Heavy metal-free, near-infrared colloidal quantum dots for efficient photoelectrochemical hydrogen generation

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\begin{abstract}
Photoelectrochemical (PEC) hydrogen generation based on colloidal quantum dots (QDs) is very promising because of its high solar energy to fuel conversion efficiency and low fabrication costs. However, its commercial development is hindered by various challenges, including the widespread use of toxic heavy metal–based QDs as sensitizers. We report an environmentally friendly, high efficiency PEC device in which the photoanode consists of a mesoporous TiO\textsubscript{2} film sensitized with heavy metal-free, near-infrared (NIR) colloidal CuInSe\textsubscript{2}/ZnS (CISeS) QDs. To reduce surface-related traps, we grew an ultrathin ZnS shell on the CISeS core QDs by cation exchange. The PEC cell based on this core/shell CISeS/ZnS QDs exhibits suppressed charge recombination and a saturated photocurrent density of ~5.3 mA/cm\textsuperscript{2} under one sun illumination (AM 1.5 G, 100 mW/cm\textsuperscript{2}). In addition, the as-prepared PEC device shows an outstanding stability, exhibiting a drop of only 23% after 9 h illumination. The success in using such core/shell CISeS/ZnS QDs paves the way to realize environment-friendly, high efficiency and cost-effective PEC devices for hydrogen production.
\end{abstract}

\section{1. Introduction}

The efficient use of solar energy for the sustainable production of clean fuels is an attractive approach to address future global energy needs. In this perspective, photoelectrochemical (PEC) hydrogen (H\textsubscript{2}) generation, which uses sunlight to produce hydrogen from water, represents a major opportunity to address this challenge [1–6]. A PEC device consists of a semiconductor photoanode, a counter electrode and an electrolyte. Electron-hole pair generation occurs when the energy of the incident photon is larger than the band gap of the electrode and an electrolyte. Electron-hole pair generation occurs when the energy of the incident photon is larger than the band gap of the semiconductor photoanode, consequently leading to hole oxidation and electron reduction. One of the most promising approaches to enhance light harvesting of TiO\textsubscript{2} is sensitization using colloidal quantum dots (QDs) [7–21]. Colloidal QDs can be easily prepared and their size/shape and chemical composition can be tuned to the NIR region (wavelength up to 2000 nm) [22,23]. Colloidal QDs can be easily controlled to obtain a wide range of optical properties, including band gaps and absorption spectra. Colloidal QDs are excellent sensitizers for PEC devices because they can absorb light in the visible/NIR regions [22,23]. Colloidal QDs have been used as photoanodes (or photocathodes) for hydrogen generation [8–16]. Among these, some wide-band-gap metal oxides (e.g. TiO\textsubscript{2}) have been demonstrated as efficient, stable and inexpensive anode materials for efficient PEC solar-to-fuel generation [17–21]. However, their large band gap (~3.2 eV for TiO\textsubscript{2}) limits absorption to the ultraviolet (UV) part of solar radiation (merely 3–5% of sunlight power density), thus preventing photoconversion in the visible and near-infrared (NIR) regions [22,23]. Sensitization using colloidal quantum dots (QDs) is one of the most promising approaches to enhance light harvesting of TiO\textsubscript{2} in the visible/NIR range, mainly due to the wide absorption of QDs, which is a good match for the solar spectrum. For example, NIR lead sulfide (PbS) QDs have a typical absorption spectrum ranging from the UV–visible to the NIR region (wavelength up to 2000 nm) [24]. More importantly, the absorption spectrum and bandgap of QDs can be easily controlled by tuning their size/shape and chemical composition [25,26]. CdS, CdSe, PbS QDs and their composite heterostructures, such as core/shell PbS/CdS QDs, or CdSe/CdS QDs have been used to sensitize TiO\textsubscript{2} for efficient PEC hydrogen generation, yielding a maximum photon-to-electron conversion efficiency of 2–3%.

\begin{acknowledgments}
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\end{acknowledgments}

