Near-Infrared Colloidal Quantum Dots for Efficient and Durable Photoelectrochemical Solar-Driven Hydrogen Production

Lei Jin, Bandar AlOtaibi, Daniele Benetti, Shun Li, Haiguang Zhao,* Zetian Mi, Alberto Vomiero,* and Federico Rosei*

Solar energy offers a huge potential for global supply of clean and sustainable energy, reducing our dependence on fossil fuels and decreasing carbon dioxide (CO₂) emissions.¹⁻⁷ Photoelectrochemical (PEC) solar-driven hydrogen (H₂) production, which converts solar energy into H₂ using semiconductors as active materials, is considered as a promising route, because H₂ is a solar fuel, which combines the advantages of high energy storage densities, ease of transportation, cost-effectiveness,⁸ and generating water as the only byproduct of H₂ use.⁹ PEC cells perform redox reactions driven by electron–hole pairs created by incident photons, namely, the holes oxidize water/hole scavengers at the surface of the photoanode, and the electrons migrate to the counter electrode to reduce water and produce hydrogen.¹⁵ The ideal PEC cell is composed of inexpensive semiconducting materials with proper electronic band structure, leading to strong sunlight absorption, effective charge separation, and high photochemical stability.

TiO₂ and ZnO are promising photocatalysts for H₂ production by water splitting due to their appropriate energy band position and stability,¹¹ yet their photoactivation requires ultraviolet (UV) light due to their wide band gap (≈3.2 eV).¹² To improve their photocatalytic activity, chalcogenide quantum dots (QDs) optically active in the visible (Vis) range have been developed to sensitize TiO₂, forming a heterostructured platform for PEC H₂ generation. These QDs could expand the absorption of solar radiation into the Vis part of the solar spectrum and also provide fast exciton dissociation and charge injection to the wide band gap semiconductor due to their proper band alignment.¹³ To maximize light absorption in the broadest spectral region, lead chalcogenide QDs were applied, with band gap in the range 1.1–1.7 eV, providing a good matching of the solar spectrum.¹⁴ Near-infrared (NIR) PbS QDs, which allow fast/efficient charge separation/injection in the whole UV, Vis, and NIR,¹⁵ can be easily grown inside a mesoporous TiO₂ film via in situ deposition techniques, yielding a solar to H₂ conversion efficiency of 1.15% in PEC systems, with a photocurrent density of 1.5 mA cm⁻² and an H₂ generation rate of 12.5 mL cm⁻² d⁻¹.¹⁶ However, PbS as a sensitizer suffers from problems of stability and high charge recombination.¹⁷ Recently, PbS QDs synthesized by a successive ionic layer adsorption and reaction (SILAR) approach and further coated by a CdS layer on TiO₂ mesoporous film have been used as a photocatalyst to produce H₂ at 60 mL cm⁻² d⁻¹ with a photocurrent density of 6 mA cm⁻² under one-sun simulated solar illumination.¹⁸ SILAR has several drawbacks, such as lack of precise control over QD size, difficulty in controlling QD coverage, slow carrier injection into TiO₂, and high charge recombination due to interfacial traps.¹⁶⁻¹⁹ These issues can be addressed by using presynthesized colloidal QDs for sensitizing the mesoporous film.²⁰ Size-tunable QDs with high quantum yield (QY) and narrow size distribution can be synthesized via an organometallic approach in an organic solvent, with the introduction of surface ligands to passivate the QD surface.²¹ A well-established approach, based on electrophoretic deposition (EPD), has been used to deposit these colloidal QDs onto mesoporous films,²² yet suffers from the degradation of the QD surface due to the damage of the protection ligand during EPD, which results in surface oxidation of QDs and their chemical etching. An elegant solution to mitigate the stability issues of colloidal QDs is to coat them with a robust inorganic shell, which inhibits surface oxidation and the formation of surface traps.²³ Here, we describe a hybrid architecture based on a TiO₂ mesoporous film, functionalized through EPD with colloidal PbS@CdS core@shell QDs, followed by further CdS capping via SILAR, targeting an efficient and stable hydrogen production.

