Structural and Photoelectrochemical Characterization of Gallium Phosphide

Semiconductors Modified with Molecular Cobalt Catalysts

by

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A Dissertation Presented in Partial Fulfillment of the Requirements for the Degree Doctor of Philosophy

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ABSTRACT

The molecular modification of semiconductors has applications in energy conversion and storage, including artificial photosynthesis. In nature, the active sites of enzymes are typically earth-abundant metal centers and the protein provides a unique three-dimensional environment for effecting catalytic transformations. Inspired by this biological architecture, a synthetic methodology using surface-grafted polymers with discrete chemical recognition sites for assembling human-engineered catalysts in three-dimensional environments is presented. The use of polymeric coatings to interface cobalt-containing catalysts with semiconductors for solar fuel production is introduced in Chapter 1. The following three chapters demonstrate the versatility of this modular approach to interface cobalt-containing catalysts with semiconductors for solar fuel production. The catalyst-containing coatings are characterized through a suite of spectroscopic techniques, including ellipsometry, grazing angle attenuated total reflection Fourier transform infrared spectroscopy (GATR-FTIR) and x-ray photoelectron (XP) spectroscopy. It is demonstrated that the polymeric interface can be varied to control the surface chemistry and photoelectrochemical response of gallium phosphide (GaP) (100) electrodes by using thin-film coatings comprising surface-immobilized pyridyl or imidazole ligands to coordinate cobaloximes, known catalysts for hydrogen evolution. The polymer grafting chemistry and subsequent cobaloxime attachment is applicable to both the (111)A and (111)B crystal face of the gallium phosphide (GaP) semiconductor, providing insights into the surface connectivity of the hard/soft matter interface and demonstrating the applicability of the UV-induced immobilization of vinyl monomers to
a range of GaP crystal indices. Finally, thin-film polypyridine surface coatings provide a molecular interface to assemble cobalt porphyrin catalysts for hydrogen evolution onto GaP. In all constructs, photoelectrochemical measurements confirm the hybrid photocathode uses solar energy to power reductive fuel-forming transformations in aqueous solutions without the use of organic acids, sacrificial chemical reductants, or electrochemical forward biasing.
DEDICATION

for my family

to Mom, for loving me unconditionally

to Dad, for imparting the joy of learning

and to Leon, who understands the significance of this journey

“As we are a doomed race, chained to a sinking ship, as the whole thing is a bad joke, let us, at any rate, do our part; mitigate the suffering of our fellow-prisoners; decorate the dungeon with flowers and air-cushions; be as decent as we possibly can.”
— Virginia Woolf, Mrs. Dalloway

“There's nothing left except to try.”
— Madeleine L'Engle, A Wrinkle in Time
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CHAPTER 1   INTRODUCTION

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1.1 Biological Inspiration

Biology provides inspiration for developing human-engineered systems to capture, convert, and store solar energy in chemical bonds.\textsuperscript{1-6} In nature, photo-initiated redox reactions drive the process of photosynthesis (Figure 1.1). Plants and other photosynthetic organisms absorb sunlight and use the energy to carry out a series of complex redox reactions and synthetic transformations, creating the foods we eat and ultimately the fossil fuels that power our modern economies. In this context, sunlight acts as a reagent in chemical reactions, and the products of the overall reaction store the sun’s energy in the form of molecular bonds. Catalytic sites, providing relatively low-energy pathways for carrying out the overall chemical transformations, facilitate the formation of these bonds and must be reduced or oxidized at least twice for each successful completion of a reaction cycle.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{figure1.png}
\caption{Schematic diagram representing the movement of electrons following illumination in photosystem II during the process of oxygenic photosynthesis.}
\end{figure}
In biological catalysis, enzymes use soft material interactions, including coordination to amino acid residues along a protein scaffold, to provide appropriate three-dimensional environments for controlling the catalytic activity and selectivity of metal centers composed of earth-abundant elements.\textsuperscript{7,8} This, in accordance with the Sabatier principle, results in examples of enzymes that have exceptionally high activities and exquisite selectivity. The reduction potentials of the active sites of iron-based enzymes span a volt, modulated by the identity and number of coordinating ligands, charges on the surrounding protein residues, and/or solvent accessibility (Figure 1.2).\textsuperscript{9,10} In a similar vein, a focus on the role of secondary coordination sphere interactions has emerged as a bioinspired design theme in synthetic molecular catalysis, providing improved routes for binding substrates, lowering transition state energies along a reaction coordinate, and releasing products.\textsuperscript{11,12}

\textbf{Figure 1.2.} Graph showing the reduction potential range of an array of iron enzymes. Adapted from Ref. 11.
1.2 Photoelectrochemical Approach

Future clean energy scenarios require effective methods for converting and storing intermittent energy sources.\textsuperscript{13,14} Taking inspiration from the solar-to-fuels paradigm in biology, scientists have set out to re-design photosynthesis for industrial applications using top-down as well as bottom-up strategies. In this context, photoelectrochemical (PEC) fuel production using sunlight as an energy input has emerged as a promising storage option that could be integrated with our existing petroleum-based infrastructure.\textsuperscript{15}

In this approach, semiconductors are used as the light-absorbing components to drive a thermodynamically uphill fuel-forming reaction. In one PEC application, the overall water-splitting reaction uses solar energy to provide the standard change in Gibbs free energy of 4.92 eV (475 kJ mol\textsuperscript{-1}) (Equation 1.1).

\begin{equation}
2H_2O (l) \rightarrow 2H_2 (g) + O_2 (g) \tag{1.1}
\end{equation}

As a four-electron process, the corresponding standard potential is $E^0 = -1.23$ V.

Although a PEC water-splitting device is composed of 2 electrodes, a cathode at which the hydrogen evolution reaction (HER) takes place and an anode at which the oxygen evolution reaction (OER) occurs, component electrodes may be studied individually in a three-electrode setup for optimization of the individual reactions (Figure 1.3). The work presented in this dissertation focuses on homogeneous-heterogeneous catalysis at a molecular-modified cathode.

Semiconductors used for reductive processes are typically p-type semiconductors, in
which addition of a dopant shifts the energy of the Fermi level closer to the valence band energy, resulting in a material in which electrons are the minority carrier. The optical band gap, $E_g$, of the semiconductor is one of the factors that determine the maximum photocurrent density, with smaller band gap materials capable of generating greater photocurrents (Figure 1.4). Commonly used semiconductors for photocathode materials include silicon, indium phosphide, gallium arsenide, and gallium phosphide, as they have energy band gaps suitable for visible light absorption. In addition, the conduction bands of these materials are thermodynamically poised to drive $H_2$ evolution or $CO_2$ reduction.

1.3 Molecular Catalysts for Hydrogen Production

At the photocathode of a water splitting cell, the hydrogen evolution half-reaction occurs (Equation 1.2):

$$2H^+ + 2e^- \rightarrow H_2$$  \hspace{1cm} (1.2)
The formation or dissociation of hydrogen at an electrode surface can present relatively large energy barriers. If an applied electrochemical potential greater than the thermodynamic potential of the reaction is required to overcome energetic barriers, the reaction operates at an overpotential. Therefore, an active area of research in the field of the photoelectrochemical generation of solar fuels focuses on strategies to interface semiconductors with appropriate electrocatalysts to reduce the overpotential requirements for generating fuels and industrially relevant chemical feedstocks.\textsuperscript{17–21} While the precious metal platinum is the state-of-the-art catalyst for HER, there has been increased interest in employing earth-abundant metals.\textsuperscript{22–26} Advances in this field include the design and
study of bio-inspired catalysts, and there is ongoing interest in controlling reaction networks in complex environments.27

Unlike traditional surface electrocatalysts such as platinum, which are an integral part of the electrode and contribute to the Fermi level, molecular catalysts are discrete entities with distinct chemical and electronic properties.5 Molecular catalysts provide local three-dimensional environments for binding substrates, lowering transition-state energies along a reaction coordinate, and releasing products. Their unique selectivity and ability to lower energy requirements for achieving chemical transformations make them attractive targets for integration with solid-state substrates for technological applications, including electrochemical and photoelectrochemical activation for generating fuel and other valuable chemical products.

1.4 Surface-Immobilized Molecular Catalysts at Semiconductors

Molecular catalysts powered by visible-light-absorbing semiconductors represent one approach in artificial photosynthesis to developing an integrated system for generating solar fuels.20,28-31 However, finding new ways to immobilize catalysts onto semiconductor surfaces and characterize the resultant hard-to-soft matter interfaces remains a major challenge.20 Addressing this obstacle provides an improved fundamental understanding of catalysis in complex environments and enables technological advancements that depend on the precise control and selectivity of molecular components.

Molecular catalysis of the HER reaction can proceed via a homolytic or heterolytic pathway. In a homolytic pathway, the product is formed through a symmetrical
bimolecular chemical step. Conversely, a heterolytic pathway involves the reaction of chemically distinct species. For example, the mechanism of HER catalysis by cobaloximes has been proposed to occur via several pathways.\textsuperscript{32–34} After reduction of the cobalt center from Co(III) to Co(I), the Co(I) species is protonated to generate a cobalt hydride, HCo(III). In the homolytic pathway, two cobalt hydride species react with one another to release hydrogen. Alternately, the HCo(III) generated in the initial protonation step can react with an acid in solution to generate hydrogen through a heterolytic pathway. It has also been proposed that the HCo(III) can be further reduced to HCo(II), which can then proceed to generate H\textsubscript{2} through a homolytic or heterolytic pathway.

Plotting the exchange current density of various metals for HER versus the metal-hydride bond strength yields a volcano plot, in which a maximum rate of exchange current density is reached at intermediate metal-hydride bond strengths, which stabilize the bond but also allow the product to be released. The mechanism through with HER occurs has important implications for surface-immobilized catalysts. If the optimal catalytic pathway is homolytic, the surface-attached catalysts must be close enough to each other and oriented in such a way as to favor the interaction of two protonated metal centers.

Addition of a catalyst to the electrode surface may provide a lower energy pathway for a reaction to occur, and/or increase the efficiency of charge transfer across the interface by capturing minority carriers at the surface. However, it is often unclear whether the role of surface-immobilized catalysts is confined to improving the rate of interfacial electron transfer, as it can also serve to alter the surface energetics that in turn affect surface recombination rates.\textsuperscript{35–37} Since electrochemical measurements give information on both
the thermodynamics and kinetics of a reaction, it can be difficult to clearly assign whether the role of the catalyst in improved photoelectrochemical performance is to change the surface energetics or to provide a lower energy pathway for the reaction.\textsuperscript{38-41} Nonetheless, thin catalyst layers have been reported to form adaptive semiconductor/electrocatalyst junctions where the catalysts serve as an independently tunable entity whose redox states changes the effective (non-equilibrium) barrier height, resulting in higher photovoltages and efficiencies relative to impermeable electrocatalysts.\textsuperscript{42,43}

In integrating molecular catalysts to semiconductors, several requirements must be considered. A prevailing paradigm in surface catalysis suggests a higher loading of active sites is crucial for optimizing reaction conditions. This parameter can be addressed by using nano- or meso-structured substrates, or by employing three-dimensional environments for the catalyst.\textsuperscript{44,45} Conversely, an emerging strategy is that employing low catalyst coverage for achieving accumulative charge separation could increase the yields of accumulated redox equivalents.\textsuperscript{46} In either case, the surface coating should be optimized so that the catalyst loading does not hinder charge transport or block light absorption.\textsuperscript{47} Colored materials, including catalysts, can screen an underpinning semiconductor by “parasitically” absorbing photons that would otherwise contribute to production of photocurrent. Conversely, colored materials are also capable of extending the light harvesting capabilities of a semiconductor through dye sensitization mechanisms.\textsuperscript{47,48} Finally, typical benchmarking parameters such as turnover number (TON) and turnover frequency (TOF) used for homogeneous catalysts are not as easily
applied to heterogeneous catalysis since it can be difficult to determine the number of catalytically active sites.

