High-performance photoelectrochemical hydrogen production using asymmetric quantum dots

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Abstract

Solar-driven photoelectrochemical (PEC) reactions using colloidal quantum dots (QDs) as photoabsorbers have shown great potential for the production of clean fuels. However, the low $H_2$ evolution rate, consistent with low values of photocurrent density, and their limited operational stability are still the main obstacles. To address these challenges, we report the heterostructure engineering of asymmetric rod/egg shaped CdSe/Cd$_x$Zn$_{1-x}$Se QDs with broad absorption and efficient charge extraction. By engineering the shell composition from pure ZnSe shells into Cd$_x$Zn$_{1-x}$Se gradient shells, the electron transfer rate increased from $4.0 \times 10^7$ s$^{-1}$ to $32.7 \times 10^7$ s$^{-1}$. Moreover, the rod/egg shaped architecture enables more efficient spatial carrier separation, yielding a saturated current density of 35 mA/cm$^2$ under AM 1.5 G one sun illumination. This value is the highest ever observed for QDs-based devices and comparable to the best-known Si-based devices, perovskite-based devices and metal oxide-based devices. Furthermore, PEC devices based on heterostructured QDs maintained 96% of the initial current density after two hours and 82% after 10 hours under continuous illumination, respectively. Our results represent a breakthrough in hydrogen production using heterostructured asymmetric QDs.

Introduction

Colloidal quantum dots (QDs) are attractive semiconductor materials for various purposes, due to their unique combination of properties: (i) size/shape/composition-tunable absorption and emission; (ii) structure-controlled charge dynamics; (iii) easy and low-energy synthetic process; (iv) possibility of multiple exciton generation (MEG) with single-photon absorption.$^1$–$^4$ Compared to bare QDs, core/shell heterostructured QDs are more sterically and electrostatically stable and flexible for display devices and optoelectronic devices such as QDs light emitting diodes (QLEDs),$^5$–$^7$ Luminescent Solar Concentrators (LSCs),$^8$–$^{10}$ QDs Solar Cells (QDSCs)$^{11}$–$^{13}$ and solar-driven water splitting$^{14}$, 15. For example, Shen et al. reported a red, green and blue QLED based on CdSe/ZnSe core/shell structures with both high brightness and high external quantum efficiency.$^7$ Meinardi et al. reported Stokes-shift-engineered CdSe/CdS QDs with “giant” shells to realize LSCs without reabsorption energy losses for device dimensions up to tens of centimetres.$^9$ Working on energy conversion and energy storage, Du et al. reported the Zn:CuInSe$_2$ QDs/TiO$_2$ as photoelectrode for the application of solar cell which achieves consistent photovoltaic performance with $\sim$ 85% photon-to-electron conversion efficiencies and highly reproducible power conversion efficiencies (PCEs) of 9–10%.$^{16}$

The reduction in cost of solar electricity or solar fuels has been driven by advances in PCEs and the reduced costs of favorable materials and fabrication. Photoelectrochemical (PEC) hydrogen ($H_2$) evolution is a low-cost, and environmentally-friendly method compared to electrolytic and electrochemical $H_2$ production, a promising alternative for $H_2$ evolution as well as solar cell by means of solar-to-fuel conversion.$^{17}$–$^{21}$ Since Fujishima and Honda reported PEC $H_2$ generation using TiO$_2$ as photoelectrode,$^{22}$ numerous studies on hydrogen production from water using metal oxide semiconductors (MOS) have
been reported, such as TiO$_2$\textsuperscript{23–26}, ZnO\textsuperscript{27–29}, SnO$_2$\textsuperscript{30–32}, etc. However, the intrinsic bandgap of MOS limits their absorption range within the UV range of the solar spectrum (only about 4%), yielding low solar-to-hydrogen (STH) efficiency. Using QDs as sensitizers for such wide-bandgap semiconductors, the absorption range can be extended up to the visible and even near-infrared range. However, the instincts of QDs still restrict the STH efficiency and stability performance. For example, the highest current density is 17.5 mA/cm$^2$ for colloidal QDs deposited photoanodes while 22.1 mA/cm$^2$ was reported for \textit{in situ} sensitized QDs/oxide based photoanodes\textsuperscript{33,34} (Table S1). This can be mainly attributed to: (i) the presence of surface traps as exciton/charge recombination centers; (ii) inefficient carrier separation as well as low carrier transfer rate; (iii) photo-corrosion, etc\textsuperscript{35}.

Until now, numerous heterostructured core/shell QDs architecture such as PbS/CdS\textsuperscript{36}, CdSe/CdS\textsuperscript{37}, CdS/CdSe\textsuperscript{38}, CuInSe/ZnS\textsuperscript{39} have been widely used as light harvesters in optoelectronic devices. For the proper selection of shell materials on a given core, two important parameters should be considered: the relative positions of the bandgaps of the core and shell semiconductors and the lattice mismatch between core and shell materials. The former determines the charge carriers’ behaviour, such as carrier confinement, carrier separation/transfer, whereas the latter is crucial for epitaxial deposition of the shell material on the core and accordingly the core/shell interface\textsuperscript{40}. Among all possible combinations of compound semiconductors, ZnSe is an ideal shell material on CdSe cores.\textsuperscript{41–43} Although the lattice mismatch between the ZnSe and CdSe (~ 6.3%)\textsuperscript{44} is larger compared to that of the CdSe/CdS (~ 3.9%), the CdSe/ZnSe core/shell system still exhibits an efficient confinement of the electrons in the core of the nanocrystals (NCs) due to the wide bandgap (~ 2.8 eV) of ZnSe and high conduction-band offset of the ZnSe shell.\textsuperscript{44} On the other hand, only a relatively small barrier exists for the holes in this system which means that the spatial separation of carriers can be improved. Nonetheless, issues such as limited electron leakage and fast electron-hole recombination in spherical QDs are still present and represent the main obstacle for the effective use of CdSe/ZnSe QDs as building blocks for optoelectronic devices. To address this issue, spherical QDs can be engineered into asymmetric QDs. In this architecture, the electron and holes can be separated in different directions, leading to accelerated carrier spatial dissociation. For example, Park et al. used type-I core/shell asymmetric heterostructured QDs as the single-dot light sources achieving high emission quantum yields and widely tunable emission color.\textsuperscript{45}

