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**CdSe on a Mesoporous Transparent Conducting Oxide Scaffold as a Photocathode**

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We report here a photocathode based on a high surface area conductive metal oxide scaffold sensitized by CdSe quantum dots attached via organic linkers. Photoreduction of methyl viologen demonstrates efficient photoreactions occurring at electrode surfaces and verifies that the high surface area scaffold is promising for use as a photocathode material**.**

Rising energy demands and the need to decrease CO2 emissions require the utilization of alternative energy resources. For solar energy to become viable on a global scale, energy storage solutions are necessitated by the intermittent and diffuse nature of sunlight. An avenue toward energy storage would be to use sunlight to create chemical bonds through the reduction of protons or CO2 to energy dense fuels, mimicking processes occurring in natural photosynthesis.[1](#_ENREF_1) This artificial photosynthetic construct would thus require a photoanode (water oxidation) and a photocathode (H+ or CO2 reduction) as shown in Figure 1. As attractive as this concept sounds, design of a practical device on a large scale remains a formidable challenge as it is important to carefully control both the band gaps and relative band edge positions of the photoanode and photocathode in order to meet the thermodynamic considerations for water splitting and absorb complementary photons to increase device efficiency.[2](#_ENREF_2)

Due to the ability to control the optical and electronic properties of semiconductor quantum dots (QDs) through size selective synthesis, QDs are ideal materials to be used for light absorption in photocathode and photoanode applications.[3](#_ENREF_5) QDs, particularly CdSe and CdS, have been used effectively in dye-sensitized solar cells where the QDs are attached to TiO2 and light absorption initiates electron injection into the TiO2 to create charge separation. These systems naturally have been applied as photoanodes for a variety of device architectures for generating current from light.[4](#_ENREF_7) For fuel production, these photovoltaic (PV) materials have been coupled to photoelectrochemical cells (PEC) using combinations of QD materials and dye-sensitized solar cells to generate the necessary photovoltage for proton reduction.[5](#_ENREF_8)



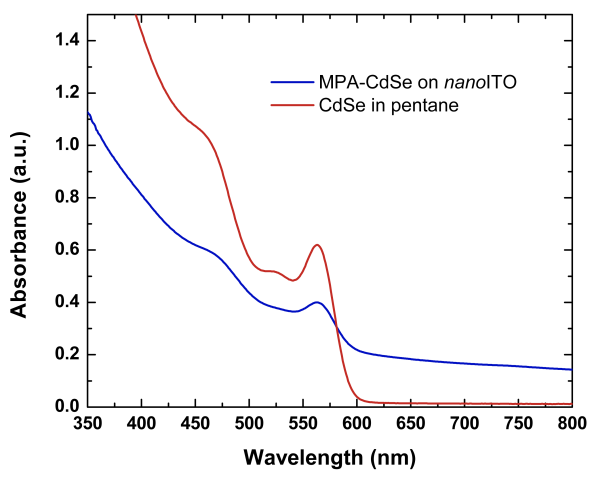
**Figure 1.** Illustration of a z-scheme device containing a photoanode for water oxidation and a photocathode for proton reduction. The electrodes may each consist of multiple components.

In addition to being utilized as sensitizers on n-type TiO2 for PV and PEC applications, QDs have also been shown to drive H+ reduction catalysts.[6](#_ENREF_10),[7](#_ENREF_12) However, examples of photocathodes where these materials are used to sensitize wide band gap p-type semiconductors and drive H+ reduction heterogeneously remain rare. One difficulty in the design of photocathodes is the relative dearth of wide band gap p-type semiconductors to use analogously to TiO2. NiO has been the most popular candidate but it is not as effective as TiO2 given issues relating to poor sensitizer loading, fast (ps) back electron transfer from the dye to injected holes, and lower carrier mobilities.[8](#_ENREF_13) Further, syntheses of high-surface area electrodes of NiO with nanoscale structural control have proven difficult. Other p-type materials, such as InP nanowire arrays, have been combined with H+ reduction catalysts for photoelectrochemical H2 production.[9](#_ENREF_14) Unfortunately, these are not quantum confined and the band gap is not tuneable.

