulation amplitude, 19.95 G; microwave power, 5 mW; sweep time, 84 s; conversion time, 41 ms; time constant, 82 ms. Each spectrum was the average of two scans. Since the signal intensity is proportional to radical concentration, the quantity of Ti³⁺ was calculated and the results of three samples are listed in Table S3. The standard used was carefully weighed out 2,2-Diphenyl-1-picrylhydrazy (DPPH) standard (Analytical grade, Sigma Aldrich). The EPR spectrum of the standard was taken under identical conditions.

Raman spectroscopy: Raman spectra were obtained using a Horiba XploRA micro Raman system with excitation laser of 638 nm. Commercial anatase TiO₂ (Sigma Aldrich, 99.8% trace metal basis) was employed instead of ALD anatase TiO₂ film for more sufficient interaction with CH₄; 3% H₂O-saturated CH₄ was circulated and enclosed in a homemade quartz cell (Schematic S2). Spectra were collected under air, CH₄/H₂O and CD₄ (99 atom% D, Assay 99%, Sigma Aldrich)/H₂O with/without illumination by UV light respectively (the same light source in PEC characterizations).

ATR-FTIR spectroscopy: ATR-FTIR spectra were recorded using a Bruker

Vertex 70 FTIR spectrometer (Billerica, MA) equipped with an MCT detector (FTIR-16; Infrared Associates; Stuart, FL). The TiO₂ coated FTO glass slide was pressed on the ATR Si prism crystal. Electrochemical experiments were carried out in a twoelectrode configuration with a Pt foil (99.95%; BASi Inc.; West Lafavette, IN) as the reference/counter electrode. 0.10 M KNO₃ (99.999% trace metals basis, Sigma Aldrich) was used as the electrolyte at room temperature and it was purged for at least one hour by either N₂ (control experiment) or CH₄ before being added into the electrochemical cell. The linear sweep voltammogram (at a rate of 20 mV \cdot s⁻¹) of ALD TiO₂ was scanned under light illumination in CH₄-saturated 1.0 M KNO₃ electrolyte in the FTIR set-up. To ensure steady-state conditions, the target potential was held at 0.3 V vs. internal Pt. The applied potential 0.3 V vs. internal Pt in Figure 5.4b would correspond to 0.9 V vs. RHE in a 3-electrode configuration. The appearance of specific adsorbed intermediates on the electrode is highly sensitive to surface heterogeneity, applied potential, and the amount of dissolved CH₄. Pressing of the working electrode against the IR transparent prism results in an electrochemical cell configuration that brings about uncertainties in the applied potential and unfavorable mass-transport conditions. As a result, while the three bands reported in Figure 5.4 were observed in multiple experiments, they did not always appear concurrently and/or with the same magnitude.

Each reported spectrum was collected at a 2 cm^{-1} spectral resolution and a 40 kHz scanner velocity with 64 scans. The spectrum collected in the beginning of PEC bulk electrolysis was used as the reference, followed by the single beam spectrum collected

at each corresponding time point. The change of optical density was calculated as follows, $\Delta mOD = -1000 \cdot \log(S_{sample}/S_{reference})$.

5.3 Selective CO production by PEC methane oxidation

A typical representation of our experimental setup is schematically shown in Figure 5.1a, where a 3-electrode configuration was employed. A TiO₂ photoelectrode (ca. 50 nm in thickness) was used as the working electrode.³⁸ A Pt wire served as the counter electrode, and the reference electrode was a saturated calomel electrode. In comparison with previous studies on photochemical oxidation of CH4,7,8,12-17 we introduced two key innovations. First, ALD grown TiO2 was studied, which shows critical differences in product selectivity when compared with TiO₂ prepared by other methods. Second, the separation of the oxidation (TiO₂ working electrode) and reduction (Pt counter electrode) reactions permitted us to focus on CH₄ oxidation without confounding effects by the reduction reactions of H₂ generation. The light source used for this body of research was a UV lamp (λ =254 nm; intensity 0.1 mW/cm²). The electrolyte was 1.0 M NaOH (pH 13.6). CH₄ was bubbled into the electrolyte under standard conditions. The solubility is expected to be ca. 0.0010 mol/kg.^{39, 40} The turnon potential was 0.2 V vs. RHE in current voltage curve. A stability test was carried out at 0.6 V vs. RHE, and no obvious decay was observed during the first 15 h. Under our

