High efficiency, Pt-free photoelectrochemical cells for solar hydrogen generation based on “giant” quantum dots

Rajesh Adhikari,1, Lei Jin,1, Fabiola Navarro-Pardo,2, Daniele Benetti,1, Bandar AlOtaibi,2, Srinivas Vanka,2, Haiguang Zhao,1,*, Zetian Mi,2, Alberto Vomiero,1,2,*, Federico Rosei,1,2,*

1. Introduction

Harvesting solar energy is a very attractive pathway to address, at least in part, the increasing demand for power [1–5]. Hydrogen (H2) has drawn considerable interest as a future energy carrier for its application as clean fuel and energy storage system. Photoelectrochemical (PEC) water splitting into H2 and oxygen using solar radiation is regarded as one of the most attractive approaches to produce H2 due to its simplicity, cost-effectiveness and environmental friendliness [1–4]. Current research focuses on developing efficient, stable, low-cost, sustainable and eco-friendly catalytic systems for H2 production. Metal-oxide semiconductors such as TiO2 and ZnO were demonstrated as promising photocatalysts for H2 evolution due to their efficient solar-to-H2 conversion and stability [6,7]. However, their activation requires UV-light (5% of incident solar spectrum) due to their large band gap (3.2 eV). Thanks to their unique optoelectronic properties and several striking features such as size-tunable band gap energy, multiple exciton generation, high absorption coefficient and broad absorption, including UV, visible and near infrared (NIR) radiation, quantum dots (QDs) have been recently developed to sensitize TiO2, providing a convenient heterostructured platform for PEC H2 production [8–12]. Various types of metal chalcogenide QDs including bare QDs or core@thin-shell QDs have been used for H2 production, such as CdS/TiO2, CdSe/TiO2, PbS@CdS/TiO2, CdS@CdSe/TiO2, CdSe@CdS/TiO2 [9–11,13–19]. While a photocurrent density of 16.2 mA/cm2 was recently demonstrated using a hybrid heterojunction [17], the limited stability of QDs during their post-purification, storage, PEC cell fabrication and operation is still a major challenge, due to their surface sensitivity to the chemical and photo-chemical/physical environment such as quenchers, light, moisture etc [20,21]. Such sensitivity induces the formation of surface defects that act as charge traps, leading to a decrease of overall device performance [20,21]. In addition, high efficiency PEC H2 production requires a strongly alkaline solution (pH ~ 13–14) [2] to minimize the over potential, which is an extreme challenge for QDs. Such environment leads to the formation of surface traps,
chemical decomposition of QDs and/or their photo corrosion especially under long-term solar illumination [8,9,16]. An elegant solution to address this challenge consists in using core@shell QDs, which possess significantly enhanced quantum yield (QY) and largely improved chemical, thermal and photo-physical stability, compared to pure QDs [9,12,22–24]. Among various types of core@shell systems, “giant” core@shell QDs [25] (in which the shell is very thick, from several up to 10 nm, and the core exhibits quantum confinement behavior) have been widely studied due to their superior chemical- and photo-stability compared to both pure QDs and thin-shell QDs [22,23,26,27]. A thicker shell can efficiently isolate the core material, insulating it from QD surface chemistry and the surrounding chemical environment [28,29]. More importantly, for suitably tailored compositions and electronic band structures, the lifetime of excitons generated in the core can be significantly longer than for pure and thin-shell QDs thanks to efficient leakage of the electrons in the shell, forming a quasi-type II band alignment [28,29]. For instance, in CdSe@CdS “giant” core@shell QDs [28,29], the electrons leak into the shell region and the holes are still confined within the core. The decrease in spatial overlap between electron and hole wave functions leads to a reduced recombination probability, resulting in a prolonged lifetime, up to ~50–100 ns [30]. Until now, only one article reported the application of “giant” core@shell CdSe@CdS QDs with a core size of 3.1 nm and shell thickness of ~6 nm for H2 production. However, a very low photocatalytic H2 generation rate was achieved, 15 times lower (0.06 mL/cm2/day under a light intensity of 8 mW/cm2) than dot-in-rod nanocrystals, due to the aggregation of QDs in the operating cell, reduction of electron density at the QD surface and consequent slow charge separation rate [30]. The optoelectronic properties of “giant” core@shell QDs are strongly dependent on the core size and shell thickness, which determine the final electronic band structure. Therefore, demonstrating the successful application of “giant” QDs suitable for high-performance operating PEC cells is still a challenge, and could represent a major improvement in the field, leading to the development of stable PEC systems for H2 generation [29].

Here we report a hybrid architecture based on a TiO2 mesoporous frame functionalized with colloidal “giant” core@shell CdSe@CdS QDs, targeting the fabrication of an efficient and stable H2 generation device. Two different core sizes were examined, keeping the shell thickness constant, to investigate the influence of core bandgap and band alignment on charge extraction and long-term stability. Electron transfer from QD to electron/hole scavengers was indirectly investigated by transient fluorescence spectroscopy. We obtained a saturated photocurrent density of ~10 mA/cm2 (equivalent to 100 mL/cm2/day of H2) in a PEC cell under one sun illumination (100 mW/cm2), which is the highest value yet reported based on colloidal “giant” core@shell CdSe@CdS QDs [30]. The as-prepared photoanode presented good stability, thanks to QD coating with an external protective ZnS shell, maintaining 65% of its initial current density after 2-h irradiation. In addition, we replaced the Pt cathode by using earth abundant and low-cost Cu2S nano-structured films, without any significant difference in the H2 generation rate. These results demonstrate the high potential of “giant” core@shell QDs and proper cell engineering in PEC photocatalysis for the development of efficient, highly stable, Pt-free, and cost-effective H2 production.

