# Photoelectrochemical Generation of Hydrogen from Water Using a CdSe Quantum Dot-Sensitized Photocathode

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Ⓢ Supporting Information

**ABSTRACT:** The present study reports photelectrochemical $H_2$ evolution using a water-solubilized $S_3$-cap-CdSe quantum dot-sensitized NiO as the photocathode and either [Co-$(bdt)_2]^-$ (bdt =1,2-benzenedithiolate) or Ni(DHLA)$_x$ (DHLA= the anion of dihydrolipoic acid) complex as the $H_2$-forming catalyst. The NiO-$S_3$-cap-CdSe/[Co(bdt)$_2$]$^-$ system produces $H_2$ with a turnover frequency of 3000 per CdSe mol·h. Faradaic efficiency for this system is essentially quantitative. Both systems are stable for more than 16 h.
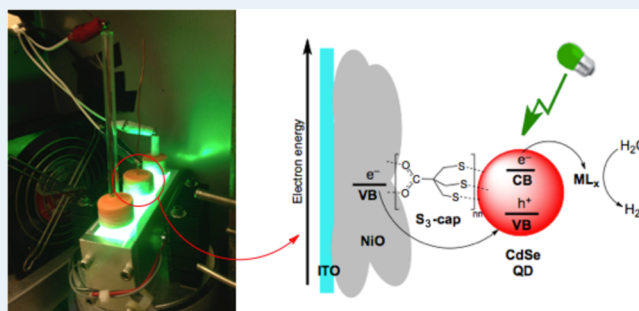


**KEYWORDS:** *photoelectrochemistry, photocathodes, quantum dots, hydrogen, solar energy, molecular catalyst*

Hydrogen is a clean, carbon-free fuel with the highest specific enthalpy of combustion of any chemical fuel. As the reductive side of water splitting, the synthesis of $H_2$ from aqueous protons requires, at a minimum, a visible light absorber or photosensitizer (PS), a $H_2$-forming catalyst, and a source of electrons. Recently, we reported a system based on water-solubilized CdSe quantum dots (QDs) as PS with Ni and Co complexes as catalysts that yielded turnover numbers (TONs) of >500 000, activity over 15 days, and a quantum yield $\varphi$ ($H_2$) of 36% using 520 nm light.[1] Others have also used II−VI QDs as light absorbers in conjunction with molecular catalysts for $H_2$ generation with impressive results.[2] However, one concern regarding these efforts, as well as many other studies that have been conducted for the light-driven generation of $H_2$,[3] is the need for a source of electrons in the form of a sacrificial electron donor for proton reduction (in the above case, ascorbic acid). In this report, we describe new studies on the photogeneration of $H_2$ in which the CdSe QDs become part of a photocathode to which electrons are supplied at a specific potential following photoinduced electron transfer from the QD to the catalyst in solution.

Until recently, precious metals such as Pt[3b,4] and Ru[5] have been used as (or in) components of most photoelectrochemical systems for $H_2$ evolution. Efforts of the past few years to find alternatives to replace noble metals as catalysts on photocathodes for $H_2$ generation have included the use of Ni,[6] NiMoZn,[7] MoS$_2$,[8] and CoS$_2$.[9] In addition to these reports, photocathodes made of Cu$_2$O[10] and graphene-based materials[11] have yielded promising results without the use of noble metals. Immobilization of molecular catalysts on p-type semiconductor surfaces has also been performed, as in the attachment of Fe carbonyl species to InP nanocrystals on a gold

cathode[12] and to p-Si as a photocathode in nonaqueous media.[13] The former study described $H_2$ production with a Faradaic efficiency of 60%, whereas the latter yielded essentially quantitative Faradaic efficiency. In another study, Mo$_3$S$_4$ clusters were connected to p-Si and reported to exhibit high photon-to-hydrogen conversion efficiency without an applied bias relative to the reversible hydrogen potential.[14]

Derivatives of the known electrochemical and photochemical cobaloxime catalyst CoCl(dmg)$_2$(pyr), where pyr = pyridine and dmg = dimethylglyoximate anion, have also been linked to semiconductor surfaces for hydrogen evolution experiments. In one, the Co catalyst is connected via Co(III) complexation to polyvinylpyridine which stabilizes p-type GaP.[15] In the other, a NiO cathode sensitized by a cyclometalated Ru phenylpyridine bis(bipyridine) derivative is used and linked to the cobaloxime catalyst via the latter's pyridyl ligand.[16] It is important to note, however, that under light-driven $H_2$-generating conditions in aqueous media, the CoCl(dmg)$_2$(pyr) catalyst has been shown to undergo ligand exchange readily,[17] thereby compromising the value of such photofunctional constructs.