L. Jin, D. Benetti, Dr. S. Li, Dr. H. G. Zhao, Prof. A. Vomiero, Prof. F. Rosei Centre for Energy, Materials and Telecommunications Institut National de la Recherche Scientifique 1650 Boul. Lionel-Boulet, Varennes QC J3X 1S2, Canada E-mail: haiguang.zhao@emt.inrs.ca; rosei@emt.inrs.ca B. AlOtaibi, Prof. Z. Mi Department of Electrical and Computer Engineering McGill University 3480 Univ. Str. W. Montreal QC H3A 0E9, Canada Dr. H. G. Zhao, Prof. A. Vomiero CNR INO SENSOR Lab Via Branze 45, 25123 Brescia, Italy Prof. A. Vomiero Department of Engineering Sciences and Mathematics Luleå University of Technology 971 98 Luleå, Sweden E-mail: alberto.vomiero@ltu.se; Prof. F. Rosei CSACS McGill University 801 Sherbrooke Str. W., Montreal, QC H3A 0B8, Canada

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Trap-mediated electron transport occurs in the TiO₂ at the QD/oxide interface (Figure 1b), and electrons are injected as light absorbers. Photogenerated exciton dissociation occurs before SILAR coating, indicating the possibility of broadening the spectral absorbance in the proposed system.[16–19] Here, we used core@shell QDs with first absorption peak around 1.4 eV to demonstrate the proof of concept. The QDs have an average diameter of ~3 nm and narrow size distribution (Figure 2a; Figure S1, Supporting Information). The blueshift of the absorption/PL peak after cation exchange is due to the shrinking of the PbS core during the replacement of Pb²⁺ by Cd²⁺.[30] The PbS core size (2.8 nm) is estimated from the position of the first excitonic peak (Figure 2b).[30] The shell thickness (0.1 nm) is estimated from the TEM dimensions of the QDs and the calculated dimensions of the core,[31] which is further confirmed by testing the Pb-to-Cd ratio with inductively coupled plasma optical emission spectrometry (ICP-OES; see the Supporting Information).

The QDs were deposited by EPD to sensitize an 0.85 to 1.54 eV (4.8 nm in diameter) PbS QDs (3 nm in diameter).[24,30] CdS,[28] PbS@CdS core@shell QDs with the CdS (core@shell/CdS), a significant charge transfer from QDs to TiO₂.[21] After further coating with a CdS/ZnS SILAR film, to elucidate the role of the QDs and evaluate the contribution of the SILAR layer to the optical properties of the device. The full list of analyzed samples is reported in Table 1.

Before SILAR coating, the core@shell QDs after EPD show strong absorption ranging from 1.2 to 3.1 eV (Figure 3b), which is very similar to its absorption spectrum in solution (Figure 2b). Further, CdS coating via SILAR (sample TiO₂/core@shell/CdS) significantly improves the absorption of the film in the 2.25–3.1 eV range (Figure 3b). Due to the large band gap of ZnS and TiO₂, their contribution to light absorption in the visible range is almost negligible (Figure 3b; Figure S3, Supporting Information). The PL shape and peak position almost remain unchanged after EPD compared to the solution (Figure 3b), indicating that EPD does not create any traps/surface defects affecting PL, thanks to the protection of the CdS shell. Compared to solution, the PL after QD uptake shows a strong decrease in intensity, most likely due to efficient charge transfer from QDs to TiO₂.[21] After further coating the core@shell QDs with the CdS (core@shell/CdS), a significant PL redshift from 1.17 to 0.92 eV (~0.25 eV) was observed, mostly due to the creation of trap states, when the surface oleic acid ligands were modified by the presence of the inorganic CdS capping. These traps can act as alternative pathways for electron transfer from QDs to TiO₂ in the PEC device.

