Eco-friendly Colloidal Quantum Dots for Efficient Photoelectrochemical Hydrogen Generation

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Abstract. Colloidal quantum dots (QDs) are very promising for fabrication of photoelectrochemical (PEC) cells to conduct hydrogen generation thanks to their low cost and tunable size/composition-dependent optoelectronic properties. However, most of current QDs-based PEC systems consist of highly toxic elements such as lead (Pb) and cadmium (Cd) that hinders their real-life usage and commercial purpose. It is hence significant to fabricate PEC cells by using non-toxic QDs as light absorbers. Herein, we synthesized eco-friendly colloidal CuInS₂ (CIS) QDs via a simple one-pot method and as-prepared CIS QDs show good light absorption in visible region. These QDs were utilized them to sensitize mesoporous TiO₂ film as the photoanode for fabrication of an efficient PEC device. The CIS QDs-based PEC cell shows a saturated photocurrent density as high as ~0.8 mA/cm² under one sun illumination (AM 1.5 G, 100 mW/cm²), suggesting that CIS QDs are favorable candidates to achieve low-cost, environment-friendly and high-performance PEC devices for hydrogen production.

1. Introduction
Conventional fossil fuels are becoming limited due to the increasing energy requirement with rapidly growing economy and population [1]. To address this issue, solar energy has attracted tremendous attention as it is the most abundant and sustainable energy on the earth [2]. It is therefore significant to convert solar energy into chemical fuels that are storable, renewable and transportable. In this perspective, hydrogen energy stands out as it is a clean chemical fuel and can be generated from earth-abundant source of water. Hence, using solar energy to efficiently conduct water splitting for hydrogen generation is an ideal and renewable approach to address the future global energy demand [3].

Semiconductor-based solar-driven photoelectrochemical (PEC) water splitting has been demonstrated as one of the available approaches to produce hydrogen since the pioneering work by Fujishima et al., which reported that semiconductor TiO₂ could be used as light harvester to produce hydrogen under the illumination of ultraviolet (UV) light [4]. While the large band gap (~3.2 eV) of TiO₂ limits its light absorption to the small part (ultraviolet region) of solar spectrum, hindering the efficient photocconversion in the visible and near-infrared (NIR) regions [5]. In order to effectively harness solar energy, colloidal quantum dots (QDs) such as CdS, CdSe, PbS etc. have been used to sensitize wide band gap TiO₂ for PEC hydrogen production as these QDs exhibit size-tunable optical properties that could extend the light absorption into the visible and NIR part of the solar spectrum.

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Meanwhile, QDs generally possess appropriate band alignment with TiO2 that results in efficient charge carriers separation and transfer at their interface [6].

However, currently, most of widely employed QDs in materials synthesis and device fabrication of PEC cells consist of heavy metals (such as Cd and Pb) [7, 8], thus leading to the environmental and health issues that limit their possible commercial applications. Therefore, QDs with comparable properties but less toxic composition are favorable. Eco-friendly QDs such as CuInS2 (CIS) QDs a direct band gap of 1.5 eV have been widely utilized for solar energy applications [9]. These QDs possess lots of advantages: 1) low-cost, large area and facile synthesis; 2) large absorption coefficients and broad light absorption; 3) tunable photoluminescence (PL) emission covering visible to NIR region. 4) high PL quantum yield and very long PL lifetime; 5) efficient charge separation/transfer and appropriate band alignment for hydrogen production. These outstanding merits render them as good candidates for optoelectronic devices such as PEC devices [10].

2. Experimental section

2.1. CIS QDs Synthesis

CIS QDs were synthesized via the method reported by Klimov’s group [11]. Typically, copper(I) iodide (1 mmol), indium acetate (1 mmol) and 1-dodecanethiol (DDT, 5 mL) were loaded in a three-necked flask (50 mL). The resulting mixture is then degassed and purged under vacuum. Subsequently, the temperature is raised to 100 °C for 10 min with vigorous magnetic stirring to completely dissolve the precursors. The reaction mixture is then heated to 230 °C to conduct the growth of CIS QDs. The flask was quenched with cold water when the color of reaction mixture turned to red. As-synthesized QDs were precipitated with addition of ethanol, centrifuged to remove redundant precursors, and re-dispersed in toluene.