experimental conditions, the measured anodic photocurrents could be due to CH₄ oxidation or H₂O oxidation or both. Care was taken to ensure that no other parasitic reactions (such as oxidation of organic impurities) contributed to the measured currents. The products of CH₄ oxidation were detected using a GC-MS (Shimadzu QP2010 Ultra, with a Carboxen 1010 PLOT column). The products of H₂O oxidation were quantified by a Clark-type BOD oxygen electrode (Thermo Scientific 9708 DOP).⁴¹ No production of H₂O₂, which was examined by iodine clock reactions, was detected. The V_{app} 's were limited within 0.4 to 1.2 V vs. RHE for this body of study, so that CO oxidation was ruled out. The possibility that H₂ oxidation contributes to the measured photocurrent was ruled out by the measurement of ca. 100% Faradaic efficiency of H₂ detection. For a typical data set as shown in Figure 5.1b, at least 3 different samples were tested for each CO or O₂ detection, and the statistical variation (the standard deviation at each V_{app} was less than 5.1%) was insignificant. Taken together, the selectivity trend as shown in Figures 5.1 and 5.3 is statistically significant.



Figure 5.1 (a) Schematic illustration of selective CH₄ oxidation to CO on a TiO₂ photoelectrode, starting with charge separation between O^{2-} and Ti⁴⁺ to produce \overline{O} Ti³⁺ upon illumination. The separation of the redox half reactions permitted us to focus on CH₄ oxidation. (b) Dependence of the CO efficiency and selectivity on the applied potentials (left axis: efficiency, %; right axis: selectivity of CO over all carbonaceous products, %). PEC bulk electrolysis was conducted on ALD TiO₂ in CH₄-saturated 1.0 M NaOH electrolyte at the corresponding applied potentials.

For the comparison of reaction selectivity under different conditions, we present the Faradaic efficiencies in Figure 5.1b. As can be seen, the detected CO and O_2 collectively account for 80% to 90% of the overall charges as measured by PEC bulk electrolysis. The unaccounted charges were attributed to the production of carbonates, the existence of which was confirmed by spectroscopic measurements. Although the amount of carbonates was too insignificant to quantify by weighing precipitates with Ba(II), the yield is estimated based on the balance of charge transferred (Figure 5.1b). It is noted that for this body of research, the most important quantitative information is the yield of CO. We see from Figure 5.1b and Figure 5.3a the following trends. *First*, the yield of CO is highly sensitive to the applied potentials. At 0.4 V vs. RHE, CO accounts for 81.9% of all charges other than O₂ formation. Given the low concentration of CH₄ (0.0010 mol/kg) under STP,^{39,40} H₂O oxidation is expected to compete favorably in receiving photogenerated holes, which explains the relatively high yield of O₂. The yield of CH₄ oxidation (such as CO) is expected to be readily improved by increasing the partial pressure of CH₄.¹⁰ By comparison, at 1.2 V vs. RHE, CO only accounts for 24.7% of all charges other than O_2 formation. **Second**, the yield is sensitive to the type of TiO₂ substrate used. For ALD grown TiO₂, at 0.6 V vs. RHE, CO accounts for 62.7% of the total charges other than O_2 formation; the yield was <4% for commercially obtained anatase TiO₂ or P25 TiO₂ nanoparticles. *Third*, we observed no CH₄ oxidation products in the absence of illumination or applied potentials or both. The observation is consistent with the understanding that the activation of the first C-H bond requires

significant energy input. It further highlights the importance of photoexcitation for CH₄ oxidation.

