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Heterostructured core/gradient multi-shell quantum dots for high-performance and durable photoelectrochemical hydrogen generation

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ABSTRACT

Colloidal Quantum dots (QDs) are considered promising light harvesters for photoelectrochemical (PEC) hydrogen generation devices due to their size tunable optoelectronic properties. However, the solar-to-hydrogen (STH) efficiency and long-term stability of devices based on QDs are still relatively low, thus limiting the commercial development. These limitations are attributed to the limited absorption range of QDs, unfavorable band energy alignment and photo-oxidation. Here we propose and realize two core/multiple-shell architecture based on CdSe/CdS/ZnS QDs. The shell composition is optimized with gradient layers, forming CdSe/CdSe_xS_{1-x}/CdS/Zn_yCd_{1-y}S/ZnS core/multiple-shell structures, which reduces the surface traps and defects of QDs and simultaneously suppresses exciton recombination by providing intermediated alloyed interlayers. The PEC device based on a mesoporous TiO₂ sensitized with two types of core/multiple-shell QDs exhibited an outstanding saturated photocurrent density of 20.5 mA/cm² for alloyed core/multiple-shell QDs, under one sun illumination (AM 1.5 G, 100 mW/cm²). To our knowledge, this is comparable to the highest value reported so far for the PEC devices based on colloidal QDs. In addition, the as-prepared PEC devices exhibited excellent stability, maintaining ~93.4 % of the initial photocurrent density after 2-hour continuous illumination (100 mW/cm²). This work provides an efficient approach for improving the performance of PEC devices through QDs structure engineering.

1. Introduction

Solar technologies that capture and transform the sun's energy can take many forms, such as solar cells, photocatalysis (PC) and photoelectrochemical (PEC) hydrogen (H₂) generation [1–4]. PEC H₂ production is a low-cost and efficient method to produce H₂ via solar irradiation compared to other approaches such as PC and photovoltaic-electrolysis (PV-E) [5,6]. Generally, a PEC device for H₂ production consists of a photoelectrode (either a photoanode or a photocathode), a counter-electrode, and an electrolyte. Recent research has focused on the design of functional semiconductors, which have suitable band alignment to absorb the solar irradiation efficiently and drive the hydrogen reduction process. The most studied photoanodes are based on metal oxides with wide-bandgap (e.g. TiO₂ [7,8], ZnO [9,10], SnO₂ [11,12]), which have high stability in neutral or alkaline

electrolytes against photo/chemical corrosion [13]. However, most metal oxides' intrinsically wide-bandgap properties limit their absorption range within the UV part of the solar spectrum (i.e. only 5 % of the total solar irradiation can be exploited). For example, anatase TiO₂, due to its wide bandgap of ~3.2 eV, can only absorb photons below 385 nm [14], leading to a low solar-to-hydrogen (STH) efficiency [15]. One possibility to address this issue is to sensitize the metal oxide using a material with smaller bandgap, which allows to increase the absorption range. Due to their broad absorption range [16,17], tunable bandgap [18], multiple exciton generation (MEG) effects [19] and high absorption coefficient, colloidal quantum dots (QDs) can be used as efficient sensitizers of metal oxides. Recently, many QDs semiconductors (e.g. PbS [20,21], CdSe [22,23], CdS [12,24], CuInSe [25,26], CuInS [25,27]) have been investigated and used to fabricate QDs/TiO₂ heterostructures for PEC H₂ evolution. In particular, to address the issues of unstable

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surface of bare QDs [28,29], core/shell structured QDs (e.g. PbSe/PbS [30,31], CdSe/CdS [32,33], PbS/CdS [20,34], CdS/CdSe [24,35], ZnTe/CdSe [36,37]) have been further developed. In this context, the core/shell QD architecture exhibits multiple favorable properties: (i) the shell material can passivate the surface of the core QDs, leading to a better steric and electrostatic stability; (ii) the shell materials and composition can be tuned to form favorable band alignment, leading to an efficient electron/hole (e^+/h^-) separation and transfer; (iii) the absorption of core/shell QDs could be enhanced compared to bare QDs, generating more excitons [38–50].

However, so far, the low saturated photocurrent density as well as the poor long-term stability limit their applications in PEC cells. Previously, we have shown that by using a CdSe/CdS architecture with an alloyed interfacial layer ($\text{CdSe/CdSe}_x\text{S}_{1-x}/\text{CdS}$), it is possible to increase the photocurrent density up to 17.5 mA/cm^2 [51]. However, the stability performance of these QDs based PEC devices still needs to be improved. Typically, one of the most important reasons for the fast degradation of QDs based devices is their surface traps/defects, which act as non-radiative recombination centers for charge carriers. More in general, the stability of QDs-based PEC devices is mainly affected by the following factors: photo-corrosion, photo-degradation and photo-oxidation. Inorganic ZnS passivated layers are often used as protective shell for QDs and metal oxides to prevent photo-corrosion. Photo-oxidation and photo-degradation are usually caused by inefficient carrier separation and unfavorable non-radiative recombination. An efficient approach is to build favorable band alignment to accelerate carrier transfer efficiency. As a result, non-radiative recombination events can be significantly reduced [52].

To address the issue of stability, a widely used approach consists in using wide bandgap semiconductors as shells (e.g. ZnS, ZnSe) [53]. Such wide bandgap semiconductors can reduce the traps states by passivating the QDs surface and play a barrier layer for prohibiting the electrons leaking to electrolyte or back into the QDs. However, if the shell is too thick, such architectures will decrease the carrier transfer efficiency. Based on these considerations, core/shell/shell QDs also known as core/multiple-shell QDs have been developed, in which a more efficient charge carrier transfer is realized due to a cascade band alignment [54].

Herein, by combining the two approaches, we demonstrate two types of graded core/multiple-shell QDs based PEC devices, $\text{CdSe}/(\text{CdS})_4/(\text{ZnS})_2$ (namely CCZ-1) QDs and $\text{CdSe}/(\text{CdSe}_x\text{S}_{1-x})_3/\text{CdS}/\text{Cd}_y\text{Zn}_{1-y}\text{S}/\text{ZnS}$ ($x = 0.5, y = 0.5$) (namely CCZ-2) QDs sensitizing mesoporous TiO_2 film for PEC H_2 generation. Under standard one sun illumination (AM 1.5 G, 100 mW/cm^2), the saturated photocurrent density of the photoanode based on CCZ-1 QDs reaches 14.2 mA/cm^2 , maintaining 84 % of its initial photocurrent density value after two-hour illumination. In contrast, alloyed CCZ-2 QDs based photoanode exhibits an outstanding photocurrent density of 20.5 mA/cm^2 and high stability, maintaining 93.4 % of its initial value after 2-hour illumination. To the best of our knowledge, the obtained photocurrent density value is comparable to the highest ever reported among all colloidal QDs based photoanodes. In addition, the stability performance indicates that the core/multiple-shell QDs are a promising candidate for future low-cost, highly efficient and stable hydrogen generation devices.