In order to address the issues of photocathode construction, we sought to design an easily tailored system with QDs anchored to a transparent and high surface-area electrode. The material of choice was a mesoporous film of tin-doped indium oxide (*nano*ITO). Electrodes of this material are easily made through spin coating a suspension of commercially available nanoparticles followed by annealing, and the electrodes have been shown to be transparent and conductive.[10](#_ENREF_15) The hypothesis for use of this material was that CdSe QDs, shown to be effective at light-driven reduction reactions (specifically the hydrogen evolution reaction) in solution,[6](#_ENREF_11) would continue to function as such when on a surface.

CdSe QDs were synthesized via a heat-up method wherein a mixture of cadmium myristate and selenium dioxide are suspended in ODE and heated to 220 °C.[11](#_ENREF_16) Addition of oleic acid to cease growth, followed by precipitation with acetone gave CdSe QDs with a 3.4 nm diameter as determined by the position of the lowest-energy excitonic transition (LEET) as has previously been reported.

In order to sensitize the electrodes with the CdSe QDs, a method of dip-coating ligand exchange was used. First, a 30 × 10 mm electrode with a 10 × 10 mm active area was immersed in a 0.1 M methanolic solution of 3-mercaptopropionic acid (MPA) for 10 min. It is known that carboxylate[12](#_ENREF_17) and phosphonate[10](#_ENREF_15) functionalities readily bind to *nano*ITO electrodes and it was surmised that the MPA would bind through the carboxylic acid. The electrode was then rinsed with methanol, dried, and dipped into a 5.0 × 10−7 M solution of CdSe QDs in pentane for 10 min. After immersion, the electrode was rinsed with pentane and visibly had turned a light orange. This two-step dipping procedure was then repeated two additional times. Figure 2 shows the UV/vis spectrum of the solution of pentane containing CdSe used to load the electrodes as well as the resulting electrode after 3 loading cycles. The UV/vis spectrum shows CdSe attached to the slide and the feature from the LEET remains centered at 563 nm with slight broadening.



**Figure 2.** UV/vis absorption of a solution of CdSe in pentane (red) and CdSe attached to a nanoITO electrode (blue). The electrode was held in the path of the beam without any solvent.

The electrodes were also characterized by electron microscopy. Figure 3 shows a picture of the *nano*ITO film before and after annealing in forming gas and after loading with CdSe (A) and SEM images of both the bare *nano*ITO film (B) and *nano*ITO film loaded with CdSe QDs (C). The images illustrate the adherence of the CdSe QDs to the film with retention of transparency. The SEM images confirm the mesoporous nature of the annealed *nano*ITO films and that attachment of the CdSe QDs to the surface has little effect on the film morphology.



**Figure 3.** A) Photograph of nanoITO electrodes (from left to right) annealed in air, after a second anneal under forming gas, and after sensitization with CdSe. B) SEM image of a nanoITO electrode as synthesized. C) SEM image of a nanoITO electrode with CdSe attached.

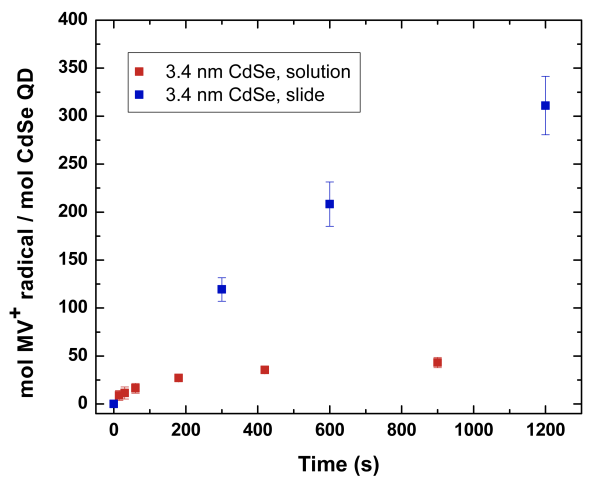
A combination of UV/vis spectroscopy and electrochemical measurements were used to determine the active surface area of the modified *nano*ITO electrodes. UV/vis spectra of CdSe bound via the MPA linker to both planar fluoride-doped tin oxide (FTO) and *nano*ITO (geometric active area of 10 mm × 10 mm) ̶ both were loaded with 3 dipping cycles ̶ were compared (Figure S1). The maximum absorbance of the LEET of the *nano*ITO slide is ca. 3× that of the LEET absorbance of the planar FTO slide. For electrochemical comparison, a viologen derivatized with a propionic acid group was anchored to both the planar FTO and *nano*ITO electrodes using the same dipping technique in a solution of 0.1 M viologen in methanol. This allows the viologen to bind to the surface of the electrodes. The viologen-derivatized electrodes were then used in a three electrode cell as the working electrode, with a platinum counter, and Ag/AgNO3 reference electrode in a 0.1 M acetonitrile solution of tetrabutylammonium hexafluorophosphate. Reductive scans show two reversible couples corresponding to the reduction of the viologen first to the radical cation followed by the di-radical (Figure S2). The amount of current passed was determined by the area under the cathodic peaks. For the *nano*ITO, the current passed was ca. 3.7× that of the planar FTO slide. Finally, choronocoulometry was used to generate Anson plots of the oxidation of ferrocene by the bare *nano*ITO electrodes to determine active surface area. For these experiments, *nano*ITO electrodes were used as the working electrode with a 10 mM ferrocene standard. A potential step experiment was used to instantaneously step to a potential sufficient to oxidize all the ferrocene. The total charge (Q) that passes during the time following a potential step is measured as a function of time (Figure S3). For a diffusionally controlled system, the charge observed following the potential step can be described by the integrated Cottrell equation, known as the Anson equation:

*Q* = 2*nFACD* ½ π -½ *t* ½

A plot of Q vs. t1/2 (Figure S4) thus gives a straight line with the slope being equal to:

2*nFACD* ½ π -½

where n is the number of moles of electrons in the redox reaction, F is Faraday’s constant, C is the concentration of substrate (ferrocene), and D is the diffusion coefficient (2.3 × 10−5 cm2/s for ferrocene under the experimental conditions). This analysis gave a surface area of 2.2× that of the geometric surface area, although this method can underestimate the active surface area of mesoporous electrodes when a fast electron transfer mediator is used.[13](#_ENREF_18)

 In order to assess the performance of the CdSe QDs for driving reduction reactions, photoreduction experiments were conducted with a suspension of CdSe QDs, MPA as a sacrificial electron donor, and methyl viologen (MV2+) as an electron acceptor. Methyl viologen was chosen as it has a first reduction potential at −0.45 V vs NHE (Figure S5), a potential that is sufficiently reducing to drive proton reduction to H2, and the radical cation generated (MV+●) is an intense purple color that can be monitored spectrophotometrically. Experiments were designed such that a QD solution could be irradiated with LEDs to generate an exciton. An electron would then transfer from the excited QD to the MV2+ and the hole would be trapped by the MPA, thus regenerating the CdSe ground state (Figure 4). The initial experiments were done as a benchmark for the surface reactions with the sensitized *nano*ITO electrodes.

**Figure 4.** Cartoon of the relative energy levels of the CdSe conduction and valence bands, the oxidation potential of the sacrificial donor (MPA), the MV2+/+● couple, and the proton reduction couple at pH = 0 (left), and diagram of the photoexcitation, reduction, regeneration cycle (right).

For each photoreduction experiment, a solution of CdSe QDs (1.6 × 10−8 mol), 5 mM [MV](I)2, and 50 mM MPA in pH 7.4 phosphate buffered aqueous solution were illuminated with a strip of LEDs (Figure S6). The reaction was monitored by UV/vis at various time points to observe the appearance of the MV+●. The radical cation has a known extinction coefficient of 13700 M−1cm−1 at 603 nm[14](#_ENREF_19) in water that could be used to calculate the amount of MV+● produced at any given time. The rate of production of MV+● was monitored over 20 minutes and the experiment was run 3 times. In order to compare to the rate of MV2+ reduction by the slide in a heterogeneous reaction, the number of moles of MV+● produced was divided by the number of moles of CdSe in the reaction. This number essentially gives the turnovers per CdSe QD where a turnover is a photon absorption followed by electron transfer to generate the MV+●. These results are plotted in Figure 5 (red squares) with error bars for the three trials, and show an increase in MV+● with time consistent with the series of events depicted in Figure 4. After 2 minutes the rate of MV+● production begins to slow and the plot begins to plateau. This behaviour likely has two main causes, the first being an imperfect seal on the vessel and a slow leak of atmosphere which will re-oxidize some of the MV+●, and the second due to the intense purple color of the solution which, at high MV+● concentrations, competitively absorbs the LED light.