5.4 The proposed reaction mechanism

Significant research efforts have been attracted to understanding the activation of CH₄. For heterogeneous catalysis, homolytic C-H dissociation has been reported as one of the activation mechanisms by hydrogen (H) abstraction on an active oxygen (O⁻) center, forming methyl radicals (\bullet CH₃).³³ How to effectively regenerate the surfaceactive oxygen species for continuous CH₄ activation was a major challenge. A solution was found in TiO₂ under photocatalytic conditions. It has been established by previous research that photo-oxidation on TiO_2 starts with charge separation between O^{2-} and Ti^{4+} , producing ${}^{\bullet}O-Ti^{3+}$.^{42, 43} The oxygen radical then attacks the C-H bond in CH₄ to yield Ti-O-CH₃. Subsequent reactions turn this species back to Ti⁴⁺-OH (or Ti⁴⁺-O²⁻ in the deprotonated form), ready for regeneration of the reactive site by photo-excitation. The oxygen radical then attacks the C-H bond in CH₄ to yield surface-adsorbed methoxy (OCH₃) species.²² The understanding is summarized in Figure 5.2. The evolution of this methoxy species and surface adsorbed CH₄ upon light illumination was detected by *in situ* Raman spectroscopy. The applied potential facilitates electron transport away from the Ti site through the conduction band of TiO₂.^{42, 43} Subsequent photoexcited electron transfers between O and Ti drive the reaction to reach a quasistable intermediate state of Ti-O=CH₂, which was observed by *in operando* attenuated total reflection-Fourier transformed infrared spectroscopy (ATR-FTIR). To explain the dependence of CO product selectivity on the type of TiO₂ substrates and the applied potentials, we hypothesize that the mechanism of Ti-O=CH₂ oxidation depends on the nature of the adjacent Ti sites. In the presence of Ti³⁺, it favors the formation of a Ti³⁺-C bond, leading to selective production of CO. An increase in CO selectivity was observed at higher light intensity, since more Ti³⁺ sites would be induced and stabilized. Otherwise, the lack of Ti³⁺ sites would favor the formation of a Ti⁴⁺-O-C bond, resulting in the formation of carbonates and, hence, complete oxidation of CH₄. The proposed mechanism shown in Figure 5.2 is inspired by recent advances on CO₂ reduction and supported by the detection of key intermediates.²⁶ The mechanism is also supported by computational calculations. Below, we present detailed evidence to support the proposed reaction mechanisms.



Figure 5.2 Proposed mechanisms of photooxidation of CH_4 on TiO_2 . The species highlighted by dotted circles have been confirmed by various spectroscopic techniques. The key distinguishing step is identified at the bottom of the catalytic cycle, where the synergistic effect between two adjacent Ti sites promote the switching of C=O-Ti to O=C-Ti, leading to selective formation of CO. Alternatively, in the absence of such a switching, CO_2 is the preferred oxidation product.