2. Results and discussion

2.1. Synthesis and characterization of “giant” core@shell QDs

CdSe QDs were synthesized via a hot injection approach [12]. The core size of the QDs can be simply modulated by changing the reaction time, as evidenced by their size-dependent photoluminescence (PL) peak position (Fig. S1) [12]. CdSe QDs with two sizes (radius ~1.85 nm, CdSe#1 and ~1.65 nm, CdSe#2) were used to synthesize “giant” CdSe@CdS core@shell QDs by a successive ionic layer adsorption and reaction (SILAR) [31] (Fig. S2, see for details the Experimental Section). XRD patterns (see Fig. S3) reveal that the CdSe has a zinc blende (ZB) crystal structure, as expected from the synthesis conditions. In the “giant” QDs, diffraction patterns are dominated by the Wurtzite (WZ) crystal structure of CdS, due to the larger volume of the CdS shell.
Table 1

<table>
<thead>
<tr>
<th>Sample</th>
<th>R (nm)</th>
<th>H (nm)</th>
<th>Abs (nm)</th>
<th>PL (nm)</th>
<th>QY (%)</th>
<th>Lifetime (ns)</th>
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<tbody>
<tr>
<td>CdSe#1</td>
<td>1.85</td>
<td>–</td>
<td>575</td>
<td>595</td>
<td>12 ± 1</td>
<td>22 ± 2</td>
</tr>
<tr>
<td>CdSe#2</td>
<td>1.65</td>
<td>–</td>
<td>550</td>
<td>568</td>
<td>10 ± 1</td>
<td>20 ± 2</td>
</tr>
<tr>
<td>Giant#1</td>
<td>1.85</td>
<td>3.2</td>
<td>630</td>
<td>647</td>
<td>50 ± 4</td>
<td>50 ± 3</td>
</tr>
<tr>
<td>Giant#2</td>
<td>1.65</td>
<td>4.3</td>
<td>600</td>
<td>618</td>
<td>40 ± 3</td>
<td>45 ± 3</td>
</tr>
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* R is the CdSe core radius.
* H is the CdS shell thickness.

Compared to the CdSe core (Fig. S3), in good agreement with results in literature [28,29], Fig. 1(a)–(f) shows the representative TEM images of bare CdSe and “giant” QDs. The “giant” QDs retain their regular uniform quasi-spherical shape after shell growth, a clear crystalline lattice and narrow size distribution (standard deviation σ < 10%, Fig. S4). HRTEM reveals high crystallinity with lattice fringes throughout the whole particle (Fig. 1(d)). The lattice distance (3.35 Å, Fig. 1(d)) corresponds to the (002) lattice spacing of the WZ crystal structure of CdS, consistent with the results from XRD.

The average core radius (R) and calculated shell thickness (H) are shown in Table 1. H equal to 3.2 nm corresponds to 10 monolayers of CdS (Giant#1) and H of 4.3 nm corresponds to 13 monolayers of CdS (Giant#2), consistent with the number of SILAR reaction cycles [31]. As seen in Fig. 1(e) and (f), the “giant” QDs are homogeneously dispersed at the surface of TiO2 nanoparticles. No QD aggregation is detected.

The absorption spectra of the as-synthesized QDs in toluene are presented in Fig. 1(g), which clearly shows the first excitonic peaks near 550 nm (CdSe), 630 nm (Giant#1), and 600 nm (Giant#2), respectively. Photoanode camera pictures in Fig. 1(h)–(j) refer to QD-sensitized TiO2 films via electrophoretic deposition (EPD), clearly confirming the successful deposition of the QDs on the TiO2 film. The thickness and final chemical composition of the as-prepared photoanode after 2 cycle ZnS coating via SILAR were further analyzed and are presented in Fig. S3. Scanning electron microscopy (SEM) cross-sectional imaging and related energy-dispersive X-ray spectroscopy (EDX) analysis (both line scan and 2D mapping) revealed the chemical composition of the anode (Fig. S5, Supporting information), further indicating the presence of QDs and ZnS in the anode and their relative molar ratio compared to Ti.

