Near-Infrared, Heavy Metal-Free Colloidal “Giant” Core/Shell Quantum Dots

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“Giant” core/shell quantum dots (g-QDs) are a promising class of materials for future optoelectronic technologies due to their superior chemical- and photostability compared to bare QDs and core/thin shell QDs. However, inadequate light absorption in the visible and near-infrared (NIR) region and frequent use of toxic heavy metals (e.g., Cd and Pb) are still major challenges for most g-QDs (e.g., CdSe/CdS) synthesized to date. The synthesis of NIR, heavy metal-free, Zn-treated spherical CuInSe2/CuInS2 g-QDs is reported using the sequential cation exchange method. These g-QDs exhibit tunable NIR optical absorption and photoluminescence (PL) properties. Transient fluorescence spectroscopy shows prolonged lifetime with increasing shell thickness, indicating the formation of quasi type-II band alignment, which is further confirmed by simulations. As a proof-of-concept, as-synthesized g-QDs are used to sensitize TiO2 as a photoanode in a photoelectrochemical (PEC) cell, demonstrating an efficient and stable PEC system. These results pave the way toward synthesizing NIR heavy metal-free g-QDs, which are very promising components of future optoelectronic technologies.

1. Introduction

Colloidal quantum dots (QDs) are very promising nanoscale systems with size/composition dependent optical and electronic properties. Such systems are attractive building blocks for optoelectronic devices due to their simple, cost-effective solution-based synthetic process. Emerging applications include QD-sensitized solar cells (QDSCs), light-emitting diodes (LEDs), luminescent solar concentrators (LSCs), photodetectors, and photoelectrochemical (PEC) cells for hydrogen production, among others.[1]

In recent years, the performance of QD-based optoelectronic devices has improved dramatically. For example, the certified power conversion efficiency (PCE) of QDSCs reached 10.6% in solid-state and 11.6% in liquid-junction devices.[2] Improving the performance of QD-based technologies is still hindered by several challenges, related, for example, to limited stability. Generally, QDs are very sensitive to surface chemistry conditions (oxidation, ligand damage, etc.) and chemical environment such as light, oxygen, moisture, and temperature.[3] Such sensitivity induces the formation of surface traps/defects, resulting in decreased chemical and optical stability of QDs during their synthesis and subsequently device fabrication and operation.[3,4] Core/shell QD architectures present an opportunity to address this challenge, as they exploit a robust inorganic shell which efficiently passivates the surface of QDs and reduces surface-related traps/defects. The shell leads to an enhanced quantum yield (QY), suppressed photobleaching and photoblinking, and significantly improved chemical, thermal, and photochemical/physical stability compared to organic ligand-capped bare QDs.[5]

Among various kinds of core/shell QDs, “giant” core/shell QDs (g-QDs) exhibit outstanding optoelectronic properties, which are largely attributed to their very thick shell (with thickness from several nanometers up to tens of nanometers).[6] In such g-QD system, the core material can be efficiently isolated from the QD’s surface and ambient chemical environment, thanks to the thick shell, leading to outstanding chemical- and photostability with respect to bare QDs and core/thin shell QDs (in general, the shell thickness of thin-shell QDs is less than 1.5 nm).[7] The very thick shell dominates the absorption spectrum of g-QDs and is able to further improve their optical properties.[8] For instance, conventional g-QDs consisting of a relatively small CdSe core and a very thick CdS shell have been shown to strongly suppress Auger recombination, improve QY, and prolong multieexciton lifetime.[6,8,9] In the g-QD systems, with appropriate tunable electronic band structure and chemical composition, the electrons are able to leak into the shell...
region, while the holes are still confined within the core region. The efficient leakage of electrons in the shell region leads to a longer lifetime of charge carriers, forming a quasi or full type-II band alignment in g-QDs.\textsuperscript{[8–10]} For example, in InP/CdS g-QDs, the wave functions of electrons and holes are spatially separated to form a fully type-II band structure.\textsuperscript{[10]} Due to these features, g-QD heterostructures such as CdSe/CdS g-QDs/MoS\textsubscript{2} (drop casting g-QDs on MoS\textsubscript{2} films grown by chemical vapor deposition) and CdSe/CdS g-QDs/Ag (drop the g-QD solution on Ag films prepared via molecular beam epitaxy) have recently emerged, showing promise for applications in energy technologies including photodetectors and LEDs.\textsuperscript{[11]}

Until now, various types of g-QDs have been reported, showing potential for both biomedical devices, e.g., fluorescent biosensors and bioimaging and optoelectronic devices including LSCs, LEDs, and PEC cells, among others.\textsuperscript{[8–10,12]} Examples include CdSe/CdS, CdSe/ZnSe, ZnSe/CdS, PbS/CdS, PbSe/CdSe, and InP/CdS. For instance, CdSe/CdS and CdSe/Zn\textsubscript{1−x}Cd\textsubscript{x}S g-QDs have been used to fabricate high performance LEDs\textsuperscript{[9a,12]} and CdSe/CdS g-QDs have been exploited to achieve large-area high-efficiency LSCs.\textsuperscript{[12c]}. Recently, CdSe/CdS g-QDs were employed to sensitize TiO\textsubscript{2} and the as-fabricated photoanode exhibited high efficiency PEC hydrogen production with good stability with respect to stable rate of H\textsubscript{2} generation during cell operation.\textsuperscript{[13]}