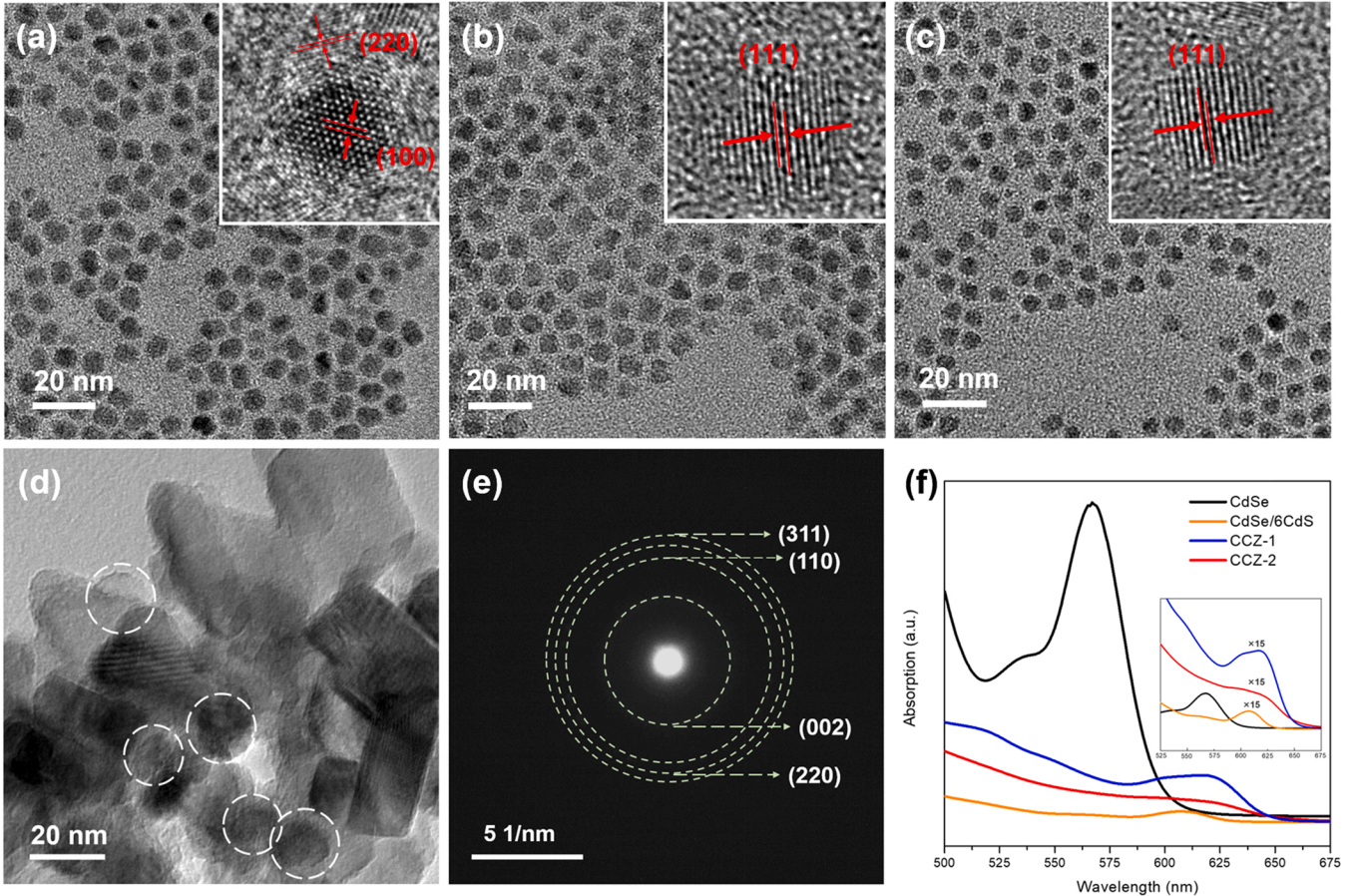


Fig. 1. TEM images of (a) CdSe/6CdS QDs, (b) CCZ-1 QDs and (c) CCZ-2 QDs where the right corner insets showed the HR-TEM images of the corresponding QDs; (d) TEM images of CCZ-2 QDs onto TiO_2 mesoporous films where the white circles indicate the position of QDs; (e) SAED spectra of CCZ-2 QDs; (f) The absorption spectrum of CdSe, CdSe/6CdS, CCZ-1 and CCZ-2 QDs (the inset shows the enlarged image of the peaks).

2. Results and discussions

2.1. Structures of QDs

The synthesis of the three types of QDs, CdSe/6CdS, CCZ-1 and CCZ-2 QDs, was achieved via a two-step procedure. First, the CdSe core QDs were synthesized by a hot-injection approach [51]. Subsequently, the heterostructured QDs were produced by successive ionic layer adsorption and reaction (SILAR) to finely control the shell thickness (details in experimental section) [55]. The CdSe morphologies were observed by transmission electron microscopy (TEM), as shown in Fig. S1. The average diameter of the CdSe core is ~ 3.4 nm with spherical morphology. Fig. 1(a)-(c) shows the TEM images of the CdSe/6CdS QDs, CCZ-1 QDs and CCZ-2 QDs, respectively. The average size of CdSe/6CdS is 7.4 ± 0.7 nm, while the average sizes of CCZ-1 and CCZ-2 QDs are 7.3 ± 0.8 nm and 6.5 ± 0.8 nm, respectively (Fig. S2). Due to the same layers of SILAR process grown for CdSe/6CdS and CCZ-1 QDs, the overall size of two types of QDs is similar. The size of CCZ-2 QDs is smaller than the sizes of both CCZ-1 QDs and CdSe/6CdS, which could be mainly due to the cation exchange process that occurs during the growth of the CdSe_{x-1-x} and $\text{Cd}_y\text{Zn}_{1-y}\text{S}$ alloyed shells, causing the shrinking of the CdSe core size [56]. In the insets of Fig. 1(a)-(c), the high-resolution TEM (HR-TEM) images indicate the (100) crystal plane ($d = 3.74$ Å) of wurtzite (WZ) structure of CdSe (PDF No. 02-0330) and (220) plane ($d = 2.06$ Å) of zinc blende (ZB) CdS for CdSe/6CdS QDs (PDF No. 01-0647). The boundary between CdSe core and CdS shell is clearly observed. For CCZ-1 and CCZ-2 QDs, the HR-TEM images reveal a lattice spacing of 3.36 Å, which corresponds to the (111) plane of the ZB crystal structure of CdS (PDF No. 01-0647). The reason for the non-visible boundary between layers for CCZ-1 and CCZ-2 QDs is due to the small lattice mismatch between the gradient layers that our TEM instrument is not able to discern. Selected area electron diffraction (SAED) pattern of CCZ-2 QDs is shown in Fig. 1(e), which indicates (002), (110) planes of WZ CdSe, (220) plane of ZB ZnS and (311) plane of ZB CdS. The SAED pattern for CdSe/6CdS and CCZ-1 QDs is shown in Fig. S3.

To further confirm the crystal structure of the QDs, X-ray diffraction (XRD) patterns were acquired (Fig. S4). The patterns reveals that the CdSe core has a WZ crystal structure, while for the CdSe/6CdS QDs, both CdSe WZ crystal structure and CdS ZB crystal structure can be identified. For CCZ-1 and CCZ-2 QDs, the CdSe core and CdS shell also present the typical WZ and ZB crystal structure, respectively, while the ZnS shell presents a ZB crystal structure.

X-ray photoelectron spectroscopy (XPS) was further used to verify the composition of QDs (Fig. S5). In XPS spectra, it can be confirmed that the presence of element Cd, Se, S and Zn in CCZ-2 QDs. Cross-sectional scanning electron microscopy (SEM) images and the corresponding energy dispersive spectroscopy (EDS) maps were also acquired conducted, providing evidence of the uniform dispersion of the CCZ-2 QDs inside the mesoporous TiO_2 film (Fig. S6).

