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Hybrid photocathodes for solar fuel production: coupling molecular fuel-production catalysts with solid-state light harvesting and conversion technologies

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Artificial photosynthesis is described as the great scientific and moral challenge of our time. We imagine a future where a significant portion of our energy is supplied by such technologies. However, many scientific, engineering and policy challenges must be addressed for this realization. Scientific challenges include the development of effective strategies to couple light absorption, electron transfer and catalysis for efficient conversion of light energy to chemical energy as well as the construction and study of structurally diverse assemblies to carry out these processes. In this article, we review recent efforts from our own research to develop a modular approach to interfacing molecular fuel-production catalysts to visible-light-absorbing semiconductors and discuss the role of the interfacing material as a protection layer for the catalysts as well as the underpinning semiconductor. In concluding, we briefly discuss the potential benefits of a globally coordinated project on artificial photosynthesis that interfaces teams of scientists, engineers and policymakers. Further, we offer cautions that such a large interconnected organization should consider. This article is inspired by, and draws largely from, an invited presentation given by the corresponding author at the Royal Society at Chicheley Hall, home of the Kavli Royal Society International Centre, Buckinghamshire on the themed meeting topic: 'Do we need a global project on artificial photosynthesis?'

1. Introduction

The concepts of artificial photosynthesis as well as improvement of photochemical fuel generation by surface modification of semiconductor surfaces are not new [1–4]. However, there are relatively few examples of photofunctional systems composed of molecular catalysts attached to visible-light-absorbing semiconductors. A promising feature of molecular catalysts is their ability to provide discrete local three-dimensional environments as well as secondary coordination spheres, for binding substrate, lowering transition-state energies along a reaction coordinate and releasing products. Thus, in accordance with the Sabatier principle, they can have exceptionally high activities and, perhaps more importantly, selectivity for catalysing a desired chemical transformation [5,6]. These are highly desirable features in the context of catalysing complex multi-electron and multi-proton reactions such as those associated with solar fuels production. However, the majority of molecular fuel-production catalysts are initially designed and optimized for operation in solution, with the use of external chemical agents or an electrode providing the driving force [7–10] and it is often uncertain how or if a selected complex may function when immobilized at a surface. Despite these challenges, there has been considerable progress towards the construction and study of systems and subsystems that use molecular components attached to mesoporous and nanoparticulate materials [11–21], biological components [22,23–33] and conductive substrates [34–37].

We have reported a modular approach to interfacing molecular fuel-production catalysts to visible-light-absorbing semiconductors, including p-type (100) GaP ($E_g = 2.26$ eV) and p-type (111) Si ($E_g = 1.12$ eV) [38–40]. Both materials have conduction bands poised negative of the H^+/H_2 redox couple [41] and are thus relevant as cathodic light-absorbing components in artificial photosynthesis [42–47]. The grafting procedure exploits the UV-induced immobilization chemistry of alkenes to a semiconductor surface [48–55] and provides a means for attaching catalytic complexes to surface-bound linking units. The modularity of this method allows independent modification of the light absorber, bridging material, anchoring functionality or catalysts. We have demonstrated the feasibility of this attachment chemistry using an appropriately functionalized nickel bisdiphosphine catalyst [56–58] for attachment to amine-modified Si and GaP substrates, as well as a cobaloxime species [59–61] for attachment to a polyvinylpyridine-modified GaP electrode (figure 1). The cobalt-based construct is photochemically active, whereas the Ni-based assembly showed significantly diminished photoperformance following chemical modification. Although a detailed understanding of all factors contributing to the diminished performance is unavailable, initial results indicate this is in large part due to structural rearrangement of the Ni complexes following surface attachment as well as degradation of the photophysical properties of the semiconductor following chemical processing. For the Co-based assembly, the use of a polymeric interface provides a protective environment that stabilizes the catalytic units as well as the underpinning semiconductor.