However, despite their great potential for high performance devices, g-QDs, still present several major limitations: (i) the available shell materials such as CdS, ZnS, ZnSe possess dominant light absorption in the ultraviolet (UV) region due to their relatively large bandgap (for instance, CdS, 2.49 eV), and the inadequate light absorption in the visible and near-infrared (NIR) region limits their use in energy technologies; (ii) the typical PL spectrum falls in the visible range (for instance, CdSe/CdS g-QDs exhibit the PL peak at less than 700 nm) which limits their application in the NIR window, for example, in NIR LEDs and deep-tissue NIR imaging; (iii) most of g-QDs currently in use contain heavy metals (such as Pb, Cd, etc.), hindering their prospective commercial developments due to health and environmental concerns, especially for biomedical applications (bioimaging and biosensors). In this perspective, heavy metal-free g-QDs such as CuInSe\textsubscript{2}/CuInS\textsubscript{2} core/shell g-QDs with absorption/PL spectrum spanning across the UV−visible−NIR regions are very promising for potential applications in both NIR biomedical and solar energy technologies such as, e.g., fluorescent biosensors, LSCs, PEC H\textsubscript{2} production.

Due to the difficulty in controlling simultaneously the reactivity of multiple precursors during the synthesis of ternary CuInS(Se) systems, recently a sequential cation exchange method was developed to grow CuInSe\textsubscript{2}/CuInS\textsubscript{2} dots in rod heterostructures.\textsuperscript{[14]} Here, we followed a similar procedure to synthesize NIR, heavy metal-free, CuInSe\textsubscript{2}/CuInS\textsubscript{2} core/shell g-QDs (CIS/CIS g-QDs) by a sequential cation exchange approach using CdSe/CdS core/shell g-QDs as initial templates.

The morphology of the as-synthesized CIS/CIS g-QDs confirms the formation of a thick CuInS\textsubscript{2} shell on the core QDs of CuInSe\textsubscript{2}. Unlike the irregular shape of typical directly synthesized CuInS(Se) QDs, we accurately controlled the spherical shape by the cation exchange method. Selected area electron diffraction (SAED) and X-ray powder diffraction (XRD) patterns indicate that the crystal structure of as-synthesized g-QDs is the wurtzite (WZ) phase, which is dominated by the shell material (i.e., CuInS\textsubscript{2}). Inductively coupled plasma optical emission spectrometry (ICP-OES) measurements indicate the full exchange of heavy metal of Cd from initial CdSe/CdS g-QD template to heavy metal-free CIS/CIS g-QDs with thickness up to 5 nm. The optical properties show tunable QD’s absorption and PL spectra in the NIR region (up to ≈1100 nm). The PL lifetime of g-QDs with various shell thicknesses was measured by transient fluorescence spectroscopy and prolonged with thicker shells, demonstrating the quasi type-II band alignment in as-synthesized g-QDs, which is consistent with simulation results. As a proof-of-concept, we fabricated photoanodes based on these NIR, heavy metal-free g-QDs for PEC hydrogen generation. The CIS/CIS g-QDs after Zn surface treatment (Zn-CIS/CIS) were deposited into a TiO\textsubscript{2} film via electrophoretic deposition (EPD). The as-fabricated photoanodes using Zn-CIS/CIS/6GdS and Zn-CIS/CIS/13GdS g-QDs as sensitizers exhibit a saturated photocurrent density as high as ≈3.1 and ≈3 mA cm\textsuperscript{−2} with very good stability, comparable to the best reported QDs-based PEC devices.\textsuperscript{[15]} These results indicate that NIR, heavy metal-free Zn-CIS/CIS g-QDs are promising materials for various cost-effective and environmentally friendly solar energy applications, such as PEC hydrogen generation.

2. Results and Discussion

2.1. Synthesis and Structure of CIS/CIS g-QDs

CdSe QDs with radius of 1.65 nm were synthesized via a hot injection approach\textsuperscript{[16]} and then used as a core for the subsequent synthesis of CdSe/CdS g-QDs using the successive ionic layer adsorption and reaction (SILAR) method.\textsuperscript{[6c]} As-prepared CdSe/CdS g-QDs then served as template to synthesize CIS/CIS g-QDs by sequential cation exchange procedures.\textsuperscript{[14]} As shown in Figure 1a, Cd\textsuperscript{++} in CdSe/CdS g-QDs was exchanged by Cu\textsuperscript{+} and as-synthesized Cu\textsubscript{2}Se/Cu\textsubscript{2}S g-QDs were partially exchanged by In\textsuperscript{3+} to form CuInSe\textsubscript{2}/CuInS\textsubscript{2} g-QDs. We further grew a very thin ZnS protective shell by cation exchange to suppress the surface defects on the QDs and enhance the colloidal stability of as-synthesized g-QDs.\textsuperscript{[16c]}

