# Fuel from Water: The Photochemical Generation of Hydrogen from Water

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CONSPECTUS: Hydrogen has been labeled the fuel of the future since it contains no carbon, has the highest specific enthalpy of combustion of any chemical fuel, yields only water upon complete oxidation, and is not limited by Carnot considerations in the amount of work obtained when used in a fuel cell. To be used on the scale needed for sustainable growth on a global scale, hydrogen must be produced by the light-driven splitting of water into its elements, as opposed to reforming of methane, as is currently done. The photochemical generation of H_2, which is the reductive side of the water splitting reaction, is the focus of this Account, particularly with regard to work done in the senior author's laboratory over the last 5 years. Despite seminal work done more than 30 years ago and the extensive research conducted since then on all aspects of the process, no viable system has been developed for the efficient and robust photogeneration of H_2 from water using only earth abundant elements. For the photogeneration of H_2 from water, a system must contain a light absorber, a catalyst, and a source of electrons. In this Account, the discovery and study of new Co and Ni catalysts are described that suggest H_2 forms via a heterocoupling mechanism from a metal-hydride and a ligand-bound proton. Several complexes with redox active dithiolene ligands are newly recognized to be effective in promoting the reaction.
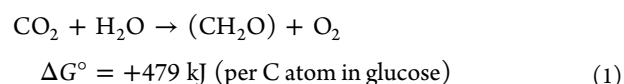
A major new development in the work described is the use of water-soluble CdSe quantum dots (QDs) as light absorbers for H_2 generation in water. Both activity and robustness of the most successful systems are impressive with turnover numbers (TONs) approaching 10^6, activity maintained over 15 days, and a quantum yield for H_2 of 36% with 520 nm light. The water solubilizing capping agent for the first system examined was dihydrolipoic acid (DHLA) anion, and the catalyst was determined to be a DHLA complex of Ni(II) formed in situ. Dissociation of DHLA from the QD surface proved problematic in assessing other catalysts and stimulated the synthesis of tridentate trithiolate (S_3) capping agents that are inert to dissociation. In this way, CdSe QD's having these S_3 capping agents were used in systems for the photogeneration of H_2 that allowed meaningful comparison of the relative activity of different catalysts for the light-driven production of H_2 from water. This new chemistry also points the way to the development of new photocathodes based on S_3-capped QDs for removal of the chemical sacrificial electron donor and its replacement electrochemically in photoelectrosynthetic cells.
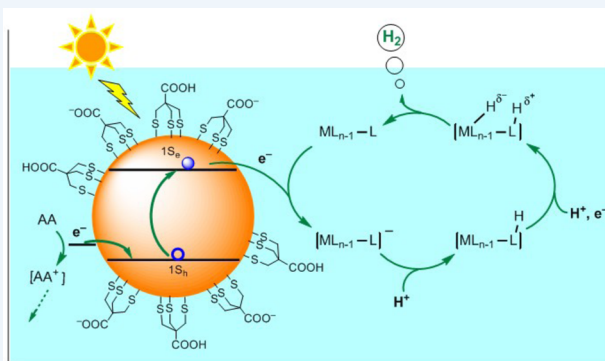
■ INTRODUCTION

The term "photosynthesis", which is defined as the use of light to drive a thermodynamically unfavorable reaction, is the basis for the conversion of solar energy into stored chemical potential energy. It is the holy grail for the production of abundant, environmentally benign energy on the scale needed for global economic development as the planet's population grows and the overall standard of living, which depends on energy use per capita, increases. Equation 1 corresponds to the well-known energy-storing reaction for natural photosynthesis involving CO_2 reduction to carbohydrates, while eq 2, which is water splitting, represents the key reaction for artificial photosynthesis (AP). Equation 2 is not the only possible AP energy-storing reaction, but it is the only one capable of fulfilling the goal of sustainable, carbon-free energy on a global scale. Both of these equations store similar amounts of energy per O_2 produced. For the development of a viable AP system based on eq 2, it is important to remember that water splitting

is indeed a redox reaction and that each half-cell reaction can be analyzed and studied separately. Eventually, the two half-cell reaction systems must be connected to allow electrons and protons to flow between them.

$$CO_2 + H_2O \rightarrow (CH_2O) + O_2$$
$$\Delta G° = +479 \text{ kJ (per C atom in glucose)} \quad (1)$$

$$2H_2O \rightarrow 2H_2 + O_2 \qquad \Delta G° = +474 \text{ kJ} \quad (2)$$

The reductive side of water splitting involves the generation of H_2 as the fuel from aqueous protons. Much has been written about H_2 as the fuel of the future with various and sundry attendant problems.[1−7] As a chemical fuel, H_2 has the highest specific energy of combustion (joules per gram), but because