Immobilization of catalysts at solid supports to form heterogeneous architectures provides several advantages. Surface immobilization allows catalysts that are normally not soluble in aqueous conditions to be employed in aqueous environments. By integrating a catalyst with a surface, less material is needed as all the catalyst is in close proximity to the electrode and can be activated more readily. In addition, immobilization may improve the stability of a molecular catalyst. For example, a cobalt diamine-dioxime cobalt catalyst grafted onto carbon nanotubes showed improved stability for hydrogen evolution compared to the solution counterpart, which may result from the disfavoring of decomposition pathways involving the interaction of two catalysts.23

1.5 Examples of Molecular Modification of Photocathodes

Molecular modification of surfaces promises enhanced selectivity and tunability for catalyzing chemical transformations at solid supports, leading researchers to investigate strategies to effectively immobilize molecular catalysts onto semiconductor surfaces and characterize the resultant modified surfaces. Reports describing strategies to directly integrate molecular catalysts for hydrogen production to visible-light-absorbing semiconductors are limited, but include: [Fe₂S₂(CO)₆] adsorbed onto indium phosphide nanocrystals,49 trinuclear molybdenum cluster salts drop-cast on Si(100)50 ferrocenophane-containing polymers deposited on Si(100) and (111),51 modified Dubois-type nickel bisdiphosphine catalysts covalently attached to amine-modified Si(100) and GaP(100),52 Negishi coupling of phosphine ligands onto Si(111) followed by
metalation,\textsuperscript{53} a metal-organic surface composed of a cobalt dithiolene polymer dropcast onto Si(100),\textsuperscript{54} and cobaloxime catalysts adsorbed onto a TiO$_2$-coated GaInP$_2$ semiconductor.\textsuperscript{55} Some of the cathode assemblies reported to date require an electrochemical bias poised negative of 0 V vs the reversible hydrogen electrode (0 V vs RHE) (i.e., an applied cathodic polarization beyond the thermodynamic potential of the H$^+$/H$_2$ half-reaction under the conditions tested to produce hydrogen). In addition, some require extreme pH operating conditions or nonaqueous conditions using relatively strong organic acids as a proton source, features that may be undesirable in the context of large-scale deployment, environmental impact, and biocompatibility. Although immobilization via drop-casting methods and other electrostatic-based deposition methods offer ease of assembly, the development of more precise surface attachment chemistries could offer additional control over diffusion, migration and convection dynamics, orientation of attached components, surface loading, passivation of the substrate, and interfacial energetics.\textsuperscript{9,23,56-65}

UV-induced grafting has been used to polymerize 4-vinylpyridine onto p-type GaP to provide surface-attached pyridine ligands for subsequent assembly of cobaloxime catalysts (Figure 1.5).\textsuperscript{66} In this construct, the polymer coating of the GaP surface likely provides protection against oxide layer passivation by restricting access to surface GaP(100) sites while providing attachment sites for assembly of the catalysts. The Co-functionalized photocathode produced 2.4 mA cm$^{-2}$ of current density at 310 mV underpotential under 100 mW cm$^{-2}$ illumination at pH 7, an improved photoperformance compared to the polyvinylpyridine-functionalized GaP photocathode, which required an
overpotential of 270 mV to achieve the same current density. This work was extended to fluorinated cobaloximes, where a similar attachment strategy was used to immobilize difluoroborylcobaloxime catalyst. The pH dependence of the photoelectrochemical responses of fluorinated and non-fluorinated cobaloximes tested at pH 7 or pH 4.5 was consistent with the electrochemical properties of the analogous non-surface-attached catalysts.

1.6 Prospects in the Molecular Modification of Semiconductors

Controlling matter and information at the nanoscale presents a challenge for science and the imagination. In this vein, integrated materials have been developed using a range of surface functionalization chemistries, and recent advances in polymer chemistry offer opportunities to tailor their structure and macromolecular properties. This dissertation presents the characterization and photoelectrochemical characterization of
photocathodes with thin-film coatings. Surface chemistry utilizing molecular components is used to build photoactive materials that include applications to artificial photosynthesis as well as emerging solar-to-fuels technologies. By integrating gallium phosphide with molecules that are well known for efficient catalysis, hybrid materials for photoelectrochemical catalytic transformations can be made. The research findings presented in the following chapters extend the work presented above, in which a polymeric brush serves as a structural interface between the soft molecular components and the semiconductor surface. It is shown that exchange of the polymeric interface from polyvinylpyridine to polyvinylimidazole results in distinct spectroscopic signatures associated with the unique molecular surface environments of the polymer films, and that the macroscopic photoelectrochemical characteristics are also influenced by the choice of polymer. Polyvinylpyridine can be UV-grafted to both the A (Ga-rich) and B (P-rich) sides of GaP(111), providing an immobilization method for cobaloximes at multiple crystal faces and yielding insights on the molecular connectivity of the polymer to GaP. The polymeric interface can also serve to coordinate cobalt porphyrin hydrogen evolution catalysts, and post-photoelectrochemical analysis shows that the catalysts retain their molecular integrity. Throughout the dissertation, structure/function relationships at interfaces are explored through surface spectroscopies and photoelectrochemical techniques, advancing knowledge of relationships between the molecular structures at surfaces and the resultant macroscopic properties. Thus, this work presents novel constructs not only for generating solar fuels, such as hydrogen, but also for studying catalysis in complex environments at hard/soft matter interfaces.
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CHAPTER 2 POLYVINYLMIDAZOLE OR POLYVINYLPYRIDINE GRAFTS ON GALLIUM PHOSPHIDE FOR COBALOXIME IMMOBILIZATION

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2.1 Introduction

Chapters 2-4 illustrate how the modular approach to semiconductor functionalization allows for versatility in the choice of component parts- polymer, semiconductor, or catalyst- and focus on surface characterization of the surface assemblies. Distinct structural details of the film composition and connectivity in the catalytic coating are revealed, illustrating the ability to effect molecular-level changes at the surface, and the photoelectrochemical (PEC) performance of the constructs is evaluated. In this chapter, it is shown that cobaloxime catalysts for hydrogen evolution can be immobilized at gallium phosphide through a polyvinylpyridine (PVP) or polyvinylimidazole (PVI) interface. Structural characterization of the modified wafers by ellipsometry as well as X-ray photoelectron (XP) and grazing angle attenuated total reflection Fourier transform infrared (GATR-FTIR) spectrosopies is used to evaluate the success of the surface attachment strategy and gain insights into the chemical composition of the surface coatings. PEC characterization, including gas chromatography (GC) analysis of the photochemical products, verifies the functionality of the hybrid constructs.

2.1.1 Gallium Phosphide

GaP is a III-V semiconductor used in optoelectronic applications with an indirect band gap of 2.26 eV and a direct band gap of 2.78 eV (Figure 2.6). Additionally, GaP has promising features as a candidate material for applications in solar fuels generation, including a capacity for achieving relatively large photovoltages. The energetic positioning of the conduction band (~ -1 V vs NHE) more than satisfies the thermodynamic requirement for driving the hydrogen evolution reaction (HER),
Figure 2.6. The air mass 1.5 global tilt solar flux spectrum (solid) and the transmission spectrum of GaP (dashed). The shaded grey area shows the integrated region of the solar spectrum from 280 nm up to the band gap of GaP, prompting researchers to investigate this material for PEC applications since the 1970s.\textsuperscript{1–9} However, its performance is limited by photocorrosion in aqueous conditions and surface defect sites that hinder efficient transfer of photogenerated minority carriers at the semiconductor|liquid junction.\textsuperscript{4} In this chapter, p-type GaP(100) substrates serve as commercially available materials for developing a catalyst attachment chemistry for integrating cobaloximes to the semiconductor via a polymeric interface.

2.1.2 Polymeric Interface

The constructs exploit the properties of olefins to undergo self-initiated photografting and photopolymerization at semiconductor surfaces as well as a variety of other hydrogen- or hydroxyl-terminated materials.\textsuperscript{10–19} The UV-induced surface grafting reaction has been used to graft monolayers or polymer brushes onto conductive and semiconductive
substrates, and several mechanisms have been proposed for the reaction. In the self-initiated photografting and photopolymerization (SIPGP) mechanism, the neat monomer acts as a photosensitizer, absorbs a photon and is excited to a triplet state, which is in equilibrium with a biradical species. The biradical species can react with a monomer in solution, propagating radical polymerization. Alternately, the biradical species can abstract a surface hydrogen atom, creating a radical surface site for surface-initiated polymerization. In addition, a surface-initiated radical mechanism has been proposed for the photografting reaction at silicon, in which incoming UV light cleaves the Si-H bond, which has a bond strength of ~ 3.5 eV, therefore requiring UV light of < 350 nm. The Si radical site can then react with the β-carbon of an alkene to form a Si-C bond. Finally, the α-carbon radical abstracts a hydrogen atom from a neighboring Si-H group, and the surface reaction is propagated across the surface in a random walk to form an alkylated monolayer.

Surface-initiated grafting can also occur under white light. Under these conditions, the proposed mechanism occurs via nucleophilic attack by the alkene to a valence band hole generated by photogenerated electron-hole separation. In a similar manner, UV excitation can result in photoemission of an electron from the semiconductor to solution, resulting in a persistent hole in the valence band subject to nucleophilic attack by the alkene. The predominant mechanism contributing to surface grafting of alkenes under UV light is ascribed to a photoemission process, as the lifetime of the hole is much longer in the photoemission mechanism compared to the exciton mechanism.

In this work, UV-initiated surface grafting and polymerization are used to prepare PVI or
Figure 2.7. Schematic representation of the attachment method used to assemble cobaloxime-modified photocathodes.

PVP grafts (Figure 2.7). Post-polymerization modification is then used to direct and assemble molecular catalysts onto built-in recognition sites—ligands—on the surface-attached polymer. Thus, the polymeric brush serves as a structural interface between the soft molecular catalysts and the hard semiconductor surface. To facilitate direct comparisons between the PVI- and PVP-functionalized materials in the work reported here, the grafts were assembled on GaP (100) wafers with identical physical properties including doping conditions, resistivity, mobility, carrier concentration and etch pit density (i.e., the wafers are cut from the same ingot).

2.1.3 Cobaloximes

Cobaloximes are a class of cobalt-containing catalysts known for catalyzing hydrogen evolution in organic and aqueous conditions and have shown promise in electrocatalysis
and solar-to-fuel applications. Since the first report of electrochemical hydrogen
evolution catalyzed by a fluorinated cobaloxime by Connolly and Espenson, cobaloximes
and their mechanism of catalysis have been extensively studied by chemical,
electrochemical, and photochemical means.\textsuperscript{30-42} Previous reports show that cobaloximes
can be assembled onto GaP via a polyvinylpyridine interface, resulting in a cathode
material that uses only photonic energy, and no external electrochemical forward biasing
or sacrificial electron donors, to generate a relatively stable current and associated rate of
hydrogen production in pH neutral aqueous solutions.\textsuperscript{43} In addition, treatment of the
PVP-functionalized GaP using cobaloxime catalyst precursors with a ligand macrocycle
that is modified at the molecular level has been shown to affect the PEC response to
illumination and pH observed at the construct level.\textsuperscript{44} Thus, the photoactivity of the
modified semiconductor can be influenced by changes to the ligand environment of the
attached cobalt complexes.

2.2 Results and Discussion

2.2.1 Wafer Preparation and Characterization

A two-step method is used to assemble catalysts at the semiconductor surface. First, UV-
induced grafting of the appropriate polymer to the GaP (100) surface yields
polyvinylimidazole-grafted GaP (PVlGaP) or polyvinylpyridine-grafted GaP (PVP(GaP)
constructs. In the second step, wet chemical treatment of the polymer-modified surface is
used to assemble cobaloximes on the polymer graft. This chemical transformation
exploits the base-promoted ligand exchange of axial X-type chloride ligands on cobalt
catalyst precursors with pendent N-type ligands on the surface-grafted polymers, yielding
cobaloxime-modified PVP|GaP (ColPVP|GaP) or cobaloxime-modified PVII|GaP (ColPVII|GaP) (Figure 2.8). Analysis of the chemically modified surfaces using XP spectroscopy provides evidence of successful functionalization with the desired molecular connectivity. Survey spectra of the PVP|GaP and PVII|GaP samples show C, N and O elements and cobaloxime-functionalized samples show additional C, O, Cl and Co elements associated with attached cobaloximes (Figure 2.8). N 1s core level XP spectra of polymer-functionalized GaP surfaces (Figure 2.9) present a single nitrogen feature centered at 398.7 for PVP|GaP corresponding to the pyridyl nitrogens of the graft. Conversely, N 1s core level spectra of PVII|GaP surfaces exhibit two distinct nitrogen features centered at 398.3 and 400.2 and having a 1:1 spectral intensity ratio arising from the two types of nitrogen environments in PVI,45–47 with the amine nitrogen feature at higher binding energies than those assigned to imine nitrogen (Table 2.1).

**Figure 2.8.** XP survey spectrum of (left) PVII|GaP and (right) ColPVII|GaP.
Figure 2.9. N 1s core level XP spectra of (top) PVI|GaP and (bottom) PVP|GaP. The solid blue (b) and solid dark blue (c) lines represent the component fit of the imine nitrogen, and the dashed blue (a) line the component fit of the amine nitrogen. The circles represent the spectral data, the gray line is the linear background, and the black line the overall fit.