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http://dx.doi.org/10.1016/j.nanoen.2016.11.053
Received 16 September 2016; Received in revised form 13 November 2016; Accepted 25 November 2016
Available online 27 November 2016
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current density in excess of 10 mA/cm² under one sun illumination (AM 1.5 G, 100 mW/cm²) [27–30]. However, heavy metals (such as Cd and Pb) are often used in PEC devices, either for QD synthesis or for anode post-treatment, thus limiting their potential applications due to environmental and health concerns. Environmentally friendly QDs (so-called green QDs), such as CuInS₂, CuInSe₂ and CuInSe₂/CdS (CISEs) etc. have been recently widely investigated for applications in energy conversion and storage. The latter exhibit outstanding properties, such as: i) simple, large-scale, cost-effective synthesis; ii) heavy metal-free QDs (without toxic elements, such as Cd, Hg and Pb etc.); iii) size- and chemical composition-dependent optoelectronic properties, including wide absorption spectrum (covering the range from UV to visible and NIR region), high absorption coefficients, efficient charge transfer rate and high charge mobility, etc.[31]; iv) favorable electronic band alignment for water reduction [31–37]. To date, few papers describe heavy metal-free NIR colloidal QDs for PEC hydrogen generation and the obtained photocurrent density is still very low (~2 mA/cm²), because of defects-induced charge trapping [38,39]. Higher currents (~18 mA/cm²) were achieved using a complicated and expensive molecular beam epitaxy approach to produce non-colloidal NIR QDs for water reduction [10]. In addition, although core/shell structured CISEs/ZnS QDs have been synthesized, there is still no report describing their use for H₂ production. It is still very challenging to achieve high efficiency PEC solar-driven hydrogen production using heavy metal-free, simple and cost-effective NIR colloidal QDs, because it is difficult to reduce surface traps and suppress charge recombination in these systems.

Here we report the fabrication of a PEC device by using NIR colloidal CISEs QDs sensitized mesoporous TiO₂ film as photoanode. The QDs were deposited into mesoporous TiO₂ film by electrophoretic deposition (EPD) to achieve intimate contact between QDs and TiO₂ nanoparticles. Subsequently, two layers of ZnS prepared via a successive ionic layer adsorption and reaction (SILAR) method were overcoated on the TiO₂/CISEs anode to prevent photocorrosion. The fabricated PEC system based on the TiO₂/CISEs/ZnS photoanode exhibited a saturated photocurrent density of ~2.57 mA/cm² under standard AM 1.5 G solar irradiation (100 mW/cm²). To suppress the surface traps of bare CISEs QDs, an ultrathin ZnS shell was grown on core CISEs QDs via cation exchange at three reaction temperatures (50, 100 and 150 °C). It was demonstrated that the CISEs QDs with Zn treatment at 100 °C exhibited optimal optical properties in terms of improved photoluminescence (PL) intensity and prolonged lifetime, resulting in strong reduction of surface defects/traps. The optimized PEC cell using this core/shell CISEs/ZnS QDs (with Zn treatment at 100 °C, denoted as Zn-CISEs QDs) showed reduced charge recombination, leading to largely improved stability and saturated photocurrent density as high as ~5.35 mA/cm² compared to bare CISEs QDs. This is the highest reported photocurrent density up to date for a heavy metal-free, NIR colloidal QD based PEC device for hydrogen generation. In addition, the Zn-CISEs QDs-based photoanode also exhibits very good stability. These results suggest that core/shell CISEs/ZnS QDs may be used to realize high efficiency, stable, low-cost and green solar driven PEC hydrogen production.

2. Results and discussion

CISEs QDs were synthesized via a thermal decomposition approach [40]. As shown in Fig. 1a, the CISEs QDs exhibit a triangular projected shape in TEM images, suggesting a pyramidal shape with average size of 5.64 nm (~0.77 nm), where the size is defined as the height of the projected triangles, consistent with the reported structure in similar reaction conditions [40].