5.5 The importance of photoexcited Ti³⁺ species

Our first task was to examine the difference between different TiO₂ substrates. Three prototypical TiO₂ substrates, namely TiO₂ by ALD (Sample 1), anatase TiO₂ (Sigma Aldrich, 99.8% trace metal basis; Sample 2), and P25 (Evonik Industries, Aeroxide TiO₂ P25; Sample 3), were compared. Electron paramagnetic resonance (EPR) spectroscopy was employed for this purpose. While the true nature of the Ti^{3+} sites may not be fully understood until later, a theoretical study by Selloni et al. has shed important light on the problem. Their results showed that photo-generated charges become self-trapped on Ti, reducing the site to become Ti³⁺. EPR detects unpaired electrons, which reports on the localized Ti³⁺ sites in TiO₂.⁴⁵ As shown in Figure 5.3b, a significantly higher intensity of the EPR signal associated with Ti³⁺ was observed for Sample 1 than the other samples,^{8, 44, 45} which is indicative of electrons trapped at the Ti³⁺ sites. It is important to note that the EPR data as shown in Figure 5.3b were obtained in an atmosphere with CH₄ (97%) and H₂O (3%), immediately after illumination (<120 s delay). Our results indicate a clear correlation of the Ti³⁺ concentration as detected by EPR with the CO selectivity as detected by GC-MS. That is, reaction routes involving Ti³⁺ would be favored when **Sample 1** is used as the substrate, which is the CO pathway as shown in Figure 5.2. Further research would be needed to fully explain the high concentration of unpaired electrons in the trapped sites in Sample 1. Possible reasons include high concentration of O vacancies or incomplete

removal of the ligands (isopropoxide).⁴⁶ It is, nevertheless, emphasized that **Sample 1** has been shown highly active and stable toward PEC water splitting, suggesting that the high concentration of Ti^{3+} does not undermine its optoelectronic properties.³⁸



Figure 5.3 Product selectivity dependence on substrates. (a) Comparison of CO selectivity on three different types of TiO₂ samples. PEC bulk electrolysis was conducted in CH₄ saturated 1.0 M NaOH electrolyte at 0.6 V vs. RHE. (b) EPR spectra showing the EPR signals consistent with the presence of Ti³⁺ in the three samples (the color coding of the spectra is the same as the left panel). Of them, ALD TiO₂ (**Sample 1**) features the highest intensity (g_⊥ = 1.99 and g_{||} = 1.96).

5.6 Probing the reaction intermediates

Next, we carried out a multimodal study to detect several key intermediates as shown in Figure 5.2. The techniques we employed include in situ Raman and in operando ATR-FTIR measurements. Among them, in situ Raman allowed us to detect Ti-O-CH₃ (Figure 5.4a), which is a product of the initial oxidation of CH₄ after photoexcitation of electrons from O 2p orbitals to Ti 3d orbitals. The Raman spectra as shown in Figure 5.4a were collected in a homemade quartz cell filled with CH₄ (97%) and H₂O (3%) at 1 atm. Without photoexcitation, we only observed a characteristic peak at 2917 cm⁻¹ that is due to free CH₄ molecules.⁴⁷ With photoexcitation, a shoulder peak at 2905 cm⁻¹ appeared, which is ascribed to adsorbed CH₄.⁴⁷ The red shift in comparison with free CH₄ is due to a weakened bond as a result of adsorption to the TiO₂ substrate. Most prominently, two satellite peaks at 2850 cm⁻¹ and 2965 cm⁻¹ gradually evolved during the *in situ* photoexcitation experiments. Similar peaks have been assigned to the C-H symmetric stretching and asymmetric stretching modes of O-CH₃ on TiO₂, respectively, in the literature.⁴⁸ These results provide strong support for the conclusion that we have obtained CH₃-O-Ti bonds upon photoexcitation under our experimental conditions. To rule out the possibility that these two satellite peaks are due to impurities, we performed Raman characterization using isotope-labelled methane (CD₄). The characteristic Raman shifts of the C-D stretching modes (1800~2500 cm⁻¹) are distinctly different from the C-H stretching modes (2800~3000

cm⁻¹).⁴⁹ Similar satellite peaks were observed, providing additional strong support for our interpretation. The proposed reaction mechanism that governs the formation of CH₃-O-Ti is illustrated in the top panel of Figure 5.4. Alternatively, Ti-O-CH₃ may be generated by an indirect oxidation of CH₄ by water oxidation intermediates, such as H₂O₂. A series of control experiments have been performed by adding H₂O₂ to the electrolyte under different conditions. The results indicate that the last suggested alternative route is unlikely.

