Semiconductor quantum dot-sensitized rainbow photocathode for effective photoelectrochemical hydrogen generation

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Contributed by Richard Eisenberg, September 7, 2017 (sent for review July 13, 2017; reviewed by Thomas E. Mallouk and Daniel G. Nocera)

The present study reports the fabrication of CdSe quantum dot (QD)-sensitized photocathodes on NiO-coated indium tin oxide (ITO) electrodes and their H₂-generating ability upon light irradiation. A well-established spin-coating method was used to deposit CdSe QD stock solution onto the surface of NiO/ITO electrodes, thereby leading to the construction of various CdSe QD-sensitized photocathodes. The present report includes the construction of rainbow photocathodes by spin-coating different-sized QDs in a sequentially layered manner, thereby creating an energetically favorable gradient for charge separation. The resulting rainbow photocathodes with forward energetic gradient for charge separation and subsequent electron transfer to a solution-based hydrogen-evolving catalyst (HEC) exhibit good light-harvesting ability and enhanced photoresponses compared with the reverse rainbow photocathodes under white LED light illumination. Under minimally optimized conditions, a photocurrent density of as high as 115 $\mu\text{A}\cdot\text{cm}^{-2}$ and a Faradaic efficiency of 99.5% are achieved, which is among the most effective QD-based photocathode water-splitting systems.

photochemical | hydrogen | photocathode | semiconductor | quantum dot

Solar-driven splitting of water is the key transformation in a non-carbon-based conversion of photon energy into stored chemical potential. Through it, abundant, environmentally benign energy can become a reality on a global scale (1–5). In a deconstruction of the challenges of solar-driven water splitting, natural photosynthesis serves as a guide with two separate photosystems for water oxidation and proton reduction as embodied in the well-known Z-scheme [in nature, the reduction half-reaction involves the conversion of nicotinamide-adenine dinucleotide phosphate (NADP⁺) into NADPH]. To achieve the reductive side of water splitting into molecular H₂, a number of approaches have been investigated (6–11).

Most extensively studied are molecular and/or materials systems in which protons are reduced in a process beginning with photoinduced electron transfer and leading to catalysis of H₂ generation, with electrons supplied chemically from a sacrificial electron donor (SED) (8, 12–19). While some of these systems have been moderately successful, the need for the SED means that they cannot simply be inserted into a viable water-splitting system. Instead, these promising systems must be modified to allow electrons to be supplied by a cathode at a particular electrochemical potential to complete the catalytic cycle. To accomplish this, a light absorber needs to be linked to the electrode so that, upon photoexcitation, electron transfer is initiated, passing ultimately to the catalyst, while the vacancy or “hole” generated upon excitation is filled from the cathode at its set potential. When paired with a photoanode for water oxidation, the resultant system produces light-driven water splitting (6).

Both photoanodes and photocathodes are currently under active study as parts of a total solar-driven water-splitting system (6, 20, 21). The photoelectrodes consist of a conductive support on which resides a semiconducting layer or assembly and a light absorber attached to it. The solution–semiconductor interface

leads to a space charge region with p-type semiconductors favored for moving electrons to the solution interface as photocathodes and n-type semiconductors favored for moving electrons to the bulk as photoanodes. In addition to the challenges of the photoelectrodes for each half-reaction of water splitting, there is also the overall “system” task of moving electrons and protons from photoanode to photocathode by separate and distinct paths (22, 23).

The use of dye-sensitized NiO photocathodes for photoelectrochemical (PEC) hydrogen generation has attracted attention in recent years (24–35), following investigations of this semiconductor for p-type dye-sensitized solar cells (DSSCs), in which electrical energy serves as the product (36–44). In several related hydrogen-generation studies, it has been found that organic chromophore-sensitized NiO photocathodes exhibit steady but low photocurrent density during irradiation in the presence of Co glyoximate catalysts (24, 25, 29).