The absorption/PL peaks of bare QDs dispersed in toluene gradually red shift after coating with a CdS shell due to the leakage of electrons [28,32] from the core to the shell region (Fig. S6). Core@shell QDs also present a longer lifetime compared to the pure CdSe QDs (Fig. S7, Table 1), which indicates that the longer recombination lifetime is observed with respect to the bare QDs, due to the efficient spatial separation of electron and hole wave functions [28,32]. In addition, “giant” QDs show a typical QY of ~40–50% in toluene solution, which is ~4-fold higher than the pure CdSe QDs, indicating the improvement of surface passivation due to the efficient protection of the thicker shell [28,29]. More importantly, the “giant” QDs show a very good PL stability as evident from the QY (see Table 1) with respect to bare QDs: in fact, no significant variation was recorded in absorbance/PL spectra of “giant” QDs after-purification and during storage at room temperature after one year. The CdSe QDs without protective shell, instead, show very poor PL stability. They must be stored at low temperature (−20 to −4 °C) and we observed that repeated post-purification severely affects their PL. Photostability under UV exposure was also increased: after exposure of the QDs under intense UV light for 4 h, no significant change in the PL signal was observed for “giant” QDs, compared to 50% decrease in intensity for CdSe QDs. In addition, “giant” QDs were very stable during the EPD process peak shape and position unchanged, compared to bare CdSe QDs, in which a significant red shift of the PL peak and an obvious red tail was found, due to the presence of traps/defects (Fig. 2(a)). In addition, the as-prepared “giant” QD-sensitized TiO2 anodes show a very good optical stability (over 2 months) compared to bare QDs, in which QDs oxidize quickly (<1 day) after deposition into the TiO2, as confirmed by the rapid drop of PL intensity with the appearance of a trap-related peak in the lower wavelength region (Fig. S8) [33]. These results indicate that the “giant” core@shell QDs present very good optical stability due to the protection of the ultra-thick CdS shell [28,29], making them suitable for potential long-term solar-driven PEC H2 production.

2.2. Charge dynamics of QDs coupled with charge scavenger

In general, photogenerated exciton dissociation occurs at the QD/oxide interface. Due to electronic band bending, the resulting electrons are driven through TiO2 toward the contact and then transported to the Pt or Cu2S counter electrode, where H2 generation takes place [19]. Meanwhile, an aqueous solution containing 0.25 M Na2S and 0.35 M Na2SO3 (pH ~13) serves as sacrificial hole scavenger [9,10,19]. Fig. 2(e) represents a scheme of the overall integrated PEC cell architecture depicting the charge carrier generation, interfacial charge transport and redox reaction that occur during the PEC test (details of redox reactions are provided in Supporting information). The energy levels of TiO2, CdSe and CdS (obtained from the literature) are also shown in Fig. 2(e) [19,32].

We investigated the electron transfer rate through transient fluorescence spectroscopy. We considered pure or “giant” core@shell QDs with different core radius, R (1.85 nm and 1.65 nm), QDs deposited into TiO2 or ZrO2 mesoporous films, with or without addition of the electrolyte. Due to its electronic band alignment, we use ZrO2 as a benchmark system, in which charge injection does not occur, and PL degradation can be uniquely attributed to radiative/non-radiative exciton recombination. The electrolyte acts as hole scavenger in a system in which electron injection does not occur, to obtain a quantitative estimate of the hole transfer rate. The PL lifetime of the three samples was investigated under excitation at λexc=444 nm, by focusing on emission at the PL peaks (Fig. 2(b–d)) [34]. The fast PL decay profile of QDs in the presence of a charge scavenger with respect to the QDs in ZrO2 is most probably due to charge transfer from QDs to charge scavenger. Energy transfer can be realistically ruled out because there is no spectral overlap between the PL of QDs and absorption of TiO2 or electrolyte (absorption of TiO2 occurs in the UV, at wavelengths below 450 nm) [30,35]. Pure CdSe QDs are considered as a benchmark, to evaluate the effect of the shell on the charge injection rate. The representative fluorescence decay curves of the PL peak centered at 570 nm of pure CdSe QDs were well fitted by a three-component exponential decay. The three lifetimes of the QDs are consistent with the reported CdSe or CdSe/CdS QDs [30,32,37]. The intensity-weighted average lifetime <τ> is estimated by the following equation: [36]

\[ <τ> = \frac{a_1τ_1^2 + a_2τ_2^2 + a_3τ_3^2}{a_1τ_1 + a_2τ_2 + a_3τ_3} \]

where \( a_i \) (i = 1, 2, 3) are the coefficients of the fitting of PL decay and \( τ_i \) (i = 1, 2, 3) are the characteristic lifetimes, respectively. In all the analyzed samples, the presence of TiO2 or electrolyte induces a decrease in lifetime, compared to the QDs in ZrO2 film, pointing to an efficient charge transfer from QDs to electron/hole scavengers (Fig. 2(b–d)). For instance, the lifetime in Giant#2 sample (R/H: 1.65 nm/4.3 nm) decreases from 43 ns in ZrO2 to 30 ns in the electrolyte. Hole transfer time constants as fast as picoseconds in “giant” QDs were recently reported, with R equal to 1.95 nm and H
equal to 2.6 nm in the presence of ferrocene ligands [34]. The electron/hole transfer rate, \( K \) is calculated on the basis of the following equation: [35].

\[
K = \frac{1}{\tau_{QDs/e or h scavenger}} - \frac{1}{\tau_{QDs/ZrO_2}}
\]