As Zn surface treatments are effective to passivate the bare CISEs QDs to reduce surface defects [33], we used a cation exchange approach to form a thin inorganic ZnS protecting shell on CISEs QDs. In parallel, for comparison, we also synthesized CdS capped CISEs QDs via a cation exchange approach. The core/shell CISEs/ZnS (with Zn treatment at 100 °C, denoted as Zn-CISEs) and CISEs/CdS (denoted as Cd-CISEs) QDs displayed similar pyramidal structure and size distribution, indicating that the Zn and Cd surface treatment does not change the overall size/structure [33]. A high-resolution transmission electron microscopy (HRTEM) image of a single Zn-CISEs QD is shown in Fig. 1(d). The measured lattice spacing of 0.327 nm lies between 0.319 nm (indexed to the (112) plane of pure CuInS₂) and 0.335 nm (indexed to the (112) plane of pure CuInS₂) that is consistent with the (112) plane of alloyed CISEs QDs, demonstrating the alloy nature of CISEs. This conclusion is also consistent with X-ray diffraction (XRD) patterns (Fig. S2a). HRTEM investigations do not allow to identify a clear interface between the CISEs core and ZnS shell, possibly due to the ultra-thin layer of ZnS (~0.1 nm) [33].

Generally, to effectively connect QDs and TiO₂, the QDs are deposited into the TiO₂ film by various techniques, such as bi-linker technique or EPD approach [41]. For bi-linker technique, various types of bifunctional molecule can efficiently link the QD to the surface of TiO₂, and the electron transfer rate at the QD/TiO₂ interface has been demonstrated to be mainly associated with the linker length, showing an exponential decay of electron transfer rate as a function of increasing length due to tunneling of electrons through the linker molecule [42,43]. In this work, the surface capping ligands of QDs are 1-dodecanethiol (DDT) and oleylamine or oleic acid with length of ~2 nm [44]. Compared to linker approach, EPD is an efficient method that leads to shrink or removal of the surface capping ligands, which results in close contact of QDs and TiO₂ for enhanced electron transfer rate, enhancing the performance of relevant QDs-based PEC devices [28,41]. Therefore, to realize high performance PEC devices, we further deposited the as-synthesized CISEs or Zn(Cd)–CISEs QDs into the mesoporous TiO₂ film by EPD.

The heterostructure of TiO₂/Zn-CISEs is displayed in Fig. 1e, which shows that the QDs are uniformly attached onto the surface of TiO₂ nanoparticles without any noticeable agglomeration. The HRTEM image of QDs/TiO₂ (Fig. 1f) demonstrates the highly intimate connection between QDs and TiO₂ nanoparticles, suggesting the possibility of a fast electron transfer rate from QDs to TiO₂, thereby improving the performance of QDs-sensitized PEC device due to the decrease of exciton recombination. In addition, there is no visible structural and/or lattice change during EPD (Fig. 1f, Fig. S2b) with respect to the colloidal Zn-CISEs QDs before EPD (Fig. 1d). Similar hybrid structures were also found for the QDs of CISEs and Cd-CISEs in the TiO₂ film. These results indicate that EPD is an efficient approach to directly deposit QDs onto the TiO₂ film with good connection [41].

The presence and distribution of QDs inside the film were further confirmed by energy-dispersive X-ray spectroscopy (EDS). Cross-section scanning electron microscope (SEM) imaging and relevant EDS mapping of the Zn-CISEs QDs-sensitized photoanode are reported in Fig. 2. The thickness of the mesoporous TiO₂ film with transparent and scattering layer is estimated to be ~13.2 μm. The Zn-CISEs QDs were found to be uniformly dispersed in the TiO₂ film. The relative mass concentration of Zn-CISEs QDs with respect to TiO₂ is reported in Fig. S3 and Table S1.

X-ray photoelectron spectroscopy (XPS) analysis (Fig. S4 and Table S2) was used to study the surface chemical bonding in the TiO₂/ Zn(Cd)–CISEs anode. A high resolution XPS (HRXPS) spectrum of Zn 2p and Cd 3d confirms the presence of Zn and Cd elements with proportion of ~23% and 14% (atomic concentration) when calculated with cationic Cu and In components. Using this Zn (or Cd) concentration and the diameter of core/shell QD from TEM images, the thickness of the shell was calculated by assuming a homogeneous shell/core coverage. The estimated shell thickness is around 0.12 nm, consistent with HRTEM results and the designed thickness of ~0.1 nm [37]. In addition, in the HRXPS spectra (Fig. S4b and d), there is no obvious peak (Zn or Cd dangling bonds) located at low binding energies, which is usually an indication of surface defects/traps during the anode
preparation, indicating that the EPD process does not introduce significant traps/defects [41].

