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Biomolecule-assisted synthesis of defect-mediated $\text{Cd}_{1-x}\text{Zn}_x\text{S}/\text{MoS}_2/\text{graphene}$ hollow spheres for highly efficient hydrogen evolution†

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Moderate efficiency and the utilization of noble metal cocatalysts are the key factors that restrict the large-scale application of photocatalytic hydrogen production. To develop more efficient photocatalysts based on earth abundant elements, either a new material strategy or a fundamental understanding of the semiconductor/cocatalyst interfaces is highly desirable. In this paper, we studied the feasibility of *in situ* formation of defect-rich cocatalysts on graphene-based photocatalysts. A facile biomolecule-assisted strategy was used to self-assemble $\text{Cd}_{1-x}\text{Zn}_x\text{S}/\text{MoS}_2/\text{graphene}$ hollow spheres. The defect-mediated cocatalyst and synergetic charge transfer around heterostructured interfaces exhibit a significant impact on the visible-light-driven photocatalytic activity of multicomponent solid solutions. With engineered interfacial defects, $\text{Cd}_{0.8}\text{Zn}_{0.2}\text{S}/\text{MoS}_2/\text{graphene}$ hollow spheres exhibited a 63-fold improved H_2 production rate, which was even 2 and 3.8 times higher than those of $\text{CdS}/\text{MoS}_2/\text{graphene}$ hollow spheres and $\text{Cd}_{0.8}\text{Zn}_{0.2}\text{S}/\text{Pt}$. Therefore, our research provides a promising approach for the rational design of high-efficiency and low-cost photocatalysts for solar fuel production.

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Introduction

Photocatalytic hydrogen evolution from water has become a challenging and significant research topic for solving the energy crisis and environmental problems. Over the last few decades, numerous semiconductor photocatalysts for H_2 production have been investigated, such as TiO_2 , ZnO , CdS and C_3N_4 .^{1–10} However, the low photocatalytic efficiency and the utilization of noble metals (such as Pt, Ru and Rh) as cocatalysts are still the key factors that restrict the large-scale industrial application of this technology.¹¹ Therefore, new material strategies are highly desirable to develop more efficient photocatalytic systems based on inexpensive and earth abundant elements.

Most recently, the thin atomic layer of MoS_2 has received great attention, due to its great potential as a low-cost alternative to Pt.^{12,13} Using density functional calculations, Hinnemann *et al.* found the same free energy with Pt and MoS_2 for hydrogen evolution.¹⁴

Using an analogue of graphene, the layer-number-dependent activity enhancement was also investigated by Ye *et al.* A drastic increase in photocatalytic H_2 evolution was observed with decreasing MoS_2 layer number, particularly for the single-layer MoS_2 .¹⁵ Coupling few-layered MoS_2 with graphene provided a new kind of cocatalyst because of superior electrical conductivity, less stacking and the large edge dimension of MoS_2 .¹⁶ The synergetic effects between MoS_2 and graphene have been well demonstrated by using TiO_2 and CdS as prototypes.^{17,18}

It has been revealed that the electrocatalytic activity of MoS_2 is derived from the undercoordinated sulfur edge sites, while their basal planes remain inert toward hydrogen evolution.¹⁹ For the MoS_2 decorated photocatalysts, their performance can be influenced by many factors, such as morphology, crystalline phase, electronic structure and defect state. In particular, recent results indicate that interfacial defects are the fundamental and intrinsic characteristics of photocatalysts, which have critical impacts on their activities.²⁰ Compared to the rich efforts in engineering the defects in photocatalysts, little attention has been paid to the possible formation of intrinsic defects in MoS_2 cocatalysts and their synergetic effects on the photocatalytic performance.²¹ It is of significance for the development of efficient MoS_2 decorated photocatalysts based on the defect chemistry mechanism.