2. Structural and functional characterization

For both the Ni- and Co-based assemblies, grazing angle attenuated total reflection Fourier transform infrared spectroscopy (GATR-FTIR) and X-ray photoelectron spectroscopy (XPS) were used to characterize successful chemical modification of the surfaces following each stage of wet-chemical processing. Figures 2 and 3 show representative GATR-FTIR and XPS spectra of hybrid-photocathode materials composed of nickel bisdiphosphine-modified p-type (111) Si wafer (1) as well as a cobaloxime-modified p-type (100) GaP wafer (2), respectively. In both examples, GATR-FTIR enables investigation of the vibrational modes of the ligand following surface immobilization and XPS confirms the presence of intact metal complexes. For a more detailed discussion of the spectra and associated assignments, see [52,53]. We note that the shakeup satellite features observed in the Ni 2p core level XPS spectrum of **1** are indicative of structural distortion, as compared with the unbound diamagnetic Ni^{II} complex, to a more paramagnetic configuration. These changes in structure, coupled with an observed sharp decrease in the minority carrier lifetime of photocathodes following chemical modification, contribute to the lack of photocatalytic activity for this assembly.

For the Co-based construct, attachment of catalysts to the polyvinylpyridine-modified semiconductor allows the modified electrode to photocatalyse what is otherwise a sluggish reaction, requiring relatively large overpotentials. For example, we have shown that a cobaloxime-modified electrode illuminated under simulated solar conditions (100 mW cm^{-2}) yields a 2.4 mA cm^{-2} current density when operated at a potential 310 mV below the equilibrium potential of the H^+/H_2 half reaction (figure 4). To obtain a similar

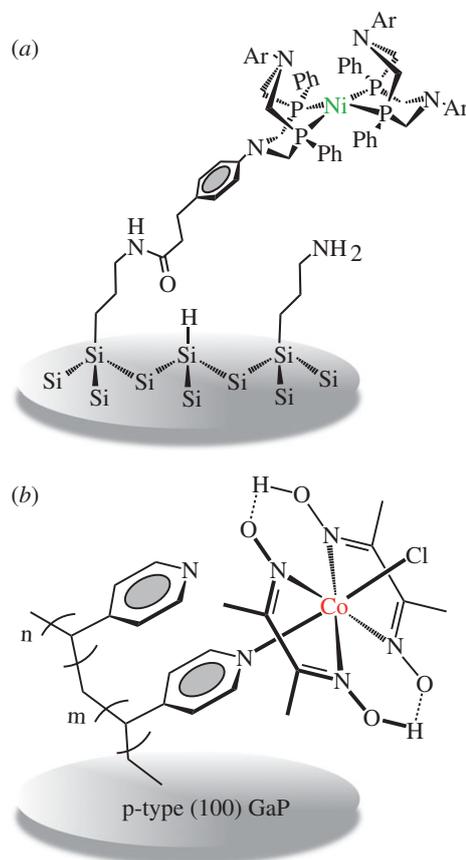


Figure 1. Schematic of (a) **1** a nickel bisdiphosphine-functionalized p-type (111) Si electrode as well as (b) **2** a cobaloxime-polymer-modified p-type (100) GaP electrode. (Online version in colour.)

photocurrent density using a polyvinylpyridine-modified electrode without catalyst treatment, a 270 mV overpotential must be applied. The generation of current at an applied underpotential indicates that only light, and no external electrochemical forward biasing or sacrificial reagents, is required to generate the photocurrent and associated hydrogen.

The Co-functionalized cathode also shows an increased stability as compared with GaP electrodes without polymer functionalization (greater than 175% increase as evidenced by the per cent decrease in photocurrent over time of the respective electrodes). We postulate that attachment of the polymer alleviates the unstable photocurrent associated with the bare GaP surface by providing a protective layer that inhibits access to otherwise reactive surface sites. Further functionalizing the electrode with cobaloxime catalysts provides additional improvement of photoperformance by lowering the required potential for achieving a selected current density. For the polymer-grafted surface, without catalysts, the lack of catalytic sites results in a greater probability for minority carrier recombination at the interface. For the catalyst-modified samples, the incorporation of active Co complexes promotes charge transfer across the interface.

Although the catalysts-polymer-modified electrodes exhibit extended stability relative to unfunctionalized GaP, the photocurrent does decline over time (figure 5). Analysis of the surface composition of the electrodes following photoelectrochemical operation indicates a loss of surface attached Co catalysts is a major contributing factor to the reduction of photoperformance during operation. Previous computational and experimental work shows the axial pyridine units of similar

