A metal–organic framework-derived Zn$_{1-x}$Cd$_x$S/CdS heterojunction for efficient visible light-driven photocatalytic hydrogen production†

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ZCS-C (ZnCdS/CdS) QDs were synthesized via low-temperature vulcanization using zeolitic imidazolate framework-8 (ZIF-8) nanoparticles as a precursor, cation exchange, and heterojunction construction. Without any precious metal as a cocatalyst, the photocatalytic hydrogen production rate of ZCS-C-3 QDs reached 2.7 mmol g$^{-1}$ h$^{-1}$ under visible light irradiation. The optimized sample exhibited an outstanding chemical stability and recyclability, which is superior to most of the reported Zn$_{1-x}$Cd$_x$S-based photocatalysts.

The exploration of novel low-carbon energy is necessary for the sustainable development of the society. Clean hydrogen is one of the most potential energy carriers to substitute traditional fossil fuels due to its high energy density, and is carbon-free and easily transportable. Since Honda and Fujishima published their research on photocatalytic water splitting on TiO$_2$ electrodes in 1972, photocatalytic hydrogen production through inexhaustible solar energy has aroused general concern, and significant research progress has been achieved during the past several decades.

Recently, metal sulfide semiconductors have been widely studied in photocatalytic hydrogen production due to their suitable electronic band structure, powerful quantum size effect and exposed active sites. As a solid solution of ZnS and CdS, Zn$_{1-x}$Cd$_x$S (ZCS) is a direct bandgap semiconductor combining the visible light responsiveness of CdS and the advantage of ZnS in the rapid separation of photogenerated electrons and holes. Moreover, compared to pristine CdS and ZnS, the ZCS also has a more adjustable and appropriate bandgap and a better photocorrosion resistance.

Multitudinous methods have been researched to manufacture ZCS solid solutions. However, these methods are complicated, or require harsh reaction conditions, and the resulting products usually have a large particle size (>10 nm) or even bulks ending up with aggregation, which depresses the photocatalytic process. It is well-known that quantum dots (QDs), which are in the nanometre range (usually 2–10 nm), have a strong light capture ability, large specific surface area and quantum confinement effect. The smaller QDs exhibit faster electron transport rates and higher photocatalytic performance because of their larger specific surface area and more active sites compared to bulk materials, and the absorption spectrum can be changed by adjusting the size of QDs. Currently, researchers have studied numerous methods for synthesizing QDs, such as chemical precipitation, sol–gel, reflux, pyrolysis, wet-chemical synthesis, and microwave-assisted synthesis. However, most of these methods require long reaction time, toxic chemicals, specialized equipment or critical reaction conditions. Therefore, the exploration of an efficient green chemical method for synthesizing ZCS QDs has attracted considerable attention in the scientific community.

Metal–organic frameworks (MOFs) are a series of promising microporous crystalline materials, which are composed of metal clusters and organic ligands. MOFs have large porosity and specific surface area, adjustable pore size and diverse surface functionality. Recently, using MOFs as sacrificial precursors for synthesizing new materials is an efficient preparation method for obtaining small and uniform nanoparticles. First, by adjusting the interaction between the metal centre and the organic ligand, the metal ions can be released under the appropriate conditions, which can be controlled to form QDs. Second, different sizes of QDs can be easily obtained by adjusting the size of MOFs. These MOF-derived materials normally have tailored compositions, versatile functionalities, and ordered structures with high surface areas and porosities, which exhibit a great efficiency in numerous applications.