As an alternative to organic chromophores or molecular metal complexes as light absorbers in DSSC photocathodes, semiconductor quantum dot (QD)-sensitized NiO photocathodes have been found to exhibit greater photostability, as well as a larger hole diffusion coefficient (45). The unique properties of QDs such as superior photostability, tunable light absorption, large extinction coefficients over a broad spectral region, and rich surface binding features have made them attractive as light-harvesting alternatives relative to molecular chromophores for photochemical hydrogen production in the presence of SEDs (12–19). To date, however, there are only limited examples using QD-sensitized NiO photocathodes for PEC hydrogen evolution

Significance

Photochemical water splitting is the most desirable transformation in a non-carbon-based conversion of photon energy into stored chemical potential. The system described here to carry out this transformation is a photoelectrochemical (PEC) cell in which CdSe quantum dots (QDs) on a NiO surface serve as light absorbers, and a metal complex in solution acts to assemble the two protons and two electrons into H₂. The present report extends prior work significantly with the construction of a “rainbow” photocathode by spin-coating different-sized QDs in a sequentially layered manner, thereby creating an energetically favorable gradient for charge separation. The resultant rainbow photocathode exhibits enhanced light-harvesting ability under white LED light illumination and an increased photoresponse relative to a single-sized CdSe QD-sensitized photocathode.

Author contributions: H.L. and R.E. designed research; H.L., C.W., G.L., and R.B. performed research; H.L., C.W., G.L., R.B., T.D.K., Y.G., and R.E. analyzed data; and H.L. and R.E. wrote the paper.

Reviewers: T.E.M., The Pennsylvania State University; and D.G.N., Harvard University.

The authors declare no conflict of interest.

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This article contains supporting information online at www.pnas.org/lookup/suppl/doi:10.1073/pnas.1712325114/-DCSupplemental.

(27, 28, 30–32, 34, 35). In these studies, the photogenerated electrons in the QDs are transferred to an anchored or solution-based hydrogen-evolving catalyst (HEC), while the holes in the QDs are filled by electrons from the p-type NiO film.

It has been reported that charge-transfer efficiency and rate in QD-sensitized PEC cells (27, 28, 30–32, 34, 35) and QD-sensitized solar cells (QDSSCs) (46–55) are critically dependent on QD size and/or the way that the QDs are deposited on the metal oxide surfaces, including the particular anchoring method. The fabrication of QD-based photoelectrodes has been carried out in a number of ways such as successive ionic layer adsorption and reaction (SILAR) (27, 28, 56–58), chemical bath deposition (CBD) (31, 35, 59, 60), electro/electrophoretic deposition (61–64), direct adsorption (65, 66), and linker-assisted assembly (30, 32, 34, 67, 68). Among these various approaches, the direct growth approach (e.g., SILAR and CBD) offers higher coverage of QDs on the porous metal oxide surface but may also introduce poorer quality and uneven size distribution of the QDs (55). In contrast, the postsynthesis assembly approach (e.g., electro/electrophoretic deposition, direction adsorption, and linker-assisted assembly) can provide excellent properties of presynthesized QDs, but low coverage of QDs on the metal oxide electrode surface is a central concern (53). Therefore, the development of a facile way to achieve both high coverage and the superior properties of presynthesized QDs remains an important objective.

In the present study, we report the fabrication of CdSe QD-sensitized photocathodes on NiO-coated indium tin oxide (ITO) electrodes and their H₂-generating ability upon light irradiation. These photocathodes were fabricated by spin-coating a colloidal QD stock solution onto the NiO surface. With this method, the coverage of QDs is well controlled, and the quality of QDs used for film preparation is assured. The present report also extends earlier studies in that CdSe QDs of different sizes and bandgaps have been employed within the same photocathode in a designed manner. Through this approach, charge separation can be enhanced, leading to H₂ production with higher efficiency. Because of the order of different sizes, and therefore colors, of the CdSe QDs employed, these electrodes are referred to as rainbow photocathodes with the smallest QDs next to the NiO layer and the largest QDs closer to the catalyst-containing solution, thereby creating an energetically favorable gradient for charge separation. Such an assembly of QDs with different sizes has been reported in the case of QD-based rainbow solar cells (49, 69–72).