Figure 1b,c displays transmission electron microscopy (TEM) images of CdSe/CdS g-QDs with 13 and 6 monolayers of CdS shell (CdSe/13CdS and CdSe/6CdS). The CdSe/CdS g-QDs exhibit a spherical shape with radius of ≈1.65 nm for CdSe and shell thickness of ≈4.2 and ≈2 nm for CdSe/13CdS and CdSe/6CdS g-QDs, respectively. The corresponding energy-dispersive X-ray spectroscopy (EDS) spectrum of CdSe/6CdS g-QDs (Figure S1a, Supporting Information) confirms the presence of elemental Cd, S, and Se, while Se is absent in the EDS spectrum of CdSe/13CdS g-QDs (Figure S1b, Supporting Information). This is attributed to a less concentrated sample in the grid during EDS measurements by TEM. Further characterization of the EDS spectrum (Figure S2a, Supporting Information) in a scanning electron microscope (SEM) and the ICP-OES analysis (Table S1, Supporting Information) both confirm the presence of elemental Se in CdSe/13CdS g-QDs.
High resolution TEM (HR-TEM) images (inset images in Figure 1b,c) of these two kinds of QDs both display a lattice spacing of $\approx 0.335$ nm that is well indexed to the (002) plane of WZ phase CdS, demonstrating the dominance of the WZ crystal structure of CdS in the CdSe/CdS g-QDs due to the larger volume of the CdS shell with respect to the CdSe core, consistent with previous reports.[8,9]

After sequential cation exchange, the TEM images of as-synthesized Zn-CISe/13CIS (Figure 1f) and Zn-CISe/6CIS (Figure 1g) g-QDs show no noticeable change of shapes and sizes compared to the CdSe/13CdS and CdSe/6CdS g-QDs, indicating an effective preservation of QD morphology using this sequential cation exchange method, consistent with the literature.[14] The latter approach is effective to control the morphologies of QDs by varying the shape/size of the initial QD templates. Unlike the directly synthesized irregular shaped CuInSe(S) QDs, the spherical shape of CISe/CIS g-QDs can be obtained by using the cation exchange approach. The TEM images of CISe/13CIS (Figure S3a, Supporting Information) and Zn-CISe/13CIS g-QDs (Figure S3b, Supporting Information) also possess similar shape and size because the Zn surface treatment only forms a very thin ZnS protective shell (<0.1 nm) and has already been demonstrated to have a negligible effect on QD morphology in previous work.[1c,4] To further support this conclusion, size histograms of CISe/13CIS and Zn-CISe/13CIS are displayed in Figure S4 (Supporting Information), showing sizes of $9.2 \pm 0.6$ and $9.2 \pm 0.7$ nm, respectively, indicating no significant size variation before and after Zn surface treatment.

The HR-TEM images (inset images in Figure 1f,g) reveal a lattice distance of $\approx 0.338$ nm, which is indexed to the (100) plane of WZ phase CuInS$_2$. The lattice distances measured in SAED patterns of CdSe/13CdS (Figure 1d) and Zn-CISe/13CIS g-QDs (Figure 1h) are well indexed to the (002), (100), (101), (110), (103), and (112) planes of WZ phase CuInS$_2$, respectively, which are typical planes with relatively high diffraction intensity in WZ CdS (JCPDS No. 00-041-1049) and CuInS$_2$ (JCPDS No. 01-077-9459). For CISe/13CIS g-QDs, the planes of WZ phase CuInS$_2$ in the SAED pattern (Figure S3c, Supporting Information) are consistent with the diffraction peaks in the XRD pattern (Figure S5, Supporting Information), indicating the formation of a very thick WZ phase CuInS$_2$ shell. Similarly, the lattice spacing in SAED patterns of CdSe/6CdS (Figure S6a, Supporting Information) and Zn-CISe/6CIS (Figure S6b, Supporting Information) g-QDs are also well indexed to the (002), (100), (101), (110), (103), and (112) planes of the WZ phase CdS and CuInS$_2$, further demonstrating the WZ crystal structure of as-synthesized Zn-CISe/CIS g-QDs.

In addition, the EDS spectra of Zn-CISe/13CIS (Figure 1e) and Zn-CISe/6CIS (Figure 1i) g-QDs both confirm the presence of all the elements including Cu, In, Se, and Zn. The residual Cd after first cation exchange of CdSe/13CdS to Cu$_2$Se/13Cu$_2$S g-QDs is measured by using ICP-OES. As shown in Table 1,
the ICP-OES analysis indicates that 99.7% (molar ratio) of Cd$^{2+}$ has been exchanged by Cu$^{+}$ in Cu$_{13}$Se/13Cu$_2$S core/shell g-QDs even with a thick shell of 13 layers of CdS. This can be considered as full exchange of Cd by Cu cations. In addition, the Cu$_{13}$Se/13Cu$_2$S g-QDs were used for In$^{3+}$ cation exchange to form CISe/13CIS g-QDs and no Cd$^{2+}$ was introduced in this synthesis process, thus the Cd$^{2+}$ in Cu$_{13}$Se/13Cu$_2$S g-QDs was almost identical as confirmed by ICP measurements, demonstrating that the as-synthesized Zn-CISe/CIS g-QDs are free of heavy metals, consistent with the literature.[14] The molar ratio of Cu/In is $\approx$ 1:1.2 in the CISe/CIS g-QDs as measured by ICP-OES (Table S3, Supporting Information). The morphology of as-prepared CISe/CIS g-QDs shows nearly identical sizes and shapes of CdSe/CdS template, indicating that the CIS shell thickness of CISe/CIS g-QDs can be controlled by tuning the CdS shell thickness of the CdSe/CdS template. Using this sequential cation exchange technique leads to a full exchange of Cd$^{2+}$ by Cu$^{+}$ and In$^{3+}$. The as-synthesized CISe/CIS g-QDs do not contain toxic heavy metals and are environmentally friendly.