Fig. 2. PL spectra of the different QDs in toluene, in sensitized TiO\(_2\) and ZrO\(_2\) film, with or without electrolyte (Ele). Transient PL spectra of (b) CdSe\#2, (c) Giant\#1 and (d) Giant\#2 QDs after deposited into TiO\(_2\), films, ZrO\(_2\) film and ZrO\(_2\) film in presence of electrolyte. The excitation wavelength is 444 nm. (e) Approximate energy levels (correspond to pH = 13) of TiO\(_2\), CdSe, CdS, together with related characteristic redox potentials. The band gap value of CdSe and CdS correspond to QD and bulk semiconductors respectively. The arrows indicate the electron and hole transfer process.

where \( \tau_{QDs/e or h scavenger} \) and \( \tau_{QDs/ZrO_2} \) are the average PL lifetimes of the QDs/TiO\(_2\) (or QDs/electrolyte) and QDs/ZrO\(_2\), respectively. The lifetime measurements in the QDs confirm that electron/hole transfer takes place from QDs to charge scavenger, and that there is no significant difference between electron \( (K_e) \) or hole \( (K_h) \) transfer rate (Table S1) in the pure QDs.
In “giant” QDs, instead, \((K_{et})\) and \((K_{ht})\) significantly differ. In fact, \((K_{et})\) is around 1.5 to 1.9-fold lower and \((K_{ht})\) is around 4-5-fold lower than in pure QDs. Decrease in both \((K_{et})\) and \((K_{ht})\) can be explained with a decrease in electron/hole density at the surface of QDs [30]. The larger decrease in \((K_{ht})\), compared to \((K_{et})\) can be explained on the basis of the electronic band structure formed in the “giant” QDs, which exhibit a quasi-type II band alignment (Fig. S9), where electrons are partially delocalized from the core to the shell, and holes are confined in the core [32,37]. As the excitons generated in the CdS shell can relax into the core on a time scale of picoseconds, there is no observed PL signal from the CdS shell even for very thick shells (over 4 nm). The recombination time for excitons generated in the CdSe core is very long in the “giant” CdSe@CdS QDs with respect to the bare CdSe QDs, as the hole in the core region needs to recombine with the electron indirectly, due to the leakage of electrons into the shell region [30]. These leaked electrons are long lived, which allows for efficient electron transfer from the QDs to the oxide, while, typically, holes remain confined in the core region and hole transfer from QDs to hole scavenger needs to tunnel through the thick CdS shell [30,32]. This effect is clearly seen in Table S1, in which \((K_{et})\) is between 1.5 and 2.5 times larger than \((K_{et})\). In general, with the increase in shell thickness, the physical barrier could slow down or even block the hole transfer [36]. In our case, the shell thickness is around ~4.4 nm and the energy levels are favorable for the hole transfer in the presence of hole scavengers. An efficient hole transfer rate can be achieved because of the faster hole transfer time (\(\sim 20\) ns) compared to exciton recombination time (\(\sim 40-50\) ns) [30,32]. As the electron scavenger of TiO\(_2\) nanoparticle and hole scavenger of Na\(_2\)S/Na\(_2\)SO\(_3\) are the same as those used in our PEC cell, our results indicate that efficient charge transfer is still possible by controlling the structure of core@shell in “giant” QDs, demonstrating the potential use of CdSe@CdS “giant” QDs in the PEC solar H\(_2\) generation.

### 2.3. PEC performance

The PEC activity of the TiO\(_2\)/QDs system toward the H\(_2\) evolution reaction (HER) was studied by using a three-electrode electrochemical cell configuration [19]. A set of linear-sweep voltammograms with respect to the (RHE) \((V_{\text{RHE}}=V_{\text{Ag/AgCl}}+0.197+\text{pH} \times 0.059)\) were recorded on different photoanodes in the dark and under simulated solar illumination (AM 1.5 G, 100 mW/cm\(^2\)). The photocurrent density in light gradually increases with the increase in voltage, until a saturated current density is obtained (Fig. 3(a)). Compared to bare QDs, the Giant#2 QDs with core size of 1.65 nm show a two-fold enhancement in the saturated photocurrent density as high as \(5\) mA/cm\(^2\) (Fig. 3(a)). The Giant#1 QDs with core size of 1.85 nm only show a ~4.4 nm and the energy levels are favorable for the hole transfer in the presence of hole scavengers. An efficient hole transfer rate can be achieved because of the faster hole transfer time (\(\sim 20\) ns) compared to exciton recombination time (\(\sim 40-50\) ns) [30,32]. As the electron scavenger of TiO\(_2\) nanoparticle and hole scavenger of Na\(_2\)S/Na\(_2\)SO\(_3\) are the same as those used in our PEC cell, our results indicate that efficient charge transfer is still possible by controlling the structure of core@shell in “giant” QDs, demonstrating the potential use of CdSe@CdS “giant” QDs in the PEC solar H\(_2\) generation.