H_2 is a noncondensable gas except at extremely low temperatures, the volume energy density (joules per liter) is less impressive. Even so, with H_2 at 70 MPa (*ca.* 10 000 psi), the *volume* energy density still exceeds all batteries, although it ranks behind hydrocarbon fuels. Despite this problem, efforts are in progress on a large pilot scale to make H_2 commercially available at 70 MPa for automotive transportation based on fuel cells.[5,8] In these efforts, H_2 is produced from natural gas, which generates about 50% less CO_2 per unit mass relative to coal, but to make this approach viable for the long-term on a global scale, the source of H_2 must be light-driven water splitting. In order to do this, one needs a light absorber or photosensitizer (PS), aqueous protons, a chemical or electrochemical source of electrons, and a catalyst at which to collect and assemble $2H^+ + 2e^-$ into H_2.

In laboratory studies of the reductive half of water splitting conducted over the last 35 years, the light absorber of choice has been a metal complex possessing a charge transfer excited state that reacts by electron transfer to a catalyst or an electron mediator.[6,9,10] Such complexes include the many variants of Ru(II) tris(bipyridine)[11,12] and bis(terpyridine) complexes,[13] Ir(III) phenylpyridine (ppy) derivatives,[14] and Pt(II) bipyridine or terpyridine acetylide complexes.[15,16] In nearly all cases, the excited state corresponds to transfer of an electron from the highest occupied molecular orbital (HOMO) in the ground state, which is metal-based, to the lowest-unoccupied molecular orbital (LUMO), which is mainly on the unsaturated heterocyclic ligand. A relatively long excited state lifetime is achieved in these complexes by efficient intersystem crossing (ISC) to the triplet manifold of excited states. Despite the wealth of studies on systems using these complexes as photosensitizers,[10,17] there exist significant problems with such chromophores such as high energy required for CT absorption, low molar absorptivities, instability during prolonged irradiation, and the use of noble metals.

In the seminal studies referred to above, the catalyst for H_2 generation consisted of metal colloids, most frequently of Pt but also of Pd, because of their low overpotentials for proton reduction.[18,19] Only in the past decade have efforts expanded greatly to use discrete metal complexes of other, more abundant elements as catalysts for H_2 evolution in photochemical systems.[17,20,21] Because of parallel interest in *electrochemical* reduction of protons,[22,23] the initial candidate complexes were generally good electrocatalysts in organic media. In this regard, the most extensively examined class of complexes was that containing cobalt with bidentate glyoximate ligands and variants thereof having polydentate ligands and in some cases, pseudomacrocyclic structures.[21,24–26] A second major class of compounds that have enjoyed particular scrutiny as possible H_2 evolution catalysts in the past decade are models of the active sites of various [Fe,Fe] and [Fe,Ni] hydrogenase enzymes. The research on these compounds as potential electrocatalysts for H_2 production has been reviewed,[27–29] and in a few cases, their activity for the light-driven generation of H_2 has been assessed.[10,17]

In this Account, studies mainly from the Eisenberg laboratory are described that concentrate on the use of other light absorbers than charge transfer metal complexes, specifically organic dyes and CdSe quantum dots (QDs), and selected complexes of Co and Ni as catalysts for the light-driven generation of H_2 from aqueous protons. These studies address some of the deficiencies found in the durability and activity of system components referenced above, their compatibilities and,

for the reductive side of water splitting, the need to carry out proton reduction in *aqueous* media.