Table 1. ICP-OES analysis results of Cu$_{13}$Se/13Cu$_2$S nanocrystals.

<table>
<thead>
<tr>
<th>Element (wavelength)</th>
<th>Correlation coefficient</th>
<th>Concentration [ppm]</th>
<th>Molar ratio (Cd:Cu)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cd (214.439 nm)</td>
<td>0.99</td>
<td>0.24</td>
<td>0.3%</td>
</tr>
<tr>
<td>Cu (324.754 nm)</td>
<td>0.99</td>
<td>45.87</td>
<td></td>
</tr>
</tbody>
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2.2. Optical Properties of CISe/CIS g-QDs

The optical properties of CISe, Zn-CISe/6CIS, and Zn-CISe/13CIS g-QDs in solution are reported in Figure 2a–c. Before the sequential cation exchange, CdSe, CdSe/6CdS, and CdSe/13CdS g-QDs show absorption spectra covering the UV to visible region with first-excitonic peaks near $\approx$ 550, 590, and 610 nm, respectively. After sequential cation exchange, the absorption spectra of CISe, Zn-CISe/6CIS, and Zn-CISe/13CIS g-QDs have shifted to the NIR region up to 1100 nm without apparent first-excitonic peaks, which are the typical absorption spectra of CuInS(Se) QDs.[16] The PL spectra of CISe,
Zn-CISe/6CIS, and Zn-CISe/13CIS g-QDs before and after sequential cation exchange further demonstrate the redshift of the g-QD's PL peaks from ≈565, 605, and 625 nm to ≈765, 1075, and 1100 nm, respectively.

In addition, as the ICP-OES measurements already demonstrated the full exchange of Cd by Cu cations, after the first step of Cu⁺ for Cd²⁺ cation exchange, the peak originating from CdSe/13CdS g-QDs disappears in the PL spectrum of the as-synthesized Cu₅Se/13Cu₅S g-QDs (Figure S7a, Supporting Information). With constant CulnSe₂ core radius, by increasing the shell thickness, the PL peak positions of the Zn-CISe/CIS g-QDs gradually redshift from ≈765 to ≈1100 nm.

Compared to CISe QDs, a large redshift of the PL peak positions was found in CISe/CIS g-QDs. In general, in a core/shell system, the electron leakage from the core into the shell region leads to a redshift of the PL peak. Such phenomenon has been observed and verified in many core/shell structured g-QDs (such as quasi-type-II CdSe/CdS or type-II InP/CdS).[8,10] To further understand the exciton dynamics of as-synthesized CISe/CIS g-QDs with different shell thickness, transient fluorescence spectroscopy was used to measure the lifetime of QDs in solution before and after sequential cation exchange, as shown in Figure S8 (Supporting Information) and Figure 2d. By increasing the shell thickness, the templates of CdSe, CdSe/6CdS, and CdSe/13CdS QDs exhibit a prolonged lifetime of ≈19, 29, and 43 ns, respectively. This extension of lifetime indicates an efficient spatial separation of holes and electrons in the g-QD system.[6b,9a]

After sequential cation exchange, the PL lifetime of bare CISe QDs and the Zn-CISe/CIS g-QDs with different shell thickness were fitted by a triexponential or biexponential decay with standard deviation less than 10%, respectively. The fitting parameters and QY of CISe, Zn-CISe/6CIS, and Zn-CISe/13CIS g-QDs were listed in Table S4 (Supporting Information). The slower lifetime of τ₁ and faster lifetime of τ₂ are typical lifetimes in this type of QDs. The bare CISe QDs exhibit an average lifetime of 200 ± 10 ns. In contrast, the Zn-CISe/6CIS and Zn-CISe/13CIS g-QDs exhibit longer average lifetimes of 230 ± 5 and 300 ± 10 ns, respectively. The longer average lifetime with increasing shell thickness in Zn-CISe/CIS g-QDs may be attributed to the efficient decrease in spatial overlap between electron and hole wave functions, leading to leakage of the electrons from the core to the shell region, resulting in suppressed recombination and leading to a prolonged lifetime. In conclusion, both the redshift of the PL peak and increasing lifetime with thicker shell of QDs demonstrate the formation of quasi-type-II band alignment of the core and shell in the Zn-CISe/CIS g-QDs after sequential cation exchange.[8,9]