As light absorbers in systems for photochemical proton reduction, semiconductor QDs offer distinct advantages over metal complexes with charge-transfer excited states and strongly absorbing organic dyes in terms of durability, absorptivity, and tunability. The last of these is achieved by variation of particle size that results in different band gaps for the semiconductor nanocrystals. Although a few studies have been reported on the preparation and characterization of CdSe

QD-sensitized photocathodes,[18] none to date has investigated the photocathode's activity with regard to the hydrogen evolving reaction (HER). Herein, we report the photoelectrochemical (PEC) generation of $H_2$ from aqueous protons by a system containing CdSe QD-sensitized NiO as the photocathode and a molecular Co or Ni complex in solution as the $H_2$-forming catalyst. The Co catalyst system exhibits essentially quantitative Faradaic efficiency for $H_2$ generation, and stability of the photocathode with either catalyst is seen for more than 16 h.

In the present study, photocathodes are fabricated via attachment of presynthesized quantum dots (diameter = 2.4 nm) to porous NiO films on ITO glass substrates. NiO films were deposited on ITO glass following the hydrothermal route reported by Odobel et al.[19] (Figure S3). Following the synthesis of CdSe QDs,[20] trioctylphosphine oxide (TOPO) ligands on the QDs were exchanged with 3-mercapto-2,2-bis(mercaptomethyl)propanoate (denoted as $S_3$-cap). It has been shown recently that the $S_3$-cap ligand binds strongly to the CdSe surface, thereby minimizing capping agent dissociation and exchange with catalyst ligands in solution.[1b] The $S_3$-cap-CdSe QDs are water-soluble and bind to the NiO surface, presumably through the carboxylate groups of the capping anions (see Supporting Information for experimental details). The presence of QDs on NiO surface is supported by scanning electron microscopy (SEM) (Figure S4) and UV/vis spectroscopy (Figure S5). Figure S6 shows the incident photon to current efficiency (IPCE) spectra of NiO-$S_3$-cap-CdSe and bare NiO films. The IPCE spectra of NiO-$S_3$-cap-CdSe roughly follows the absorption spectra of CdSe QDs in solution reaching a maximum value of 7.8% at 450 nm. This value is lower than the previously reported value of 18 for NiO-CdSe films due to lesser amounts of CdSe QDs on the NiO film by the attachment method using $S_3$-cap as compared to the direct attachment method previously used.[21]

Figure 1 shows the proposed operation of the photocathode. It is known from previous reports that the valence band (VB)
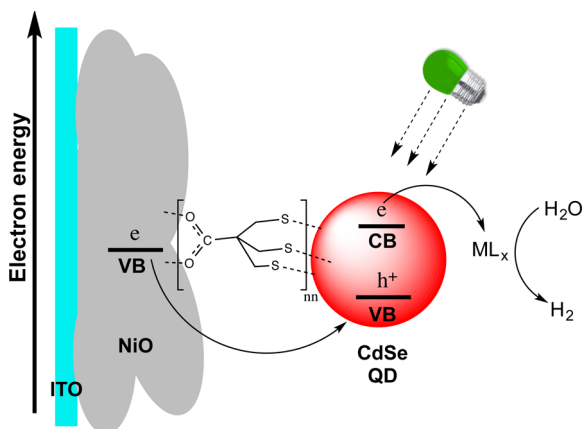


**Figure 1.** Scheme for electron transfer processes occurring in CdSe quantum dot-sensitized photocathode in the presence of the catalyst $ML_x$ (either $Ni(DHLA)_x$ or $[Co(bdt)_2]^-$) in solution.