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ZnS QDs in our study. Moreover, ZCS QDs \( (x = n_{\text{Cd}}/n_{\text{Zn+Cd}}) \) were synthesized via the cation exchange method with ZnS QDs. Unfortunately, due to the poor migration efficiency of photo-generated carriers, there is still much more space to improve the photocatalytic performance of pristine ZCS. Therefore, numerous strategies, such as instance doping, loading cocatalysts, morphology control and introducing heterojunctions, have been put forward to promote the rate of hydrogen evolution in photocatalysis efficiently. Li et al. modified a ZnCdS/CdS heterojunction via phosphorus-doping and surface modulation by adopting the novel VS\(_2\) as the cocatalyst that exhibited synergistic effects for improving the photocatalytic activity of the heterojunction. Yousaf et al. designed the heterostructure of \( \alpha \)-Fe\(_2\)O\(_3\)/Zn\(_{0.4}\)Cd\(_{0.6}\)S, which showed a visible light photocatalytic H\(_2\) production rate as high as 536.8 \( \text{mol h}^{-1} \) \( \text{g}^{-1}\). Among the various proposed strategies, constructing heterostructure photocatalysts has been proven as one of the most promising ways. Due to the different Fermi energy levels of different semiconductor materials, a potential difference is formed at the contact interface, which is beneficial to the effective separation of the photogenerated electron–hole pairs, and its photoelectrochemical performance is far superior to single-component materials.

In consideration of the appropriate energy band matching and the rapid migration of charge carriers at the contact interface, CdS is regarded as a typical candidate due to its narrow bandgap of 2.4 eV and suitable band position. In addition, the construction of heterojunctions can effectively suppress the ultrafast surface/bulk recombination of the photogenerated charge carriers and the photo-corrosion, originating from the irreversible hole-driven oxidation reaction in the CdS photocatalysts.

In our study, based on the consideration that small-sized semiconductor heterojunction materials can effectively suppress the recombination of photogenerated electron–hole pairs, the Zn\(_{1-x}\)Cd\(_x\)S/CdS (ZCS-C-X) QDs composites were rationally synthesized via vulcanization using ZIF-8 as the sacrificial template, cation exchange and heterojunction construction processes. Under a visible-light irradiation (\( \lambda > 420 \text{ nm} \)), the optimized ZCS-C-3 sample exhibited the highest hydrogen production rate without adding any cocatalyst, which could be attributed to multiple merits, including the suitable band-gap structure, large specific surface area, and short electron migration distance.

Scheme 1 illustrates the synthetic procedure for the preparation of ZCS-C-X QDs via the soft template method and the cation exchange strategy. First, ZIF-8 was used to synthesize ZnS QDs as a sacrificial template due to the moderate Zn–N bond strength and simple preparation method. Moreover, the high affinity of Zn\(_{2+}\) towards S\(^{-2}\) was beneficial to promote the formation of ZnS. In consideration of the stability of ZIF-8 in water, using deionized water as a dispersant and thiourea (TAA) as the S source, the synthesis of ZnS QDs was completed under mild conditions. As the solubility product constant of CdS is relatively smaller than that of ZnS \( \left[ K_{\text{sp}}(\text{CdS}) = 8.0 \times 10^{-27}; K_{\text{sp}}(\text{ZnS}) = 1.6 \times 10^{-24} \right] \), a typical hydrothermal cation exchange process has been performed to convert the resulting ZnS QDs into ZCS QDs. The ratio of Zn and Cd could be easily adjusted by tuning the amount of the Cd\(_{2+}\) precursor. Based on the actual molar ratio of Zn and Cd obtained by an inductively coupled plasma optical emission spectrometer (ICP-AES), the molar percentages of Cd in ZCS QD were nearly equivalent to the theoretical values (Table S1†). As shown in Fig. S1† after a series of photocatalytic hydrogen evolution tests, the Zn\(_{0.5}\)Cd\(_{0.5}\)S sample showed the highest production rate, and then, different amounts of CdS were deposited on Zn\(_{0.5}\)Cd\(_{0.5}\)S to form the ZCS-C-X QDs heterojunction.