2.3. Wave Function in CISe/CIS g-QDs

To theoretically describe the quasi type-II characteristics and understand the prolonged lifetime of the CISe/CIS g-QDs, we calculated the wave functions of the electrons and holes in the QDs based on the bulk band alignment (Figure 3a,b). Details of calculations are described in the Experimental Section. The light emission process in the CISe/CIS g-QDs is attributed to either the recombination of the 1S electrons and the 1S holes or the recombination of the 1S electrons to the impurity holes in the core, or both.[8] Our calculations show that the Eigen energy of the 1S electron exceeds the energy barrier of the shell layer with thickness of 1–6 nm. As a consequence, electrons have a great probability of being found outside the CISe core, compared to a bare CISe-QD. By increasing the thickness of the CISe shell, more electrons are likely to leak into the shell region. In contrast, the 1S valence band holes are still well confined in the core for both a bare CISe-QD and a CISe/CIS-QD. And the probability profile of the 1S hole remains nearly unchanged with increasing shell layer thickness (from 1 to 6 nm). To qualitatively demonstrate the PL lifetime of the core/shell QDs, we calculated the squared overlap integral of the 1S electron and 1S hole as a function of shell thickness. The squared overlap integral (OI) is given by

\[ OI(h_{shell}) = \frac{\left| \int \psi_{electron}(r) \psi_{hole}(r) \, dr \right|^2}{\int \left| \psi_{electron}(r) \right|^2 \, dr \int \left| \psi_{hole}(r) \right|^2 \, dr} \]  

for 1S electron and 1S hole, and

\[ OI(h_{shell}) = N_{impurity}^{-1} \int_{V_{core}} OI_0 \left( r_{impurity} \right) \, dV_{impurity} \]  

with

\[ OI_0 \left( r_{impurity} \right) = \frac{\left| \int \psi_{electron}(r) \psi_{hole}(r_{impurity}) \psi_{impurity}(r_{impurity}) \, dr \right|^2}{\int \left| \psi_{electron}(r) \right|^2 \, dr \int \left| \psi_{hole}(r_{impurity}) \right|^2 \, dr \int \left| \psi_{impurity}(r_{impurity}) \right|^2 \, dr} \]  

for 1S electron and impurity hole (see the Experimental Section for description of impurity holes). Here \( \psi_{electron} \) and \( \psi_{hole} \) are wave functions of 1S electron state and hole state, respectively, and \( N_{impurity} = 18 \) is the number of impurities in the CISe core. We assume a weak interaction between the impurity hole states. The lifetime of fluorescence emission should be proportional to the inverse of the squared overlap function. Figure 3c shows that the squared overlap integral decreases with increasing shell layer thickness, proving that the lifetime should increase with increasing shell thickness. This trend is in qualitative agreement with the experimental measurements (PL and lifetime).

The as-prepared CISe/CIS g-QDs exhibit a broad absorption spectrum up to 1100 nm, PL spectrum in the second biological window of 1100–1400 nm, and longer lifetime as high as ≈300 ns compared to generic biomolecules with lifetime of around several nanoseconds, which make them a great candidate for NIR deep-tissue imaging/sensors compared to toxic CdSe/CdS g-QDs, since they are made of nontoxic elements. In addition, the quasi type-II nature of CISe/CIS g-QDs makes them superior candidates in solar technologies such as photovoltaics and hydrogen production as the electrons can efficiently transfer to the electron scavengers. The wide absorption spectrum (up to NIR region) of CISe/CIS g-QDs has a significant overlap with the solar spectrum, presenting great potential to boost the PCE in such g-QD based devices.
As a proof-of-concept, we fabricated a CISe/CIS g-QD based photoanode (detailed information for the fabrication procedure is shown in the Experimental Section) for PEC hydrogen production. To fabricate the g-QD-sensitized photoanode, the as-prepared Zn-CISe/CIS g-QDs were deposited into the mesoporous TiO$_2$ films via EPD. TEM image and corresponding EDS spectra of TiO$_2$/Zn-CISe/CIS g-QD heterostructure are shown in Figure S10 (Supporting Information), demonstrating that the QDs (denoted by white dashed circles) are homogeneously dispersed on the surface of TiO$_2$ nanoparticles without any noticeable aggregation.