CdS has been proven to be a potential visible-light-driven photocatalyst for water splitting. However, the photocorrosion

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process, environmental risk of toxic cadmium and fast recombination of charge carriers largely limit its scalable application. Recent studies indicate that coupling CdS with a wide-band-gap semiconductor, for example ZnS, In_2S_3 , and NiS, is an effective strategy to suppress the photocorrosion, decrease the used amount of cadmium, and increase the charge carrier separation. As an emerging and promising multicomponent metal sulphide, $\text{Cd}_{1-x}\text{Zn}_x\text{S}$ might provide more opportunities for developing highly efficient and less-toxic photocatalysts, due to the controllable band structure, improved stability and improved charge separation efficiency.^{22–24} Furthermore, it was also motivated by the well-matched coordination mode between CdS and ZnS, tunable band gap width and band edge position.^{25,26} Bearing all these in mind, we aim to investigate the feasibility of integrating defective MoS_2 with $\text{Cd}_{1-x}\text{Zn}_x\text{S}$ solid solutions.

Here, novel $\text{Cd}_{1-x}\text{Zn}_x\text{S}/\text{MoS}_2/\text{graphene}$ nanoarchitectures were chosen as model materials to demonstrate the concept of defect-rich cocatalyst decorated synergetic photocatalysts. Due to the unique characteristics of large surface area, good permeability and multiscattering of incidence light, hollow structures are always attractive during photocatalyst design. Besides the high conductivity of graphene, using $\text{MoS}_2/\text{graphene}$ as defective cocatalysts can also provide more active defect sites for reactions. Therefore, $\text{Cd}_{1-x}\text{Zn}_x\text{S}/\text{MoS}_2/\text{graphene}$ hollow spheres should be a strong candidate for high-efficiency photocatalysis. A biomolecule-assisted method, a facile strategy for template-free self-assembly of hollow spheres, was used to integrate $\text{Cd}_{1-x}\text{Zn}_x\text{S}$ solid solutions with defective MoS_2 and graphene.²⁷ It was found that defect-rich MoS_2 decorated hollow spheres exhibited significantly enhanced capability for photocatalytic H_2 evolution. The optimal H_2 production rate of $2.97 \text{ mmol h}^{-1} \text{ g}^{-1}$ was 64 times higher than that of blank $\text{Cd}_{0.8}\text{Zn}_{0.2}\text{S}$, which was even 3.8 times higher than that of $\text{Cd}_{0.8}\text{Zn}_{0.2}\text{S}/\text{Pt}$. We believe that our research offers a promising prospective to develop defective MoS_2 decorated multicomponent solid solutions as photocatalysts for high-efficiency and low-cost H_2 production.

Experimental section

Fabrication of $\text{Cd}_{1-x}\text{Zn}_x\text{S}/\text{MoS}_2/\text{graphene}$ hollow spheres

All chemicals were of analytical grade, and used as received without further purification. Graphene oxide (GO) solution was synthesized from natural graphite powder by a modified Hummers' method. $\text{Cd}_{1-x}\text{Zn}_x\text{S}/\text{MoS}_2/\text{graphene}$ hybrids were fabricated through a one-pot hydrothermal reaction. In a typical synthesis of $\text{Cd}_{0.8}\text{Zn}_{0.2}\text{S}/\text{MoS}_2/\text{graphene}$ solid solution, 0.8 mmol $\text{Cd}(\text{OAc})_2$ and 0.2 mmol $\text{Zn}(\text{OAc})_2$ were added to distilled water (20 mL). After the ultrasonic treatment for 0.5 hour, 10 mL of graphene oxide solution (with the concentration of 0.2 mg mL^{-1}), 4 mmol cysteine and 0.2 mmol sodium molybdate were added into the solution under vigorous stirring, respectively. After stirring for 1 h, the mixture was transferred into a 50 mL Teflon-lined stainless steel autoclave and heated at 453 K for 24 h. After cooling naturally, the precipitates were collected by centrifugation, washed with distilled water and ethanol, and dried in a

vacuum oven at 333 K for several hours. For comparison, composites with different material components were also fabricated by changing the weight ratio of reaction reagents.