2.2. Optical properties of QDs

The optical properties of the as-synthesized QDs were characterized by absorption and photoluminescence (PL) spectrum. As shown in Fig. 1(f), the first-excitonic absorption peak is located at 607 nm for CdSe/6CdS QDs. For CCZ-1 QDs, the first-excitonic absorption peak is located

at 616 nm, while for CCZ-2 QDs, the peak is slightly redshifted to 618 nm. The PL spectrum also shows a similar red-shift attributed to the successful epitaxial growth of CdS and ZnS (or alloyed layers) shells (Fig. S7) [53–55]. Fig. S8 and Table 1 show the lifetime of different QDs in toluene. The lifetime of CdSe QDs is 16.5 ns while for CdSe/6CdS QDs, CCZ-1 QDs, and alloyed CCZ-2 QDs is 22.5 ns, 23.8 ns and 21.3 ns, respectively. Compared with CdSe QD, the core/shell structures present longer lifetimes, which proves that the shell coating offers an improved carrier separation and thus a longer charge carrier lifetime. There is no significant difference of lifetime among the three core/shell (or core/multiple shells) QDs.

2.3. Carrier dynamics

Generally, under solar irradiation, upon photoexcitation, electron and hole pairs will generate in the QDs and dissociate at the QDs/ TiO_2 interfaces. The electrons will transfer from the CdSe core to CdS shell for CdSe/6CdS core/shell QDs while the electrons will further leak into ZnS shell region for CCZ-1 and CCZ-2 QDs. Subsequently, due to a favorable electronic band bending, the electrons will be injected into TiO_2 and then transferred to the counter-electrode (Pt) through the FTO to produce H_2 . Meanwhile, the holes which serves as hole scavenger will be extracted from QDs to the electrolyte ($\text{Na}_2\text{S}/\text{Na}_2\text{SO}_3$) ($\text{pH} \sim 13$). Fig. S9 shows the schematic diagram of CCZ-1 QDs/ TiO_2 based photoanode, indicating the bandgap and band position of CdSe, CdS and ZnS [32,57,58]. According to a previous report [32], the CdSe/6CdS forms a Quasi-type II band alignment core/shell architecture where the electrons can leak from CdSe core to CdS shell. It is important to control the thickness of the ZnS layer, otherwise, if the ZnS shell is not thin enough, due to the large conduction band offset between CdS and ZnS, the electrons will remain confined in the CdS shell region [59]. The holes still can be injected into the electrolyte due to strong driving force provided by the alkaline electrolyte ($\text{pH} \sim 13$, ~ 0.93 V (E vs SHE)) which means that the carrier spatial separation is more efficient than that in CdSe/CdS QDs. Fig. 2(a) shows the schematic diagram of CCZ-2 QDs based photoanode for PEC H_2 generation. The difference between CCZ-2 and CCZ-1 QDs is the presence of additional intermediate layers CdSe_{x-1-x} between CdSe, CdS and $\text{Cd}_y\text{Zn}_{1-y}\text{S}$ between CdS and ZnS for CCZ-2 QDs. Such intermediate layers can increase the carrier transfer efficiency by reducing the energy barriers (band offset) between two semiconductor materials and also reducing the lattice mismatch at the interfaces. Thus, the recombination can be suppressed owing to more efficient carrier separation as well as fewer defects at the interfaces. Moreover, such structure also has the advantage of passivating the QDs surface via coating with wide bandgap semiconductors, leading to fewer recombination centers on the surface of QDs.

To further investigate the carrier dynamics of the three types of QDs, the PL lifetimes of TiO_2 and ZrO_2 mesoporous films sensitized with QDs, with and without presence of electrolyte were collected and the charge carrier transfer rate can be calculated based on lifetime [60]. Due to the high energy band offset of ZrO_2 where electrons in QDs cannot be transferred to ZrO_2 , ZrO_2 can be used as a benchmark to compared with lifetime of QDs/ TiO_2 . The only reason for PL quenching in QDs/ ZrO_2 is attributed to carrier recombination events [61]. First, the average lifetime τ is calculated following the equation:

Table 1
QDs size and optical properties of the different QDs.

QDs	Diameter of core (nm)	Overall size (nm)	Abs peak position (nm)	PL peak position (nm)	Average electron lifetime in toluene (ns)
CdSe	3.4	3.4	567	583	16.5
CdSe/6CdS	3.4	7.4 ± 0.7	607	618	22.5
CCZ-1	3.4	7.3 ± 0.8	616	625	23.8
CCZ-2	3.4	6.5 ± 0.8	618	632	21.3