Cross-section SEM imaging and corresponding EDS analysis of the Zn-CISe/6CIS g-QD-sensitized photoanode are displayed in Figure 4. The thickness of the mesoporous TiO$_2$ film is estimated to be $\approx 20.5$ µm (Figure 4a). EDS spectra (Figure 4b) and 2D EDS mapping (Figure 4c–i) exhibit the presence of Cu, In, Se, S, Zn, Ti, and O, consistent with the chemical composition in the Zn-CISe/CIS g-QD-sensitized photoanode. The element of In has overlapped EDS signal with Sn, leading to the richer EDS signal of In at the surface. Similarly, due to the relatively low molar concentration of Se in the g-QDs, the EDS signal of Se is weaker in the TiO$_2$ film compared to other elements, such as In and Cu. The observed stronger Se signal in the substrate with respect to that in the TiO$_2$ film is due to the additional contribution from the O signal because of elemental Se overlapping with O (Figure 4d). The relative mass concentration of Zn-CISe/6CIS g-QDs with respect to TiO$_2$ is reported in Figure 4b (the content of Zn is much higher as we deposited 2 ZnS layer on the QDs-based photoanode to protect photocorrosion), whereas semiquantified QD loading amounts in the TiO$_2$ film are presented in the EDS line scan (Figure 4j, measured along the yellow line in Figure 4a). In parallel, cross-sectional SEM imaging and relevant EDS analysis of Zn-CISe/13CIS g-QD-sensitized photoanode are reported in Figure S11 (Supporting Information). All the EDS analyses demonstrate the uniform dispersion of g-QDs in the TiO$_2$ film.

The approximate band alignment and schematic diagram of Zn-CISe/CIS g-QD-sensitized photoanode for PEC cells is illustrated in Figure 5a. The Zn-CISe/CIS g-QDs can form a favorable band alignment with TiO$_2$ for efficient charge dissociation of photogenerated carriers at the QD/TiO$_2$ interface, where photoexcited holes oxidize the sacrificial agent (Na$_2$S and Na$_2$SO$_3$) in the electrolyte and the electrons are injected into TiO$_2$, collected by the fluorine doped tin oxide (FTO) electrode and transferred to the Pt counter electrode for water reduction to produce hydrogen.[1a]
Figure 5b,c displays the photocurrent density as a function of applied potential for Zn-CISe/13CIS and Zn-CISe/6CIS g-QD-sensitized photoanodes in the dark (black curve), under continuous (red curve) and chopped (blue curve) illumination (AM 1.5G, 100 mW cm\(^{-2}\), 30 cm from the sun simulator to PEC cell), which exhibits a saturated photocurrent density.
of ≈3 and 3.1 mA cm⁻² obtained at ≈0.8 V versus the reversible hydrogen electrode (RHE), respectively. For comparison, the CISe QD-sensitized photoanode only shows a saturated photocurrent density of ≈1.5 mA cm⁻² (Figure S12, Supporting Information). The Zn-CISe/13CIS and Zn-CISe/6CIS g-QD-sensitized photoanodes exhibit higher photocurrent density than bare CISe QD-sensitized photoanode, which we attribute to both their enhanced light absorption and quasi type-II band alignment. The PEC cell based on the bare TiO₂ photoanode (Figure S13, Supporting Information) exhibits a saturated photocurrent density of ≈0.25 mA cm⁻², which is much lower compared to the QD-sensitized photoanodes (≈1.5, 3, and 3.1 mA cm⁻²), indicating that the QD loading in the TiO₂ mesoporous film is the dominant contribution to the enhancement of saturated photocurrent density. The saturated photocurrent density of Zn-CISe/13CIS and Zn-CISe/6CIS g-QD-sensitized photoanodes are higher than previous reports of green NIR QDs (CuInSeS, Ag₂S, and CuInS₂ QDs with photocurrent density of ≈0.3, 0.6, and 2 mA cm⁻², respectively) sensitized photodevices for hydrogen generation.\(^\text{[16a,19]}\) The incident-photon-to-current efficiency (IPCE) was derived from current-voltage measurements (Figure S14, Supporting Information). The results are consistent with the broad NIR absorption of the Zn-CISe/CIS g-QDs, with contribution to IPCE originating from the UV-vis and NIR region, up to 1000 nm.

We further measured the PEC performance of photoanodes sensitized by intermediate products of Cu₂Se, Cu₂Se/6CuInS₂, and Cu₂Se/13CuInS₂ QDs (Figure S15, Supporting Information), showing saturated photocurrent of ≈0.8, 0.85, and 0.55 mA cm⁻², respectively, which are much lower than the Zn-CISe/CIS g-QDs. While, the PEC cells using CdSe, CdSe/6CdS, and CdSe/13CdS QD-sensitized photodevices exhibit much higher photocurrent of ≈4.5, 6, and 7 mA cm⁻² (Figure S16, Supporting Information) than that of the Zn-CISe/CIS g-QDs. However, the highly toxic heavy metal of Cd hinders their potential applications due to environmental and health concerns.