Characterization

Powder X-ray diffraction (XRD) studies were recorded on a Bruker D8 focus Advance diffractometer with a $\text{Cu K}\alpha$ source ($\lambda = 0.15418 \text{ nm}$). The morphology of the products was characterized by field emission scanning electron microscopy (FESEM, JSM-7600F, JEOL) and high-resolution transmission electron microscopy (HR-TEM, JEOL-2010). The Brunauer–Emmett–Teller (BET) specific surface areas of the samples were analyzed by nitrogen adsorption-desorption (Micromeritics ASAP 2460, USA). X-ray photoelectron spectroscopy (XPS) measurements were carried out on ESCALA-B220I-XL apparatus at a base pressure of $1 \times 10^{-9} \text{ mbar}$, and an X-ray source of $\text{Al K}\alpha$. Electron spin resonance (ESR) analysis was performed on a Bruker E500 spectrometer. A Cary 5000 UV-vis-NIR spectrometer from Varian, America was used to obtain the UV-vis-NIR diffuse reflectance spectra (DRS) of the photocatalysts. The Raman spectra were obtained on a laser micro-Raman spectrometer (Horiba JobinYvon T64000). The 532 nm radiation from a 20 mW air-cooled argon ion laser was used as the exciting source. The laser diameter was $1 \mu\text{m}$ and the laser power at the sample position was 4.0 mW. The photoluminescence (PL) spectra were recorded at room temperature using a fluorescence spectrophotometer (Hitachi F-4500) made in Japan, at an exciting wavelength of 325 nm.

Photocatalytic H_2 evolution

Photocatalytic activity was tested on a gas-closed circulation system equipped with a 300 W Xenon lamp (PLS-SXE300C, Beijing Perfectlight Co.) for irradiation experiments with visible light ($\lambda > 420 \text{ nm}$). In a typical measurement, 50 mg of a photocatalyst was dispersed in 96 mL of distilled water containing 4 mL of lactic acid as a sacrificial reagent. After purging with nitrogen for 30 minutes to remove dissolved air, the reaction vessel was connected to the online system and exposed to visible light irradiation. Hydrogen gas evolution was measured using a gas chromatograph (SP-6890, Shanghai Tech-comp, nitrogen as a carrier gas) with a thermal conductivity detection (TCD) instrument.

Photoelectrochemical measurements

5 mg of samples and 10 μL of Nafion solution (5 wt%) were dispersed in 1 mL water/isopropanol mixed solvent (3 : 1 v/v) by sonication for at least 30 min to form a homogeneous solution. Then 50 μL of the catalyst solution was drop-casted onto the FTO electrodes (with the area of 1 cm^2) and left to dry in air at room temperature.

Photoelectrochemical measurements were performed using a three-electrode configuration. The FTO glass loaded with samples was used as a working electrode. A platinum plate and a Ag/AgCl electrode was used as a counter and a reference electrode, respectively. 0.2 M Na_2SO_4 aqueous solution was used as the electrolyte. The electrical impedance spectra (EIS) and Mott–Schottky plots at a frequency of 1000 Hz were measured

using an electrochemical workstation (Gamry electrochemical workstation, Interface 1000).

Results and discussion

A series of $\text{Cd}_{1-x}\text{Zn}_x\text{S}/\text{MoS}_2/\text{graphene}$ composites with different Cd/Zn ratios were synthesized, and their XRD patterns were compared with blank $\text{Cd}_{0.8}\text{Zn}_{0.2}\text{S}$. In Fig. 1, it can be seen that the variation of the elemental component results in different diffraction patterns. The $\text{Cd}_{0.2}\text{Zn}_{0.8}\text{S}/\text{MoS}_2/\text{graphene}$ composite exhibits a cubic structure, with left-shifted peaks (for example, from 28.56° to 27.82°) compared to that of cubic ZnS (JCPDS No. 01-677). The systematic shift indicates that the Cd ion is successfully incorporated, due to the larger ionic radius of Cd^{2+} (0.95 nm) compared to Zn^{2+} (0.74 nm). As the x increases, the phase structure of products obviously changes from sphalerite to wurtzite structure. The successive shift of XRD patterns to that of hexagonal CdS (JCPDS 01-647) indicates the formation of $\text{Cd}_{1-x}\text{Zn}_x\text{S}$ solid solution. Due to the relatively low amount and low diffraction intensity, no characteristic diffraction peak corresponding to graphene is observed in the composites, which is similar to the literature reports. The absence of the peak corresponding to MoS_2 indicates that MoS_2 nanosheets in the composites are highly dispersed and contain only few layers, which are too thin to be detected by XRD.²⁸