In this work, we demonstrate high-performance PEC devices based on asymmetric CdSe/ZnSe core/shell QDs with intermediate alloyed layers. Two rod-shaped CdSe/Cd$_x$Zn$_{1-x}$Se alloyed core/shell QDs were synthesized (denoted as CdSe/Cd$_x$Zn$_{1-x}$Se#1 and CdSe/Cd$_x$Zn$_{1-x}$Se#2 QDs) with different ratio of Cd/Zn in each layer. For PEC devices based on QDs, the saturated photocurrent density is 30 mA/cm$^2$ for CdSe/Cd$_x$Zn$_{1-x}$Se#1 QDs and 35 mA/cm$^2$ for CdSe/Cd$_x$Zn$_{1-x}$Se#2 QDs, respectively, which are much higher than that obtained from CdSe/6ZnSe QDs (8.8 mA/cm$^2$) under one sun illumination (AM 1.5 G, 100 mW/cm$^2$). Meanwhile, the as-prepared PEC device exhibited good operational stability (maintained ~ 96% of its initial value after 2-h illumination and 82% after 10-h illumination). These results are promising
towards the use of asymmetric QDs as light harvesters for PEC H₂ generation cells as well as other optoelectronic devices.

**Results and discussion**

Heterostructured asymmetric QDs were synthesized by coating a shell on the CdSe QDs seed using the successive ion layer adsorption and reaction (SILAR) method. Details are included in the Experimental Section. For all the samples, six layers were coated on identical CdSe seeds. For the core/shell/shell QDs, the feeding ratio of Cd(oleate)/Zn(oleate) is 1:1 for CdSe/CdₓZn₁₋ₓSe/ZnSe QDs (named as CdSe/CdₓZn₁₋ₓSe #1) and gradient ratio for CdSe/CdₓZn₁₋ₓSe/ZnSe QDs (x = 0.9, 0.8, 0.7, 0.5, 0.3, 0 for each layer) (named as CdSe/CdₓZn₁₋ₓSe #2). The structural details are displayed in Table S2. Other than CdSe/ZnSe core/shell architecture, CdS and ZnS can also be used as shell materials on the CdSe core seed. The CdSe/CdS structure offers a small lattice mismatch between the two materials, leading to less recombination at the interfaces. The band alignment between the core and shell can also be tuned by controlling the size of core and the thickness of the shell. Thus, carrier separation and transfer can be optimized. Thanks to its wide bandgap (~ 3.6 eV), ZnS can efficiently passivate the core surface and provide carrier confinement, leading to reduced photoluminescence (PL) quenching and higher photoluminescence quantum yield (PLQY). Thus, several types of core/shell, core/shell/shell QDs (CdSe/CdS, CdS/ZnS, CdSe/CdS/ZnS) and their corresponding alloyed QDs (CdSe/CdSeS/CdS, CdSe/CdZnSe/CdZnS/ZnS, CdSe/CdSeS/CdS/CdZnS/ZnS) were designed and synthesized to compare their optical properties, carrier dynamics, PEC efficiency and stability performance.

**Morphology and structure of QDs**

The morphology and structure of asymmetric QDs were characterized by transmission electron microscopy (TEM). Other than spherical-shaped QDs, rod/egg-shaped QDs were found for the CdSe/CdₓZn₁₋ₓSe #1 and CdSe/CdₓZn₁₋ₓSe #2 (shown in Figure S1 and Fig. 1a). In Figure S1a, f and Fig. 1a, the TEM images show that three types of QDs were dispersed uniformly and the average size of the QDs are shown in Figure S2 where the length and width of CdSe/6ZnSe are 8.9 ± 1 nm and 4.3 ± 0.3 nm, respectively. For two core/shell/shell QDs, the long axis length is 8.3 ± 1.2 nm and the short axis length is 4.6 ± 0.5 nm for CdSe/CdₓZn₁₋ₓSe #1 while 9.0 ± 1.3 nm in length and 4.7 ± 0.7 nm in width for CdSe/CdₓZn₁₋ₓSe #2. The overall size increases with the addition of alloyed layers. Figure S1b-d, g-i and Fig. 1b-d show atomically resolved aberration-corrected high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) images and corresponding energy dispersive spectroscopy (EDS) elemental maps of Cd, Zn, Se and single Se for three types of QDs. From these images, we determined that the QDs composition consists of Cd, Zn, Se. Figure 1e and Figure S1e, j show the elemental profiles of Cd, Zn and Se of a typical QD by the direction of orange arrows in the dark-field STEM image. The results in Figure S1e confirm that Cd and Se are dispersed evenly from 1 to 5 nm in the orange arrow direction while Zn is not present in the first 4 nm, confirming the core/shell structure of CdSe/6ZnSe QDs while the same phenomenon is observed in Fig. 1e. X-ray photoelectron spectroscopy
(XPS) was used to further verify the chemical composition of as-prepared QDs (Figure S3). The XPS spectrum reveals peak positions at 412 and 405 eV which were assigned to Cd 3d\(^{3/2}\) and Cd 3d\(^{5/2}\), respectively. In addition, the peak of Se is located at 55 eV and 53.5 eV, corresponding to Se 3d\(^{3/2}\) and Se 3d\(^{5/2}\), respectively while peaks at 1045 eV and 1022 eV are attributed to Zn 2p\(^{1/2}\) and Zn 2p\(^{3/2}\), respectively. The XPS results prove the existence of elemental Cd, Se, Zn, consistent with STEM mapping.