Table 2.1 N 1s Binding Energies (eV)

<table>
<thead>
<tr>
<th>Construct</th>
<th>Imine nitrogen</th>
<th>Amine nitrogen</th>
<th>Co-imine nitrogen</th>
<th>Co-amine nitrogen</th>
<th>Glyoximate nitrogen</th>
</tr>
</thead>
<tbody>
<tr>
<td>PVP</td>
<td>GaP</td>
<td>398.7</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>ColPVP</td>
<td>GaP</td>
<td>398.6</td>
<td>--</td>
<td>400.6</td>
<td>--</td>
</tr>
<tr>
<td>PVI</td>
<td>GaP</td>
<td>398.3</td>
<td>400.2</td>
<td>--</td>
<td>400.0</td>
</tr>
<tr>
<td>ColPVI</td>
<td>GaP</td>
<td>398.4</td>
<td>400.0</td>
<td>399.0</td>
<td>400.0</td>
</tr>
</tbody>
</table>
The assembly of cobaloximes on the PVP or PVI grafts gives rise to additional nitrogen features at higher binding energies in the N 1s core level spectra. Spectral fitting of the XP data facilitates assignment of the individual contributions (Figure 2.10). For ColPVIIGaP, a spectral contribution at 400.6 eV is assigned to pyridyl nitrogens on the graft that are coordinated to cobalt centers of attached cobaloximes and the contribution centered at 400.0 eV is indicative of the N 1s features of the cobaloxime glyoximate ligands. The remnant contribution at 398.6 eV is assigned to pyridine units on the polymer chains that are not coordinated to cobalt centers. For ColPVIIGaP surfaces, assembly of Co centers to imidazole units on the polymer graft contribute to the peaks at 399.0 eV and 400.6 eV, while the contributions at 398.4 eV and 400.6 eV are assigned to remnant imidazole nitrogens on the polymer that are not coordinated to cobalt centers. The prominent peak at 400.0 eV is assigned to glyoximate nitrogens of the cobaloximes. For both the ColPVIIGaP and ColPVPIGaP surfaces, the Co:Cl spectral intensity ratio is 1:1, corroborating the proposed synthetic mechanism in which one of the axial chloride ligands on the Co-precursor complex is replaced with a nitrogen-containing ligand on the polymer graft. In this mechanism, charge balance of the cobalt complex when replacing chloride, an anionic X-type ligand, with a neutral L-type ligand is accounted for by the base-promoted conversion of the dimethylglyoxime ligand to the dimethylglyoximate monoanion. As anticipated, the Co 2p core level spectra signal shows the expected 15 eV splitting and 2:1 ratio of the 2p$_{3/2}$ and 2p$_{1/2}$ peaks (Figure 2.11), consistent with the Co$^{3+}$ oxidation state of the grafted complex.$^{48,49}$ The collective information regarding the
Figure 2.10. N 1s core level spectra of (top) CoPVI|GaP and (bottom) CoPVP|GaP. The solid blue (b) and solid dark blue (c) lines are the component fits for the unbound imine, the dotted blue line (a) the component fit for the unbound amine, the solid red (f) and solid dark red (h) lines the component fit for the bound imine, and the dotted red line (e) the component fit for the bound amine. The dashed red (d) and dashed dark red (g) line are the component fits for the glyoximate contributions. The circles represent the spectral data, the gray line is the Shirley background, and the black line is the overall fit.
elemental identity and chemical composition obtained from XPS analysis provides confirmation of the synthetic efforts.

Surface analysis using GATR-FTIR spectroscopy provides further structural characterization of the modified GaP substrates, including direct observation of vibrational modes associated with the grafted polymers and assembly of intact cobaloxime complexes. FTIR spectra following the photochemical treatment of freshly cleaned and etched GaP surfaces with 4-vinylpyridine or N-vinylimidazole show distinct C-H and C-N modes in the 1400 to 1600 cm\(^{-1}\) range indicative of successful polymerization, and unique from the C-H and C-N vibrations associated with monomeric 4-vinylpyridine or N-vinylimidazole (Figure 2.12). Additionally, there is a lack of the pronounced feature at 1371 cm\(^{-1}\) associated with the C=C bond of the vinyl group monomer\(^{50}\) and instead a peak at 1454 cm\(^{-1}\), indicative of the planar deformation vibration of the CH\(_2\) groups along the polymer chain backbone, is observed.\(^{51}\)
Figure 2.12. GATR-FTIR spectra of PVI|GaP (blue) and PVP|GaP (dotted dark blue) grafted onto gallium phosphide, as well as unmodified GaP (dashed black). Spectra are normalized for comparison.

Treatment of the polymer-grafted surfaces with a solution of the catalyst precursor, Co(dmgH2)(dmgH)Cl2, gives rise to new vibrational modes on the surface that are ascribed to the formation of intact cobaloxime catalyst. These modes are distinct from those observed in the FTIR spectrum of the Co(dmgH2)(dmgH)Cl2 precursor but are nearly identical to the vibrational modes observed in spectra of the model molecular catalysts Co(dmgH)2(Py)Cl or Co(dmgH)2(meIm)Cl (Figure 2.13a). In particular, measurements of the NO\(^\cdot\) stretching frequency of the cobaloxime-functionalized surfaces provide direct spectroscopic evidence supporting assembly of the cobaloxime units at the pendant pyridyl or imidazole sites of the polymer graft. For the Co(dmgH2)(dmgH)Cl2 precursor complex the NO\(^\cdot\) stretch occurs at 1225 cm\(^{-1}\), however for the model cobaloximes Co(dmgH)2(Py)Cl and Co(dmgH)2(meIm)Cl, this mode is centered at 1240 or 1237 cm\(^{-1}\), respectively. FTIR spectra of the polymer-functionalized GaP surfaces
Figure 2.13. (a) FTIR transmission spectra of Co(dmgH)$_2$Cl$_2$ in KBr (green), Co(dmgH)$_2$(Py)Cl in KBr (dashed dark red), and Co(dmgH)$_2$(meIm)Cl in KBr (red), as well as (b) GATR-FTIR absorbance spectra of CoPVIIGaP (red), CoPVPIIGaP (dashed dark red), and GaP following a fresh HF etch (dashed black). Insets show the NO$^-$ region.
following wet chemical treatment with a solution of Co(dmgH₂)(dmgH)Cl₂ show a strong NO⁻ vibration at 1241 cm⁻¹ for PVP-functionalized GaP and at 1240 cm⁻¹ for PVI-functionalized GaP (Figure 2.13b), values that closely match those of the model catalysts within the 4 cm⁻¹ resolution of the spectroscopic scans. Additionally, there is no pronounced peak at 1225 cm⁻¹, indicating that minimal to no precursor complex remains in or on the cobaloxime-modified GaP following ultrasonic cleaning of the samples.

Thus, FTIR analysis indicates effective assembly of cobaloxime units using the built-in recognition sites of the polymer grafts, in agreement with our surface analysis using XP spectroscopy.

Information on the length of the PVP or PVI polymer grafts is provided by spectroscopic ellipsometry measurements, yielding a PVP thickness of 10 nm and a PVI thickness of 6 nm on the GaP (100) substrates (Figure 2.14). Using these film thickness values, the corresponding pyridyl and imidazole site density can be estimated given the bulk polymer

![Figure 2.14](image-url)  
**Figure 2.14.** Spectra obtained from ellipsometry measurement (red) of PVIIGaP at 69° (top) and 74° (bottom) and model fit to data (black dash).
density (1.15 g cm\(^{-3}\) for PVP and 1.25 g cm\(^{-3}\) for PVI) is representative of the solvent-free layer density. For a 10 nm thick solvent-free PVP layer the corresponding maximum site density is 6.6 \times 10^{15} \text{ cm}^{-2} or 11 \text{ nmol cm}^{-2}. In the case of a 6 nm thick solvent-free PVI layer the maximum site density is 4.8 \times 10^{15} \text{ cm}^{-2} or 8 \text{ nmol cm}^{-2}. The larger film thickness of PVP grafts with respect to those obtained for the PVI grafts is consistent with previous reports of lower grafting concentrations reported for the UV polymerization of PVI relative to PVP.\(^{45,52}\) The identity of the polymer graft thus can be used to control the physical characteristics at the mesoscale in addition to the chemical identity of the ligand sites at the nanoscale.

2.2.2 Photoelectrochemical Performance

PEC performance of the assembled constructs is evaluated by fabricating photocathodes from the functionalized and unmodified constructs (Figure 2.15). All measurements are performed in aqueous solutions buffered at pH 7 (0.1 M phosphate buffer) in the dark and at AM1.5 illumination using a 100 W solar simulator with a sample size consisting of at least 4 individually tested electrodes. The polymer-grafted GaP electrodes (PVP|GaP and PVI|GaP) produce a photocurrent density of 0.68 \pm 0.18 mA cm\(^{-2}\) and 0.43 \pm 0.02 mA cm\(^{-2}\), respectively, when polarized at 0 V vs RHE. For the cobaloxime-modified GaP electrodes, polarized at 0 V vs RHE, the current density is 1.3 \pm 0.05 mA cm\(^{-2}\) for PVP|GaP and 1.2 \pm 0.08 mA cm\(^{-2}\) for PVI|GaP. For the cobaloxime-modified samples, a positive shift in the potential needed to reach a selected current density (with \(V_{on}\) defined as the potential required to achieve a current density of 1 mA cm\(^{-2}\)) is observed as compared to the potential required using electrodes containing only the polymer graft.
Figure 2.15. Linear sweep voltammograms of PVP\(\text{I}\)GaP (dark blue), PVI\(\text{I}\)GaP (blue), Co\(\text{I}\)PVP\(\text{I}\)GaP (dark red) and Co\(\text{I}\)PVI\(\text{I}\)GaP (red) working electrodes at pH 7 in the dark (dotted lines) and with 100 mW cm\(^{-2}\) illumination (solid and dashed lines). An unmodified GaP electrode under illumination is shown for comparison (black).

Table 2.2 PEC Characteristics

<table>
<thead>
<tr>
<th>Construct</th>
<th>(V_{oc}) (V vs RHE)</th>
<th>(V_{on})* (V vs RHE)</th>
<th>(J) at 0 V vs RHE (mA cm(^{-2}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>GaP(100)</td>
<td>0.57 ± 0.03</td>
<td>-0.037 ± 0.06</td>
<td>0.86 ± 0.01</td>
</tr>
<tr>
<td>PVP\text{I}GaP</td>
<td>0.57 ± 0.01</td>
<td>-0.068 ± 0.09</td>
<td>0.68 ± 0.18</td>
</tr>
<tr>
<td>CoPVP\text{I}GaP</td>
<td>0.61 ± 0.05</td>
<td>+0.24 ± 0.04</td>
<td>1.3 ± 0.05</td>
</tr>
<tr>
<td>PVI\text{I}GaP</td>
<td>0.53 ± 0.05</td>
<td>-0.14 ± 0.02</td>
<td>0.43 ± 0.02</td>
</tr>
<tr>
<td>CoPVI\text{I}GaP</td>
<td>0.58 ± 0.02</td>
<td>+0.073 ± 0.05</td>
<td>1.2 ± 0.08</td>
</tr>
</tbody>
</table>

*where \(V_{on}\) is defined here as the potential required to achieve a 1 mA cm\(^{-2}\) current density.
and without cobaloxime modification. For the PVP-grafted electrodes, cobaloxime modification yields a $+310 \pm 100$ mV shift in $V_{on}$ while for PVI-grafted electrodes, cobaloxime modification yields a $+210 \pm 50$ mV shift in $V_{on}$. Likewise, $V_{on}$ for CoLPVPlGaP electrodes wafers that are tested in a three-electrode configuration is 170 mV positive of those obtained using CoLPVPlGaP electrodes (Figure 2.15 and Table 2.2). The measured open-circuit photovoltages ($V_{oc}$) of the electrodes are also consistent with the increased photoactivity of the electrodes following cobaloxime addition.

Analysis of the headspace of the PEC cell by gas chromatography (Figure 2.16) after 60 minutes of chronoamperometry at a voltage slightly positive of 0 V vs RHE confirms the formation of $H_2$ gas with a near-unity faradaic efficiency for the cobaloxime-modified electrodes. For comparison, electrochemical measurements using solutions of the

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**Figure 2.16.** Gas chromatogram of 5 mL of headspace before (black dash) and after (red) bulk electrolysis of CoLPVPlGaP working electrodes at pH 7 with 100 mW cm$^{-2}$ illumination for 1 hour at 0 V vs RHE.
cobaloxime model compounds \( \text{Co(dmgH)}_2(\text{meIm})\text{Cl} \) and \( \text{Co(dmgH)}_2(\text{Py})\text{Cl} \) recorded in acetonitrile solutions show that structural modifications to the ligand environment (axial coordination to imidazole vs. pyridine) result in a 60 mV shift of the \( \text{Co}^{II}/\text{Co}^I \) redox couple to more negative potentials (Figure 2.17), illustrative of the ligand environment’s effect on the redox properties of the cobaloxime catalysts. For the cobaloxime-modified GaP substrates reported here, the differences in PEC performance in aqueous environments may in part be due to the inherent difference in activity of the cobaloximes in the grafted polymer environment (PVI vs. PVP).