The photoreduction quenching experiments were repeated with the same composition of pH 7.4 aqueous solution containing MPA and [MV](I)2 but instead of a suspension of CdSe QDs, a *nano*ITO slide that had been loaded with three cycles of dipping was added to the vessel. The same illumination experiment was conducted, again showing the generation of MV+● with time. Data from these trials are also plotted in Figure 5 (blue squares) with error bars from 3 separate experiments. In order to calculate the moles of CdSe on the slide, a geometric approximation was made. Given that the packing efficiency of circles in a 2-D space is 91%; the diameter of the dots (3.4 nm) and the geometric surface area of the electrode (1 cm2) were used to calculate the number of CdSe QDs that could be placed in that area. This number was then multiplied by 4, given that the actual active area of the mesoporous *nano*ITO electrode was found to be 2 – 5 times that of the geometric surface area which gives 1.8 × 10−17 mol of QDs (9 orders of magnitude *less* than in the solution experiments). While this gave an estimate as to the number of CdSe QDs on the surface, it is important to note that it likely *overestimates* the number of QDs on the surface, given that the packing efficiency of the QDs in the mesoporous film is much less than 91%. Strikingly, the reduction of the MV2+ to MV+● is not impeded at the surface and the number of molecules of MV+● produced per QD is an order of magnitude larger than the QD suspension. These data are indicative of the ability to drive important reduction reactions photochemically at the surface of an electrode.

**Figure 5.** Plot of the generation of MV+● over time using a white LED with both a suspension of CdSe (red) and a nanoITO slide with attached CdSe (blue) in pH = 7.4 aqueous phosphate buffer with 5 mM MV2+ and 50 mM MPA.

Finally, we wanted to replace the sacrificial donors used in the system with an electrochemical bias. Since in an overall water-splitting device electrons would be delivered via wire to a photocathode for fuel production, photoelectrochemical reduction of MV2+ would represent a proof of concept for use of this material as a photocathode. For these experiments, a *nano*ITO slide derivatized with CdSe QDs was used as a working electrode in a 3-electrode cell with the solution containing the same mixture of MV2+ and phosphate buffer, but without MPA. Reactions were run under Ar to prevent any air oxidation of generated MV+●. A bias of −0.30 V vs Ag/AgCl was applied to the slide to generate driving force for electron transfer from the electrode into the VB of CdSe as diagrammed in Figure 6, and the reaction was illuminated with white LEDs. Even after 1 h of irradiation, however, no MV+● was observed spectrophotometrically.

**Figure 6.** Cartoon of the relative energy levels of the CdSe conduction and valence bands, the oxidation potential held at the electrode, the MV2+/+● couple, and the proton reduction couple at pH = 0.

For the photoelectrochemical experiments, it is likely that an electron transfer to MV2+ after irradiation occurs rapidly (*k1*, Scheme 1). The timescale of this reaction has been shown to be on the fs – ps timescale,[15](#_ENREF_20) and the previously described quenching studies confirm this reaction will occur. However, unlike when there is a sacrificial donor in high concentration in solution, the hole left in the VB of the CdSe must be filled by an electron transferred from the *nano*ITO surface through the organic ligands anchoring the QD to the electrode (*k2*, Scheme 1), all before back electron transfer from the MV+● to the hole in the VB of the CdSe can occur (*kr1*, Scheme 1). This BET process is also likely fast and out competes productive electron transfer from the electrode.

Although photoelectrochemical experiments have proven unsuccessful, the quenching experiments demonstrate the viability of reduction reactions occurring at photocathode surfaces sensitized with QDs. In order to overcome the deleterious BET reactions preventing photoelectrochemical reduction, a thin p-type transparent semiconductor may need to be deposited on the *nano*ITO (Figure S7) using techniques such as electrodeposition and ALD, which has already been done for n-type semiconductors like TiO2 on *nano*ITO.16 One advantage of the *nano*ITO is it provides the high surface area structure while remaining transparent, which avoids the need to make bulk wide band gap and nanostructured p-type materials. It is also advantageous to have only a thin layer of p-type semiconductor so that charges may be quickly extracted for more efficient devices.