Figure 1f-h show high resolution STEM (HR-STEM) images of CdSe/6ZnSe, CdSe/Cd\(_x\)Zn\(_{1-x}\)Se#1 QDs and CdSe/Cd\(_x\)Zn\(_{1-x}\)Se#2 QDs, respectively and their corresponding crystal structures are modeled below the HR-STEM images. In the central core domain of CdSe/6ZnSe QDs (Fig. 1f) and CdSe/Cd\(_x\)Zn\(_{1-x}\)Se#2 QDs (Fig. 1h), the measured interplanar d-spacing and angle is ~ 3.5 Å and 71°, respectively. This suggests that the core is viewed along the [110] zone axis and the crystal plane can be indexed with \{111\} according to the lattice parameters (a = 6.08) of CdSe (PDF NO. 00-019-0191). Typical cubic close-packed atomic planes (…ABCABC…) can be observed, consistent with zinc blende (ZB) CdSe. In the shell of CdSe/6ZnSe QDs, the ZnSe grows along the [111] direction layer by layer. Due to the crystalline slip, local hexagonal close-packed atomic planes (…ABAB…) are formed. Selected area electron diffraction (SAED) patterns (Figure S4) and X-ray diffraction (XRD) patterns (Figure S5) also support the mix of ZB and wurtzite (WZ) crystal structures. In Fig. 1g, the measured interplanar d-spacing is ~ 3.5 Å and ~ 2.1 Å with an angle of ~ 90°, corresponding to the (111) and (220) plane of the ZB crystal structure of CdSe, respectively. They also can be indexed with the (0002) and (1120) planes of WZ ZnSe. Therefore, no crystal boundary is observed in the HR-STEM image (Fig. 1g). In WZ ZnSe, (0002) is the close-packed plane, which has the lowest surface energy. Therefore, the growth rate along the (0002) direction is faster than other directions, which results in rod/egged-shaped QDs. Due to the existence of WZ ZnSe in two types of alloyed QDs, CdSe/Cd\(_x\)Zn\(_{1-x}\)Se#1 QDs and CdSe/Cd\(_x\)Zn\(_{1-x}\)Se#2 QDs are also turning into rod/egged shape with similar growth mechanism.

**Optical properties**

The optical properties of QDs were measured by acquiring UV-vis absorption and PL spectra. Figure 2a shows the absorption spectra of CdSe and of the three types of core/shell QDs. The absorption of the CdSe QDs ranges from 300–600 nm with a first-excitonic absorption peak located at 554 nm. After SILAR, the first-excitonic absorption peak of the CdSe/6ZnSe QDs shifted to 552 nm, however core/shell/shell QDs showed an extended absorption ranging from 300–650 nm with peak centered at 612 nm for CdSe/Cd\(_x\)Zn\(_{1-x}\)Se#1 and 625 nm for CdSe/Cd\(_x\)Zn\(_{1-x}\)Se#2, respectively. There was a double peak appearance for both CdSe/Cd\(_x\)Zn\(_{1-x}\)Se#1 and CdSe/Cd\(_x\)Zn\(_{1-x}\)Se#2 QDs, indicating the asymmetric structure of QDs\(^{49,50}\). Overall, the absorption range as well as the first-excitonic absorption peak all shifted to longer wavelength after the addition of alloyed shells. The absorption range and first-excitonic absorption peak for all types of QDs are listed in Table S3.

The same phenomenon is shown in the PL spectrum (Fig. 2b) where the PL peaks blue-shifted from 592 to 578 nm after ZnSe shell coating. Such results indicate a decrease in core size due to the cation
exchange process, leading to a poorly defined core-shell interface\textsuperscript{51}. For two types of alloyed QDs, the PL peaks shift to 642 and 649 nm for CdSe/Cd\textsubscript{x}Zn\textsubscript{1−x}Se#1 and CdSe/Cd\textsubscript{x}Zn\textsubscript{1−x}Se#2 QDs, respectively. Such red-shift indicates that the alloyed shell could improve the electron leakage which is consistent with previous reports.\textsuperscript{52}

For comparison, the UV-vis and PL spectra of CdSe/CdS, CdS/ZnS, CdSe/CdS/ZnS and their corresponding alloy QDs are shown in Fig. 2c-d. The peak position of both UV-vis and PL spectra as well as the absorption range are shown in Table S3. The peak positions in UV-vis absorption spectra and PL spectra all shift towards longer wavelengths for alloyed QDs compared to their pure-shell QDs. In addition, the absorption range can also be broadened by adding alloyed shells due to the increasing concentration of CdSe in the shell.\textsuperscript{53}

As shown in Fig. 2e, the PL lifetimes of QDs dispersed in toluene were tested to investigate the carrier dynamics of CdSe and three types of core/shell QDs. The results are shown in Table 1. The average electron lifetime of CdSe/ZnSe is 14.3 ns, shorter compared to 22.6 ns of CdSe core. Instead, core/shell/shell QDs have a prolonged lifetime of 48.8 ns for CdSe/Cd\textsubscript{x}Zn\textsubscript{1−x}Se#1 QDs and 58.5 ns for CdSe/Cd\textsubscript{x}Zn\textsubscript{1−x}Se#2 QDs, respectively. This observation indicates a shorter electron lifetime with pure ZnSe shell coating while prolonged lifetime with alloyed shell coating which is due to strong electron leakage, as reported previously.\textsuperscript{42}

