

Investigations of Metal Oxide Photocathode Protection Layers and Interfacial Charge Transfer Rates on Graphene Electrodes

Thesis by

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Abstract

Coatings of HfO_2 , Ta_2O_5 , TiO_2 , and Nb_2O_5 were evaluated as protection layers for p-InP photocathodes in aqueous acidic electrolytes. Each candidate protection layer was characterized based on several criteria: interfacial conduction of photogenerated electrons, thermodynamic and kinetic stability of the overlayer throughout the relevant potential and pH range for cathodic fuel-forming half-reactions, and inhibition of the primary anodic and/or chemical dissolution processes that limit electrode stability. Both conduction of photogenerated electrons and inhibition of anodic oxidation were evaluated using $\text{V}^{3+/2+}$ in 5.0 M HCl(aq) as a one-electron redox couple with a potential close to that of hydrogen evolution in acidic media. Failure modes due to cathodic plating of metal, as well as anodic dissolution and chemical dissolution processes, were evaluated for photocathodes made from etched p-InP, platinized p-InP, and p-InP photoelectrodes that had been coated with the various oxide films and then platinized for use in photoelectrochemical hydrogen evolution in acidic aqueous electrolytes. Nb_2O_5 best met all of the previously specified criteria, in contrast, TiO_2 was found to be thermodynamically and kinetically unstable in acid over the potential range relevant for the hydrogen evolution and/or CO_2 reduction electrochemical half-reactions. The protocols developed in this work are broadly applicable for determining the effectiveness of other materials and semiconductors as protection layers for photocathodes.

The electrochemical charge transfer rate at mechanically exfoliated graphene electrodes have also been investigated to probe the coupling distance into the electrode by which redox species in solution electronically couple. Scanning electrochemical cell microscopy (SECCM) was used to measure the rates of charge transfer and to reduce the effect

of graphene defects on the electrochemical measurements. The rates of charge transfer with $\text{Co(en)}_3^{3+/2+}$, $\text{Ru(NH}_3)_6^{3+/2+}$, and $\text{IrCl}_6^{2-/3-}$ redox couples were determined on graphene with different thicknesses, suggesting a coupling distance of 0.3 nm. However, real coupling distance may differ due to the convoluting effects of surface defects, errors inherent to SECCM, and uncertainty in the thickness of graphene.

Published Content and Contributions

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Chapter 1: Introduction

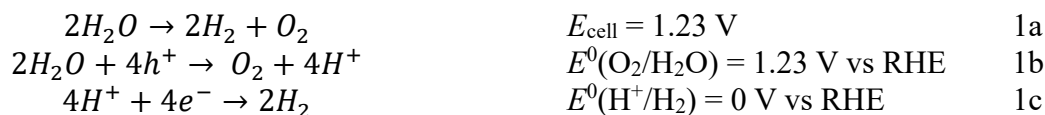
Hydrogen for solar energy storage

As society looks to move toward a renewable energy dominated energy system, the need for storage options has become increasingly important.¹ The energy from the sun and wind can more than easily provide enough energy to power the global energy requirements, but the sun does not always shine, and the wind does not always blow, so energy storage solutions are necessary for reliability.^{1,2} Plants solve this issue by storing extra energy in chemical bonds in the form of sugars. Taking inspiration from nature, chemical fuels that could be used at a large enough scale to support the global energy needs can be found. These candidates include carbon-based fuels, hydrogen, and ammonia.³ There are already industrial processes to convert the various fuels interchangeably, including steam reforming and the Haber-Bosch process, so producing one chemical fuel is enough to generate the various chemical fuels.^{4,5} Plants, which capture sunlight and convert the energy into carbon-based fuels, are the basis of current fossil fuels and modern energy infrastructure. However, the oxidized carbon is released as carbon dioxide, leading to global warming and is dispersed throughout the atmosphere.⁵ Current catalysts to convert CO₂ to carbon-based fuels have also faced chemical selectivity problems, producing a mixture of chemical species rather than any one desired product.⁶ For these reasons, producing carbon-based fuels are difficult. The oxidation of nitrogen is also problematic in that harmful NO_x compounds can be formed. Thus, hydrogen is a promising chemical fuel, though it is not without its problems. Hydrogen gas is extremely explosive if handled improperly, and water splitting can require chemically harsh conditions which makes designing long lasting stable water splitting devices difficult.⁷ Hydrogen does have the benefit that the feedstock, water, is readily available and concentrated (55.5 M). When hydrogen is used as a fuel, the resulting combustion products consist of just water, making it a very clean burning fuel.

Electrochemically generated fuels

Hydrogen can be produced electrochemically by splitting water into hydrogen and oxygen ([Equation 1a](#)). On one side of the electrochemical cell, the anode oxidizes water to form oxygen

(Equation 1b, OER), while on the other side, the cathode reduces the water to produce hydrogen (Equation 1c, HER)



The sum of the half reactions gives the overall Equation 1a of water splitting, requiring at least 1.23 V to split water. In electrochemical studies, the electrode used to perform the reaction of interest is also called the working electrode while the electrode used to perform the other half reaction is called the counter electrode. A third reference electrode is often added to the cell to provide a stable reference potential and to determine the electrochemical potential of the other electrodes. Ideally, no current is allowed to flow through the reference electrode to avoid disturbing the potential of the reference electrode. Supporting electrolyte is also added to the system to minimize solution resistance and prevent migration.⁸

Since water splitting is a multi-electron reaction, extra energy in addition to the thermodynamically required 1.23 V are required to do the reaction. This additional energy, or overpotential, of water splitting is generally quite high without the use of catalysts. Common catalysts for HER and OER include noble metals such as Pt, Ru, and IrO_x, but work has been done to find catalysts with lower overpotentials for HER or OER, and to find earth abundant alternatives.^{9,10} To provide the energy to perform water splitting, an external bias can be applied to the anode and cathode, or semiconductor photoelectrodes can be used to harness the energy in sunlight.

Semiconductor properties

The classification of semiconductors vs. insulators and metals is based on the difference between the valence band and conduction band. While metals have no gap between the valence band and conduction band, semiconductors have a small (~1-3 eV) band gap. This allows electrons in the valence band to be excited by photons in the visible range into the conduction band. Insulators on the other hand, have large band gaps and essentially no electron conduction is observed. Common semiconductors include silicon (Si, $E_g = 1.12 \text{ eV}$), gallium arsenide (GaAs, $E_g = 1.42 \text{ eV}$), indium phosphide (InP, $E_g = 1.34 \text{ eV}$), and gallium indium phosphide (GaInP, $E_g = \sim 1.85 \text{ eV}$).¹¹ GaAs, InP, and GaInP are examples of III-V semiconductors. Ternary and quaternary

III-V semiconductors, such as GaInP and GaInAsP, respectively, have the advantage that the band gaps of such materials can be tuned by changing the ratio of the atomic species while staying lattice matched to the underlying substrate, allowing high quality light absorbers to be grown epitaxially.¹¹

A key consequence of these band gaps is that photons absorbed by the semiconductor must have an energy greater than or equal to the band gap. The absorption of the photon photoexcites an electron from the valence band to the conduction band, leaving behind a hole, or a positively charged pseudo-particle which can behave similarly to an electron. After being photogenerated, these electrons and holes quickly thermally relax to the conduction band minima and valence band maxima respectively. Any extra energy in the photon that was used to excite the electron above the conduction band minimum is lost as thermal energy and cannot be used for work. The selection of the band gap is therefore a balancing act of having a low enough band gap to allow many photogenerated carriers to be formed, while having a high enough band gap to not lose too much energy to thermal relaxation. This balance applied to the solar spectrum is known as the Shockley-Queisser limit, and for a single junction solar cell, is about 33% at a band gap of 1.34 eV.^{12,13} For photovoltaic devices, efficiencies for Si single crystal single junction devices have reached 26.1%, and efficiencies for GaAs have reached 29.1% for single crystal single junction devices.¹⁴ Multijunction III-V cells with solar concentrators have reached up to 47.6%.¹⁴ Solar fuels systems have reached sustained solar-to-fuel efficiencies in excess of 10%, and have shown efficiencies in excess of 19% for short periods.^{15–17}

In addition to the conduction band and valence band, semiconductors have a Fermi level, or a hypothetical energy level at which an electron would have a 50% chance of occupying if such a level were to exist. That is to say, the Fermi level indicates the distribution of electrons in the valence and conduction band at equilibrium, or the free energy of an electron in the semiconductor. Dopant atoms can be added to the semiconductor to add electrons (n-type dopants) or holes (p-type dopants), which shifts the equilibrium distribution of the electrons in the valence and conduction band, and subsequently, the Fermi level. The ability to change the free energy of an electron in a semiconductor by simply changing the dopant density allows the semiconductor to behave in interesting ways that can be harnessed for multiple applications central to the modern world, including computers, LED lights, and solar panels.

When semiconductors come into contact with another material, mobile electrons or holes from the dopant atoms move across the interface until the Fermi levels of the semiconductor and contacting material equilibrates, leaving behind the immobile dopant ions. This region of charged immobile dopant ions creates an electric field at the interface which can cause the valence band and conduction band to “bend” (Figure 1-1). The band bending spatially separates photoexcited electrons from the photoexcited holes, preventing the recombination of the charge carriers and allowing the photoexcited charge carriers to perform useful work. Mobile photoexcited electrons in the conduction band try to move to the lowest energy position, and so the bending of the conduction band can lead to movement of electrons towards or away from the interface for p-type semiconductors or n-type semiconductors, respectively (Figure 1-1). The photocurrent can be harnessed as the charge carriers cross the interface to perform electrochemical reactions of interest such as water splitting or CO₂ reduction.

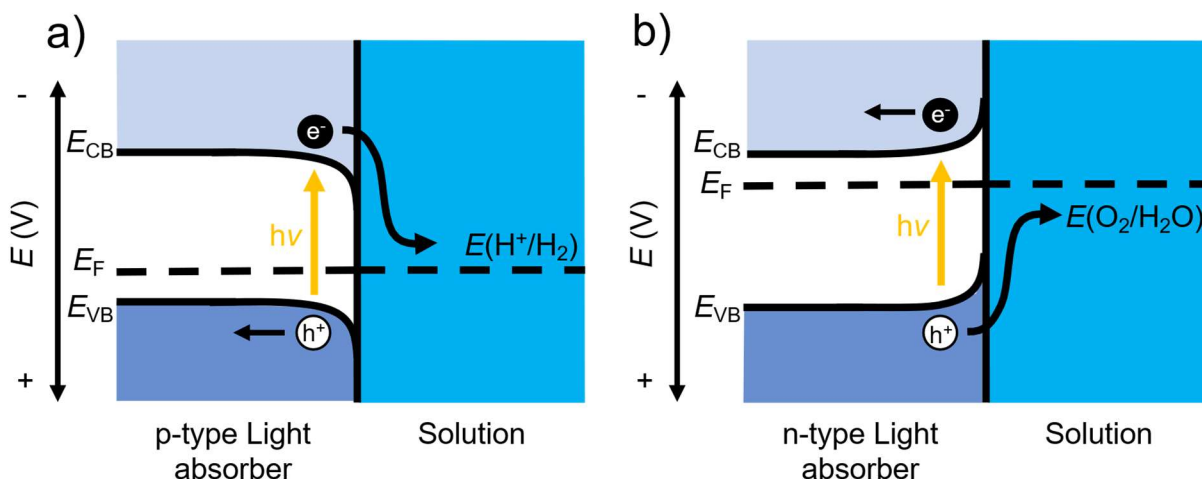


Figure 1-1: Band bending diagram at a p-type semiconductor/liquid interface, and at an n-type semiconductor/liquid interface.

The effects of non-equilibrium phenomena such as external bias, photoexcitation, and recombination, on charge transfer, carrier statistics, and quasi-fermi levels are important for the understanding of semiconductors, but require significantly more in depth discussion than can be described here.^{8,18,19} In short, the band bending formed at the interface as a result of the equilibration process creates a diode, which allows current to flow in one direction while blocking current flowing in the other direction. Application of an external bias, to a first order, bends the

bands more, or un-bends the band. The following diode equation describes the current-voltage behavior of semiconductor junctions.

$$J = J_{ph} - J_0 \left[\exp \left(-\frac{qV}{nkT} \right) - 1 \right]$$

Where J is the current density, J_{ph} is the additional current density induced by the photoexcitation of electron-hole pairs, J_0 is the reverse-bias saturation current, q is the charge of an electron, V is the applied bias, n is the diode quality factor, k is the Boltzman constant, and T is the temperature. The absorption of light by the semiconductor creates electron-hole pairs which can contribute to the photocurrent linearly with the number of photoexcited charge carriers, though at high level injection, higher order terms need to be accounted for.²⁰ The excitation of electron-hole pairs disrupts the equilibrium carrier statistics in a semiconductor, making the concept of a fermi level invalid. Instead, two quasi-fermi levels are used to describe the carrier statistics of the electrons and holes independently. The effects of different recombination mechanisms, such as bulk recombination, depletion region recombination, surface state recombination, tunnelling, and electron transfer can manifest as different J_0 and n in the diode equation. Critically, these recombination mechanisms limit the amount of work that can be extracted from photoexcited charge carriers. In the absence of other recombination mechanisms, bulk recombination will always be present, limiting the photovoltage of photoexcited charge carriers. Non-ideal phenomena such as fermi-level pinning and dipoles can also contribute to complications at the semiconductor interface.^{18,19,21,22}

Photoelectrochemical Cell Design and Photoelectrode stability

Photoelectrochemical cells (PEC) are devices designed to combine the topics discussed above in order to absorb light, separate charges, and produce useful solar fuels all in one device, just like plants. One of the first PEC devices utilized TiO_2 to produce solar driven water splitting in acidic and alkaline aqueous electrolytes.²³ To ensure intrinsically safe operation by ensuring that the $\text{H}_2(\text{g})$ and $\text{O}_2(\text{g})$ do mix at any point in space or time in the operating cell, a separator is used to prevent the recombination of the products back into the reactants.²⁴ Since water splitting produces H^+ at the anode and is consumed at the cathode, the separator must selectively allow the conduction of H^+ or OH^- ions. If a different ion was used to charge balance the system, such as K^+ or Cl^- , the ions would accumulate on one side of the PEC, eventually leading to concentration gradients that

prevent any further current flow and fuel formation. Additionally, the PEC must be operated in highly acidic or alkaline conditions to prevent pH gradients across the device that would reduce the efficiency of the device.²⁴

Unfortunately, strong acid and alkaline are not particularly suitable environments for many of the common semiconductors, especially under diurnal cycles of solar intensity changes.^{25–27} The thermodynamically stable forms of the elements that make up the semiconductors are different from the desired crystalline phase, leading to corrosion of the semiconductor during operation (Figure 1-2).^{25,28,29} The photodecomposition of many semiconducting materials in these aqueous electrolytes were identified and categorized by Gerischer based on the corrosion potentials of the semiconductor relative to the conduction and valence band positions.^{30,31} Due to this fundamental instability, only specific systems for solar fuel energy conversion have been shown to be stable in aqueous electrolytes. n-CdS and n-CdSe were shown to be stable in aqueous solutions containing X_2^{2-}/X^{2-} where $X = S, Se, \text{ and } Te$.^{32–34} Using these same aqueous solutions, n-GaAs, n-GaP, and n-InP have been stabilized,^{35,36} but the toxic nature of the solutions and specificity of the electrochemical systems makes systems which can produce fuels directly without the additional complications of coupled redox systems difficult.

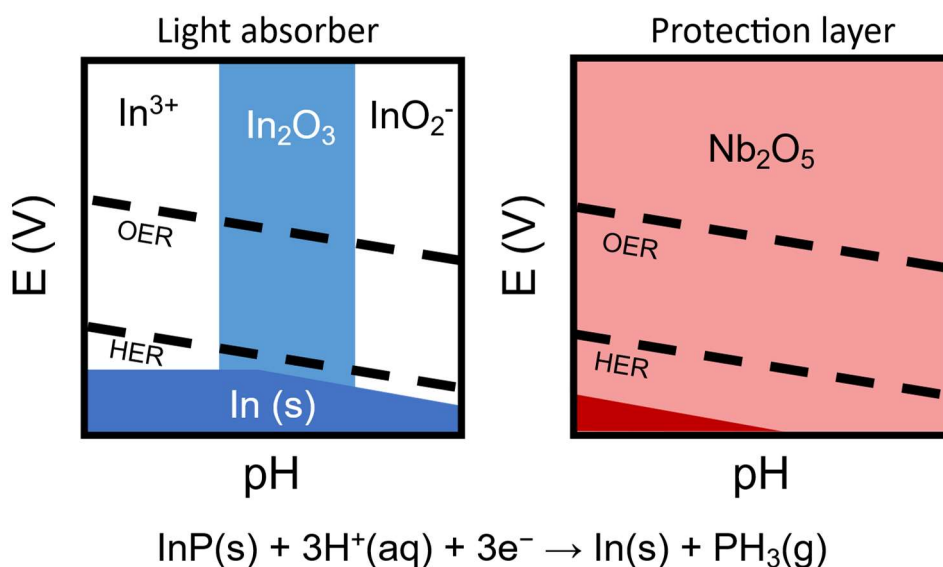


Figure 1-2: Simplified pourbaix diagrams of InP, an example light absorber, and Nb_2O_5 , an example protection layer.^{25,28,29}

To solve this instability, barrier layers have been explored as a method to physically separate the corrosive aqueous electrolyte from the light absorbing semiconductor while still allowing charge transfer for the photoexcited charge carriers into solution. Previous studies have found that TiO₂ coated Si photoanodes were able to prevent corrosion for upwards of 2000 hrs in 1 M KOH.³⁷ In this case, the TiO₂ protection layers allow the photoexcited holes to conduct through oxygen vacancies in the TiO₂ and into the OER catalyst.³⁸ Further studies have found success with various transparent, conductive metal oxides such as NiO_x, CoO_x, SnO_x, and NiCoO_x, with TiO₂ barrier layers attracting the most attention.^{39–43}

Photocathodes on the other hand, have not had the same level of development, and do not currently have barrier layers that have been shown to be stable in the relevant conditions.

The corrosion mechanisms in III-V semiconductors such as InP, GaAs, and InGaP have been elucidated and characterized to primarily consist of dark anodic dissolution and cathodic plating of metals.^{44,45} For InP, metal plating occurs when ions that have been leached from the surface cathodically plate as a metallic In, since the metallic phase is thermodynamically favorable compared to InP at reducing potentials. Anodic dissolution can occur due to chemical or electrochemical oxidation of the surface.⁴⁴ For GaAs, cathodic dissolution occurs due to the thermodynamic and kinetic instability of the surface, resulting in leaching of the Ga and As atoms into solution, either stoichiometrically or preferentially, depending on the specifics of the electrolyte and catalyst used.⁴⁵ GaInP exhibited a combination of cathodic plating and dissolution of the surface similar to InP. The Ga plating potential is more negative than that of In, resulting in the In plating first and affecting the surface chemistry more than Ga.⁴⁶ As a result, by studying the properties of protection layers on InP, the results can be readily extended to GaInP.

In a bare semiconductor surface, the corrosion potential can be 3 places relative to the conduction and valence bands of the semiconductor which dictate the photostability of the semiconductor as defined by Gerisher.^{30,31} If the corrosion potential is above the conduction band minima, then the semiconductor is stable, since any photoexcited electrons will thermalize to the conduction band minima and not be able to reach the corrosion potential. If the corrosion potential is between E_{cb} and E_{vb} , then the semiconductor is quasistable depending on the kinetics of the corrosion reaction. For example, p-InP is cathodically protected in the presence of Pt since the Pt allows hydrogen to kinetically outcompete the corrosion reaction.⁴⁴ In the third case, the corrosion

potential is below E_{vb} , resulting in an unstable material that will actively decompose, since electrons from the valence band can readily react to corrode the material.

Though the fundamental characteristics of a hypothetical barrier layer are thought to be understood, we have yet to show that they work (Figure 1-3). When a protection layer is placed on the surface of the semiconductor, the relative potentials between $E_{cb}(SC)$ and $E_{cb}(PL)$ can affect charge transfer across the SC/PL interface. If $E_{cb}(SC) \gg E_{cb}(PL)$, then photoexcited electrons must overcome an energetic barrier to cross the interface. On the other hand, if $E_{cb}(SC) < E_{cb}(PL)$, then photoexcited electrons can cross the interface without significant energetic barriers (Figure 1-3). Several metal oxides and their conduction band locations relative to the conduction band location of p-InP are shown in Figure 1-4. In addition to the ability to conduct photoelectrons, barrier layers for photocathodes should be optically transparent, hole blocking, chemically stable, and electrochemically stable.

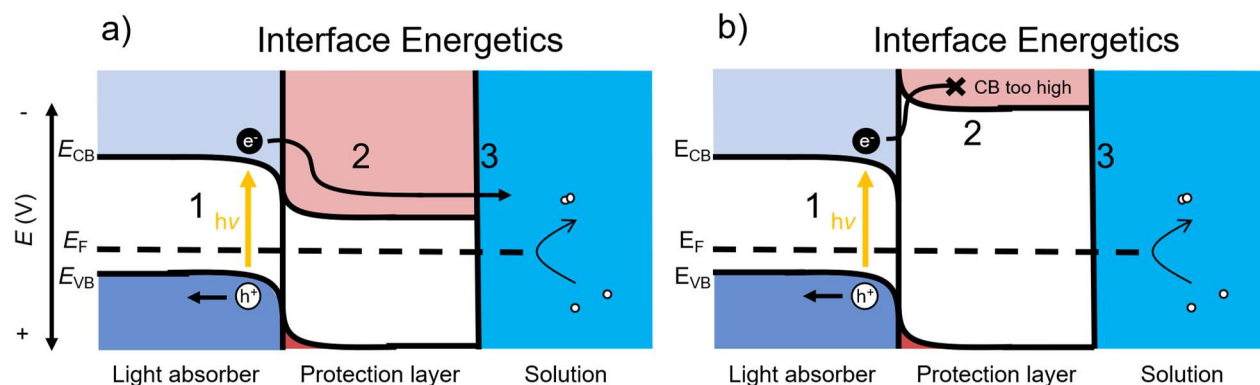


Figure 1-3. Schematic of band alignments and hypothesized electron transfer between a p-type light absorber and protection layer. (a) In the first case, the conduction band of the protection layer, $E_{CB}(PL)$, is positive of the conduction band of the semiconductor light absorber, $E_{CB}(SC)$, allowing facile electron conduction into the protection layer. (b) In the second case, the $E_{CB}(PL)$ is too negative compared to the $E_{CB}(SC)$, creating an energy barrier for electron transfer between the semiconductor and protection layer.

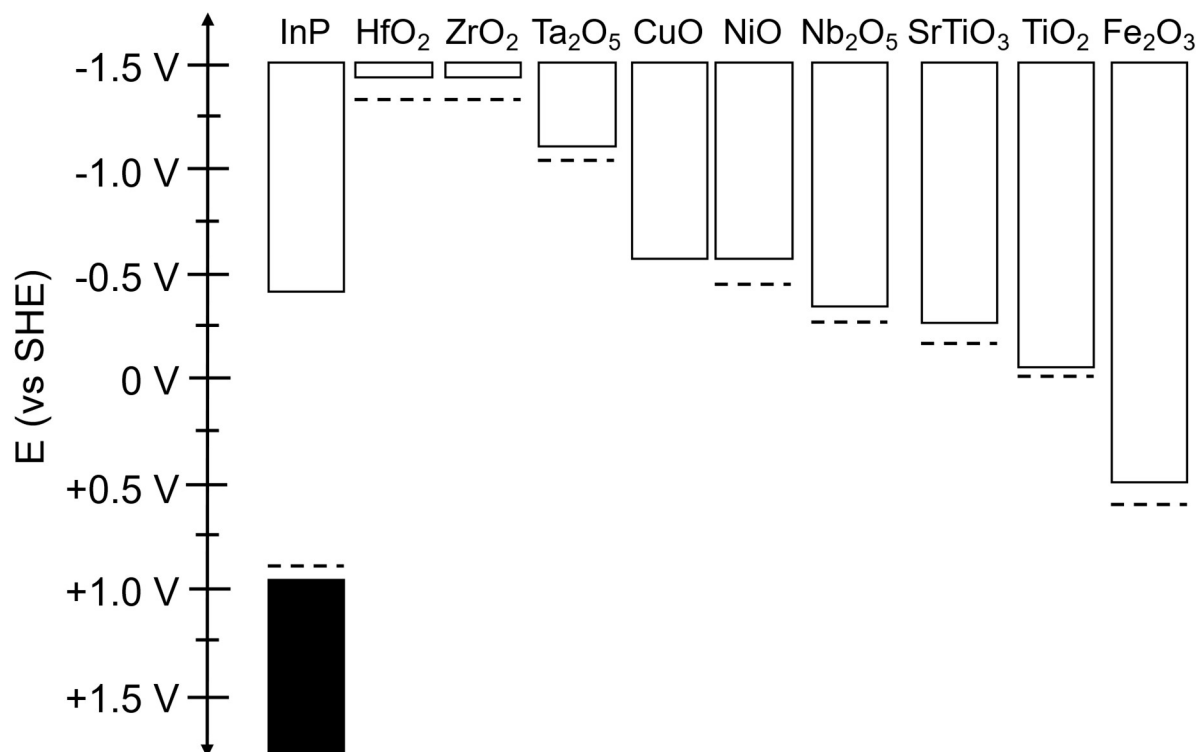
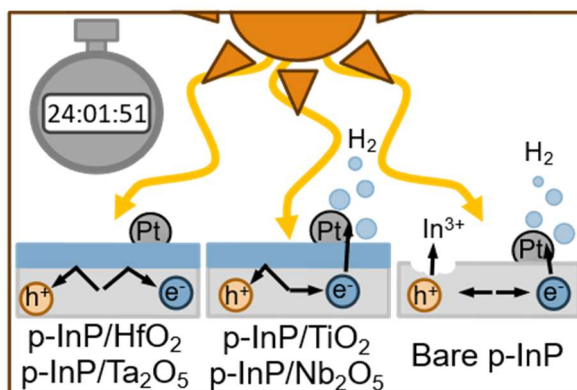


Figure 1-4. Approximate conduction band edges for different metal oxide protection layer candidates relative to p-InP.

Scope of Thesis

This thesis aims to understand the electrochemical behavior of photocathode protection layers and the rate of electrochemical charge transfer reactions that occur at heterogeneous interfaces. Chapter 2 discusses the key properties necessary for p-InP protection layers, such as Nb₂O₅ and TiO₂, to prevent the main failure modes of photocathodes and protocols to evaluate the effectiveness of protection layers. By evaluating a series of metal oxide protection layers with various conduction band edges, the hypothesis of the criteria from photoanode protection layers can be evaluated to see if they can be extended to photocathodes. Chapter 3 investigates the rate of electrochemical charge transfer at graphene electrodes. The coupling length in the Fermi Golden Rule formulation of Marcus theory was investigated using graphene electrodes and scanning electrochemical cell microscopy to determine if the coupling length could be experimentally determined.

Chapter 2: Chemically and Electrochemically Stable Nb₂O₅ Protection Layers for Hydrogen Evolution by p-InP Photocathodes in Acidic Electrolytes



Content for this chapter was adapted from:

- **Ye, A. Z.;** Covelli, D.; Struzyk, A. A.; Bean, P. J. L.; Shen, X. E.; Lewis, N. S. “Nb₂O₅ Protection Layers for Hydrogen Evolution by p-InP Photocathodes in Acidic Electrodes” Accepted to The Journal of Physical Chemistry C. <https://doi.org/10.1021/acs.jpcc.5c07292>.

Semiconductor photoelectrodes are generally unstable in the electrolytes required for safe, efficient oxidation of H_2O to $\text{O}_2(\text{g})$, in conjunction with the reduction of H_2O and/or CO_2 to produce solar fuels.^{7,19,47} Many semiconducting photoanodes have been stabilized by protection layers, with an emphasis on use of TiO_2 deposited by atomic layer deposition (ALD).^{43,48,49} TiO_2 is stable thermodynamically under alkaline conditions at positive potentials,²⁵ thus enabling photoanodes to efficiently sustain the oxygen-evolution reaction. Moreover, 50-60 nm thick TiO_2 films formed by atomic layer deposition provide facile hole conduction to a variety of water oxidation catalysts while protecting the underlying semiconductor from corrosion in 1.0 M $\text{KOH}(\text{aq})$.^{38,43,50,51} Specifically, Si microwire array photoanodes have yielded high photoelectrode energy-conversion efficiencies for $\text{O}_2(\text{g})$ production for thousands of hours of continuous operation under simulated sunlight.³⁷

In contrast to photoanodes, protection layers for fuel-forming photocathodes do not require a defect band to effect rapid hole conduction but instead should allow conduction of photogenerated electrons at or near the potential of the reversible hydrogen electrode (RHE). Moreover, instead of anodic passivation or corrosion by dissolution, the failure modes of photocathodes include cathodic plating of metal, reductive dissolution of the atomic constituents of the semiconducting photoelectrode, and chemical dissolution and dark anodic corrosion at open circuit.^{30,44-46} Additionally, photocathode protection layers need to be stable chemically and electrochemically under more negative potentials than are experienced by photoanodes performing water oxidation.

