Energetics and efficiency analysis of a cobaloxime-modified semiconductor under simulated air mass 1.5 illumination
Energetics and efficiency analysis of a cobaloxime-modified semiconductor under simulated air mass 1.5 illumination†

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We report on the energetics and efficiency of a p-type (100) gallium phosphide (GaP) semiconductor functionalized with molecular hydrogen production catalysts via polymer grafting. The catalysts belong to the cobaloxime class of compounds that have recently shown promise in electrocatalysis and solar-to-fuel applications. Attachment of the complex to a semiconductor surface allows direct photoelectrochemical (PEC) measurements of performance. Under simulated air mass 1.5 illumination, the catalyst-modified photocathode yields a 0.92 mA cm\(^{-2}\) current density when operating at the equilibrium potential for the hydrogen production half reaction. The open circuit photovoltage (V\(_{OC}\)) is 0.72 V vs. a reversible hydrogen electrode (RHE) and the fill factor (FF) is 0.33 (a 258% increase compared to polymer-modified electrodes, without cobaloxime treatment). The external quantum efficiency (EQE), measured under a reverse bias of +0.17 vs. RHE, shows a maximum of 67% under 310 nm illumination. Product analysis of the head-space gas yields a lower limit on the Faradaic efficiency of 88%. In addition, the near linear photoresponse of the current density upon increasing illumination indicates that photocarrier transport to the interface can limit performance. These results give insights into the design of improved photocatalytic constructs with additional performance gains.

Introduction

Artificial photosynthesis is a long-sought goal in solar energy research.\(^1\)–\(^3\) By splitting water into oxygen and a source of reducing equivalents (protons and electrons) for producing a fuel, two problems are addressed: energy storage and the production of a potential carbon-neutral transport fuel.\(^4\)–\(^7\) However, effective strategies to interface light capture and conversion technologies with emerging catalysts for energy storage remain an outstanding scientific challenge.\(^8\),\(^9\) In biology, enzymes catalyze a myriad of technologically relevant chemical reactions by providing discrete three-dimensional environments (molecular catalysts) for binding substrates, releasing products, and lowering transition-state energies along a reaction coordinate.\(^10\),\(^11\) Thus, in accordance with the Sabatier principle, they can have exceptionally high activities and, perhaps more impressively, selectivity for specific chemical transformations. However, not every aspect of biology should necessarily be a target of chemical mimicry.\(^12\) For example, in photosynthesis the efficiency of the initial light capture and charge separation steps is near unity, but losses due to inherited metabolic processes and use of intermediate energy carriers reduce the overall energy conversion efficiency to less than a few percent.\(^13\),\(^14\)

Human-engineered systems could bypass such constraints by having fewer energy transduction steps with improved interfaces. This will require strategies to engineer bulk materials and surfaces with enhanced electronic quality, stability and catalytic functionality.\(^15\)–\(^19\) The development of advanced materials and techniques for manipulating matter on the nanoscale has allowed significant advances toward mimicking favorable aspects of the chemistry of biological systems into human-engineered constructs.\(^15\)–\(^43\) However, a majority of molecular fuel catalysts are currently designed and optimized for operation in solution, with the use of external chemical agents or an electrode providing the driving force.\(^20\)–\(^25\) Thus, it is often uncertain how or if a given complex will function when immobilized on a conductive electrode or semiconductor surface. Understanding the properties that promote favorable photocatalytic function is hampered by a lack of functional systems and subsystems.

We have recently reported a modular approach to interfacing visible-light absorbing semiconductors, including p-type (100) GaP and p-type (111) Si, with fuel production catalysts.\(^40\)
The grafting procedure exploits the UV-induced immobilization chemistry of alkenes to a semiconductor surface,44–50 providing a means for attaching molecular catalytic complexes to surface bound linkers. The modular aspect of this method allows independent modification of the light absorber, bridging material, anchoring functionality, or catalysts as new materials and discoveries emerge. In addition, we have also reported a photo-functional construct composed of cobalt-containing hydrogen production catalysts interfaced to a polyvinylpyridine-modified GaP surface (Co–PVP–GaP) (Fig. 1).36 The catalysts belong to the cobaloxime class of compounds that have recently shown promise in electrocatalysis, both in solution and immobilized on conductive substrates as well as solar-to-fuel applications in systems using molecular sensitizers, wide-bandgap semiconductors or biological photosystems.27–34