**Figure 2.17.** Cyclic voltammograms of \( \text{Co(dmgH)}_2(\text{meIm})\text{Cl} \) (green) and \( \text{Co(dmgH)}_2(\text{Py})\text{Cl} \) (red) recorded in 0.1 M tetrabutylammonium hexafluorophosphate in acetonitrile at a scan rate of 100 mV s\(^{-1}\) with a glassy carbon working electrode at room temperature and ferrocene as an internal standard with \( E_{1/2} \) taken as 0.40 V vs NHE. Data are normalized for comparison. Data collected by Samuel Jacob.
2.2.3 Turnover Frequency

An estimate of the per cobalt center turnover frequency (TOF) of the cobaloxime-modified electrodes can be arrived at using the following assumptions: 1) there is uniform surface coverage of the graft and uniform distribution of cobaloximes along the depth of the polymer graft, 2) the film thickness determined by ellipsometry is representative of the solvent-free thickness of the film, and 3) all cobalt centers are active and are the only sites of hydrogen production. Given the first and second set of conditions, cobalt loading of the films can be estimated from the associated XP spectroscopy and ellipsometry data. In the case of the CoLPVPiGaP construct, the spectral intensity ratio of the nitrogen contribution at 400.6 eV, assigned to pyridyl nitrogen coordinated to cobalt centers, and the remnant peak at 398.6 equate to a 30% loading of cobalt centers to pyridyl groups on the PVP graft. An analysis of spectral intensity ratio of the nitrogen contributions using CoLPVIIGaP samples indicates that 35% of the available imidazole sites on the PVI graft are associated with an attached cobaloxime. An analysis of the total Co:N ratios yields identical loadings. If the cobaloximes are, however, not distributed evenly along the nitrogen sites of the grafted brushes but are instead concentrated toward the upper portions of the polymer (i.e. away from the underpinning semiconductor surface), then our analysis results in an overestimate of the loading due to signal attenuation of nitrogen sites located at lower depths along the polymer. Likewise, if solvent remains in the brush following cleaning and drying, then the calculated FT represents an upper limit on the site density.
Using cobaloxime loadings obtained from the analysis described above, the current densities measured in three-electrode polarization experiments using cobaloxime-modified GaP electrodes give information on the activity of the electrodes per number of cobaloximes assembled on the polymer grafts. For example, the current density of 1.3 mA cm\(^{-2}\), measured at 0 V vs. RHE and under 1 sun illumination, for the CoLPVPGaP electrode yields a TOF of 2.1 s\(^{-1}\), and the current density of 1.2 mA/cm\(^2\) for the cobaloxime-PVI functionalized electrode, measured under similar conditions, gives a TOF of 2.4 s\(^{-1}\). This analysis represents the activity of the electrode per amount of cobalt present, regardless of the activity of individual centers. If not all cobaloxime centers are active or equally active, as could likely be the case for the inherently heterogenized molecular components reported here, our analysis could underestimate the TOF of individual cobaloxime sites. Conversely, if there are other sites of hydrogen production on the surface the TOF could be overestimated for individual cobaloxime sites. For comparison, a 1.0 mM solution Co(dmgH)\(_2\)(Py)Cl at a graphite electrode poised at -0.90 V vs. Ag/AgCl in 1,2-dichlorethane in the presence of 0.2 M Et\(_3\)NH(BF\(_4\)) (a sacrificial reductant) yielded \(\approx\)100 turnovers in 2.5 hours with no visible degradation of the catalyst. Previous reports, however, indicate that immobilized catalysts can have significantly higher turnover ability compared to their solution counterpart. In a report by Artero and coworkers using cobalt diimine-dioxime catalysts grafted onto carbon nanotubes polarized at -0.59 V vs. RHE in acetate buffer (pH 4.5) a TOF of \(\approx\)2.2 s\(^{-1}\) is reported. The authors speculate that immobilization of the catalyst prevents inactivation through dimerization and enhances electron transfer dynamics from the conductive electrode to
the catalytic site.\textsuperscript{53} Similarly, a more recent report by Turner and coworkers assigns a TOF of 1.9 s\textsuperscript{-1} to 3.4 s\textsuperscript{-1} using an isonicotinic acid-modified cobaloxime catalysts adsorbed on a TiO\textsubscript{2}-coated GaInP\textsubscript{2} electrode operating at 0 V vs. RHE in an basic aqueous solution (pH 13).\textsuperscript{54}

### 2.3 Conclusions

Cobaloxime catalysts for hydrogen production have been assembled on the surface of GaP(100) using both PVP and PVI grafts. The variation of the polymeric interface affects the photoelectrochemical performance of the constructs. Surface-sensitive spectroscopic analyses verify the successful synthesis of cobaloximes on the polyvinylpyridine or polyvinylimidazole grafts using molecular assembly at recognition sites on the surface-attached polymers. PEC characterization of the cobaloxime-modified assemblies shows a marked increase in per geometric area hydrogen production rates as compared to results obtained using electrodes without cobaloxime functionalization. This work illustrates the versatility of the polymer graft as an interface for controlling structure at the nano- and mesoscales as well as functional performance at the macroscale as evidenced by PEC characterization of the photocathodes assembled from the modified wafers. The imidazole- and pyridyl-grafted cobaloxime constructs are both capable of achieving a current density greater than 1 mA cm\textsuperscript{-2} when polarized at potentials positive of the reversible hydrogen electrode (RHE) and thus under reverse biased conditions, achieving 1 mA cm\textsuperscript{-2} at +0.24 V vs. RHE for the pyridyl-based construct and +0.073 V vs. RHE for the imidazole-based assembly. The cobaloxime-PVP architecture shows improved per geometric area photocurrent production over the cobaloxime-PVI construct, achieving a
13.4 ± 1.0% higher photocurrent density for electrodes polarized at the potential of the reversible hydrogen electrode. Yet the imidazole graft is 60% the length and more conservative in use of cobaloxime complexes, containing 80% the number of cobalt centers per geometric area. The more effective use of cobalt in the PVI-assembly is evidenced in the per-cobalt TOF analysis of the ColPVI\textsubscript{I}GaP and ColPVI\textsubscript{I}GaP photocathodes, estimated at 2.1 s\textsuperscript{-1} and 2.4 s\textsuperscript{-1} respectively. Future work will focus on an improved understanding of surface coverage and distribution of cobaloximes along the polymer graft using angle-resolved XP spectroscopy measurements, which should enable a refined model and assessments of the loadings and per cobalt TOFs achieved using these hybrid constructs. This work illustrates the potential to control and optimize the properties of visible-light-absorbing semiconductors using polymeric overlay techniques coupled with the principles of synthetic molecular design. Key features of the construct include the use of polymer-functionalized semiconductors, the assembly of molecular components at the polymeric interface, a modular architecture, and PEC operation in aqueous conditions (an imperative for the photoelectrochemical reduction of water).

2.4 Experimental Methods

2.4.1 Materials

Single crystalline p-type gallium phosphide wafers were purchased from University Wafers. The material is single side polished to an epi-ready finish. The p-type Zn-doped GaP(100) wafers have a resistivity of 0.2 Ω cm\textsuperscript{-2}, a mobility of 66 cm\textsuperscript{2} V\textsuperscript{-1} s\textsuperscript{-1}, and a carrier concentration of 4.7 x 10\textsuperscript{17} cm\textsuperscript{-3}, with an etch pit density of less than 8 x 10\textsuperscript{4} cm\textsuperscript{-2}. Preparation of all wafers began with initial degreasing with an acetone-soaked cotton
swab followed by consecutive ultrasonic cleaning in acetone and isopropanol for 5 minutes each followed by drying under a nitrogen stream. The wafers were then exposed to an air-generated plasma (Harrick Plasma, USA) at 30 W for 2 minutes. Finally the wafers were etched in buffered hydrofluoric acid (6:1 HF:NH_4F in H_2O) for 5 minutes followed by rinsing with distilled methanol and drying under a nitrogen stream then storing under vacuum (−750 Torr). All reagents were purchased from Aldrich. Isopropanol was cleanroom grade and used as received. Dichloromethane, methanol and vinylimidazole were freshly distilled before use. All solvents were stored over the appropriate molecular sieves prior to use. Milli-Q water (18.2 MΩ·cm) was used to prepare all aqueous solutions.

2.4.2 Cobaloxime Synthesis

*Synthesis of Co(dmgH_2)(dmgH)Cl_2 and Co(dmgH)_2(py)Cl*. These complexes were prepared by Samuel Jacob according to a previously reported procedure.\textsuperscript{55}

*Synthesis of Co(dmgH)_2(meIm)Cl*. These complexes were prepared by Samuel Jacob. A suspension of Co(dmgH_2)(dmgH)Cl_2 (1.1 g, 3.0 mmol) and 1-methylimidazole (0.58 g, 7.0 mmol) was vigorously agitated in 60 mL of chloroform. After 10 minutes, water (30 mL) was added and the mixture was stirred for 2.5 h. The mixture was filtered and washed with 60 mL portions of water using a separatory funnel until the aqueous layer was clear. The organic layer was concentrated under reduced pressure and precipitated with the addition of ethanol. The crude product was recrystallized from dichloromethane and ethanol yielding a brown crystalline solid (45% yield). \textsuperscript{1}H NMR (400 MHz, CDCl_3):
2.39 (12H, s, CH₃), 3.60 (3H, s, ArCH₃), 6.66-6.67 (1H, m, ArH), 6.73-6.74 (1H, m, ArH), 7.27 (1H, s, ArH), 18.43-18.51 (2H, brs, OH). UV-vis (CH₂Cl₂) 252, 297, 355 nm.

2.4.3 Wafer Functionalization

The freshly etched wafers were placed into a quartz flask containing the appropriate argon-sparged monomer (N-vinylimidazole or 4-vinylpyridine) and purged with argon for 15 minutes, after which they were placed into a UV chamber and irradiated with shortwave (254 nm) light for 2 hours.¹¹,¹⁸,⁵⁶ The resultant graft serves a dual purpose, offering a protection layer for the underpinning GaP surface⁴⁷,⁵⁷ and providing multiple sites for subsequent assembly of cobaloxime catalysts at the polymeric interface. Following the UV-induced attachment, the wafers were ultrasonically cleaned in freshly distilled methanol and dried under a nitrogen stream then stored under vacuum (-750 Torr). Cobaloxime functionalization was achieved using wet-chemical treatment of the polymer-modified substrate with a methanolic solution of Co(dmgH₂)(dmgH)Cl₂ (1 mM) and 1 mM triethylamine (TEA). After 12 hours, the wafers were removed from the reaction mixture, ultrasonically cleaned in freshly distilled methanol, dried under a nitrogen stream and stored under vacuum (-750 Torr).

2.4.4 Wafer Characterization

XPS was performed using a monochromatized Al Kα source (hv = 1486.6 eV) operated at 63 W with a takeoff angle of 0° relative to the surface normal and a pass energy for narrow scan spectra of 20 eV at an instrument resolution of 700 meV. Survey spectra are collected with a pass energy of 150 eV. Spectral fit was analyzed using CASA software and all spectra were calibrated by adjusting adventitious carbon to 284.8 eV. Curves were
fitted using a linear background for polymers and Shirley background for cobaloxime-functionalized films. N 1s components were constrained to a fwhm of 1.3 eV.

Grazing angle attenuated total reflection Fourier transform infrared spectroscopy (GATR-FTIR) was performed using a VariGATR accessory (Harrick Scientific) with a Ge crystal plate installed in a Bruker Vertex 70. Samples were pressed against the Ge crystal to ensure effective optical coupling. Spectra were collected using 256 scans under a dry nitrogen purge at 4 cm$^{-1}$ resolution with a GloBar MIR source, a broadband KBr beamsplitter and a liquid nitrogen cooled MCT detector. Background measurements were obtained from the bare Ge crystal and the data processed using OPUS software. GATR measurements were baseline corrected for rubberband scattering.

Film thickness (FT) was determined using a J.A. Woollam Variable Angle Spectroscopic ellipsometer with a spectral range of 200 nm-1200 nm. Measurements were taken at 69° and 74° incidence angles and analysis performed using Complete EASE software. The model used to determine the FT of surface-grafted polyvinylimidazole was composed of a GaP substrate layer (Palik), a GaP oxide layer (Zollner) with a fixed thickness of 1.01 nm and a Cauchy layer for the polymer film of each sample.

**2.4.5 Electrode fabrication**

GaP working electrodes were fabricated by applying an indium gallium eutectic (Aldrich) to the backside of a wafer, then fixing a copper wire to the back of the wafer using a conductive silver epoxy (Circuit Works). The copper wire was passed through a glass tube, and the wafer was insulated and attached to the glass tube with Loctite 615 Hysol Epoxi-patch adhesive. The epoxy was allowed to fully cure before testing the electrodes.
2.4.6 Photoelectrochemical Characterization

PEC characterization was performed using 100 mW cm\(^{-2}\) illumination from a 100 W Oriel Solar Simulator equipped with an AM1.5 filter. Three-electrode linear sweep voltammetry and bulk electrolysis experiments (chronoamperometry) were performed with a Biologic potentiostat using a platinum coil counter electrode, a Ag/AgCl, NaCl (3 M) reference electrode (0.21 V vs. NHE) and GaP working electrodes (including GaP following acid etch, polymer-grafted GaP and cobaloxime-modified GaP) in a PEC cell containing a quartz window. The supporting electrolyte was 0.1 M phosphate buffer (pH 7). Linear sweep voltammograms were recorded at sweep rates of 100 mV s\(^{-1}\) under a continuous flow of 5% hydrogen in nitrogen. Chronoamperometry was performed with the working electrode and at -0.61 V vs. Ag/AgCl, positive of 0 V vs. RHE, where E vs. RHE = E vs. NHE + 0.05916 x pH (V) = E vs. Ag/AgCl + 0.05916 x pH +0.21 (V).

2.4.7 Hydrogen Detection

Gas analysis was performed via gas chromatography (GC) using an Agilent 490 Micro GC equipped with a 5 Å MolSieve column at a temperature of 80°C and using argon as the carrier gas. Gas samples were syringe-injected using 5 mL aliquots of headspace gas collected with a gas-tight Hamilton syringe from a sealed PEC cell both prior to and following 60 min of three-electrode photoelectrolysis using a cobaloxime-modified working electrode polarized at +0.013 V vs. RHE. Prior to the experiment the cell was purged for 30 min with argon before sealing. The retention time of hydrogen was confirmed using a known calibrated source obtained from a standard lecture bottle containing a hydrogen and argon mixture.
2.5 References


(44) Leung, J. J.; Warnan, J.; Nam, D. H.; Zhang, J. Z.; Willkomm, J.; Reisner, E. Photoelectrocatalytic H₂ Evolution in Water with Molecular Catalysts Immobilised on p-Si via a Stabilising Mesoporous


CHAPTER 3  SOLAR HYDROGEN PRODUCTION USING MOLECULAR CATALYSTS IMMOBILIZED ON GALLIUM PHOSPHIDE (111)A OR (111)B POLYMER-MODIFIED PHOTOCATHODES

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3.1 Introduction

The crystal face of GaP(100) terminates with a mixed phase of Ga and P sites, while the (111A) and (111B) faces consist of surfaces with predominantly atop Ga or atop P, respectively. Both faces are subject to oxidative and corrosive processes; however methods have been developed to chemically protect and passivate these otherwise structurally unstable surfaces, including treatment with (NH$_4$)$_2$S$_x$, alklylation or allylation with subsequent secondary functionalization of the A-side, and alkyl halide reactions with the P sites via a Williamson ether synthesis on the B-side. An attachment strategy that can be utilized across multiple crystal face orientations may be useful in interfacing molecular catalysts to nanostructured materials that terminate with a range of indices, thereby permitting a relatively dense loading of catalysts and relieving the turnover frequency (TOF) of individual active sites required to achieve a selected current density.