Results and Discussion

QDs of CdSe capped by tri-*n*-octylphosphine oxide-capped CdSe (CdSe-TOPO) QDs were synthesized as reported in ref. 12 and confirmed by TEM images to have quite uniform size distributions (*SI Appendix*, Fig. S1). Water solubilization of the CdSe QDs was achieved by ligand exchange reactions with 3-mercaptopropionic acid (denoted as S3) in methanol under N₂ atmosphere, yielding CdSe-S3 QD light absorbers, as detailed in *SI Appendix, Materials and Methods* (15, 17, 73).

Fig. 1. SEM images of (A) the bare NiO/ITO electrode and (B) the CdSe-S3/NiO/ITO electrode.

Fig. 2. Energy diagram and working principle of the CdSe QD-sensitized NiO/ITO photocathode in the presence of hydrogen-evolving catalyst (HEC) at pH 6.0.

UV-Vis spectra show that the ligand exchange process does not significantly affect the size of CdSe QDs (17) (*SI Appendix*, Fig. S2).

The mesoporous p-type NiO/ITO electrodes in the present work were prepared differently from the hydrothermal method used in our previous study (32) and was carried out by doctor-blading a commercial Ni-nanoxide paste onto a clean conductive ITO substrate, followed by calcinations at 450 °C for 1 h. The crystallinity, morphology, and composition of the prepared NiO films were characterized by various techniques. SEM images show that the surface of the ITO glass substrate is evenly covered with a layer of porous NiO film of several microns thickness (Fig. 1A), and corresponding energy-dispersive X-ray spectroscopy (EDS) analysis confirms its elemental composition (*SI Appendix*, Fig. S3A). Powder X-ray diffraction patterns reveal high crystallinity of the as-synthesized NiO film (*SI Appendix*, Fig. S3C). X-ray photoelectron spectroscopy (XPS) analysis further confirms its chemical purity with a +2 oxidation state of Ni and complete absence of metallic Ni⁽⁰⁾ (74) (*SI Appendix*, Fig. S4).

Design of Single-Sized CdSe-S3-Sensitized Photocathode. The sensitization of the NiO/ITO electrode by CdSe-S3 QDs was achieved using the spin-coating method (see *SI Appendix, Materials and Methods*, for details). An obvious change in film color is observed after deposition of CdSe-S3 QDs (*SI Appendix*, Fig. S6). The sensitization process does not affect the crystallinity of the NiO/ITO film (*SI Appendix*, Fig. S3C), but it does cause a roughening of the film surface (Fig. 1B), indicating the attachment of CdSe-S3 QDs. Powder X-ray diffraction patterns do not show the diffraction peaks of CdSe QDs due to their low surface coverage on the film (*SI Appendix*, Fig. S3C). However, EDS and XPS measurements (*SI Appendix*, Figs. S3B and S5) clearly suggest the presence of Cd and Se elements on the surface of the NiO film with oxidation states of +2 and −2, respectively. Deconvolution of the Cd 3d peak yield multiple peaks, which can be attributed to different chemical environments of the Cd²⁺ ions. The XPS signal of S originates from the S3 capping ligands (*SI Appendix*, Fig. S5). The NiO films and CdSe-sensitized NiO films (see below) were converted to electrodes by making ohmic contact with a copper microalligator clip stabilized with conductive

Fig. 3. Chopped-light chronoamperometric measurements on bare NiO/ITO electrode (black) and CdSe-S3-520-nm-sensitized NiO/ITO photocathode prepared by the spin-coating method with 120- μ L (blue line), 60- μ L (red line), and 20- μ L (magenta line) stock solution loading. Conditions: 10 μ M TBA[Co(bdt)₂] catalyst, 0.2 M air saturated HMTA/HCl buffer at pH 6.0 with 0.1 M KCl, green LED light source (intensity: 180 mW), and applied bias potential 0 V vs. Ag/AgCl in 3 M NaCl.

copper foil tape covered by polyimide film tape (see *SI Appendix, Materials and Methods*, for details and *SI Appendix, Fig. S6*).