of NiO lies at +0.54 V vs RHE.[22] The VB and the conduction band (CB) of CdSe QDs with a 2.4 nm diameter is ca. +1.10 and −1.30 V versus RHE, respectively.[23] Upon absorption by the QD of a photon of greater than band gap energy, an electron is promoted to the CdSe CB from which it is transferred to the catalyst in solution. The catalyst is either

$[Co(bdt)_2]^-$ (bdt = 1,2-benzenedithiolate), or in situ generated $Ni(DHLA)_x$ (DHLA = dihydrolipoic acid anion) (Figure S1). The reduction potentials for $[Co(bdt)_2]^-$ and $Ni(DHLA)_x$ under the operating conditions are +0.016 V and −0.75 V versus RHE, respectively. The reduced metal complex initiates proton reduction to $H_2$ that proceeds via intermediates generated from subsequent protonation and reduction steps (the latter involving another excited QD) in aqueous solution. As the VB edge of the CdSe QDs lies lower than the NiO VB edge (Figure 1), hole transfer from CdSe to the NiO VB occurs, corresponding to electron transfer *from* the NiO VB *to* the $S_3$-cap-CdSe-QD VB, thereby preventing oxidative decomposition of the QD semiconductor. Figure S7 shows the open-circuit potentials (OCP) of the NiO-$S_3$-cap-CdSe photocathode versus Ag/AgCl (Sat KCl) under dark and illumination ($\lambda$ = 520 nm) conditions. Upon illumination, the OCP shifts toward more positive potential, consistent with the p-type conductivity of the NiO-$S_3$-cap-CdSe electrode. The magnitude of the difference between the values of the OCP in the dark and under illumination shows that the photocathode has a photovoltage ($V_{ph}$) of 214 mV at 0.15 W light intensity (without considering the kinetic overpotential under operating conditions).

The catalytic onset potential was determined by linear sweep voltammetry for four different photoelectrochemical systems. These are shown in Figure 2 for the following: (a) bare NiO
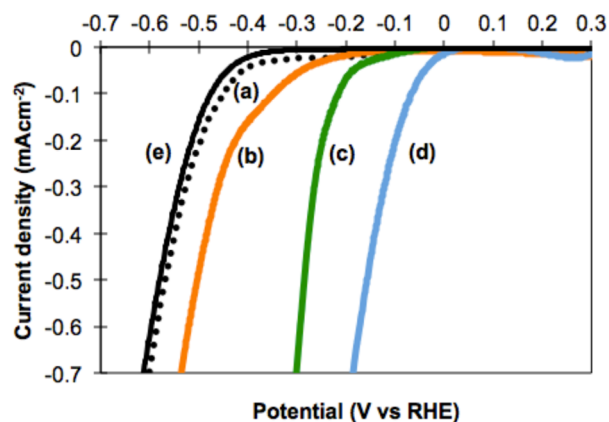


**Figure 2.** Linear sweep voltammograms under 520 nm LED light (150 mW) illumination of (a) bare NiO film; (b) NiO-$S_3$-cap-CdSe; (c) NiO-$S_3$-cap-CdSe with $Ni(DHLA)_x$; and (d) NiO-$S_3$-cap-CdSe with $[Co(bdt)_2]^-$. LSV labeled (e): NiO-$S_3$-cap-CdSe without illumination at pH = 6, 0.1 M KCl solution.

film; (b) NiO-$S_3$-cap-CdSe; (c) NiO-$S_3$-cap-CdSe with Ni-$(DHLA)_x$; (d) NiO-$S_3$-cap-CdSe with $[Co(bdt)_2]^-$. Under illumination, the NiO-$S_3$-cap-CdSe electrode onset potential is distinctly more positive (−0.2 V vs RHE) relative to the bare NiO onset potential value (−0.35 V vs RHE). The electrode systems having catalysts present exhibit even more positive onset potentials, being −0.10 V versus RHE for the electrode with $Ni(DHLA)_x$ (c) and 0.0 V versus RHE for the electrode with $[Co(bdt)_2]^-$ (d). For (c) and (d), respectively, these values correspond to positive shifts of nearly 100 and 200 mV relative to the NiO-$S_3$-cap-CdSe electrode, showing that the addition of metal complexes for $H_2$ formation significantly enhances photocathode performance.