The ZIF-8 nanoparticles were fabricated according to the reported method based on the rapid nucleation of the reaction system. The transmission electron microscopy (TEM) image reveals that the as-prepared ZIF-8 had an average nanoparticle size of 200 nm (Fig. 1a), and possessed a uniform rhombic dodecahedral morphology. The high-resolution transmission electron microscopy (HRTEM) image of ZnS QDs shows that their lattice fringe spacing is 0.311 nm, which could correspond to the (111) facet of cubic ZnS (Fig. S2†). The particle size distribution of Zn\(_{0.7}\)Cd\(_{0.3}\)S QDs was about 6.2 ± 0.1 nm (Fig. S3†). Compared to Zn\(_{2+}\) (0.74 Å), the Cd\(_{2+}\) had a larger radius (0.97 Å), which resulted in an increased edge lattice dis-
tance of the Zn_{0.7}Cd_{0.3}S crystals (d = 0.318 nm). From the Fig. 1b and c, the TEM and HRTEM images of ZCS-C-3 exhibited two obvious stripes with different d-spacing of the crystalline lattice at ca. 0.317 nm and 0.336 nm, which were in good agreement with the (111) facet of cubic Zn_{0.7}Cd_{0.3}S and the (002) facet of hexagonal CdS, respectively (marked with arrows in Fig. 1c). The high-angle annular dark field scanning transmission electron microscopy (HAADF-STEM) image of ZCS-C-3 clearly revealed that the CdS nanocrystals are closely connected to the surface of Zn_{0.7}Cd_{0.3}S QDs (Fig. 1d).

From the powder X-ray diffraction (PXRD) patterns of the obtained samples, all diffraction peaks are consistent with the simulated crystal data, which demonstrates the successful synthesis of ZIF-8 (Fig. 2a). Apart from this, the transformation from ZIF-8 to ZnS QDs can be certified by the PXRD pattern of the as-prepared ZCS-C-3 composite with a specific surface area of approximately 180.4 cm$^2$ g$^{-1}$ (Fig. 2d). In addition, the colour changed from yellow to orange (Fig. S4†). The UV-vis spectra show that ZCS-C-X has two energy bands, corresponding to the absorption of Zn$_{0.7}$Cd$_{0.3}$S solid solution and CdS QDs. The results demonstrate that the bandgap of ZCS-C-X QD photocatalysts can be precisely adjusted with the varying CdS via the hydrothermal method. Based on the above-mentioned results, with the increase of the CdS content, the $E_g$ of obtained ZCS-C-X QDs narrowed significantly in the range of 2.16–2.42 eV (Fig. 2d).

The specific surface areas were calculated from the N$_2$ isotherms at 77 K via the BET method. Fig. S5† shows that the specific surface area of Zn$_{0.7}$Cd$_{0.3}$S is approximately 180.4 cm$^2$ g$^{-1}$ through the BET test, which can be attributed to the small size of QDs. Compared to Zn$_{1-x}$Cd$_x$S QDs synthesized by other methods, such as high temperature pyrolysis and solvothermal method, Zn$_{1-x}$Cd$_x$S QDs derived from ZIF-8 as the precursor had a larger specific surface area, which was attributed to the inheritance of the MOF porosity. This advantage enabled the ZCS-C-3 composite with a specific surface area of 150.5 cm$^2$ g$^{-1}$ to absorb more reactive substrates and have more reactive sites, thereby enhancing photocatalytic activity.

The photocatalytic hydrogen production performance of all samples was investigated by solid UV-vis diffuse absorption spectroscopy (Fig. 2c). A continuous and noticeable red-shift of the absorption edges could be observed with an increase in the content of CdS in ZCS-C-X QDs. In addition, the colour changed from yellow to orange (Fig. S4†). The UV-vis spectra show that ZCS-C-X has two energy bands, corresponding to the absorption of Zn$_{0.7}$Cd$_{0.3}$S solid solution and CdS QDs. The results demonstrate that the bandgap of ZCS-C-X QD photocatalysts can be precisely adjusted with the varying CdS via the hydrothermal method. Based on the above-mentioned results, with the increase of the CdS content, the $E_g$ of obtained ZCS-C-X QDs narrowed significantly in the range of 2.16–2.42 eV (Fig. 2d).