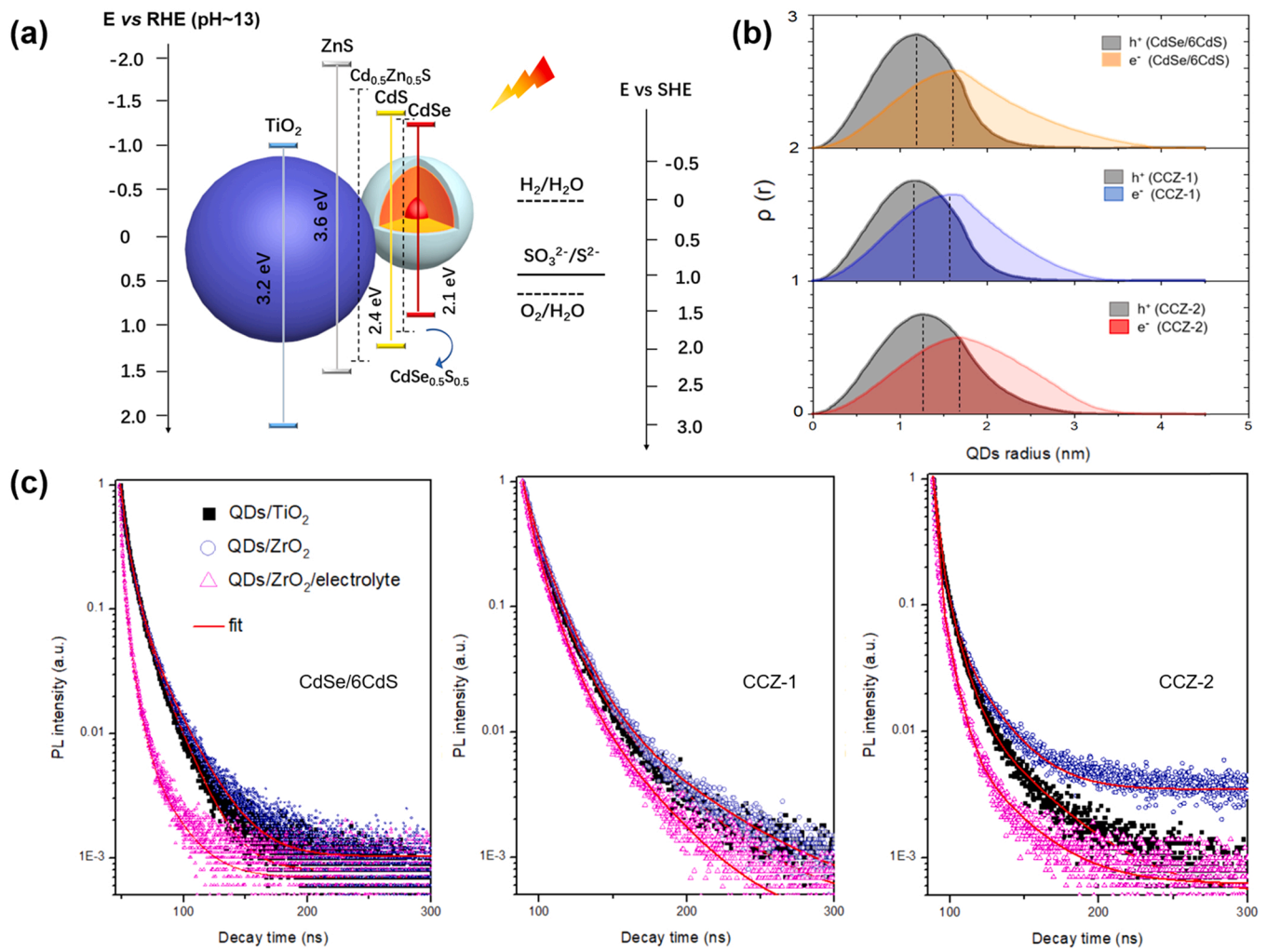


Fig. 2. (a) Representative schematic graph of CCZ-2 QD and QD based photoanode where the band gap of band position were shown for CdSe, CdS, ZnS and TiO₂ (the band position of alloyed shells were estimated according to the composition of the layers); (b) Carrier dissociation value $\rho(r)$ as a function of QD radius in CdSe/6CdS, CCZ-1 and CCZ-2 QDs (dash lines indicate the positions of the peaks for comparison); (c) PL lifetime spectra in the presence of an electrolyte of CdSe/6CdS, CCZ-1, and CCZ-2 QDs after being deposited onto TiO₂ films, ZrO₂ films, and ZrO₂ films in electrolyte.

$$\langle \tau \rangle = \frac{a_1 \tau_1^2 + a_2 \tau_2^2 + a_3 \tau_3^2}{a_1 \tau_1 + a_2 \tau_2 + a_3 \tau_3} \quad (3)$$

Subsequently, the electron/hole transfer rate (K_{et}/K_{ht}) can be calculated according to the measured average lifetime of as-synthesized QDs on different substrates by using the following equations:

$$\frac{K_{et}}{K_{ht}} = \frac{1}{\langle \tau \rangle_{QDs - TiO_2/ZrO_2} (electrolyte)} - \frac{1}{\langle \tau \rangle_{QDs - ZrO_2}} \quad (4)$$

Where K_{et} (or K_{ht}) is referring to the electron transfer rate (or hole transfer rate) while $\langle \tau \rangle_{QDs/TiO_2}$ and $\langle \tau \rangle_{QDs/ZrO_2}$ are corresponding to average lifetime of QDs on the substrates of TiO₂ films and

ZrO₂ films. The $\langle \tau \rangle_{QDs/ZrO_2}$ (electrolyte) represents the average lifetime of QDs/ZrO₂ films immersed in the electrolyte. All the lifetime values and calculated carrier transfer rates are listed in Table 2.

Typically, the lifetime of QDs-TiO₂ and QDs-ZrO₂ of CCZ-1 QDs are 14.3 ns and 15.2 ns, respectively, both higher compared to that of the CdSe/6CdS QDs. This result indicates that the ZnS shells serve as carrier transfer barrier where the electrons and holes are confined in the CdSe core and CdS shell regions. Similarly, the calculated K_{et} and K_{ht} are both smaller compared to that of the CdSe/6CdS QDs, which confirms the confinement effect provided by the ZnS shells. Instead, for alloyed CCZ-2 QDs, compared to CCZ-1 QDs, the K_{et} is 9 times larger while the K_{ht} value is 9.3, respectively. These data indicate that band alignment in CCZ-2 QDs is optimized by the alloyed intermediate layers which provided a favorable band structure for the carrier separation and transfer, leading

Table 2
Average electron lifetime with TiO₂ or ZrO₂ (in electrolyte) and the calculated charge transfer rate.

QDs	Lifetime of QDs/TiO ₂ (ns)	Lifetime of QDs/ ZrO ₂ (ns)	Lifetime of QDs/ ZrO ₂ in electrolyte (ns)	Calculated electron transfer rate K_{et} (10 ⁷ s ⁻¹)	Calculated hole transfer rate K_{ht} (10 ⁷ s ⁻¹)
CdSe/6CdS	9.9	10.8	4.2	0.8	14.3
CCZ-1	14.3	15.2	11.4	0.4	2.2
CCZ-2	7.0	9.5	3.2	3.6	20.4

suppressed charge recombination events [51,62].

To better understand the process of the carrier dissociation, we calculated the stationary Schrödinger equation in spherical geometry to solve the theoretical electron-hole wave functions. The $[\rho(r)]$ represented the calculated spatial probability distribution of electron wave function $\psi_e(r)$ and hole wave function $\psi_h(r)$ as a function of QDs radius (nm) is shown in Fig. 2(b). The dash lines in the graph indicate the peak position of functions for easier comparison. When compared to CdSe/6CdS core/shell QDs, both $\psi_e(r)$ and $\psi_h(r)$ of CCZ-1 QDs exhibit reduced carrier leakage according to the left-shift of the dash lines. This result is consistent with the former demonstration that the confinement effect caused by the ZnS shells. For alloyed CCZ-2 QDs, $\psi_e(r)$ and $\psi_h(r)$ show enhanced carrier leakage due to the right-shift of the dash lines when compared to CdSe/6CdS and CCZ-1 QDs. This phenomenon also provides evidence that the band alignment is optimized via band engineering of alloyed layers. Tables S1 shows the overlapping areas of three types of QDs. The e-h overlapping area increases from 62 % for CdSe/6CdS QDs to 67 % for CCZ-1 QDs due to the enhancement of confinement. The e-h overlapping area value of CCZ-2 QDs further increases up to 70 % because the carrier transfer efficiency improves, so both electrons and holes have more probability to leak to the shell regions. In summary, from the wavefunction model of three types of QDs, the ZnS

shell in CCZ-1 QDs offers carrier confinement via wide-bandgap shell coating compared to CdSe/6CdS QDs, while CdSe_xS_{1-x}, Cd_yZn_{1-y}S intermediated alloyed shells in CCZ-2 QDs provide faster pathway for carriers to leak out.

2.4. PEC performance

As a proof of concept, the three types of QDs were used as light harvesters in TiO₂ based photoanodes for PEC H₂ generation. First, the QDs were deposited onto mesoporous TiO₂ films by electrophoretic deposition (EPD) for 2 h under 200 V [63]. Prior to the PEC measurements, 2 SILAR cycles of ligand exchange and 2 cycles of passivation ZnS capping were conducted. The main function of post ZnS capping layer is to prevent photocorrosion. Meanwhile, it still can be a blocking barrier preventing the back electrons transfer from TiO₂ or QDs into the electrolyte [20]. The PEC performance of the QDs/TiO₂ photoanode system towards the H₂ generation reaction was evaluated in a typical three-electrode configuration with Na₂S (0.25 M) and Na₂SO₃ (0.35 M) as hole scavengers. All the PEC and stability measurements were carried out in dark and under simulated sun irradiation (AM 1.5 G, 100 mW/cm²). Ag/AgCl electrode was used as the reference electrode while a Pt sheet was used as counter electrode and. A set of linear-sweep