III-V semiconductor alloys, such as alloys of GaAs, InP, and/or GaP, can have band gaps (E_g) of ~ 1.7 eV, and thus would provide photocathodes that could be paired with oxygen-evolving Si photoanodes to produce a tandem photoelectrochemical cell with nearly optimal energy-conversion efficiency for solar fuel production.^{11,52} At very negative potentials, p-type GaInP and p-InP undergo photocorrosion by plating of metallic In.^{44,46,53-55} However, p-InP (and p-GaInP) can be kinetically stabilized for H_2 production by addition of a Pt catalyst that prevents the minority-carrier quasi-Fermi level from becoming sufficiently negative in potential to reduce InP to In^0 .^{44,56} p-InP is thus a Type II semiconductor as classified by Gerischer,^{30,31} and consequently under continuous simulated solar illumination, p-InP/Pt photoelectrodes provide stable, 12% efficient photoelectrodes for H_2 production in 1.0 M $\text{HCl}(\text{aq})$.⁵⁶ Nanopillars of p-InP protected by 5 nm TiO_2 and coated with Ru as a catalyst for the hydrogen-evolution reaction (HER) have

exhibited stable photocurrent for H₂ evolution for >4 h in 1 M HClO₄(aq) at 0.23 V vs RHE.⁵⁷ p-GaP photocathodes coated with reactively sputtered Nb₂O₅ and a Pt HER catalyst yielded stable photocurrents for <16 h under illumination at 0.63 V vs RHE in 1 M HClO₄(aq).⁵⁸ Also, n⁺p-Si photocathodes that were spin-coated with Nb₂O₅ followed by deposition of a NiPt catalyst produced stable photocurrents for 100 h at 0 V vs RHE in 0.5 M H₂SO₄.⁵⁹ Notably, due to cathodic protection, p-GaP, p-Si, and n⁺p-Si photocathodes are kinetically stabilized by Pt and consequently yield stable photocurrents while effecting the HER in acid,^{46,60,61} confounding conclusions regarding potential benefits of a protection layer for such systems. The primary failure mode of kinetically stabilized p-InP/Pt and related III-V/catalyst photocathodes is irreversible reduction of the interfacial oxide in conjunction with anodic dissolution and/or chemical dissolution of the photoelectrode material at or near open-circuit in the dark, as opposed to degradation while passing cathodic current under illumination near the maximum power point of the cell.^{44,46,56}

In this work, a series of metal oxides (TiO₂, Nb₂O₅, HfO₂, and Ta₂O₅) with different band gaps and conduction band-edge positions was systematically evaluated as protection layers for p-InP photocathodes. Desirable properties include facile conduction of photogenerated electrons for reduction reactions at potentials near RHE, chemical and electrochemical stability under acidic conditions, and the ability to suppress the relevant primary failure modes of chemical dissolution and anodic dissolution near the open-circuit potential in the dark. The approach moreover illustrates a protocol to determine the effectiveness of a protection layer for photocathodes that are kinetically stabilized from decomposition under continuous illumination and consequently should exhibit a stable photocurrent for extended time periods when operated solely under those specific test conditions without any protection layer present.

Conduction of photogenerated electrons

Figure 2-1a shows the current density vs potential (*J-E*) behavior in 350 mM V^{3+/2+}-5.0 M HCl(aq) of illuminated p-InP photocathodes coated with ~50 nm of ALD-deposited TiO₂, Nb₂O₅, HfO₂, or Ta₂O₅. The metal oxides were deposited using 1000 cycles of tetrakis(dimethylamido)titanium(IV) (TDMAT) at 150 °C for TiO₂, 1200 cycles of (t-butylimido)tris(diethylamino)niobium(V) (TBTDEN) at 250 °C for Nb₂O₅, 460 cycles of tetrakis(dimethylamino)hafnium(IV) (TDMAH) at 150 °C for HfO₂, and 1100 cycles of pentakis(dimethylamino)tantalum(V) (PDMAT) at 150 °C for Ta₂O₅. The complete deposition

conditions and electrode fabrication procedures are listed in Table 2-S1 as well as in the supporting information. 50 nm was chosen to minimize pinholes in the barrier layers^{43,62} and to maximize conductivity of the barrier layers. However, the film thickness could be optimized further in specific cases such as for anti-reflective coatings or to reduce the resistance of the films to obtain enhanced performance. The Nernstian potential of the cell, $E(V^{3+/2+})$, was -0.46 V vs SCE. Etched p-InP as well as p-InP coated with Nb₂O₅ or TiO₂ exhibited light-limited current densities of -10 mA cm⁻² at -0.7 V vs SCE. In contrast, p-InP coated with HfO₂ or Ta₂O₅ produced $|J| = <0.5$ mA cm⁻² at potentials <-0.8 V vs SCE (Figure 2-1a). p-InP/TiO₂ and p-InP/Nb₂O₅ electrodes produced photovoltages that were ~560 mV and ~400 mV, respectively, less than the photovoltages produced by etched p-InP electrodes. Mott-Schottky analyses derived from the differential capacitance vs potential behavior of p-InP, p-InP/TiO₂, and p-InP/Nb₂O₅ contacts produced flat-band potentials, E_{fb} , of 0.64 V, 0.58 V, and 0.50 V vs SCE, respectively (Figure 2-S1a and 2-S2). The dopant densities of the Mott-Schottky fits were in accord with the dopant density specified by the manufacturer (Figure 2-S1). The InP/TiO₂ electrodes showed visible thinning of the TiO₂ coating after an hour of electrochemical testing in the $V^{3+/2+}$ -5.0 M HCl(aq) solution. The HfO₂ and Ta₂O₅ were too resistive to obtain reliable Mott-Schottky behavior, and the TiO₂ data may be confounded by the rapid dissolution of the film at or near the pH values of interest.

X-ray photoelectron spectroscopy (XPS) confirmed the composition and oxidation state of the ALD-deposited metal oxides. The p-InP/Ta₂O₅ sample had a Ta 4f_{7/2} binding energy of 25.9 eV attributable to Ta₂O₅, and the p-InP/HfO₂ sample had a Hf 4f_{7/2} binding energy of 16.7 eV attributable to HfO₂.⁶³ The p-InP/Nb₂O₅ sample had a Nb 3d_{5/2} binding energy of 207.3 eV indicative of Nb₂O₅, and the p-InP/TiO₂ sample had a Ti 2p_{3/2} binding energy of 458.5 eV indicative of TiO₂ (Figure 2-S3).⁶³ These ALD-deposited metal oxide films were amorphous, as indicated by x-ray diffraction (XRD) data.

In 5.0 M HCl(aq), $V^{3+/2+}$ is a one-electron redox couple that allows oxidation and reduction at the surface of the photocathodes without concurrent corrosion of p-InP. $V^{3+/2+}$ yields high efficiency junctions with p-InP photoelectrodes, and both forms of the $V^{3+/2+}$ redox species are very soluble in aqueous acid, minimizing mass transport issues that could limit the photocurrent density.⁶⁴ Both forms of the redox couple have optical absorptions dominated by optically forbidden d-d transitions, and the $V^{3+/2+}$ system thus also minimizes any reduction in photocurrent

due to absorption by the redox species in the electrolyte, while being within 0.2 V of RHE in acidic media.⁶⁴ Other redox couples such as methyl viologen ($E^0(\text{MV}^{2+/+}) = -0.446$ V vs the standard hydrogen electrode, SHE)⁶⁵ and $\text{Eu}^{3+/2+}$ ($E^0(\text{Eu}^{3+/2+}) = -0.34$ V vs SHE)⁶⁶ have redox potentials further from $E(\text{H}^+/\text{H}_2)$ than $\text{V}^{3+/2+}$ ($E(\text{V}^{3+/2+}) = -0.22$ V vs SHE). MV^+ moreover absorbs strongly throughout the visible region of the spectrum even at modest (>1 mM concentrations in the electrolyte). Furthermore, $\text{Eu}^{3+/2+}$ is only quasi-reversible in many aqueous solutions.⁶⁶

Figure 2-S4 presents a band diagram scheme depicting the relative positions of the conduction bands and redox potentials. The potential of the conduction-band edge, E_{cb} , of HfO_2 , and $E_{\text{cb}}(\text{Ta}_2\text{O}_5)$, are much more negative than $E_{\text{cb}}(\text{InP})$, creating a substantial energetic barrier that inhibits the transfer of photogenerated electrons across the p-InP/metal oxide interface (Figure 2-S4).⁶⁷⁻⁶⁹ In contrast, $E_{\text{cb}}(\text{TiO}_2)$ and $E_{\text{cb}}(\text{Nb}_2\text{O}_5)$ are close to $E_{\text{cb}}(\text{InP})$ as evidenced by the similar flat-band potentials measured by Mott-Schottky analysis (Figure 2-S1). The relative band-edge positions for the various oxides determined by ultraviolet photoelectron spectroscopy, UPS, are consistent with the observed behavior, although ultra-high vacuum methods do not fully account for the pH dependence of the flat-band potentials of metal oxides in aqueous solutions due to protonation reactions of the surface or any differences in protonation state between the oxide/liquid and oxide/p-InP interfaces.^{70,71} Table 2-S4 lists literature values of E_{cb} for HfO_2 , Ta_2O_5 , TiO_2 , Nb_2O_5 , and InP. The band gap of Nb_2O_5 depends on the crystal phase, but E_{g} for Nb_2O_5 is typically ~ 3.5 eV,^{72,73} as compared to $E_{\text{g}} \sim 3.0$ eV for rutile TiO_2 .^{74,75} The potentials of the valence-band edge (E_{vb}) of metal oxides are generally dominated by the energy of the O 2p level, so E_{vb} is relatively constant between different metal oxides.^{74,76-78} Consequently, the difference in E_{g} between Nb_2O_5 and TiO_2 is expected to yield $E_{\text{cb}}(\text{Nb}_2\text{O}_5) < E_{\text{cb}}(\text{TiO}_2)$. Consistently, $E_{\text{cb}}(\text{InP})$ is ~ -0.4 V vs RHE, $E_{\text{cb}}(\text{TiO}_2)$ is ~ 0.1 - 0.2 V vs RHE, and $E_{\text{cb}}(\text{Nb}_2\text{O}_5)$ is ~ -0.3 V vs RHE (Figure 2-S4).^{78,79}

The difference in electrochemical response between TiO_2 -, Nb_2O_5 -, HfO_2 -, and Ta_2O_5 -coated p-InP photocathodes (Figure 2-1a) is consistent with expectations that lowered energetic barriers at the protection layer/liquid interface improve the conduction of photogenerated electrons into the $\text{V}^{3+/2+}$ - 5.0 M $\text{HCl}(\text{aq})$ solution. The difference in the photovoltages produced by the p-InP, p-InP/ TiO_2 and p-InP/ Nb_2O_5 electrodes is also consistent with the measured differences in E_{fb} in conjunction with the different energetic barriers between the metal oxide protection layers and the $\text{V}^{3+/2+}(\text{aq})$ - 5.0 M $\text{HCl}(\text{aq})$ electrolyte. The more negative value of $E_{\text{cb}}(\text{Nb}_2\text{O}_5)$ relative to $E_{\text{cb}}(\text{TiO}_2)$

is expected to produce a higher energetic barrier for reduction of V^{3+} by TiO_2 -coated electrodes than by Nb_2O_5 -coated electrodes (Figure 2-S4, 2-S5a and 2-S6), in accord with the J - E behavior observed in Figure 2-1a. Relative to an etched Ni electrode, Ni/ TiO_2 and Ni/ Nb_2O_5 electrodes exhibited shifts of ~ -400 mV and ~ -250 mV, respectively, in the J - E behavior for reduction of $V^{3+/2+}(aq)$ (Figure 2-S5a), in accord with expectations for $E_{cb}(Nb_2O_5) < E(V^{3+/2+}) < E_{cb}(TiO_2)$. The photocurrent density observed on all of the p-InP electrodes is less than the maximum theoretical photocurrent density ($\sim 28 \text{ mA cm}^{-2}$)⁵⁶ under 100 mW cm^{-2} of simulated solar illumination due to a long path length in the blue-violet $V^{3+/2+}$ solution and optical reflection losses.

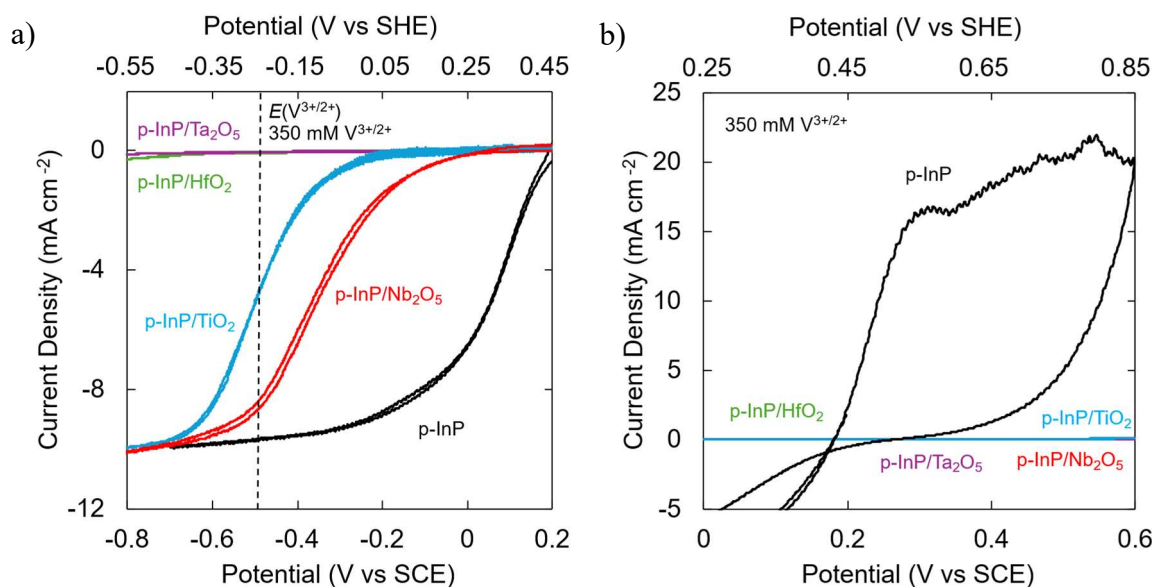


Figure 2-1. J - E behavior of (a) the cathodic region and (b) the anodic region of illuminated p-InP electrodes coated with different barrier layers in a 350 mM solution of $V^{3+/2+}$ in 5.0 M HCl(aq). The solution potential was -0.46 V vs SCE.

Effect of pinholes on photoelectrochemical activity

Figure 2-1b shows the J - E behavior of p-InP/ TiO_2 , p-InP/ Nb_2O_5 , p-InP/ HfO_2 , and p-InP/ Ta_2O_5 electrodes at potentials positive of the open-circuit potential, E_{oc} , in contact with 350 mM $V^{3+/2+}$ - 5.0 M HCl(aq). Etched p-InP electrodes passed $>20 \text{ mA cm}^{-2}$ of anodic current density at $E > 0.3$ V vs SCE, whereas under the same conditions the samples coated with metal oxide protection layers passed $<1 \text{ mA cm}^{-2}$ of anodic current density. Stable photocurrents for kinetically stabilized photocathodes performing the HER could be obtained with a fully insulating oxide overlayer by

flow of charge through pinholes or uncoated areas of the photoelectrode of interest, without substantially affecting the primary failure mode of such systems, so identifying the role of pinholes on the photoelectrochemical behavior is important in understanding the conductivity of these barrier layers. The small limiting anodic current density of the coated p-InP electrodes indicates that the metal oxide coatings suppress transfer of holes from the semiconductor to the electrolyte, reducing the rate of anodic dissolution of InP. The data demonstrate that the interfacial charge transfer occurs predominantly through the Nb₂O₅ films.

The remaining anodic current density is consistent with exposure to the electrolyte of ~0.1% of the surface area of the coated samples, based on studies of GaAs photoanodes that were coated with oxides deposited in air by ALD.^{62,80} The change in photovoltage between the etched p-InP electrodes and the coated p-InP electrodes (Figure 2-1a) indicates that the voltametric behavior is determined by the p-InP/oxide/liquid interfacial structure as opposed to being determined by pinhole-exposed areas that produce direct contact between the p-InP and the V^{3+/2+} electrolyte. Furthermore, the mutually similar light-limited current densities observed for TiO₂-coated, Nb₂O₅-coated, and etched p-InP electrodes indicate that electrons flow through the coated areas of the TiO₂- and Nb₂O₅-coated samples as opposed to flowing solely through pinholes in the protection layers.

Stability of p-InP/Nb₂O₅ Photocathodes for Hydrogen Evolution

Figure 2-2a shows the J - t behavior of p-InP, p-InP/Pt, p-InP/Nb₂O₅, and p-InP/Nb₂O₅/Pt electrodes held at 0 V vs RHE in 1.0 M H₂SO₄(aq) under 100 mW cm⁻² of simulated solar illumination. Within 30 min, the cathodic current density of etched p-InP electrodes decreased from ~6 mA cm⁻² to <0.1 mA cm⁻². Under these conditions a visible film of off-white/grey In/InO_x, indicative of photocorrosion, formed rapidly on the etched p-InP electrode.⁴⁴

p-InP/Nb₂O₅ electrodes initially exhibited cathodic current densities of $|J| < 0.1$ mA cm⁻², with a steady increase in cathodic current density after 6 h to $|J| > 1$ mA cm⁻². The current density fluctuated over the remaining 18 h of the experiment. The gradual increase in current density after the initial 6 h of the p-InP/Nb₂O₅ electrode is consistent with reduction of the Nb₂O₅ layer into a more conductive phase, and/or cathodic plating of In⁰ at exposed pinhole sites. In⁰ is a relatively inactive catalyst for the HER but may catalyze the HER more effectively than Nb₂O₅. In contrast,

p-InP/Pt and p-InP/Nb₂O₅/Pt electrodes produced $J = -17 \text{ mA cm}^{-2}$ for 24 h of continuous operation at 0 V vs RHE.

InP/TiO₂ and InP/TiO₂/Pt electrodes held at 0 V vs RHE in 1.0 M H₂SO₄(aq) for 24 h under 100 mW cm⁻² illumination resulted in dissolution of the TiO₂ film. Figures S7 and S8 show optical images and XPS data of TiO₂-coated electrodes before and after electrochemical testing, indicating that TiO₂ was no longer present after electrochemical testing.

HfO₂ and Ta₂O₅ did not facilitate interfacial electron flow at negative potentials even with a one-electron redox couple in solution (Figure 2-1), so these materials are unsatisfactory as photocathode protection layers despite their chemical stability at or near $E(\text{H}^+/\text{H}_2)$ in acidic electrolytes.²⁵ According to the Pourbaix diagrams, TiO₂ is thermodynamically stable at $E(\text{H}^+/\text{H}_2)$ under alkaline conditions but corrodes at $E(\text{H}^+/\text{H}_2)$ in acidic conditions.²⁵ The rapid dissolution of the TiO₂ film (Figure S7 and S8) under operating conditions for the HER underscores the ambiguity associated with phenomenological stability measurements, such as the number of consecutive hours of photocurrent stability, for photocathodes that are kinetically stabilized in the absence of any protection layer. Nb₂O₅ is thermodynamically stable over the entire pH and potential range of interest,^{25,59,81} in contrast to TiO₂ and other metal oxides with $E_{\text{cb}} < E(\text{H}^+/\text{H}_2)$ in 1.0 M H₂SO₄(aq), such as BaTiO₃, SrTiO₃, and SnO₂.^{25,28,29,77} Hence, of the metal oxides tested, on the basis of chemical stability Nb₂O₅ was the most suitable oxide for use as a protection layer for p-InP.

TiO₂ displays an optical absorption peak at 375 nm that is associated with Ti³⁺ defects.⁸² When held at or near $E(\text{H}^+/\text{H}_2)$ in 1.0 M H₂SO₄(aq), the TiO₂ film formed a visible blue color (Figure 2-S9a).⁸² In contrast, spectroelectrochemical measurements showed that the Nb₂O₅ sample did not exhibit a distinctive absorption in this spectral range under potential control at 0 V vs RHE (Figure 2-S9b). Consistently, in 1.0 M H₂SO₄(aq), electrochromism of Nb₂O₅ onsets at potentials <0 V vs RHE,⁸³ whereas electrochromism of TiO₂ onsets at ~0.2 V vs RHE.⁸² Both oxides showed an increased background absorption throughout the potential sweep that resulted from scattering by evolved H₂ gas bubbles. Electrochromism of TiO₂ requires time to develop at steady state and thus affect the spectral absorption of the barrier layer.⁸² Additionally, the spectrum of the light source used in these experiments, an ENH-type tungsten halogen lamp with a dichroic rear reflector,⁸⁴ is red-shifted compared to the Air Mass 1.5 solar spectrum.⁸⁵ Hence, unlike TiO₂, Nb₂O₅ films do

not decrease the light-limited photocurrent density or result in trap states near the conduction-band edge while effecting the HER in aqueous electrolytes.

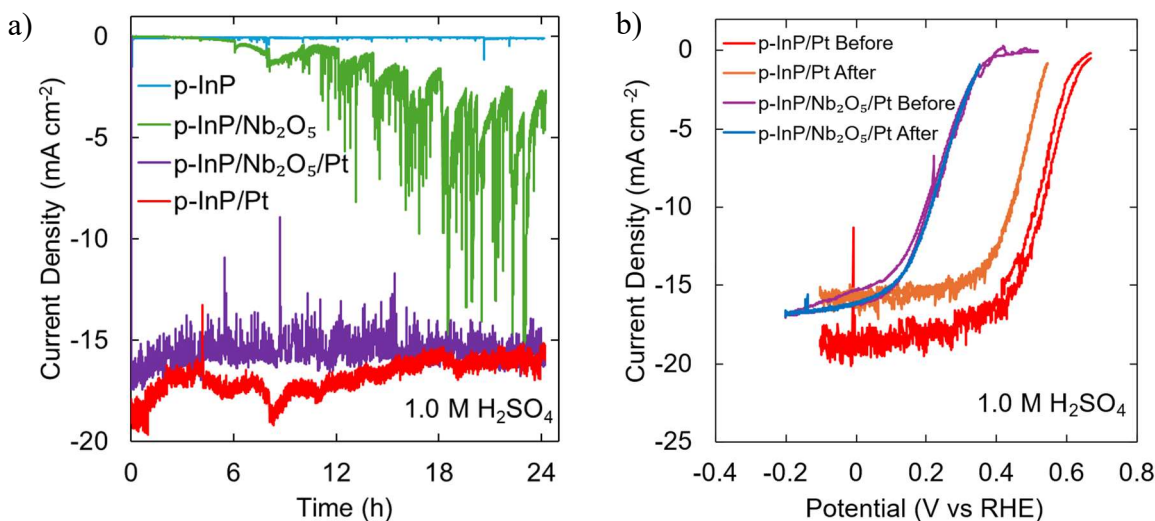


Figure 2-2. (a) J - t behavior of p-InP electrodes with Nb₂O₅ with or without Pt in 1.0 M H₂SO₄(aq) held at 0 V vs RHE under illumination. (b) J - E behavior of p-InP/Pt and p-InP/Nb₂O₅/Pt electrodes before and after the 24 h hold.

Figure 2-2b shows the J - E behavior of p-InP/Pt and p-InP/Nb₂O₅/Pt electrodes before and after, respectively, 24 h at 0 V vs RHE. Figure S10 shows the J - E behavior of p-InP and p-InP/Nb₂O₅ electrodes before and after, respectively, 24 h at 0 V vs RHE. After 24 h of continuous operation, the open-circuit potential, E_{oc} of the p-InP/Pt electrode decreased from 650 mV to 550 mV vs RHE, whereas the E_{oc} of the p-InP/Nb₂O₅/Pt electrodes remained at ~350 mV vs RHE (Figure 2-2a). Mott-Schottky analysis indicated that the flat-band potential in contact with 1.0 M H₂SO₄(aq) was 0.96 V, 0.89 V, and 0.82 V vs RHE, respectively, for p-InP/Pt, p-InP/TiO₂/Pt, and p-InP/Nb₂O₅/Pt electrodes (Figure 2-S1b). Compared to platinized Ni electrodes, Ni/TiO₂/Pt and Ni/Nb₂O₅/Pt electrodes exhibited overpotentials of ~100 mV and ~150 mV, respectively, for reduction of protons in 1.0 M H₂SO₄(aq) (Figure 2-S5b), although the Ni/TiO₂/Pt electrodes appeared to be more resistive than the Ni/Nb₂O₅/Pt electrodes at comparable thicknesses of these two oxide films. This behavior is consistent with expectations for $E_{cb}(\text{TiO}_2) \sim 0.1\text{-}0.2$ V vs RHE, whereas $E_{cb}(\text{Nb}_2\text{O}_5)$ is ~ -0.3 V vs RHE.

After 24 h at 0 V vs RHE under continuous 100 mW cm⁻² of simulated solar illumination, p-InP and p-InP/Pt electrodes showed XPS emissions ascribable to In⁰ and InO_x (Figure 2-S11 and

2-S12). No In XPS emissions were detectable on either the p-InP/Nb₂O₅/Pt or p-InP/Nb₂O₅ electrodes following 24 h of continuous illumination at 0 V vs RHE (Figure 2-S11 and 2-S12). p-InP/Nb₂O₅/Pt and p-InP/Pt electrodes both showed emissions ascribable to In⁰/InO_x after 24 h in the dark at E_{oc} (Figure 2-S13).

Scanning electron micrographs (SEM) showed substantial corrosion and roughening of the surface of etched p-InP held under illumination at 0 V vs RHE in 1.0 M H₂SO₄(aq), whereas under the same conditions the corrosion of p-InP/Nb₂O₅ electrodes was confined to pinholes where the Nb₂O₅ layer did not fully cover the p-InP substrate (Figure 2-S14).

The chemical and anodic dissolution corrosion behavior was quantified by inductively coupled mass spectrometry (ICP-MS) data for p-InP, p-InP/Pt, p-InP/Nb₂O₅, and p-InP/Nb₂O₅/Pt electrodes held under 100 mW cm⁻² of simulated solar illumination for 24 h at 0 V vs RHE as well as for electrodes held at open-circuit in the dark (Figure 2-3). Etched p-InP electrodes exhibited an order of magnitude greater dissolved In³⁺ in the solution than did the kinetically stabilized p-InP/Pt electrodes (Figure 2-3a). For the electrodes held at open-circuit in the dark, the E_{oc} for p-InP/Pt electrodes varied from -0.2 V vs RHE to 0.3 V vs RHE, whereas E_{oc} for p-InP/Nb₂O₅/Pt electrodes varied from -0.1 V vs RHE to 0.05 V vs RHE. In the dark at open circuit, the dissolution rate of p-InP/Pt electrodes was 2.3 nm h⁻¹, whereas p-InP/Nb₂O₅/Pt electrodes exhibited a dissolution rate of <0.05 nm h⁻¹ (Figure 2-3b). Table 2-S5 lists the current density, photovoltage, and dissolution rates obtained from the experiments in this work. Specifically, the ALD-coated Nb₂O₅ films substantially reduce the rates of the primary failure mode of p-InP photocathodes. The Nb₂O₅ films thus block interfacial hole transfer and suppress the primary failure mode of p-InP electrodes in the dark in addition to facilitating kinetic stabilization of the photoelectrode for the HER under illumination.⁴⁴ The remaining dissolution is ascribable to pinholes that are known to occur on oxide films deposited in air using ALD to form protection layers for photoanodes.⁶² In contrast to phenomenological measurements of photocurrent stability, measurements of the rate of the primary dissolution failure mode in both the light and dark presented herein allow quantitative calculation of the durability of these protected photocathodes for any combination of selected operational conditions and substrate thicknesses.

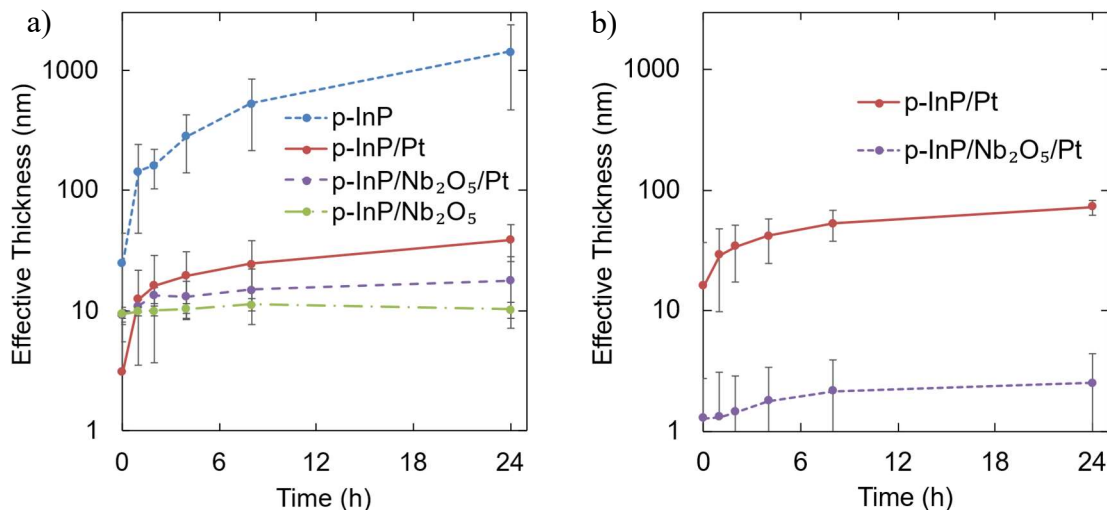


Figure 2-3. ICP-MS data of the (a) effective dissolution thickness of p-InP over time during 24 h at 0 V vs RHE, and (b) effective dissolution thickness of p-InP over time during 24 h at open circuit in the dark.