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The photocatalytic hydrogen production performance of all samples was examined in an Na$_2$S-Na$_2$SO$_3$ aqueous solution without any noble metal cocatalyst under visible light ($\lambda > 420$ nm). The pure CdS behaved with a low $H_2$ evolution rate of only 0.062 mmol g$^{-1}$ h$^{-1}$ because of its rapid recombination of photogenerated carriers and severe photoinduced corrosion. Similarly, the photocatalytic activity of pristine Zn$_{0.7}$Cd$_{0.3}$S was only 0.11 mmol g$^{-1}$ h$^{-1}$. Fig. 3a shows the photocatalytic
hydrogen evolution performance for all ZCS-C-X samples. With the gradually increasing CdS content, the photoactivities of ZCS-C-X samples presented a volcano shape, and the optimized ZCS-C-3 exhibits the highest H₂ production rate of 2.7 mmol g⁻¹ h⁻¹, corresponding to an apparent quantum efficiency (AQE) equal to 3.84% per 5 mg at 400 nm. In order to investigate the chemical stability and durability, the test of photocatalytic H₂ production over ZCS-C-3 QDs was performed for four consecutive reaction cycles under visible light irradiation. After four cycles, the heterostructure exhibits an ignorable downtrend in photocatalytic activity (Fig. 3b). The XRD and HRTEM characterizations of the photocatalyst after cycling also revealed that the original crystallinity, structure, and morphology were completely retained (Fig. S6 and S7†). The above-mentioned results manifested the superior durability and stability of ZCS-C-3 QDs. Table S2† shows the photocatalytic activities of a few Zn₁₋ₓCdₓS-based photocatalysts reported in recent years. Through comparison, it was found that ZCS-C-3 QDs had a relatively high photocatalytic performance.

The composition and the surface chemical state of the ZCS-C-3 composites were investigated by X-ray photoelectron spectroscopy (XPS). In Fig. 4a, the full survey spectrum indicates that the composites mainly contains Zn, Cd and S elements, as it was expected. The C 1s at 284.6 eV is used as a reference to correct the binding energies of other elements. As shown in the normalized high resolution Zn 2p spectra (Fig. 4b), the peaks corresponded to the typical binding energies of the Zn²⁺ oxidation states [centered at 1044.5 eV and 1021.5 eV]. From Fig. 4c, the XPS spectrum of Cd 3d shows that two peaks at 411.9 eV and 405.1 eV are attributed to the Cd 3d₃/₂ and Cd 3d₅/₂ of ZCS-C-3, respectively, which are in agreement with the literature data for Cd²⁺ in CdS. The curves of the S 2p region can be deconvoluted into two peaks, which represented that the S element was in the sulfide state. In Fig. 4d, the high-resolution XPS signals of S 2p₁/₂ and S 2p₃/₂ for the ZCS-C-3 sample are around 162.8 eV and 161.6 eV, respectively, which are the same with the values of S in pristine ZnS and CdS. Furthermore, compared to Zn₀.₇Cd₀.₃S QDs, the binding energies of Zn 2p, Cd 3d, and S 2p of ZCS-C-3 shifted to higher values by 0.2 eV, respectively. The up-shift of these peaks of ZCS-C-3 manifests that there is not only a strong interaction and compact interfacial contact between Zn₀.₇Cd₀.₃S QDs and CdS QDs, but also a charge flow from Zn₀.₇Cd₀.₃S to CdS.

To gain an insight into the separation efficiency of photogenerated charge pairs, photoluminescence (PL) emission spectra of these samples were recorded at an excitation wavelength of 400 nm. In Fig. 5a, with the increase of the CdS content, the PL intensity decreased firstly and then increased, which was coincident with the photoactivity test. This trend indicated that among all samples, the photo-generated electron and hole recombination rate of ZCS-C-3 was the lowest. In order to explore the charge separation efficiency of the samples under working conditions, photocurrent measurements and electrochemical impedance spectroscopy (EIS) tests...
were carried out. In Fig. 5b, the ZCS-C-3 QDs heterostructure exhibited a much higher photocurrent response compared to other samples, which was consistent with the results of PL and photocatalytic tests, indicating the improved charge carrier separation efficiency of ZCS-C-3 QDs. Moreover, the Nyquist plots measured at the 0.5 V bias potential and the simulated electrical equivalent-circuit model of all the samples are summarized in Fig. 5c and d. Compared to other samples, the ZCS-C-3 QDs exhibited the smallest semicircle with the lowest $R_{ct}$ ($R_{ct} = 2462 \ \Omega$; Table S3†), which had the same trend as the photocurrent response data. This result also supports the lower charge-transfer resistance and the faster charge kinetics of the ZCS-C-3 QDs heterostructure, and makes the interpretation of the enhanced photocatalytic behaviour.42 The steady-state surface photovoltage (SPV) spectrum (Fig. S8†) shows that the SPV value of ZCS-C-3 is much higher than that of CdS, indicating that more photoinduced electron–hole pairs are transferred onto the surface of ZCS-C-3.43 The above discussion solidly indicated that the obtained QDs heterostructure played a crucial role in broadening light absorption, prompting charge carrier transfer, retarding recombination, and enhancing the photocatalytic activity.