The colloidal PbS QDs were first synthesized via hot-injection methods. Subsequently, the PbS@CdS core@shell QDs were obtained via a cation exchange approach and then dispersed in toluene, with typical QY of 40%–80%.[10] By controlling the initial size of PbS QDs and the cation exchange parameters such as reaction temperature and time, we were able to produce core@shell QDs with the first absorption peak tunable from 0.85 to 1.54 eV (Figure 2d). Based on the electron affinity of TiO₂ (~4.1 eV), which is favorable for water reduction, and consolidated results,[21] electrons of colloidal PbS QDs are demonstrated to be efficiently transferred into the TiO₂ as long as the first excitonic absorption peak is above 0.9 eV (4.8 nm in diameter). This low limit for light absorption is below most in situ SILAR grown QDs, indicating the possibility of broadening the spectral absorbance in the proposed system.[16–19]

Figure 1. a) Scheme of the PEC device. b) Energy levels (at pH = 13) of TiO₂,[27] PbS QDs (3 nm in diameter),[24,30] CdS,[28] related characteristic redox potentials,[29] and the arrows indicate the electrons and holes transfer process.
for exciton recombination and PL generation, in addition to the standard direct band gap emission, namely, trap emission (route 1 and route 3 in Figure 3a, respectively). On the other hand, a dramatic enhancement of integrated PL intensity as high as 52-fold was observed after CdS coating (core@shell/CdS), indicating strong inhibition of electron transfer into TiO$_2$. For samples with identical optical density at the same excitation wavelength, the integrated fluorescence intensities of core@shell in TiO$_2$ are reduced to about one-fiftieth of the core@shell QDs in solution, indicating that QD-TiO$_2$ electron transfer is still the dominant process in core@shell/CdS, even if less effective, compared to core@shell before SILAR.

The PEC behavior of the TiO$_2$/core@shell/CdS/ZnS system in the dark and under illumination using a conventional three-electrode configuration with an Ag/AgCl (saturated KCl) reference electrode and Pt counter electrode is shown in Figure 3d. An aqueous solution containing 0.25 M Na$_2$S and 0.35 M Na$_2$SO$_3$ (pH = 13) serves as sacrificial hole scavenger. To rule out any effects of TiO$_2$, a 425 nm long-pass filter was used to measure the photoresponse under AM 1.5G illumination (100 mW cm$^{-2}$) (Figure 3c) (the final real light intensity should be less than 100 mW cm$^{-2}$ due to the cutoff of light below 425 nm). The photocurrent density for the bare TiO$_2$ photo-anode under full sun illumination without the 425 nm cutoff filter was used to measure the photoresponse under AM 1.5G illumination (100 mW cm$^{-2}$) (Figure 3c) (the final real light intensity should be less than 100 mW cm$^{-2}$ due to the cutoff of light below 425 nm). The photocurrent density for the bare TiO$_2$ photo-anode under full sun illumination without the 425 nm cutoff filter is 0.5 mA cm$^{-2}$. When the filter is applied, almost no photocurrent is observed any longer, indicating that the UV radiation matching the TiO$_2$ energy gap $E_g$ is responsible for the previously observed photocurrent.
In the TiO$_2$/CdS/ZnS system, a saturated photocurrent density of 4.5 mA cm$^{-2}$ was obtained at $\approx$ 0.2 V versus reversible hydrogen electrode (RHE), comparable with a previous report for the same structure.[34] In the TiO$_2$/core@shell sample, we recorded a saturated photocurrent density of 2 mA cm$^{-2}$, which is boosted to 7.3 mA cm$^{-2}$ in the case of TiO$_2$/core@shell/CdS/ZnS. This value is higher than the sum of the pure TiO$_2$/core@shell (2 mA cm$^{-2}$) and TiO$_2$/CdS/ZnS (4.5 mA cm$^{-2}$), suggesting a cooperative action in the composite photoanode between the NIR QDs and the overcoating layer. PbS QDs improve the visible and NIR-light absorption (550–1000 nm), and the photogenerated electrons in the composite system can be effectively transferred to TiO$_2$ nanoparticles, with an increase of more than 3.5 times in the photocurrent density.