This chapter presents the functionalization of GaP(111) with cobaloxime for hydrogen production using a chemical attachment strategy that can be deployed on both the A and B crystal faces (Figure 3.18). It has been shown that polyvinylimidazole (PVI) confers stability to metal surfaces and in these efforts, it serves the dual role of providing a linkage to molecular catalysts as well as a protective layer for the underpinning GaP. As compared to unmodified electrodes, cobaloxime modification yields a greater than four-fold increase in the photocurrent density measured for electrodes polarized at zero volts versus the reversible hydrogen electrode (0 V vs. RHE). Chronoamperometry coupled with gas analysis measurements show the photocurrent
densities are relatively stable, with a drop off of less than 1% over 55 minutes following an initial decrease of up to 12% during the first 5 minutes of photoelectrochemical (PEC) characterization, and that the current produced is associated with a nearly quantitative production of hydrogen gas. This work illustrates the promise of these constructs to produce a fuel using only light as an energy input with no requirement of forward electrochemical biasing, sacrificial reagents or extreme pH conditions. Additionally, the modular assembly method allows modification of components as new materials and discoveries emerge. In particular, and as illustrated in this chapter, the ability to export the grafting chemistry across a selection of crystal face orientations is a desirable feature.

Figure 3.18. Schematic of cobaloxime linked to either the GaP(111)A face or the GaP (111)B face through surface-grafted polyvinylimidazole.
in the context of functionalizing the inherently multi-faceted surfaces of nanostructured light-harvesting materials which have shown great promise in emerging light capture and conversion technologies due to their relatively large aspect ratios and short minority-carrier diffusion lengths.\textsuperscript{22–26}

3.2 Results and Discussion

3.2.1 Wafer Preparation and Characterization

Cobaloxime-modified GaP(111) wafers are assembled via a two-step process. First, PVI is grafted onto gallium phosphide wafers using surface-initiated polymerization of the vinylimidazole monomer under shortwave UV light.\textsuperscript{27–30} Second, surface-attached cobaloxime complexes are formed using a wet chemical treatment that exchanges one of two chloride ligands from the complex Co(dmgH\textsubscript{2})(dmgH)Cl\textsubscript{2} with an imidazole ligand on the PVI graft. Sample preparation starts with placing clean, freshly etched GaP wafers into a quartz flask containing the monomer under argon. The flask is then illuminated with UV light (254 nm) for 2 hours before removing and cleaning the polymer-functionalized wafers with successive solvent washes followed by drying under a stream of nitrogen. The polymer-modified wafers are then placed in a sealed flask containing an argon-sparged methanolic solution that is 1 mM in triethylamine and 1 mM Co(dmgH\textsubscript{2})(dmgH)Cl\textsubscript{2}. After 12 hours, the catalyst-modified wafers are removed from the flask and cleaned with successive solvent washes followed by drying under a stream of nitrogen then under vacuum. Following the PVI-grafting procedure, spectroscopic ellipsometry measurements, performed in air, yield a polymer thickness of 6 nm. An upper limit on the imidazole unit site density can be provided given the bulk PVI density.
(1.25 g cm\(^{-3}\))\(^{31}\) is representative of the solvent-free layer density. Thus, for a 6 nm thick PVI layer, the maximum site density is \(5 \times 10^{15} \text{ cm}^{-2} = 8 \text{ nmol cm}^{-2}\).

Surface analysis using grazing angle attenuated total reflection (GATR-FTIR) spectroscopy provides compelling evidence for successful chemical functionalization of the GaP(111) surfaces. GATR-FTIR spectra of unmodified GaP(111A) and GaP(111B) as well as spectra collected following photochemical grafting of vinylimidazole, yielding PVIIGaP (111A) or PVIIGaP (111B), and spectra collected following assembly of cobaloximes, yielding ColPVIIGaP (111A) or ColPVIIGaP (111B), are shown in Figure 3.19. For the GaP samples functionalized only with PVI, and prior to attachment of catalysts, distinct IR absorbance bands associated with multimode in-ring C=C as well as in-ring C=N stretches of PVI are observed at 1500 cm\(^{-1}\). In addition, the distinct 1373 cm\(^{-1}\) peak of the C=C stretch associated with the vinyl group of the monomer is not pronounced on the PVI-functionalized wafers. Instead, a new peak indicative of the planar deformation vibration of the CH\(_2\) groups in the polymer chain\(^{32}\) and centered at 1454 cm\(^{-1}\), is present.

Following treatment of PVIIGaP surfaces with the Co(dmgH\(_2\))(dmgH)Cl\(_2\) solution, unique vibrational modes characteristic of imidazole units coordinated to cobaloxime complexes are detected, including a peak at 1570 cm\(^{-1}\) characteristic of the C=N stretches on the glyoximate ligands of cobaloximes coordinated to an axial imidazole.\(^{33}\) Furthermore, unlike the C=N and C=C vibrations of the imidazole ring observed at 1500 cm\(^{-1}\) on PVIIGaP samples, additional vibronic features appear at 1517 cm\(^{-1}\) on samples of and ColPVIIGaP(111B) associated with the C=N and C=C vibrations of imidazole units.
Figure 3.19. FTIR transmission spectra of (a and c) N-vinylimidazole monomer in KBr (blue) as well as a powder sample of the model cobaloxime catalyst, Co(dmgH)₂(meIm)Cl, in KBr (red). GATR-FTIR absorbance spectra of (b) the (111)A-face and (d) (111)B-face of unmodified GaP (black dash) polyvinylimidazole-grafted GaP (blue) and cobaloxime-modified GaP (red). The spectra shown in parts a and c are identical and included to facilitate comparisons.

Coordinated to cobalt centers. This 17-wavenumber difference is consistent with previously reported IR spectra of metals coordinating to PVI. Finally, and as described in the following sentences, comparison of the NO\(^-\) stretching region in spectra of ColPVII\(\text{GaP}\) with spectra of Co(dmgH)\(_2\)(dmgH)Cl\(_2\) and Co(dmgH)\(_2\)(meIm)Cl, a model cobaloxime compound bearing an axial N- methylimidazole unit, affords a direct
spectroscopic method of confirming successful synthesis of intact cobaloxime complexes on the polymeric interface. The FTIR spectrum of the precursor material, Co(dmgH$_2$)(dmgH)Cl$_2$, used to assemble the attached cobalt complexes to the PVI-functionalized electrode includes a strong NO$^-$ stretch at 1225 cm$^{-1}$. However, this feature is not pronounced in the spectrum of PVI-GaP samples following treatment with Co(dmgH$_2$)(dmgH)Cl$_2$. Instead the strong NO$^-$ stretching frequency is observed at 1239 cm$^{-1}$ on the surface of the A and B wafers, a value more consistent with that observed for the NO$^-$ stretch at 1237 cm$^{-1}$ measured for the cobaloxime model compound, Co(dmgH)$_2$(meIm)Cl. All spectra are collected at 4 cm$^{-1}$ resolution and the lack of apparent peak features centered at 1225 cm$^{-1}$ in spectra of CoPVIIGaP surfaces indicate that minimal to no residual Co(dmgH$_2$)(dmgH)Cl$_2$ remain following ultrasonic cleaning of the samples. In addition, the close alignment of the spectral features of CoPVIIGaP samples with those obtained for powders of the model cobaloxime compound indicates that that surface-assembled cobaloxime species have a vibrational structure similar to that of the non-surface-attached model compound.

Sample analysis using X-ray photoelectron (XP) spectroscopy provides further evidence of successful surface functionalization. Survey XP spectra of PVIIGaP samples show the presence of additional O, N, and C elements as compared to spectra of unfunctionalized GaP. In contrast to the Ga 2p and P 2p core level XP spectra of wafers with a native oxide layer (Figure 3.20), the spectral features associated with gallium oxide and phosphate are significantly reduced following the H$_2$SO$_4$ etching and subsequent polymer grafting procedure, despite the samples being exposed to air following the polymer-
Figure 3.20. XP spectra of the Ga 2p (left) and P 2p (right) regions of unmodified GaP (111)A (top) and GaP(111)B (bottom). The circles are the spectral data, and the solid lines represent the background (gray), component fit (green), and overall fit (black).

grafting step (Figure 3.21). For the untreated GaP (111A) and GaP (111B) wafers, the Ga 2p$_{3/2}$ spectral intensity ratios, $A_{Ga-O}/A_{Ga-P}$, are 0.08 and 0.49, and the P 2p spectral intensity ratios, $A_{P-O}/A_{P-Ga}$, are 0.04 and 0.12, respectively. By contrast, inspection of the XP core level spectra for PVIIGaP surfaces show a significant attenuation of the substrate
Figure 3.21. XP spectra of the Ga 2p (left) and P 2p (right) regions of polymer-modified GaP (111)A (top) and GaP(111)B (bottom). The circles are the spectral data, and the solid lines represent the background (gray), component fit (blue), and overall fit (black).

Signals due to the presence of the grafted molecular layer. On the PVI GaP A face, the $A_{Ga-O}/A_{Ga-P}$ ratio is 0.06 and there is no detectable phosphate feature. On the PVI GaP B face, both the gallium signal and phosphate feature are unapparent. In the C 1s core level XP spectra of the polymer-functionalized wafers, a shakeup satellite appearing 6 eV higher in binding energy than the C 1s feature centered at 284.8 eV is indicative of $\pi/\pi^*$
bonding of aromatic polymers. Lastly, the N 1s core level XP spectra of PVI|GaP samples show two features centered at ~400 and 398 eV with near-equal spectral intensity as anticipated for the 1:1 ratio of amine and imine nitrogens associated with imidazole units on the PVI graft (Figure 3.22a and 3.22c). This is in sharp contrast to

Figure 3.22. N 1s core level spectra of (a) PVI|GaP(111)A, (b) ColPVI|GaP(111)A, (c) PVI|GaP(111)B, and (d) ColPVI|GaP(111)B. Circles represent the spectral data. Solid and dash lines are background (gray), component (red or blue), and overall (black) fits to the experimental data.
spectra reported on GaP samples following grafting of PVP where only a single nitrogen feature is observed at 398.7 eV.\textsuperscript{35,36}

Survey XP spectra of ColPVI\textsubscript{11}GaP samples confirm the presence of additional Co and Cl elements associated with attached cobaloximes. Analysis of the Co and Cl spectral intensities obtained from core level XP spectra, following the application of appropriate sensitivity factors, yields a measured Co:Cl ratio of 1:1. However, the measured Co:Cl ratio using a Co(dmgH\textsubscript{2})(dmgH)Cl\textsubscript{2} powder sample is 1:2. These ratios are consistent with the proposed attachment mechanism invoking a base-promoted conversion of the dimethylglyoxime ligand of Co(dmgH\textsubscript{2})(dmgH)Cl\textsubscript{2} to a dimethylglyoximate monoanion and the associated replacement of one of the axial X-type chloride ligands with an L-type nitrogen ligand on the PVI-polymer brush.

Additional structural confirmation is provided by comparison of the N 1s and Co 2p core level spectra of ColPVI\textsubscript{11}GaP samples which yields a Co:N spectral intensity ratio of 1:11 and 1:10 on the 111A and 111B modified surfaces, indicating that 28\%-32\% of the imidazole units on the polymer graft are coordinated to a Co center, provided there is an evenly distributed loading of Co sites along the ~6 nm depth polymer coat. Further, unlike the N 1s core level spectra obtained for PVI\textsubscript{11}GaP surfaces which show only two distinct nitrogen features with approximately equal spectral intensity, N 1s core level spectra of ColPVI\textsubscript{11}GaP samples can be fit with three additional nitrogen contributions assigned to imine, amine and glyoximate nitrogens coordinated to the Co centers of the cobaloximes (Figure 3.22b and 3.22d). As measured in previous reports, coordination of cobalt centers to a surface-grafted PVP-polymer brush is associated with displacement of
the N 1s feature assigned to attached pyridyl nitrogens to higher binding ratios estimated from the Co:N spectral intensities. Finally, the Co 2p core level spectra of CoPVIIGaP samples show samples show peaks centered at 780.0 eV (2p$_{3/2}$) and 795.0 eV (2p$_{1/2}$), a 2:1 branching and no apparent shakeup satellite structures, all features indicative of the Co$^{3+}$ species.$^{37,38}$

3.2.2 Photoelectrochemical Performance

Photoactivity of the electrode assemblies is assessed via electrochemical characterization in aqueous solutions buffered at pH 7 (0.1 M phosphate buffer) in the dark and upon AM1.5 illumination using a 100 mW cm$^{-2}$ solar simulator. For the 111 samples reported here, all A and B face constructs are prepared using wafers cut from the same ingot resulting in samples that achieve a similar saturating photocurrent when under equal illumination conditions, thus simplifying the comparison of results obtained using the photoelectrodes. The doping conditions of these wafers as well as the light source used for illumination differ from previous reports from, and both of these factors can affect the maximum attainable current density (Figure 3.23). Figures 3.24a and 3.24b show the three-electrode polarization curves obtained using surface-functionalized GaP working electrodes. For the cobaloxime-modified electrodes, the photocurrent measured at 0 V vs. RHE is significantly higher than those achieved testing unmodified or polymer-only treated electrodes, with the PVIIGaP electrodes having a current density of 0.32 ± 0.04 and 0.30 ± 0.08 mA cm$^{-2}$ and the CoPVIIGaP electrodes having a current density of 0.89 ± 0.02 and 0.89 ± 0.03 mA cm$^{-2}$ for the A and B face, respectively (Table 3.3). Consistent with the increased photoactivity of the molecular catalyst-modified electrodes, the
Figure 3.23. Linear sweep voltammograms of working electrodes using GaP substrates with the varied properties and illumination conditions.