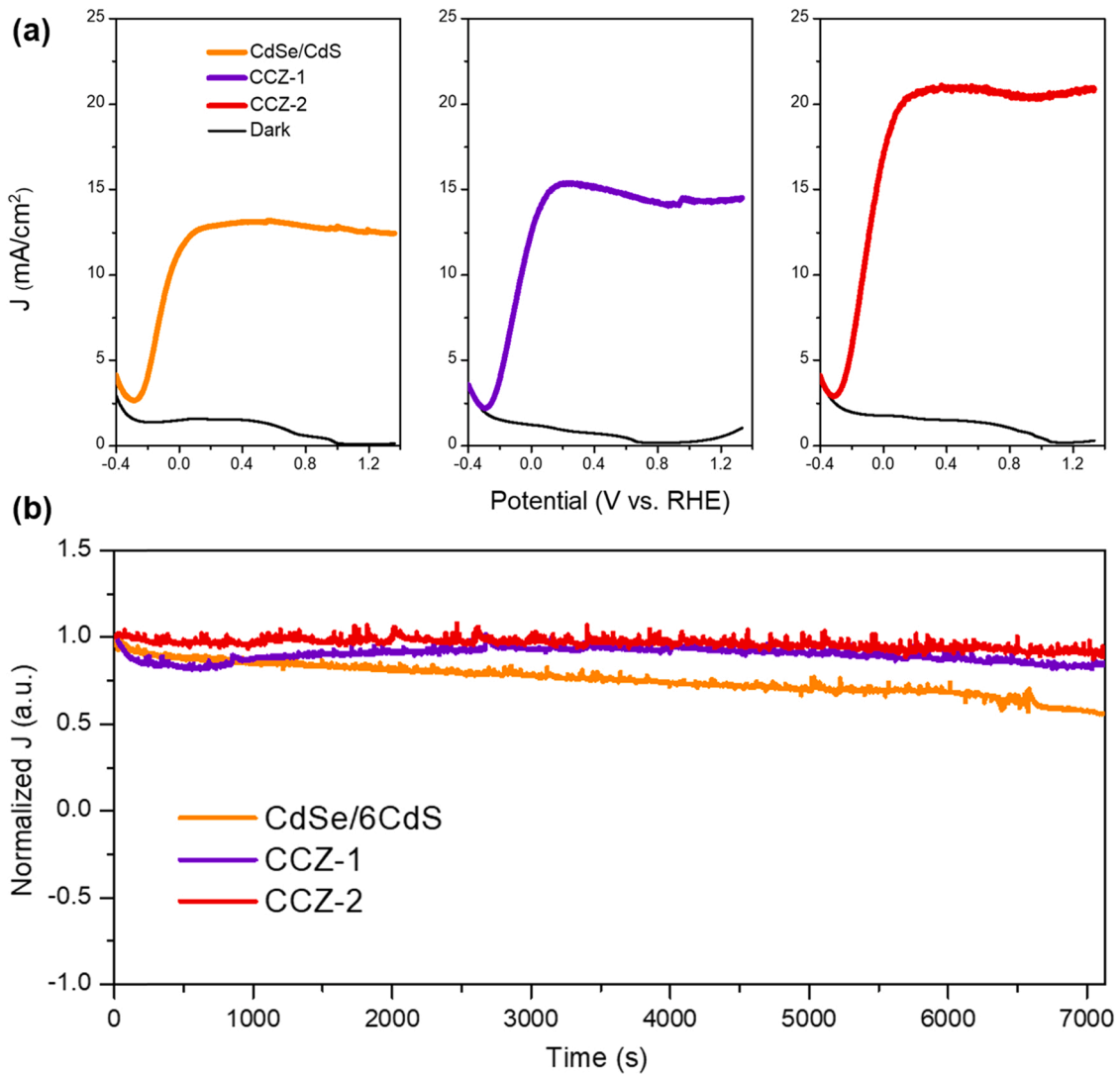


Fig. 3. Photocurrent density as the function of potential applied based on TiO₂ sensitized by (a) CdSe/6CdS QDs; (b) CCZ-1 QDs; (c) CCZ-2 QDs under dark (black curves) and continuous illumination (AM 1.5 G, 100 mW/cm²) (chromatic curves); (d) stability performance of the photoanodes based on CdSe/6CdS QDs, CCZ-1 QDs and CCZ-2 QDs with the bias of 0.6 V vs RHE under standard on sun illumination (100 mW/cm²).

voltammograms (LSV) were acquired using the representative photoanodes. With increasing voltage, the saturated photocurrent density (J_{ph}) was obtained for three types of QDs based photoanodes. Fig. 3 shows the LSV data of TiO₂ sensitized with CdSe/6CdS QDs CCZ-1 QDs and CCZ-2 QDs under dark and continuous illumination (AM 1.5 G, 100 mW/cm²). The CdSe/6CdS based photoanode displayed a J_{ph} of 12.6 mA/cm². For CCZ-1 QDs, the photoanode can achieve a J_{ph} of 14.2 mA/cm². The increased photocurrent density compared to the CdSe/6CdS based photoanode is mainly attributed to the enhancement of the absorption as well as the surface passivation effect provided by the ZnS shells. As a result, the surface traps are largely suppressed and fewer non-radiative recombination events occur on the QDs surface. The J_{ph} of the photoanode based on the alloyed CCZ-2 QDs reaches a value as high as 20.5 mA/cm², dramatic improvement compared to the other two types of QDs. Thanks to the double alloyed shells, the energy barrier between the different semiconductor materials (CdSe, CdS and ZnS) is significantly reduced, leading to more efficient carrier transfer. At the same time, the alloyed shells also have a passivation effect reducing the surface defects accordingly.

As mentioned previously, long-term stability is a critical factor for this type of device. In this work, the stability measurements were carried out at the bias of 0.6 V vs RHE for 2 h under continuous one sun illumination. According to Fig. 3(d), ~55 % of the initial photocurrent density value was maintained for the CdSe/6CdS QDs based photoanode. Meanwhile, ~84 % of the initial photocurrent density value was observed for the CCZ-1 QDs based photoanode, while an unprecedented stability performance was achieved for the alloyed CCZ-2 QDs based photoanode, with retention of ~93.4 % of the initial photocurrent value after 2 h of continuous illumination (100 mW/cm²). This outstanding stability performance is mainly attributed to the presence of the intermediate alloyed layers that can act as fast pathways for carrier transfer. As a result, the hole accumulation is largely reduced in the valence band, in turn leading to a reduced photo-oxidation of the photoanodes. Moreover, the ZnS (or alloyed layers) also play an important role of passivating the QDs surface. Thus, the recombination caused by the surface traps and defects can be dramatically suppressed.

In the literature, several works reported colloidal QDs based photoanodes for PEC H₂ generation. Some typical results are listed in Table 3 for comparison. In this work, we focused on improving the photocurrent density as well as long-term stability. To the best of our knowledge, the highest photocurrent density based on colloidal QDs was 17.5 mA/cm² while 22.1 mA/cm² based on in-situ QDs [51,64]. Here, the CCZ-2 alloy QDs based photoanode can achieve a J_{ph} as high as 20.5 mA/cm² under one illumination. More importantly, there are few works focusing on improving the stability performance of colloidal QDs based anode which is crucial for developing a robust technology for H₂ evolution from water. In Table 3, the 2-hour value was used as reference as it is the most common value reported for stability performance. So far, few studies reported over 90 % of the initial value of the photocurrent density. Basu [65] reported an unprecedented stability performance of 96 % after 2-hour measurement, but with a low photocurrent density of 4.7 mA/cm². Similarly, Adhikari [33] reported a photoanode of CdSe/CdS/Pb_xCd_{1-x}S/CdS/TiO₂ with retention of 94.9 % of the initial photocurrent value of 8 mA/cm² after 2 h. To summarize, the alloyed CCZ-2 QDs based photoanode not only achieves an extremely high

photocurrent density, but also maintains one of the best stability performances among all colloidal QDs based photoanodes.