In the assembly reported here, catalyst attachment to a polymer-modified semiconductor (PVP–GaP) allows direct measurement of photoelectrochemical performance. Co–PVP–GaP catalyzes what is otherwise a sluggish reaction, requiring relatively large overpotentials to achieve similar rates when using electrodes without cobaloxime treatment. For example, in a previous report16 we showed that a Co–PVP–GaP electrode under 100 mW cm$^{-2}$ illumination using a Newport Oriel Apex illuminator source yields a 2.4 mA cm$^{-2}$ current density when poised at a potential 310 mV below the equilibrium potential of the H$^+$/H$_2$ redox couple. To achieve a similar photocurrent density using a PVP–GaP working electrode (without catalyst treatment), a 270 mV overpotential must be applied. The production of current at an underpotential indicates that only light, and no external electrochemical forward biasing, is required to generate the photocurrent and associated hydrogen. In addition, the Co-functionalized material shows an increased stability compared to bare GaP (a > 175% increase), evidenced by the percent decrease in photocurrent over time in Co–PVP–GaP versus GaP (without cobaloxime–polymer modification). Herein, we report a more detailed energetics and efficiency analysis of these constructs including photovoltaic parameters, quantum efficiency and Faradaic efficiency obtained using modified- and unmodified-GaP substrates under selected illumination conditions and applied bias potentials.

Results and discussion

Component optical and electronic properties

GaP is a midsize optical band gap (indirect $E_g = 2.26$ eV) semiconductor with a conduction band (CB) edge poised $\sim 1$ V negative of the hydrogen production half reaction. Thus, in addition to commercial importance in light emitting diode technologies, GaP is a promising candidate material for applications in solar-fuel generator technologies.51–57 Although, the band gap of this material limits the fraction of total solar photons available for absorption, the energetic positioning of GaP’s CB is an attractive feature for investigation of interfaces to fuel production catalysts that may require significant overpotentials.

The transmission spectra of the GaP wafer used in this study as well as the air mass 1.5 global tilt (AM 1.5G) solar spectrum$^{58}$ are shown in Fig. 2. The conduction band and valence band positions of GaP as well as the theoretical maximum photocurrent density set by its optical properties are shown in Fig. 3. Information on other p-type semiconductors (InP and Si) is included for comparison. Integration of the AM 1.5G solar spectrum up to the GaP absorption threshold yields a photon flux of $6.0 \times 10^{16}$ photons s$^{-1}$ m$^{-2}$. If all available photons give rise to current, the maximum theoretical photocurrent density is 9.6 mA cm$^{-2}$. However, actual photocurrent densities are always lower given reflection and transmission losses (Fig. 4) as well as other “parasitic” processes$^{59}$ that preclude absorbed photons from being converted to charge carriers moving through a potential. In addition, catalysts immobilized on a surface can also absorb a fraction of the incident photons.$^{60}$ An absorption spectrum of a model cobaloxime catalyst, Co(dmgH)$_2$PyCl, recorded as an acetonitrile solution is shown in Fig. S1 (ESI†). The complex shows characteristic absorption features of the Co$^{III}$ complex,28 including high-energy absorption bands with $\lambda_{max}$ at 223 nm and 253 nm corresponding to spin-allowed intraligand ($\pi-\pi$) transitions.

The p-type character of the modified-semiconductor electrodes used in these experiments precludes analysis of the constructs as dark electrocatalysts. A cyclic voltammogram of the model

![Fig. 1](https://example.com/fig1.png)  
**Schematic depiction of a cobaloxime-modified GaP semiconductor.** Illumination of the hybrid construct with visible light generates a photovoltage that drives hydrogen production at the cobaloxime-modified surface.

![Fig. 2](https://example.com/fig2.png)  
**The air mass 1.5 global tilt solar flux spectrum (solid) and the transmission spectrum of the GaP substrates used in these experiments (dashed).** The shaded grey area shows the integrated region of the solar spectrum from 280 nm up to the band gap of GaP ($E_g = 2.26$ eV = 549 nm), representing the theoretical maximum number of photons ($6.0 \times 10^{16}$ photons s$^{-1}$ cm$^{-2}$) that can be collected.
compound Co(dmgH)2PyCl (Fig. S2, ESI†) recorded in a 0.1 M TBAPF$_6$ acetonitrile solution at a glassy carbon working electrode shows a chemically irreversible redox process with $E_p = -0.98$ V vs. Fe/Fe$^+$ ($-0.34$ V vs. NHE)$^{31}$ assigned to the Co$^{III}$/Co$^{II}$ redox couple, and a chemically reversible redox process with $E_{1/2} = -1.46$ V vs. Fe/Fe$^+$ ($-0.82$ V vs. NHE) assigned to the Co$^{III}$/Co$^{II}$ relay. These measurements are consistent with previous reports on this complex$^{28}$ and give an approximation of the photovoltage required to access these couples during catalytic operation. However, values obtained using a homogenous complex in organic solvents may be significantly different from those of analogous surface immobilized species (i.e. heterogenized-homogenous catalysts) in aqueous environments. Nonetheless, in the experiments reported here the relatively negative potential of the GaP conduction band should ensure thermodynamically favorable conditions for photoactivating attached cobaloxime complexes.