1 (solid line) illuminated with a Newport Oriel Apex illuminator (100 mW cm\(^{-2}\)) using Co-PVP-modified Zn doped p-GaP(100) with a resistivity of 1.17 x 10\(^{-1}\) Ω.cm, a mobility of 77 cm\(^2\) V\(^{-1}\) s\(^{-1}\), and a carrier concentration of 6.95 x 10\(^{17}\) cm\(^{-3}\).36 2 (dotted line) illuminated with a Solar Light PV cell test simulator (100 mW cm\(^{-2}\)) using the same electrode described in 1.39 3 (dashed-dotted line) illuminated with a Solar Light PV cell test simulator (100 mW cm\(^{-2}\)) using Co-PVP-modified Zn doped p-GaP(100) with a resistivity of 5.5 x 10\(^{-2}\) Ω.cm, a mobility of 54 cm\(^2\) V\(^{-1}\) s\(^{-1}\), and a carrier concentration of 2.2 x 10\(^{18}\) cm\(^{-3}\).35 4 (dashed-dotted line) illuminated with a LSC-100 Series Oriel Solar Simulator equipped with an AM1.5 filter (100 mW cm\(^{-2}\)) using Co-PVI-modified Zn doped p-GaP(100) with a resistivity of 4.6 x 10\(^{-2}\) Ω.cm, a mobility of 50 cm\(^2\) V\(^{-1}\) s\(^{-1}\), and a carrier concentration of 2.7 x 10\(^{18}\) cm\(^{-3}\) (chapter 2).
measured open-circuit photovoltages (as determined by the zero-current value in the linear sweep voltammograms) of the PVI\textsubscript{1}GaP electrodes are 0.56 ± 0.02 V vs. RHE and 0.58 ± 0.04 V vs. RHE for the A and B faces, respectively; with an increase to 0.64 ± 0.02 following cobaloxime-modification of A-face electrodes and to 0.65 ± 0.02 following cobaloxime-modification of B-face electrodes (Table 3.3). The minimum sample size of each photocathode type reported (GaP, PVI\textsubscript{1}GaP and Co\textsubscript{1}PVI\textsubscript{1}GaP) included testing of three distinct electrode assemblies. The polymer-only functionalized electrodes show a slightly greater deviation in their current-voltage responses as compared to results obtained using Co\textsubscript{1}PVI\textsubscript{1}GaP assemblies, especially in the B-face.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure3.png}
\caption{Linear sweep voltammograms of (a) GaP(111)A and (b) GaP(111)B working electrodes following polyvinylimidazole grafting (blue) and cobaloxime attachment (red). All measurements were performed at pH 7 in the dark (dashed-dotted lines) or under 100 mW cm\textsuperscript{-2} illumination (solid lines).}
\end{figure}
samples. It has previously been shown that the B face of GaP(111) is more prone to residual oxide coverage following initial etching and cleaning,\textsuperscript{40} which may provide an explanation for the slightly increased variability in the data reported here for the PVIIGaP(111B) electrodes. However, following cobaloxime attachment the electrodes prepared on either face show nearly identical current and voltage responses with minimal variability of results between individually fabricated electrodes. For all catalyst-modified photocathodes reported here, hydrogen production is confirmed via gas chromatography analysis of the headspace, showing near-unity faradaic efficiency. The photocurrent response and associated rate of hydrogen production for both the A and B faces functionalized GaP(111) wafers are nearly identical. The measurements also show that the photocurrent over an hour is relatively stable, with a decrease of less than 1% over 55 minutes following an initial drop off of up to 12% during the first 5 minutes of photoelectrochemical (PEC) characterization (Figure 3.25). Previous computational

<table>
<thead>
<tr>
<th>Construct</th>
<th>$V_{oc}$ (V vs RHE)</th>
<th>$J$ at 0 V vs RHE (mA cm$^{-2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>GaP(111)A</td>
<td>0.02 ± 0.02</td>
<td>0.22 ± 0.06</td>
</tr>
<tr>
<td>PVIIGaP(111)A</td>
<td>0.56 ± 0.02</td>
<td>0.32 ± 0.04</td>
</tr>
<tr>
<td>ColPVIIGaP(111)A</td>
<td>0.64 ± 0.02</td>
<td>0.89 ± 0.02</td>
</tr>
<tr>
<td>GaP(111)B</td>
<td>0.53 ± 0.06</td>
<td>0.22 ± 0.06</td>
</tr>
<tr>
<td>PVIIGaP(111)B</td>
<td>0.02± 0.04</td>
<td>0.30 ± 0.08</td>
</tr>
<tr>
<td>ColPVIIGaP(111)B</td>
<td>0.58 ± 0.02</td>
<td>0.89 ± 0.03</td>
</tr>
</tbody>
</table>
and experimental studies show that redox cycling of cobaloxime solutions can result in the dissociation of N-containing ligands from cobalt centers, and the loss of current during the initial 5 minutes of PEC characterization of the cobaloxime-modified assemblies reported here may in part be due to loss of loosely bound catalysts located at electrolyte-exposed edges of the polymer that are not protected by the encapsulating environment of the polymer.\textsuperscript{36}

3.2.3 Turnover Frequency

The data obtained from ellipsometry, XP spectroscopy, and PEC measurements allow an estimate of the TOF of the ColPVI|GaP construct per cobalt center. For example, an electrode operating at a 0.9 mA cm\textsuperscript{-2} current density (a value representative of that measured using ColPVI|GaP electrodes polarized at 0 V vs. RHE) with a 6 nm PVI graft

![Figure 3.25](image.png)

**Figure 3.25.** Three-electrode electrolysis measurements using cobaloxime-modified GaP(111)A (dashed) and cobaloxime-modified GaP(111)B (solid) working electrodes polarized at 0 V vs RHE. All measurements were performed at pH 7 under 100 mW cm\textsuperscript{-2} illumination.
and 30% attachment to cobaloxime catalysts yields a TOF of 7,000 per hour per cobalt center, assuming that all the cobalt centers are photoelectrochemically active. For comparison, a TOF of 8,000 per hour was reported by Artero and coworkers using an analogous cobaloxime species surface grafted to an electroactive carbon support polarized at -0.59 V vs. RHE\textsuperscript{41} and a TOF of 1.9 per second was reported by Turner et al.\textsuperscript{42} using a cobaloxime catalyst assembled on a TiO\textsubscript{2}-coated GaInP\textsubscript{2} semiconductor poised at 0 V vs RHE.

3.3 Conclusions

In conclusion, cobaloxime catalysts are successfully assembled on both crystal faces of gallium phosphide 111 by employing a vinylimidazole polymer brush interface. Structural analysis of the reported assemblies is performed using spectroscopic ellipsometry, GATR-FTIR, and XP spectroscopies. PEC characterization of the modified cathodes shows significant improvement of the photoperformance for hydrogen production of GaP electrodes following polymeric cobaloxime modification, obtaining a current density of ≈1 mA cm\textsuperscript{-2} when polarized at 0 V vs. RHE. Our measurements indicate that a slightly higher loading of catalysts can be achieved via functionalization of the B face with respect to results obtained on A face modified samples. Yet, the photoelectrochemical characterization of samples using A or B face modification show nearly identical photoperformance under the conditions tested, illustrating that factors other than catalyst loading can limit photoactivity. Previous light intensity dependence measurements obtained using CoLPVPlGaP samples show a near-linear response of the current measured at 0 V vs. RHE, indicating that in such hybrid constructs, photocarrier
transport to the interface may in part limit the performance of the Co-modified GaP photocathodes. Although the mechanistic details of vinyl group attachment chemistry are not settled,\textsuperscript{43–49} molecular binding appears to occur over bridging oxygen atoms on GaP (100) surfaces.\textsuperscript{50} A similar attachment chemistry may occur for the functionalized GaP (111A) and GaP (111B) constructs reported in this work, consistent with the similarity in catalysts-polymer loadings and photoelectrochemical performance achieved using these substrates as well as the analysis of surface oxygen content performed prior to and following surface functionalization. Efforts to further analyze the loading, mesoscale architecture, surface energetics (thermodynamics) and activity of catalysts (kinetics) are underway. Nonetheless, attachment chemistry reported in this chapter is not limited to a specific crystal face of gallium phosphide, a promising feature regarding the applicability of this attachment strategy across varying crystal face orientations.

3.4 Experimental Methods

3.4.1 Materials

Single crystalline p-type gallium phosphide wafers were purchased from University Wafers. The material was single side polished to an epi-ready finish. The p-type GaP(111)A wafers have a resistivity of 0.046 \(\Omega\) cm, a mobility of 50 cm\(^2\) V\(^{-1}\) s\(^{-1}\), and a carrier concentration of 2.7 x 10\(^{18}\) cm\(^{-3}\). The etch pit density was less than 9.5 x 10\(^4\) cm\(^{-2}\). The p-type Zn-doped GaP(111)B(±0.5\(^\circ\)) wafers have a resistivity of 0.054 \(\Omega\) cm, a mobility of 46 cm\(^2\) V\(^{-1}\) s\(^{-1}\), and a carrier concentration of 2.5 x 10\(^{18}\) cm\(^{-3}\). The etch pit density was less than 2.0 x 10\(^4\) cm\(^{-2}\).
3.4.2 Synthesis

All syntheses were carried out under an argon atmosphere using Schlenk techniques unless otherwise stated. All reagents were purchased from Aldrich. Isopropanol was cleanroom grade and used as received. Dichloromethane, methanol, and vinylimidazole were freshly distilled before use. All solvents were stored over the appropriate molecular sieves prior to use. Milli-Q water (18.2 MΩ cm) was used to prepare all aqueous solutions. The cobaloxime syntheses was carried out as described in Section 2.4.2.

3.4.3 Wafer Preparation

All wafers were initially degreased with an acetone-soaked cotton swab. GaP(111) wafers were further cleaned using consecutive ultrasonic treatments in a series of solvents (acetone, 1 min; methanol, 1 min; dichloromethane, 30 s; methanol, 1 min; and water, 1 min), followed by a 30 s etch in concentrated sulfuric acid.\textsuperscript{40} Unmodified wafers used for XPS analysis were thoroughly degreased but not acid-etched.

3.4.4 Wafer Functionalization

The freshly etched wafers were put into an argon-sparged solution of N-vinylimidazole and exposed to 254 nm UV light for 2 h. After thoroughly rinsing with methanol, the wafers were dried under N\textsubscript{2} and stored under vacuum. Cobaloxime functionalization was achieved by covering the PVI\textsubscript{2}GaP wafers with an argon-degassed solution of Co(dmgH)\textsubscript{2}(dmgH)Cl\textsubscript{2} and triethylamine (1 mM in each) in methanol and allowing them to react overnight. The wafers were rinsed with methanol, then ultrasonically treated in
methanol for 1 min, followed by rinsing with isopropanol, and drying under N₂ then vacuum.

### 3.4.5 Electrode Fabrication

GaP working electrodes were fabricated by applying an indium–gallium eutectic (Aldrich) to the backside of a wafer and then fixing a copper wire to the back of the wafer using a conductive silver epoxy (Circuit Works). The copper wire was passed through a glass tube, and the wafer was insulated and attached to the glass tube with Loctite 615 Hysol Epoxi-patch adhesive. The epoxy was allowed to fully cure before testing the electrodes.

### 3.4.6 Instrumentation

**UV–Vis Spectroscopy.** Ultraviolet–visible (UV–vis) optical spectra were recorded on a Shimadzu SolidSpec-3700 spectrometer with a D2 (deuterium) lamp for the ultraviolet range and a WI (halogen) lamp for the visible and near-infrared regions. Transmission and reflectance measurements were performed with an integrating sphere.

**NMR Spectroscopy.** Nuclear magnetic resonance (NMR) spectra were recorded on a Varian NMR spectrometer operating at 400 MHz. Unless otherwise stated, all spectra were collected at room temperature.

**FTIR Spectroscopy.** Grazing angle attenuated total reflection Fourier transform infrared spectroscopy (GATR-FTIR) was performed using a VariGATR accessory (Harrick Scientific) with a Ge crystal plate installed in a Bruker Vertex 70. Samples were pressed against the Ge crystal to ensure effective optical coupling. Spectra were collected using
256 scans under a dry nitrogen purge with a 4 cm\(^{-1}\) resolution, GloBar MIR source, a broadband KBr beamsplitter, and a liquid nitrogen cooled MCT detector. Background measurements were obtained from the bare Ge crystal, and the data were processed using OPUS software. GATR measurements were baseline-corrected using an ATR correction for a germanium crystal and a sample with a refractive index of 1.43. Spectra from model compounds in pressed KBr pellets were acquired with the same settings but using transmission mode.