The as-prepared QDs show the typical absorption spectrum of the CISeS material, covering the broad wavelength range from ~400 nm up to 1000 nm (Fig. 3a) [40]. No significant change in the absorption spectra was recorded after cation exchange (Fig. 3a), consistent with the ultrathin shell thickness. The bandgap of Zn-CISeS, Cd-CISeS and CISeS QDs was calculated to be ~1.49, 1.48 and 1.51 eV, according to Tauc plots (inset in Fig. 3a), respectively. These values are in good agreement with the bandgap derived from the PL peak (1.46 eV), taking into account the Stokes shift between the first excitonic absorption peak and the emission peak (Fig. S6) [37].

As the heavy metal of Cd in Cd-CISeS QDs could lead to possible health and environment issues, we further investigated and highlighted the environment-friendly Zn-CISeS QDs. The thickness of ZnS shell on core CISeS QDs was tuned by controlling the Zn-treatment temperatures (i.e. 50, 100 and 150 °C) based on identical reaction time (10 min). The ZnS shell thickness was estimated based on the overall size of QDs measured by TEM and the molar ratio of Zn/(Cu+In) calculated by EDS (Fig. S7) or XPS analysis (Fig. S4), by assuming a uniform coverage of the shell on the QD core. Shell thicknesses of ~0.04, 0.12 and 0.2 nm were obtained at 50, 100 and 150 °C, respectively. As shown in Fig. 3c, the CISeS QDs before and after Zn treatment (with increasing temperatures) exhibit similar absorption spectra with slight blue-shift, consistent with the increasing thickness of ZnS and decreasing core radius of CISeS QDs [45]. The PL spectra of CISeS QDs after Zn surface treatment at various temperatures show no significant change of PL peak positions, but largely improved PL.

Fig. 1. TEM images of (a) CISeS QDs; (b) Cd-CISeS and (c) Zn-CISeS QDs showing analogous pyramidal structure and nearly same sizes. Inset images of (a), (b) and (c) display schematic diagrams of QDs structures of CISeS, Cd-CISeS and Zn-CISeS, respectively. (d) HRTEM image of an individual Zn-CISeS QD with lattice spacing of 0.327 nm. (e) TEM image of TiO2/Zn-CISeS heterostructure with uniform dispersion of Zn-CISeS QDs (white dashed circle presents a single QD on the surface of TiO2). (f) HRTEM of TiO2/single Zn-CISeS QD heterostructure (higher magnification image of the white line circle in (e)).

Fig. 2. (a) Cross-sectional SEM image of Zn-CISeS QDs-sensitized photoanode. EDS mapping analysis of all the elements in relevant TiO2/Zn-CISeS/ZnS electrode including (b) Ti, (c) O, (d) Zn, (e) Cu, (f) In, (g) Se and (h) S.
Fig. 3. (a) Absorption spectra of CISeS in toluene before and after Zn (Cd) treatment. The inset image exhibits the extrapolation of Tauc plots ((αhν)² versus photon energy (hν)). (b) Band alignment and schematic diagram of Zn-CISeS QDs-sensitized photoanode. Absorption and PL spectra (c) and lifetime (d) of CISeS QDs with Zn treatment at different temperatures. (e) UPS full spectrum of the Zn-CISeS QDs deposited on mesoporous TiO₂. Corresponding high resolution UPS spectrum of (f) high binding energy cut-off (determining Fermi level) and (g) low binding energy cut-off (determining valence band maximum).
intensity as compared to bare CISeS QDs due to improved surface passivation. Consistently, CISeS QDs with Zn treatment exhibit prolonged lifetime compared to bare QDs (Fig. 3d). The detailed information of PL spectra and lifetime of these CISeS QDs with different Zn treatment temperatures were summarized in Table S4, confirming that the Zn-CISeS treated at 100 °C show the highest PL intensity and the longest PL lifetime. This demonstrates that surface traps/defects on CISeS QDs were successfully suppressed by growing a very thin ZnS shell at 100 °C [33].