Next, we conducted *in operando* ATR-FTIR measurements to probe the reaction intermediates in the subsequent oxidation steps. Similar to the implementations by Hamann *et al.*,⁵⁰ we carried out the experiments by pressing the working electrode against the IR-transparent Si ATR crystal. The electrolyte sandwiched between TiO₂ and Si was either saturated with CH₄ or N₂ (as a control). The IR data were collected at a constant applied potential of 0.3 V (vs. Pt counter electrode) under illumination. They are presented in Figure 5.4b after correction for background absorption. We focused our attention on the region between 1700 cm⁻¹ and 2300 cm⁻¹ because the IR absorption beyond 2700 cm⁻¹ is cut off by a long-pass IR filter in front of the detector and other regions (below 1600 cm⁻¹, 2300 cm⁻¹ to 2700 cm⁻¹) are interfered by broad H₂O and CO₂ absorptions. Within the observation window, three distinct peaks at 1735, 1763, and 2065 cm⁻¹ were observed, but only in the presence of CH₄. All three peaks exhibited an obvious dependence on the illumination duration, strongly suggesting that they are due to photooxidation reactions on the surface of TiO₂. Of them, the most prominent peak at 1763 cm⁻¹ is assigned to the C=O stretch due to surface adsorbed formic acid species.⁵¹⁻⁵⁴ The peak at 1735 cm⁻¹ is assigned to the C=O stretch due to surface adsorbed formaldehyde species, where the oxygen adatoms are coordinated to Ti atoms.^{51, 54, 55} The peak at 2065 cm⁻¹ is assigned to the C=O stretch due to surface adsorbed CO species.^{56, 57} The assignments of these peaks are supported by literature reports. The importance of these reaction intermediates to the overall reactions is illustrated in the proposed catalytic cycle (Figure 5.2).



Figure 5.4 In situ Raman and FTIR detection of key reaction intermediates. (a) In situ Raman spectra of samples in dark (left) and in light (right) confirm the H₃C-O-Ti species as a result of the initial oxidation of CH₄. No electrical potential was applied. (b) Evolution of H₂C=O-Ti, Ti-CO and HCOO(H)-Ti surface species as a function of time as detected by FTIR. The IR data were collected at $V_{app} = 0.3$ V (vs. Pt counter electrode) under illumination.

5.7 The implications to parallel CO₂ reduction reaction

Our investigations of the catalytic cycle highlight the importance of the Ti³⁺ site adjacent to Ti-O=CH₂ in promoting CO formation. This understanding is consistent with the potential dependence we observed. At relatively high applied potentials (e.g., 1.2 V vs. RHE), photoexcited electrons are readily removed from the Ti^{3+} site, which would favor the pathway leading to CO_2 (or carbonate) formation. At less positive potentials (e.g., 0.4 V vs. RHE), the higher concentration of Ti³⁺ sites facilitates the formation of Ti-C(H)=O bonds, leading to CO formation. In essence, the switching between Ti-O-C and Ti-C-O bonding appears to be critical to the selectivity for CO production. The conclusion reminds us of parallel studies on CO₂ reduction by metal catalysts. It is well accepted that the reaction starts with a M-C bond (where M represents the metal catalytic center). Computational results suggest that formation of more reduced products such as CH₄ or CH₃OH often requires switching from M-C-O to M-O-C bonding (Figure 55.);²⁴ otherwise, the reaction favors the formation of CO. While experimental evidence to explicitly verify this understanding is still missing, multiple computational studies provide strong supports for this hypothesis.^{24, 58, 59} The switching likely proceeds through a concerted mechanism with adjacent metal sites, in a similar fashion to our proposed mechanism as shown in Figure 5.5. We suggest that insights into CO₂ reduction could be drawn from studies of CH₄ oxidation, given the similarities of the key steps.



Figure 5.5 The switching between Ti-O-C and Ti-C-O bonding is critical to the selective production of CO from CH_4 (top). In parallel studies of CO_2 reduction, the selective production of CH_4 or CH_3OH may proceed by switching between M-C-O and M-O-C bonding in a similar fashion (bottom). The key steps are highlighted in the dotted boxes.