\textit{X-ray Photoelectron Spectroscopy.} X-ray photoelectron spectroscopy (XPS) was performed using a monochromatized Al K\(\alpha\) source (hv = 1486.6 eV), operated at 63 W, on a Kratos system at a takeoff angle of 0° relative to the surface normal and a pass energy for narrow scan spectra of 20 eV, at an instrument resolution of approximately 700 meV. Survey spectra were collected with a pass energy of 150 eV. Spectral fitting was performed using Casa XPS analysis software. Spectral positions were corrected by shifting the primary C 1s core level position to 284.8 eV, and curves were fit with quasi Voigt lines following Shirley background subtraction. All N 1s fits were constrained to a full width at half-maximum (fwhm) value of less than 1.3 eV.

\textit{Electrochemistry.} Cyclic voltammetry was performed with a Biologic potentiostat using a glassy carbon (3 mm diameter) disk, a platinum counter electrode, and a silver wire pseudoreference electrode in a conventional three-electrode cell. Anhydrous acetonitrile (Aldrich) was used as the solvent for electrochemical measurements. The supporting electrolyte was 0.1 M tetrabutylammonium hexafluorophosphate. The solution was deoxygenated by bubbling with argon. The working electrode was cleaned between
experiments by polishing with alumina (50 nm diameter) slurry, followed by solvent rinses. The potential of the pseudoreference electrode was determined using the ferrocenium/ferrocene redox couple as an internal standard and adjusting to the normal hydrogen electrode (NHE) scale (with $E_{1/2}$ taken as 0.40 V vs NHE).

**Photoelectrochemistry.** Photoelectrochemical (PEC) characterization was performed using 100 mW cm$^{-2}$ illumination from a 100 W Oriel Solar Simulator equipped with an AM 1.5 filter. Linear sweep voltammetry and three-electrode electrolysis (chronoamperometry) were performed with a Biologic potentiostat using a platinum coil counter electrode, a Ag/AgCl, NaCl (3 M) reference electrode (0.21 V vs NHE), and GaP working electrodes (including GaP following acid etch, PVI-grafted GaP, and cobaloxime-modified GaP) in a modified cell containing a quartz window. The supporting electrolyte was 0.1 M phosphate buffer (pH 7). Linear sweep voltammograms were recorded at sweep rates of 100 mV s$^{-1}$ under a continuous flow of 5% hydrogen in nitrogen. Open-circuit photovoltages were determined by the zero current value in the linear sweep voltammograms. Chronoamperometry was performed with the working electrode polarized at −0.610 V vs Ag/AgCl, slightly positive of 0 V vs RHE, where $E$ vs RHE = $E$ vs NHE + (0.05916 V) (pH) (V) = $E$ vs Ag/AgCl + (0.05916 V) (pH) + 0.21 V.

**GC Analysis.** Gas analysis was performed via gas chromatography (GC) using an Agilent 490 Micro GC equipped with a 5 Å MolSieve column at a temperature of 80 °C and argon as the carrier gas. Gas samples were syringe-injected using 5 mL aliquots of headspace gas collected with a gastight Hamilton syringe from a sealed PEC cell both prior to and following 10 min of three-electrode photoelectrolysis using a cobaloxime-
modified working electrode polarized at 0 V vs RHE. Prior to the experiment the cell was purged for 30 min with argon before sealing. The retention time of hydrogen was confirmed using a known source of hydrogen obtained from a standard lecture bottle containing a hydrogen and argon mixture.

Ellipsometry. Film thickness (FT) was determined using a J. A. Woollam variable angle spectroscopic ellipsometer with a spectral range of 200–1200 nm. Measurements were at 70°, 75°, and 80° incidence angles, and analysis was done using VASE software. The model used to determine the FT of surface-grafted polyvinylimidazole was composed of a GaP substrate layer (Aspnes), a GaP oxide layer (Zollner) with a fixed thickness of 1.01 nm, and a Cauchy layer for the polyvinylimidazole film of each sample. The Cauchy coefficients for GaP(111)A were A = 1.414 and B = −0.034, and the FT of the Cauchy layer was determined to be 6.2 ± 0.2 nm with an MSE of 8.356.

The Cauchy coefficients for GaP(111)B were A = 1.371 and B = 0.008, and the FT of the Cauchy layer was determined to be 6.5 ± 0.2 nm with an MSE of 3.745. In this analysis, the thickness of the oxide layers is based on ellipsometry measurements performed on unfunctionalized GaP(111)A and GaP(111)B surfaces. However, the vast majority of the oxide is likely formed during transportation and handling of the sample in air (up to 10 min) following the etching process and subsequent ellipsometry measurement. The process of photografting and polymerizing N-vinylimidazole onto freshly etched GaP, under inert conditions, should give an oxide layer much thinner than the average oxide FT of 1.01 nm; thus these values provide an upper limit of any oxide formation on polyvinylimidazole-grafted GaP.
3.5 References

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CHAPTER 4  COBALT PORPHYRIN-POLYPYRIDYL SURFACE COATINGS
FOR PHOTOELECTROSYNTHETIC HYDROGEN PRODUCTION

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4.1 Introduction

The use of a surface-grafted organic coating to assemble molecular catalysts for hydrogen evolution to a visible-light-absorbing semiconductor is reported in this chapter. This approach combines features of solid-state light capture and conversion materials with molecular components for enhancing photoelectrochemical fuel production. The materials used to assemble the hybrid photocathode include GaP as the underpinning semiconductor, 4-vinylpyridine as the monomeric unit used to form a polypyridine surface coating (PPy), and 5,10,15,20-tetra-p-tolylporphyrin cobalt(II) (CoTTP) as a molecular component for enhancing photoelectrochemical hydrogen production.

Metalloporphyrins serve important roles in biology as reactive sites for driving enzymatic reactions and as components in emerging molecular-based materials with applications to energy transduction.\(^1\)\(^{-}\\(^{20}\) As electrocatalysts, they are capable of chemically transforming protons into hydrogen as well as converting carbon dioxide into carbon monoxide and/or hydrocarbons such as methane and ethylene when electrochemically activated in solution or immobilized at a conductive substrate polarized at an appropriate potential (Figure 4.26). A synthetic methodology for directly grafting metalloporphyrins onto GaP using precursor complexes bearing a 4-vinylphenyl surface attachment group at the beta position of the porphyrin macrocycle has been previously reported.\(^21\) The cobalt porphyrin-modified photocathodes are active for hydrogen production, evolving the product gas at a rate of \(\approx 10 \text{ μL min}^{-1} \text{ cm}^{-2}\). Comparison of the total surface cobalt porphyrin concentrations with the amount of hydrogen produced indicate the HER activity per metal site is among the highest reported for a molecular-modified
Figure 4.26. Voltammograms of 5,10,15,20-tetra-p-tolylporphyrin cobalt(II) (CoTTP) recorded in 0.1 M tetrabutylammonium hexafluorophosphate in dimethylformamide and 0 mM tosic acid (green solid line), 10 mM tosic acid (green dashed line) or CO$_2$ (black dashed line) at a scan rate of 250 mV s$^{-1}$ using a glassy carbon working electrode at room temperature and ferrocene as an internal standard. Data collected by Diana Khusnutdinova.

This work shows that an initially deposited organic interface consisting of repeating pyridyl units can provide molecular recognition sites that self-assemble cobalt porphyrins onto the polypyridine-modified GaP surface. This provides an alternate and streamlined method for interfacing cobalt porphyrins to a semiconductor that does not require synthetic modifications to the porphyrin macrocycle to install a surface-grafting functional group. Thus, the attachment strategy also enables application of porphyrins bearing substituents that are chemically incompatible or complicated by installment of the vinylphenyl functionality.
4.2 Results and Discussion

4.2.1 Wafer Preparation and Characterization

The cobalt porphyrin-polypyrrole-modified GaP semiconductors (CoTTP|PPy|GaP) described in this report are prepared using a two-step method (Figure 4.27) leveraging the UV-induced surface grafting chemistry of alkenes\textsuperscript{22–29} to apply an initial thin-film polypyrrole surface coating, followed by wet-chemical treatment to assemble the cobalt porphyrin units. During this process, freshly cleaned and etched GaP(100) wafers are placed in an argon-sparged solution of 4-vinylpyridine under shortwave UV illumination for 2 hours before removing and cleaning the functionalized wafers with successive solvent washes followed by drying under a stream of nitrogen. The resulting polypyrrole-modified substrates (PPy|GaP) are then exposed to a 1 mM solution of CoTTP in toluene under an argon atmosphere for 18 hours, forming the cobalt porphyrin-modified wafers, CoTTP|PPy|GaP.

Analysis of CoTTP|PPy|GaP surfaces using grazing angle attenuated total reflection Fourier transform infrared (GATR-FTIR) spectroscopy confirms that cobalt centers of the porphyrin macrocycles coordinate to pyridyl nitrogen sites of the PPy graft (Figure 4.27). In addition to characteristic vibrational features associated with C-H and C-N vibrations of surface-grafted pyridyl units as well as the C\textsubscript{β}-H, C\textsubscript{α}-N, and C=C vibrations of the porphyrin macrocycle, a prominent absorption band is measured at 1009 cm\textsuperscript{-1}. Absorption bands appearing in the region from 1019-1004 cm\textsuperscript{-1} in the IR spectra of metalloporphyrins are ascribed to in-plane porphyrin deformation. This region is sensitive to both the elemental nature of the metal center as well as local coordination.
Figure 4.27. (left) Schematic representation of the synthetic method used to prepare the PPy|GaP and CoTTP|PPy|GaP samples. (right) GATR-FTIR absorbance spectra of the (a) 1700-950 cm\(^{-1}\) region of unfunctionalized GaP (black), PPy|GaP (blue), and CoTTP|PPy|GaP (purple), including (b) an expanded plot of the 1022-987 cm\(^{-1}\) region in spectra of CoTTP|PPy|GaP.
environment due to inductive and mesomeric effects.\textsuperscript{30,31} The feature at 1009 cm$^{-1}$ on CoTTP|PPy|GaP surfaces, labeled as $\nu_{\text{Co-N}}$ (Figure 4.27b), is particularly diagnostic of cobalt porphyrin complexes coordinated to an axial pyridyl unit\textsuperscript{32} and thus provides structural information on the bonding motif of the surface-immobilized cobalt porphyrins.

Further information on the composition and structure of the modified surface, including film thickness, pyridyl site density, loading efficiency (defined here as the fraction of pyridyl sites coordinated to a cobalt center), and associated cobalt concentration per geometric area is gained using complementary methods of ellipsometry, inductively coupled plasma mass spectrometry (ICP-MS) and X-ray photoelectron (XP) spectroscopy. Spectroscopic ellipsometry measurements of PPy|GaP surfaces are used to determine the film thickness and provide an estimate of the pyridyl site density. For the samples in this report, the obtained film thickness is $1.45 \pm 0.17$ nm. Given the bulk polyvinylpyridine density ($1.15 \text{ g cm}^{-3}$) is representative of the solvent-free film, the calculated pyridyl site density is $1.57 \pm 0.18 \text{ nmol cm}^{-2}$.

ICP-MS measurements following acid digestion of PPy|GaP samples indicate no significant cobalt is present. However, following attachment of cobalt porphyrin complexes, the Co surface concentration is estimated to be $0.39 \pm 0.08 \text{ nmol cm}^{-2}$. The reported cobalt surface concentration takes into account that the synthetic method (UV-induced grafting of 4-vinylpyridine followed by wet chemical treatment with a CoTTP solution) and the reaction vessel geometry used in this report yields samples with cobalt porphyrin assembled on both sides of the single-side polished GaP wafers. The total
cobalt, including contributions from the front and back side of the GaP wafer and as measured by ICP-MS following acid digestion of CoTTP|PPy|GaP samples, is $0.59 \pm 0.12$ nmol cm$^{-2}$. Thus, the total cobalt contribution of CoTTP|PPy|GaP samples is nearly identical to that estimated and previously reported\textsuperscript{8c} for CoP-GaP samples (0.59 nmol cm$^{-2}$) in which no attempt was made to distinguish contributions from the front and back side of the GaP wafer and thus represents an upper limit. However, XP spectroscopic analysis of the polished and unpolished faces of CoTTP|PPy|GaP samples prepared \textit{via} UV illumination from the polished side of the wafer indicate the surface cobalt concentration on the unpolished (non-directly illuminated) side of the wafer is 33% lower than that of the polished (directly illuminated) side of the wafer, yielding the reported cobalt concentration of $0.39 \pm 0.08$ nmol cm$^{-2}$ on the polished face. These measurements indicate 25 ± 5% of the pyridyl units on the CoTTP|PPy|GaP surface are coordinated to a porphyrin cobalt center, equating to a total N/Co ratio of 4.1 ± 0.8. This ratio, as measured by ICP-MS and ellipsometry, is used to establish the N 1s background in XP spectroscopy and assists in guiding the component fitting. This method of combining information obtained from ICP-MS, ellipsometry and XP spectroscopy is particularly useful in analyzing thin-film surface coatings on GaP as the N 1s spectrum contains background components arising from Ga 3d (Auger) LMM lines (Figure 4.28).\textsuperscript{33} As compared to XP spectra of unfunctionalized GaP or PPy|GaP samples, spectra of the CoTTP|PPy|GaP samples show additional Co and N contributions. After applying
Figure 4.28. N 1s core level XP spectra of unfunctionalized GaP (black) and PPy|GaP (blue).