Ultraviolet photoelectron spectroscopy (UPS) with He I radiation (21.21 eV) was further used to estimate the Fermi level and maximum valance band energy level of various QDs and TiO2 [46,47]. The UPS analysis of the Zn-CISeS QDs/TiO2 sample is illustrated in Fig. 3e-g. Fig. 3e reports the UPS full spectrum of TiO2/Zn-CISeS and Fig. 3f shows a high binding energy cut-off of 16.9 eV, which determines the Fermi level of Zn-CISeS QDs on TiO2 located at ~4.31 eV with respect to the vacuum level. The high resolution UPS spectrum of low binding energy cut-off from 0 to 4 eV is displayed in Fig. 3g, suggesting that the valence band maximum is at ~5.71 eV with respect to vacuum. According to the band gap of Zn-CISeS QDs derived from their absorption spectra (Fig. 3a), the calculated conduction band minimum is ~4.22 eV. The precise band alignment and schematic diagram of Zn-CISeS QDs-sensitized photoanode for PEC cell is illustrated in Fig. 3b. The Zn-CISeS QDs is able to form a type II band alignment with TiO2 that is favorable for the dissociation of photoexcited carriers at the QDs/TiO2 interface, where photogenerated holes oxide the sacrificial agent (Na2S and Na2SO3) in the electrolyte and electrons are injected into TiO2 and are subsequently collected by the FTO electrode. Finally, they migrate to the Pt counter electrode for water reduction [48]. The band alignment and schematic investigations of CISeS and Cd-CISeS QDs-modified TiO2 are shown in Fig. S8, both presenting favorable band energy levels for water reduction.

Fig. 4 displays the PEC performance of CISeS, Zn-CISeS and Cd-CISeS QDs-sensitized photoanodes in dark, under continuous and chopped illumination using a typical three electrode configuration with working electrode (as-fabricated photoanodes), Ag/AgCl (saturated with KCl) reference electrode and Pt counter electrode. Prior to PEC measurements, an additional inorganic ZnS layer is deposited on the TiO2/QDs by SILAR following the EPD process, to prevent photocorrosion of the electrodes [28]. As shown in Fig. 4a, under dark conditions (without any illumination), no significant current density is produced (> 0.4 V); while a saturated photocurrent density of ~2.57 mA/cm2 is obtained at a potential of 0.6 V versus the reversible hydrogen electrode (RHE) under standard AM 1.5 G illumination (100 mW/cm2, ~30 cm from the sun simulator to PEC cell) for the TiO2/CISeS/ZnS system. This value is comparable with a NIR PbS QDs/TiO2 based anode and 8-fold higher than the similar CISeS QDs based cathode for hydrogen generation [28,38]. To choose the proper number of SILAR cycles, various ZnS layer cycles (1, 2, 4 and 6) were performed on the same TiO2/CISeS anode prepared with identical QDs solution and EPD time (15 min). The relevant J-V curves are shown in Fig. S10, indicating that the 2-cycle ZnS SILAR deposition is prone to...
inhibit photocorrosion and maximize PEC performance.

However, the stability of this bare QDs based PEC cell is still limited. After 2 h of continuous illumination under one sun, the photocurrent density dropped to 38% of its initial value. Generally, QDs are sensitive to the surface defects created during device operation that act as charge traps, leading to a low photocurrent efficiency and limited long-term stability [49,50]. A promising solution to address this challenge consists in using core/shell structured QDs, which have shown significantly enhanced photocurrent and stability in a QDs based PEC system, such as CdTe/CdS or PbS/CdS core/shell QDs based PEC system [28,51]. Recently, core-shell ClSeS/ZnS(CdS) QDs have been explored as potential light absorbers in QDs based solar cells, due to their excellent properties such as reduced surface traps, suppressed charge recombination and enhanced photonic and chemical stability [33,37]. The efficiency of a solar cell is largely improved by using core/shell QDs even with a very thin shell layer (in general, less than 0.1 nm) of ZnS or CdS [33,37]. Herein, we further use the core/shell structured ClSeS/Zn(Cd)S QDs as photosensitizers to fabricate the PEC cell (detailed information for fabrication of core/shell QDs is shown in Supporting Information). In the following, all the anodes were fabricated using the TiO2 film containing one transparent layer and one scattering layer and the anodes after QDs deposition were further capped with 2 cycles of ZnS. The as-prepared TiO2/Zn-ClSeS/ZnS (Fig. 4b) and TiO2/Cd-ClSeS/ZnS (Fig. 4e) photoanodes exhibit a large enhancement of saturated photocurrent density of ~4.27 mA/cm2 and ~4.62 mA/cm2 respectively compared to bare QDs, elucidating the effective passivation of surface traps on ClSeS QDs and suppression of charge recombination in Zn-ClSeS and Cd-ClSeS QDs-sensitized photoelectrodes.