2.2. Fabrication and Characterization of QDs-based PEC Device

Fluorine doped tin oxide (FTO) glass substrates were cleaned ultrasonically with acetone, ethanol and deionized (DI) water and then dried in N2 gaseous flow. A compact TiO2 blocking layer was subsequently deposited on FTO substrates by spin coating at 6000 r.p.m. for 30 s utilizing the commercial solution (Ti-Nanoxide BL/SC). The as-prepared TiO2 films were annealed at 500 °C on a hot plate for 30 min and naturally cooled down to room temperature. Then, titania paste containing ~20 nm nanoparticles in diameter (18 NR-T) was tape-casted on FTO substrates and fully spread out for 15 min. As-prepared electrodes were dried at 120 °C for 6 min and sintered at 500 °C for 30 min in a furnace and cooled down to room temperature.

CIS QDs were deposited into mesoporous TiO2 film by using electrophoretic deposition (EPD) technique. A pair of TiO2 FTO substrates were put in diluted CIS QDs solution with a distance of ~1 cm. An applied voltage of 150 V was supplied between these two electrodes for 60 min. Toluene is used to rinse the as-deposited TiO2/FTO electrodes to remove the absorbed QDs at the end of the EPD process. Successive ionic layer adsorption and reaction (SILAR) method was then used to deposit two-monolayer ZnS on as-deposited TiO2/QDs electrode to prevent photocorrosion. Finally, the photoanode’s surface (excluding the active area, which is around 0.2 cm²) was sealed with epoxy resin to complete device fabrication.

The PEC performance of the QDs-sensitized photoanode is evaluated by a typical three-electrode configuration with an Ag/AgCl reference electrode (saturated with KCl), a Pt counter electrode and an as-fabricated working electrode. The photoanode was then completely dipped into the electrolyte containing sacrificial hole scavenger (0.25 M Na2S and 0.35 M Na2SO3 (pH~13)). The measured potentials (versus Ag/AgCl) via an electrochemical workstation (PARSTAT 3000A-DX with 20 mV/s sweep rate) were converted to the potentials versus the reversible hydrogen electrode (RHE) by using the following formula V_{RHE}=V_{Ag/AgCl}+0.1976+ph<0.059. Photoreponse of as-fabricated photoanodes were measured under simulated sunlight (1 sun=AM 1.5 G, 100 mW/cm²) employing a Class AAA Solar Simulator (SAN-EI, XES-50S1). A Si reference diode was used to determine the
distance between photoelectrode and solar simulator before each measurement for calibration of the standard 1 Sun illumination (100 mW/cm²).

3. Results and discussion
The optical properties of as-synthesized CIS QDs dispersed in toluene are shown in Figure 1 and 2. Figure 1 exhibits the broad absorption spectra of CIS QDs with absorption band edge extended to ~620 nm, indicating the excellent light absorption of CIS QDs, especially in visible region. This visible light absorption is comparable to other widely used toxic QDs such as CdS and CdSe QDs [12], while the CIS QDs possess the intrinsically non-toxic nature, which is encouraging for their real-life applications.

![Figure 1. UV-vis spectra of CIS QDs dispersed in toluene.](image)

As-prepared CIS QDs show clearly bright red-light emission under illumination of UV light (Inset image in Figure 2), demonstrating that these QDs can be excited to produce charge carriers (i.e. electrons and holes) which leads to radiative recombination for red-light emission [10]. To further verify this conclusion, PL spectra of CIS QDs is carried out and exhibited in Figure 2, presenting a PL emission peak at ~660 nm that lies between the wavelength range of red light (i.e. 620 to 750 nm). All these optical characterizations suggest that CIS QDs are capable to harvest visible light and provide photogenerated charge carriers, which are favorable for optoelectronic devices.