Figure 3. a) Photoelectron transfer pathways of PbS QDs through the band gap recombination (1); trap recombination (3); transfer to TiO$_2$ (2) or recombination with electrolyte (4). b) UV–vis–NIR absorption spectra of the bare TiO$_2$ film (TiO$_2$) and the TiO$_2$ films sensitized by CdS SILAR film (CdS), colloidal PbS@CdS QDs (TiO$_2$/core@shell) and colloidal PbS@CdS QDs followed by CdS SILAR treatment (TiO$_2$/core@shell/CdS). The inset table of (b) indicates the integrated absorption area for various thin films. The PL spectra of the sensitized photoanode before (TiO$_2$/core@shell) and after CdS SILAR coating (TiO$_2$/core@shell/CdS) are also shown in normalized form. The PL intensity of TiO$_2$/core@shell was multiplied by a factor of 52 to match the one of TiO$_2$/core@shell/CdS. Current density–potential dependence of the TiO$_2$ film c) and the TiO$_2$-QD film photoanode d) under irradiation with long-pass filter ($\lambda$ > 425 nm).
states of core@shell/CdS after ZnS treatment and/or the consumption of the sacrificial reagents (S$_2$$^-$$^-, $SO$_3$$^-$$^-$). These results suggest that the CdS shell can largely enhance the photostability of the PbS core, benefi ting from its isolation. Such a high stability under intense illumination offers good potential for combination with solar concentrator technology or solar thermal energy. In addition, the increasing temperature produced by solar thermal energy could decrease the necessary energy for electrolytic H$_2$ production. As a consequence, the electrolysis of water could be substantially enhanced.

To optimize the PEC cell, a TiO$_2$ blocking layer using commercial formulation (see the Supporting Information) was deposited between the mesoporous TiO$_2$ and FTO. A saturated photocurrent density of 11.2 mA cm$^{-2}$ was observed for 100 mW cm$^{-2}$ light intensity (Figure 4c), most likely due to improved compactness and uniformity of the blocking underlayer. Assuming a Faradaic efficiency of unity, the corresponding hydrogen generation rate is around 112 mL cm$^{-2}$ d$^{-1}$, which is 86% higher than the reported PEC system using SILAR PbS/CdS QDs (60 mL cm$^{-2}$ d$^{-1}$) and is unprecedented for NIR QD-based PEC for H$_2$ generation. To confirm the contribution of infrared photons to the photocurrent, the incident photon to current efficiency (IPCE) was derived by current–voltage measurements (see the Supporting Information and Figure 4d). The results are consistent with the broad NIR absorption of the QDs (Figure 3b), with signifi cant contribution to IPCE originating from the NIR region, up to 750 nm.

An external bias is still needed in our PEC system, and a substantial improvement can be expected in a stand-alone design (Figure 1a), namely, a photovoltaic absorber unit that can be used to provide the needed bias, so that solar energy is the only source to achieve electrocatalytic H$_2$ production. We applied a series of two homemade dye-sensitized solar cells (DSSCs), providing an external open circuit voltage of ≈1.4 V (Figure S5, Supporting Information), which can be used as an external bias. No signifi cant differences were found for the PEC behavior of the photoanode by using either the external bias supported or by using the solar cells, indicating that it is
possible to make a PEC for H₂ production using solar radiation as the only energy source.