**Band alignment analysis**

Generally, as shown in Fig. 3a, upon solar irradiation QDs absorb photons with energy higher than the bandgap, subsequently yielding excitons. The photogenerated electron and hole pairs will then dissociate at the QDs/TiO\textsubscript{2} interface. The electrons will leak from the CdSe core to ZnSe or Cd\textsubscript{x}Zn\textsubscript{1−x}Se alloyed shells and are injected into TiO\textsubscript{2} due to favorable electronic band bending. Finally, electrons will be collected and transferred to the counter-electrode where reduction of water molecules takes place, generating H\textsubscript{2} on the surface of Pt catalysts. Meanwhile, the holes will be extracted from the QDs to the Na\textsubscript{2}S/Na\textsubscript{2}SO\textsubscript{3} electrolyte (pH ~ 13), which serves as hole scavenger.

We used ultra-violet photoelectron spectroscopy (UPS) to analyze the core/shell band alignment of three types of QDs (Figure S7)\textsuperscript{54}. The positions of the conduction band (CB) and valence band (VB) of CdSe core are −3.41 eV and −5.66 eV, respectively with bandgap of 2.25 eV. After coating with a ZnSe shell, the CB shifted positively to −2.90 eV while VB shifted negatively to −5.81 eV with band gap of 2.91 eV. For two types of alloyed QDs, the CB shifted negatively to −3.96 eV and −4.06 eV for CdSe/Cd\textsubscript{x}Zn\textsubscript{1−x}Se#1 and CdSe/Cd\textsubscript{x}Zn\textsubscript{1−x}Se#2 QDs, respectively, which is attributed to the addition of Cd in alloyed shells. Similarly, the VB shifted to −6.51 eV and −6.61 eV for CdSe/Cd\textsubscript{x}Zn\textsubscript{1−x}Se#1 and CdSe/Cd\textsubscript{x}Zn\textsubscript{1−x}Se#2 QDs, respectively. Such phenomena indicate that the overall bandgap of alloyed QDs becomes narrower (both 2.55 eV for alloyed QDs compared to 2.91 eV). As shown in Fig. 3b, the red square indicates the overall band position of CdSe/Cd\textsubscript{x}Zn\textsubscript{1−x}Se#2 QDs according to the UPS results. The band positioning shows that
electrons can be successfully injected from QDs to TiO$_2$ thanks to favorable band alignment. Due to the high CB offset of ZnSe, the shell serves as both physical barrier and energy barrier to slow down the electron transfer rate. Due to the gradient interfacial Cd$_x$Zn$_{1-x}$Se layer, the large energy barrier is significantly reduced, thus the electrons have a higher probability to leak out.

To quantitatively analyze the carrier transfer behavior, we used ZrO$_2$ mesoporous films as benchmark to estimate the electron/hole transfer rate, using the following Eq. 5:$^5$$^6$

$$\frac{K_{et}}{K_{ht}} = \frac{1}{<\tau>_{QDs - TiO_2/ZrO_2\ (electrolye)}} - \frac{1}{<\tau>_{QDs - ZrO_2}}$$

Where $K_{et}$ and $K_{ht}$ are the electron and hole transfer rate, respectively. Transient PL spectroscopy was used to monitor the PL decays of the QDs, QDs/TiO$_2$, QDs/ZrO$_2$ and QDs/ZrO$_2$/electrolyte. Figure 3c-e show the PL lifetime spectra of three types of core/shell QDs. The average lifetimes of three types of QDs in different conditions and the corresponding carrier transfer rates are listed in Table 1. For alloyed QDs, $K_{et}$ reaches $24.2 \times 10^7$ s$^{-1}$ (CdSe/Cd$_x$Zn$_{1-x}$Se#1) or $32.7 \times 10^7$ s$^{-1}$ (CdSe/Cd$_x$Zn$_{1-x}$Se#2 QDs), which is $\sim 6$ times and $\sim 8$ times faster than that of the CdSe/6ZnSe QDs. Such large improvement is attributed to the presence of an intermediated gradient shell, which lowers the transfer energy barrier, yielding a faster electron transfer rate. The electron transfer rate of CdSe/Cd$_x$Zn$_{1-x}$Se#2 QDs was then compared to that of other types of alloyed QDs. According to Figure S9 and Table 1, the $K_{et}$ is $3.6 \times 10^7$ s$^{-1}$ for CdSe/CdSeS/CdS/CdZnS/ZnS QDs, $2.6 \times 10^7$ s$^{-1}$ for CdSe/CdSeS/CdS QDs and $4.5 \times 10^7$ s$^{-1}$ for CdSe/CdZnS/CdZnS/ZnS QDs, respectively which is much lower than that of CdSe/Cd$_x$Zn$_{1-x}$Se#2 QDs ($32.7 \times 10^7$ s$^{-1}$). When comparing the hole transfer rate ($K_{ht}$) of three types of QDs, higher $K_{ht}$ for two alloyed QDs is observed: from $23.7 \times 10^7$ s$^{-1}$ for CdSe/6ZnSe QDs to $30.2 \times 10^7$ s$^{-1}$ for CdSe/Cd$_x$Zn$_{1-x}$Se#1 QDs and $30.1 \times 10^7$ s$^{-1}$ for CdSe/Cd$_x$Zn$_{1-x}$Se#2 QDs. The minor change in the $K_{ht}$ compared to $K_{et}$ occurs because the VB of CdSe and ZnSe are closer ($\sim 0.1$ eV difference).$^{42}$ Thus, the gradient shell no longer plays a critical role in facilitating the hole transfer in a strong alkaline electrolyte (pH $\sim$ 13) with a large hole-driven force. In other words, such gradient alloy intermediate layers yield a faster electron transfer rate yet have a minor influence on the hole transfer rate.
Table 1
Optical and dynamic parameters of as-prepared QDs.