In the following, we focus on using Zn-ClSeS QDs because they are green NIR QDs with a comparable photocurrent density to that of toxic Cd-ClSeS QDs. In addition to the TiO2/Zn-ClSeS (100 °C Zn treatment)/ZnS photoanode with photocurrent density of ~4.27 mA/cm2, the TiO2/Zn-ClSeS (50 °C)/ZnS photovoltaic cell shows a saturated photocurrent density of ~2.57 mA/cm2. This indicates that the ZnS thin shell of ClSeS QDs with Zn treatment at 50 °C suppresses the surface defects/traps on ClSeS QDs. In contrast, the TiO2/Zn-ClSeS (150 °C)/ZnS photoanode has a very low saturated photocurrent density of ~1.75 mA/cm2 (Fig. S11b), suggesting that the ClSeS QDs with Zn treatment at 150 °C created a relatively thick ZnS shell on ClSeS QDs that hinders electron/hole transfer due to the wide band gap of ZnS [52]. Detailed information on the PEC performance of core ClSeS QDs with different ZnS shell thicknesses are summarized in Table S5. It is concluded that the optimal ZnS shell on ClSeS QDs can efficiently suppress the surface defects/traps and lead to improved device performance, while relatively thick ZnS shell results in a large tunneling barrier due to its wide band gap and electronic band positioning, inhibiting electron/hole transfer [52]. Further optimization of Zn-ClSeS (100 °C) based PEC cell including the improved TiO2 film uniformity and QDs concentration in film lead to a maximum photocurrent density of ~5.3 mA/cm2 (Fig. S12). In previous work using heavy metal-free, NIR colloidal bare ClSeS and core/shell ZnClSeS QDs as sensitizers, the ClSeS QDs-sensitized photoanode led to a saturated photocurrent density of ~2.57 mA/cm2 upon exposure to standard AM 1.5 G solar illumination (100 mW/cm2, ~30 cm from sun simulator to PEC cell). To reduce surface traps of core ClSeS QDs, we added an inorganic ZnS surface passivation by cation exchange. The QDs were effectively deposited into the mesoporous TiO2 film by EPD, showing intimate connection between QDs and TiO2 nanoparticles. UPS spectra show appropriate band alignment of the QDs and TiO2 and the as-fabricated core/shell Zn-ClSeS QDs-sensitized photoanode demonstrates efficient charge separation and transport, leading to a saturated photocurrent density of ~5.3 mA/cm2 (the highest value to date for environment-friendly, NIR colloidal QDs for hydrogen generation). The stability of the TiO2/Zn-ClSeS/ZnS system is comparable to the best reported anode based on QDs [56,57]. Overall the Zn-ClSeS QDs are a promising system for environment-friendly, cost-effective, robust and highly efficient solar driven hydrogen production, paving the way for broader and deeper investigations of green QDs for high performance PEC systems. Future developments should focus on tuning the Cd composition, such as CuSnSeS and CuZnSeS QDs to promote electron transport, engineering the shell structure (ZnSe or ZnS etc.) and shell thickness to enhance the efficiency and stability of PEC devices. In addition, other types of heavy metal-free QDs such as AgInS2, AgInTe2, AgS/ZnS and InP/ZnS etc. with absorption and/or PL spectrum covering the UV-visible-NIR region are promising candidates for solar energy applications, which may be employed to fabricate QDs-sensitized photoelectrodes for high efficiency solar hydrogen production.