SYSTEMS USING ORGANIC DYES AS PHOTOSENSITIZERS

Within a decade after the seminal studies on light-driven production of H_2 using Ru tris diimine photosensitizers, systems were reported that employed more strongly absorbing organic dyes in that role. In these reports, it appeared that a heavy atom substituent on the dye was necessary because only systems containing the halogenated dyes such as eosin Y (EY) gave notable yields of H_2 whereas a system with the unsubstituted parent dye, fluorescein (Fl), yielded only small amounts of H_2 upon irradiation.[30–32] The need for the heavy atom was attributed to the necessity of intersystem crossing (ISC) to the long-lived $^3\pi\pi^*$ excited state for electron transfer to the Pt catalyst. However, these systems decomposed within 3–5 h with cessation of H_2 evolution.
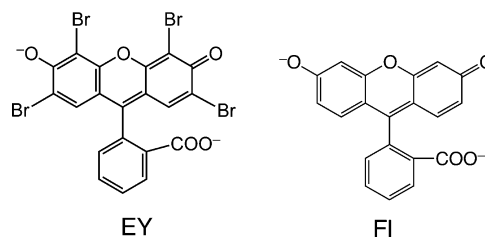
Following the initial studies of the light-driven production of H_2 using $CoCl(pyr)(dmgH)_2$ where pyr = pyridine and dmgH = dimethylglyoximate anion as the catalyst,[33] a system that contained EY as the photosensitizer together with this catalyst was assembled and studied.[34] The system was notable in that it contained no platinum group elements in its components while exhibiting greater activity than previously reported for this catalyst. However, overall system durability was not good; H_2 production, which could be prolonged with added dmgH ligand, ceased within 10 h.[34]

A different set of organic dyes, shown as **P1**, was next examined based on the facts that (a) the chalcogen atoms in **P1** are part of the core dye structure and not simply substituents, (b) they exhibited stability under prolonged visible-light irradiation, and (c) derivatives of them had been found to produce photocurrent when attached to TiO_2 indicating photoinduced electron transfer.[35,36] When examined in systems for the light-driven generation of H_2, the Se derivative (**P1-Se**) was much more active than **P1-S**, while the parent dye, **P1-O**, was totally inactive for H_2 generation.[37] Mechanistic and photochemical studies revealed that the initial step for this system after light absorption involved reductive quenching by triethanolamine (TEOA), rather than by electron transfer from PS* to the catalyst. Instead, the catalyst is reduced by electron transfer from PS$^-$ with regeneration of the neutral dye. However, it was also determined that PS$^-$ decomposes on the order of minutes if no catalyst or oxidizing agent for the reduced dye is present.

The fact that the system with $CoCl(pyr)(dmgH)_2$ containing **P1-Se** was much more active than those of its O and S analogs for H_2 production indicated a need to access the long-lived $^3\pi\pi^*$ excited state of the dye for bimolecular electron transfer, whereas the photocurrent data suggested fast electron transfer from the $^1\pi\pi^*$ state since **P1-O** does not undergo significant ISC, and **P1-S** does so more poorly than **P1-Se**.[35] The basis of

P1

X = O, S, Se

1a R = H
1b R = Cl
1c R = CF₃

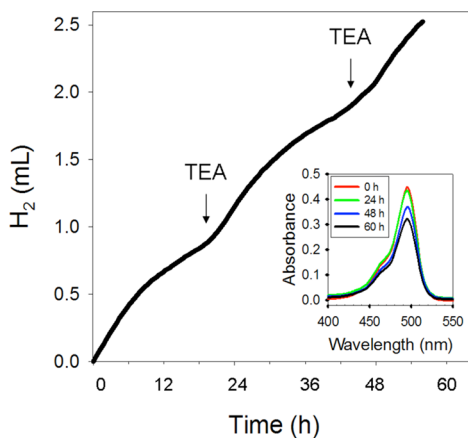1d

2

3a

3b

4a R″ = H
4b R″ = CH₃
4c R″ = OCH₃
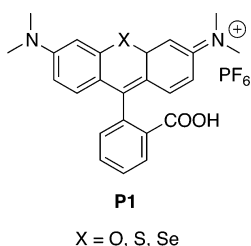
the difference was reconciled by transient absorption measurements that indicated H-aggregation of the dyes in the photocurrent measurements whereas for H_2 generation, the dyes were not aggregated, leading to the $^3\pi\pi^*$ state for bimolecular chemistry and H_2 formation.[38]
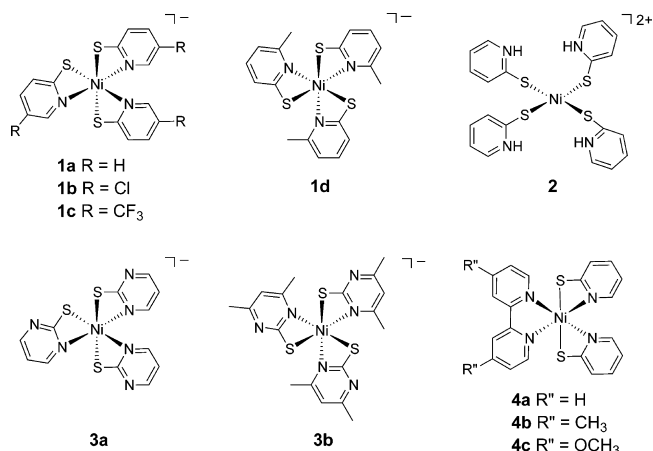
■ NEW COBALT AND NICKEL CATALYSTS