For photoelectrochemical hydrogen production of the NiO-$S_3$-cap-CdSe/$[Co(bdt)_2]^-$ photocathode system, irradiation

under 520 nm LED light was conducted with a bias of $-0.28$ V versus RHE in a 0.1 M KCl with pH 6 buffer in 1:1 CH$_3$CN/H$_2$O solution. Under these conditions, current density obtained from a controlled potential coulometry experiment remained around $-2$ mA cm$^{-2}$, whereas in the dark, the current density was almost negligible (Figure 3a). Existence of current under
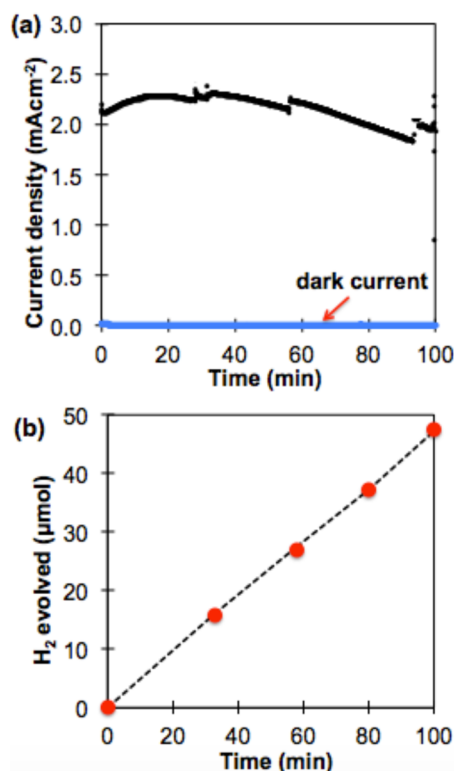


**Figure 3.** (a) Controlled potential bulk photoelectrolysis experiments for NiO-S$_3$-cap-CdSe/[Co(bdt)$_2$]$^-$ under light and dark conditions (slight discontinuities of current at 30, 60, 100 min are due to disturbance from gas withdrawal from the airtight 3-chamber cell for GC analysis); (b) Experimentally observed (red circles) and theoretically calculated (black dashed line) hydrogen production vs time for NiO-S$_3$-cap-CdSe with [Co(bdt)$_2$]$^-$ ($1.85 \times 10^{-4}$ M) at pH 6 in 0.1 M KCl and applied potential of $-0.28$ V vs RHE.

illumination results from effective electron transfer to the metal complex catalyst from the conduction band of the excited QDs. Figure 3(b) shows the amount of H$_2$ evolved at the photocathode based on gas chromatographic (GC) analysis of the headspace with time. The dashed line represents the theoretical amount of H$_2$ that would be produced if all charge that passed through the photocathode was used for proton reduction. A Faradaic efficiency of $100\% \pm 2$ was thus obtained for 2 h of H$_2$ production. The turnover number (TON) and the turnover frequency (TOF) for H$_2$ production with respect to [Co(bdt)$_2$]$^-$ were $400 \pm 30$ and $30 \pm 2$ h$^{-1}$, and with respect to the S$_3$-cap CdSe nanoparticles on the NiO surface, TON and TOF were approximately $35000 \pm 600$ and $3000 \pm 100$ h$^{-1}$ respectively. The same photocathode system without illumination produced no H$_2$.

Although hydrogen production for the NiO-S$_3$-cap-CdSe/[Co(bdt)$_2$]$^-$ photocathode system increases with increasing catalyst concentration up to 0.185 mM, activity decreases beyond that value. For example, a change of [Co(bdt)$_2$]$^-$ concentration from 0.185 mM to 0.27 mM results in a decrease

in H$_2$ produced after 3 h of irradiation from 83.8 $\mu$mol to 32.1 $\mu$mol (Table S1), with a slight decline in Faradaic efficiency to 91%. This change may be due to an inner-filter effect because the S$_3$-cap-CdSe QDs and [Co(bdt)$_2$]$^-$ in solution exhibit considerable spectral overlap (Figure S8). Although the molar extinction coefficient for CdSe (64000 M$^{-1}$cm$^{-1}$) is much greater than that for [Co(bdt)$_2$]$^-$ (3000 M$^{-1}$cm$^{-1}$), the concentration of [Co(bdt)$_2$]$^-$ in the solution is higher than that of the QDs as part of the photocathode. It was also found that at lower pH, the photocathode becomes deactivated after 30 min as a result of CdSe dissolution under acidic conditions (Figure S10). Faradaic efficiency for hydrogen production decreases drastically below pH 6 (Table S2).