Fig. 2 depicts the general energy diagram and working principle of the CdSe QD-sensitized NiO/ITO photocathode, which has been tested and used by both us and others (30–32). Upon irradiation, the electrons from the valence band (VB) of CdSe QDs are excited to the conduction band (CB), followed by electron transfer to the anchored or solution-based HEC for proton reduction to H₂. In the present study, the HEC is the solution-based complex TBA[Co(bdt)₂], where bdt is benzene-1,2-dithiolate and TBA is tetra-*n*-butyl ammonium, that has been found by us to be an effective catalyst for H₂ generation (15, 75). The photogenerated holes left in the VB of CdSe are then filled by electrons from the VB of the p-type NiO film at a poised potential. The occurrence of this process is supported by open circuit potential measurements (*SI Appendix, Fig. S7*). A photovoltage of around 250 mV is observed upon green LED light irradiation at 180-mW light intensity.

As mentioned above, the particular method used to anchor/deposit QDs on the metal oxide electrode surfaces can critically affect both the charge-transfer efficiency and rate (27, 28, 46, 47). Therefore, we compared the performance of CdSe QD-sensitized photocathodes fabricated using the spin-coating, SILAR, and in situ ligand-exchange methods as detailed in *SI Appendix, Materials and Methods*. Chopped-light chronoamperometric measurements on these different photocathodes is shown in *SI Appendix, Fig. S8*. In the absence of CdSe QDs, no photocurrent is observed for bare NiO/ITO electrode. However, with sensitization by CdSe QDs, cathodic photocurrent is seen immediately upon green LED (530-nm) light irradiation for all three photocathodes at 0 V vs. Ag/AgCl in an air-saturated aqueous buffer solution. The photocurrent from the photocathode prepared by the spin-coating method (75 μ A·cm⁻²) is clearly superior to those obtained from analogous photocathodes made by the SILAR method (54 μ A·cm⁻²) and the in situ ligand-exchange method (24 μ A·cm⁻²). Also, the photocurrent obtained from the photocathode made by the SILAR method was found to slowly diminish with time (*SI Appendix, Fig. S8*, magenta line).

Controlled potential photoelectrolysis was also used to evaluate the relative performances of the various photocathodes with Co(bdt)₂⁻ as HEC (see *SI Appendix, Materials and Methods* and *Fig. S9*). Although more charge was passed for photocathodes made by the SILAR and in situ ligand-exchange methods, the Faradaic efficiencies (77.4% and 36.3%, respectively) that were calculated through quantification of evolved H₂ gas as described under *SI Appendix, Materials and Methods*, are significantly lower than that of the photocathode made by the spin-coating method (Faradaic efficiency, 99.6%). These experimental results can be attributed to the poorer quality of CdSe deposition with the SILAR method as well as lower CdSe coverage and the existence of the organic TOPO ligand with the in situ ligand-exchange method. Based on these observations, further studies of CdSe QD-sensitized photocathodes were conducted solely on samples prepared using the spin-coating method.

The spin-coating method also allowed us to control the loading of CdSe-S3 QDs on the NiO/ITO electrode surface by simply varying the amount of the stock solution used for the coating. Linear sweep voltammograms (LSVs) of CdSe-S3-sensitized NiO/ITO photocathodes in which the QDs were maximally absorptive at 530 nm exhibited significant photocurrent enhancement upon green LED light irradiation (*SI Appendix, Fig. S10*). An increase in the loading quantity of CdSe-S3-520-nm QDs from 20 μ L (0.3 nmol·cm⁻²) to 120 μ L (1.8 nmol·cm⁻²) on the electrode surface yielded a substantial increase in photocurrent density from 35 to 108 μ A·cm⁻² (Fig. 3), which represents one of the highest photocurrent values achieved in QD-based photocathode systems (27, 28, 30–32, 34, 35).