The complex $Co(bpy)_3^{2+}$ and other Co complexes having bidentate glyoximate ligands or derivatives have been used as "first generation" noble-metal-free catalysts for H_2 generation, and reviews of these catalysts are available.[21,39] In their modes of action, the formation of Co^I and Co^{III}−H intermediates was proposed to be the two key steps for H_2 generation.[40] Although a number of cobaloxime complexes were good initial catalysts, their activity was greatly limited,[34,37,41,42] and under the conditions for light-driven generation of H_2, they were found to undergo ligand exchange.[43]

To develop new robust catalysts for proton reduction in view of possible ligand deactivation, two different approaches were followed. First, the nickel complex $[Ni(pyS)_3]^-$ (1a, pyS = pyridine-2-thiolate), which mimics the [Fe,Ni] hydrogenase active site, was found to have impressive catalytic activity for the light-driven production of H_2 in homogeneous systems with Fl as the photosensitizer and triethylamine (TEA) as the sacrificial electron donor in basic 1:1 EtOH/H_2O.[44] Over 5000 turnovers relative to catalyst were obtained, and system activity was maintained with periodic additions of TEA (Figure 1). In order to probe this system more deeply, closely related pyridyl- and pyrimidylthiolate complexes of Ni(II) (1−4) were examined for both light-driven and electrocatalytic H_2 production.[45]

While the oxidative quenching rate constant of Fl* by the Ni catalysts was determined to be 2−3 orders of magnitude greater than the reductive quenching rate constant of Fl* by TEA, the initial photochemical step in the H_2 generating system was reductive quenching by a factor of ∼100 due to the relative concentrations of TEA and catalyst, the former being 10^5 greater than the latter. In this case, Fl⁻ generated from reductive quenching was found to undergo rapid decomposition, which limits the long-term performance of the system. However, when TEA concentration was lowered until the oxidative quenching rate given by $k_Q[\text{catalyst}]$ was greater than the reductive quenching rate ($k_Q'[\text{TEA}]$), the system became much more robust with an unabated rate of H_2 production over 60 h and more than 70% of the initial Fl still in solution (Figure 1).

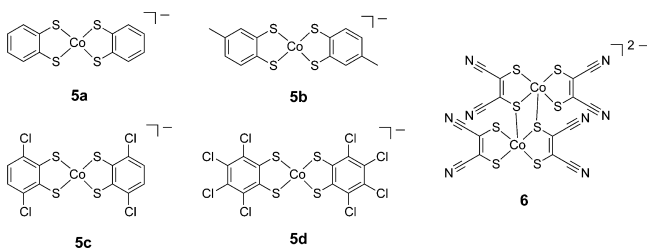The proton reduction mechanism by 1a is shown in Scheme 1. The first step involves a reversible protonation on the

Scheme 1. Proposed Mechanism of Hydrogen Formation by Complex 1a
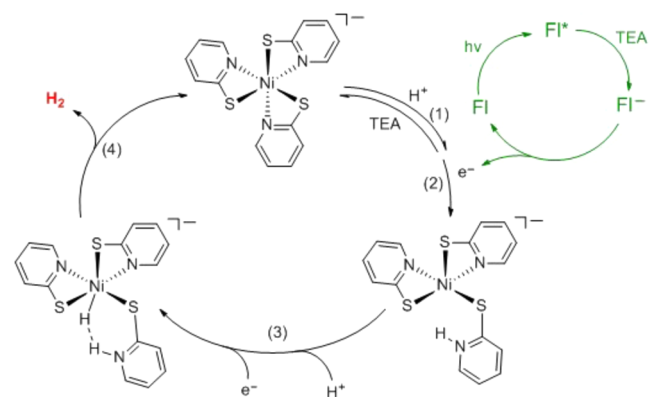
pyridylthiolate ligand. The protonation site was proposed to be the pyridyl N atom based on square planar complex 2 in which the pyridylthiolates are monodentate and protonated. Protonated 1a can then accept an electron from the reduced Fl to generate a Ni^I species. Further protonation and reduction occur before the turnover-limiting step, with the proposed order of steps based on consideration of the overall charge of the complex and resultant tendency to reduction. The H−H bond forming step involves a hetero coupling between a Ni hydride intermediate and the protonated pyridyl ligand, which is the reverse of hetero splitting of H_2 modeled by an IrH(pySH) complex isolated by Morris and co-workers.[46] The hetero