The differences between the photovoltages of the etched, TiO₂-coated, and Nb₂O₅-coated p-InP photocathodes can be primarily attributed to differences in E_{fb} in conjunction with differences in the energetic barriers between the metal oxide protection layer and the solution (Figure 2-S4 and 2-S6). $E_{cb}(\text{Nb}_2\text{O}_5) < E(\text{V}^{3+/2+})$, so reduction of V^{3+} to V^{2+} by electrons photoinjected into the Nb₂O₅ protection layer is thermodynamically favorable. The J - E behavior of Ni/Nb₂O₅ electrodes shows residual kinetic barriers for V^{3+} reduction that result in ~250 mV overpotential to produce cathodic current densities of 1-10 mA cm⁻² (Figure 2-S5a). In contrast, $E_{cb}(\text{TiO}_2) > E(\text{V}^{3+/2+})$, so reduction of V^{3+} by photoinjected electrons in the TiO₂ protection layer has both thermodynamic and kinetic barriers. Consistently, the J - E behavior of Ni/TiO₂ electrodes shows a ~400 mV overpotential to produce cathodic current densities of 1-10 mA cm⁻² for reduction of V^{3+} in 5.0 M HCl(aq) (Figure 2-S5a). $E_{cb}(\text{TiO}_2)$ is close to $E(\text{H}^+/\text{H}_2)$ and $E_{cb}(\text{Nb}_2\text{O}_5) < E(\text{H}^+/\text{H}_2)$, so Ni/TiO₂/Pt and Ni/Nb₂O₅/Pt interfaces exhibit lower overpotentials for H^+ reduction than for reduction of V^{3+} (Figure 2-S4, 2-S5b, 2-S6). Metals with a low work-function, such as Ni, yield low interfacial barriers for hole conduction at TiO₂/1.0 M KOH(aq) interfaces relative to metals with a high work function, such as Ir, that form rectifying contacts to TiO₂ deposited by ALD and thus yield low photovoltages for O₂(g) production in 1.0 M KOH(aq).³⁸ Hence, optimization of the interfacial charge-transfer kinetics between the protection layer and 1.0 M H₂SO₄(aq) would be expected to

minimize the ~ 100 mV and ~ 150 mV interfacial overpotentials of the p-InP/TiO₂/Pt and p-InP/Nb₂O₅/Pt photocathodes, respectively, for the HER in 1.0 H₂SO₄(aq) (Figure 2-S5b).⁸⁶

The remaining difference in photovoltage between the various protected p-InP photocathodes arises predominantly from the electrical characteristics of the interface between the p-InP and the oxide protection layer. In contact with 1.0 M H₂SO₄(aq), the open-circuit voltage of p-InP/Nb₂O₅/Pt photocathodes is lower than that of p-InP/Pt photocathodes. However, the photovoltage of p-InP electrodes is beneficially affected by formation of a submonolayer of interfacial InO.^{64,87} For example, a photovoltage of ~ 0.65 V is obtained when titanium (IV) isopropoxide (TTIP) is used as the ALD precursor to form TiO₂ protection layers on p-InP photocathodes.⁸⁸ Hence, interfacial engineering of the intervening oxide through the insertion of ultrathin layers or interfacial dipoles and of the InP band-edge positions could improve the photovoltage of the p-InP/Nb₂O₅/Pt photoelectrodes while retaining the beneficial stability characteristics of the Nb₂O₅ protection layer. Improvement of the metal oxide/catalyst contact through careful selection of catalyst deposition method and composition may also minimize the overpotentials at the oxide/catalyst/liquid interface. Due to the large pH stability window of Nb₂O₅, Nb₂O₅ may be also suitable as a protection layer for a variety of solar fuels reduction reactions such as N₂ reduction or CO₂ reduction. Moreover, p-GaInP shares primary failure modes with p-InP, but p-GaInP is more resistant to metal plating than p-InP due to the more negative plating potential of Ga relative to In.^{25,89} Hence, extension of Nb₂O₅ protection layers to p-GaInP, which has a near-optimal band gap of $E_g = 1.7$ eV for use in a tandem photoelectrode structure for fuel formation,^{11,49,52,55} should reasonably be expected. Stabilization of p-GaInP would therefore provide a last missing component of a first-generation prototype tandem full photoelectrochemical cell that efficiently splits water for extended periods of time into separate streams of H₂ and O₂.^{5,11,49,90}

In summary, ALD-deposited barrier layers suitable for the protection of photocathodes need to conduct photogenerated electrons, block interfacial transfer of holes, and be stable in acidic or alkaline solutions at potentials near RHE. The band alignment between Nb₂O₅ and p-InP facilitates conduction of photogenerated minority carriers through the protection layer, to effect fuel-forming reductive half-reactions. The Nb₂O₅ blocks interfacial hole transfer and consequently inhibits anodic dissolution of p-InP photocathodes, resulting in a lower rate of InP dissolution in the dark

at open circuit than kinetically stabilized p-InP photocathodes, which are cathodically protected only under illumination. Furthermore, Nb₂O₅ is stable over the range of negative potentials and pH values required for efficient, safe water splitting. Relative to TiO₂, the shift in E_{cb} of Nb₂O₅ advantageously minimizes the electrochromism, blue-coloration and trap-state filling at potentials near RHE where the reductive half-reactions for fuel formation proceed, and additionally minimizes the energetic barrier for photogenerated minority-carrier electrons to reduce water to H₂ relative to the energies of the trap-state levels or the conduction-band edge energy of the oxide in the protection layer. The data demonstrate that the interfacial charge flows predominantly through the Nb₂O₅ films and moreover allow quantitative evaluation of the effects of residual pinholes in the film on suppressing the primary failure mode, anodic and/or chemical dissolution, of p-InP photocathodes being used for hydrogen evolution in acid. The protocols described in this work should also be useful in identification of other barrier layer materials for photocathode protection.

Non-aqueous testing of p-InP electrodes

In an attempt to probe the effect of barrier layers on the surface energetics of p-InP, non-aqueous studies in acetonitrile were performed. Assuming the Fermi levels are not pinned, the built-in voltage, V_{bi} , of bare p-InP should depend on the solution potential while protected surfaces should be isolated from the solution potential, preventing large changes to V_{bi} . Ferrocene ($E^0(\text{Fc}^{+/0}) = 0.541 \text{ V vs SHE}$), decamethylferrocene ($E^0(\text{Fc}^{*+/0}) = 0.073 \text{ V vs SHE}$), and cobaltocene ($E^0(\text{Cp}_2\text{Co}^{+/0}) = -0.79 \text{ V vs SHE}$) were chosen to effect the solution over a wide potential range.²¹ Ideally, the V_{bi} for a bare p-InP electrode should be close to 0 V for ferrocene and >1 V for cobaltocene. However, the V_{bi} of bare p-InP did not change significantly, V_{bi} only slightly decreased by 0.25 V in the Fc solution compared to Cp₂Co (Figure 2-4). TiO₂-coated p-InP displayed a similar magnitude change, though positive compared to bare p-InP.

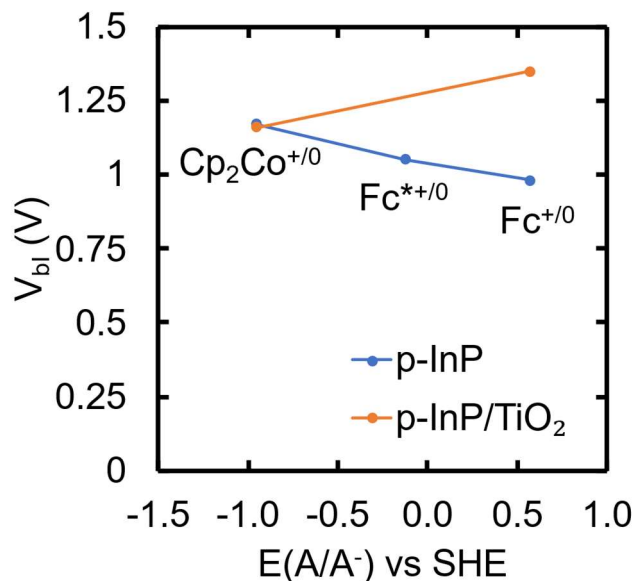


Figure 2-4. Built in voltages for p-InP and p-InP/TiO₂ electrodes in acetonitrile with different redox couples in solution.

The relative pinning of p-InP was likely a result of oxide contamination from the presence of O₂ or H₂O. The Fc redox couple also likely oxidized the surface of the bare p-InP, further worsening the problem. Though care was taken to avoid oxygen and water contamination, the formation of sub-monolayer InPO_x is known to affect the photovoltage of p-InP electrodes.⁸⁷ The oxide usually beneficially improves the photovoltage of p-InP electrodes compared to oxide-free surfaces, and is, in some cases, required for the operation of p-InP photocathodes.⁶⁴ This oxide however, prevents the solution potential from directly influencing the V_{bi} of even bare p-InP electrodes, making this method of determining the conformality of barrier layers in non-aqueous electrolytes difficult. Through more careful control and water/air free etching of the p-InP surface, it may be possible to prevent the formation of InPO_x and to observe an un-pinned p-InP surface. However, due to the inherent inability to distinguish between InPO_x pinning and barrier layer isolation, non-aqueous studies as a method to characterize the conformality of barrier layers and effect of pinholes on the surface energetics of p-InP may not be possible.

The method discussed earlier in this chapter using V^{3+/2+}-HCl(aq) was used to overcome the problems found in the non-aqueous redox method. InPO_x is soluble in acidic conditions, resulting in an un-pinned bare p-InP surface^{44,64} and allowing coated samples to be distinguished from uncoated samples (Figure 2-1).

Additional Future Directions

Further characterization of the interfaces such as the InP/InPO_x and MO_x/Catalyst interfaces could provide useful insight into the low photovoltages and large overpotentials observed for p-InP/TiO₂ and p-InP/Nb₂O₅ electrodes. Different ALD precursors for the MO_x protection layer may allow favorable InPO_x formation or doping of the metal oxide.⁸⁸ No evidence of mid-gap defect states were observed in the XPS of TiO₂ and Nb₂O₅ films that were fabricated with the nitrogen containing ALD precursors (TDMAT and TBTDEN), and previous studies have shown that the presence of defect states does not vary with deposition method.⁹¹ However, the use of oxygen containing ALD precursors such as titanium isopropoxide (TTIP) or niobium ethoxide may affect the formation of mid-gap states, providing an alternative hypothesis for the low photovoltages that were observed for the coated p-InP samples. The oxidizing conditions in the ALD may also lead to the formation of unexpected InPO_x that could be avoided using different deposition methods or deposition conditions such as sputtering. Sputtering may also produce crystalline metal oxide barrier layers which have different conduction band locations than the amorphous materials studied here.^{92,93} Furthermore, lower work function catalysts such as Ru, NiP, and CoP may provide better charge transfer between the protection layer and catalyst by forming an ohmic contact between the metal oxide and catalyst. Alternatively, a thin interlayer of a metal that forms an ohmic contact with the metal oxide protection layer, such as Ni, can be used as an interfacial layer to promote charge transfer between the metal oxide and catalyst.³⁸ Once the interfacial energetics at the metal oxide barrier layers have been investigated, the extension of the photocathode protection layers to p-GaInP should be straightforward due to the similar corrosion mechanisms of p-InP to p-GaInP. This application of photocathode protection layers would allow fully stable tandem PEC devices to be fabricated and the demonstration of highly efficient and stable solar-to-hydrogen devices.

In addition, the effectiveness of these protection layers should also be characterized in base, where the kinetic stabilization of p-InP does not occur in the presence of Pt. Despite the predicted stability of Nb₂O₅ in base by the Pourbaix diagrams,²⁵ initial studies showed some flaking and delamination of the amorphous Nb₂O₅ film when p-InP/Nb₂O₅/Pt electrodes were tested in 1.0 M KOH (Figure 2-5). It should be noted however, that this flaking is distinct from the dissolution observed in TiO₂, which isotropically dissolved from the surface of the p-InP in acidic pH under reducing bias (Figure 2-S7). The flaking of the film may not be related to the stability of the Nb₂O₅,

but rather the $\text{Nb}_2\text{O}_5/\text{InP}$ interface. Different fabrication methods or post processing need to be explored to allow Nb_2O_5 to be stable in KOH . When TiO_2 was used as the protection layer in 1.0 M $\text{KOH}(\text{aq})$, no obvious thinning of the film or delamination was observed, but the photocurrent decayed from 5 mA cm^{-2} to $< 1 \text{ mA cm}^{-2}$ (Figure 2-6). The lower photocurrent may be an indication that InP corroded from the pinholes and subsequently plated onto the TiO_2/Pt surface, reducing the photocurrent significantly over time. These electrodes, however, were not rigorously characterized, and more work needs to be performed to fully understand the behavior of these protection layers in alkaline electrolytes.

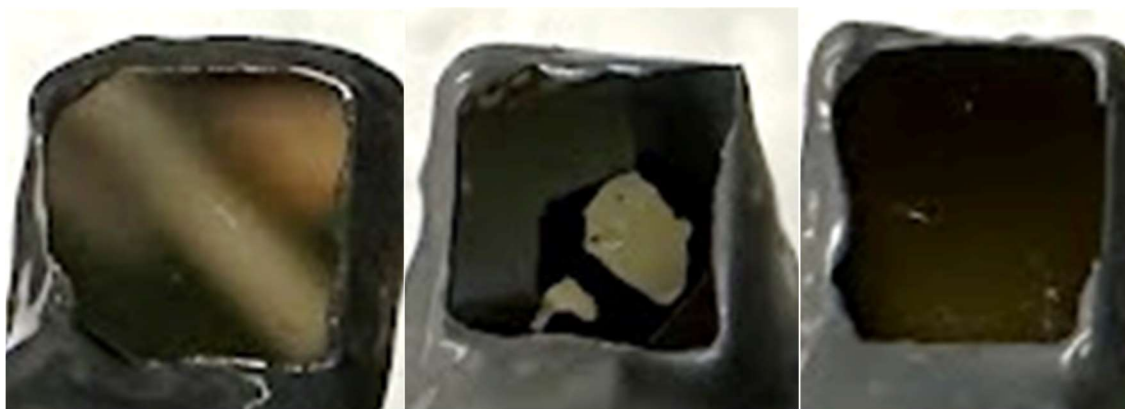


Figure 2-5. Optical images of (a) as prepared $\text{p-InP/Nb}_2\text{O}_5/\text{Pt}$ electrodes alongside $\text{p-InP/Nb}_2\text{O}_5/\text{Pt}$ electrodes held at reducing potentials in (b) 1 M KOH and (c) 1 M H_2SO_4 for 2 h. There is distinct delamination of the Nb_2O_5 layer on the electrode held in 1 M KOH which is not present on the electrode tested in 1 M H_2SO_4 .

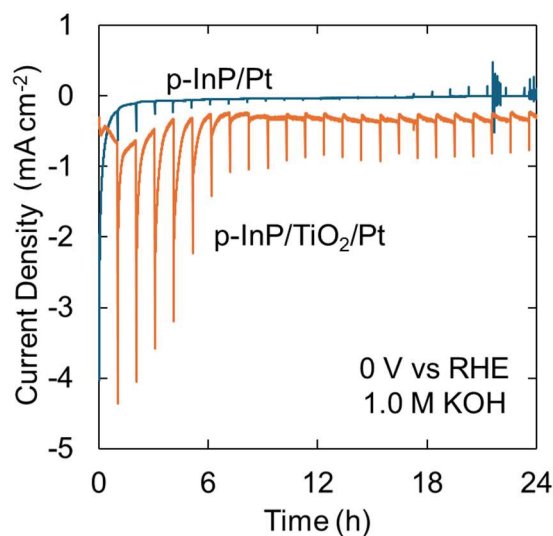


Figure 2-6. *J-t* behavior for p-InP/Pt and p-InP/TiO₂/Pt electrodes in 1.0 M KOH held at 0 V vs RHE for 24 h.

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Experimental Methods

Materials

p-type InP wafers (ATX Inc.) were (100)-oriented, single-side polished, and Zn-doped ($N_d = 1.8 \times 10^{17} \text{ cm}^{-3}$). The following reagents were used as received: bromine (Br_2 , ACS reagent grade, Sigma Aldrich), methanol (CH_3OH , 99.8%, ACS, VWR Analytical), ammonium hydroxide (NH_4OH , 28-30%, ACS, Sigma Aldrich), conductive silver paint (PELCO, Ted Pella, Inc), epoxy (Hysol-9460), vanadium (V) oxide (V_2O_5 , >99.6% trace metal basis, Sigma Aldrich), zinc (Zn, granular, Acros Organics), mercury (Hg, 99.9998%, Alfa Aesar), potassium tetrachloroplatinate (II) (K_2PtCl_4 , 99.9% - Pt, STREM), potassium chloride (KCl, ACS, Macron), hydrochloric acid (HCl, ACS, Sigma Aldrich), nitric acid (HNO_3 , ACS, Sigma Aldrich), sulfuric acid (H_2SO_4 , 95.0-98.0%, ACS, JT Baker), hydrogen (H_2 , UHP, Airgas), oxygen (O_2 , UHP, Airgas), argon (Ar, UHP, Airgas) and nitrogen (N_2 , UHP, Airgas). The niobium precursor ((t-butylimido)tris(diethylamino)niobium(V), 98%+, STREM), titanium precursor (tetrakis(dimethylamido)titanium(IV), 99.999%, Sigma Aldrich), hafnium precursor (tetrakis(dimethylamino)hafnium(IV), 98%+, STREM), and tantalum precursor (pentakis(dimethylamino)tantalum(V), 98%+, STREM), were loaded into new ALD cylinders in a N_2 -purged glovebox that contained <10 ppm O_2 . Ultrahigh purity water (18.2 M Ω cm, Thermo Scientific Nanopure system) was used as the oxidant during ALD and for making electrochemical solutions. The H_2SO_4 was diluted with water to 1.0 M for electrochemical experiments.

InP Etching and Ohmic Contact

Ohmic back contacts were made to p-type InP wafers via a two-step sputtering and subsequent annealing process. First, 10 nm of Zn was sputtered onto the wafers, followed by 90 nm of Au. Sputter deposition was performed in a custom-built RF sputtering system with a base pressure of 5×10^{-7} Torr. The sample was rotated during the deposition, and sputtering was performed under 2 mTorr Ar at 60-70W, at a rate of $0.8 \text{ \AA s}^{-1}$ as measured by a quartz microbalance, until the desired film thickness was obtained. The sample was then annealed under forming gas for 10 min at 400 °C.

Prior to electrochemical measurements and before the deposition of protection layers, the p-InP electrodes or wafers were etched in 0.04% (by volume) $\text{Br}_2/\text{CH}_3\text{OH}$ for 30 s, followed by 1:1

(by volume) $\text{NH}_4\text{OH}/\text{H}_2\text{O}$ for 30 s, and then rinsed with pure CH_3OH for 10 s. The etching and rinsing cycles were repeated twice, and the p-InP was dried under a stream of N_2 . The etching solutions were made fresh before use, since Br_2 is volatile and light sensitive, and NH_3 is also volatile.

Metal Oxide Deposition

Niobium oxide was deposited via a Cambridge Nanotech Savannah S200 Atomic Layer Deposition (ALD) System. The TBTDEN was heated to 120 °C, the H_2O was kept at room temperature, and the reactor was heated to 250 °C. The deposition consisted of 0.15 s pulses of TBTDEN, a 15 s purge with 20 sccm N_2 , 0.015 s of H_2O , and a 60 s purge. Approximately 1200 cycles were used to deposit ~50 nm of Nb_2O_5 . The thickness of the Nb_2O_5 film was determined across a wavelength range of 380-890 nm at 65, 70, and 75° angles, using a J.A. Woolam Co ellipsometer with the CompleteEASE software.

The other metal oxides TiO_2 , HfO_2 , and Ta_2O_5 were deposited in an analogous manner using slightly different parameters (Table 2-S1).

Table 2-S1. ALD parameters for metal oxide depositions

Metal Oxide	TiO_2	HfO_2	Ta_2O_5	Nb_2O_5
Precursor Temperature	90 °C	90 °C	120 °C	120 °C
Reactor Temperature	150 °C	150 °C	150 °C	250 °C
Precursor Pulse Duration	0.15 s	0.15 s	0.15 s	0.15 s
Purge Duration Following Precursor Pulse	15 s	15 s	15 s	15 s
Water Pulse Duration	0.015 s	0.015 s	0.015 s	0.015 s
Purge Duration Following Water Pulse	15 s	15 s	15 s	60 s
Approximate Deposition Rate (Number of cycles used for 50 nm films)	0.5 Å/cycle (1000 cycles)	1.1 Å/cycle (460 cycles)	0.45 Å/cycle (1100 cycles)	0.4 Å/cycle (1200 cycles)

Electrode fabrication

For electrochemical measurements, the back contact to the InP sample was attached to a coiled, tin-plated Cu wire (McMaster-Carr) using Ag paint. The electrode was then allowed to dry for at least 1 h and the Cu wire was then threaded through a piece of glass tubing (Corning Incorporated, Pyrex tubing, 7740 glass). The sample was encapsulated in, and sealed to, the glass tube using Hysol-9460 epoxy, which was allowed to dry overnight under ambient conditions. The exposed area of each electrode was then imaged using a high-resolution optical scanner (Epson Perfection V370 with a resolution of 1200 dpi), and the geometric areas of the electrodes (typically 0.07-0.10 cm²) were analyzed using ImageJ software.

For Ni electrodes, glass slides were cleaned with isopropyl alcohol and dried under a stream of N₂(g). 50 nm Ni was then evaporated onto the glass slides with a Denton Explorer 14 electron-beam metal evaporator with a base pressure of <10⁻⁶ torr using an accelerating voltage of 10 kV and 70 mA deposition current. The Ni-coated glass slides were then cut and used to make electrodes in the same manner as the InP samples.

Electrochemical Testing

Before use, electrochemical cells were cleaned using a 3:1 volume ratio of HCl:HNO₃. Electrochemical measurements were performed without IR compensation using a SP-200 potentiostat (BioLogic Science Instruments). The light source was an ENH-type W-halogen lamp, and the intensity was calibrated to be equivalent to 100 mW cm⁻² of Air Mass 1.5 illumination using a calibrated silicon photodiode (FDS100-Cal, Thor Labs) that was placed at the same position as the working electrode.

A three-electrode set-up with a graphite rod as the counter electrode, and an SCE reference electrode (CHI, Inc) was used for cells that contained V^{3+/2+} in 5.0 M HCl(aq). The cell was purged with N₂(g) before and during collection of electrochemical data. Cathodic *J-E* behavior was measured with a scan rate of 50 mV s⁻¹ starting from -0.46 V vs SCE ($\sim E(V^{3+/2+})$) to a potential of < -0.6 V vs SCE, then to *E*_{oc}, and finally to -0.46 V vs SCE. The anodic *J-E* behavior was measured at a scan rate of 50 mV s⁻¹ from -0.46 V vs SCE ($\sim E(V^{3+/2+})$) to 0.6 V vs SCE and ending at -0.46 V vs SCE.

For stability measurements in 1.0M H₂SO₄(aq), a Teflon compression cell was used to avoid the leaching of ions through the epoxy of glass body electrodes. A peristaltic pump was used to dislodge gas bubbles from the surface of the electrode. A Pt wire RHE was used as the reference electrode, and the counter electrode was a separate Pt wire that was separated from the main compartment using a ground glass frit. The cell was purged with H₂ before and during the experiment, and the cell was stirred. 200 μ L of the electrolyte was removed from the hydrogen outlet for ICP-MS analysis periodically without replacement. The overall cell volume was 30 mL. *J-E* behavior of the electrodes was determined periodically every 2 h by first interrupting the chronoamperometry with a short 15 s open circuit condition to measure E_{oc} . Then, the *J-E* behavior was measured by starting from $E_{start} = E_{oc} - 30$ mV to a vertex potential of < 0 V vs RHE and ending at $E_{end} = E_{oc} - 80$ mV. These potentials were chosen to minimize the anodic current through the electrode. Two *J-E* scans were collected during each current interruption. Voltammetry was collected at a scan rate of 50 mV s⁻¹.

Electrodeposition of Pt

Pt nano-islands were electrodeposited in a two-electrode configuration using a Pt(II) solution (5 mM K₂PtCl₄ in 0.5 M KCl) at a current density of -0.2 mA cm⁻² until 20 mC cm⁻² had passed. The electrodeposition was performed under ~ 1 Sun of simulated solar illumination. A Pt wire was used as the counter electrode. Pt(IV) should not be as the Pt precursor, since K₂PtCl₆ is not soluble in KCl and can oxidize the p-InP surface, resulting in a lower photovoltage for p-InP.

Preparation of V^{3+/2+} Solutions

A V^{3+/2+} solution that contained a total vanadium concentration of 350 mM was prepared by stirring V₂O₅ in water and slowly adding, over several hours under a N₂ purge, concentrated HCl dropwise to the solution until a 5.0 M HCl(aq) solution was obtained. The dissolved V⁵⁺ was then reduced to V²⁺ by adding a Zn (Hg) amalgam until the V was fully reduced. The color of the solution turned from orange to green and finally to blue violet. The solution potential was then brought from -0.51 V vs SCE to -0.46 V vs SCE by bubbling O₂ into the cell.

Mott-Schottky

Mott-Schottky measurements were performed using an SP-200 potentiostat (BioLogic Science Instruments) in contact with 350 mM V^{3+/2+}-5.0 M HCl(aq) or 1.0 M H₂SO₄(aq) under a

stream of flowing N₂(g) or H₂(g), respectively. The impedance data were collected in the dark in the reverse bias region with a sinusoidal wave amplitude of 10 mV over a frequency range of 10 kHz to 10 Hz. The impedance measurements were fit to a model circuit consisting of a resistor in series with a component consisting of a resistor and capacitor in parallel. The potential dependence of the differential capacitance was analyzed using the Mott-Schottky equation:

$$C_d^{-2} = \frac{2}{qA^2\epsilon_0\epsilon_r N_d} \left(E_{app} + V_{bi} - \frac{k_B T}{q} \right)$$

Here, C_d is the differential capacitance, q is the unsigned charge of an electron, A is the area of the electrode, ϵ_0 is the vacuum permittivity, ϵ_r is the relative permittivity of the semiconductor, N_d is the dopant concentration of the semiconductor, E_{app} is the applied electrode potential, V_{bi} is the built-in voltage in the semiconductor, k_b is the Boltzmann constant, and T is the temperature of the electrode while the impedance data were collected. A relative permittivity of $\epsilon_r = 8.8$ was used for InP. The slopes of the Mott-Schottky relationship were used to calculate the dopant density, N_d . The dopant density extracted from the slope of C_d^{-2} vs E_{app} was then compared to the dopant density of the sample provided by the manufacturer, to verify the accuracy of the fit to the Mott-Schottky data.

SEM

Scanning-electron micrographs (SEMs) were obtained using a calibrated Nova NanoSEM 450 (FEI) at an accelerating voltage of 5 kV with a working distance of 5.0 mm and an in-lens secondary electron detector.

XPS

X-ray photoelectron spectroscopy (XPS) was performed using a Kratos Axis Ultra system with a base pressure of 3×10^{-9} Torr in the analysis chamber. A 150 W monochromatic Al K α source was used to irradiate the sample with X-rays (1486.6 eV). For maximum depth sensitivity, the hemispherical analyzer was oriented for detection along the sample surface normal. The data were analyzed using CasaXPS software. A Shirley background was used for all spectra, and all peaks were referenced to adventitious C at a binding energy of 284.8 eV. The Pt⁰ peak of the Pt 4f spectra was fit using an asymmetric peak shape (LA(1.2, 85, 70) in CasaXPS). All other peaks were fit using a 50% Gaussian/50% Lorentzian Voigt-function (LA(50) in CasaXPS).

UV-Vis

Ultraviolet-visible spectroscopy between 190-1100 nm was performed on an Agilent 8453 UV-vis Spectrometer. 50 nm of either Nb₂O₅ or TiO₂ was deposited on fluorine-doped tin oxide (FTO, Tec 8) samples that were then cut into 1 cm x 5 cm pieces. The pieces were used as part of a single compartment 3-electrode cell with the coated FTO acting as the working electrode, along with a Pt wire counter electrode and a 3.0 M KCl Ag/AgCl reference electrode. The electrolyte was 1.0 M H₂SO₄(aq). The UV-Vis was blanked after holding the working electrode for 15 min at 0.8 V vs Ag/AgCl. The potential was swept from 0.8 V vs Ag/AgCl to -0.8 V vs Ag/AgCl at 5 mV s⁻¹, and UV-Vis spectra were taken every 2 s.

ICP-MS

ICP-MS was performed using an Agilent 8800 Triple Quadrupole ICP-MS system. Calibration samples were prepared by diluting standard solutions for ICP with water having a resistivity of 18.2 MΩ cm. All samples were diluted using 5% (~0.8 M) nitric acid to pH < 2. The concentration of In dissolved in the electrolyte sample was then used to calculate the equivalent depth of InP removed from the InP electrode normalized by the geometric electrode surface area.

Non-aqueous experiments

Non-aqueous experiments were performed in a dry glovebox containing < 5 ppm O₂. Dry acetonitrile was extracted from a solvent purification system and stored over dried 3Å molecular sieves. Molecular sieves were dried under vacuum at 150 °C overnight. LiClO₄ was dried by fusion, heating a small amount of LiClO₄ under vacuum to 240 °C.⁹⁴ Care was taken during the fusing process to remove any metal contamination because LiClO₄ is a strong oxidizer, so contact with metals can lead to an explosion. A blast shield was also employed as a safety precaution.