3. Conclusions and perspectives

In summary, we fabricated and characterized photoanodes which use heavy metal-free, NIR colloidal bare ClSeS and core/shell ZnClSeS QDs as sensitizers. The ClSeS QDs-sensitized photoanode led to a saturated photocurrent density of ~2.57 mA/cm2 upon exposure to standard AM 1.5 G solar illumination (100 mW/cm2, ~30 cm from sun simulator to PEC cell). To reduce surface traps of core ClSeS QDs, we added an inorganic ZnS surface passivation by cation exchange. The QDs were effectively deposited into the mesoporous TiO2 film by EPD, showing intimate connection between QDs and TiO2 nanoparticles. UPS spectra show appropriate band alignment of the QDs and TiO2 and the as-fabricated core/shell Zn-ClSeS QDs-sensitized photoanode demonstrates efficient charge separation and transport, leading to a saturated photocurrent density of ~5.3 mA/cm2 (the highest value to date for environment-friendly, NIR colloidal QDs for hydrogen generation). The stability of the TiO2/Zn-ClSeS/ZnS system is comparable to the best reported anode based on QDs [56,57]. Overall the Zn-ClSeS QDs are a promising system for environment-friendly, cost-effective, robust and highly efficient solar driven hydrogen production, paving the way for broader and deeper investigations of green QDs for high performance PEC systems. Future developments should focus on tuning the Cd composition, such as CuSnSeS and CuZnSeS QDs to promote electron transport, engineering the shell structure (ZnSe or ZnS etc.) and shell thickness to enhance the efficiency and stability of PEC devices. In addition, other types of heavy metal-free QDs such as AgInS2, AgInTe2, AgS/ZnS and InP/ZnS etc. with absorption and/or PL spectrum covering the UV-visible-NIR region are promising candidates for solar energy applications, which may be employed to fabricate QDs-sensitized photoelectrodes for high efficiency solar hydrogen production.

4. Experimental section

4.1. Materials

Copper(I) iodide (CuI), indium(III) acetate (In(Ac)3), 1-dodecanethiol (DDT), oleylamine (OLA), selenium (Se) powder, oleic acid (OA), 1-octadecene (ODE), cadmium oxide (CdO), zinc acetate dehydrate (Zn(Ac)2×2H2O), Triton™ X-100, acetone, methanol, ethanol, toluene, sodium sulfide nonahydrate (Na2S×9H2O) and sodium sulfate (Na2SO3) were purchased from Sigma-Aldrich. Ti-Nanoxide BL/SC was obtained from Solaronix. Titania paste containing ~20 nm nanoparticles in diameter (18 NR-T) and a mixture of active anatase particles (~20 nm) and larger anatase scatter particles (~450 nm) paste (18 NR-500) were purchased from Dyesol (Queanbeyan, Australia). All chemi-

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4.2. CuInSe$_2$$_{1-x}$ quantum dots (CISEs QDs) synthesis

CISEs QDs were synthesized according to the method described by Hunter McDaniel et al. with slight modifications [40]. Typically, CuI (1 mmol) and In(acac)$_3$ (1 mmol) were mixed with DDT (5 mL) and OLA (1 mL) in a 50 mL flask and degassed under vacuum at 90 °C for 30 min. The temperature was then raised to 140 °C and maintained for 15 min to fully dissolve the precursors. Meanwhile, OLA /DDT-Se solution (2 M) was prepared by mixing Se (2 mmol) powder with OLA (1.5 mL) and DDT (0.5 mL) at room temperature under N$_2$ flow. Subsequently, the reaction mixture was heated to 210 °C and OLA /DDT-Se solution (2 M) was injected dropwise via syringe. The temperature was maintained at 210 °C for 10 min to conduct QD nucleation, and then the flask was heated quickly to a growth temperature of 235 °C, maintained for 20 min. The reaction was then quenched with cold water. The as-synthesized QDs were precipitated with ethanol, centrifuged to eliminate unreacted precursors, and re-dispersed in toluene. The purification process was repeated at least twice and the final product was dispersed in toluene and stored at −10 °C for further characterization.