<table>
<thead>
<tr>
<th>QDs</th>
<th>Abs. (nm)</th>
<th>PL (nm)</th>
<th>Lifetime in toluene (ns)</th>
<th>Electron transfer rate $K_{et}$ $(10^7 \text{ s}^{-1})$</th>
<th>Hole transfer rate $K_{ht}$ $(10^7 \text{ s}^{-1})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CdSe/6ZnSe</td>
<td>552</td>
<td>578</td>
<td>14.3</td>
<td>4.0</td>
<td>23.7</td>
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<tr>
<td>CdSe/Cd$<em>{x}$Zn$</em>{1-x}$Se#1</td>
<td>612</td>
<td>642</td>
<td>48.8</td>
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<tr>
<td>CdSe/Cd$<em>{x}$Zn$</em>{1-x}$Se#2</td>
<td>625</td>
<td>649</td>
<td>58.5</td>
<td>32.7</td>
<td>30.1</td>
</tr>
</tbody>
</table>

Theoretical calculation of wavefunction in QDs

To confirm the structure of three types of core/shell QDs and the corresponding carrier dynamics inside the QDs, we obtained the wave function of electrons and holes in QDs by solving the stationary Schrödinger equation in a rod/egg-shaped geometry where $r$ represents two short axes and $z$ represents long axes. The values of width and length of QDs were measured using from TEM images (9 nm for the length and 4.5 nm for the width). Figure 4a and d show the simulated area of electrons and holes in the three types of QDs where the colours represent the probability density in certain areas. Figure 4b-c and e-f shows the electron and hole distribution probability inside the QDs as the function of QDs axis ($r$ or $z$), represented by $\psi_e^2(r)$, $\psi_e^2(z)$, $\psi_h^2(r)$ and $\psi_h^2(z)$. According to the Figs. 4b-c, the probability of electrons in both $r$ and $z$ axis $\psi_e^2(r)$ and $\psi_e^2(z)$ for CdSe/Cd$_{x}$Zn$_{1-x}$Se#1 QDs show an increasing electron leakage compared to CdSe/6ZnSe QDs, resulting from the intermediated alloyed shells (shown in Figure S10). For CdSe/Cd$_{x}$Zn$_{1-x}$Se#2 QDs, with gradient shell composition, both $\psi_e^2(r)$ and $\psi_e^2(z)$ exhibit a more efficient electron leakage compared to the other two QDs. such phenomena indicate that a more favorable band alignment was obtained by adding gradient alloyed shells, leading to a more efficient electron transfer rate. Similarly, $\psi_h^2(r)$ and $\psi_h^2(z)$ of alloyed QDs also show an increasing probability for hole transfer to the outer area of the QDs. In summary, the theoretical calculations of wavefunction of three types of QDs confirm that a more favorable band alignment was attained with the addition of alloyed shells, leading to faster electron/hole transfer rate (consistent with former results) which suppresses exciton recombination inside the QDs.

Based on the above results, we deduce that the non-spherical structure is favourable for the spatial separation of electrons and holes. Meanwhile in the $r$ direction, the physical barrier of the asymmetric QDs is largely reduced compared to spherical QDs. Together with the aligned valence energy levels, the holes can efficiently transfer into the electrolyte through the thinner alloyed shell in the $r$ axis, whereas electrons mostly leak through the $z$ axis. In other words, the asymmetric QDs structure improves the carrier spatial separation, leading to suppressed exciton recombination.

Photoelectrochemical performance
We fabricated photoanodes by depositing QDs into mesoporous TiO$_2$ films using electrophoretic deposition (EPD)\textsuperscript{57}, forming QDs/TiO$_2$ heterostructures. After the ligand exchange and ZnS protection layer via SILAR, several types of QDs based photoanodes were assembled for PEC measurements. For all the anodes, we kept identical parameters for anode preparation, post-treatment and PEC configuration. In general, the photocurrent density ($J$) gradually increases with the increase of applied voltage until a saturated photocurrent density ($J_{ph}$) is obtained. As shown in Fig. 5a, a $J_{ph}$ of 8.8 mA/cm$^2$ can be obtained for the photoanode based on CdSe/6ZnSe. Remarkably, the CdSe/Cd$_x$Zn$_{1-x}$Se#1 QDs based photoanode reaches $J_{ph}$ values as high as 30.0 ± 1.0 mA/cm$^2$. When the alloyed layers are further optimized by adding gradient layers, the CdSe/Cd$_x$Zn$_{1-x}$Se#2 QDs based photoanode exhibits unprecedented champion $J_{ph}$ values of 35 mA/cm$^2$ with average value of 33 ± 2.0 under one sun illumination (AM 1.5 G, 100 mW/cm$^2$), which is the highest photocurrent density among all QDs based PEC cells to date. To confirm the data obtained, we prepared more than 10 samples for PEC measurements. Figure 5b shows the $J_{ph}$ distribution for the three types of QDs and the inset figure shows the $J_{ph}$ of each measurement for CdSe/Cd$_x$Zn$_{1-x}$Se#2 QDs.