In order to further explore the advantages of the QDs heterojunction, time-resolved PL spectroscopy was used to monitor the fluorescence lifetime (Fig. 6a). Due to the long lifetime of the separated electrons and holes, the emission decay of the ZCS-C-3 sample was expected to be the slowest among the samples.44 The emission lifetimes of all samples were obtained by fitting the decay curves (Table S4†). The $\tau_{AVE}$ (ZCS-C-3) is 19.95 ns, which has a longer carrier lifetime than other samples. This also proved its highest charge separation efficiency in the photocatalytic reaction process. In general, a longer emission lifetime also indicates a relatively longer apparent carrier migration distance, which can effectively reduce the rapid annihilation of charge carriers, thereby promoting the photocatalytic reaction.

Combining the band gap calculated by the Tauc plot and the XPS valence band spectrum of Zn$_{0.7}$Cd$_{0.3}$S and CdS (Table S5†, Fig. 6b), the valence band (VB) position and conduction band (CB) position of Zn$_{0.7}$Cd$_{0.3}$S are calculated at 1.58 eV and $-1.24 \ \text{eV}$, whereas the CdS is located at 1.67 eV and $-0.46 \ \text{eV}$, respectively. Based on the experimental calculation results, Scheme 2 shows the charge transfer and separation mechanism of the ZCS-C-3 QDs heterojunction. The photogenerated holes located at the VB of CdS migrate to the local acceptor state in Zn$_{0.7}$Cd$_{0.3}$S, and the photogenerated electrons located at the CB of Zn$_{0.7}$Cd$_{0.3}$S are transferred to CdS. The photoexcited charge carriers formed by the ZCS-C-3 heterostructure prepared via the in situ method can significantly curb their recombination, and enhance the utilization efficiency of charge carriers.

To explore the charge transfer process at the interface of Zn$_{0.7}$Cd$_{0.3}$S and CdS qualitatively, the ZnS-CdS heterojunction model was constructed. The charge density differences obtained by subtracting the electronic charge of a hybrid ZnS-CdS heterojunction from that of the isolated ZnS and CdS layers were calculated, as shown in Fig. 6c and d. The yellow and green colors represent electron accumulation and depletion, respectively. Clearly, there was a distinct charge redistribution at the interface region, where the electrons mainly located at the ZnS part. Therefore, in the heterojunction region, a polarized field was generated from CdS to the ZnS, which was beneficial for the separation of photon-generated carriers. The photon-generated electrons are transferred towards CdS part with the inducement of the heterojunction polarized field.45

In summary, a method of using MOFs as a single precursor under mild conditions to construct ZCS-C-X QDs through low-
temperature vulcanization, cation exchange and heterojunction construction has been achieved. ZCS-C-3 QDs possessed abundant reactive sites, close interface contact and efficient separation of photo-generated electrons and holes, which greatly improved the photocatalytic hydrogen production activity. Under visible-light irradiation (\( \lambda > 420 \) nm) and cocatalyst-free conditions, the hydrogen evolution rate of ZCS-C-3 can reach 2.7 mmol g\(^{-1}\) h\(^{-1}\), which is better than that of most reported Zn\(_{1-x}\)Cd\(_x\)S-based photocatalysts. The synthesis approach can potentially provide a reference for developing or fabricating other energy/environment-related, efficient, and stable metal chalcogenide QD photocatalysts.

**Conflicts of interest**

There are no conflicts to declare.

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**Notes and references**