**Construct photoelectrochemical properties**

Three-electrode current density–voltage ($J$–$V$) responses and associated power curves of a cobaloxime-modified electrode under simulated AM 1.5 solar illumination are shown in Fig. 5. The GaP substrates used in these experiments are Zn doped with a resistivity of $5.5 \times 10^{-2}$ Ω cm, a mobility of 54 cm$^2$ V$^{-1}$ s$^{-1}$ and a carrier concentration of $2.2 \times 10^{18}$ cm$^{-3}$. Co–PVP–GaP working electrodes show significant improvement in photo-performance compared to electrodes without catalyst modification. Under simulated AM 1.5 illumination, Co–PVP–GaP yields a 0.92 mA cm$^{-2}$ current density when operating at the equilibrium potential for the hydrogen production half reaction. For comparison, electrodes without cobalt treatment show a 0.42 mA cm$^{-2}$ and 0.19 mA cm$^{-2}$ current density for GaP and PVP–GaP respectively. In these experiments, under simulated AM 1.5 illumination, the open circuit potential ($V_{OC}$) for the GaP, PVP–GaP, and Co–PVP–GaP electrodes is 0.69 V, 0.68 V, and 0.72 V vs. RHE respectively. Comparison of the $V_{OC}$ values obtained for PVP–GaP and Co–PVP–GaP photoelectrodes reveals a positive shift that is indicative of increased catalytic activity following incorporation of the Co catalyst. The fill factor (FF), defined as the maximum power output divided by the product of the $V_{OC}$ and the short-circuit current density ($J_{SC}$) with respect to the desired half reaction, improves dramatically for the Co catalyst functionalized electrodes. The fill factor of the Co–PVP–GaP electrode is 0.33 (a 119% and 258% increase as compared to GaP and PVP–GaP respectively). Due to the steep increase in operating photocurrent densities that are produced by small changes in the FF of a photocathode and/or photoanode, even small changes in FF can have a significant effect on the solar-to-hydrogen efficiencies of a complete two-electrode assembly.

The $J$–$V$ response of PVP–GaP and Co–PVP–GaP upon increasing illumination intensity is shown in Fig. 6. For the Co–PVP–GaP electrode, increasing illumination intensity results in relatively little change in the $V_{OC}$ or FF. However, the $J_{SC}$ increases approximately linearly with illumination intensity (Fig. 7), indicating that photocarrier transport to the interface can limit the performance of the Co-modified GaP photocathodes. A similar trend is observed for PVP–GaP, albeit at overall lower photocurrent densities (Fig. S3, ESI†). As reported in a previous publication,$^{16}$ even higher current densities
can be obtained for Co–PVP–GaP, reaching 2.4 mA cm\(^{-2}\) at a 310 mV underpotential, when using a Xenon lamp illumination source without an AM 1.5 filter and after optimizing the doping of the GaP wafers (Fig. S4 and S5, ESI†).

Photocurrents were also measured under monochromatic light at selected potentials. External quantum efficiencies were calculated using the measured values of the photocurrents and the intensity of the illumination source. The spectral response of the external quantum efficiency (EQE) of PVP–GaP and Co–PVP–GaP electrodes poised at +0.17 V vs. RHE are shown in Fig. 8. A measurable photocurrent is observed at wavelengths lower than \(\sim 550\) nm, consistent with the GaP indirect band gap. Likewise, the sharp rise in photocurrent at wavelengths lower than \(\sim 450\) nm is characteristic of the GaP direct band gap (2.8 eV). Using the QE data, the calculated electron flux (i.e. current) produced by PVP–GaP and Co–PVP–GaP samples poised at +0.17 V vs. RHE under AM 1.5G illumination is shown in Fig. 9. Integration of the spectra yields current densities of \(8.9 \times 10^{15}\) electrons s\(^{-1}\) cm\(^{-2}\) = 0.14 mA cm\(^{-2}\) and \(6.4 \times 10^{15}\) electrons s\(^{-1}\) cm\(^{-2}\) = 1.0 mA cm\(^{-2}\) for PVP–GaP and Co–PVP–GaP, respectively, indicating that the solar simulator used in the \(J–V\) measurements closely approximates AM 1.5G conditions. Comparison of the AM 1.5G solar flux, integrated over 280–4000 nm (\(4.3 \times 10^{17}\) photons s\(^{-1}\) cm\(^{-2}\)), with the Co–PVP–GaP electron flux (shown in Fig. 9) yields an overall EQE of 1.5%. Considering only photons in the GaP actinic range, from 280 to 549 nm (Fig. 1), the EQE is 11%.