To confirm the alloy effect on other types of core/shell QDs, we also synthesized CdSe/ZnS, CdSe/CdS, CdSe/CdS/ZnS core/shell QDs and their corresponding alloyed QDs, CdSe/CdZnSe/CdZnS/ZnS, CdSe/CdSeS/CdS, CdSe/CdSeS/CdS/CdZnS/ZnS and spherical CdSe/Cd$_x$Zn$_{1-x}$Se QDs. All types of QDs were used 6 monolayers for the shells with different composition via SILAR process. We then used them as sensitizers for TiO$_2$ for PEC H$_2$ generation. The results are shown in Fig. 5c-d and Figure S11. The $J_{ph}$ is observed to increase with alloyed shells compared to pure-shell QDs. However, the highest $J_{ph}$ based on other types of alloyed QDs is only 22 mA/cm$^2$ (CdSe/CdSeS/CdS QDs), much lower than 35 mA/cm$^2$ obtained from CdSe/Cd$_x$Zn$_{1-x}$Se#2 QDs.

To investigate the morphology effect, spherical CdSe/CdZnSe/ZnSe QDs with the same structure/composition were compared with rod/egg shaped CdSe/CdZnSe/ZnSe QDs. The $J_{ph}$ based on spherical CdSe/CdZnSe/ZnSe QDs can reach up to 26.5 mA/cm$^2$ which is still lower than that of rod/egg shaped CdSe/CdZnSe/ZnSe (CdSe/Cd$_x$Zn$_{1-x}$Se#1 and CdSe/Cd$_x$Zn$_{1-x}$Se#2 QDs) QDs. Such unprecedented results of CdSe/Cd$_x$Zn$_{1-x}$Se#2 QDs compared to CdSe/ZnSe QDs and other types of alloyed QDs can be attributed to: (i) the enhanced absorption range by adding alloyed gradient shells, leads to more absorbed photons from solar irradiation; (ii) as ZnSe is a wide bandgap semiconductor, it allows a more efficient passivation effect for the QDs surface compared to CdS and the overall band gap of the shell could be reduced by adding Cd in ZnSe, lowering the CB energy offset from the core to the shell; (iii) compared to the spherical shape, asymmetric rod/egg shaped QDs with intermediate alloyed shells improve the electron transfer efficiency (more than 7 times faster than other types of alloyed QDs), and simultaneously separate the carriers in different axis direction, leading to fewer carrier spatial overlap and exciton recombination.
Thus, the asymmetric QDs exhibited an outstanding $J_{ph}$ compared to other types of CdS/ZnS shelled QDs and spherical QDs with similar structure and composition. The obtained $J_{ph}$ in this work is comparable to the state-of-art of all semiconductors as PEC photoelectrodes as shown in Table 2. The highest $J_{ph}$ (35 ± 2.0) obtained using asymmetric QDs is close to the one obtained with photoanodes based on Si, and higher compared to values from photoanodes based on perovskites, and other bulk semiconductors such as metal oxides, nitrides, sulfides, etc.
Table 2
Best current density values for PEC H$_2$ evolution.

<table>
<thead>
<tr>
<th>Photoelectrode</th>
<th>Reaction electrolyte</th>
<th>$J_{ph}$ (mA/cm$^2$)</th>
<th>Reference electrode</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>CdSe/Cd$<em>x$Zn$</em>{1-x}$Se QDs/TiO$_2$</td>
<td>0.35 Na$_2$S$_3$/0.25 M Na$_2$S</td>
<td>35 (0.6 V)</td>
<td>Ag/AgCl</td>
<td>This work</td>
</tr>
<tr>
<td>n-Si/SiO$_x$/Al$_2$O$_3$/Pt/Ni</td>
<td>1 M KOH</td>
<td>28.5 (1.6 V)</td>
<td>Hg/HgO</td>
<td>58</td>
</tr>
<tr>
<td>n-Si/SiO$_x$/Co/CoOOH</td>
<td>1 M KOH</td>
<td>35 (0.6 V)</td>
<td>Ag/AgCl</td>
<td>59</td>
</tr>
<tr>
<td>SrTiO$_3$/p-Si</td>
<td>0.5 M H$_2$SO$_3$</td>
<td>35 (0.6 V)</td>
<td>Ag/AgCl</td>
<td>60</td>
</tr>
<tr>
<td>b-Si/TiO$_2$/Co(OH)$_2$</td>
<td>1 M NaOH</td>
<td>32.3 (1.48 V)</td>
<td>calomel</td>
<td>61</td>
</tr>
<tr>
<td>CoO$_x$/p$^+$/n-Si</td>
<td>1 M NaOH</td>
<td>30.8 (1.23 V)</td>
<td>Hg/HgO</td>
<td>62</td>
</tr>
<tr>
<td>MoSe$_2$/ p$^+$/n-Si</td>
<td>1 M HBr</td>
<td>30 (0.3 V)</td>
<td>Ag/AgCl</td>
<td>63</td>
</tr>
<tr>
<td>n-Si/PEDOT: PSS</td>
<td>hydrogen iodide</td>
<td>28.8 (0.3 V)</td>
<td>Ag/AgCl</td>
<td>64</td>
</tr>
<tr>
<td>n$^+$/p-Si microwire/SiO$_2$</td>
<td>0.1 M H$_2$SO$_4$</td>
<td>34 (0 V)</td>
<td>Ag/AgCl</td>
<td>65</td>
</tr>
<tr>
<td>p$^+$/n-Si/SiO$_2$</td>
<td>1 M KOH</td>
<td>31.2 (1.23 V)</td>
<td>/</td>
<td>66</td>
</tr>
<tr>
<td>np$^+$/Si/SiO$_x$/NiFe</td>
<td>1.0 M KOH</td>
<td>30.7 (1.23 V)</td>
<td>/</td>
<td>67</td>
</tr>
<tr>
<td>MAPbI$_3$ with proline</td>
<td>0.5 M H$_2$SO$_4$</td>
<td>21.7 (0 V)</td>
<td>calomel</td>
<td>68</td>
</tr>
<tr>
<td>CH$_3$NH$_3$PbI$_3$</td>
<td>0.5 M H$_2$SO$_4$</td>
<td>18 (0 V)</td>
<td>calomel</td>
<td>69</td>
</tr>
<tr>
<td>BiVO$_4$/Ni:FeO$_x$</td>
<td>0.5 M K$_3$BO$_3$</td>
<td>6.4 (1.23 V)</td>
<td>Ag/AgCl</td>
<td>70</td>
</tr>
<tr>
<td>Cu$_3$BiS$_3$</td>
<td>0.2 M Na$_2$HPO$_4$/Na$_2$PO$_4$</td>
<td>7 (0 V)</td>
<td>Ag/AgCl</td>
<td>71</td>
</tr>
<tr>
<td>In:GaN/Ta$_3$N$_5$/Mg:GaN</td>
<td>1 M KOH</td>
<td>9.3 (1.23 V)</td>
<td>Hg/HgO</td>
<td>72</td>
</tr>
<tr>
<td>CdIn$_2$S$_4$</td>
<td>0.5 M Na$_2$SO$_4$</td>
<td>5.73 (1.23 V)</td>
<td>Ag/AgCl</td>
<td>73</td>
</tr>
</tbody>
</table>