**Scheme 1. Electron Transfer Following Photoexcitation.**

Conclusions

We have shown the ability to use CdSe QDs to functionlize high surface area, transparent electrodes for photo-driven reduction reactions. The electrodes were made out of *nano*ITO which is a transparent conducting oxide that can easily be applied to glass substrates to create high surface area scaffolds which are necessary for photoelectrochemical water splitting device designs. Sensitized electrodes were used to photochemically reduce MV2+ which demonstrated the ability to drive reactions at the surface of the electrodes using light. Although the current version of the sensitized electrodes were not able to photoelectrochemically reduce MV2+, these materials represent an important step toward second generation devices where electrode morphology does not need to be controlled by a semiconducting material that also must act as light absorber, thus removing some of the challenging limitations in finding new p-type materials and dyes for photocathode applications.

Notes and references

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1. E. S. Andreiadis, M. Chavarot-Kerlidou, M. Fontecave and V. Artero, *Photochem. Photobiol.*, 2011, **87**, 946.

2. J. H. Alstrum-Acevedo, M. K. Brennaman and T. J. Meyer, *Inorg. Chem.*, 2005, **44**, 6802; D. Gust, T. A. Moore and A. L. Moore, *Acc. Chem. Res.*, 2009, **42**, 1890; M. G. Walter, E. L. Warren, J. R. McKone, S. W. Boettcher, Q. Mi, E. A. Santori and N. S. Lewis, *Chem. Rev.*, 2010, **110**, 6446.

3. P. V. Kamat, *J. Phys. Chem. C*, 2008, **112**, 18737; M. Shalom, I. Hod, Z. Tachan, S. Buhbut, S. Tirosh and A. Zaban, *Energy Environ. Sci.*, 2011, **4**, 1874.

4. P. V. Kamat, *J. Phys. Chem. Lett.*, 2013, **4**, 908.

5. V. González-Pedro, I. Zarazua, E. M. Barea, F. Fabregat-Santiago, E. de la Rosa, I. Mora-Seró and S. Giménez, *J. Phys. Chem. C*, 2013, **118**, 891; O. Khaselev and J. A. Turner, *Science*, 1998, **280**, 425.

6. H. Zhu, N. Song, H. Lv, C. L. Hill and T. Lian, *J. Am. Chem. Soc.*, 2012, **134**, 11701; L. Amirav and A. P. Alivisatos, *J. Phys. Chem. Lett.*, 2010, **1**, 1051.

7. Z. Han, F. Qiu, R. Eisenberg, P. L. Holland and T. D. Krauss, *Science*, 2012, **338**, 1321.

8. I. Barceló, E. Guillén, T. Lana-Villarreal and R. Gómez, *J. Phys. Chem. C*, 2013, **117**, 22509.

****9. L. Gao, Y. Cui, J. Wang, A. Cavalli, A. Standing, T. T. T. Vu, M. A. Verheijen, J. E. M. Haverkort, E. P. A. M. Bakkers and P. H. L. Notten, *Nano Lett.*, 2014, **14**, 3715.

10. G. Hoertz Paul, Z. Chen, A. Kent Caleb and J. Meyer Thomas, *Inorg. Chem.*, 2010, **49**, 8179.

11. O. Chen, X. Chen, Y. Yang, J. Lynch, H. Wu, J. Zhuang and Y. C. Cao, *Angew. Chem., Int. Ed.*, 2008, **47**, 8638.

12. B. H. Farnum, Z. A. Morseth, A. M. Lapides, A. J. Rieth, P. G. Hoertz, M. K. Brennaman, J. M. Papanikolas and T. J. Meyer, *J. Am. Chem. Soc.*, 2014, **136**, 2208.

13. M. M. Collinson, *ISRN Analytical Chemistry*, 2013, **2013**, 21.

14. T. Watanabe and K. Honda, *J. Phys. Chem.*, 1982, **86**, 2617.

15. A. J. Morris-Cohen, M. D. Peterson, M. T. Frederick, J. M. Kamm and E. A. Weiss, *J. Phys. Chem. Lett.*, 2012, **3**, 2840.

16. L. Alibabaei, B. H. Farnum, B. Kalanyan, M. K. Brennaman, M. D. Losego, G. N. Parsons and T. J. Meyer, *Nano Lett.*, 2014, **14**, 3255.