![Figure 2. PL spectra of CIS QDs. Inset image exhibits the bright red-light emission under illumination of UV light.](image)
These eco-friendly CIS QDs were subsequently deposited into mesoporous TiO₂ via EPD approach to fabricate QDs-sensitized photoanode in a PEC device for solar-driven hydrogen production. The estimated band alignment and schematic diagram of PEC cells based on CIS QDs-sensitized photoanode is displayed in Figure 3. The formation of CIS QDs and TiO₂ creates a type II band alignment which is beneficial for the dissociation of photoexcited carriers. Upon illumination, the CIS QDs are excited to generate electron-hole pairs that are separated at the interface of QDs/TiO₂, then the photogenerated holes oxide the sacrificial agent (Na₂S and Na₂SO₃) in the electrolyte and the electrons are injected into TiO₂. Subsequently, these electrons were collected by the conductive FTO and finally transfer to the Pt counter electrode for water reduction and hydrogen generation [13].

![Figure 3. Band alignment and schematic diagram of CIS QDs-sensitized photoanode.](image)

The photoresponse of CIS QDs-sensitized photoanodes under chopped illumination using a typical three electrode system with working electrode (as-fabricated photoelectrodes), Ag/AgCl (saturated with KCl) reference electrode and Pt counter electrode is shown in Figure 4. To prevent the photocorrosion of as-fabricated photoanodes, before PEC measurements, two monolayers of additionally inorganic ZnS are deposited on TiO₂/QDs via SILAR method following the EPD process. As exhibited in Figure 4, the optical image of CIS QDs-modified photoelectrode shows the uniform color of QDs in the TiO₂ film, indicating the effective sensitization of these photoanodes via CIS QDs.

![Figure 4. Photocurrent density as a function of bias potential (versus RHE) for the CIS QDs-sensitized photoanodes under chopped AM 1.5G one-sun (100 mW/cm²) illumination. Inset image shows the optical image of CIS QDs-modified photoelectrode.](image)
More importantly, under chopped standard AM 1.5G illumination (100 mW/cm²), a saturated photocurrent density of ~0.8 mA/cm² is attained at a potential of 0.6 V versus the reversible hydrogen electrode (RHE) for the CIS QDs-sensitized photoanodes. This value is much higher than previous work by using CuInSeS QDs for PEC device, showing saturated photocurrent of ~0.3 mA/cm² [14]. We confirmed that the photoresponse is derived from CIS QDs rather than bare TiO₂ electrode which only exhibits a saturated photocurrent density of ~0.25 mA/cm² [15], which is much less than the ~0.8 mA/cm² of our QDs-decorated sample.

4. Conclusion
In summary, we synthesized eco-friendly colloidal CIS QDs by using a facile one-step approach. Optical properties of these QDs indicate the outstanding visible light absorption and ability to create photoexcited charge carriers. As-prepared “green” CIS QDs were used as photosensitizers to fabricate photoanodes via EPD method. The heterostructured CIS QDs/TiO₂ photoelectrodes show efficient charge separation and transport, leading to a saturated photocurrent density of ~0.8 mA/cm² under standard 100 mW/cm² AM 1.5G solar illumination. These results indicate that CIS QDs are promising candidates for low-cost, environment-friendly, and high efficiency solar-driven PEC hydrogen generation. Future optimizations include tuning the composition of QDs and/or constructing core/shell structure (e.g. CIS/ZnS QDs) to improve the charge carriers transport, suppress the charge recombination of QDs and enhance device stability. Moreover, other eco-friendly QDs such as AgInS₂, AgInSe₂ and CuInTeSe QDs etc. with broad light absorption can be used to fabricate high efficiency QDs-based PEC device for hydrogen generation.

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