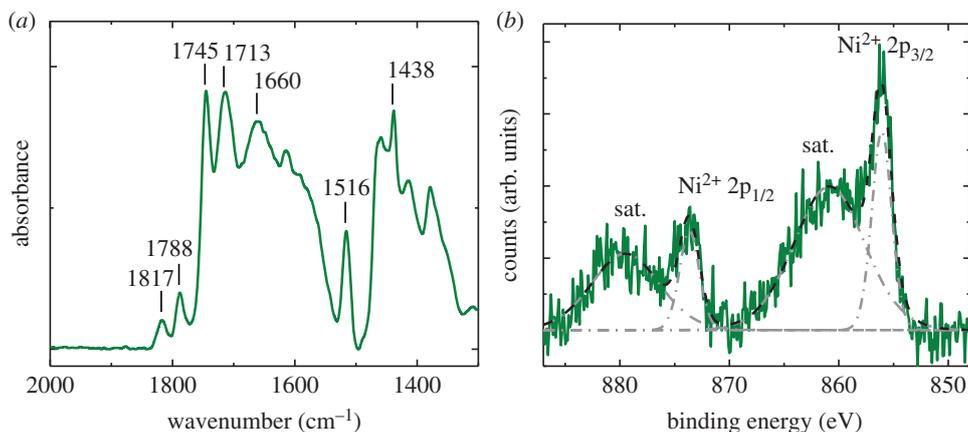


Figure 2. (a) GATR-FTIR spectrum of construct **1** as well as (b) Ni 2p core level spectrum of construct **1** (green, solid), including the component (grey, dash dot) and overall (black, dash) fits. (Online version in colour.)

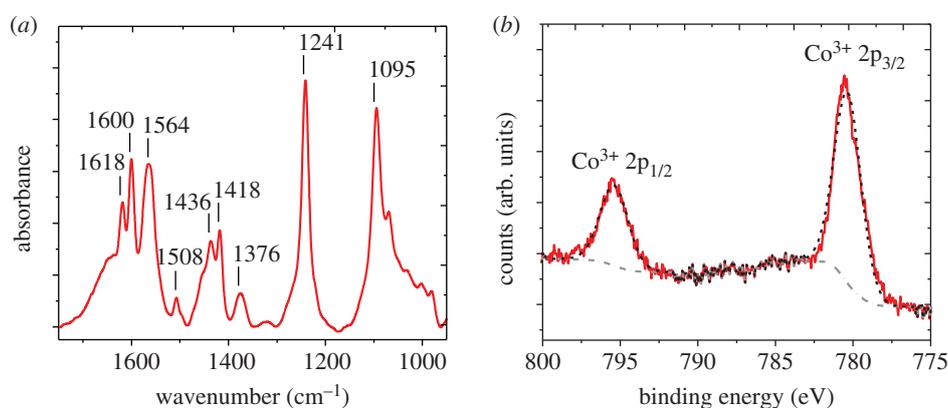


Figure 3. (a) GATR-FTIR as well as (b) Co 2p core level spectra of construct **2** (red, solid), including the component (grey, dash dot) and overall (black, dash) fits. (Online version in colour.)

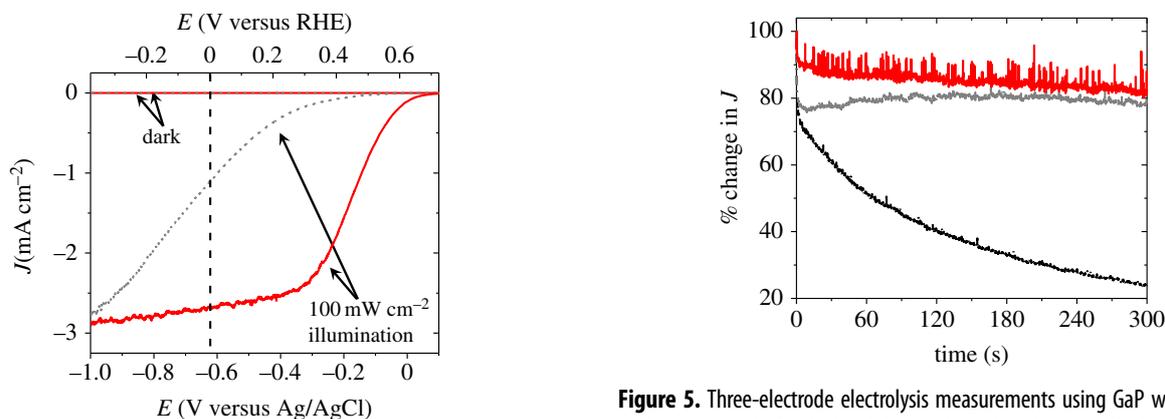


Figure 4. Linear sweep voltammograms of working electrodes composed of **2** (red, solid) as well as a polyvinylpyridine-modified GaP substrate without catalyst modification (grey, dash), and an unmodified GaP electrode following buffered HF treatment (black, dash dot). All data were recorded at pH 7 in the dark or with 100 mW cm^{-2} illumination. (Online version in colour.)