5.8 Summary

In conclusion, we have observed highly selective CO production by CH_4 photoelectrochemical oxidation. Only with a moderately positive applied potentials (between 0.4 and 1.2 V vs. RHE) and on ALD-grown TiO₂ did we obtain a high yield of CO production. EPR studies revealed that the key difference between ALD-grown TiO₂ and commercially obtained samples is the concentration of Ti³⁺ sites. We propose that the adjacent Ti³⁺ sites to the Ti-C=O bond are key to the high selectivity for CO formation. Spectroscopic evidence from *in situ* Raman and FTIR spectroscopy provides strong support to the proposed mechanism. The feasibility of the proposed mechanism is also supported by computational studies as well. The proposed mechanism draws similarities to heterogeneous CO_2 reduction reactions. Together, the results highlight the importance of synergistic effects in promoting complex chemical reactions such as CH_4 oxidation and CO_2 reduction. The photooxidation reaction as presented here opens up new doors toward highly selective reforming of CH_4 for high-value industrial chemicals such as CO.

5.9 Reference

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Chapter 6: Conclusions

Solar energy is considered as one of the most ideal renewable energies, which can meet the rising energy demand of human beings. Given its intermittent nature, it is desired to convert solar energy in chemical bonds for ease of storage, transportation and utilization. Photoelectrocatalysis promises a direct route for solar-to- chemical energy conversion. Despite decades of intense research, the efficiency remains low. In addition with discovering new material candidates, significant efforts (this research for instance) have been devoted to understanding the mechanisms behind the low performance.

We focused on controlling the surface band alignment to improve the photovoltage. Comparing with conventional p type semiconductors as photocathodes for PEC water splitting, Cu₂O stands out. It is non-toxic, cost effective and earth abundant, with a direct band gap of 2 eV. However, a fundamental challenge is energy mismatch of Cu₂O with water reduction potential, that the valence band edge is too negative to provide high photovoltage. A pn heterojunction can be formed to address this challenge. As an earth abundant material, ZnS is an n-type semiconductor and has a more negative Fermi level than water reduction potential. Under illumination, an

enhanced built-in field is supposed to be created, that thermodynamically improves photovoltage. Under illumination, Cu₂O with ZnS shows an anodic shift in onset potential as 0.68V vs. RHE, over 0.61V for bare Cu₂O. OCP measurements help understand that thermodynamically greater photovoltage can be generated, since larger measured open-circuit potential for Cu₂O/ZnS is seen in light. Additionally, flat band potential measurements including illuminated OCP measurement under various light intensities and Butler method demonstrate 120mV shift for Cu₂O/ZnS can be observed. The same trend exhibits on fully earth abundant Cu₂O based photocathodes with NiMo/CoMo decoration.

We then focused on understanding the influence of surface chemical species on surface kinetics and energetics. We apply hematite as platform, systematically compare {012} and {001} facets exposed photoanode on particle level. Since surface chemical species are sensitive to atomic structure, we are aiming to provide insights about how different exposed facets contribute to surface kinetics and energetics. The combination of IMPS and OCP measurement have been adopted to probe the surface kinetics and energetics accordingly. From kinetics perspective, although **hematite {012}** exhibit better charge transfer rate constant, on the other hand, these more active sites also act as surface hole/electron recombination centers. From energetics perspective, undesired Fermi level pining is induced on **hematite {012}**, resulting in smaller band bending. These revealed information could help understand the influence of surface chemical species on the current-voltage characteristics.