Ferrocene (Fc), decamethylferrocene (Fc*), and cobaltocene (Cp₂Co) were used as redox couples with the corresponding redox pair. Ferrocene and cobaltocene were purified by vacuum sublimation, whereas cobaltocenium was recrystallized from acetonitrile and dried under vacuum.⁹⁴ Ferrocenium was prepared by oxidizing ferrocene in diethyl ether with p-benzoquinone in the presence of HBF₄ and dried under vacuum.⁹⁵ Decamethylferrocene and decamethylferrocenium were prepared in a similar manner to ferrocene and ferrocenium, respectively.²¹

Solutions contained 50 mM and 2 mM of the desired oxidized and reduced redox pair, respectively. 1.0 M LiClO₄ was used as the supporting electrolyte in all solutions. A Pt wire poised at the Nernstian potential of the solution was used as the reference electrode, and a separate Pt mesh electrode was used as the counter electrode. The light source was an ELH-type W-halogen lamp, and the intensity was calibrated to be equivalent to 100 mW cm⁻² of Air Mass 1.5 illumination using a calibrated silicon photodiode (FDS100-Cal, Thor Labs) that was placed at the same position as the working electrode. The solution was stirred throughout the experiment.

Supporting Figures

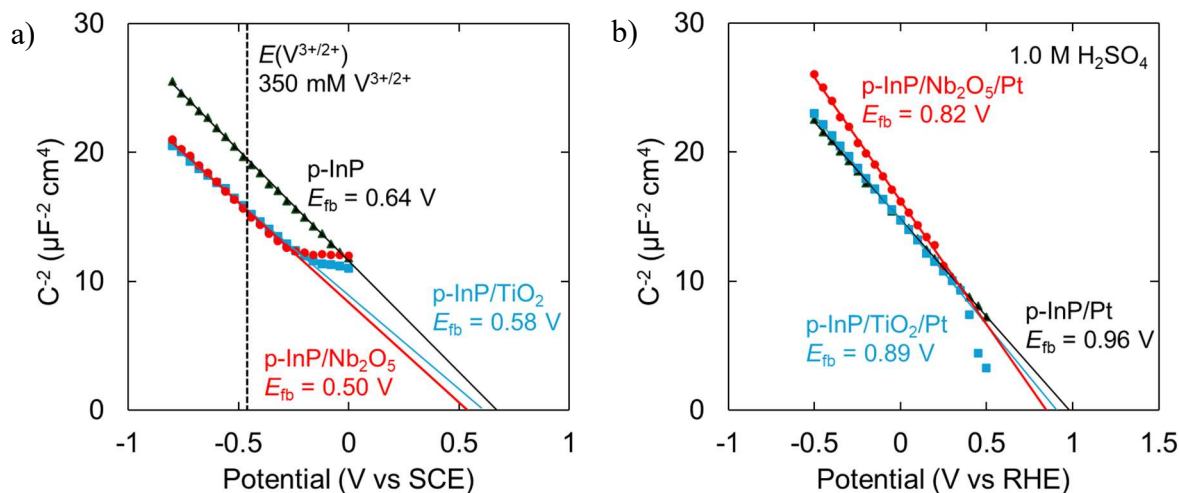


Figure 2-S1. Mott-Schottky analyses for (a) samples of p-InP, p-InP/Nb₂O₅, and p-InP/TiO₂ measured in the dark while in contact with 350 mM $\text{V}^{3+/2+}$ -5.0 M HCl(aq) , and (b) samples of p-InP/Pt, p-InP/Nb₂O₅/Pt, and p-InP/TiO₂/Pt measured in the dark while in contact with 1.0 M $\text{H}_2\text{SO}_4(\text{aq})$. The dopant density derived from the fits ($N_{\text{d}} = 6.98 \times 10^{17} \pm 0.67 \times 10^{17} \text{ cm}^{-3}$) is in accord with the dopant density specified by the manufacturer ($N_{\text{d}} = 1\text{-}8 \times 10^{17} \text{ cm}^{-3}$). Bode plots of the impedance data from which these fits were extracted are shown in Figure 2-S2.

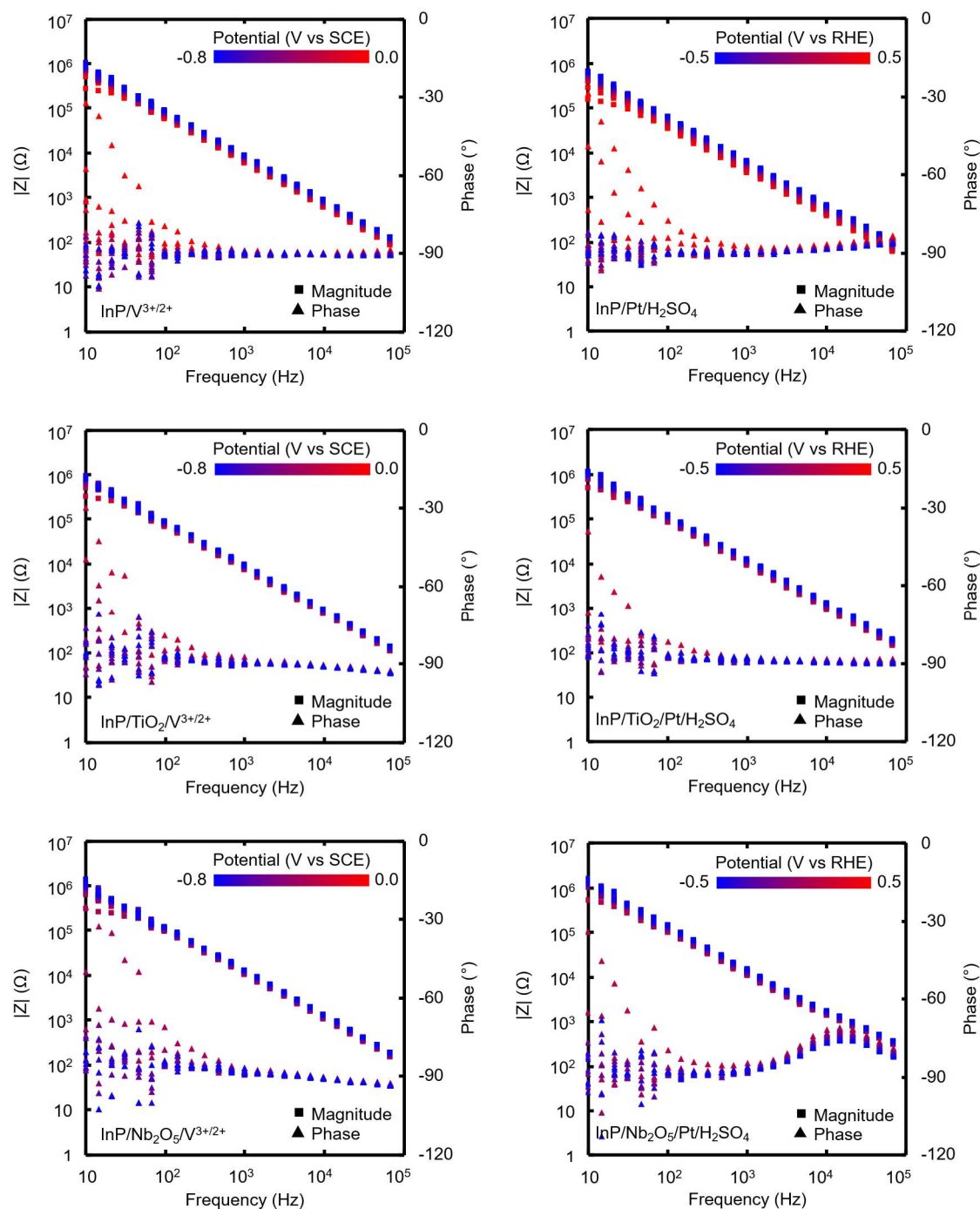


Figure 2-S2. Bode plots of the electrochemical impedance spectra data used to extract the Mott-Schottky fits in Figure 2-S1.

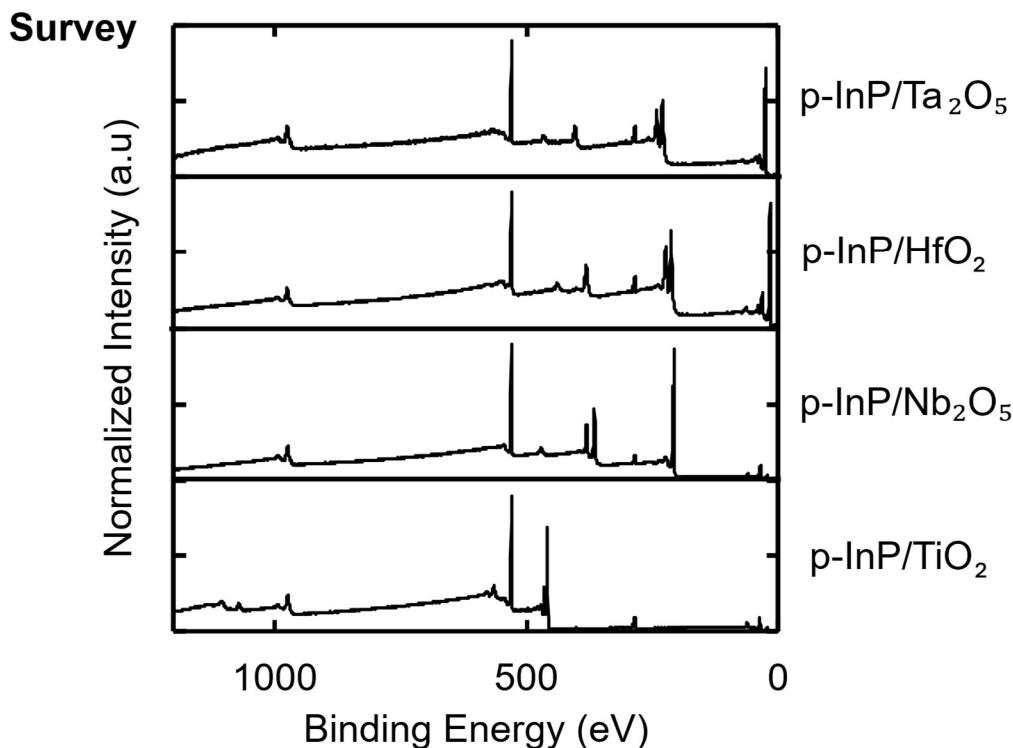


Figure 2-S3. XPS data of as-prepared samples of p-InP/TiO₂, p-InP/Nb₂O₅, p-InP/HfO₂, and p-InP/Ta₂O₅. The InP/Ta₂O₅ sample had Ta 4f_{7/2} and 4f_{5/2} binding energies of 25.9 eV and 27.8 eV respectively, both with a FWHM of 0.96 eV. The InP/HfO₂ sample had Hf 4f_{7/2} and 4f_{5/2} binding energies of 16.7 eV and 18.3 eV respectively, both with a FWHM of 1.05 eV. The InP/Nb₂O₅ sample had Nb 3d_{5/2} and 3d_{3/2} binding energies of 207.3 eV and 210.1 eV respectively, both with a FWHM of 0.94 eV. The InP/TiO₂ sample had Ti 2p_{3/2} and 2p_{1/2} binding energies of 458.5 eV and 464.3 eV and FWHM of 0.99 eV and 1.96 eV, respectively. No In signals were detectable.

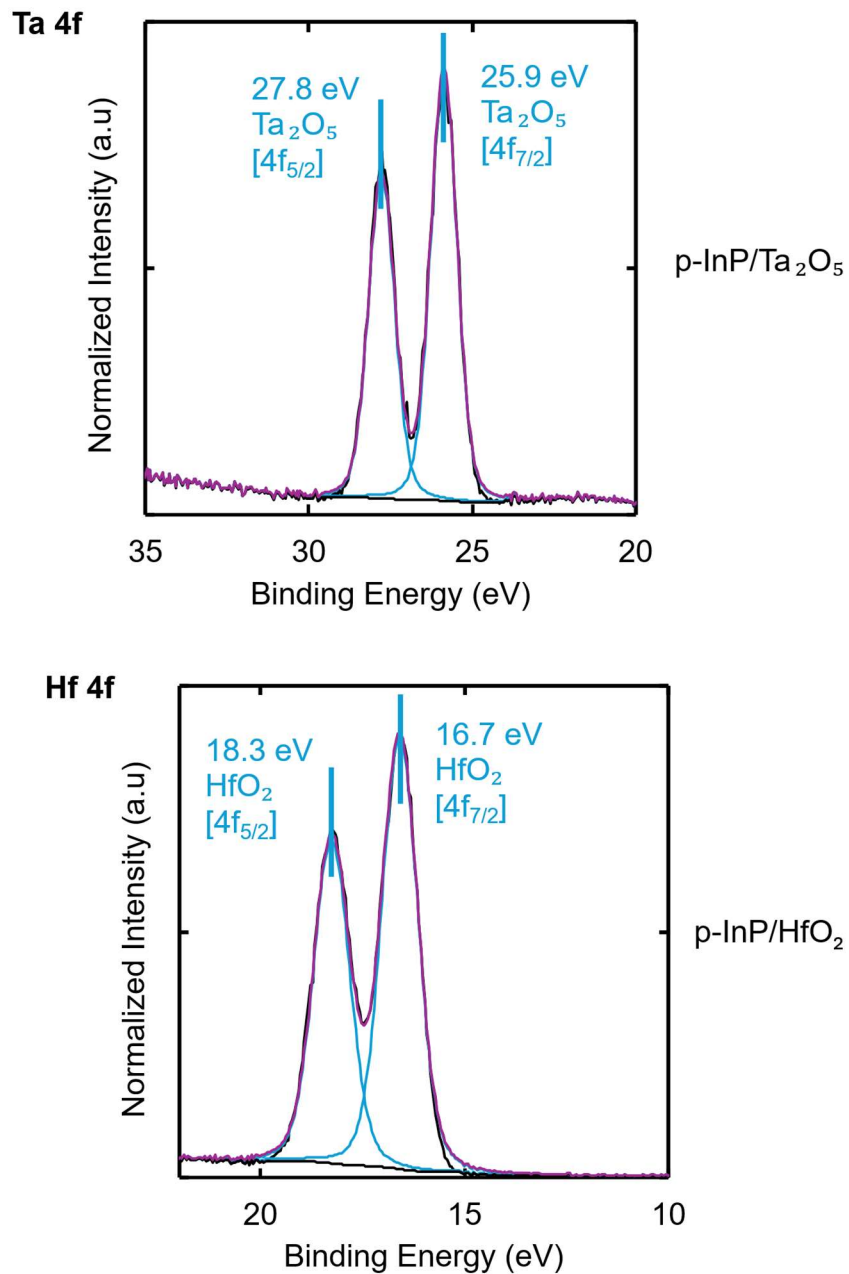


Figure 2-S3. (continued) XPS data of as-prepared samples of p-InP/TiO₂, p-InP/Nb₂O₅, p-InP/HfO₂, and p-InP/Ta₂O₅. The InP/Ta₂O₅ sample had Ta 4f_{7/2} and 4f_{5/2} binding energies of 25.9 eV and 27.8 eV respectively, both with a FWHM of 0.96 eV. The InP/HfO₂ sample had Hf 4f_{7/2} and 4f_{5/2} binding energies of 16.7 eV and 18.3 eV respectively, both with a FWHM of 1.05 eV. No In signals were detectable.

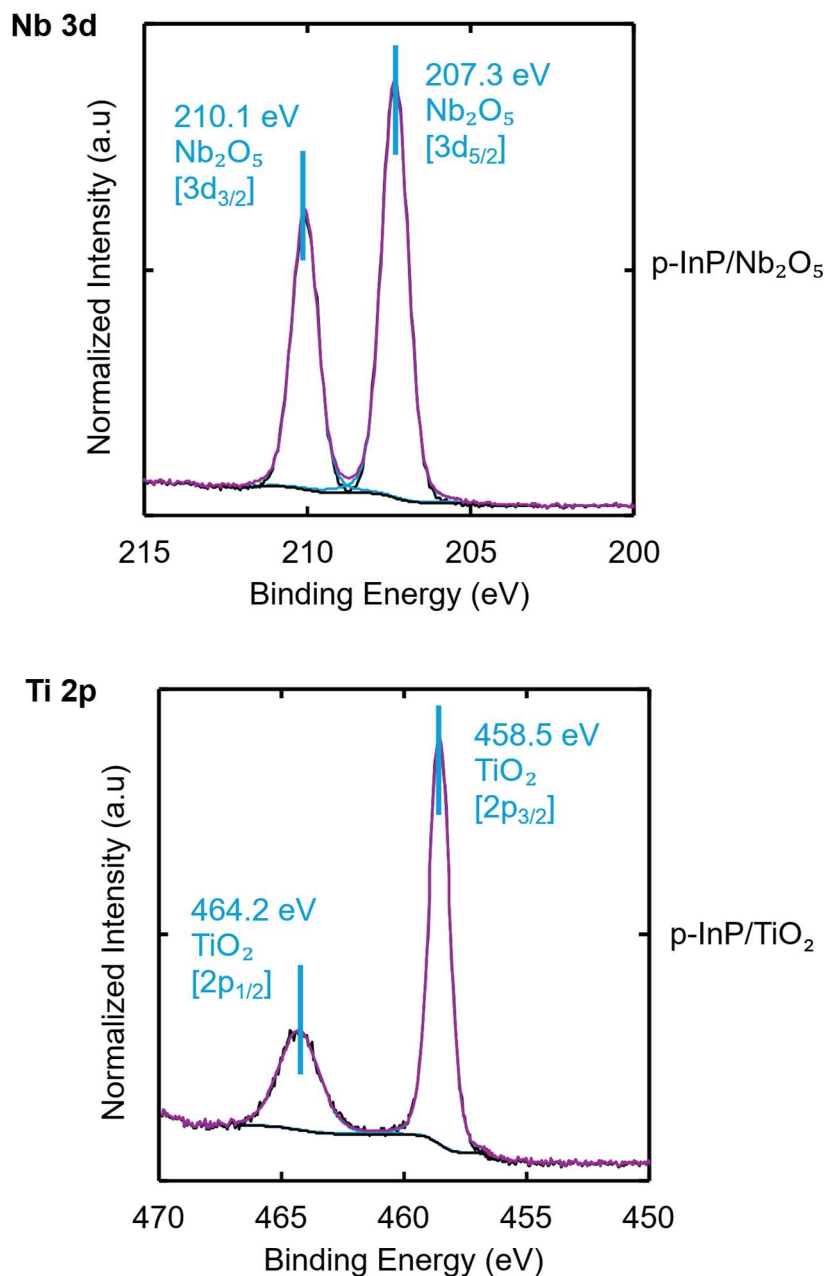


Figure 2-S3. (continued) XPS data of as-prepared samples of p-InP/TiO₂, p-InP/Nb₂O₅, p-InP/HfO₂, and p-InP/Ta₂O₅. The InP/Nb₂O₅ sample had Nb 3d_{5/2} and 3d_{3/2} binding energies of 207.3 eV and 210.1 eV respectively, both with a FWHM of 0.94 eV. The InP/TiO₂ sample had Ti 2p_{3/2} and 2p_{1/2} binding energies of 458.5 eV and 464.3 eV and FWHM of 0.99 eV and 1.96 eV, respectively. No In signals were detectable.

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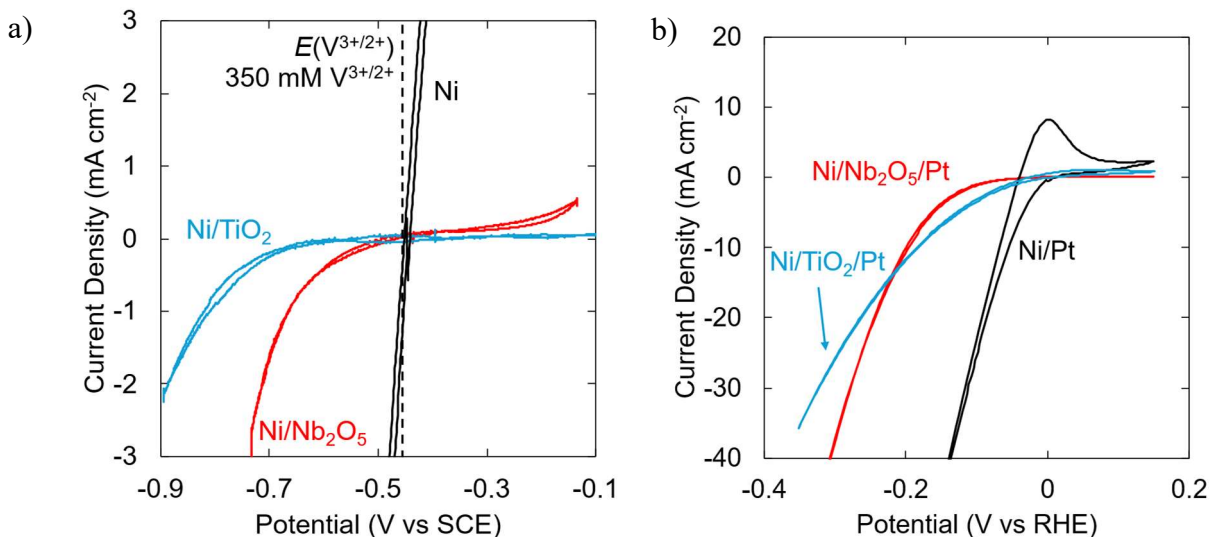


Figure 2-S5. *J-E* behavior of Ni electrodes coated with Nb₂O₅ and TiO₂, respectively, in (a) 350 mM V^{3+/2+}-5.0 M HCl(aq) and (b) in 1.0 M H₂SO₄(aq). $E(V^{3+/2+}) = -0.46$ V vs SCE, and the scan rates were 50 mV s⁻¹. The electrodes in b) were platinized. The Ni/TiO₂ and Ni/Nb₂O₅ contacts were verified to be ohmic using Ni/TiO₂/Ni and Ni/Nb₂O₅/Ni electrodes. However, the Ni/TiO₂ films were more resistive than the Ni/Nb₂O₅ films, leading to a negative shift in the *J-E* characteristics for Ni/TiO₂ electrodes relative to Ni/Nb₂O₅ electrodes. The resistance of the TiO₂ films (5.0 Ω cm²) and the resistance of the Nb₂O₅ films (2.4 Ω cm²) were determined using Ni/MO_x/Ni electrodes.

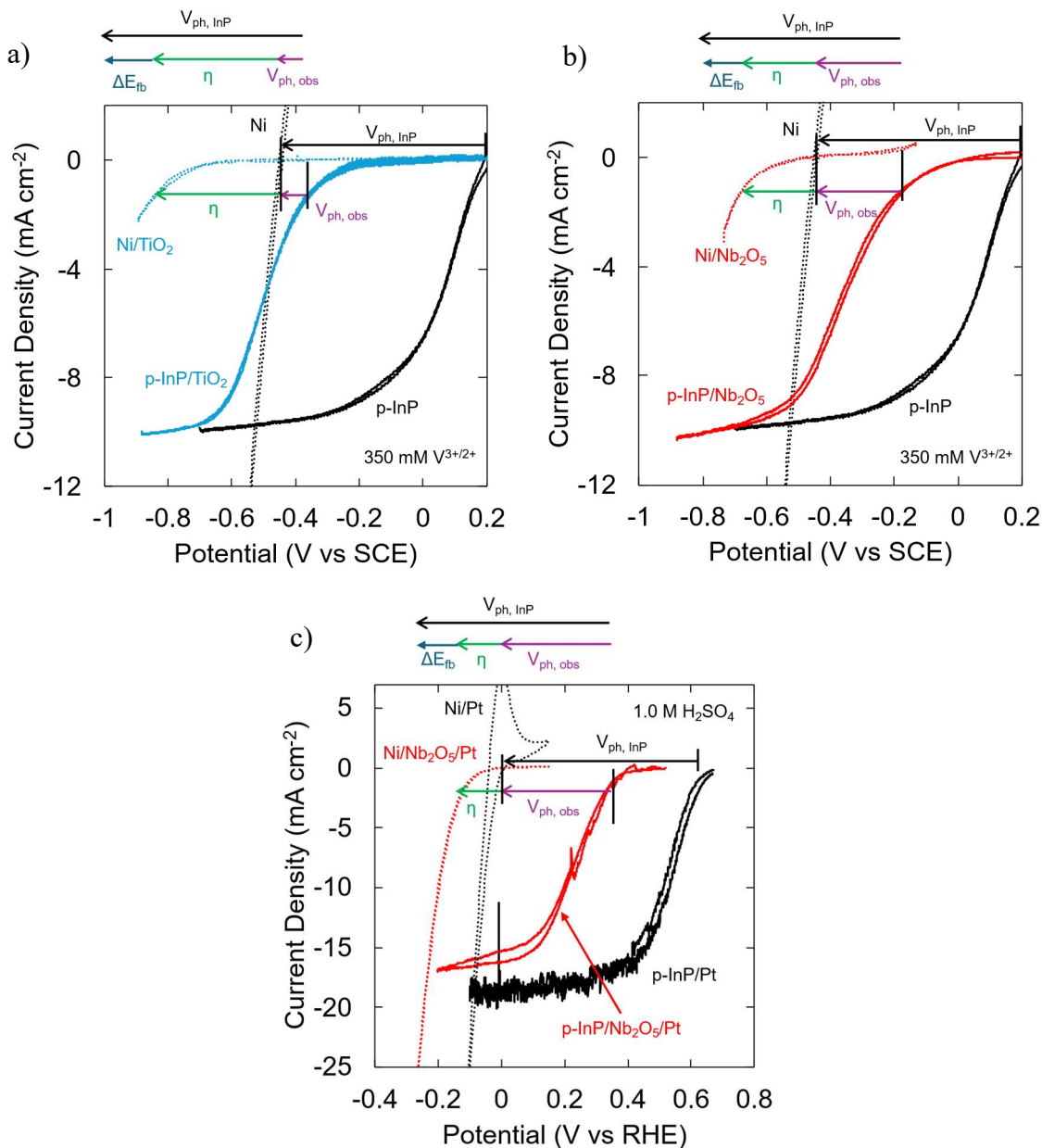


Figure 2-S6. $J-E$ behavior in 350 mM $\text{V}^{3+/2+}$ -5.0 M HCl(aq) (Figure 2-1a and 2-S5a) of Ni and p-InP electrodes, respectively, with and without (a) Nb_2O_5 coatings or (b) TiO_2 coatings. $J-E$ behavior in 1.0 M $\text{H}_2\text{SO}_4(\text{aq})$ of (c) platinized Ni and p-InP electrodes, respectively, with and without a Nb_2O_5 coating (Figure 2-2b and 2-S5b). The sum of the observed photovoltage of the coated p-InP samples, $V_{\text{ph, obs}}$, the overpotential at the $\text{MO}_x/\text{solution}$ interface, η , and the difference in flat-band potentials, ΔE_{fb} , (Figure 2-S1) is approximately equal to the photovoltage of the etched p-InP, $V_{\text{ph, InP}}$. Equivalently, the observed photovoltage of the coated p-InP samples, $V_{\text{ph, obs}}$, is approximately equal to the photovoltage of the etched p-InP samples, $V_{\text{ph, InP}}$, minus the

overpotential at the $\text{MO}_x/\text{solution}$ interface, with an additional subtraction to correct for the difference in flat-band potentials measured by Mott-Schottky analysis between the coated and etched p-InP electrodes, ΔE_{fb} .

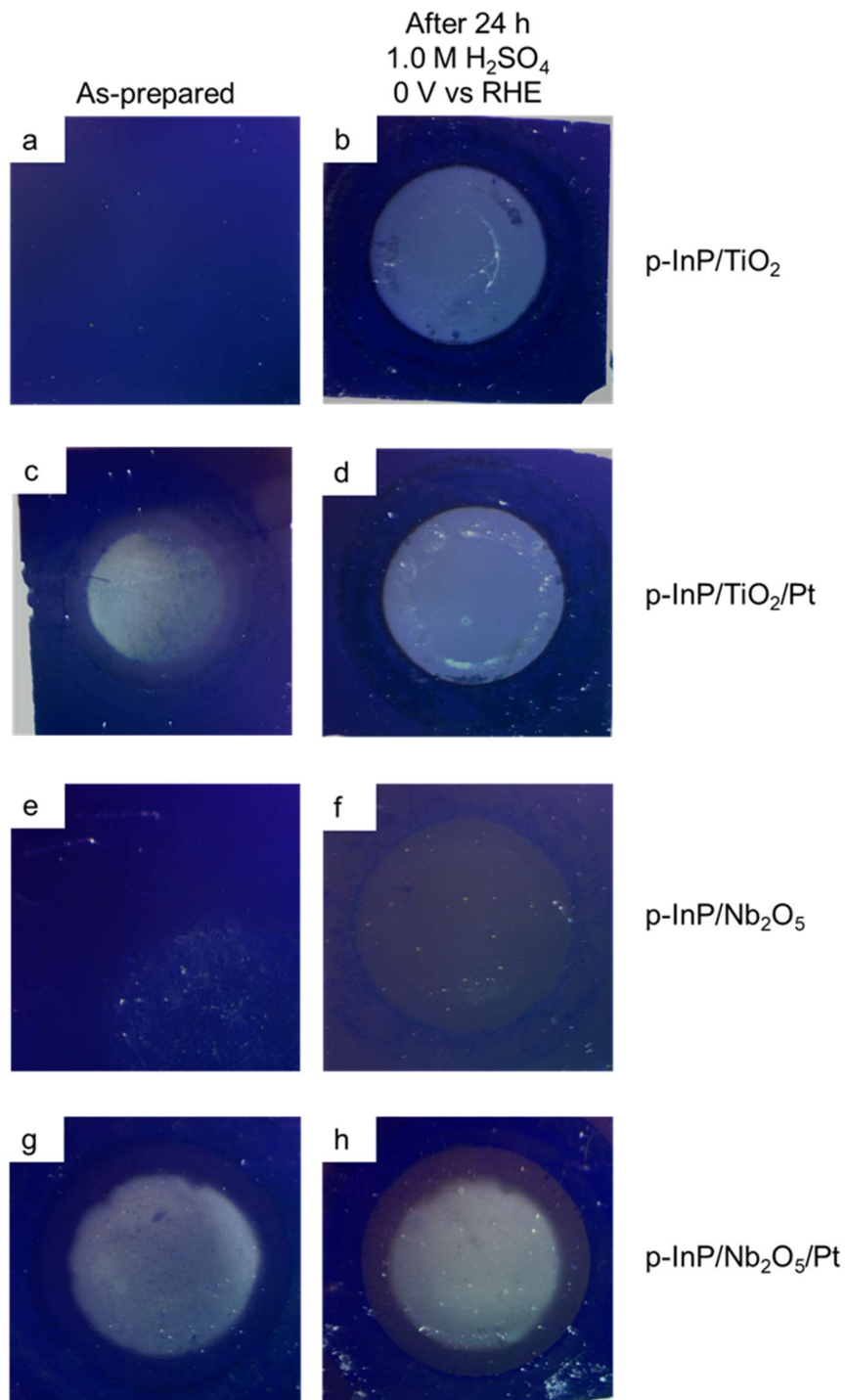


Figure 2-S7. Optical images of as-prepared (a) p-InP/TiO₂, (c) p-InP/TiO₂/Pt, (e) p-InP/Nb₂O₅, and (g) p-InP/Nb₂O₅/Pt electrodes alongside optical images of (b) p-InP/TiO₂, (d) p-InP/TiO₂/Pt, (f) p-InP/Nb₂O₅, and (h) p-InP/Nb₂O₅/Pt electrodes after 24 h at 0 V vs RHE in 1.0 M H₂SO₄(aq). The (bluish) bare and platinized TiO₂ in contact with the H₂SO₄ in the center of the electrode completely disappeared after electrochemical testing, leaving behind exposed InP. The

bare and platinized Nb_2O_5 in contact with the H_2SO_4 in the center of the electrode remains unchanged after electrochemical testing. XPS analysis of these samples further support this conclusion, as shown in Figures S8, S11, and S12. TiO_2 dissolves rapidly under HER conditions in acid and thus is not suitable as a durable protection layer for photocathodes performing the HER in aqueous acidic electrolytes. The observation of stable photocurrents for oxide overlayers that rapidly dissolve, like TiO_2 , underscores the difficulty in forming conclusions regarding beneficial effects of a protection layer based solely on stable photocurrents in systems that are kinetically stabilized for the HER in the absence of a protection layer.