The morphology of the $\text{Cd}_{0.8}\text{Zn}_{0.2}\text{S}/\text{MoS}_2/\text{graphene}$ sample was examined by SEM and TEM. As shown in Fig. 2a, abundant spherical nanoparticles can be clearly seen. The appearance of collapsed shells and broken spheres with clear hollow interior voids indicates the hollow nature of as-synthesized products. As shown in Fig. S1 (ESI[†]), the calculation based on 100 separate particles indicates that the size of hollow spheres is mainly distributed in the range of 200–1000 nm, with an average diameter of 750 nm. One typical hollow sphere is studied in Fig. 2b, with the diameter of 800 nm and a shell thickness of 50 nm. And the outer

Fig. 2 SEM (a), TEM (b) and HRTEM (c and d) images of $\text{Cd}_{0.8}\text{Zn}_{0.2}\text{S}/\text{MoS}_2/\text{graphene}$ hollow spheres.

and inner regions of spheres display different brightness, which further confirms the characteristic of hollow structured materials. It is obvious that the shell of the hollow sphere is composed of loosely packed nanoparticles, resulting in a coarse surface. The high-resolution TEM image of the assembled shell is shown in Fig. 2c. The diameter of each nanoparticle is estimated to be about 20 nm. Well-defined crystallinity of nanoparticles with a lattice spacing of 0.33 nm is seen, which is close to that of the (002) plane of wurtzite $\text{Cd}_{1-x}\text{Zn}_x\text{S}$. The presence of graphene nanosheets in the composites is approved by the presence of 2-D structures and the characteristic wrinkles on the edges. The uniform distribution of small $\text{Cd}_{1-x}\text{Zn}_x\text{S}$ nanoparticles on graphene substrates proves the formation of graphene-based hollow structures with intimate interfacial contact. Furthermore, HR-TEM images in Fig. 2c and d show the existence of typical layered structures with the interlayer distance of 0.62 nm, corresponding to the (002) planes of hexagonal MoS_2 .²⁹ The advantage of *in situ* growth can be well demonstrated by the homogeneous dispersion of crystalline MoS_2 cocatalysts on both the surface of $\text{Cd}_{1-x}\text{Zn}_x\text{S}$ nanoparticles and graphene substrates, which can provide sufficient active sites for efficient charge separation and transfer.

The use of cysteine molecules and alkaline sodium molybdate plays an important role in the formation of hollow structured materials, which is consistent with our recent research of $\text{CdS}/\text{MoS}_2/\text{graphene}$ composites.²⁷ Generally, the growth of hollow spheres is facilitated by increasing the concentration of alkaline additives (Mo precursor). In the control experiments, the yield of hollow structures gradually decreases when the ratio of Zn increases. It seems that the self-assembly process is dependent on the type of metal ions. As shown in Fig. S2a (ESI[†]), for the ratio of Cd/Zn = 4 : 1, only $\text{Cd}_{0.8}\text{Zn}_{0.2}\text{S}$ nanoparticles with irregular morphology are observed without the addition of GO and sodium molybdate. The utilization of GO shows no influence on the morphology of metal sulfide, resulting in the deposition of $\text{Cd}_{0.8}\text{Zn}_{0.2}\text{S}$ nanoparticles on the surface of graphene (Fig. S2b, ESI[†]). When a certain amount of sodium molybdate is added as

Fig. 1 XRD patterns of $\text{Cd}_{1-x}\text{Zn}_x\text{S}/\text{MoS}_2/\text{graphene}$ composites and blank $\text{Cd}_{0.8}\text{Zn}_{0.2}\text{S}$ nanoparticles.

both the precursor for MoS₂ and the weakly alkaline additive, Cd_{0.8}Zn_{0.2}S/MoS₂/graphene hollow structures can be obtained (Fig. 2). When Cd_{0.8}Zn_{0.2}S is totally replaced by MoS₂, sheet-like MoS₂/graphene products are formed, as shown in Fig. S2c (ESI†). These results also indicate that a series of hollow structured metal sulfides/MoS₂ composites can be fabricated *via* the biomolecule-assisted strategy. The self-assembly of CuInS₂/MoS₂/graphene hollow spheres further confirms this, as shown in Fig. S2d (ESI†).