The possibility of [Co(bdt)$_2$]$^-$ binding directly to the surface of the S$_3$-cap-CdSe QDs was examined as follows. A photocathode that had been employed in one of the NiO-S$_3$-cap-CdSe/[Co(bdt)$_2$]$^-$ photoelectrochemical reactions was used to carry out a new PEC experiment without any added [Co(bdt)$_2$]$^-$. It was observed that H$_2$ was produced with this system, but with a 50% decrease in Faradaic efficiency. The linear sweep voltammogram (LSV) of the previously used photocathode exhibited a new feature occurring at $-0.1$ V versus RHE, which is absent from that of the initial NiO-S$_3$-cap-CdSe photocathode (Figure S11). In FT-IR spectra of the photocathode thin films before and after the initial H$_2$-generating reaction, it was found that new bands appeared between 800 and 1000 cm$^{-1}$, consistent with the presence of aromatic groups on the surface of the electrode (Figure S13). These results suggest that some of the Co catalyst remains attached to the surface of the photocathode after irradiation and H$_2$ generation. This is similar to a literature report on the binding of $\mu-$sulfido metal complexes to a semiconductor surface[12] in which [Fe$_2$($\mu$-S)$_2$(CO)$_6$] attachment to InP nanocrystals was determined by fluorescence quenching and FT-IR spectroscopy. Further investigation is necessary to establish the exact nature of [Co(bdt)$_2$]$^-$ attachment to the surface because the complex does not have simple sulfido ligands.

In the initial study on H$_2$ production by DHLA-capped-CdSe QDs with a Ni$^{2+}$ salt present, the active catalyst was proposed to be an in situ formed Ni(DHLA)$_x$ complex.[1a] A subsequent study using S$_3$-cap-CdSe QDs confirmed this idea.[1b] The NiO-S$_3$-cap-CdSe photocathode system with Ni(DHLA)$_x$ as the catalyst was therefore examined photoelectrochemically with 520 nm irradiation and an applied potential of $-0.18$ V versus RHE. Figure 4 shows the current density versus time graph for this experiment. The current density obtained remained close to 0.1 mA cm$^{-2}$ for 16 h, whereas under dark conditions the value decreased dramatically. The catalytic onset potential for Ni(DHLA)$_x$ is more negative compared to [Co(bdt)$_2$]$^-$ (Figure 2). This may due to less effective electron transfer from the CdSe QDs to Ni(DHLA)$_x$ relative to [Co(bdt)$_2$]$^-$. Based on reduction potentials for Ni(DHLA)$_x$ and [Co(bdt)$_2$]$^-$, the driving force for electron transfer to the latter is much greater than that for the former. For NiO-S$_3$-cap-CdSe/Ni(DHLA)$_x$ system, the amount of H$_2$ evolved, as determined by GC analysis, was 6.3 $\mu$mol, giving a TOF of 8 per mol of Ni(DHLA)$_x$ h$^{-1}$ and a TON with respect to the photosensitizer of $6000 \pm 300$. A Faradaic efficiency of $82 \pm 10\%$ was obtained for H$_2$ production.

The structure of the in situ formed Ni(DHLA)$_x$ catalyst is uncertain, but aspects of the Ni coordination can be deduced from solution spectroscopic studies.[24] In $^1$H NMR spectra of
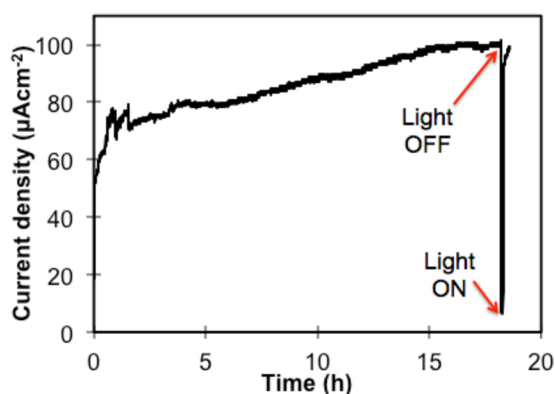
**Figure 4.** Extended controlled potential bulk photoelectrolysis experiments for NiO-S$_3$-cap-CdSe with Ni(DHLA)$_x$ (1.0 × 10$^{-4}$ M) in 0.1 M KCl pH 6 at −0.18 V vs RHE. Notice that at 18 h the current under illumination recovers after a brief dark period, indicating the stability of the QDs on the surface of NiO electrode.