Finally, to estimate the evolved H₂ volume in real condition based on as-synthesized QDs, a gas chromatograph system was further carried out together with *J-t* curves to compare the produced H₂ with calculated H₂ volume. As shown in Fig. S11, the calculated H₂ volume and measured H₂ volume are shown. Then the Faradaic efficiency is roughly calculated according to the equation shown in the Supporting information where ~80 % of the η_{FE} is obtained within 60 min PEC operation.

2.5. The effect of ZnS shell thickness

On one hand, a shell of a wide bandgap semiconductors such as ZnS can reduce the traps and defects on the QDs surface, improving the optoelectronic properties [59]. On the other hand, the wide bandgap shells can also act as a barrier inhibiting electron injection into the metal oxide. Thus, it is critical to investigate the ZnS shell thickness effect on PEC devices for which effect of the surface passivation and electron injection are both considered. For this reason, CdSe/4CdS QDs capped with different ZnS thicknesses (1–3 monolayer) were designed and synthesized via SILAR.

According to Fig. 4(a)–(c), TEM images show that the size of QDs increases with thicker ZnS shell. Typically, the diameter of QDs with different ZnS shell thickness is 7.0 ± 0.9 nm for CdSe/4CdS/ZnS QDs, 7.3 ± 0.8 nm for CdSe/4CdS/2ZnS QDs and 7.7 ± 1 nm for CdSe/4CdS/3ZnS QDs, respectively (Fig. S12). These values of QDs size indicates that the ZnS shells are successfully grown on the CdS surface by SILAR. Fig. S13 shows the UV–vis absorption spectra of CdSe/4CdS/ZnS QDs, CdSe/4CdS/2ZnS QDs and CdSe/4CdS/3ZnS QDs, in which the first-excitonic absorption peak is located at 591 nm, 601 nm and 603 nm, respectively. This observation reveals that a red-shift is induced by thicker ZnS shells, which is consistent with the former results.

Subsequently, we investigated the carrier dynamics of the colloidal QDs with different ZnS shells. Fig. S14 shows the lifetime of three QDs in toluene where the average lifetime is prolonged from 22.0 ns for CdSe/4CdS/ZnS QDs to 24.8 ns for CdSe/4CdS/2ZnS QDs, then further increasing to 25.0 ns for CdSe/4CdS/3ZnS QDs. The reason for such increased average lifetime is the stronger electron confinement provided by the thicker ZnS shell. Fig. 4(d)–(f) reports the PL spectra of three QDs after deposition onto TiO₂, ZrO₂ with/without the presence of the electrolyte. According to Fig. 4(d)–(f) and the Table 4, the average electron lifetime with ZrO₂ increased from 19.8 ns for CdSe/4CdS/ZnS QDs to 27.9 ns for CdSe/4CdS/2ZnS QDs and 26.3 ns for CdSe/4CdS/3ZnS QD, respectively. These results shown in Table S2 confirm the stronger confinement of electrons with thicker ZnS shells. For the calculated electron and hole transfer rate, K_{et} is both 1.6×10^7 s⁻¹ for the CdSe/4CdS/2ZnS QDs and CdSe/4CdS/3ZnS QDs, which is faster than the K_{et} of CdSe/4CdS/ZnS QDs. A similar phenomenon is observed for the hole transfer rate. The K_{ht} is both 2.6×10^7 s⁻¹ for CdSe/4CdS/2ZnS QDs and CdSe/4CdS/3ZnS QDs, higher than that of CdSe/4CdS/ZnS QDs.

Finally, mesoporous TiO₂ was sensitized with the three QDs and the PEC actively measured. According to Fig. 4(g), the J_{ph} of the three QDs is 12.5 mA/cm² for CdSe/4CdS/ZnS QDs, 14.2 mA/cm² for CdSe/4CdS/2ZnS QDs and 8.6 mA/cm² for CdSe/4CdS/3ZnS QDs, respectively. The

Table 3
Previous work of colloidal QDs based photoanode for PEC H₂ generation.

QDs	Metal oxide	Electrolyte	Saturated photocurrent density (mA/cm ²)	Stability performance	Ref
PbS/CdS	TiO ₂	Na ₂ S/Na ₂ SO ₃	11.2	70 % after 2 h	[20]
CdS/CdSe	TiO ₂	Na ₂ S/Na ₂ SO ₃	16	83 % after 4 h	[24]
CdSe/Pb _x Cd _{1-x} S/CdS	TiO ₂	Na ₂ S/Na ₂ SO ₃	8	94.9 % after 2 h	[33]
CdSe/CdSe _x S _{1-x} /CdS	TiO ₂	Na ₂ S/Na ₂ SO ₃	17.5	~70 % after 2 h	[51]
CdSe/CdS	SnO ₂	Na ₂ S/Na ₂ SO ₃	4.7	96 % after 2 h	[65]
CdSe/CdSe _x S _{1-x} /CdS/Cd _y Zn _{1-y} S/ZnS	TiO ₂	Na ₂ S/Na ₂ SO ₃	20.5	93.4 % after 2 h	This work