The elemental composition of Cd_{0.8}Zn_{0.2}S/MoS₂/graphene was investigated by XPS. Based on the atomic percentage of elements in the composites, the molar ratio of Mo/(Cd + Zn) was determined to be 0.19, which agrees well with the concentration of precursor. In Fig. S3a (ESI†), the survey scan spectrum confirms the co-existence of Zn, Cd, S, Mo, C and O elements. The binding energy located at 404.1 and 410.8 eV can be attributed to Cd 3d_{5/2} and Cd 3d_{3/2}, respectively (Fig. 3a). The splitting energy of 6.7 eV between them indicates that the chemical state of Cd is Cd²⁺.^{30,31} The Zn 2p_{3/2} and Zn 2p_{1/2} peaks at 1021.1 and 1044.2 eV confirm the presence of Zn element in the form of Zn²⁺ (Fig. 3b). The Auger parameter is useful for distinguishing coordination environments around the atom. The Auger parameter can be calculated using the maximum of the Zn 2p_{3/2} main peak and the maximum of the L₃L_{4,5}M_{4,5} Zn Auger peak (Fig. S4, ESI†). The Auger parameter of Cd_{0.8}Zn_{0.2}S/MoS₂/graphene hollow spheres is determined to be 2011.1 eV. This value is different from that of metallic zinc (2013.8 eV), confirming the formation of zinc-based sulfides in the solid solutions.^{32,33}

Fig. 3 XPS spectra of Cd_{0.8}Zn_{0.2}S/MoS₂/graphene hollow spheres. (a) Cd 3d, (b) Zn 2p, (c) Mo 3d, (d) O 1s, and (e) S 2p spectra. (f) ESR spectra of Cd_{0.8}Zn_{0.2}S and Cd_{0.8}Zn_{0.2}S/MoS₂/graphene hollow spheres.

Mo and S elements in the composite were further confirmed by the high-resolution Mo 3d, Mo 3s and S 2p spectra, respectively. The Mo 3d spectrum can be deconvoluted into five single peaks. The features in Fig. 3c at 225.8, 228.6, and 231.9 eV are associated with the S 2s, Mo⁴⁺ 3d_{5/2}, and Mo⁴⁺ 3d_{3/2} core levels in MoS₂.^{34–37} Peaks located at around 230.2 and 233 eV are also observed, which can be assigned to Mo⁵⁺, indicating the formation of structural defects in the Cd_{0.8}Zn_{0.2}S/MoS₂/graphene composites.³⁸ The presence of Mo⁵⁺ can also be confirmed by the overlapped peaks in the Mo 3s spectrum (Fig. S3b, ESI†). Fig. 3d shows the O 1s spectrum, the presence of the Mo–O bond in the composites can be deduced from the peak at 531.5 eV. As reported, the incorporation of oxygen into the lattice of MoS₂ ultrathin nanosheets can oxidize unsaturated Mo into Mo⁵⁺. The formation of defect-rich MoS₂ results in an obvious change in the S 2p spectrum in Fig. 3e. Those peaks at around 161.3 and 162.5 eV can be assigned to the S^{2–} 2p_{3/2} and S^{2–} 2p_{1/2} lines of MoS₂.^{39,40} The S 2p doublet at 162 and 163.5 eV is attributed to S₂^{2–} 2p_{3/2} and S₂^{2–} 2p_{1/2}, which confirms the formation of abundant unsaturated S atoms.^{41–43} To confirm the above results, the S 2s spectrum was further studied. As shown in Fig. S5a (ESI†), four sets of peaks are observed, which can be, respectively, assigned to S^{2–} 2s, S₂^{2–} 2s, Mo⁵⁺ 3d doublets and Mo⁴⁺ 3d doublets. It further confirms the formation of defective structures in MoS₂ co-catalysts. As the sulfur edge plays an important role in the hydrogen evolution reaction, superior activity of defective MoS₂ cocatalysts can be expected.^{21,44} The restoration of graphene from graphene oxide is studied by the C 1s spectrum. In Fig. S5b (ESI†), the peak can be deconvoluted into three peaks at 284.6 eV (sp²-bonded carbon C–C or C=C), 287.6 eV (carbonyls C=O) and 288.7 eV (carboxyl O–C=O) respectively. In comparison to graphene oxide, the decreased peak intensities of C=O and O–C=O indicate the substantial reduction of graphene oxide into graphene, which agrees well with the Raman results in Fig. S6 (ESI†).⁴⁵ The above results confirm the formation of defect-rich Cd_{1–x}Zn_xS/MoS₂/graphene heterostructures *via* a one-pot hydrothermal reaction.