Confirmation of hydrogen production and a measure of the Faradaic efficiency was performed via analysis of the head-space gas using a gas chromatograph equipped with a thermal conductivity detector (see Methods section). Following 30 minutes of simulated AM 1.5 illumination of a Co–PVP–GaP electrode poised at +0.17 V vs. RHE, a lower limit on the Faradaic efficiency of 88% was determined.

Experimental

Materials and methods

Single crystalline (100) GaP wafers were purchased from ITME, Warsaw, Poland. The wafers were Zn doped p-type with a resistivity of \(5.5 \times 10^{-2}\) Ω cm, a mobility of \(54\) cm\(^2\) V\(^{-1}\) s\(^{-1}\) and a carrier concentration of \(2.2 \times 10^{18}\) cm\(^{-3}\). The etch pit density (EPD) was \(3.7 \times 10^4\) cm\(^{-2}\). The wafers used for the
Faradaic efficiency measurement were also from ITME with a resistivity of $2.93 \times 10^{-4} \, \Omega \, \text{cm}$, a mobility of $70 \, \text{cm}^2 \, \text{V}^{-1} \, \text{s}^{-1}$, a carrier concentration of $3.05 \times 10^{17} \, \text{cm}^{-3}$ and an etch pit density (EPD) of $5.7 \times 10^4 \, \text{cm}^{-2}$. The material was single side polished to an epi-ready finish. Diced semiconductor samples were degreased by wiping the surface with an acetone soaked cotton swab and sonication in acetone and isopropanol, followed by drying under flowing nitrogen. Samples were then exposed to an air-generated oxygen plasma (Harrick Plasma, USA) at 30 W for 2 min. Surface oxide layers were then removed in a glove box by immersion of the plasma-treated samples in buffered hydrofluoric acid (6:1 HF:NH$_4$F in H$_2$O) for 5 min, followed by rinsing with anhydrous methanol and drying under vacuum. All syntheses were carried out under an argon atmosphere using Schlenk techniques or in a nitrogen glove box. All reagents were purchased from Aldrich. All solvents were stored over the appropriate molecular sieves prior to use. Milli-Q water was used to prepare all aqueous solutions. The cobaltaxole catalyst precursor, Co(dmgH)$_2$(dmgH)Cl$_2$, and the cobaloxime catalyst, Co(dmgH)$_2$PyCl, were prepared according to a previously reported procedure.

Preparation of polyvinylpyridine-grafted GaP. Freshly cleaned and etched [see Materials section] (100) GaP wafers were placed in a quartz flask and covered with inhibitor-free 4-vinylpyridine. The flask was illuminated with UV light (254 nm, SPECTROLINE(R) E-SERIES UV LAMP) for 2 h with the polished surface of GaP facing the light source. The modified wafers were then washed with copious amounts anhydrous methanol before drying under vacuum.

Preparation of cobaloxime-modified GaP. PVP-grafted wafers of (100) GaP were dipped in a solution of Co(dmgH)$_2$(dmgH)Cl$_2$ (1 mM in methanol) in the presence of triethyamine (1 mM in methanol) overnight. The modified wafers were rinsed with anhydrous methanol and isopropanol (99%) before drying under nitrogen.

Preparation of working electrodes. Wafers were sonicated in isopropanol (99%). 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 epoxy was allowed to dry overnight before testing the electrodes.

Instrumentation and experimental details

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

NMR. Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker 500/54 Ascend spectrometer operating at 500 MHz. Unless otherwise stated, all spectra were collected at room temperature.