complexes can become labile during redox cycling [62–64]. However, in our assembly, the polymeric support used to assemble the catalyst may provide additional stability by encapsulating cobalt complexes at redox-active sites within the polymer that are abundant in free-pyridine units, favouring reformation of the complex over loss to bulk solution. An improved understanding of the resulting stability and strategies to further increase the robustness of such constructs is underway.

Figure 5. Three-electrode electrolysis measurements using GaP working electrodes composed of **2** (red, solid), a polyvinylpyridine-modified GaP substrate without catalyst modification (grey, dash), and an unmodified GaP electrode following buffered HF treatment (black, dash dot). All measurements were performed at $+0.17 \text{ V}$ versus RHE using continuous simulated solar illumination. (Online version in colour.)

3. Energetics and efficiency analysis

We have also reported an energetics and efficiency analysis of the cobaloxime-modified photocathode [38]. These results give a lower limit on the Faradaic efficiency of 88% (figure 6) and confirm that the light-absorber component of the hybrid photocathode is a major bottleneck to obtaining higher current densities. The external quantum efficiency of cobaloxime-

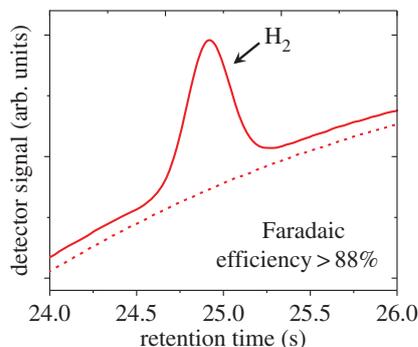


Figure 6. Gas chromatograms of 10 μl aliquots of head-space gas collected from a sealed photoelectrochemical cell both prior to (dash) and following (solid) 30 min of three-electrode photoelectrolysis using a cobaloxime-modified working electrode poised at +0.17 V versus RHE. These results give a lower limit on the Faradaic efficiency of 88%. (Online version in colour.)

modified cathodes, measured at +0.17 versus RHE, displays 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 (1.5% as measured over the entire wavelength range of the solar spectrum from 200 to 4000 nm). Additional performance gains may be obtained using semiconductors with improved spectral coverage of the solar spectrum. Of course, the use of such light absorbers will likely require incorporation of catalysts capable of operating with relatively lower potential requirements for the transfer of electrons as well as protons [61].

4. Conclusion and closing remarks

The work reviewed here illustrates the potential to directly couple molecular catalysts for hydrogen production with solid-state light harvesting and conversion materials. Despite these promising results, discovering new semiconducting and catalytic materials as well as improved methods to immobilize catalysts on semiconductor surfaces remains an

area where much work is needed. Achieving these goals will require development of new chemistries and interfaces between the relevant components at the construct and device level as well as effective interfaces between researchers, team managers and leaders at the organizational level [65–77].

A global project on artificial photosynthesis may provide the governance structure, guidance and organizational retooling required of the discovery needed to address this grand challenge. However, caution should be taken not to undermine the important contributions of small groups and independent researchers working on unconventional, yet potentially transformative science. Such a global organization should also take inspiration from nature, as does the science and technology—*artificial photosynthesis*—it seeks to achieve. In biology, healthy large-scale systems are not monocultures, but rather are diverse systems. In seeking to develop a future technology in which the ‘winning’ strategy is unknown, it may be wise to select a diverse approach and not prematurely or arbitrarily choose a winning method or set of operating conditions.

As the research efforts of artificial photosynthesis have evolved from the study of isolated components to the construction of subsystems and devices, there has been an increasing focus on stability. In this review, we illustrate one potential approach to improving the stability of hybrid constructs that combine diverse materials, i.e. hard solid-state semiconductors and soft organic interfaces. However, it is worth asking what the warranty is on a biological leaf. In the lower limit, the D1 complex which houses the manganese-based water oxidation catalyst lasts for approximately 30 min before it must be repaired. The ability of biological systems to repair, reproduce and evolve extends this warranty to approximately 3 billion years and counting. From this perspective, we still have much to learn from biology.

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