Figure 5d displays the photocurrent density as a function of time for TiO₂/CISe/ZnS (black curve), TiO₂/Zn-CISe/6CIS/ZnS (red curve), and TiO₂/Zn-CISe/13CIS/ZnS (blue curve) photoanodes measured at 0.8 V versus RHE under standard AM 1.5G solar illumination (100 mW cm⁻²). To better understand the percentage of decay trend, we divide the maximum photocurrent density of the photoanodes to make the curves decay from the value of 1. The bare CISe QD based PEC cell shows a rapid decay of photocurrent density, ≈30% drop from the initial photocurrent density only after ≈0.2 h illumination, while the Zn-CISe/6CIS and Zn-CISe/13CIS g-QD based PEC cells show only ≈31% and ≈20% drop from the initial photocurrent density even after 2 h illumination. This improvement is due to the formation of a very thick CuInS₂ shell on the CuInSe₂ core for enhanced chemical- and photostability in this type of NLR, heavy metal-free g-QDs during the anode preparation by EPD and further cell operation in corrosive electrolyte (pH of 12.5). The photostability of the PEC system based on Zn-CISe/6CIS and Zn-CISe/13CIS QD-sensitized photoanodes is comparable with the best reported PEC photoanodes of CdSe/CdS (Figure S17, Supporting Information). This approach is quite reliable, because the only difference in our g-QD based PEC system is the type of g-QDs, and all other components including electrolyte, counter electrode, and reference electrode (Ag/AgCl) are the same. The evolution of H₂ shows a nearly linear increase over time and is in good agreement with the theoretical curve (Figure S17, Supporting Information). The calculated H₂ values are ≈24.3 and ≈26.5 mL cm⁻² d⁻¹, respectively, for Zn-CISe/6CIS and Zn-CISe/13CIS g-QD based PEC cells.

3. Conclusions and Perspectives

We demonstrated the synthesis of Zn-CISe/CIS g-QDs made of nontoxic elements using the sequential cation exchange approach. Morphology investigations confirmed the thick shell of CuInS₂ and WZ crystal structure of as-synthesized g-QDs. The spherical shape of CISe/CIS g-QDs can be accurately preserved and the shell thickness can be controlled by tuning the width of the CdSe/CdS g-QDs template. ICP-OES measurements demonstrate the full exchange of heavy metal of Cd from an initial CdSe/CdS g-QDs template to a final product consisting of heavy metal-free Zn-CISe/CIS g-QDs. The optical properties of such g-QDs are characterized by tunable absorption, PL peak, and lifetime in the NIR region by varying the width of the CdSe/CdS g-QDs template. The PEC performance of photoanodes sensitized with Zn-CISe/CIS g-QDs shows an outstanding saturated photocurrent density as high as ≈3.1 mA cm⁻². The stability of the as-fabricated QD-sensitized photoanode is comparable to the best reported QD-based anodes.\(^\text{[15]}\)

Based on these results, we conclude that NLR, heavy metal-free Zn-CISe/CIS g-QDs are promising for PEC solar driven hydrogen generation. Future improvements may focus on tuning the shell thickness (varying the number of SILAR cycles) and structure (using an alloyed shell) of this type of NIR, green g-QDs and exploring more relevant NIR deep-tissue imaging and optoelectronic applications (such as solar cells, LSCs, LEDs, etc.).

4. Experimental Section

**Materials:** Tetraakis(acetonitrile)copper(I)hexafluorophosphate ([Cu₅(CN)₄][PF₆]), indium chloride (InCl₃, 98%), sulfur (100%), oleic acid (OA), 1-octadecene (ODE), 1-dodecanethiol (DDT), oleylamine (OLA) (technical grade, 70%), hexadecyltrimethylammonium bromide (CTAB), cadmium oxide (99%), selenium (20%, 99.999%), tricetylphosphine oxide (TOPO), tricetylphosphine (TOP) (97%), cadmium oxide (CdO), Triton X-100, acetone, methanol, ethanol, toluene, zinc acetate dehydrate (Zn(OAc)₂ × 2H₂O), sodium sulfide nonhydrate (Na₂S × 9H₂O), and sodium sulfite (Na₂SO₃) were purchased from Sigma-Aldrich. Titania paste containing a mixture of active anatase particles (≈20 nm) and larger anatase scatter particles (≈450 nm) paste (18 NR-AG) was obtained from Dyesol (Queanbeyan, Australia). The mesoporous TiO₂ paste was obtained from Dyesol (Queanbeyan, Australia). The titania paste was made by the sol–gel method using tetraethyl orthosilicate (TEOS) as the sol precursor and H₂O as the gelation media.
of FTO substrates by using the tape-casting technique and following. The same titania paste (18 NR-AO) was then deposited again on top tape-casted on FTO substrates and kept in air for 12 min, to obtain a down to room temperature. Titania paste containing a mixture of as-synthesized CISe/CIS g-QDs were precipitated with ethanol, allowed to react for 4 h with stirring. Finally, 5 mL DDT was added and mixture was heated to 100 °C and maintained for 2 min. OA and 1 mmol of Zn(Ac)2 dissolved in 4 mL of ODE), and the reaction proceeded for 2.5 h, followed by dropwise injection of 0.2 mmol sulfur in ODE with same volume. The shell was then annealed for 10 min. All subsequent shells were annealed at 240 °C for 10 min following dropwise injection of the Cd(OA)2 dispersed in ODE. Sulfur/Cd(OA)2 injection volumes for shell deposition were approximated as the lowest unoccupied molecular orbital and holes (m+), respectively, for the bulk theoretical method. The theoretical shrodinger equation for the 1S states of electron and hole was solved in COMSOL (a commercial software for finite element simulation). The bulk values for the effective masses of electrons (m0) and holes (m0) were used, namely, m0 = 0.090m and m0 = 0.73m for CuInSe2, and m0 = 0.16m and m0 = 0.85m for CuInS2, where m0 is the electron mass at rest in vacuum. The potentials for electrons and holes as a function of position were approximated as the lowest unoccupied molecular orbital and the highest occupied molecular orbital levels, respectively, for the bulk materials. For CuInSe2, these levels are −0.56 eV; respectively, for CuInS2, these levels are −0.49 and −0.92 eV, respectively. The bandgaps for CuInSe2 and CuInS2 were 1.04 and 1.53 eV.
The barriers between the CuInSe₂ and CuInS₂ regions were taken as 0.21 and 0.28 eV for the conduction and valence bands. Figure S18 (Supporting Information) shows the band diagrams. The interaction between electrons and holes was neglected in the calculations. The wave functions were computed from the effective-mass Schrödinger equation