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![Fig. 3. Photocurrent density-potential dependence of TiO\(_2\) sensitized by CdSe, Giant#1 (R/H 1.85/3.2), Giant#2 (R/H 1.65/4.3) (a) without and (b) with ZnS (2 cycles) in the dark and under AM 1.5 G illumination at 100 mW/cm\(^2\), employing Pt as the counter electrode. (c) Average photocurrent density for Giant#2 as a function of ZnS cycles. (d) Measured photocurrent density of Giant#2 (R/H 1.65/4.3), with different ZnS SILAR cycles and without ZnS, as a function of time at 0.2 V vs. RHE under 100 mW/cm\(^2\) illumination with AM 1.5 G filter.](image-url)
saturated photocurrent density of 1 mA/cm². An enhancement of the saturated photocurrent density can be observed for all the samples after capping with a ZnS layer (2 cycles) formed by SILAR (Fig. 3(b); Fig. S10(a) and (b)). The photocurrent density of Giant#2 reaches \( \approx 10 \text{ mA/cm}^2 \) (equivalent to \( \text{H}_2 \) generation rate of 60 mL/cm²/day) at 0.1 V vs RHE, which is the highest value ever achieved and 120 times higher than the previously reported value in “giant” CdSe@CdS QDs under the same conditions of light irradiation [30]. Typically, cadmium/lead chalcogenide QDs suffer from photodecomposition and/or photocorrosion in aqueous media. ZnS has been demonstrated as an efficient corrosion-resistant layer to protect the QDs during hydrogen evolution [8]. To investigate the possible current density contribution due to oxidation of anode materials, we analyzed the chemical bonding of Cd, S and Se before and after PEC measurements using X-ray photoelectron spectroscopy (XPS) on the sample TiO₂/Giant#2 QDs/ZnS (Fig. 4). Before the PEC, the spectrum of Zn 2p (Fig. 4(b)) shows two peaks at 1044.82 eV and 1021.79 eV with a splitting of 23.03 eV, indicating the Zn ion was mainly in the form of the state Zn(II) [38]. The S 2p (Fig. 4(c)) core level spectrum given in Fig. 4 indicates that the S 2p has a doublet structure which corresponds to S 2p 3/2 and 2p 1/2 orbitals of divalent sulfide ions (S²⁻) located at 161.23 and 162.23 eV [39]. The Cd 3d (Fig. 4(d)) core level XPS spectrum has two sharp peaks located at 404.79 eV and 411.55 eV, assigned to Cd 3d 5/2 and Cd 3d 3/2 respectively. A typical splitting energy of 6.7 eV was observed, consistent with the previously reported values for CdS [39,40]. After PEC, the valence states of all three elements present no significant change (Fig. 4), otherwise, additional peaks would be present due to the newly formed oxidative status of Cd, S, Se or Zn. No significant variation of chemical status is detected before and after PEC measurement, indicating no obvious oxidation, which is consistent with the unchanged color of the photoanode, as shown in the photo (Fig. 4(a)). This conclusion is further confirmed by cyclic voltammetry (CV) measurements, under identical conditions as PEC testing (Fig. S13). No response is detected in the range 0.6 to 1.0 eV, indicating that the origin of the obtained current is water reduction, other than oxidation of the anode.

\( \text{H}_2 \) evolution was further measured during the PEC measurement for Giant#2 (R/H 1.65/4.3), with two ZnS SILAR cycles. The produced \( \text{H}_2 \) gas was detected using a gas chromatograph (GC) equipped with a thermal conductivity detector. Argon gas was used as the carrier gas for GC analysis. The evolution of \( \text{H}_2 \) exhibits a nearly linear increase over time (Fig. 5). The \( \text{H}_2 \) evolution is also
calculated from the measured current (details in Supporting information). The measured and calculated H2 evolution are in very good agreement, and that the measured H2 value is around 80% of that calculated value based on the current (Fig. 5), which confirms that the obtained current is mainly due to the water reduction. The difference between the measured and calculated value of H2 might be due to gas leakage in our home-made prototype experimental system. Our enhanced photocurrent density indicates that the ZnS layer can significantly protect the QDs against the photodecomposition and/or photocorrosion. Since the photocurrent increased dramatically after the ZnS coating, ZnS can effectively suppress charge recombination at the surface trap states on the QDs and facilitate electron flow from QD to TiO2 (electron acceptor) [8,19,41], which is further confirmed by the enhanced electron transfer rate in the anode after ZnS coating (Fig. S11 and Table S1). A more detailed possible explanation is shown in the Supporting Information. The low photocurrent density in the CdSe QD-based PEC cell is quite possibly due to charge trapping, as the CdSe QDs are more sensitive to the surface chemical or photo environmental conditions [9,11,12,30]. The low photocurrent density of Giant#1 sample might be due to its lower driving force for H2 reduction reaction (Fig. S9) because of the lower energy gap of its core, compared to Giant#2, due to its larger core size, and of the alignment of its conduction band. For sample Giant#1 this means that the QDs geometry is not very favorable to fulfill thermodynamic and kinetic requirements to split water in generating H2 and O2 and the geometry must be carefully controlled during the synthesis of core@shell QDs.