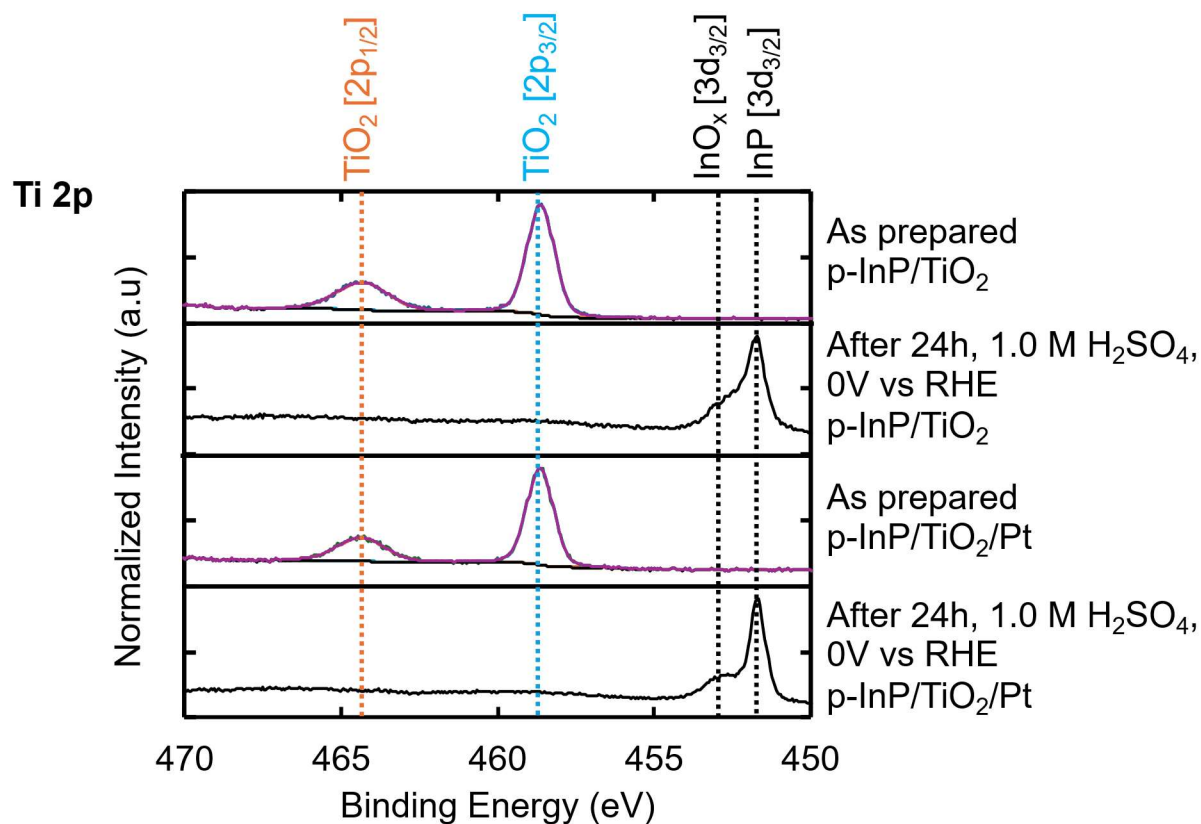


Figure 2-S8. XPS data for samples of p-InP/TiO₂ and p-InP/TiO₂/Pt electrodes, before and after, respectively, 24 h at 0 V vs RHE in 1.0 M H₂SO₄(aq). After electrochemical testing, the TiO₂ has completely dissolved and no Ti 2p XPS signal was detected. Instead, In 3d XPS signals were detected, indicating the presence of exposed InP.

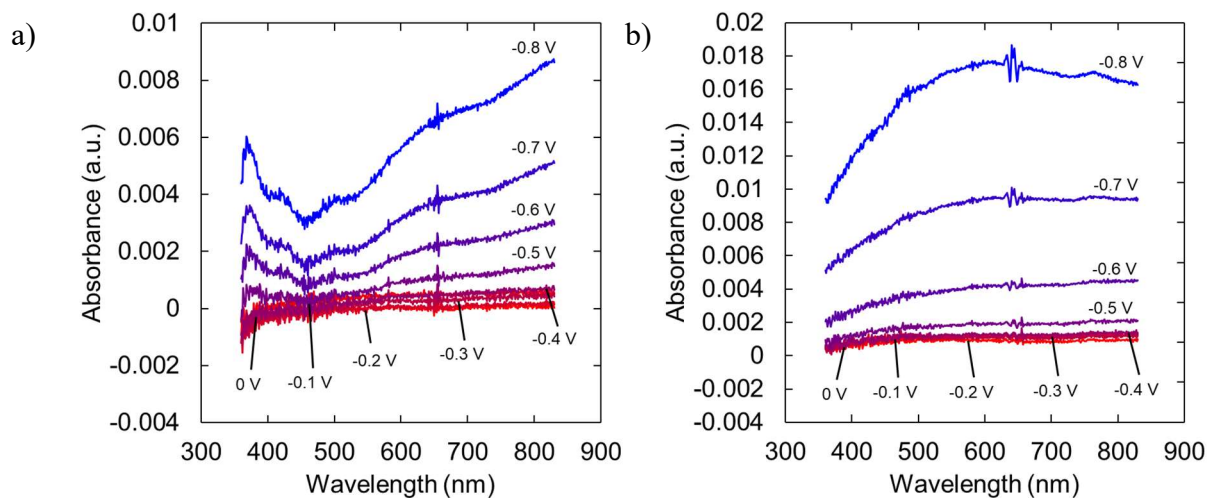


Figure 2-S9. UV-Vis spectra for (a) TiO₂-coated fluorine-doped tin oxide (FTO) and (b) for Nb₂O₅-coated FTO at different potentials in 1.0 M H₂SO₄(aq). The spectra were measured while the samples were swept at 5 mV s⁻¹ from 0.8 V to -0.8 V vs Ag/AgCl. The spectrum of the samples held at 0.8 V vs Ag/AgCl for 15 min was subtracted from the data to obtain the data presented in this figure.

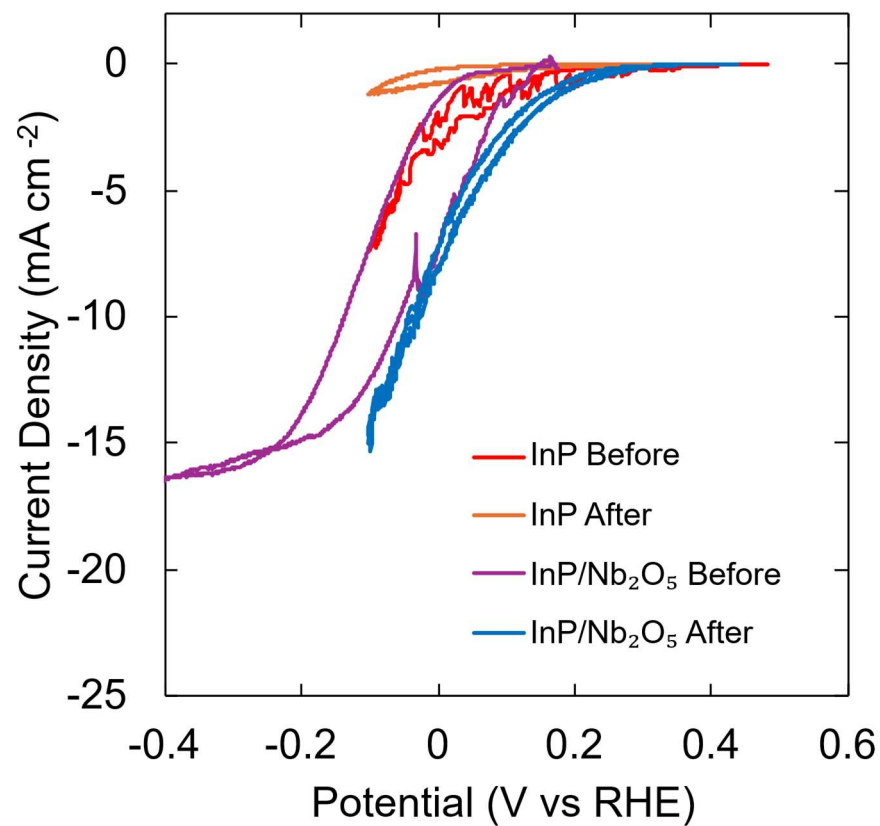


Figure 2-S10. *J-E* behavior of p-InP and p-InP/Nb₂O₅ electrodes before and after 24 h at 0 V vs RHE in 1.0 M H₂SO₄(aq) under illumination.

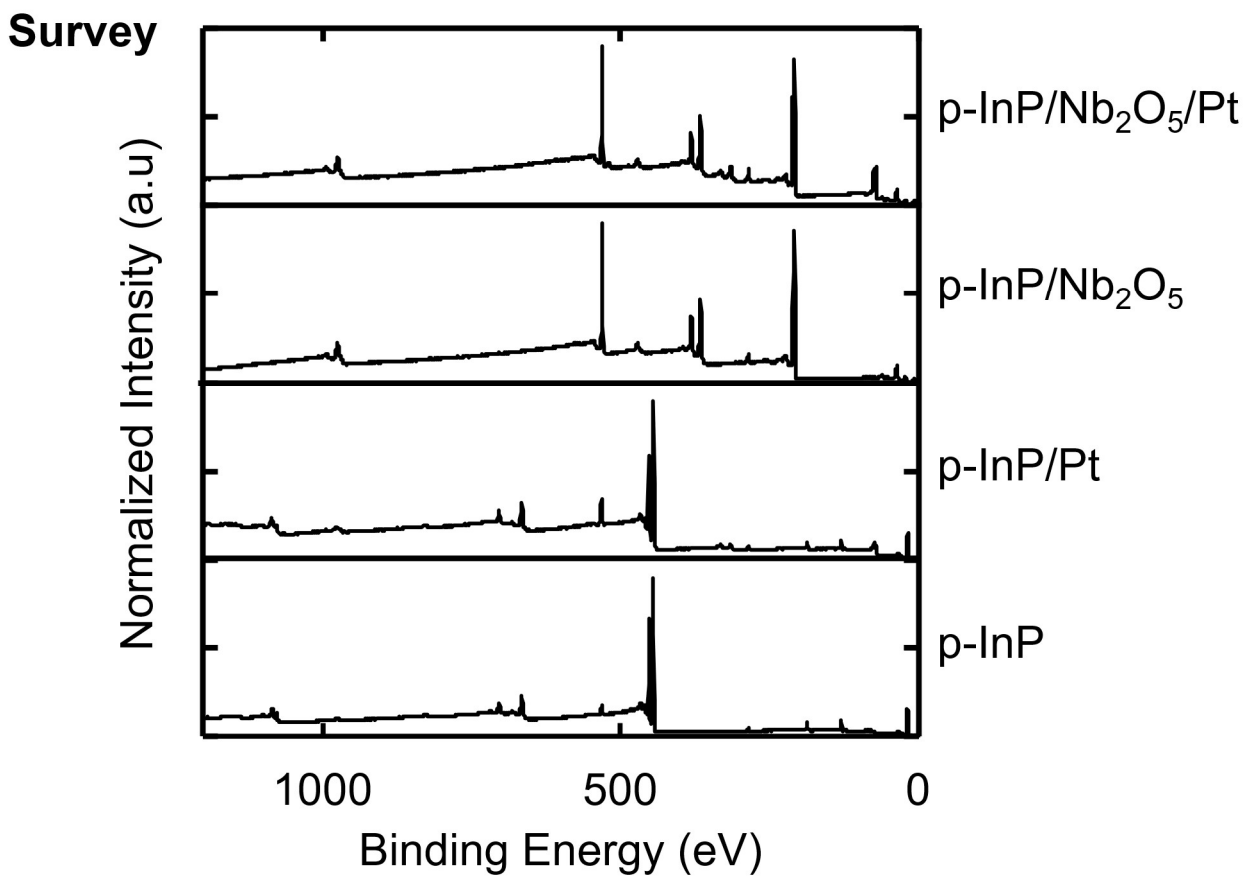


Figure 2-S11. XPS data for as-prepared samples of p-InP, p-InP/Pt, p-InP/Nb₂O₅, and p-InP/Nb₂O₅/Pt electrodes before any electrochemical testing. The peak locations and areas are listed in Tables 2-S2 and 2-S3.

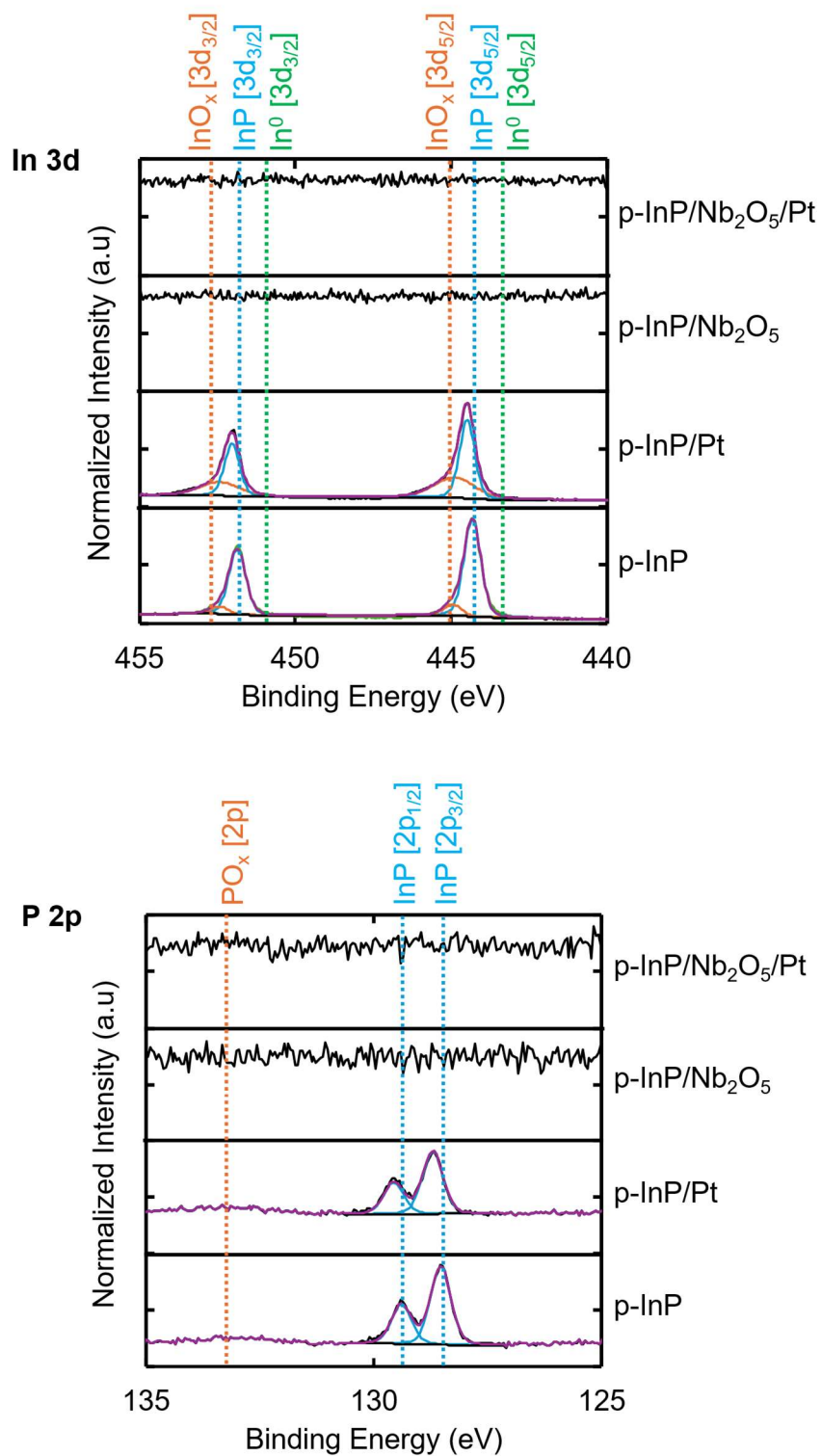


Figure 2-S11. (continued) XPS data for as-prepared samples of p-InP, p-InP/Pt, p-InP/Nb₂O₅, and p-InP/Nb₂O₅/Pt electrodes before any electrochemical testing. The peak locations and areas are listed in Tables 2-S2 and 2-S3.

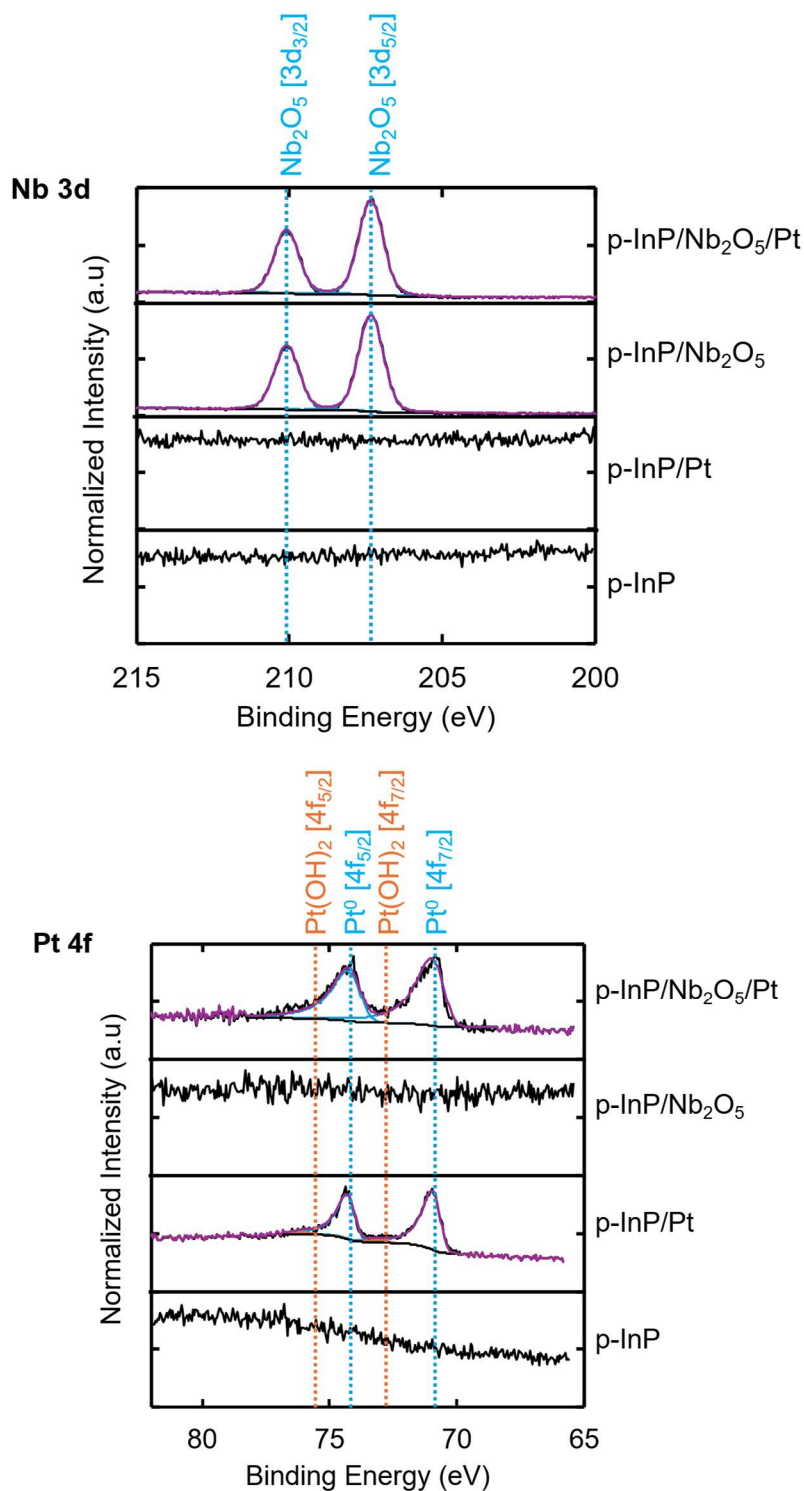


Figure 2-S11. (continued) XPS data for as-prepared samples of p-InP, p-InP/Pt, p-InP/Nb₂O₅, and p-InP/Nb₂O₅/Pt electrodes before any electrochemical testing. The peak locations and areas are listed in Tables 2-S2 and 2-S3.

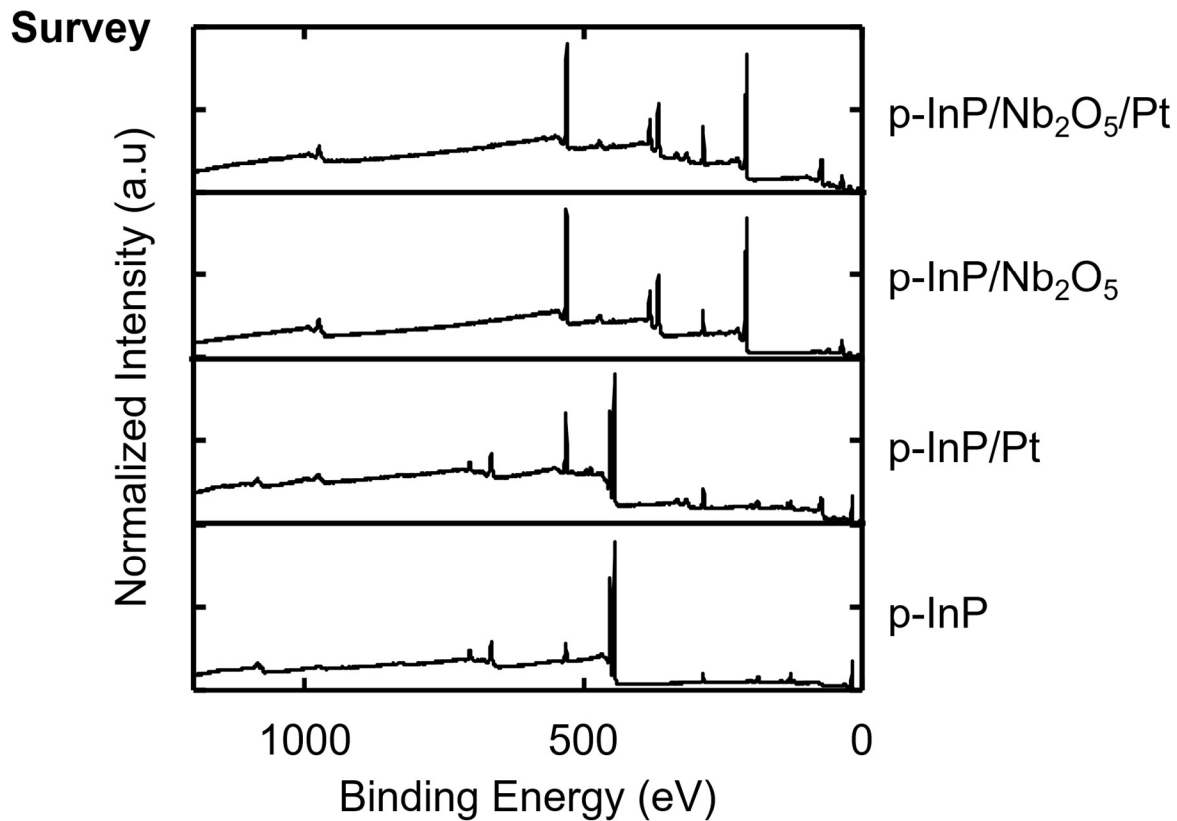


Figure 2-S12. XPS data for samples of p-InP, p-InP/Pt, p-InP/Nb₂O₅, and p-InP/Nb₂O₅/Pt held at 0 V vs RHE in 1.0 M H₂SO₄(aq) for 24 h under illumination. The peak locations and areas are listed in Tables 2-S2 and 2-S3.

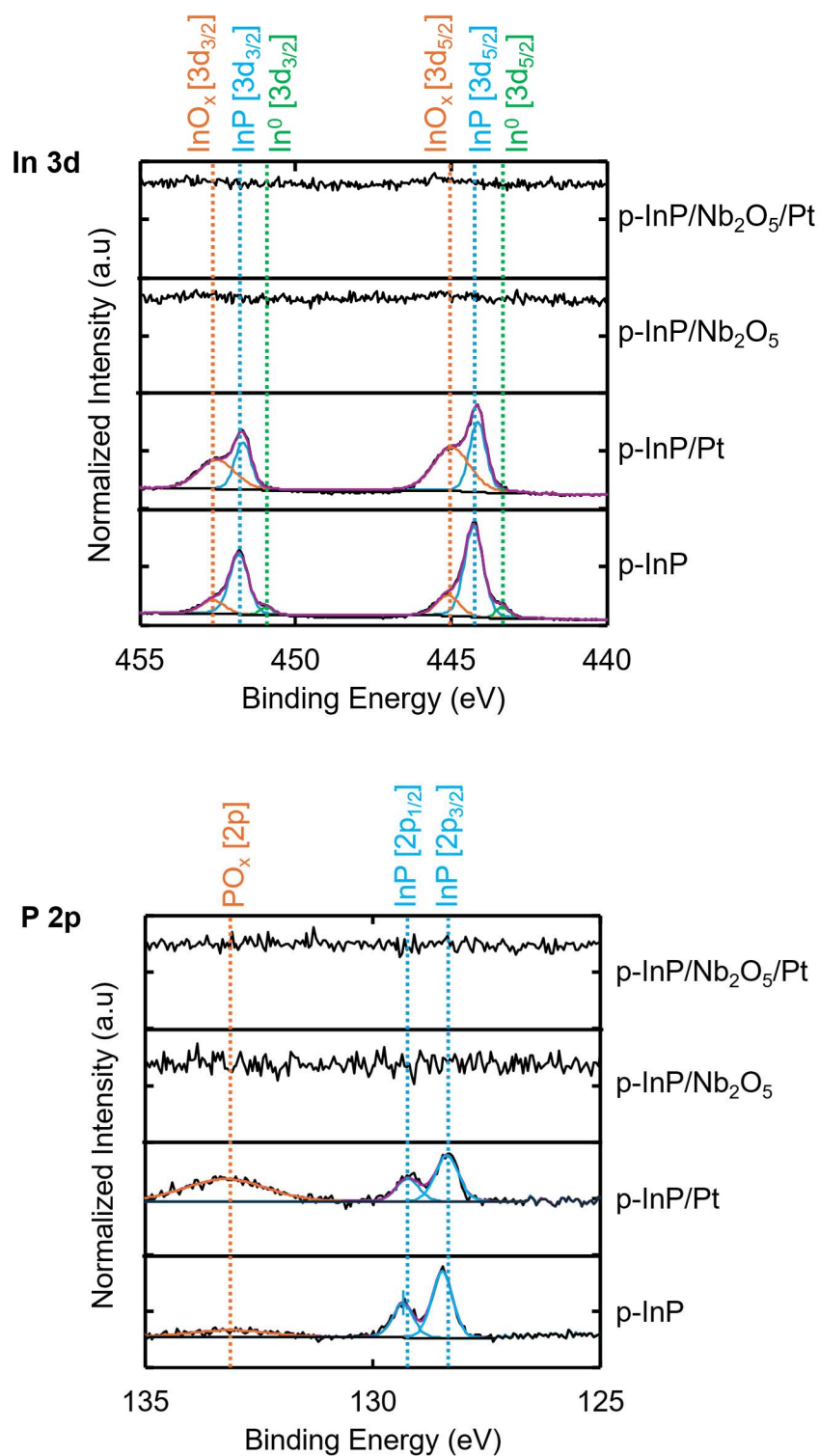


Figure 2-S12. (continued) XPS data for samples of p-InP, p-InP/Pt, p-InP/Nb₂O₅, and p-InP/Nb₂O₅/Pt held at 0 V vs RHE in 1.0 M H₂SO₄(aq) for 24 h under illumination. The peak locations and areas are listed in Tables 2-S2 and 2-S3.