In summary, we proposed an optimized heterostructured photoanode, to be applied in PEC cells, based on NIR-active core@shell QDs, further capped with a CdS layer and a passivating ZnS external shell. The hybrid heterostructured photoanode can produce a photocurrent density as high as 11.2 mA cm⁻² (equivalent to 112 mL cm⁻² d⁻¹ H₂) by cyclic voltammetry in a three-electrode configuration under 100 mW cm⁻² AM 1.5G illumination, being a good candidate architecture for solar hydrogen generation. Photocurrent measurements confirmed the contribution of colloidal NIR QDs and CdS layer to H₂ generation, extending light collection to the NIR region of the solar spectrum. Additionally, irradiation under both standard and high intensity illumination demonstrated the good stability of the system compared to other QD-based systems in the literature, suggesting the possibility of application in solar concentrators. We further demonstrated the possibility of integrating our PEC cell in a stand-alone device by coupling it with properly sized DSSCs to supply an external bias. Future development of water splitting by using NIR-active QDs can focus on the optimization of charge transfer by suitable engineering of the composition/thickness of the external shell and of the surface capping agents (application of halides can be a very promising route). Other strategies to increase the efficiency of PEC systems rely on tuning core size to further broaden light absorption to the NIR region and on the removal of surface traps (for instance, by controlled annealing). Proper capping is also a key strategy to increase the long-term stability of these systems, which is still an open issue.

Experimental Section

A detailed description of the experimental methods is available in the Supporting Information.

QD Synthesis: PbS QDs with diameter ≈3.0 nm were synthesized by hot injection method by using oleic acid (OA) as ligand.[43] PbS@CdS QDs were synthesized via a cation exchange method.[44] The PbS@CdS was washed by ethanol and redispersed in toluene. The redispersion–precipitation procedure was repeated twice.

TiO₂ Film Preparation: A thin and compact TiO₂ layer was spin coated on FTO-coated glass at 2000 rpm for 60 s by using the commercial solution Ti-NanoXide BL/SC (Solaronix) or using TiO₂ flat film precursor solution.[45] Then, the films were annealed in air at 500 °C for 30 min after drying and cooled down to room temperature. A 20 nm particle size paste named as 18NR-T (paste A, from Dyesol) and a blend of active anatase particles (~20 nm) and larger anatase scatter particles (up to 450 nm) paste (18 NR-AO, paste B, from Dyesol) were tape casted, forming a mesoporous film with thickness ~12 µm, as measured by contact profilometry.

EPD of the QDs on the TiO₂ Film: A pair of TiO₂ FTO slides were vertically immersed in the QDs solution and facing each other with a distance of 1 cm. A voltage of 200 V was applied for 120 min.[10] The samples were then rinsed several times with toluene and dried with N₂ at room temperature. Four monolayer (ML) CdS and 2 ML ZnS were subsequently deposited using SILAR.[14,16]

Characterization: The morphology of PbS@CdS QDs was characterized using a JEOL 2100F TEM. The composition of the films was measured on a freshly cleaved cross-section of the TiO₂ layers after EPD, using an Atmospheric Thin Window (ATW) EDX detector in an FEI Sirion high-resolution SEM system operated at 10–15 kV accelerating voltage (133 eV resolution at 5.9 keV). Absorption spectra were acquired with a Cary 5000 UV–Vis–NIR spectrophotometer (Varian) with a scan speed of 600 nm min⁻¹. Fluorescence spectra were taken with a Fluorolog-3 system (Horiba Jobin Yvon) and the excitation wavelength was set at 430 nm. The Pto-Cd ratio was determined by using ICP-OES (Perkin Elmer Model Optima 7300 DV). The PEC performance of the photoelectrodes was evaluated in a typical three-electrode configuration, with 0.25 M Na₂S and 0.35 M Na₂SO₃ as the sacrificial hole scavengers. All potentials measured with respect to Ag/AgCl were converted to the RHE scale.[19,47] The IPCE was derived from current–voltage measurements using different band-pass optical filters (see the Supporting Information).[47]

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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