The loading effect of CdSe QDs on resulting photocurrent density was also observed in the case of the CdSe-S3-530-nm-sensitized NiO/ITO photocathode systems (*SI Appendix, Fig. S11*), where a photocurrent enhancement from 37 to 87 μ A·cm⁻² was achieved upon an increase in the loading quantity of CdSe-S3-530-nm QDs from 20 μ L (0.3 nmol·cm⁻²) to 60 μ L (0.9 nmol·cm⁻²). In addition, different-sized CdSe-S3 QDs for photocathode sensitization produced different photocurrent responses under otherwise-identical conditions (*SI Appendix, Fig. S12*). For example, the CdSe-S3-530-nm-sensitized photocathode showed the best photocurrent enhancement upon green light irradiation, whereas the CdSe-S3-485-nm-sensitized photocathode yielded the lowest one. In light of the spectral overlap of the UV-Vis absorption of the different-sized QDs with the green LED light source, behavior of this type was expected (12).

To better investigate photocathode performance, controlled potential photoelectrolysis was carried out at an applied bias

Fig. 4. (A) Current density vs. time curve of controlled potential photoelectrolysis on CdSe-S3-520-nm-sensitized NiO/ITO photocathode; (B) Corresponding theoretically calculated (black line) and experimentally observed (red square) hydrogen evolution vs. time curve. Conditions: 10 μ M TBA[Co(bdt)₂] catalyst, 0.2 M HMTA/HCl buffer at pH 6.0 with 0.1 M KCl, degassed with N₂/CH₄, green LED light source (intensity: 180 mW), applied bias potential of -0.44 V vs. RHE, and 120 μ L of QDs stock solution used for film sensitization.

Fig. 5. Schematic illustration of different-sized CdSe QD-sensitized NiO/ITO rainbow photocathode as well as the energy levels of different-sized CdSe QDs and electron transfer process between them.

potential of -0.44 V vs. reversible hydrogen electrode (RHE) to explore its stability and efficiency for PEC hydrogen evolution. Fig. 4 reveals that upon green LED light irradiation the photocurrent density of CdSe-S3-520-nm-sensitized NiO/ITO photocathode slowly approaches a steady value of $113 \mu\text{A}\cdot\text{cm}^{-2}$ and remains basically unchanged for 5 h of irradiation (Fig. 4A). The evolved hydrogen gas produced during photoelectrolysis was quantified using gas chromatography. During the 5-h period, $8.4 \mu\text{mol}$ of H_2 gas was produced corresponding to a turnover number (TON) of 140 vs. the $[\text{Co}(\text{bdt})_2]^-$ catalyst (Fig. 4B), with accumulated charge of 1.63 C passed, corresponding to a calculated Faradaic efficiency of $\sim 99.8\%$ and a quantum yield of $\sim 0.29\%$ based on the absorbed photons. A change in the applied bias potential to a less negative value (-0.24 V vs. RHE) yielded both a decrease in the total charge passed through the external circuit (0.36 C, *SI Appendix, Fig. S13*) and a reduction in the Faradaic efficiency for H_2 generation ($\sim 49.7\%$, *SI Appendix, Fig. S13*), that can be attributed to less efficient hole transfer from the VB of CdSe QDs to NiO film, and therefore greater unproductive side reactions.

Previous studies have shown that an in situ-generated $\text{Ni}(\text{DHLLA})_x$ complex also works as a catalyst for hydrogen evolution when using water-soluble CdSe QDs as light absorbers and ascorbic acid as the SED (12, 16, 19), and in our initial report on CdSe QD-sensitized photocathodes, $\text{Ni}(\text{DHLLA})_x$ was also used as a catalyst for H_2 generation (32). In the present investigation, $\text{Ni}(\text{DHLLA})_x$ -catalyzed H_2 PEC measurements were repeated with all three different-sized CdSe-S3-sensitized photocathodes. As shown in *SI Appendix, Fig. S14*, these photocathodes with the $\text{Ni}(\text{DHLLA})_x$ catalyst also exhibit photocurrent density enhancement upon green LED light irradiation, with more charge passed through the external circuit relative to measurements made using $[\text{Co}(\text{bdt})_2]^-$ as the catalyst. The calculated Faradaic efficiencies ranged from 84.1% to 100.1%, but careful examination of the charge accumulation curves all display upward curvature suggesting the possibility that a catalyst more active than $\text{Ni}(\text{DHLLA})_x$ may be formed over time, as mentioned later.