The stability of the photoanodes was investigated under 100 mW/cm2 AM 1.5 G illumination in 0.25 M Na2S and 0.35 M Na2SO3 (pH ∼13) aqueous solution. A photocurrent (and mole of H2) versus time evolution of the PEC system at 0.2 V vs. RHE is shown in Fig. 3(c) (and Fig. 5, respectively). The photocurrent density in CdSe QDs without ZnS layer rapidly decays to ∼1.1 mA/cm2 within 20 min, only maintaining 54% of the initial photocurrent. For the giant QDs without ZnS coating, the photocurrent density only keeps 30% of its initial value after 20 min. Their poor PEC stability is due to the hole-induced self-oxidative decomposition of the metal chalcogenide [5,18]. Possible reactions during the entire PEC process are discussed in Supporting information. As the hole in the “giant” QDs needs to tunnel through the thicker CdS shell, the hole accumulation leads to the QDs surface oxidation. For the photoanode based on the bare CdSe QDs and covered by a two-cycle ZnS protective layer, the photocurrent density first decreased and then stabilized at ∼72% of its original value after 2 h, rendering a stabilized photocurrent density of 3.9 mA/cm2. These results indicate that the ZnS layer can significantly stabilize the QDs against surface oxidation under long-term irradiation and have comparable stability to the best values reported in the literature [18]. In the “giant” QD-based photoanode with 2 cycle ZnS coating, the photocurrent density gradually decreases during 2-h illumination. In 2 h, the current density decreases to 5.2 mA/cm2 (∼52% of its initial value). Further increasing the ZnS coating to 3 cycles can significantly improve the stability of the PEC cell. After 2-h illumination, the photocurrent still maintains 65% of its initial value (Fig. 3(c)). Based on the above observation, we speculate that specific numbers of ZnS SILAR cycles are required for the complete passivation of the giant QDs. Here, it is possible that 2-cycle ZnS coating did not cover the “giant” QDs completely as they have larger sizes compared to bare CdSe. This is consistent with the highest stability observed for 3 ZnS SILAR passivation cycles [42]. Therefore, it is necessary to optimize the number of ZnS SILAR treatments for the best performance in terms of stability and efficiency, which of course is determined based on the type and size of the QDs employed for PEC applications.

Another important observation relates to the counter electrode, which is usually made of Pt. The latter is rare, expensive and is known to be poisoned in the presence of sulfur-containing compounds, making it rapidly lose its catalytic properties [43,44]. For this reason, we replaced Pt with Cu2S, which was obtained by treating a sputter-deposited Cu thin film with polysulfide (details for preparation of Cu2S are described in Section 4). As seen in Fig. 6 (a), after polysulfide treatment, the cathode develops a nanostructured morphology with a high density of hexagonal nanoflakes (Inset in Fig. 4(a)). This morphology has been previously found and used in QD solar cells and has been related to improved charge collection from the electrolyte [35]. There are only a few reports of application of Cu2S in PEC for water splitting [45], and they are mainly obtained by growing Cu2S on brass by treatment with HCl and polysulfide [42,43]. According to EDX analysis, the atomic percent ratio of Cu:S was found to be 68:32, confirming a stoichiometry very close to Cu2S. No significant differences were found in terms of the PEC photocurrent-voltage behavior of the photoanode by using either Pt or Cu2S (Fig. 6(b) and Fig. S12), indicating that it is possible to construct a Pt-free PEC cell by employing a low-cost Cu2S cathode for H2 generation.

3. Conclusions and perspectives

In summary, we designed a “giant” CdSe@CdS QDs sensitized TiO2 photoanode architecture for efficient H2 production. Structural investigations confirmed the formation of “giant” QDs with thick shell. PL and charge transfer dynamics further confirmed that band structure engineering is possible by varying shell thickness during synthesis and such tuning in band alignment results in an efficient charge transfer in the operating system. In addition, this novel photoanode demonstrated excellent PEC properties with significant enhancement in photocurrent density. We also demonstrated the possibility of applying a Cu2S counter electrode, much cheaper than Pt, which proved to be very promising for the development of Pt-free PEC. Our work shows great potential for the development of “giant” QDs as light harvesting components with high efficiency and good stability for solar to H2 energy conversion, which in turn will pave the way for stable, low cost and efficient photoelectrode materials.

Fig. 5. H2 evolution of Giant#2 (R/H 1.65/43), with two ZnS SILAR cycles as a function of time at 0.2 V vs. RHE under 100 mW/cm2 illumination with AM 1.5 G filter. The evolution of H2 exhibits a nearly linear increase over time (solid red curve). H2 evolution is also calculated from the measured current (solid black curve).
4. Experimental section

4.1. Materials

Sulfur (100%), oleylamine (OLA) (technical grade, 70%), cadmium oxide (99%), oleic acid (OA), Rhodamine 6G and octadecene (ODE), selenium pellet (≥ 99.999%), trioctyl phosphine oxide (TOPO), trioctyl phosphine (TOP) (97%), hexamine nitrate hexahydrate (98%), sodium sulfide (Na2S), sodium hydroxide, sodium sulfate (Na2SO3), toluene, methanol, acetone, ethanol and isopropanol (IPA) were obtained from Sigma-Aldrich Inc. Ti-Nanoxide BL/SC was bought from Solaronix. Titania paste (code 18 NR-AO) consisting of a blend of active anatase particles (≈ 20 nm in diameter) and larger anatase scattering particles (up to 450 nm in diameter) was supplied by Dyesol (Queanbeyan, Australia). Fluorine doped tin oxide (FTO) coated glass substrates with sheet resistance 10 Ω/square were bought from Pilkington glasses. All chemicals were used as purchased.