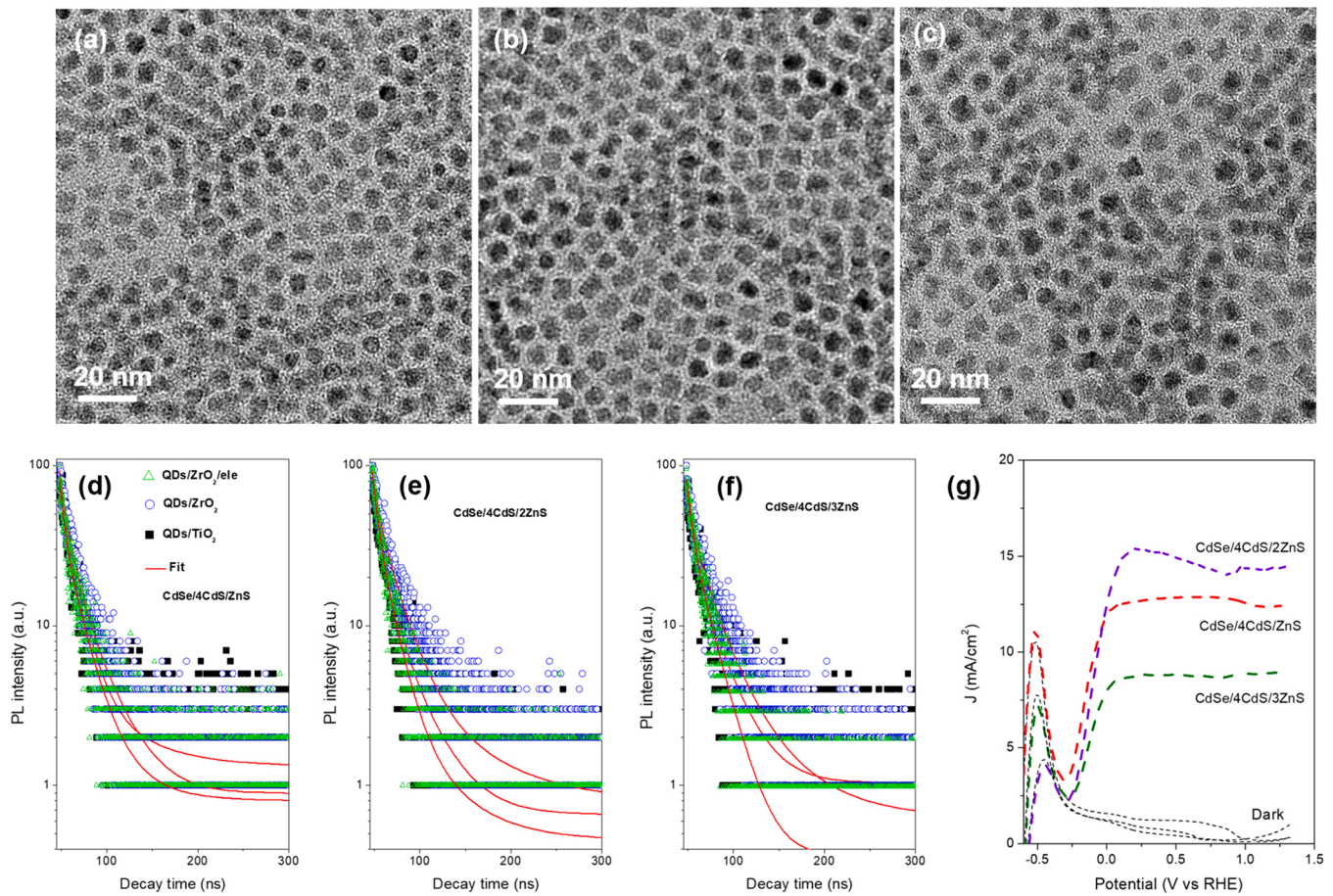


Fig. 4. TEM images of (a) CdSe/4CdS/ZnS QDs, (b) CdSe/4CdS/2ZnS QDs and (c) CdSe/4CdS/3ZnS QDs; (d)-(f) PL spectra of CdSe/4CdS/ZnS QDs, CdSe/4CdS/2ZnS QDs and CdSe/4CdS/3ZnS QDs with different substrates (TiO₂ films, ZrO₂ films and ZrO₂ films with electrolyte); (g) Photocurrent density as the function of potential applied of TiO₂ sensitized with (a) CdSe/4CdS/ZnS QDs, CdSe/4CdS/2ZnS QDs and CdSe/4CdS/3ZnS QDs under dark (dash black curves), and under continuous illumination (AM 1.5 G, 100 mW/cm²) (dash chromatic curves).

Table 4
Average lifetime with TiO₂ or ZrO₂ (in electrolyte) and the calculated charge transfer rate.

QDs	Lifetime of QDs/TiO ₂ (ns)	Lifetime of QDs/ZrO ₂ (ns)	Lifetime of QDs/ZrO ₂ in electrolyte (ns)	Calculated electron transfer rate K_{et} (10 ⁷ s ⁻¹)	Calculated hole transfer rate K_{hr} (10 ⁷ s ⁻¹)
CdSe/4CdS/ZnS	19.6	19.8	16.7	0.1	1.0
CdSe/4CdS/2ZnS	18.9	27.9	16.7	1.6	2.6
CdSe/4CdS/3ZnS	18.6	26.3	15.5	1.6	2.6

PEC measurement results indicate that 2 cycles of ZnS shell thickness present an optimal value of shell thickness for both the passivation of the surface and the charge carrier transfer. In other words, 1 cycle of ZnS shell is too thin for passivating the surface while 3 cycles of ZnS shell is too thick for the electron/hole injection from QDs to TiO₂. As a result, unfavorable non-radiative recombination will happen in the region of the ZnS shell. we conclude that 2 ZnS monolayers are the optimized shell thickness for PEC device, leading to a higher saturated photocurrent density of 14.2 mA/cm².

3. Conclusions and perspectives

In summary, we reported two types of core/multiple-shell QDs, CCZ-1 and alloy CCZ-2 QDs for efficient and stable PEC H₂ generation. Based on Quasi-type II CdSe/CdS core/shell QDs, a wide bandgap

semiconductor ZnS shell was coated to form the core/shell/shell architecture, providing a cascade Type I band alignment for surface passivation as well as efficient carrier transfer. As a result, the saturated photocurrent density based on CCZ-1 QDs can reach values of 14.2 mA/cm². Based on the CCZ-1 core/shell/shell QDs structure, an optimized gradient band alignment was obtained by adding intermediate alloyed layers. An unprecedented saturated photocurrent density of 20.5 mA/cm² was achieved based on alloyed CCZ-2 QDs under one sun illumination. More importantly, ~93.4 % of the initial photocurrent density was maintained after 2-hour continuous illumination, a promising stability performance. The main reason for the significant improvement of the PEC and stability performance was found to be the surface passivation provided by the wide band ZnS shell, together with the presence of the alloyed layers that could provide a shorter pathway for carriers charge transfer, dramatically suppressing unfavorable recombination

events. These results indicate that the heterostructure based on metal oxides and alloyed core/multiple-shell QDs metal oxide can be a promising photoanode candidate for highly efficient and stable H_2 generation devices. Future directions will focus on optimizing the core size, alloyed shell thickness and composition for improvement of PEC devices. Moreover, heavy metal composition needs to be replaced with less harmful elements in PEC cells.

4. Experimental sections

4.1. Materials

Oleic acid (OA, 90 %), oleylamine (OLA, 90 %), cadmium oxide (99 %), cetyltrimethyl ammonium bromide (CTAB), sodium sulfite (Na_2SO_3), titanium tetrachloride ($TiCl_4$), sodium sulfide nonahydrate ($Na_2S \cdot 9 H_2O$), zirconium oxide (ZrO_2) were purchased from Sigma-Aldrich Inc. Trioctyl phosphine (TOP, 90 %), zinc acetate dehydrate [$Zn(CH_3COO)_2 \cdot 2 H_2O$] were obtained from Aladdin Inc. Sulfur (S) powder (99.5 %), selenium (Se) pellet (> 99.999 %), octadecene (ODE), trioctylphosphine oxide (TOPO, 90 %), alpha-terpineol were purchased from Macklin Inc. Toluene, ethanol, methanol and isopropanol (IPA) were obtained from Chinasun Specialty Products Co., Ltd. TiO_2 paste containing anatase nanoparticles with the size of ~ 20 nm (18 NR-T) and a mixed anatase particle of size from ~ 20 nm up to 450 nm larger scattering particle (18 NR-AO) were obtained from Greatcell Solar Materials Pty Ltd. All the chemicals and solvent were used directly without any further purification.

4.2. Synthesis of CdSe, core/shell and core/multi-shell QDs

For the synthesis of CdSe QDs core, hot-injection approach was applied following previous report with minor modification. First, the ~ 0.4 mmol Cd-OA precursor was prepared by dissolving CdO powder in oleic acid solution under 240 – 260 °C with continuous stirring. After the temperature of the reaction cell cooled down to below 50 °C, ~ 1 g TOPO was slowly added into the cell for adequate integration. Subsequently, the cell was raised to over 300 °C and kept under certain temperature for a while. Then 4 mL Se-TOP (4 mmol) solution was quickly injected into cell for nucleation of small dots. The ideal size of the dots was achieved by controlling the growth temperature and reaction time. Finally, ethanol was added into the cell with purification for several times and kept in toluene.

To synthesize CdSe/CdS core/shell and CdSe/CdS/ZnS core/multiple-shell QDs, SILAR method was applied. Prior to the SILAR process, Cd (or Zn) and S precursor was prepared by dissolving CdO powder (or ZnO) in OA and ODE at 240 – 260 °C while the sulfur powder dissolving in ODE under room temperature. For the deposition of CdS shells, the Cd-OA/ODE was added into the cell under slow rate while reacted under 240 °C for ~ 2 h. Subsequently, the S-ODE was added under same temperature and grow for another 10 min. Same process was repeated several times until the ideal thickness was reached. For the growth of ZnS shells, the procedure was similar while the temperature was adjusted to ~ 230 °C. For the synthesis of alloyed core/multi-shell QDs, the anion precursor (or cation precursor) was used with the mixture of Cd/Zn-(OA) $_2$ (or Se/S-ODE).