Design of CdSe-S3-Sensitized Rainbow Photocathode. Previous studies on QDSSCs using an assembly of different-sized QDs in a sequentially layered manner have indicated that such an architecture of QDs can significantly enhance light harvesting over a broader spectral range and may increase charge carrier rate unidirectionally (49, 69–71). Those studies prompted us to construct such photocathodes using the spin-coating method, and based on the color variation of CdSe QDs with size, we refer to them as rainbow photocathodes.

Fig. 5 illustrates the CdSe QD-sensitized NiO/ITO rainbow photocathode and the underlying principle for its operation based on the VB and CB levels for the CdSe QDs of different sizes and the electron-transfer processes between them. In the desired rainbow photocathode, the smallest QDs are spin-coated next to the NiO layer while the largest QDs are deposited closer to the catalyst-containing solution, thereby creating a forward energetic gradient favorable for charge separation (76). Previous studies reported that the CB position of different-sized CdSe QDs depends highly on their sizes while the VB position is nearly independent of the QD size in the diameter range of 2.1–4.2 nm. With an increase of CdSe QD size from 2.1 to 4.2 nm, the magnitude in the uphill shift of the VB level is very small (≤ 0.1 eV) (77, 78). Upon illumination, the photogenerated electrons will preferentially flow toward the HECs, while the holes left in the VB will be filled by electrons from the NiO layer. With this design in mind, the rainbow photocathode containing four different-sized CdSe-S3 QDs in successive layers were constructed (see *SI Appendix, Materials and Methods*, for details). The successive sizes of the CdSe QDs from the NiO surface is based on their first excitonic absorption peaks located at 485, 500, 520, and 530 nm, respectively. To confirm the hypothesis that a forward energetic gradient would be favorable for charge separation and electron transfer toward HECs, a reverse rainbow photocathode was also fabricated, in which the largest QDs were spin-coated next to the NiO layer while the smallest QDs were deposited closer to the catalyst-containing solution, thereby creating an unfavorable energetic gradient for electron movement toward the HECs.

The PEC performances of both forward and reverse rainbow photocathodes were initially evaluated under green LED light illumination. LSV results show that both forward and reverse rainbow photocathodes exhibit obvious photocurrent enhancement upon green light irradiation (*SI Appendix, Fig. S15*), but the photocurrent enhancement ($\sim 79 \mu\text{A}\cdot\text{cm}^{-2}$) obtained for the forward rainbow photocathode is much higher (~ 2.7 times) than that achieved for the reverse rainbow photocathode ($\sim 29 \mu\text{A}\cdot\text{cm}^{-2}$) (*SI Appendix, Fig. S16*). Subsequent controlled potential photoelectrolysis at an applied bias potential of -0.44 V vs. RHE further proves the superior performance of the forward rainbow photocathode relative to the reverse rainbow photocathode, as revealed by the higher cumulated charges passed through the external circuit, as well as by its unit Faradaic efficiency (*SI Appendix, Fig. S16*). The calculated external quantum yields

Fig. 6. (A) Chopped-light chronoamperometric measurements on CdSe-S3-sensitized NiO/ITO rainbow photocathodes with forward energetic gradient (red line) and reverse energetic gradient (black line) at applied bias potential of 0 V vs. Ag/AgCl in 3 M NaCl in air-saturated buffer solution; (B) the corresponding charge vs. time curves from controlled potential bulk photoelectrolysis; the Inset indicates the Faradaic efficiency. Conditions: $10 \mu\text{M}$ TBA $[\text{Co}(\text{bdt})_2]^-$ catalyst, 0.2 M HMTA/HCl buffer at pH 6.0 with 0.1 M KCl, degassed with N_2/CH_4 , white LED light source (intensity: 350 mW), and applied bias potential of -0.44 V vs. RHE.

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