the appropriate relative sensitivity factors, the N 1s to Co 2p spectral intensity ratio of 8.0 ± 0.8 yields a loading efficiency of 26 ± 6%, a value consistent with that determined by the ellipsometry and ICP-MS analysis. In addition, unlike the single component observed in the high-energy resolution N 1s spectra of PPy|GaP samples (Figure 4.28), spectra obtained using CoTTP|PPy|GaP samples can be deconvoluted into three components (Figure 4.29b). Based on the relative signal intensities and binding energies associated with these components, the contributions centered at 398.5, 399.0, and 399.7 eV are assigned to remnant pyridinic nitrogens of the surface graft, porphyrin pyrrolic nitrogens bound to cobalt centers, and pyridinic nitrogens bound to cobalt centers, respectively. Further, the ≈3:4:1 spectral intensity ratios associated with the three components are consistent with both the 4:1 ratio of cobalt-pyrollic to cobalt-pyridinic nitrogen centers anticipated for a cobalt porphyrin coordinated to a pyridyl unit, as well as the 26 ± 6%
Figure 4.29. (a) Molecular structure of a CoTTP unit coordinated to polypyridine. (b) High-energy resolution XP spectrum of the N 1s region of CoTTP|PPy|GaP. Solid lines represent the background (gray), component (blue, green, and red), and overall (black) fits to the experimental data (circles). Shading indicates the component area assigned to remnant pyridinic nitrogens (blue), porphyrin pyrrolic nitrogens bound to cobalt centers (green), and pyridinic nitrogens bound to cobalt centers (red). (c) High-energy resolution XP spectrum of the Co 2p$_{3/2}$ region of CoTTP|PPy|GaP.
loading efficiency determined by comparison of the total N 1s and Co 2p\textsubscript{3/2} spectral intensity contributions. Finally, high-energy resolution XP spectra of the Co 2p region (Figure 4.29c) show peaks centered at 780.1 eV (2p\textsubscript{3/2}) and 795.3 eV (2p\textsubscript{1/2}) with the anticipated 2:1 branching ratio and 15.2 eV splitting.\textsuperscript{34} The Co 2p\textsubscript{3/2} signal also shows satellite peaks at higher binding energies, consistent with the presence of cobalt species in the +2 oxidation state and the unpaired spin of the porphyrin cobalt center resting state.\textsuperscript{35}

4.2.2 Photoelectrochemical Performance

The PEC performance of custom-built working electrodes composed of CoTTP|PPy|GaP is assessed using three-electrode electrochemical techniques, including chronoamperometry (Figure 4.30a) and linear sweep voltammetry (Figure 4.30b), performed in buffered pH neutral aqueous conditions in the dark and under air mass 1.5 simulated solar illumination. Modification of GaP photocathodes with a cobalt porphyrin-polypyriddyl surface coating results in a significant anodic shift of the open-circuit photovoltage (V\textsubscript{oc}), moving from +0.57 ± 0.02 V vs RHE for the unmodified GaP electrodes to +0.65 ± 0.02 V vs RHE. Within the experimental error of the measurements, the current density of -1.27 ± 0.04 mA cm\textsuperscript{-2} achieved for CoTTP|PPy|GaP samples polarized at 0 V vs RHE (i.e. at the H\textsuperscript{+}/H\textsubscript{2} equilibrium potential) is identical to that reported using GaP samples modified with a directly attached cobalt porphyrin.\textsuperscript{21} Thus the intervening polypyriddyl surface coating does not diminish the performance gains afforded by cobalt porphyrin surface modification yet reduces the synthetic efforts required for assembly. In addition, the saturating photocurrent shows a linear increase upon increasing illumination intensity, indicating that the PEC activity at 0 V vs RHE
Figure 4.30. (a) Chronoamperogram of a CoTTP|PPy|GaP working electrode polarized at 0 V vs RHE under alternating (200 mHz) non-illuminated and illuminated conditions. (b) Linear sweep voltammograms of CoTTP|PPy|GaP working electrodes recorded in the dark (dashed line) and under simulated 1-sun illumination (solid line). The dotted vertical line at 0 V vs RHE represents the equilibrium potential of the H⁺/H₂ couple. The calculated HER activity per cobalt center is included on the right ordinate axis. (c) Gas chromatograms of a 5 mL aliquot of the headspace drawn from a sealed PEC cell using a CoTTP|PPy|GaP working electrode polarized at 0 V vs RHE before (dashed line) and after (solid line) 30 min of AM1.5 illumination. All measurements were performed using a three-electrode configuration in 0.1 M phosphate buffer (pH 7).
is in part limited by the photon flux. Characteristic of a photosynthetic assembly, these results confirm that light, and no electrochemical forward biasing or use of sacrificial redox reagents, is the energy input required to generate the photocurrent. Production of hydrogen is confirmed via gas chromatography analysis of headspace samples taken from a sealed PEC cell containing a CoTTP|PPy|GaP working electrode polarized at 0 V vs RHE under simulated solar illumination (Figure 4.30c). Under these conditions, hydrogen is produced at a rate of \( \approx 10 \, \mu \text{L min}^{-1} \, \text{cm}^{-2} \) with a faradaic efficiency of 93 ± 3%. Given the cobalt porphyrin surface concentration (0.39 ± 0.08 nmol cm\(^{-2}\)) determined by XP spectroscopy, ellipsometry, and ICP-MS, this equates to a HER activity per cobalt center of 17.6 \( \text{H}_2 \) molecules s\(^{-1}\) Co\(^{-1}\). During bulk electrolysis measurements, hydrogen bubbles accumulate on the electrode surface and diminish the surface area of the working electrode exposed to electrolyte, resulting in a decrease of current density over time. Removal of bubbles during or following PEC characterization restores the current density to a value nearly identical to that achieved for a freshly prepared electrode.

In addition, samples were prepared for post-PEC analysis using a customized three-electrode cell equipped with a quartz window and spring-loaded copper support to secure the GaP wafer, thus negating the need to encase the sample in epoxy. The electrodes were polarized at 0 V vs RHE for a minimum of 3 min under 1-sun illumination. Samples were rinsed with Mill-Q water and dried under vacuum before GATR-FTIR measurements. The observation of a prominent \( \nu_{\text{Co-N}} \) in-plane porphyrin deformation mode in GATR-FTIR spectra of samples following bulk electrolysis indicates cobalt porphyrins maintain their molecular integrity and coordination to pyridyl sites (Figure 4.31).
**Figure 4.31.** GATR-FTIR absorbance spectra showing the $v_{\text{Co-N}}$ region of the CoTTP|PPy|GaP before photoelectrochemical characterization (top, purple), following exposure to buffer (middle, dark red), and after photoelectrochemical characterization (bottom, green).

Additional insights regarding the performance gains afforded by cobalt porphyrin-polypyridyl surface modification come from analysis of the photovoltaic performance parameters derived from the voltammetry measurements, including those performed on control samples of working electrodes composed of unfunctionalized GaP and PPy|GaP (Figure 4.32 and Table 4.4). Although CoTTP|PPy|GaP shows an enhanced $V_{oc}$ compared to unmodified GaP, similar $V_{oc}$ gains are obtained following only application of the thin-
Figure 4.32. Linear sweep voltammograms of unfunctionalized GaP (black), PPy|GaP (blue), and CoTTP|PPy|GaP (purple) working electrodes. Circles represent the maximum power point. Dashed horizontal and dashed vertical lines represent the current density and potential, respectively, at the maximum power points.

Table 4.4 PEC Characteristics

<table>
<thead>
<tr>
<th>Construct</th>
<th>Open Circuit Voltage (V vs RHE)</th>
<th>Short Circuit Current (mA cm$^{-2}$)</th>
<th>Maximum Power Point (mW cm$^{-2}$)</th>
<th>Fill Factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>GaP(100)</td>
<td>0.57 ± 0.02</td>
<td>0.22 ± 0.06</td>
<td>0.11 ± 0.05</td>
<td>0.21 ± 0.08</td>
</tr>
<tr>
<td>PPy</td>
<td>GaP</td>
<td>0.64 ± 0.04</td>
<td>0.32 ± 0.04</td>
<td>0.15 ± 0.04</td>
</tr>
<tr>
<td>CoTTP</td>
<td>PPy</td>
<td>GaP</td>
<td>0.65 ± 0.02</td>
<td>0.89 ± 0.02</td>
</tr>
</tbody>
</table>
film polypyridyl surface coating (Figure 4.32). These results contrast to those reported using GaP semiconductors with thicker polymer coatings (on the order of ≈10 nm)\textsuperscript{37–40} where the $V_{oc}$ instead decreases following pyridyl group modification of the GaP surface. It is speculated that this is in part due to a larger resistance and poorer ion conductivity associated with the thicker organic coatings.\textsuperscript{41–43} Nonetheless, although the $V_{oc}$ of the PPy|GaP and CoTTP|PPy|GaP electrodes is similar, the fill factor (ff) of the JV response under illumination nearly doubles following treatment with CoTTP, moving from 0.21 ± 0.08 for unfunctionalized GaP to 0.23 ± 0.07 for PPy|GaP, and further increasing to 0.39 ±0.07 for CoTTP|PPy|GaP (Figure 4.32 and Table 4.4). Due to the steep increase in operating photocurrent densities that are produced by changes in ff, this can have a significant effect on performance in a photoelectrosynthetic cell.\textsuperscript{44}

### 4.3 Conclusions

In summary, surface-sensitive spectroscopic methods verify our synthetic efforts dedicated to construction of a hybrid composite material that structurally interfaces a cobalt porphyrin hydrogen evolution catalyst to a visible light-absorbing semiconductor using surface-attached pyridyl groups as molecular recognition sites. Complementary methods of ellipsometry, ICP-MS, and XP spectroscopy are used to quantify the surface cobalt concentrations and the fraction of pyridyl sites coordinated to cobalt centers. The synthetic methods used to obtain these assemblies demonstrate design principles for furthering hard-to-soft matter interface chemistry and set the stage to better understand the structure and function relationships of molecular-modified semiconductors. Key features of the construct reported here include the relative ease of synthetic preparation
made possible by application of a thin-film organic coating that uses pyridyl groups to assemble cobalt porphyrins on a GaP semiconductor surface, yielding a hybrid cathode that uses solar energy to drive reductive fuel-forming reactions in aqueous solutions without the use of organic acids or sacrificial chemical reductants. Thus, this work introduces a highly useful, yet easily accessible, motif for preparing and studying molecular-modified semiconductors. In order to elucidate the effect of the polymeric interface, studies using different bases and polymeric architectures to assemble CoTTP as well as other catalysts are underway.

4.4 Experimental Methods

4.4.1 Materials

All reagents were purchased from Sigma-Aldrich. Dichloromethane, hexanes, methanol, and toluene were freshly distilled before use. Milli-Q water (18.2 MΩ·cm) was used to prepare all aqueous solutions. Single crystalline p-type Zn-doped gallium phosphide (100) wafers (University Wafers) were single side polished to an epi-ready finish. The GaP(100) wafers have a resistivity of 0.16 Ω·cm, a mobility of 69 cm² V⁻¹ s⁻¹, and a carrier concentration of 4.5 x 10¹⁷ cm⁻³, with an etch pit density of less than 5 x 10⁴ cm⁻².

4.4.2 Synthesis

The compounds 5,10,15,20-tetra-p-tolylporphyrin (TTP) and 5,10,15,20-tetra-p-tolylporphyrin cobalt(II) (CoTTP) were synthesized by Diana Khusnutdinova and Sylvia Nanyangwe using modified versions of previously reported procedures.⁴⁵,⁴⁶
4.4.3 Wafer preparation

The use of 4-vinylpyridine as a precursor for surface functionalization of GaP has been previously reported.\textsuperscript{21,38,40,47,48} Briefly, diced semiconductor samples were etched with buffered hydrofluoric acid before exposure to an argon-sparged solution of the neat monomer 4-vinylpyridine under 254 nm UV light for 2 h. The PPy-functionalized samples were then soaked for 18 h in a CoTTP solution (1 mM) in toluene.

4.4.4 Wafer characterization

Surface characterization of the wafers was carried out using ellipsometry, grazing angle attenuated total reflection Fourier transform infrared spectroscopy (GATR-FTIR), X-ray photoelectron (XP) spectroscopy, and inductively coupled plasma mass spectrometry (ICP-MS).

4.4.5 Photoelectrochemistry

Photoelectrochemical (PEC) experiments were performed in 0.1 M phosphate buffer (pH 7) under AM 1.5 irradiation. A three-electrode configuration with GaP working electrodes (including GaP following buffered hydrofluoric acid treatment, polypyridine-modified GaP, and cobalt porphyrin-modified GaP) was used in a cell containing a quartz window. HER activity was calculated assuming unity faradaic efficiency, although this was confirmed at only one point (0 V vs RHE). Samples for post-PEC analysis were prepared using a customized three-electrode cell equipped with a quartz window and spring-loaded copper support to secure the GaP wafer, thus negating the need to encase the sample in epoxy. An indium-gallium eutectic was applied between the copper support and GaP sample. The electrodes were polarized at 0 V vs RHE for a minimum of 3 min under 1-sun
illumination. Samples were rinsed with Mill-Q water and dried under vacuum before GATR-FTIR measurements. All PEC experiments were conducted under a continuous flow of 5% hydrogen in nitrogen.

4.4.7 Gas chromatography

Gas chromatography (GC) was used to analyze aliquots of headspace gas taken from a sealed PEC cell both prior to and following 30 min of bulk electrolysis at 0 V vs RHE. The 93% faradaic efficiency reported is likely a lower limit and does not correct for loss of hydrogen from the cell or during the sampling procedure.
4.5 References


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