4.2. QD synthesis

CdSe QDs of two different diameters (1.65 nm and 1.85 nm) were synthesized by using the hot injection approach [12] Typically, TOPO (1 g) and Cd-oleate (0.38 mmol, 1 mL) in 8 mL of ODE were purged by N2 at room temperature for 30 min. The reaction system was evacuated for 30 min at 100 °C, and then the temperature was raised to 300 °C. The mixture of TOP-Se (4 mmol, 4 mL), 3 mL of OLA, and 1 mL of ODE at room temperature was quickly injected into the Cd-oleate suspension under vigorous stirring. The reaction cell was quenched with cold water after injection. Ethanol (20 mL) was added, then the suspension was centrifuged, the supernatant was removed and, finally, the QDs were dispersed in toluene. As synthesized QDs hereafter are labeled as CdSe#1 for CdSe QDs having 1.85 nm in radius and CdSe#2 for 1.65 nm in radius, respectively.

Synthesis of CdSe@CdS giant QDs. Deposition of CdS layers on CdSe QDs was obtained by SILAR, similar to the procedure described in Ghosh et al. [31] Two different giant CdSe@CdS QDs were synthesized by growing CdS monolayers over the CdSe#1 and CdSe#2 cores. Typically, in a 100 mL round-bottom flask, OLA (5 mL), ODE (5 mL) and CdSe QDs (≈ 2 × 10⁻⁷ mol in hexane) were degassed at 110 °C for 30 min. The reaction flask was re-stored with N2 and the temperature was further raised to 240 °C with stirring. The Cd(OA)2 dispersed in ODE (0.25 mL, 0.2 M) was added dropwise and the mixture allowed to react for 2.5 h, followed by dropwise addition of 0.2 M sulfur in ODE with same volume. The shell was further annealed for 10 min. All subsequent shells were annealed at 240 °C for ~ 10 min following the injection of sulfur and ~ 2.5 h following dropwise addition of the Cd(OA)2 in ODE. Sulfur/Cd(OA)2 addition volumes for shell addition cycles 1–13 were as follows: 0.25, 0.36, 0.49, 0.63, 0.8, 0.98, 1.18, 1.41, 1.66, 1.92, 2.2, 2.51 and 2.8 mL, respectively. The reaction was cooled to room temperature using cold water. Ethanol was added, then the suspension was centrifuged and the supernatant was removed. The QDs were then dispersed in toluene for further characterization and labeled hereafter as Giant#1 for CdSe#1 with 10 cycle CdS QDs and Giant#2 for CdSe#2 with 13 cycle CdS QDs, respectively (details of the core@shell size are presented in Table 1).

4.3. TiO2 film preparation

FTO glass substrates were cleaned with triton, a mixture of methanol, acetone, IPA (1:1:2), thoroughly rinsed with deionized water and dried in a N2 stream. A thin and compact TiO2 layer was spin coated on FTO glass substrates at 2000 r.p.m. for 30 s by using the solution Ti-Nanoxide BL/SC (Solaronix), followed by annealing in air at 500 °C for 30 min and cooled down to room temperature. Subsequently a commercial TiO2 paste, a blend of small anatase particles (~ 20 nm in diameter) and larger anatase particles (up to 450 nm in diameter) paste (18 NR-AO), was deposited on top of the compact TiO2 layer by tape casting and dried in air for 15 min. The photoanodes were then fired on a hot plate at 120 °C for 6 min. A second layer of 18 NR-AO paste was then deposited on the top, following the same procedure. The electrodes were subsequently sintered according to the following temperature profile: 325 °C/5 min, 375 °C/5 min, 450 °C/15 min and 500 °C/30 min, forming films with total thickness ~14 μm, as measured by contact profilometry and SEM cross-sectional analysis [19,33].

4.4. ZrO2 film preparation

ZrO2 films were prepared by using commercial ZrO2 nanopowder (Aldrich, particle size ~ 100 nm). A single layer ZrO2 film was deposited on FTO glass by tape casting and then annealed in
air at 450 °C for 30 min. We studied the electron transfer rate by using transient fluorescence spectroscopy on QDs deposited into TiO₂ or ZrO₂ mesoporous films. The ZrO₂/QDs film serves as a benchmark sample, in which the energy levels do not favor electron/hole transfer. The hole transfer rate in this experiment was monitored by immersing the ZrO₂/QDs film into the Na₂S/Na₂SO₃ solution (pH ~ 13) as a hole scavenger.

4.5. EPD of the QDs on the TiO₂ film and ZnS coating

As prepared TiO₂ films on FTO substrate were vertically immersed in the QD dispersion in such a way that the deposited films were facing each other. The distance between them was adjusted at 1 cm and a direct current (DC) bias of 200 V was applied for 120 min [19,33]. To wash off unbounded QDs after the EPD process, the samples were rinsed several times with toluene and dried with N₂ at room temperature. The ZnS capping layer was formed using the SILAR process, as follows. In a typical SILAR deposition cycle, Zn²⁺ ions were deposited from an ethanolic 0.1 M solution of Zn(NO₃)₂ [19]. The sulfide source was 0.1 M solution of Na₂S in water. A single SILAR cycle consisted of 1 min of dip-coating the TiO₂ working electrode into the metal precursors (Zn²⁺), and subsequently into the sulfide solutions. After each bath, the photoanode was thoroughly rinsed by immersing it in the corresponding solvent (ethanol or water) respectively, to remove the chemical residuals from the surface and then drying with a N₂ gun. Two SILAR cycles were applied to form the capping ZnS layer.