To compare the real PEC H$_2$ evolution process with the theoretical values derived from $J_{ph}$ based on alloyed QDs, we measured the H$_2$ evolution rate using gas chromatography (GC) under one sun irradiation. According to Fig. 6a and the equation for the calculation of the faradaic efficiency ($\eta_{FE}$) (shown in the Experimental section), a final $\eta_{FE}$ of ~ 82% can be calculated for our system with
operation time of one hour. The incident photon-to-electron conversion efficiency (IPCE) was further measured and calculated based on the IPCE equation (shown in supporting information). As shown in Fig. 6b, for CdSe/Cd_{x}Zn_{1−x}Se#1 and CdSe/Cd_{x}Zn_{1−x}Se#2 QDs, from 650−700 nm, the IPCE decreases sharply and the values are close to 0, in agreement with the UV-vis absorption spectra. For CdSe/6ZnSe QDs, the initial drop position is blue-shifted to 600 nm which is attributed to the narrower absorption range. From the wavelength of 450 to 650 nm, IPCE value of two alloyed QDs are higher than CdSe/6ZnSe QDs while the IPCE for CdSe/Cd_{x}Zn_{1−x}Se#2 QDs is higher than that of CdSe/Cd_{x}Zn_{1−x}Se#1 QDs which illustrates a more efficient carrier transfer efficiency due to more favorable band alignment.

The stability performance is another critical factor for the application of PEC H\textsubscript{2} generation. Stability tests were conducted under 0.6 V bias vs RHE with continuous one sun intensity (AM 1.5 G, 100 mW/cm\textsuperscript{2}) solar irradiation (shown in Fig. 6c). The CdSe/ZnSe QDs based photoanode only shows a photocurrent retention of 58\% after 2-h continuous illumination. This is mainly due to the photo-oxidation of the QDs where electrons and holes cannot be transferred out of the QDs due to unfavourable band alignment. For two alloyed QDs, the CdSe/Cd_{x}Zn_{1−x}Se#1 QDs based photoanode can maintain ~ 78\% of the initial current density value after 2-h solar irradiation. Such improvement is attributed to the favourable band alignment between core and shell obtained by adding alloyed shells. As a result, self-oxidation and recombination can be largely reduced inside the QDs, leading to better stability performance. For CdSe/Cd_{x}Zn_{1−x}Se#2 QDs, ~ 96\% of the initial photocurrent can be preserved after 2-hour continuous illumination, and even after 10 hrs ~ 82\% of the initial J_{ph} is maintained. Such gradient band alignment can largely improve the carrier transfer rate, leading to fewer hole accumulation and accordingly reduced photo-oxidation and photo-recombination. We also compared the stability performance of CdSe/Cd_{x}Zn_{1−x}Se#2 QDs to other types of alloyed QDs under 2-h illumination which is shown in the inset of Fig. 6c. Due to the fastest electron transfer rate and efficient surface passivation effect, the CdSe/CdZnSe/ZnSe (CdSe/Cd_{x}Zn_{1−x}Se#2) QDs still exhibit the best stability performance among all alloyed QDs.

**Conclusions and perspectives**

In conclusion, we report the synthesis of continuous gradient structured asymmetric CdSe/Cd_{x}Zn_{1−x}Se colloidal QDs. The latter were used as sensitizers for TiO\textsubscript{2} for solar-driven PEC H\textsubscript{2} evolution. The PEC cell exhibits a remarkable saturated photocurrent density of more than 30 mA/cm\textsuperscript{2} for CdSe/CdS_{x}Zn_{1−x}Se#1 QDs and 35 mA/cm\textsuperscript{2} for CdSe/CdS_{x}Zn_{1−x}Se#2 QDs, respectively under one sun illumination (AM 1.5 G, 100 mW/cm\textsuperscript{2}). These values are two times higher than the present record in colloidal QDs-based photoanodes. The unprecedented value of current density is comparable to state-of-the-art performances of Si-based photoelectrodes. The corresponding faraday efficiency calculated based on theoretical and experimental H\textsubscript{2} evolution volume is ~ 82\%. Further, the photoanode based on the QDs can maintain ~ 96\% of the current density after 2 hours, and more than ~ 82\% after 10 hours. These results indicate that
such asymmetric continuous gradient heterostructured QDs are very promising towards high performance solar-to-fuel conversion efficiency and also can be potentially used for other applications.