Electrochemistry. Cyclic voltammetry was performed with a Biologic potentiostat using a glassy carbon (3 mm diameter) disc, 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 0.10 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 pseudo-reference electrode was determined using the ferrocenium/ferroce redox couple as an internal standard. The voltammograms were recorded at sweep rates of 100 mV s$^{-1}$. Linear sweep voltammetry and three-electrode electrolysis (chronoamperometry) were performed with a Biologic potentiostat using a platinum counter electrode, a Ag/AgCl, NaCl (3 M) reference electrode (0.21 V vs. NHE), and GaP working electrodes (including GaP following buffered HF treatment, PVP–GaP and Co–PVP–GaP) in a modified cell containing a quartz window. The supporting electrolyte was 0.1 M phosphate buffer (pH = 7). Measurements were performed under a continuous flow of 5% hydrogen in nitrogen. Photoelectrochemical (PEC) testing was performed using a Solar Light PV Cell Test Simulator model 16S-300-005V4.0 Xenon lamp with an AM 1.5 filter and an XPS-300 power supply under 100 mW cm$^{-2}$ illumination. All data were recorded following initial light dark testing.

Quantum efficiency measurements. Incident photon to current efficiency (IPCE) was measured under a bias of +0.17 V vs. RHE in the wavelength range relevant to GaP’s band gap. The experimental setup consisted of an NIST calibrated silicon photodiode FDS100 to calibrate the light intensity, an Oriel Xenon 150W lamp with a Newport 69907 power supply, an Oriel Cornerstone 130 1/8 m monochromator, a 200/1 mm grating (slit width was 2 mm for a resolution of 0.5 nm), a Gamry Instruments Reference 600 potentiostat/galvanostat ZRA and a Keithley 2400 SourceMeter.

Faradaic efficiency measurements. Hydrogen was detected via gas chromatography (GC) using a micro GC (Agilent 490). A Co–PVP–GaP electrode was placed in a glass electrochemical cell with a quartz window and purged with argon for 30 min before sealing the vessel. Argon (15 mL) was withdrawn from the cell with a syringe and replaced with an equivalent volume of methane (99%) analytical internal standard (Aldrich). The potential was then set to +0.17 V vs. RHE and held at that value for 30 min to accumulate the product. An aliquot of the headspace gas was withdrawn with a syringe and injected into the GC.

Conclusions

Under simulated AM 1.5 illumination, Co–PVP–GaP yields a 0.9 mA photocurrent density when poised at a potential 170 mV below the equilibrium potential of the H$^+$/H$_2$ redox couple. These results indicate that only light, and no external electrochemical forward biasing, is required to generate the photocurrent. For PVP–GaP, the lack of active catalytic sites results in a greater probability of minority carrier recombination at the interface. Therefore, a more negative applied potential, which increases the surface band bending and suppresses charge carrier recombination, is required to achieve a given photocurrent density.
The EQE of Co–PVP–GaP, measured at +0.17 vs. RHE, shows a maximum of 67% under 310 nm illumination. However, the band gap of GaP (2.26 eV) significantly limits the total number of solar photons that can be collected and the overall EQE (1.5%). The J–V response upon increasing illumination indicates that photocarrier transport to the interface can limit the performance of Co–PVP–GaP under simulated AM 1.5 illumination, indicating that additional performance gains may be obtained by using semiconductors with improved spectral coverage of the solar spectrum. Of course use of such light absorbers may require incorporation of catalysts capable of operating with relatively lower potential requirements.

The work reported here illustrates the potential to directly couple human-engineered catalysts for fuel production with light capture and conversion materials. The modular aspect of our assembly method should allow researchers to use and adapt this chemistry as new materials and discoveries emerge. This approach could allow catalysts made from earth-abundant elements, tethered over photocathodes, to replace the use of precious metal catalysts currently implemented in many solar-spectrum. Of course use of such light absorbers may require incorporation of catalysts capable of reducing net carbon dioxide emissions.

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Notes and references

58 At the time of writing, the air-mass 1.5 global tilt (AM 1.5G) solar spectrum, from the ASTM G173-03 data set, is available online at http://rredc.nrel.gov/solar/spectra/am1.5/.
61 All redox potentials were measured relative to ferrocenium/ferrocene (Fc+/Fc). To facilitate comparison with previous reports on the electrochemistry of Co(dmgH)2PyCl, the Fc+/Fc couple is taken as (0.40 V vs. SCE) then adjusted to NHE (SCE vs. NHE = 0.24 V). We advise caution in directly comparing literature values reported in V vs. NHE as conversion factors from the actual reference electrode used in the experiment and experimental conditions are not always consistent.
63 dmgH = dimethylglyoximate monoanion; dmgH2 = dimethylglyoxime; py = pyridine.