Figure 1. H_2 production from systems containing 1a (40 μM), Fl (0.5 mM), and TEA (7 mM) in EtOH/H_2O 1:1 (5.0 mL) at pH 12 upon irradiation with 520 nm LED. The arrows indicate when 0.1% v/v of TEA was added after sufficient TEA had been consumed to slow H_2 evolution. Inset: UV−vis absorption spectra measured during photolysis.

coupling mechanism is similar to what has been proposed previously in which a pendant nitrogen base acts as a proton relay to assist H−H bond formation in [FeFe]-hydrogenase models and nickel bis(diphosphine) complexes as catalysts.[47−51] This H_2 formation step is proposed to be rate-limiting, which is consistent with the observation that a higher rate for H_2 generation was obtained when the ligand was more electron-donating based on the notion that the more basic nickel hydride intermediate facilitates the hetero coupling step.

The second approach for the discovery of new catalysts for making H_2 focused on complexes of redox active ligands in which at least one of the electrons needed for proton reduction was not stored at the catalyst's metal center. Unsaturated 1,2-dithiolene ligands have long been known to form complexes that undergo reversible one-electron changes due in part to ligand redox behavior.[52,53] Based on this approach, it was found that the cobalt complex [TBA][Co(bdt)$_2$] (**5a**, where TBA = tetrabutylammonium, bdt = 1,2-benzenedithiolate) functions well as a catalyst for proton reduction.[54] A TON of 2700 was obtained with this catalyst in 8 h in the presence of Ru(bpy)$_3^{2+}$ and ascorbic acid (AA) in 1:1 CH_3CN/H_2O at pH 4.0. Later, a series of cobalt complexes with different dithiolene ligands (**5**, **6**) were also found to be active catalysts for H_2 generation.[55] Both reductive and oxidative quenching of the $^3PS^*$ by AA and cobalt bis(dithiolene) catalyst were observed in these systems, but reductive quenching was determined to be dominant during H_2 production. This meant that during photolysis, [Ru(bpy)$_3$]$^+$ was generated, which served to reduce the Co catalyst as well as a subsequently formed intermediate. Even though the systems based on **5** and **6** were more active than previous molecular systems, both PS and catalysts were found to decompose within 10 h.


Electrochemical experiments were used to elucidate the proton reduction mechanism of the cobalt bis(dithiolene) catalysts. In the presence of either CF_3COOH or tosic acid, these complexes were found to be active electrocatalysts to produce H_2 with quantitative Faradaic efficiency in 1:1 CH_3CN/H_2O. The catalytic wave was observed at a more negative potential than the Co(dithiolene)$_2^{-/2-}$ reduction, suggesting that following the initial reduction and protonation, a second, turnover-limiting reduction and protonation occur to form H_2 (Scheme 2). A computational study of these catalysts by Hammes-Schiffer[56] suggested that following initial reduction of **5a** to the dianion, two protonations occur on different sulfur donors followed by a second reduction (Scheme 2). Prior to the release of H_2, an intramolecular proton shift takes place, yielding a formally Co(III) hydride with an adjacent protonated sulfur (Scheme 2). The formation of H_2 occurs via a heterocoupling step (H$^+$ + H$^-$) similar to that proposed for Ni catalyst **1a**.

Interestingly, the analogous Ni(bdt)$_2^-$ (**7**) complex exhibits poor catalytic behavior for the light-driven generation of H_2 whereas the closely related complexes Ni(mp)$_2^-$ (**8**), Ni(abt)$_2$