Declarations

Author contributions


Acknowledgement

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References


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Figures

Figure 1

Structure of asymmetric QDs. a, TEM image of CdSe/Cd$_x$Zn$_{1-x}$Se#2 QDs. b, HAADF-STEM image of the CdSe/Cd$_x$Zn$_{1-x}$Se#2 QDs. c, Energy dispersive spectroscopy elemental maps of Cd, Zn, Se and (d) Se in the same CdSe/Cd$_x$Zn$_{1-x}$Se#2 QDs shown in (b). e, Elemental profiles of Cd, Zn and Se in a typical QD from the arrow shown below; HR-STEM image and the corresponding crystal structure simulation of (f) CdSe/6ZnSe QDs; (g) CdSe/Cd$_x$Zn$_{1-x}$Se#1 QDs; (h) CdSe/Cd$_x$Zn$_{1-x}$Se#2 QDs.
Figure 2

Optical properties of heterostructured QDs. UV-vis absorption spectra of (a) CdSe/6ZnSe, CdSe/Cd$_x$Zn$_{1-x}$Se#1 and CdSe/Cd$_x$Zn$_{1-x}$Se#2 QDs. b, CdSe/CdS, CdSe/ZnS, CdSe/ZnSe and CdSe/CdS/ZnS QDs and corresponding alloyed QDs; PL spectra of (c) CdSe/6ZnSe, CdSe/Cd$_x$Zn$_{1-x}$Se#1 and CdSe/Cd$_x$Zn$_{1-x}$Se#2 and (d) CdSe/CdS, CdSe/ZnS, CdSe/ZnSe and CdSe/CdS/ZnS QDs and corresponding alloyed QDs. e, PL decay spectra of CdSe/6ZnSe, CdSe/Cd$_x$Zn$_{1-x}$Se#1 and CdSe/Cd$_x$Zn$_{1-x}$Se#2 QDs in toluene.
**Figure 3**

**Energy diagram and charge transfer.** **a,** Schematic represented diagram of PEC H$_2$ evolution based on QDs photoanode. **b,** Band alignment of CdSe/Cd$_x$Zn$_{1-x}$Se#2 with TiO$_2$ and FTO where the red square indicates the band position of overall QDs. **c-e,** PL decay spectra of (c) CdSe/6ZnSe QDs (d) CdSe/Cd$_x$Zn$_{1-x}$Se#1 QDs (e) CdSe/Cd$_x$Zn$_{1-x}$Se#2 QDs with different substrates.
**Figure 4**

**Wavefunction in QDs.** a, Schematic diagram electrons spatial probability of 1/4 QDs in a r/z coordinate for CdSe/6ZnSe, CdSe/Cd$_x$Zn$_{1-x}$Se#1 and CdSe/Cd$_x$Zn$_{1-x}$Se#2 QDs. b-c, Electrons spatial probability of CdSe/6ZnSe, CdSe/Cd$_x$Zn$_{1-x}$Se#1 and CdSe/Cd$_x$Zn$_{1-x}$Se#2 QDs as the function of r (short axis) and z (long axis); (e) Schematic diagram holes spatial probability of 1/4 QDs in a r/z coordinate for CdSe/6ZnSe, CdSe/Cd$_x$Zn$_{1-x}$Se#1 and CdSe/Cd$_x$Zn$_{1-x}$Se#2 QDs. e-f, Holes spatial probability of CdSe/6ZnSe, CdSe/Cd$_x$Zn$_{1-x}$Se#1 and CdSe/Cd$_x$Zn$_{1-x}$Se#2 QDs as the function of r (short axis) and z (long axis). The color in (a) and (d) indicates the probability of electrons and holes in certain region.
Figure 5

PEC behaviors. **a**, Photocurrent-voltage dependence for CdSe/6ZnSe, CdSe/Cd$_x$Zn$_{1-x}$Se#1 and CdSe/Cd$_x$Zn$_{1-x}$Se#2 QDs under dark and under continuous one sun illumination (AM 1.5 G, 100 mW/cm$^2$). **b**, Photocurrent density distribution for three types of QDs while the inset shows the photocurrent density histogram of CdSe/Cd$_x$Zn$_{1-x}$Se#2 QDs. **c**, Photocurrent-voltage dependence for CdSe/ZnSe, CdSe/ZnS, CdSe/CdS and CdSe/CdS/ZnS QDs under dark and under continuous one sun illumination (AM 1.5 G, 100 mW/cm$^2$). **d**, Photocurrent-voltage dependence for CdSe/CdZnSe/ZnSe, CdSe/CdZnSe/CdZnS/ZnS, CdSe/CdSeS/CdS and CdSe/CdSeS/CdS/CdZnS/ZnS QDs under dark and under continuous one sun illumination (AM 1.5 G 100 mW/cm$^2$).
Figure 6

H₂ evolution based on heterostructured QDs device. a, Theoretical and experimental H₂ evolution of CdSe/CdₓZn₁₋ₓSe#2 QDs/TiO₂ photoanodes during 2 hours under one sun illumination (AM 1.5 G, 100 mW/cm²) with a bias of 0.6 V vs RHE. b, IPCE spectra of CdSe/6ZnSe, CdSe/CdₓZn₁₋ₓSe#1 and CdSe/CdₓZn₁₋ₓSe#2 QDs. c, Stability performance of three types of QDs for 2-hour and 10-hour continuous illumination under the bias of 0.6 V vs RHE.

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