Furthermore, we integrated Ir based WOCs on hematite to facilitate water oxidation kinetics. We demonstrated that the functionalization of a heterogenized molecular Ir WOC or heterogeneous oxide (IrO_x) on hematite photoanode resulted in 200 mV cathodic shift on onset potential with relatively high stability in acidic solutions. However, it is challenging to uncover the main reasons of the performance enhancement with surface catalysts, due to their cumulative effects and the interface complexities, The lacking of fundamental understanding makes it difficult to further improve these systems for practical applications. It is already demonstrated that application of catalysts could alter thermodynamics or kinetics (or both) of electrodes. Although intense research efforts have been contributed to reveal the role of heterogeneous catalysts, their functionalities still remain unclear due to their undefined molecular structures and working mechanisms. And, this deficiency can be filled by the community of molecular catalysts which preserve clear molecular structures and the probing techniques are rather abundant. Herein, we systematically compared the two aforementioned Ir WOCs. IMPS helps distinguish between changes in the rates of charge transfer and surface states recombination to assess the effects of the surface modification by het-WOC and IrO_x. One of the major assumptions of IMPS is, the light should be mainly absorbed within the depletion layers so that the diffusion of minority carriers towards the depletion layer from the bulk can be neglected. From our results, het-WOC gave rise in derived k trans within the low applied potential window 0.5 V -1.2 V vs. RHE, which indicated a better charge transfer from surface states to electrolyte

leading to the formation of oxygen. While derived k_{rec} remained, implying the surface states preserved identical. In stark contrast, lower derived k_{rec} for IrO_x was observed, which suggested suppression of surface states recombination further leading to better charge separation. Surprisingly, IrO_x shown higher derived k_{tran} due to the redox characteristics. IMPS results revealed that het-WOC might solely serve to provide additional pathways for promoting the forward reaction kinetics, and IrO_x completely replaced original electrode/electrolyte interface which promised both enhanced forward and reduced back reaction kinetics. As complementary information, PEIS was also utilized where potential is modulated at a certain light intensity. Two distinct equivalent circuit models were established based on IMPS results, at which the major components included charge transfer resistance and capacitance of catalyst layer. Simulated data shown that charge transfer resistance reduced for both WOCs, much higher capacitance of IrO_x was measured but for het-WOC only by a small margin. This discrepancy confirms mechanistic differences between het-WOC and IrO_x. In addition, we applied kinetic isotope effect measurements to distinguish the rate determining step of water oxidation for each case.

Lastly, we demonstrated selective CH_4 conversion on photo-excited TiO_2 through PEC approach as a prototypical platform. Photo-excited metal oxide surface promises a feasible and substantial route to generate oxygen radical at ambient conditions. The initial successes were undermined by low yield and poor selectivity to less-value product CO_2 . These fundamental challenges draw the urgent need of identifying surface

bound intermediates and reaction pathways, addressing 1) CH₄ activation on photoexcited metal oxide catalyst surface; 2) involved reaction intermediates; 3) active sites to control selectivity to value-added product. In this dessertation, we reported the first demonstration of selective CH₄ oxidation to CO under mild conditions on a photoexcited TiO₂ prepared by ALD. In addition, the PEC approach brings bonus to effectively separate excited charges to catalytic surface, and provide continuous photoelectro-generation of oxygen active site for catalytic C-H cleavage. More importantly, detailed mechanistic investigations at molecular level were carried out by the combination of experimental (Raman, Infrared spectroscopy, EPR spectroscopy) efforts. It is revealing the formation of methoxy species proceeded through radical activation, and tuning selectivity offered by active Ti species and anodic applied potentials under PEC working conditions. Furthermore, a binding switch from metaloxygen (M-O) to metal-carbon (M-C) was observed in the process of CH₄ to CO, which might shed light on controlling the selectivity of the reverse CO_2/CO reduction towards CH₄ (in Scheme 1). We believe the knowledges generated in this work will provide insights on developments of CH₄ conversion catalyst under mild reaction conditions to achieve high yield and selectivity, also provide a generalized model for guiding the design of heterogeneous catalyst for specific reactions such as CO₂ reduction.

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