Scheme 2. Proposed Mechanism of Hydrogen Formation by Complex 5a
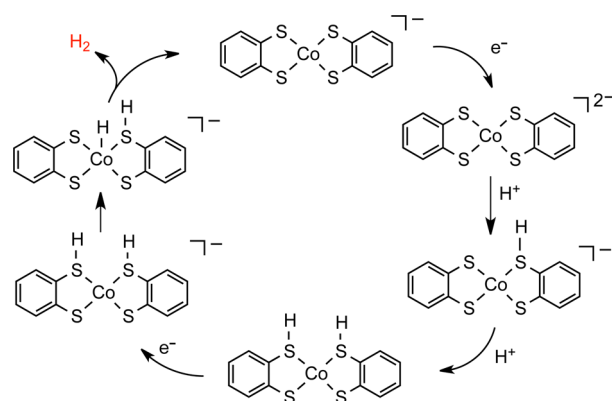
(**9**), and Ni(mpo)$_2$ (**10**) (where mp = 2-mercaptophenolate, abt = 2-amidobenzenethiolate, and mpo = 2-mercaptopyridine-N-oxide) have all been found to be active and durable catalysts for H_2 formation.[57] The poor performance of **7** results from the fact that its electrocatalytic wave is highly cathodic, which means that the catalytic intermediate cannot be reduced by either PS* or PS$^-$. Complex **10**, which functions under aerobic conditions in sea and river water, does not necessarily have a redox active ligand but may function via dechelation with the O donor acting as a proton shuttle for a heterocoupling mechanism.
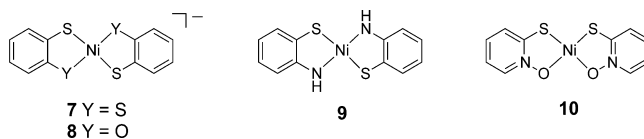

■ SYSTEMS USING QD PHOTOSENSITIZERS

In view of the photoinstability of organic dye systems for H_2 generation, attention shifted to another class of light absorbers that had the promise to be more durable as well as highly active. The properties of quantum confined semiconductor nanoparticles have been extensively studied,[58] and it was known that they could be made water-soluble by attachment of appropriate capping agents.[59−62] The particular semiconductor material that was used to initiate these studies was CdSe as prepared from Cd(OAc)$_2$ and (octyl)$_3$PSe (TOPSe) in the presence of (octyl)$_3$PO (TOPO).[63] Replacement of the lipophilic TOPO stabilizers by capping agents such as 3-mercaptopropionic acid (MPA) and dihydrolipoic acid (DHLA) had been reported to render the CdSe quantum dots water-soluble.[64−66] Our initial studies proceeded with DHLA because as a potential bidentate ligand, DHLA was thought to bind more strongly to the semiconductor surface. Early attempts with CdSe−DHLA quantum dots, Ni(NO$_3$)$_2$ as a possible catalyst precursor, and AA as the sacrificial electron donor yielded truly impressive results when irradiated with 520 nm light using an LED light source.[67] Initial turnover frequencies of >7000 h^{-1} and overall turnovers of 600 000 or more were obtained. A quantum yield of ∼36% was determined for the system with a durability that lasted for weeks. Replacement of Ni(NO$_3$)$_2$ by colloidal Ni yielded minimal H_2 generation upon irradiation, suggesting that the catalyst was a complex of Ni^{2+}.

The nature of the system was probed by stopping irradiation after 24 h followed by separation of the reaction solution from

the CdSe−DHLA QDs by centrifugation. Neither the solution nor the QDs alone with ascorbic acid present produced H$_2$ upon irradiation, but both could be reconstituted in terms of activity by adding the other component as shown in Figure 2.
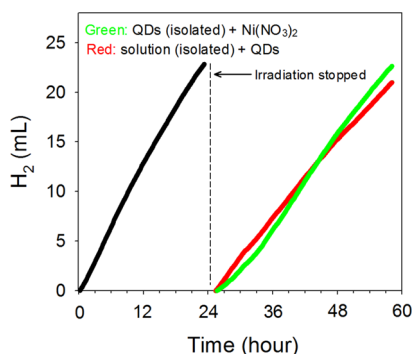
Figure 2. H$_2$ production from system containing CdSe−DHLA QDs (540 nm) (4.0 μM), Ni(NO$_3$)$_2$ (4.0 μM), and AA (0.5 M) in H$_2$O (5.0 mL), pH 4.5, 520 nm LED light. After 24 h, irradiation was stopped and QDs were separated from solution.

Atomic absorption spectroscopy indicated that the catalyst containing Ni^{2+} had not formed at the surface of the nanoparticles, and thus the system appeared to be biphasic: colloidal nanoparticles as photosensitizers and a solution-based catalyst for generating hydrogen. The exact nature of the solution catalyst was unknown, even though examples of hexanuclear nickel thiolate complexes had been reported as active catalysts for H$_2$ production in electrocatalytic and light-driven systems.[68,69]

Examination of the solutions containing CdSe−DHLA QDs by ^{1}H NMR spectroscopy revealed that DHLA was dissociating from the QD surface to the extent of 8−14 molecules of DHLA per QD. Somewhat unexpectedly, when catalyst **1a** described above was used in place of Ni(NO$_3$)$_2$ for H$_2$ generation, no significant difference was found in the level of system activity for making H$_2$. In view of the known formation constants for Ni(DHLA)$_x^{z-}$ complexes,[70] it was postulated that the active catalyst for H$_2$ formation was actually a Ni(DHLA) complex and that when **1a** was used in the system, ligand substitution of DHLA for pyS$^-$ produced the same catalyst as when Ni(NO$_3$)$_2$ was employed, yielding the same overall system activity.