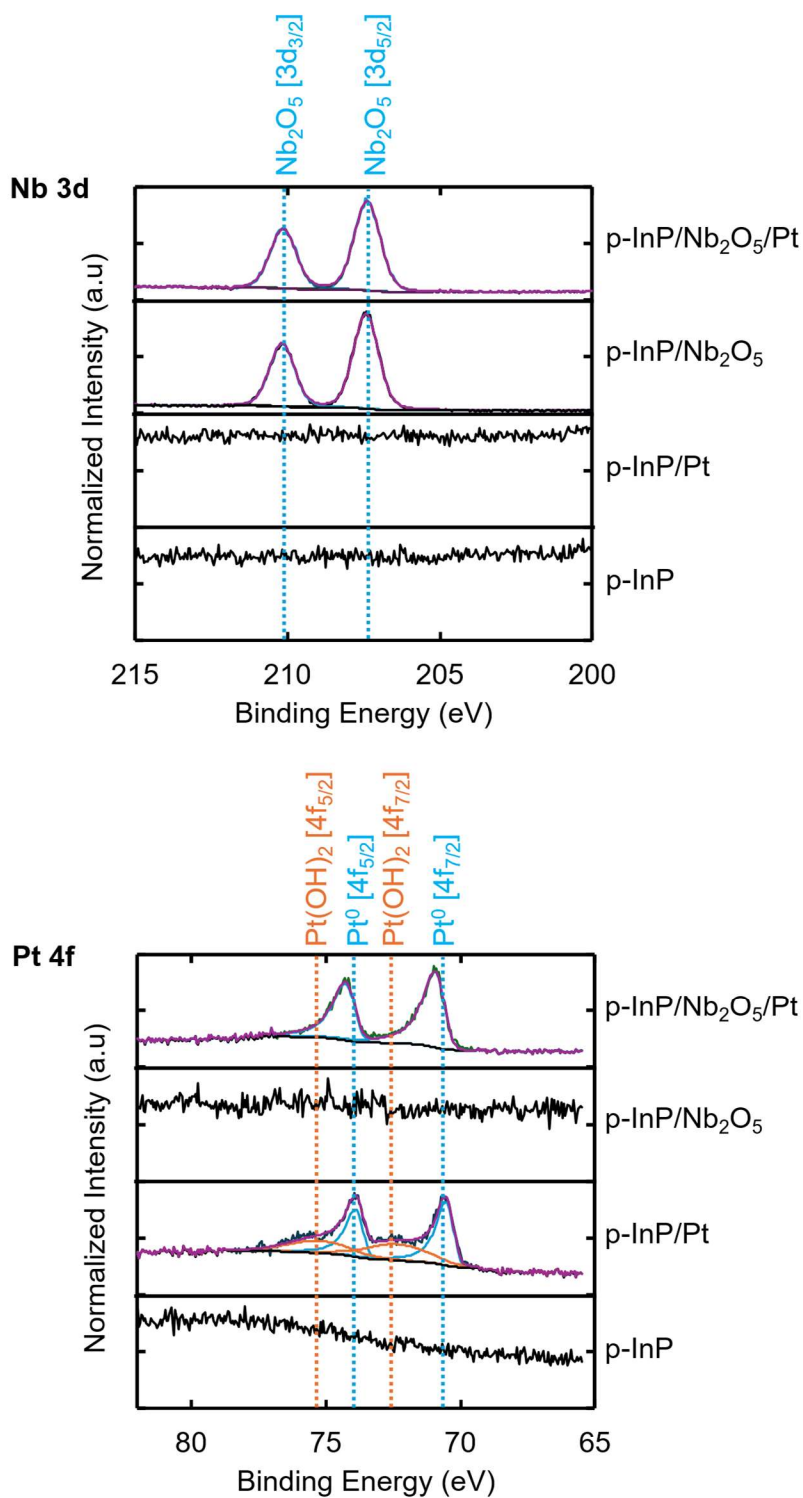


Figure 2-S12. (continued) XPS data for samples of p-InP, p-InP/Pt, p-InP/Nb₂O₅, and p-InP/Nb₂O₅/Pt held at 0 V vs RHE in 1.0 M H₂SO₄(aq) for 24 h under illumination. The peak locations and areas are listed in Tables 2-S2 and 2-S3.

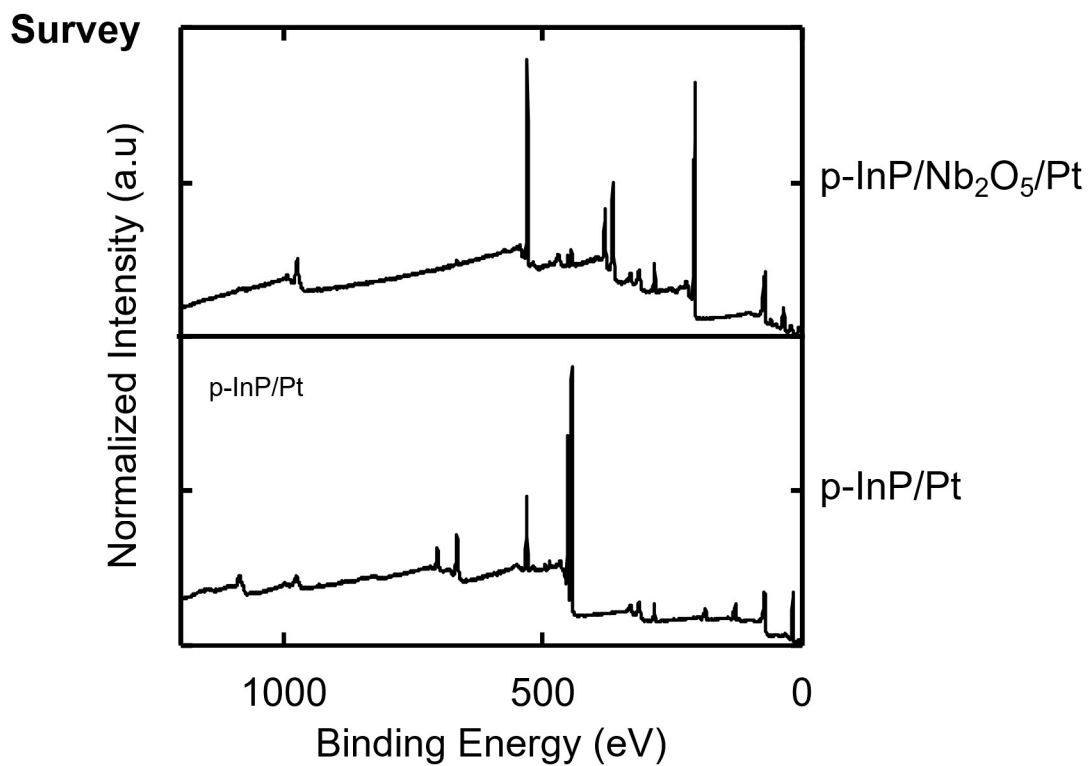


Figure 2-S13. XPS data for samples of p-InP, p-InP/Pt, p-InP/Nb₂O₅, and p-InP/Nb₂O₅/Pt held at open circuit in contact with 1.0 M H₂SO₄(aq) for 24 h in the dark. The peak locations and areas are listed in Tables 2-S2 and 2-S3.

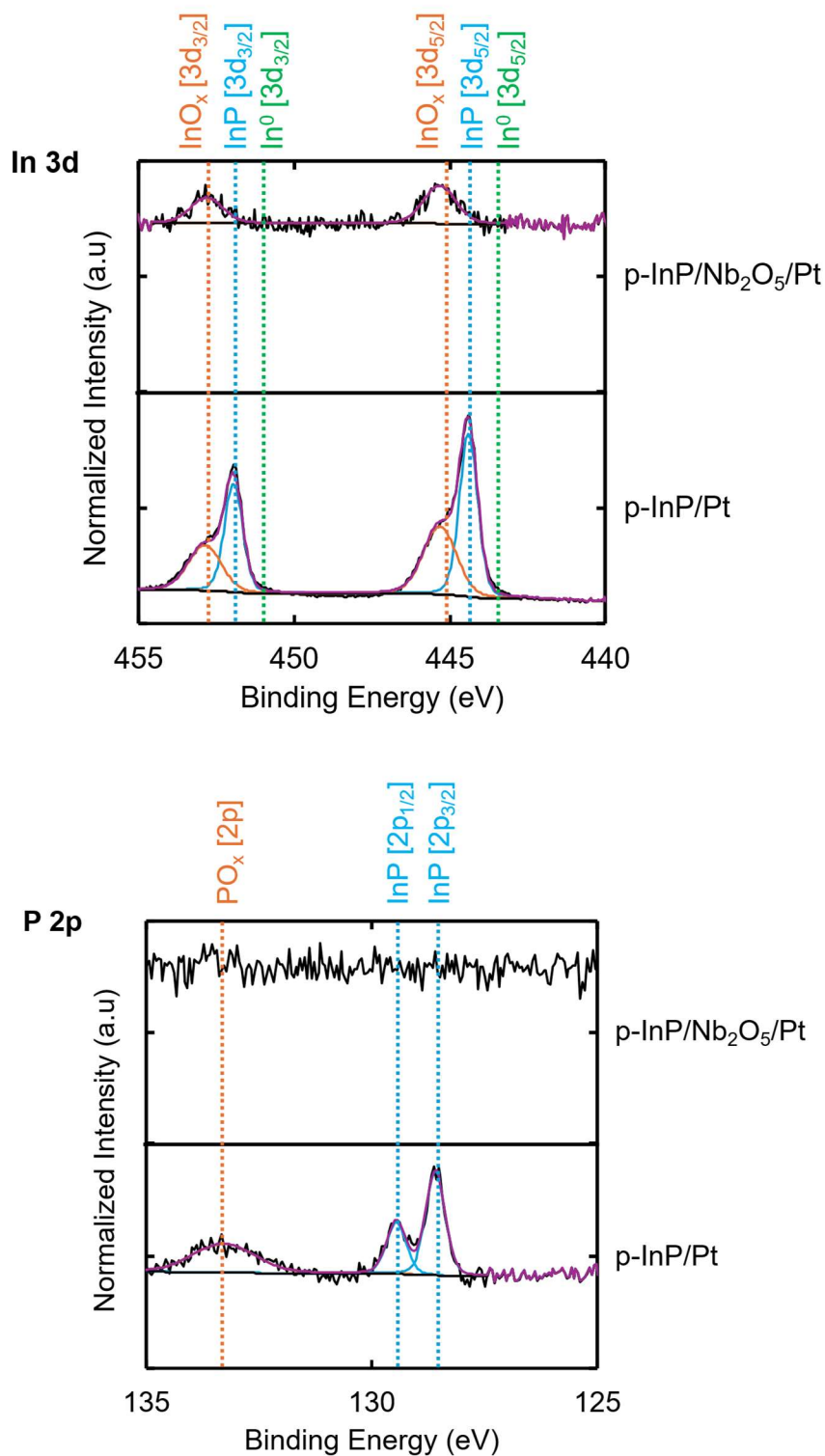


Figure 2-S13. (continued) XPS data for samples of p-InP, p-InP/Pt, p-InP/Nb₂O₅, and p-InP/Nb₂O₅/Pt held at open circuit in contact with 1.0 M H₂SO₄(aq) for 24 h in the dark. The peak locations and areas are listed in Tables 2-S2 and 2-S3.

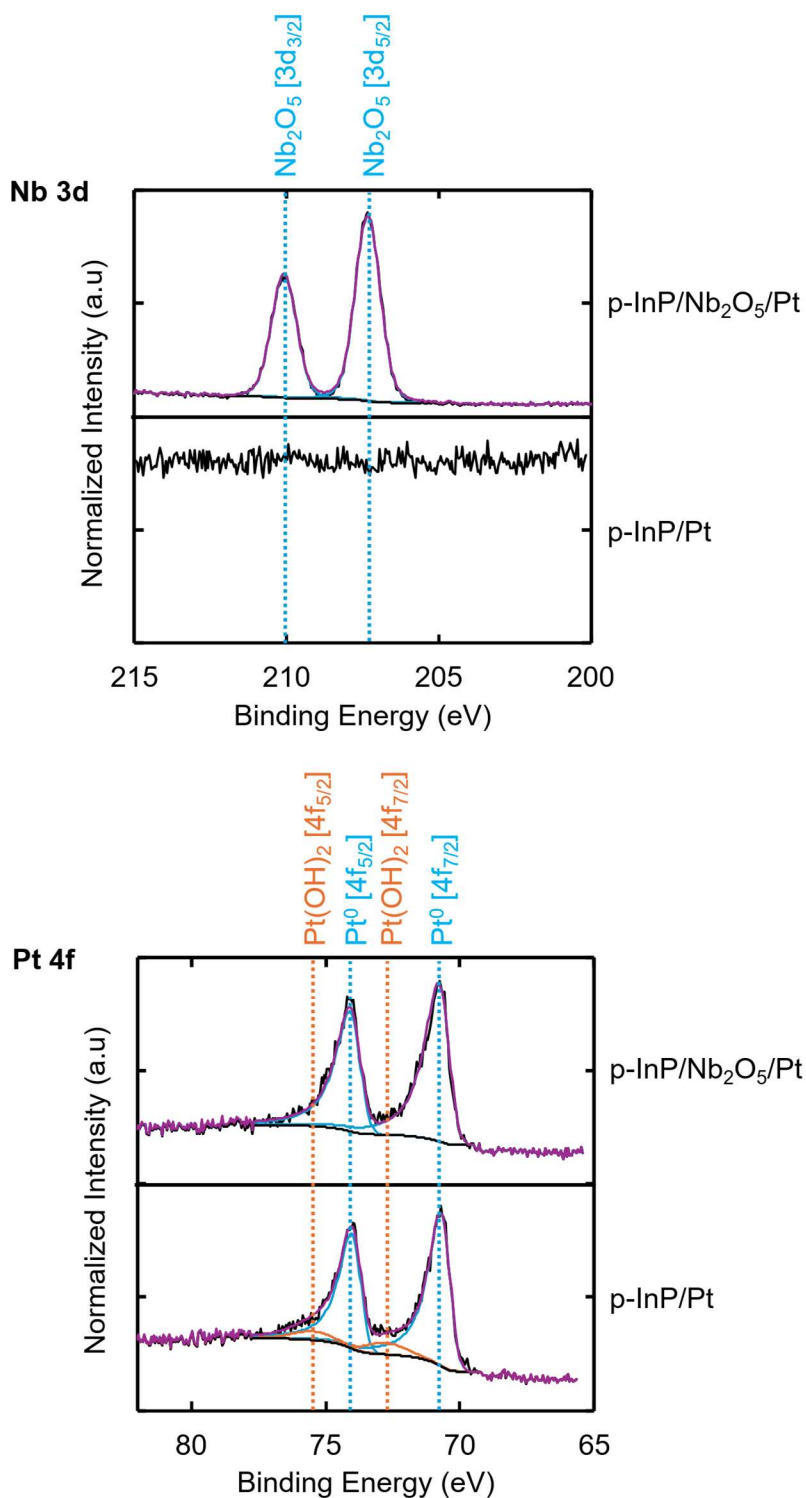


Figure 2-S13. (continued) XPS data for samples of p-InP, p-InP/Pt, p-InP/Nb₂O₅, and p-InP/Nb₂O₅/Pt held at open circuit in contact with 1.0 M H₂SO₄(aq) for 24 h in the dark. The peak locations and areas are listed in Tables 2-S2 and 2-S3.

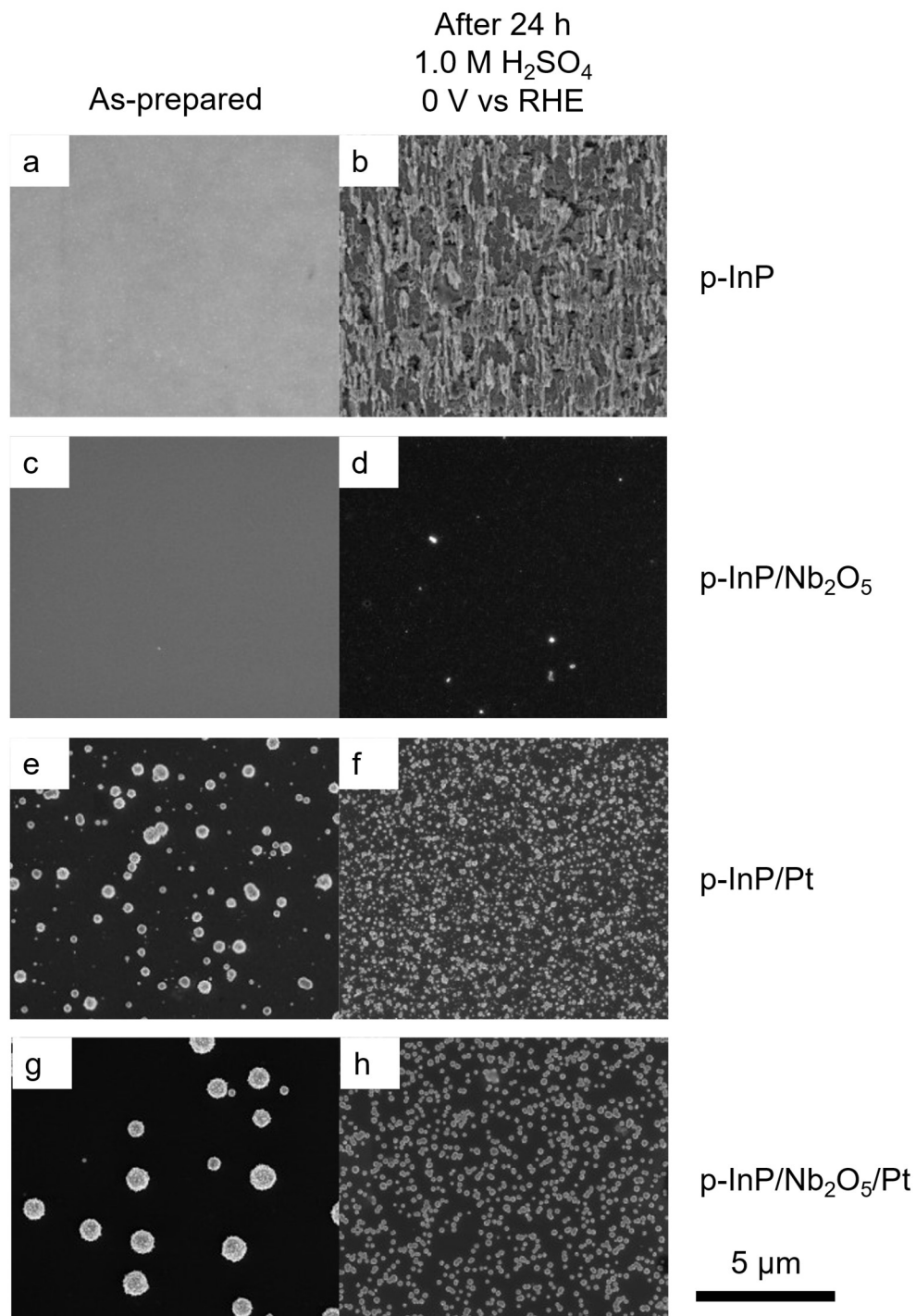


Figure 2-S14. SEM micrographs of as-prepared (a) etched p-InP, (c) p-InP/Nb₂O₅, (e) p-InP/Pt, and (g) p-InP/Nb₂O₅/Pt. SEM micrographs of (b) p-InP, (d) p-InP/Nb₂O₅, (f) p-InP/Pt, and (h) p-InP/Nb₂O₅/Pt electrodes after a potential hold at 0 V vs RHE in 1.0 M H₂SO₄(aq) for 24 h under illumination. The scale bar is 5 μm. The surface of the etched p-InP electrodes (a and b) showed more morphological changes than the Nb₂O₅-coated p-InP electrodes (c and d) after

electrochemical testing. The small surface features in (d) emerged after the reductive potential hold. These features in (d) are not Pt, due to no Pt emissions detectable by XPS (Figure 2-S12). The underlying surface of the p-InP/Pt electrodes (e and f) and p-InP/Nb₂O₅/Pt electrodes (g and h) were smooth, although the size distribution of particles changed after electrochemical testing. The particles in (e, f, g, and h) are Pt, as evidenced by the presence of Pt emissions in the XPS data (Figure 2-S12). The change in morphology of the Pt nanoparticles is consistent with detachment and subsequent re-deposition of the Pt during the reductive electrochemical testing, as is commonly observed in fuel cell testing.⁹⁶

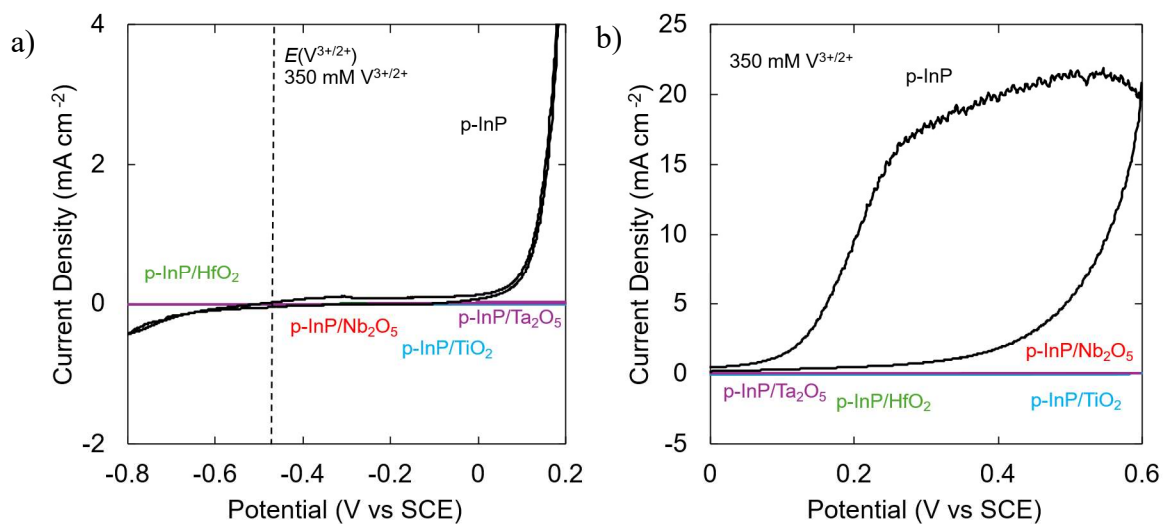


Figure 2-S15. J - E behavior of (a) the cathodic region and (b) the anodic region of p-InP electrodes coated with different barrier layers in $350 \text{ mM V}^{3+/2+}$ - 5.0 M HCl(aq) in the dark. The solution potential was -0.46 V vs SCE , and the scan rate was 50 mV s^{-1} .

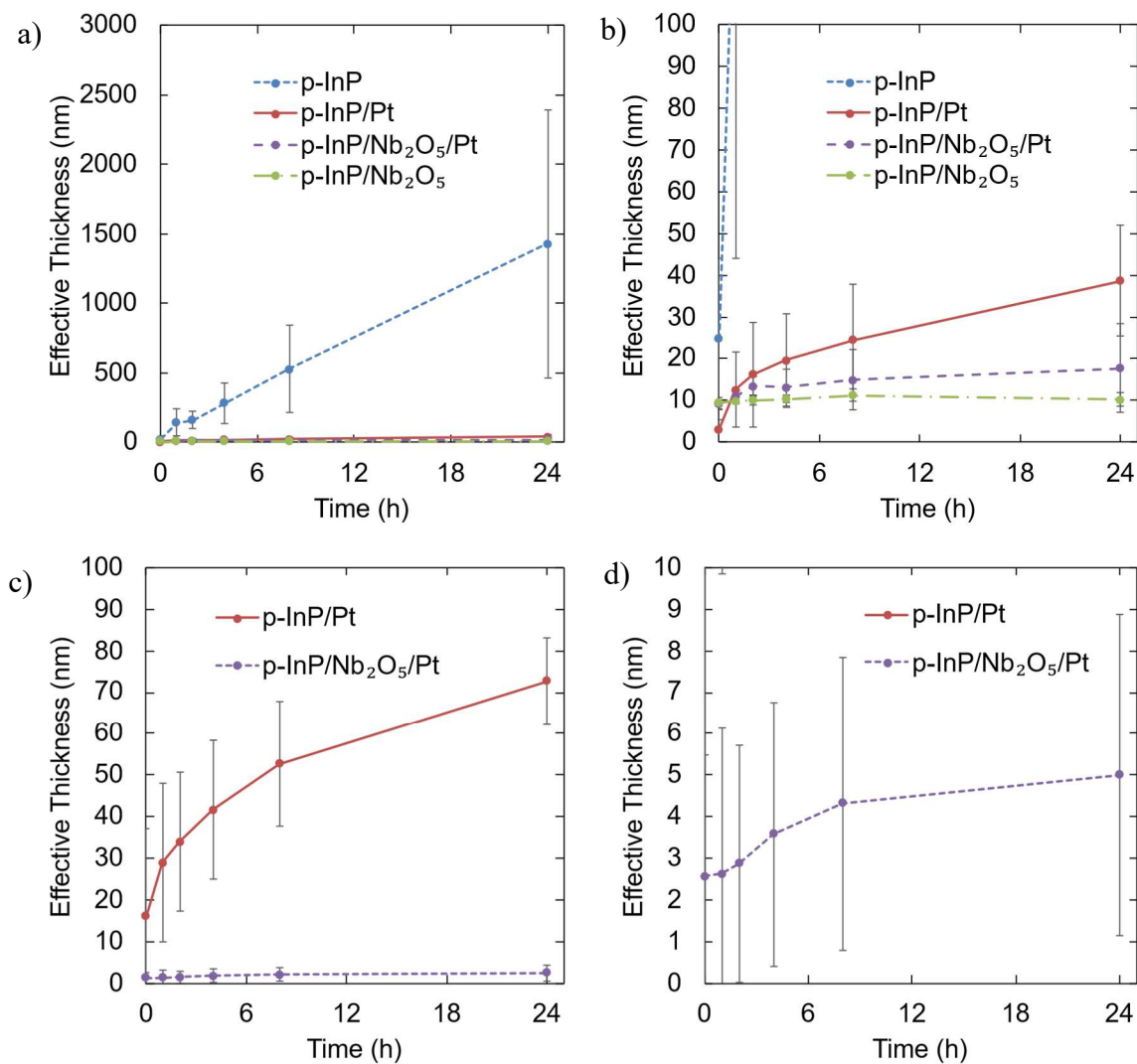


Figure 2-S16. Linear scale plots of Figure 2-3. ICP-MS data of the (a, b) effective dissolution thickness of p-InP over time during 24 h at 0 V vs RHE, and (c, d) effective dissolution thickness of p-InP over time during 24 h at open circuit in the dark.

Table 2-S2. XPS peak positions from Figures 2-S11, 2-S12, and 2-S13. Binding energies and full width half max (FWHM) are in eV. Binding energies were referenced against C 1s = 284.8 eV.

Electrode	In 3d				P 2p				Nb 3d				Pt 4f			
	Species	5/2	3/2	FWHM	Species	3/2	1/2	FWHM	Species	5/2	3/2	FWHM	Species	7/2	5/2	FWHM
Figure 2-S11. As-prepared electrodes																
p-InP	InP	444.3	451.9	0.64	InP	128.5	129.4	0.53	-	-	-	-	-	-	-	-
	InO _x	445.0	452.4	0.67												
p-InP/Pt	InP	444.4	452.0	0.58	InP	128.7	129.6	0.52	-	-	-	-	Pt ⁰	71.0	74.3	0.71
	InO _x	444.9	452.4	1.56												
p-InP/Nb ₂ O ₅	-	-	-	-	-	-	-	-	Nb ₂ O ₅	207.3	210.1	0.94	-	-	-	-
p-InP/Nb ₂ O ₅ /Pt	-	-	-	-	-	-	-	-	Nb ₂ O ₅	207.3	210.1	0.94	Pt ⁰	71.0	74.3	1.10
Figure 2-S12. Electrodes held at 0 V vs RHE for 24 h under illumination																
p-InP	In ⁰	443.4	450.9	0.50	InP	128.5	129.3	0.53	-	-	-	-	-	-	-	-
	InP	444.3	451.8	0.72	PO _x	133.1		2.05								
	InO _x	445.1	452.7	0.87												
p-InP/Pt	InP	444.1	451.7	0.62	InP	128.4	129.2	0.61	-	-	-	-	Pt ⁰	70.3	73.7	0.64
	InO _x	445.0	452.5	1.38	PO _x	133.2		2.11					Pt(OH) ₂	72.4	75.2	2.74
p-InP/Nb ₂ O ₅	-	-	-	-	-	-	-	-	Nb ₂ O ₅	207.4	210.2	0.97	-	-	-	-
p-InP/Nb ₂ O ₅ /Pt	-	-	-	-	-	-	-	-	Nb ₂ O ₅	207.4	210.1	1.00	Pt ⁰	71.0	74.3	0.82
Figure 2-S13. Electrodes held at E_{oc} for 24 h in the dark																
p-InP/Pt	InP	444.4	452.0	0.70	InP	128.6	129.5	0.51	-	-	-	-	Pt ⁰	70.8	74.0	0.81
	InO _x	445.3	452.9	1.25	PO _x	133.3		1.62					Pt(OH) ₂	72.8	75.5	1.81
p-InP/Nb ₂ O ₅ /Pt	InO _x	445.3	452.8	1.22	-	-	-		Nb ₂ O ₅	207.3	210.1	0.97	Pt ⁰	70.8	74.1	0.90

Table S3. XPS peak areas from Figures 2-S11, 2-S12, and 2-S13. Areas are in CPSeV, and relative areas are percentages. Binding energies were referenced against C 1s = 284.8 eV.