the species formed upon mixing Ni$^{2+}$ with DHLA, sharp resonances are observed indicating that the species formed is diamagnetic (Figure S16). This observation suggests that the coordination environment around the metal ion is square planar and that DHLA ligands are bound to Ni$^{2+}$ through S donors. To exclude the possibility of the carboxylate group of DHLA participating in coordination to Ni$^{2+}$, the UV/vis spectrum of Ni$^{2+}$ with 1,3-propanedithiolate was obtained and found to be virtually identical to the spectrum of the Ni(DHLA)$_x$ complex (Figure S18). This result is consistent with ligand binding to Ni$^{2+}$ solely through the DHLA S donors.[1a] The presence of the uncoordinated carboxylate group also makes possible the binding of Ni(DHLA)$_x$ directly to the NiO surface on the photocathode. A photoelectrochemical experiment was conducted using the NiO-S$_3$-cap-CdSe cathode system previously employed with Ni(DHLA)$_x$ as the catalyst, but this time without any added Ni(DHLA)$_x$. In this case, a negligible amount of H$_2$ was produced with a 3% Faradaic efficiency, indicating the amount of any directly attached Ni(DHLA)$_x$ is relatively insignificant.

To date, most reports on II−VI semiconductor nanoparticles as sensitizers for photoelectrochemical studies involve the photoanode,[25] in which absorption of light by the photosensitizer leads to electron injection into an n-type oxide semiconductor and subsequently to an external electrical circuit. A disadvantage of this approach for solar-to-chemical energy conversion is degradation of the photosensitizer resulting from oxidizing "holes" that migrate to the photoanode surface.[26] Conversely, through the use of S$_3$-cap-CdSe QDs on a NiO film, light absorption leads to electron transfer to the solution-based catalyst and hole transfer from CdSe QD to NiO, thereby avoiding oxidation at the QD surface. The long-term stability of the photocathodes described here were demonstrated by controlled potential electrolysis experiments at −0.18 V vs RHE. Figures 4 and S9 show that photocurrent is stable for more than 16 h with either metal complex catalyst, indicating the robustness of the photoelectrochemical systems. Photocurrent measurements were also conducted before and after the 16 h irradiation as a function of photon flux on NiO-S$_3$-cap-CdSe films and the observed photocurrent response remained the same within experimental error, demonstrating the stability of the photocathode. (Figure S19) These

photocathodes were used twice before any significant degradation was observed.

In conclusion, the present study reports an active photoelectrochemical system consisting of a S$_3$-cap-CdSe QD photocathode and a Ni or Co molecular catalyst. Photocathode fabrication is found to be straightforward. Catalytic onset potentials of the H$_2$ evolving reaction shift to more positive values upon the addition of molecular catalysts. With the [Co(bdt)$_2$]$^-$ catalyst, 100% Faradaic efficiency for H$_2$ production is achieved, and stable photocurrent for more than 16 h is obtained in systems with either catalyst, giving evidence of the robustness of the photoelectrochemical system.

## ■ ASSOCIATED CONTENT

**S** Supporting Information

The following file is available free of charge on the ACS Publications website at DOI: 10.1021/cs5021035.

Experimental details; characterizations of NiO-S$_3$-cap-CdSe film (UV−visible absorbance, XRD, IPCE, and SEM); concentration and pH dependence of NiO-S$_3$-cap-CdSe photocathode with [Co(bdt)$_2$]$^-$; experimental data on [Co(bdt)$_2$]$^-$ attachment; spectroscopic characterization of Ni(DHLA)$_x$ (PDF)

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**Author Contributions**
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**Notes**
The authors declare no competing financial interest.

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