4.3. Zn and Cd-treated CISEs QDs

Zn and Cd-treated CISEs QDs were synthesized following a modified cation exchange procedure [33]. Typically, for CISEs QDs treated with Zn$^{2+}$, 0.25 M Zn-oleate solution was first prepared by dissolving 3 mmol of OA and 1 mmol of Zn(acac)$_2$ in 4 mL of ODE. Five milliliters of the QDs re-dispersed in ODE were then added to 4 mL of 0.25 M Zn-oleate solution and the reaction mixture was heated to 50 (100 or 150 °C) and maintained for 10 min. For cation exchange with Cd$^{2+}$, 0.25 M Cd-oleate was prepared by dissolving 3 mmol of OA and 1 mmol of CdO in 4 mL of ODE. Five milliliters of the QDs in ODE were then added to 4 mL of 0.25 M Cd-oleate solution and the reaction mixture was heated to 65 °C for 5 min. The reaction was then quenched with cold water and the as-synthesized QDs were precipitated with ethanol, centrifuged to eliminate unreacted precursors, and re-dispersed in toluene. The purification process was repeated at least twice and the final product was dispersed in toluene and stored at −10 °C for further characterization.

4.4. Preparation of TiO$_2$ films

Cleaning Fluorine doped tin oxide (FTO) glass substrates (Pilkington TEC 8, sheet resistance 6–9 Ω/square) was conducted ultrasonically for 15 min in Triton™ X-100, acetone and ethanol, respectively, followed by deionized (DI) water rinse and dried in N$_2$ gaseous flow. The cleaned FTO glass substrates were then treated in a UV-ozone cleaner for 10 min to further eliminate surface organic contaminations. Subsequently, a blocking layer of TiO$_2$ was deposited on FTO substrates by spin coating at 6000 r.p.m. for 30 s utilizing the commercial solution Ti-Nanoxide BL/SC. After the drying process was completed, the as-deposited TiO$_2$ films were annealed at 500 °C on the photoanode in our three-electrode system, before each measurement, a Si reference diode (Sciencetech) was used to adjust the potentials versus the reversible hydrogen electrode (RHE) in electrochemical measurements by an electrochemical workstation (CHI-760D) equipped with a twin Al source and subsequently analyzed by CasaXPS software. Ultraviolet photoelectron spectroscopy (UPS) measurements were performed on a VG ESCALAB 3 Mark II high vacuum system, and EDS mapping was carried out in a FEI Sirion high resolution scanning electron microscope (HRSEM) system equipped with an Atmospheric Thin Window (ATW) energy dispersive X-ray spectroscopy (EDS) detector.

A three-electrode system consisting of a Pt counter electrode, an Ag/AgCl reference electrode (saturated with KCl) and an as-fabricated working electrode was used to assess the PEC performance of the QD-sensitized photoanode. The photoanode was then fully dipped into the electrolyte containing 0.25 M Na$_2$S and 0.35 M Na$_2$SO$_3$ (pH=12.5), which served as sacrificial hole scavenger to prevent QDs photocorrosion. The following formula $V_{RHE} = V_{Ag/AgCl} + 0.1976 + pH \times (0.059)$ was used to convert the measured potentials (versus Ag/AgCl) to the potentials versus the reversible hydrogen electrode (RHE) in electrochemical measurements by an electrochemical workstation (CHI-760D with 20 mV/s sweep rate). Photocurrent density-voltage (J-V) curves were measured under simulated sunlight (1 sun=AM 1.5 G, 100 mW/cm$^2$) employing a Compact Solar Simulator Class AAA (Sciencetech SLB-300A). To guarantee the standard 1 Sun illumination (100 mW/cm$^2$) on the photoanode in our three-electrode system, before each measurement, a Si reference diode (Sciencetech) was used to adjust the distance (typically, the distance between the reactor and the lamp is around 20 cm) between photoanode and solar simulator before each measurement. The distance from sun simulator to PEC cell is around 30 cm.

Acknowledgements

We acknowledge funding from the Natural Science and Engineering Research Council of Canada (NSERC, Discovery Grants) and the...
Supplementary data associated with this article can be found in the online version at doi:10.1016/j.nano.2016.11.053.

References

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