Electrode	In 3d			P 2p			Nb 3d			Pt 4f		
	Species	Area	Relative Area	Species	Area	Relative Area	Species	Area	Relative Area	Species	Area	Relative Area
Figure 2-S11. As-prepared electrodes												
p-InP	InP	1979	89.5	InP	5439	100.0	-	-	-	-	-	-
	InO _x	232	10.5									
p-InP/Pt	InP	2207	58.9	InP	6827	100.0	-	-	-	Pt ⁰	802	100.0
	InO _x	1542	41.1									
p-InP/Nb ₂ O ₅	-	-	-	-	-	-	Nb ₂ O ₅	5401	100.0	-	-	-
p-InP/Nb ₂ O ₅ /Pt	-	-	-	-	-	-	Nb ₂ O ₅	3285	100.0	Pt ⁰	364	100.0
Figure 2-S12. Electrodes held at 0 V vs RHE for 24 h under illumination												
p-InP	In ⁰	132	6.5	InP	3358	78.9	-	-	-	-	-	-
	InP	1486	20.0									
	InO _x	404	73.5									
p-InP/Pt	InP	644	42.3	InP	2231	47.2	-	-	-	Pt ⁰	422	55.3
	InO _x	877	57.7									
p-InP/Nb ₂ O ₅	-	-	-	-	-	-	Nb ₂ O ₅	3912	100.0	-	-	-
p-InP/Nb ₂ O ₅ /Pt	-	-	-	-	-	-	Nb ₂ O ₅	3257	100.0	Pt ⁰	704	100.0
Figure 2-S13. Electrodes held at E_{oc} for 24 h in the dark												
p-InP/Pt	InP	1060	57.3	InP	2499	63.7	-	-	-	Pt ⁰	867	88.9
	InO _x	790	42.7									
p-InP/Nb ₂ O ₅ /Pt	InO _x	78	100.0	-	-	-	Nb ₂ O ₅	3629	100.0	Pt ⁰	783	100.0

Table S4. Literature values of E_{cb} for HfO_2 , Ta_2O_5 , TiO_2 , Nb_2O_5 , and InP . The absolute potential of the standard hydrogen electrode, SHE, was taken to be 4.43 V vs vacuum.⁹⁷ The band edges of metal oxides shift with pH, so E_{cb} have also been listed vs RHE where appropriate. $E_{cb}(\text{HfO}_2)$ is consistently found to be much more negative than $E_{cb}(\text{InP})$. $E_{cb}(\text{amorphous Ta}_2\text{O}_5)$ was found to be ~ -1.1 V vs SHE, 0.7 V more negative than $E_{cb}(\text{InP})$. $E_{cb}(\text{crystalline Ta}_2\text{O}_5)$ was determined to be -0.5 V vs SHE, which is different than the band-edge positions measured for amorphous films, likely due to the differing morphologies. An average of these values places $E_{cb}(\text{Ta}_2\text{O}_5)$ at -1.0 V vs SHE. $E_{cb}(\text{TiO}_2)$ is usually found to be ± 0.1 V vs RHE (a value of 0.1 V vs SHE was used for $E_{cb}(\text{TiO}_2)$). $E_{cb}(\text{amorphous Nb}_2\text{O}_5)$ was determined to be 0.15 V more negative than $E_{cb}(\text{amorphous TiO}_2)$, and $E_{cb}(\text{nanoparticle Nb}_2\text{O}_5)$ was found to be 0.2 V more negative than $E_{cb}(\text{nanoparticle TiO}_2)$. In acetonitrile, $E_{cb}(\text{crystalline Nb}_2\text{O}_5)$ was determined to be 0.78 V more negative than $E_{cb}(\text{crystalline TiO}_2)$. An average of these values places $E_{cb}(\text{Nb}_2\text{O}_5)$ at -0.3 V vs SHE. $E_{cb}(\text{InP})$ is generally found to be ~ -0.03 V vs SHE for the bulk material, though surface effects can shift $E_{cb}(\text{InP})$ as negative as -0.53 V vs SHE. A value of -0.4 V vs SHE was used for $E_{cb}(\text{InP})$. The literature values support the relative placements of E_{cb} shown in Figure 2-S4.

Deposition Method	Contacting phase	E_{cb} (V vs SHE)	Ref
HfO₂			
ALD (amorphous)	0.5 M H ₂ SO ₄ (aq)	-1.59 (-1.57 V vs RHE)	98,99
ALD	Si	-2.07	100
Sputtering	Si	-2.55	101
Ta₂O₅			
Plasma enhanced CVD	Si	-1.23	102,103
ALD (amorphous)	Si	-1.13	102,104
Reactive Sputtering	Nb ₂ O ₅	-0.8 V vs $E_{cb}(\text{Nb}_2\text{O}_5)$	105
Anodized Ta	CH ₃ CN	~ -0.95	106
Oxidized Ta foil (crystalline)	0.5 M K ₂ SO ₄ , H ₂ SO ₄ (aq), pH = 0	-0.50 (-0.5 V vs RHE)	107
TiO₂			
Spin-coat	HClO ₄ (aq), pH = 1.9	0.14 (0.25 V vs RHE)	71
ALD (amorphous)	1 M HClO ₄ , pH $\approx$ 0	0.04 (0.04 V vs RHE)	88
ALD (amorphous)	1 M H ₂ SO ₄ , pH $\approx$ 0	-0.1 (-0.1 V vs RHE)	108
ALD (amorphous)	1 N KOH(aq), pH = 13.6	-0.79 (0.01 V vs RHE)	79
Nanoparticles	0.5 M Na ₂ SO ₄ , pH $\approx$ 7.2	-0.52 (-0.1 V vs RHE)	109
Electrospinning (crystalline)	CH ₃ CN	-0.23	110,111

Nb ₂ O ₅			
ALD (amorphous)	1 N KOH(aq), pH = 13.6	-0.94 (-0.14 V vs RHE)	79
Nanoparticles	0.5 M Na ₂ SO ₄ , pH ≈ 7.2	-0.72 (-0.3 V vs RHE)	109
Electrospinning (crystalline)	CH ₃ CN	-1.1– -1.01	110
InP			
-	Vacuum	-0.03	112
-	Au	-0.53	113

Table S5. Summary of key experimental results

Electrode	V_{ph} (mV)	J_{ph} (mA cm ⁻²)	InP Dissolution Rate (nm h ⁻¹)
350 mM V ^{3+/2+} -5.0 M HCl(aq)			
p-InP	650	9.97	-
p-InP/HfO ₂	-	0.26	-
p-InP/Ta ₂ O ₅	-	0.11	-
p-InP/TiO ₂	90	9.95	-
p-InP/Nb ₂ O ₅	250	10.10	-
24 h hold at 0 V vs RHE in 1.0 M H ₂ SO ₄ (illuminated)			
p-InP	- → -	6.45 → 0.08	58.5
p-InP/Nb ₂ O ₅	20 → 20	0.03 → 3.08	1.48
p-InP/Pt	650 → 550	18.8 → 15.6	0.03
p-InP/Nb ₂ O ₅ /Pt	350 → 350	16.8 → 16.1	0.35
24 h hold at E_{oc} in 1.0 M H ₂ SO ₄ (dark)			
p-InP/Pt	-	-	2.36
p-InP/Nb ₂ O ₅ /Pt	-	-	0.05

Chapter 3: Exploration of Fermi Golden Rule

Approach to Heterogeneous Electron Transfer

This project was done in collaboration with Jake M. Evans, Hyunjin Kim, Kamsy L. Anderson, and Martin A. Edwards. Hyunjin Kim's expertise with graphene electrodes was very helpful in the fabrication of graphene electrodes. Thanks to the help and expertise of Prof. Edwards and Kamsy, the SECCM measurements on graphene electrodes were able to be performed. Jake traveled to the University of Arkansas to do the measurements and was invaluable in acquiring the rate measurements. I worked on the initial SECCM attempts, fabricated and characterized the graphene electrodes, and analyzed the electrochemical data.

Introduction

Understanding heterogeneous charge transfer is crucial for being able to predict and improve rates of reactions at semiconductor/liquid junctions and most electrochemical interfaces, including in photovoltaics, batteries, and catalysts.^{8,36,114–119} One of the simplest models for characterizing the relationship between the rate of electron transfer and potential is the Butler-Volmer model.⁸ In this model, the change in potential is used to correct the free energy curve, which is assumed to be linear near the activated complex. This model is then used to correct the forward and backward rate relative to a standard rate constant at equilibrium.

$$i = F A k^0 [C_O(0, t) e^{-\alpha (E - E^{0'})} - C_R(0, t) e^{(1-\alpha) f (E - E^{0'})}]$$

In this equation, i is the current, F is Faraday's constant, A is an Arrhenius factor, k^0 is the standard rate constant, $C_O(0, t)$ and $C_R(0, t)$ are the concentrations of the oxidant and reductant at the surface of the electrode, α is the transfer coefficient, $f = \frac{F}{RT}$, and $E^{0'}$ is the potential where the forward and reverse rate constants have the same value. The linearized form of the Butler-Volmer equation for a one electron reaction when there are no mass transfer limitations and at large overpotentials (>118 mV), allows the parameter α , to be determined. This plot of $\log|i|$ vs η , or a Tafel plot, gives two branches, an anodic and cathodic branch with slopes of $\frac{(1-\alpha)F}{2.3RT}$ and $\frac{-\alpha F}{2.3RT}$ respectively. In the linear region where mass transport does not

limit the reaction rate and the backwards reaction is small, a Tafel plot can be fit to determine the transfer coefficient for the reaction.

In the case that the reaction is highly reversible, the reaction will no longer be limited by the electron transfer kinetics, but rather the mass transfer of the system. Under these conditions, rate measurements of the system will be of the mass-transfer properties of the system rather than the electron transfer kinetics. Additionally, the Butler-Volmer equation is based on macroscopic concepts, so while useful for understanding reaction mechanisms, the Butler-Volmer equation cannot be used to predict kinetics affected by microscopic properties. More advanced models of electron transfer at heterogeneous interfaces exist, which allow rates of reactions at different electrode materials to be understood.

Marcus theory, a microscopic electron transfer theory, has been successful at describing many electron transfer reactions including the prediction of the inverted region.^{120–123} The original theory, however, was used to describe outer-sphere homogeneous redox reactions. Through the application of Fermi's golden rule, Marcus theory has been extended to heterogeneous reactions and to account for quantum effects.^{124–126} In general, the Fermi's golden rule formulation uses the classical Marcus limit of interfacial electron transfer to describe the kinetics of these processes.

$$k^0(E) = \frac{4\pi^2}{h\sqrt{4\pi kT\lambda_m}} \overline{H_{AB,m}^{\circ 2}} \beta_m^{-1} \rho_{m,eff} I(\lambda_m, E)$$

Here, k^0 is the rate constant as a function of the potential, E , h is Plank's constant, k is Boltzman's constant, T is the temperature, λ_m is the reorganization energy of the reaction, $\overline{H_{AB,m}^{\circ 2}}$ represents the square of an integral coupling of all reactant and product states across all energies, β_m is the coupling attenuation factor, $\rho_{m,eff}$ is the effective density of states, and $I(\lambda_m, E)$ is a definite integral that weights the rate of reaction across all energies. The λ_m describes the reorganization energy required to change the redox species from one oxidation state to another, while $\overline{H_{AB,m}^{\circ 2}}$ describes the interactions between the electrode and the redox species. The exponential decrease in rate as the distance between the redox species and electrode surface is increased has been explicitly characterized using β_m . Notably, the effective density of states is related to the bulk density of states, ρ_m , by a coupling length, δ , that

expresses the distance into the electrode surface that the electronic coupling between redox species and the electrode is effective. Once the rate at any given energy level has been described, it is integrated across energy, $I(\lambda_m, E)$, to determine the overall rate. In a metal, there are viable energy states that contribute to the rate up to the Fermi level, while in a semiconductor, only the energy levels around the conduction band contribute significantly to the electron transfer rate.

Although many of the other parameters can be derived or estimated from experiments, the quantity δ does not have a strong experimental backing to estimate its value.^{127–130,120} Estimation of the effective penetration length as the length of the redox species' wavefunctions, results in the value of δ to be about 0.3 nm. For example, this approximation gives an $\rho_{m,eff}$ of about 0.27 states eV⁻¹ in gold and the rest of the states in the “bulk” of the electrode do not affect the rate of reaction.¹³¹ However, this parameter has not been explicitly determined through experiments. To determine this quantity, electron transfer rate constants must be made as a function of electrode thickness with atomic-layer precision. 2D graphene may allow this quantity to be experimentally determined since the addition of more layers will allow greater coupling and $\rho_{m,eff}$ until the “bulk” is reached.

Previous measurements of rate constants at highly oriented pyrolytic graphite (HOPG) has shown that the theoretically predicted rate constants of HOPG matches well with experimental observations (Figure 3-1).¹³² Measured rate constants on graphene however, have spanned multiple orders of magnitude, likely a result of defects or wrinkles.^{133–136} Using van der Waals heterostructure fabrication techniques and localized scanning electrochemical cell microscopy (SECCM),^{137–142} the measurement of defect-free basal plane graphene could be possible. SECCM is a localized electrochemical technique that allows an electrochemical cell to be confined to the tip of a nano-pipette, allowing the area of the electrode to be <100 nm in diameter to be studied, which should in principle allow defects to be avoided. SECCM was previously used to study rates of reaction on graphene electrodes, with one study showing that the rates plateaued at ~6 layers of graphene (~3 nm),¹⁴³ and another study showed that the twist angle of bilayer graphene electrodes affected the rate of electron transfer.¹⁴⁴

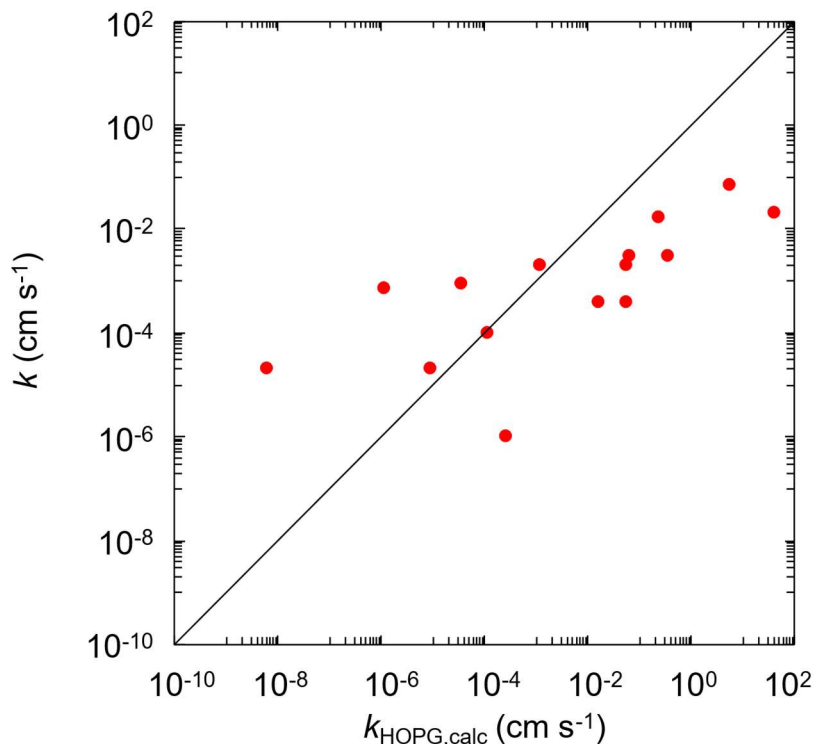


Figure 3-1. Rate of electron transfer rate constants for various redox species on HOPG vs predicted rate constants from the Fermi's golden rule formulation. Data from Ref ^{126,132}.

In this work, the rate of electrochemical electron transfer at mechanically exfoliated graphene was measured using SECCM to analyze the electrode thickness dependence of electron transfer kinetics, allowing determination of the coupling length in the Fermi's Golden Rule equation. Due to the electrochemical spatial localization provided by SECCM, SECCM allows defects on graphene to be identified and isolated from other measurements made on non-defective regions.

Fabrication of Graphene electrode samples

The fabrication of graphene van der Waals heterostructure samples were prepared through a dry stamping fabrication procedure with custom stamps made of polycarbonate and polydimethylsiloxane (PDMS). Mechanically exfoliated graphene flakes were stamped onto hexagonal boron nitride (h-BN) and electrically contacted with a graphite contact to a e-beam evaporated gold pad (Figure 3-2). Graphene flakes were exfoliated onto 20 nm SiO₂/Si wafers, allowing the thickness of small layer-graphene flakes to be identified optically before transferring them onto h-BN. The full procedure is described in the Experimental Methods

section. Samples were characterized by atomic force microscopy (AFM) and Raman spectroscopy (Figure 3-3). For graphene, the intensity ratio of the G-band and 2D-band depends exponentially with the graphene thickness, and the shape of the 2D-band is indicative of the graphene thickness.^{145,146} By calculating the ratio of the intensity of the two characteristic peaks and the shape of the 2D-band, the thickness of the graphene sample was determined for each sample. The D-band shown is a result of the underlying h-BN and is present on bare h-BN without any graphene. This overlapping of the h-BN D-band peak and graphene D-band peak made determining the defect density of fabricated graphene devices using Raman difficult.¹⁴⁵

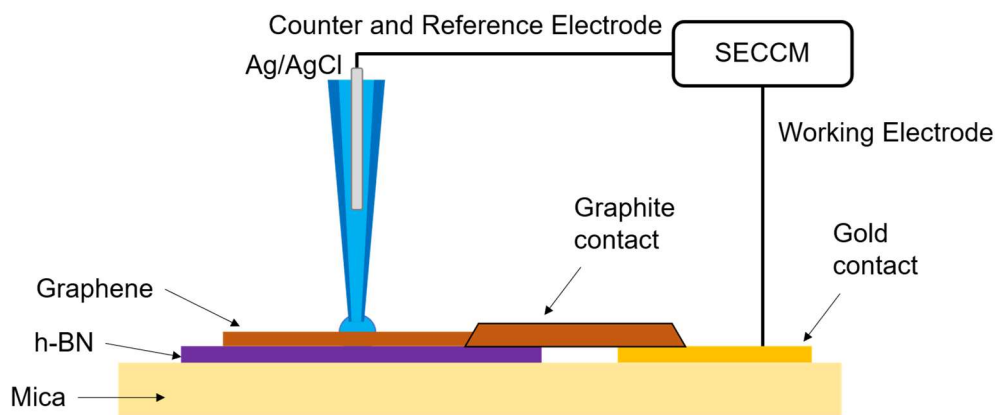


Figure 3-2. Cross-section diagram of graphene electrode and experimental setup for SECCM measurements of electron transfer rate constant

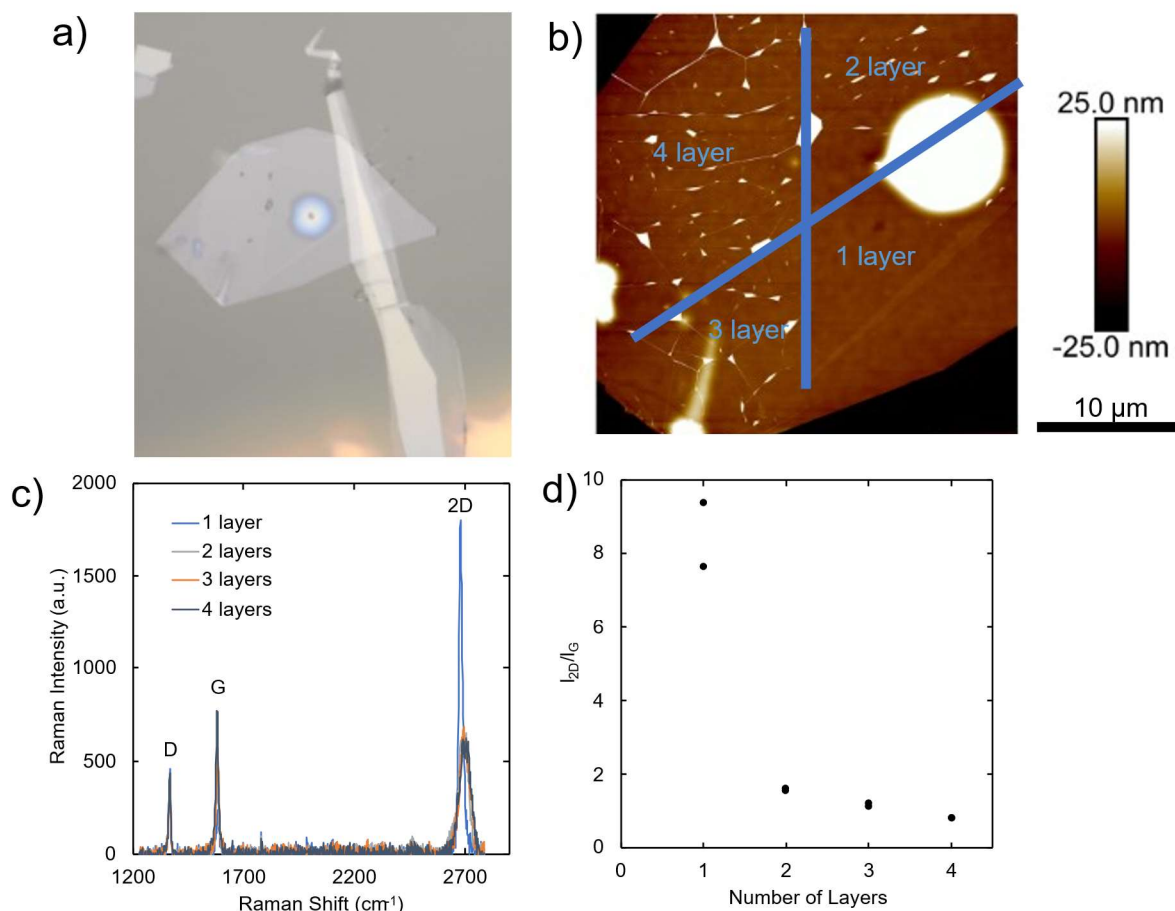


Figure 3-3. (a) Optical image and (b) AFM micrograph of a graphene electrode with regions of varying thickness. (c) Raman spectra of the graphene in the different regions and (d) ratio of the intensity of the 2D/G bands for the different thickness found in each region.

Considerations for SECCM Measurements

Although electrochemical cells generally have 3 electrodes, in SECCM and other microelectrode electrochemical experiments, the reference electrode can simultaneously act as the reference and counter electrode, simplifying the electrochemical cell. The low currents produced at the working electrode mean that the reference electrode can maintain a constant potential even if it is acting as the counter electrode. To make a 3-electrode cell in SECCM, a double barrel pipette is needed, in which a thin glass wall separates the reference and counter electrode. The small inner diameter of these double barrel pipettes, however, can lead to difficulties in filling the pipettes. A combination of pre-soaking the pipettes in piranha solution to make them hydrophilic, filtering the solution, and mechanical agitation of the pulled pipettes

was developed to fill double barrel pipettes, but the separation of the reference electrode and counter electrode is unnecessary. Instead, a single barrel pipette that only contains the solution of interest and a quasi-reference electrode can be used.

The main issue, however, is that the piezoelectric motors for positioning the tip need to be extremely accurate. Because the pipette tip and sample do not make electrical contact until the tip is almost touching the sample in SECCM, any inaccuracy of the positioning of the tip can lead to the tip crashing into the sample and breaking the pipette tip (Figure 3-2). The CHI 920D that was initially used was designed for scanning electrochemical microscopy, SECM, where exact positioning of the pipette tip is not necessary due to the continuous feedback throughout the microelectrode approach toward the surface that provides information on the proximity of the tip to the electrode surface. This inaccuracy in the pipette positioning led to many instances of snapping the pipette tip before measurements could be performed, simply because the instrument was not designed with SECCM in mind. By the time the pipette tip was close to the working electrode, it was only one or two piezo steps away from crashing. Through slower tip approach speeds and an alternate approach procedure, the breaking of tips was minimized, but the inaccuracy of the piezoelectric motors would still often lead to broken tips (Figure 3-4).

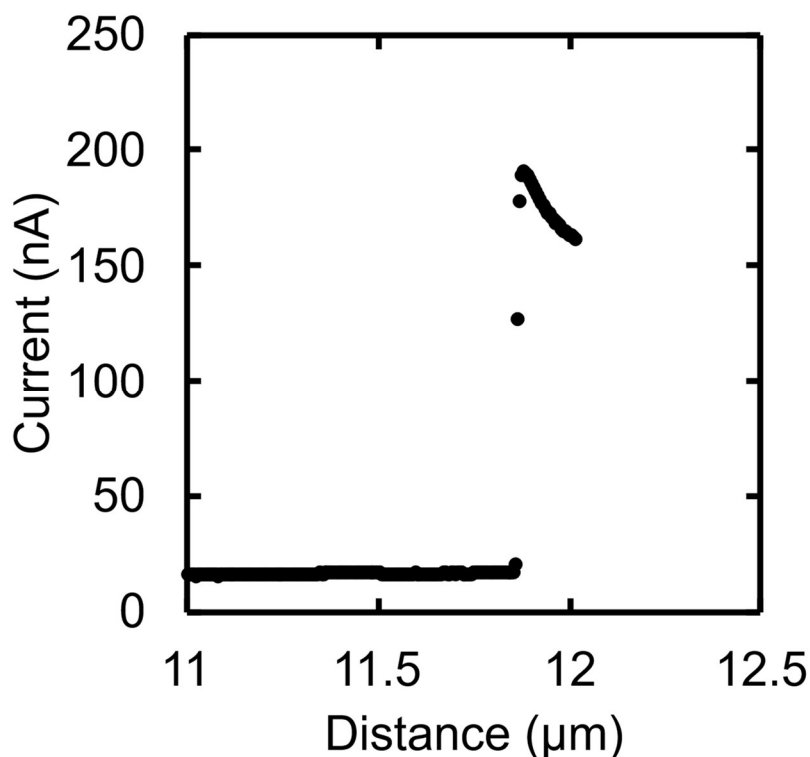


Figure 3-4. Current-distance behavior of a micropipette approaching a working electrode surface on SECCM. Contact between the micropipette and the working electrode surface requires precise positioning of the tip to the electrode surface.

Analysis of SECCM voltammograms

To determine the rate constant of the graphene electrodes, the I - E behavior can be fit to semi-empirical equations that allow the electron transfer rate constants to be extracted. The general equations used to model the steady-state I - E behavior of hemispherical electrodes can be modified to account for the difference in mass transport at an SECCM tip. Since ultramicroelectrodes have nearly hemispherical mass transport, mass transport limitations do not impact the I - E behavior as much in microelectrodes as compared to planar electrodes, allowing electron transfer rate constants for even very reversible redox couples to be extracted.⁸ If the rate of electron transfer is significantly faster than the mass transport kinetics, then the reaction will appear to be reversible, making determination of the electron transfer rate constant impossible. The scan rate used to measure the I - E behavior was sufficiently slow (10 mV/s) to ensure a steady-state approximation for the working electrode. The current as a fraction of the limiting current for a hemispherical electrode at steady state is as follows:

$$\frac{i}{i_{lim}} = \frac{\kappa}{1 + \kappa(1 + \xi^2\theta)}$$

Where i is the current, and i_{lim} is the limiting current.⁸ κ is the ratio of the forward rate constant to the steady-state mass-transfer coefficient, ξ^2 is the ratio of the diffusion constants of the oxidized and reduced forms of the redox species in solution, and θ is the ratio of the backward to forward rate constants.⁸

$$\kappa = \frac{r_0 k_f}{D_0}$$

$$\xi^2 = \frac{D_O}{D_R}$$

$$\theta = \frac{k_b}{k_f} = e^{\frac{F}{RT}(E-E^{0'})}$$

Here, r_0 is the radius of the hemispherical electrode, k_f is the forward rate constant, k_b is the backwards rate constant, D_O is the diffusion constant for the oxidized redox species, D_R is the diffusion constant for the reduced redox species, F is the Faraday's constant, R is the ideal gas constant, T is the temperature in Kelvin, E is the potential, and $E^{0'}$ is the thermodynamic reduction potential of the redox species. Assuming Butler-Volmer kinetics, k_f can be expressed as a function of the fundamental rate constant, k^0 , and E :

$$k_f = k^0 \exp \left[-\frac{\alpha F}{RT} (E - E^{0'}) \right]$$

Where α is the transfer coefficient.⁸ The limiting current at an SECCM tip is a function of the geometry at the tip and can be found by modifying the limiting current at a hemispherical electrode.¹⁴⁷

$$i_{lim}^{hem} = 2\pi r_{0,eff} n F D_O c_{b,o}$$

$$i_{lim}^{SECCM} = i_{lim}^{hem} (1 - \cos(\gamma))$$

Where $r_{0,eff}$ is the equivalent radius of a hemispherical electrode, n is the number of electrons transferred, and $c_{b,o}$ is the bulk molar concentration of the oxidized redox species solution, γ is the half-angle of the pipette (here assumed to be approximately 7.5°).¹⁴⁷ $r_{0,eff}$ can also be determined from the pipette radius, r_p , or vice-versa.¹⁴⁷

$$r_{0,eff} = \frac{r_p}{\tan(\gamma)}$$

Using these equations, the limiting current can be fit to determine $r_{0,eff}$, and the shape of the normalized I - E curve can be fit to determine k_0 .^{8,147} For the redox couples used in this work, ξ is assumed to be unity, and since D_0 and $E^{0'}$ are known for each species, the fitting can be done through a simple least squares regression for the best-fit value of k_0 and α .