4.3. Anode preparation

First, the FTO glass was cleaned with Triton ultrasonically for at least 30 min. And cleaned with methanol, IPA, ethanol and DI-water for several times each with 30 min and finally dried with N_2 flow. Afterwards, the clean FTO was placed in a petri dish filled with $TiCl_4$ (50 mM) solution under ~ 75 °C for 0.5 h for the deposition of TiO_x blocking layer. Then the anodes were annealing under 500 °C for 0.5 h. For depositing the TiO_2 mesoporous films with transparent and scattering layers, a blend of smaller TiO_2 nanoparticles (~ 20 nm) (18 NR-T) and

larger nanoparticles (~ 450 nm) paste (18NR-AO) were deposited via doctor blade technique. After every deposition, the anodes were placed on a hot plate under 120 °C for several minutes. Finally, the anodes were placed in an oven under 500 °C for 30 min

4.4. EPD process and ZnS capping layer growth

The as-prepared anode with mesoporous films were immersed in QDs dispersion vertically with the distance of 0.5 – 1 cm. Then a direct bias (current) of 200 V was involved between two poles for 2 h. To remove the unabsorbed QDs on the surface of anodes, toluene was used to wash the surface several times and finally the anodes were dried under N_2 flow. Before ZnS coating, ligand exchange was first conducted to replace OA/OLA long chain with CTAB. Typically, the anodes were placed immersing in methanolic cetyl-trimethyl ammonium bromide solution for 1 min and rinsed with methanol and toluene. Finally, the anodes were dried with N_2 flow. For the deposition of ZnS layers, 0.1 M methanolic zinc acetate dehydrate solution and 0.1 M methanol/water ($1/1$ v/v) Na_2S solution were prepared. With the sequence of Zn^{2+} and S^{2-} dipping, the anodes were kept in every solution for 1 min and wash with the same solvent after every dipping. In our system, two SILAR cycles were applied for the anodes to grow capping layers.

4.5. ZrO_2 film preparation

For preparing the ZrO_2 paste, 1 g commercial ZrO_2 nanopowder was first grind for 2 h and then mixed with ~ 6 mL ethanol and 0.6 g ethyl cellulose under continuous stirring. Subsequently, 1 mL water and 1 mL alpha-terpineol were further added. The paste was stirring for at least 24 h and remove the solvent with a pump until the paste became thick enough. For depositing the ZrO_2 films, the procedure was the same with deposition of TiO_2 films. Finally, the ZrO_2 films were annealing under 500 °C for 30 min. The ZrO_2 /QDs films were conducted under the same EPD process with bias of 200 V for 2 h.

4.6. Characterizations

The UV-Vis absorption measurement was conducted with a Perkin Elmer model Lambda 750. Fluorescence spectra of QD solution were obtained on Fluorescence Spectrometer (NIR-VIS, FL3) with excitation at 400 nm. TEM was carried out on FEI Tecnai TF20 transmission electron microscope with an acceleration voltage of 200 kV. X-ray diffraction (XRD) patterns were recorded by a Bruker D8 powder X-ray diffractometer (Germany) with Ni-filtered Cu $K\alpha$ radiation (40 kV, 40 mA). The average lifetime of the QDs measurement was conducted in the time-correlated single-photon counting (TCSPC) mode with a laser of 455 nm. XPS data were collected on X-ray photoelectron spectrometer (Kratos AXIS UltraDLD) using a monochromatic Al $K\alpha$ (1486.6 eV) X-ray source. All the XPS spectra were calibrated based on the C $1s$ peak at 284.8 eV of adsorbed carbon. The spectra were analyzed by using Casa XPS software. SEM images and EDS mapping were taken from Supra 55 Zeiss scanning electron microscope.

The theoretical simulation (wave functions of the carriers in QDs) was calculated by solving the stationary Schrödinger equation with a model of spherical geometry. Here are the bulk values for the effective masses of electrons [$m(\text{electron})^\#$] and holes [$m(\text{hole})^\#$]. For CdSe, $m(\text{electron})^\# = 0.13 m(\text{electron})$ and $m(\text{hole})^\# = 0.45 m(\text{hole})$. For CdS, $m(\text{electron})^\# = 0.21 m(\text{electron})$ and $m(\text{hole})^\# = 0.68 m(\text{hole})$. While for ZnS, $m(\text{electron})^\# = 0.28 m(\text{electron})$ and $m(\text{hole})^\# = 0.49 m(\text{hole})$ where $m(\text{electron})$ ($m(\text{hole})$) is the electron ($m(\text{hole})$) mass in vacuum. The potentials for holes and electrons as a function of position were approximated as the highest occupied molecular orbital (HOMO) levels and the lowest unoccupied molecular orbital (LUMO), respectively. These levels are -3.71 and -5.81 eV for CdSe, -3.3 and -5.8 eV for CdS and -2.5 eV and -6.1 eV for ZnS, respectively. The potentials in the outer range of the QDs were set as -9.8 eV and 0 eV for holes and

electrons, respectively.

The PEC performance in an electrochemical workstation (CHI 760) in a three-electrode system while QDs/TiO₂ as the working electrode, Pt as the counter electrode and Ag/AgCl as the reference electrode. The active area of the photoanode was about ~0.12 cm² with the other parts covered by non-conductive epoxy. The electrolyte was used Na₂S (0.25 M) and Na₂SO₃ (0.35 M) (pH~13). The potential during the measurement was converted to the RHE scale from the potential based on reference electrode according to the equation:

$$V_{\text{RHE}} = V_{\text{Ag/AgCl}} + 0.197 + \text{pH} \times (0.059) \quad (1)$$

The light source was using a Xenon High Brightness Cold Light Source (XD300) equipped with an AM 1.5 filter. The photoanodes were placed from the center of the lamp at a distance of 10–20 cm. Before each test, the intensity of the light was adjusted strictly to 100 mW/cm² by using a thermopile. All the *J-V* measurements were carried out at a sweep rate of 20 mV/s.

For the H₂ evolution measurement, it was carried out by using a GC7890T system under the *J-t* curve mode with N₂ as carrier gas under one sun illumination intensity. The Faradaic efficiency (η_{FE}) was estimated based on calculated gas volume and measured volume following the equation below:

$$\text{Faradaic efficiency}(\eta_{\text{FE}}) = \frac{V_{\text{measured gas}}}{V_{\text{calculated gas}}} \quad (2)$$

CRediT authorship contribution statement

Kanghong Wang: Methodology, Investigation, Data curation, Writing – original draft, Writing – review & editing. **Yi Tao:** Methodology, Investigation, Data curation. **Zikun Tang:** Methodology, Investigation, Data curation. **Daniele Benetti:** Data curation, Writing – review & editing, Supervision, Project administration. **François Vidal:** Methodology, Writing – review & editing. **Haiguang Zhao:** Data curation, Writing – review & editing, Supervision, Project administration. **Federico Rosei:** Writing – review & editing, Supervision, Project administration, Funding acquisition. **Xuhui Sun:** Writing – review & editing, Supervision, Project administration, Funding acquisition.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data Availability

Data will be made available on request.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the

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