\[ \mathbf{\hat{H}} \mathbf{\psi} = E \mathbf{\psi} \]  

(4)

In solving this equation, the appropriate boundary conditions at the interfaces were applied. Finally, the wave functions were normalized such that \( \int |\mathbf{\psi}|^2 \, dV = 1 \).

The wave function of an impurity hole state is described by a Gaussian function

\[ \mathbf{\psi}_{\text{hole}}(r) = A \exp \left( -\frac{(r - r_{\text{impurity}})^2}{2L_h^2} \right) \]  

(5)

where, \( r_{\text{impurity}} \) is the position of impurity in the CIS core; the coefficient \( A \) is determined by \( \int |\mathbf{\psi}_{\text{hole}}|^2 \, dV = 1 \); and the scale of hole \( L_h \) is far less than the QD radius (here, we assume \( L_h = 0.3 \) nm). Considering the spherical symmetry of the wave function of 1S electrons, the squared overlap function of Equation (2) in the main text can be simplified as

\[ \text{OI}=N_{\text{impurity}} \int_0^{L_h} \mathbf{\psi}_{\text{core}}(r) \mathbf{\psi}_{\text{impurity}}(r) \, dr \]  

\[ \approx \frac{3}{R_{\text{core}}} \int_0^{L_h} \mathbf{\psi}_{\text{core}}(r) \mathbf{\psi}_{\text{impurity}}(r) \, dr \]  

(6)

where \( r_{\text{impurity}} \) is the distance of the impurity site from the center of the core. In the experiment, the Cu and In atoms in the core are off-stoichiometry (Cu:In = 1:1.2). Then, the numbers of Cu atoms and In atoms in the core can be estimated using the mass density and molar mass of CIS as \( N_{\text{Cu}} = 176 \) and \( N_{\text{In}} = 212 \). The number of In atoms that occupy the Cu sites is given by \( N_{\text{impurity}} = N_{\text{Cu}} - 18 \).

IPCE Calculation: The IPCE describes the ratio of photogenerated electrons collected by the electrodes over the number of incident monochromatic photons. To derive the IPCE values, current-voltage measurements were performed using different band-pass optical filters. IPCE can be calculated by using the following equation

\[ \text{IPCE} = \frac{J \lambda}{P} \times 100 \]  

(7)

where \( J \) is the photocurrent density, \( P \) is the incident radiation intensity at a given wavelength, \( \lambda \) is the wavelength of the incident photon, \( c \), \( h \), and \( e \) are the speed of light, Planck’s constant, and the elementary electric charge, respectively. To confirm the contribution of infrared photons to the photocurrent, band-pass filters with wavelength center at 405, 460, 505, 694, 785, 855, 940 nm were applied. For each filter, the incident radiation intensity at the position of the sample was measured by Newport power-meter.

Theoretical Calculation of \( \text{H}_2 \) Evolution: The theoretical number of moles of hydrogen was obtained according to Faraday’s law\(^{[24]} \)

\[ q = nF \]  

(8)

With the definitions of electrolysis based on the following equations

\[ n = \frac{m}{m_e} \quad \text{and} \quad q = \int_{t_i}^{t_f} i \, dt \]  

(9)

where \( n \) is the number of equivalents, \( m \) is the mass of the substance liberated at an electrode in grams (g), \( m_e \) is the molar mass of the substance in grams per mol (g mol\(^{-1}\)), i.e., \( n \) equals to the number of moles. A common assumption on the current being constant over time, allows to the mathematical equivalent that can be simplified as\(^{[23]} \)

\[ n = \frac{1}{2} \frac{1}{F} \frac{1}{2} \frac{1}{F} \]  

(10)

where \( z \) is the number of transferred electrons per mole of water (i.e., \( z = 2 \)), \( q \) is the electric charge in coulombs (C), \( F \) is the Faraday constant (i.e., 96 484.34 C mole\(^{-1}\)), \( l \) is the photocurrent in amperes (A), and \( t \) is time in seconds (s).

The saturated photocurrent density (Figure S5b,c) and integrated the current density (Figure 5d) were used, and the theoretical hydrogen generation rate of Zn-CIS/6CIS and Zn-CIS/13CIS g-QD-sensitized photoanode is ~24.3 and ~26.5 mL cm\(^{-2}\) d\(^{-1}\), respectively.

Supporting Information

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

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Conflict of Interest

The authors declare no conflict of interest.

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