The mode of operation of the CdSe−DHLA system also appeared to be different from that found using organic dyes in our study.[34,37,43−45] The organic photosensitizer excited state functioned by electron transfer from the sacrificial donor to the dye (reductive quenching) to form PS$^-$, which in turn reduced the catalyst. However, upon excitation of CdSe QDs in the presence of known electron mediators (methyl viologen and a related diquat), the characteristic colors of the corresponding radical cations were readily observed and confirmed spectroscopically. The results indicate that in contrast to the organic dye-based systems, the CdSe−DHLA system acts by electron transfer *from the QD to the catalyst* (oxidative quenching).

Consistent with the reducing ability of an electron in an excited CdSe−DHLA QD being determined by the conduction band (CB) edge, the activity of these QD-based systems was found to depend on nanoparticle size with smaller QDs (<3 nm in diameter) being more active than larger ones. With ∼5.6 nm CdSe−DHLA QDs as light absorbers, the system was unable to produce H$_2$ upon irradiation. The basis for this observed size-

dependent behavior lies in the fact that with increasing particle size, the QD bandgap decreases with the conduction band electron becoming less reducing, ultimately reaching a point at which it can no longer reduce the molecular catalyst.

The results for H$_2$ generation using CdSe−DHLA QDs as light absorbers and **5a** as the catalyst were both interesting and unexpected. The initial activity of **5a** was greater than that obtained with Ni(NO$_3$)$_2$ but rapidly declined to a nearly inactive level (Figure 3). However, the addition of more **5a** to
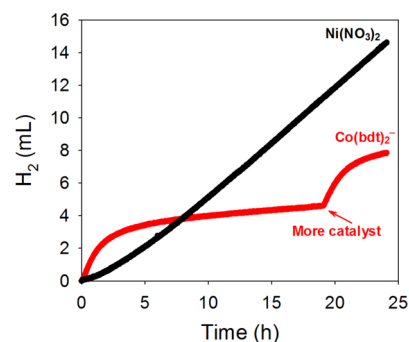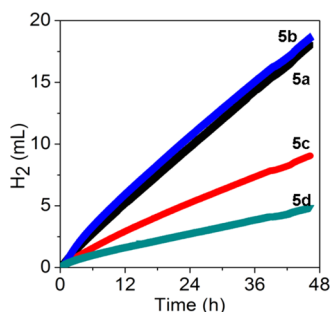

Figure 3. H$_2$ production from a system containing CdSe−DHLA QDs (540 nm) (6.0 μM) and AA (0.5 M) in pH 4.5 H$_2$O (5.0 mL) with 1.0 μM Ni(NO$_3$)$_2$ (black) or 1.0 μM **5a** (red), 520 nm LED at 15 °C. Additional 1.0 μM **5a** after 20 h restored the activity (red).

the solution restored activity that again declined rapidly. A spectroscopic study of the system revealed that the decline in H$_2$-generating activity correlated with the disappearance of **5a** from the solution, which in turn was postulated to result from substitution of the bdt ligand by DHLA that dissociated from the QD surface.[69] This dissociation, while making possible the formation of the active Ni(DHLA) catalyst in the initial QD-based system, was therefore problematic by hindering an investigation of other possible molecular catalysts in the photogeneration of H$_2$ with these light absorbers.

To address this problem, tridentate trithiolate capping agents **S1** and **S2** were synthesized and examined as part of the H$_2$ generating systems.[71] The initial results using CdSe QDs with **S1** or **S2** as the capping agent showed that tridentate binding rendered the capping agent essentially inert to dissociation and, in doing so, allowed a clear demonstration that the initially observed catalyst was a Ni(DHLA) complex. Specifically, 520 nm irradiation of a system containing CdSe−**S1** and Ni(NO$_3$)$_2$ yielded only small amounts of H$_2$, but when 3 equiv of DHLA was added to the sample, H$_2$ evolution was seen at a similar rate to that of the CdSe−DHLA system. The same was true with **1a** as the catalyst; added DHLA substituted for pyS$^-$ and led to the same rate of H$_2$ evolution as with Ni(NO$_3$)$_2$. It is important to note that for **1a**, the systems based on Fl and QD light absorbers function differently. With Fl, reductive quenching occurs with subsequent electron transfer from the reduced photosensitizer to the catalyst, whereas with QD light absorbers, electron transfer takes place from the CdSe QD to the catalyst. The fact that **1a** does not function well with the S$_3$-capped QDs indicates that the CB electron in CdSe is insufficiently reducing to transfer to **1a**.