SECCM of $\text{Ru}(\text{NH}_3)_6^{3+/2+}$ on multi-layered graphene sample

Figure 3-5 shows the I - E behavior of graphene in contact with 5 mM $\text{K}_3\text{Ru}(\text{NH}_3)_6$ as measured by SECCM. Different regions of the graphene electrode were approached by the SECCM pipette tip to target regions of different thicknesses as seen in Figure 3-3. The limiting current for the I - E behavior was consistently less than 1 pA, and the $E_{1/2}$ for these

measurements regardless of the graphene electrode thickness, was ~ -0.55 V vs Ag/AgCl ($E^{0'}(\text{Ru}(\text{NH}_3)_6^{3+/2+}) = -0.184$ V vs Ag/AgCl).

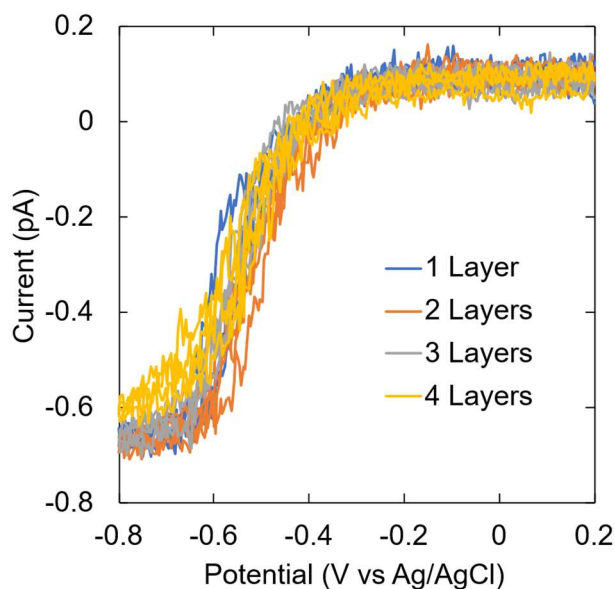


Figure 3-5. *I-E* behavior of (a) monolayer, (b) bilayer, (c) trilayer, and (d) four-layer graphene working electrodes collected via SECCM at 10 mV/s in 5 mM $\text{K}_3\text{Ru}(\text{NH}_3)_6$, 100 mM KCl solution.

The effective hemispherical radius, $r_{0,eff}$, was calculated from the limiting current and the pipette radius was calculated from $r_{0,eff}$ (Table 3-1). The effective hemispherical radii were consistently ~ 30 nm, and the calculated pipette radii were ~ 4 nm. The pipette radii suggest that the pipette was small enough to avoid defects in the graphene flakes. The pipette radius, however, is much smaller than the expected radius for a nanopipette and may be the result of an incorrect assumption in the geometry of the pipette. That said, the difference between the $E_{1/2}$ and $E^{0'}$ observed in Figure 3-5 indicates that the reaction was quasi-reversible or irreversible on graphene, satisfying the assumption of non-reversibility necessary for determining the electron transfer rate constant.

Table 3-1. Effective hemispherical radius and pipette tip radius calculated from electrochemical data.

Graphene layers	$r_{0,eff}$ (nm)	r_p (nm)
1	32.8	4.3
2	33.8	4.5
3	33.3	4.4

4	29.8	3.9
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Figure 3-6 shows the normalized I - E behavior of the graphene electrodes with different thicknesses and the resulting fits. Table 3-2 lists the fitted k^0 and α , and Figure 3-7 shows the fitted values graphically. The fits match the measured I - E behavior quite well, and the fitted α values are all quite close to 0.5. The fitted k^0 value for single layer graphene is about $4.10 \times 10^{-3} \text{ cm s}^{-1}$ whereas the fitted k^0 value for multi-layer graphene is $1.66 \times 10^{-2} \text{ cm s}^{-1}$. These fits show no clear dependence of the measured rate of electron-transfer on increasing graphene electrode thickness. Furthermore, there is a slight negative correlation of k^0 on α . When α is set to 0.5 and k^0 is re-fitted to the data, there is even less dependence of k^0 with graphene electrode thickness.

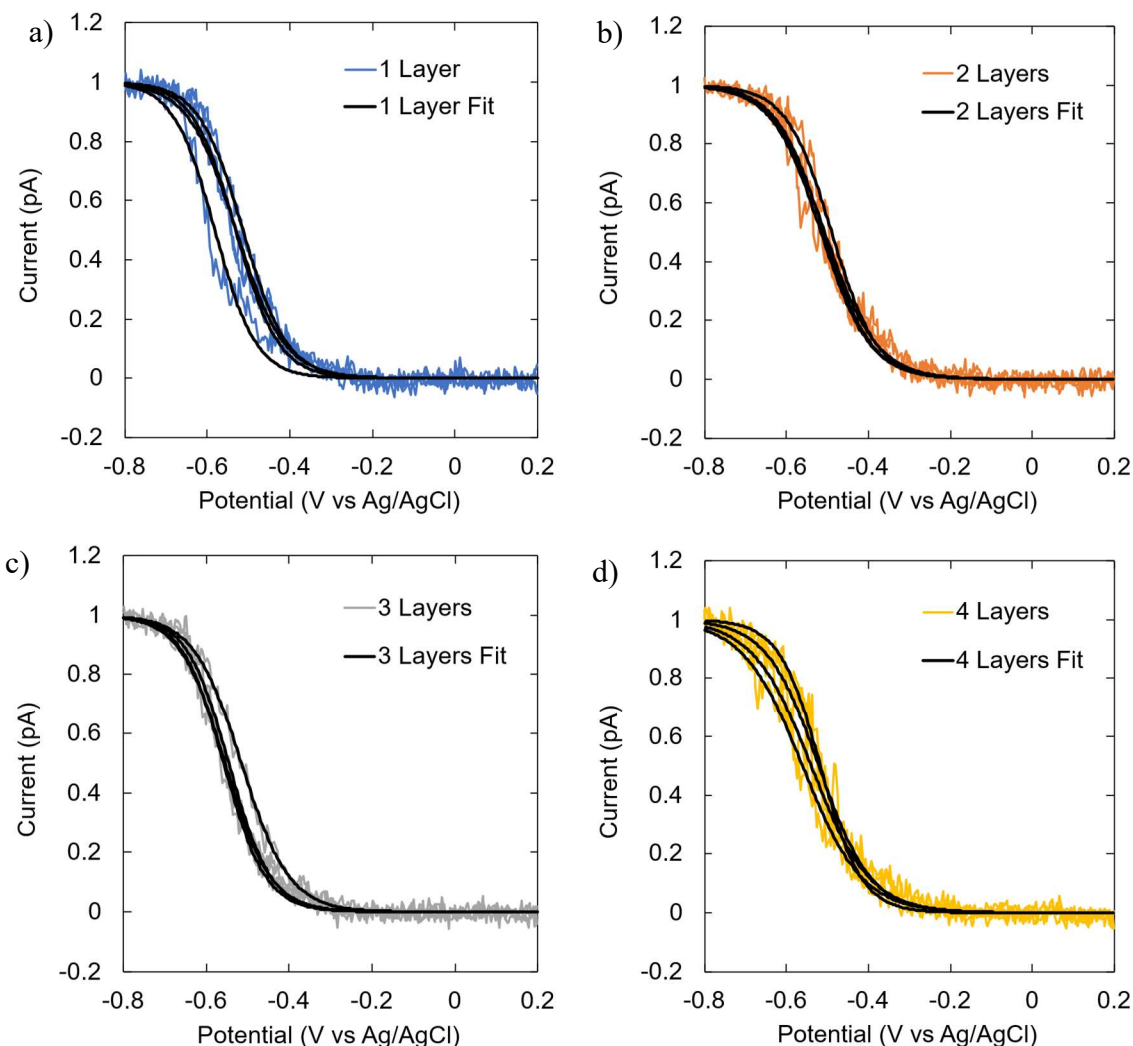


Figure 3-6. *I-E* behavior (colored lines) of (a) monolayer, (b) bilayer, (c) trilayer, and (d) four-layer graphene working electrodes collected via SECCM at 10 mV/s in 5 mM $\text{K}_3\text{Ru}(\text{NH}_3)_6$, 100 mM KCl solution with resulting fits (black lines).

Table 3-2. Fundamental rate constant and transfer coefficient calculated as a function of graphene electrode thickness

Graphene layers	k^0	α
1	4.10×10^{-3}	0.48
2	1.13×10^{-2}	0.44
3	3.67×10^{-3}	0.48
4	1.66×10^{-2}	0.37

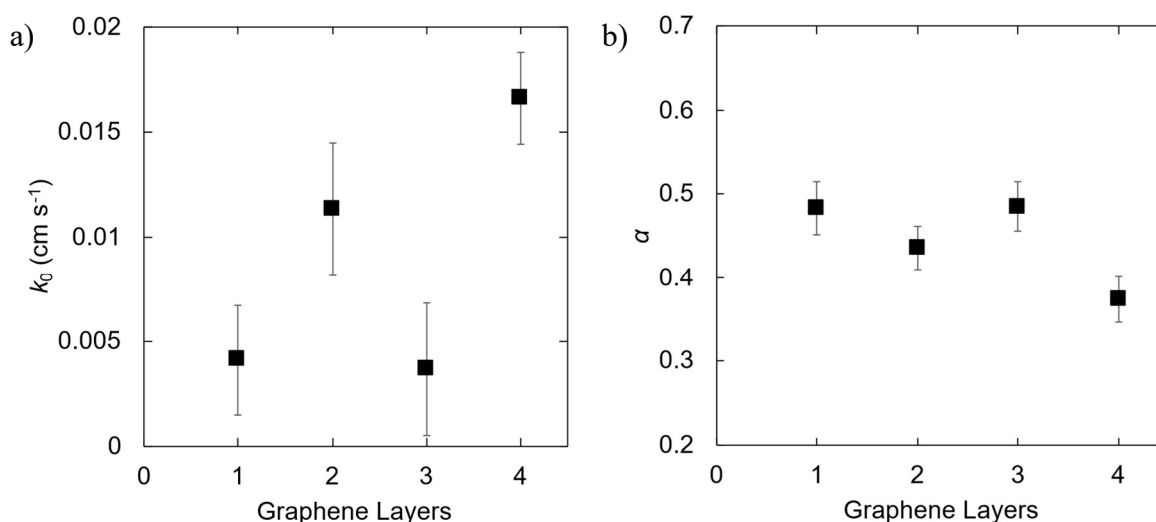


Figure 3-7. (a) Fundamental rate constant and (b) transfer coefficient calculated via the fits in Figure 3-6 as a function of graphene electrode thickness.

The value of k^0 determined here on single layer graphene is several orders of magnitude greater than the predicted value of k^0 of $\text{Ru}(\text{NH}_3)_6^{3+/2+}$ on HOPG ($3.8 \times 10^{-5} \text{ cm s}^{-1}$)¹⁴⁸ and previously measured values of k^0 on HOPG ($9.0 \times 10^{-4} \text{ cm s}^{-1}$).¹³² The value of α is between 0.4 and 0.5, indicating a symmetric electron transfer reaction as expected for $\text{Ru}(\text{NH}_3)_6^{3+/2+}$.⁸ At face value, the lack of dependence of k^0 with graphene thickness indicate that the distance into the electrodes that redox species couple with the electrode, δ , is less than or equal to the thickness of one graphene layer. The difference between measured and predicted values for

$k^0(\text{Ru}(\text{NH}_3)_6^{3+/2+})$, however, indicates that there may be defects dominating the electrochemical behavior of these measurements. These defects may be a result of wrinkles or tears introduced in the electrode fabrication procedure (Figure 3-3). The small tip radius should reduce the likelihood of defects, but the chance is still non-zero. It is also difficult to determine if the measurement has been confounded by contact with a defect in SECCM, since the defect may only be a few atoms large. Furthermore, measurements during SECCM may introduce defects and warping because of contact with the electrode surface. The solution in the pipette tip may wick out onto the surface of the electrode and dry up, leading to salt deposits on the surface of the graphene electrode that can warp of the surface of the graphene.

The thickness of single-layer graphene layer has been previously estimated by AFM to be between 0.4 nm and 1.7 nm.^{146,149} This error can be as largely attributed to inaccuracies caused by substrate-graphene interactions and graphene-tip interactions that can change the measured thickness.¹⁴⁹ When these interactions are reduced, AFM measurements agree with transmission electron microscopy measurements in approximating the thickness of single-layer graphene as about 0.3nm. This value is the same value used to approximate the value of δ when predicting the electron transfer rate constants on HOPG.^{131,148} The graphene thickness however, limits the ability of this technique to determine the value of δ with a precision of greater than 0.3 nm. It is possible that the coupling of the redox couple with the electrode was limited to a single atomic layer, leading to the inconsistent and lack of dependence of the electron transfer rate constant on the graphene thickness, since the coupling of the electrochemical species only occurs at the very first atomic layer.

SECCM of other redox species

Figure 3-8 shows the rate of electron transfer for different redox species measured on single layer graphene and HOPG. The measured rate constants are listed in Table 3-3. The rate of electron transfer for $\text{Co}(\text{en})_3^{3+/2+}$ and $\text{Ru}(\text{NH}_3)_6^{3+/2+}$ increased on HOPG compared to single-layer graphene by a factor of ~ 4 , but the rate of electron transfer decreased on HOPG compared to single-layer graphene for $\text{IrCl}_6^{2-/3-}$ by a factor of 8. The measured rate constants on both HOPG and single-layer graphene by SECCM, however, were much greater than previously measured rate constants on basal plane HOPG.¹³²

Table 3-3. Fundamental rate constants for $\text{Co(en)}_3^{3+/2+}$, $\text{Ru(NH}_3)_6^{3+/2+}$, and $\text{IrCl}_6^{2-/3-}$ on HOPG and single layer graphene measured by SECCM.

Redox Couple	$k^0(\text{HOPG}) (\text{cm s}^{-1})$	$k^0(\text{Single-layer Graphene}) (\text{cm s}^{-1})$	$k^0(\text{HOPG Literature})^{132} (\text{cm s}^{-1})$
$\text{Co(en)}_3^{3+/2+}$	1.02×10^{-2}	2.29×10^{-3}	2.0×10^{-5}
$\text{Ru(NH}_3)_6^{3+/2+}$	1.66×10^{-2}	4.10×10^{-3}	9.0×10^{-4}
$\text{IrCl}_6^{2-/3-}$	2.12×10^{-2}	1.85×10^{-1}	3.0×10^{-3}

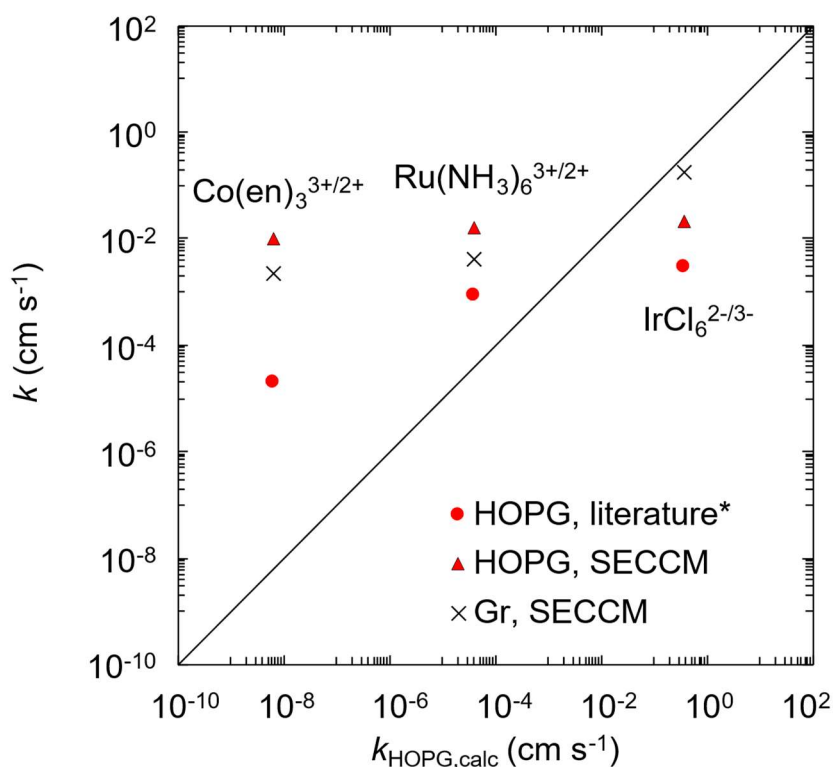


Figure 3-8. Rate of reactions, k^0 , measured by SECCM on HOPG and graphene compared to literature values of rates on HOPG. *Literature values from Ref ¹³².

The difference between the predicted, expected, and measured values of k^0 on both HOPG and single-layer graphene makes it difficult to determine the relationship between graphene thickness and k^0 . As discussed, the influence of defects, though unlikely with the SECCM, cannot be ruled out and would significantly impact the measured rate constants on these surfaces. As seen in the AFM of the graphene samples, there is some warping of the electrode due to bubbles trapped between the graphene and h-BN surfaces (Figure 3-3b). These defects in the graphene fabrication process are common,^{150,151} and though the likelihood of these

defects can be reduced through annealing or holding under vacuum as was done as was done for the fabrication of these samples, they are difficult to eliminate completely. Previous studies on graphene have noted a 10-fold increase in rate of electron transfer as a result of defects and edge sites.¹³⁶ Another possible source of error, are adventitious carbon left from the transfer process that may affect the electron transfer kinetics.¹³⁵ These sources of error in addition to the inconclusive reports of the dependence of graphene thickness on electron transfer make performing these measurements without confounding defects difficult.^{133,134,143}

Conclusions

The rate of electron transfer at graphene electrodes of varying thickness was measured using SECCM to explore the effective coupling length of redox species in solution into heterogeneous electrodes. The Fermi Golden Rule approach for heterogeneous electron transfer at heterogeneous electrodes assumes a coupling length of 0.3 nm into the electrode. Localized electrochemical measurements on van der Waals heterostructure graphene electrodes with single to multi-layer graphene were performed to test the thickness dependence of electron transfer kinetics while avoiding possible defects. The rate of electron transfer measured with $\text{Ru}(\text{NH}_3)_6^{3+/2+}$, $\text{Co}(\text{en})_3^{3+/2+}$, $\text{IrCl}_6^{2-/3-}$ did not show convincing evidence of thickness dependence, although some evidence of a negative correlation with α was observed. Measurements on HOPG similarly showed no significant difference compared to single-layer graphene for these redox species. The effective coupling length was then estimated to be 0.3 nm as was originally estimated. This conclusion, however, is tempered with confounding issues with uncertainties associated with the graphene layer thickness, and the impact of defects or surface contamination on the rate of electron transfer. Future work on this may be able to account for or eliminate the effects of defects on the graphene surface, but due to the inherent thickness of graphene, measurements will only be able to determine the effective coupling thickness in increments of 0.3 nm, or the thickness of a single graphene layer.

Experimental Methods

Materials

The following materials were used as received: HOPG (SPI-1, SPI), bulk mica (grade V-5, SPI supplies), HBN (Trivial Transfer HBN, 1 layer, ACS Materials), polydimethylsiloxane (PDMS, 10:1, SYLGARD 184), polycarbonate (Sigma-Aldrich), chloroform (ACS, Sigma-Aldrich), N-methyl-2-pyrrolidone (NMP, anhydrous 99.5%, Sigma-Aldrich), isopropyl alcohol (IPA, ACS, StatLab), glass capillaries (borosilicate, Sutter), hexaamineruthenium (III) chloride ($\text{Ru}(\text{NH}_3)_6\text{Cl}_3$, 98%, Sigma-Aldrich), silver wire (Ag, 99.9985%, Alfa Aesar), potassium chloride (KCl, ACS grade, EMD), conductive silver paint (PELCO, Ted Pella, Inc), and nitrogen (N_2 , UHP, Airgas).

Preparation of graphene electrodes

Graphene flakes were mechanically exfoliated from bulk highly ordered pyrolytic graphite by repeatedly cleaving with standard adhesive tape and then adhered to Si/SiO₂ (20 nm). Substrates were prepared by cleaving bulk mica to be flat on both sides, then 3 nm Ti was deposited as an adhesion layer using a Denton Explorer 14 electron beam metal evaporation system (base pressure $< 1 \times 10^{-6}$ Torr, 40 mA deposition current, 10 kV accelerating voltage). 40 nm Au was then deposited to make the final contact (150 mA deposition current). A physical mask was used to make circular contacts. A custom PDMS stamp was used to fabricate and transfer the van der Waals heterostructure (Figure 3-S1).

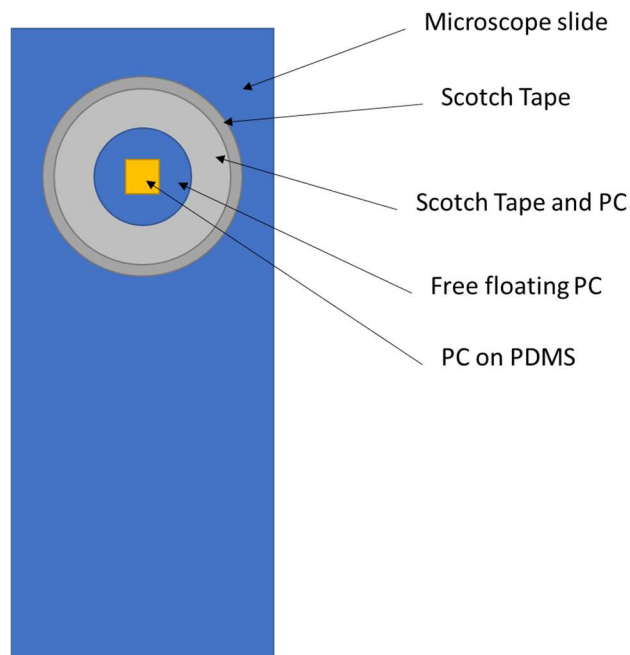


Figure 3-S1. Diagram of custom transfer stamp used to pick up exfoliated graphene flakes.

The stamp was made with a PDMS base and polycarbonate film draped over the PDMS base. To make the PDMS base, 4g/0.4g of PDMS were mixed and allowed to set in a 10 cm petri dish for 24 h. 3-4 mm squares of PDMS were cut out using a clean razor blade and placed in the center of a glass slide about 1.5 cm from the top edge. The glass slides were cleaned with IPA prior to use to avoid dust and blemishes. To fabricate the polycarbonate film, a 6 wt% polycarbonate solution in chloroform was prepared, and 7 drops of the polycarbonate solution was placed along the face of a clean glass slide. A second glass slide was then placed on top of the first, creating a thin bubble free layer of polycarbonate between the two glass slides. The two glass slides were then quickly slid across each other to create a thin film of polycarbonate on top of each glass slide. After the polycarbonate had dried for a few days, a 1 cm diameter circle was cut into the film using a razor blade and the surrounding polycarbonate was removed. A piece of scotch tape with a hole punched in the middle was then placed over the polycarbonate circle. The scotch tape and polycarbonate film were then carefully removed from the glass slide, and placed on top of the PDMS base, making sure to avoid any dust, bubbles, or wrinkles on the polycarbonate film. The stamp was then heated for 5 min at 80 °C to remove any remaining wrinkles.

These stamps were then used to fabricate the van der Waals heterostructures (Figure 3-S2). First, flakes of hexagonal boron nitride (HBN) were picked up at 90 °C, and then graphene was picked up using the HBN at 60 °C. The excess scotch tape was then cut off, and the polycarbonate film with the HBN/graphene was picked up, flipped upside down, and placed on a new PDMS base. The polycarbonate was then dissolved using NMP and IPA, leaving the assembled HBN/graphene stack on a clean PDMS base. The HBN/graphene stack was then placed on a mica substrate next to the Au contact at 60 °C.

A graphite contact was fabricated by mechanically exfoliating HOPG and selecting a thin (in width) sample. The thin graphite contact was then picked up using a PDMS stamp and aligned such that it connected the Au contact and graphene stack, then dropped on to the stack at 60 °C to make the full electrode stack. Electrical contact was made by adhering Cu metal to the Au contact with conductive Ag paste. The Cu metal was then connected to the working electrode contact of the AFM.

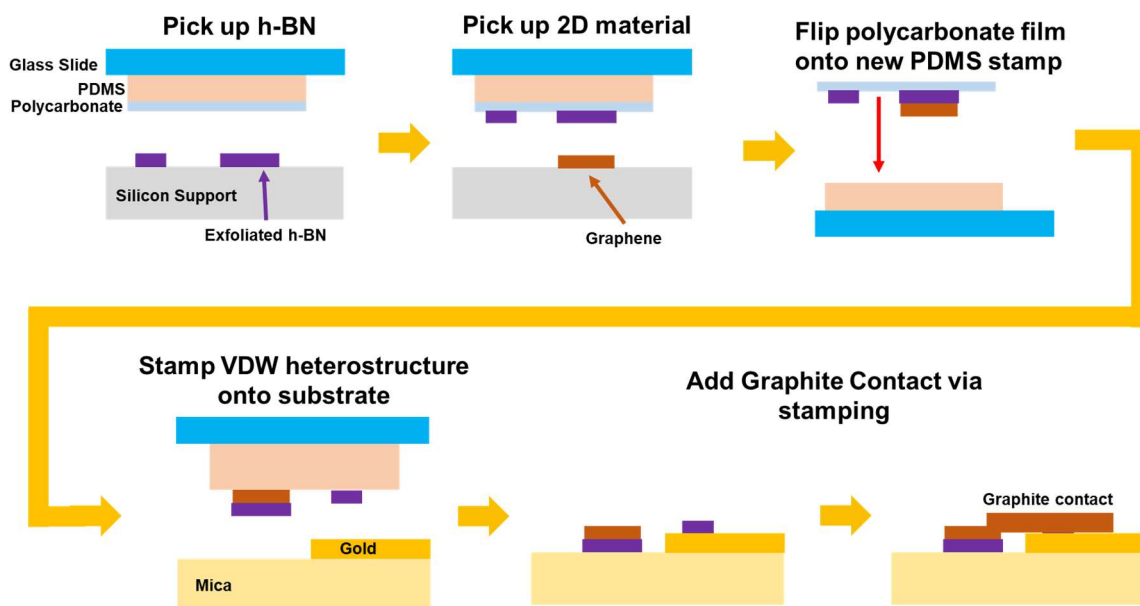


Figure 3-S2. Diagram of stamping procedure to create van der Waals heterostructure

Preparation of nanopipettes

Nanopipettes were prepared using a Sutter P-2000 micropipette puller. Capillaries used to create nanopipettes were flame-polished borosilicate glass with a filament with nominal outer diameter of 1.2 mm, inner diameter 0.69 mm, and 10 cm in length (Sutter part number BF120-

69-10). Pipettes were pulled using the settings in Table 3-S1. Aqueous solutions of 5 mM hexaamineruthenium (III) chloride and 100 mM potassium chloride were prepared in a 25 mL volumetric flask. Solutions were re-made each day due to decomposition of the ruthenium compound. Nanopipettes were filled with solution using a syringe with a filter and microfil flexible needle (WPI M28G-5). Mechanical and thermal agitation was required to completely fill nanopipettes. Thermal agitation was performed by filling the pipettes as above, then setting them on a hot plate set to low heat with pulled tip hanging off of the edge as in literature.¹⁵² Mechanical agitation was accomplished via rubbing of tweezer grips on nanopipettes at the non-pulled ends. This occasionally resulted in fractured tips due to high vibration so care was taken in this approach. The presence of bubbles and quality of the pipette filling was checked with an optical microscope.

Table 3-S1. Sutter P-2000 settings for micropipette pulling

HEAT	FIL	VEL	DEL	PUL
350	4	50	225	150

Preparation of AgCl wires

To make the Ag/AgCl wires, silver wires were oxidized in saturated NaCl to produce a nominal thickness of 10 μm . The counter electrode for the silver oxidation was a Pt wire. The wires were stored in saturated KCl in the dark. Prior to use, Pt wires were flame cleaned and then dipped in aqua regia (3:1 HCl:HNO₃) for 3 seconds. The Pt wires were then rinsed off with deionized water.

SECCM Procedure

SECCM measurements were performed with a Park NX12 AFM equipped with SICM head. Filled pipettes were attached to the SICM head, and then a Ag/AgCl wire was inserted into the pipette to form the counter/reference electrode. The camera and focus were adjusted to focus on the pipette tip, then the focal plane was lowered slightly below the visible tip. The head was lowered until the sample was in focus, then contact was achieved electrochemically using the “form cell” procedure using the settings in Table 3-S2. The “threshold” value can be adjusted depending on expected pipette diameter, where smaller pipette diameters generate less

current. Once contact was achieved, desired mapping parameters were input, if desired, and cyclic voltammetry was performed from +0.2 V vs reference to -0.8 V vs reference at 10 mV/s to achieve approximately steady-state conditions.

Table 3-S2. Form cell settings for SECCM contact in Park NX12

THRESHOLD	SPEED	FORM CELL BIAS	END BIAS
1.5 pA	0.5 $\mu\text{m s}^{-1}$	-1.0 V	0.0 V

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