4.6. Cu₂S cathode fabrication

The cathode was fabricated by sputtering 35 nm of Cu on an FTO-coated glass substrate using a copper target in a Cressington 208HR High Resolution Sputter Coater, equipped with a thickness controller [35]. The process was conducted under Argon, at 80 mA and 0.01 mbar using a rotating disk, the distance between the target and the samples was 15 cm and the thickness was achieved by using five coating layers in multiples of 7 nm. Cu coated FTO glasses were subsequently immersed in an aqueous polysulfide electrolyte (aqueous 1 M Na₂S, 1 M S and 0.1 M NaOH) for 10 min to form Cu₂S [35]. Afterwards, the polysulfide excess was removed and washed by dipping in 10 mL of distilled water for 2 min. The samples were dried under the fume cupboard for 10 min.

4.7. Characterization

Small angle X-ray diffraction (XRD) of extensively purified QDs was carried out with a Philips X’pert diffractometer using a Cu Kα辐射 source (λ=0.15418 nm). High resolution transmission electron microscopy (HRTEM) images of QDs and QD-sensitized TiO₂ film were collected by using a JEOL 2100F TEM. The morphology of Cu₂S/FTO was characterized using JSM-7401F scanning electron microscope (SEM) and the chemical composition of Cu₂S was characterized by energy-dispersive X-ray spectroscopy (EDS) analysis.

Absorption spectra were acquired with a Cary 5000 UV–vis-NIR spectrophotometer (Varian) with a scan speed of 600 nm/min. Fluorescence spectra were taken with a Fluorolog®-3 system (Horiba Jobin Yvon) and the excitation wavelength was set at 430 nm. The PL lifetime of QDs in solution or in film was measured using a time-correlated single-photon counting (TCSPC) mode with a 444 nm laser. The decay curves were fitted using a three-component exponential decay.

XPS was performed in a VG Escalab 220i-XL equipped with hemispherical analyzer, applying a Twin Anode X-Ray Source, on sample Giant#2 (2 cycle of ZnS coating) before and after 30-min PEC measurement under 1 Sun. The spectra acquisition parameters (channel exposition, number of scans, analyzer parameters, etc.) were selected to provide the best energy resolution and signal/noise ratio. Zn 2p, S 2p and Cd 3d photoelectron lines were acquired during the experiment. The C 1 s peak (BE=284.8 eV) was used as an internal reference line to accurately determine the positions of other spectral lines. The fine structure of the photoelectron lines was treated using Casa XPS software (2.3.15 Version).

The PEC performance of the photoelectrodes was evaluated in a typical three-electrode configuration, consisting of a QD-TiO₂ thick film working electrode, a Pt or Cu₂S counter electrode, and a saturated Ag/AgCl reference electrode [29,33]. A Cu wire was used to connect FTO with the outer circuit. Insulating epoxy resin was used to cover the sample’s surface except for the active area, to avoid any direct contact between the electrolyte and the conducting back-contact and/or the connecting wire. Subsequently the sample was fully immersed in the electrolyte containing 0.25 M Na₂S and 0.35 M Na₂SO₃ (pH ~ 13) as the sacrificial hole scavenger. All potentials, measured with respect to the reference electrode of Ag/AgCl during the PEC measurements, were converted to scale according to the following equation \( V_{\text{RHE}} = V_{\text{Ag/AgCl}} + 0.197 + \text{pH} \times (0.059) \) [37]. The photocurrent was measured using a 150 W Xenon lamp as light source with an AM 1.5 G filter. The sample was placed at a distance of 2 cm from the lamp case (~7 cm far from actual bulb). Prior to each measurement, light intensity monitored by a thermopile and adjusted to ~100 mW/cm². All the current versus potential measurements were carried out at a 20 mV/s sweep rate.

H₂ evolution was measured during the PEC experiment. The produced H₂ gas was detected using a GC (Shimadzu GC-8A) equipped with a thermal conductivity detector. Argon gas was used as the carrier gas for GC analysis. An air tight syringe was used for sampling from the vacuum sealed chamber.

The area of various samples ranges between 0.25 and 0.40 cm². For an individual sample, the area of anode with area of 0.25 ± 0.02 cm² show the photocurrent. Considering the number of parameters and constraints such as the area of the FTO glass, the TiO₂ film formed on FTO via tape casting, the deposition of QDs on the film by EPD, and device fabrication for the PEC experiment, 0.40 cm² was the maximum area we could achieve in our laboratory [46,47].

CV was carried out at 20 mV/s for one or two cycles for the Giant#2 samples with or without ZnS coating under dark condition. The electrolyte used was a solution containing 0.25 M Na₂S and 0.35 M Na₂SO₃. All potentials, measured with respect to the reference electrode of Ag/AgCl, were converted to the reversible hydrogen electrode (RHE) scale.

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Appendix A. Supplementary material

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References