S1   **S2**
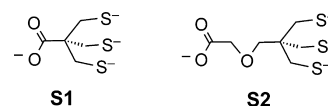
The results for systems using $Co(bdt)_2^-$ were also consistent with the importance of ligand exchange at the catalyst. For systems containing either CdSe−**S1** or CdSe−**S2** as light absorber, H_2 evolution proceeded at a high rate and with good durability using $Co(bdt)_2^-$ (**5a**) as the catalyst but declined significantly in activity when 2 equiv of DHLA was added to the systems.[71] These results also meant that with inert CdSe−**S1** and CdSe−**S2** QDs, different catalysts could be assessed in terms of activity and durability without the competing negative effects of ligand substitution at the catalyst center. In Figure 4,

Figure 4. H_2 production from a system containing CdSe−**S1** QDs (520 nm) (3 μM) and AA (0.5 M) in H_2O (5.0 mL) at pH 4.5 with 520 nm LED at 15 °C using different cobalt catalysts (3 μM): **5b** (blue), **5a** (black), **5c** (red), and **5d** (green).

the results are presented for four different Co bis-(benzenedithiolate) derivatives shown as **5a**−**5d**. The activities of these catalysts are indeed different and correlate with the 1-/2-reduction potentials for the complexes, with the more difficult to reduce complexes being more active. While additional mechanistic study is needed with these and related catalysts, we think that the more difficult-to-reduce catalysts lead to the more reactive hydrides for heterocoupling with a ligand-attached proton to form H_2.

Recently, Wu and co-workers have studied similar H_2-generating systems using CdTe or CdSe QDs capped with MPA for water solubility as the PS and $CoCl_2$ or $Fe_2(\mu$-$S)_2(CO)_6$ as the precatalyst.[72−74] The Co^{2+} ion was proposed to bind to the QD surface with the amount of bound Co^{2+} corresponding to 0.13 wt % with respect to the QDs (approximately three to four Co per QD). The notion of an integrated system differs from our conclusions with regard to QD-sensitized H_2 generation and may be due to the higher concentration of metal ion used in their experiments. However, since the MPA ligand can dissociate from the QD surface, it is possible that the active catalysts generated by Wu and co-workers are Co or Fe MPA-containing complexes.

CONCLUSIONS AND PROSPECTS

In this Account, we have described work over the past 5 years mainly in the senior author's laboratory on the light-driven generation of hydrogen from water. There has been impressive and insightful progress elsewhere on this subject, as well as on the electrochemical reduction of protons to H_2. Extensive referencing of the latter is not possible due to space limitations, but seminal reports and key reviews are cited.[23,39,50,75] The significant growth in the activity and durability of solution-based H_2-forming catalysts has been coupled with increasing insight into how they function, both experimentally and computationally. The mechanism for H_2 formation proceeds in the systems examined here via a hetero coupling of metal-

bound hydride and free or ligand-attached proton. Complexes with unsaturated or redox-active ligands appear to be a particularly fertile area for future inquiry, and there is good reason to think that even more active and durable catalysts remain to be discovered. The use of QD photosensitizers is also at a relatively early stage with only a few compositions such as CdSe having been employed. Other semiconductors, capping agents, quantum-confined shapes, and interconnections remain to be examined. The possibility of arrays of QD photo-sensitizers to absorb light from the solar spectrum more effectively is both logical and promising. Of course, as more active and robust systems are developed for H_2 generation from aqueous protons, removal of the sacrificial donor is essential, and such systems must then be connected to a water oxidation module in a genuine photosynthetic electrochemical cell with electrons and protons moving from photoanode to photo-cathode via controlled and separate paths. The scale of progress over the past 5+ years suggests that viable systems for the reductive side of water splitting will become available over the next decade, and with the development of a hydrogen infrastructure as mentioned earlier for fuel cell cars and stationary fuel cell operation, we may indeed be moving positively to a solar future.

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Notes

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