ESR analysis was further carried out to confirm the formation of defects and identify the defect species in Cd_{0.8}Zn_{0.2}S/MoS₂/graphene hollow spheres. As shown in Fig. 3f, six weak hyperfine lines with *g* values around 2.10, 2.06, 2.018, 1.98, 1.94 and 1.90 are easily observed, which can be ascribed to the instant crystal field of metal sulfides.⁴⁶ A signal located at *g* = 1.995 was also detected, indicating the formation of Cd- or Zn-vacancies in the Cd_{0.8}Zn_{0.2}S solid solution.^{47,48} Differently, Cd_{0.8}Zn_{0.2}S/MoS₂/graphene hollow spheres exhibit strong ESR signals. Based on the literature, the signal located at *g* = 1.95 approaches that of signal B in molybdenum sulfides.⁴⁹ Bensimon *et al.* found that oxygen might be involved in this resonance signal. The formation of oxidized molybdenum compounds could result in Mo⁵⁺ atoms in special surroundings with axial symmetry, which is consistent with XPS results.⁴⁸ Furthermore, the signal with *g* = 1.996 should be the overlapped signals of Mo⁵⁺ in MoS₂ and Cd or Zn-vacancies in Cd_{0.8}Zn_{0.2}S. All the results prove that defect-rich MoS₂ decorated Cd_{0.8}Zn_{0.2}S/MoS₂/graphene hollow spheres were successfully fabricated. It is

Fig. 4 UV-vis diffuse reflectance spectra (a) and BET adsorption-desorption isotherms (b) of $\text{Cd}_{0.8}\text{Zn}_{0.2}\text{S}$ nanoparticles and $\text{Cd}_{0.8}\text{Zn}_{0.2}\text{S}/\text{MoS}_2/\text{graphene}$ hollow spheres.

believed that the cut-off in the stacks could provide more active sites for catalysis. As a result, few-layer MoS_2 with defective electronic structures should be a promising candidate for cocatalysts for photocatalytic hydrogen evolution.

Fig. 4a shows the UV-vis diffuse reflectance spectra of $\text{Cd}_{0.8}\text{Zn}_{0.2}\text{S}$ and $\text{Cd}_{0.8}\text{Zn}_{0.2}\text{S}/\text{MoS}_2/\text{graphene}$ hollow spheres. It can be seen that blank $\text{Cd}_{0.8}\text{Zn}_{0.2}\text{S}$ can only absorb visible light below the wavelength of 550 nm, corresponding to the band gap of 2.26 eV. The presence of MoS_2 and graphene in $\text{Cd}_{0.8}\text{Zn}_{0.2}\text{S}/\text{MoS}_2/\text{graphene}$ composites is attributed to increased visible light absorption. Due to the formation of defective structures, the narrowed band gap of MoS_2 can significantly improve the near-infrared light absorption. Therefore, more efficient utilization of solar energy is expected for defect-rich $\text{Cd}_{0.8}\text{Zn}_{0.2}\text{S}/\text{MoS}_2/\text{graphene}$ hollow spheres.

The influence of $\text{MoS}_2/\text{graphene}$ on the BET surface area of the typical $\text{Cd}_{0.8}\text{Zn}_{0.2}\text{S}/\text{MoS}_2/\text{graphene}$ composite was surveyed using N_2 adsorption-desorption isotherms. As shown in Fig. 4b, the special BET surface area of $\text{Cd}_{0.8}\text{Zn}_{0.2}\text{S}$ nanoparticles is $35.35 \text{ m}^2 \text{ g}^{-1}$, which is significantly increased to $46.66 \text{ m}^2 \text{ g}^{-1}$ in $\text{Cd}_{0.8}\text{Zn}_{0.2}\text{S}/\text{MoS}_2/\text{graphene}$ hollow spheres because of the introduction of two-dimensional $\text{MoS}_2/\text{graphene}$ and their hollow structure. It is well known that a high surface area could also increase surface active sites and charge transfer of a photocatalyst, resulting in the photocatalytic activity improvement.

The synergistic effect of graphene and defect-rich MoS_2 cocatalysts on the photocatalytic property of the multicomponent solid solution was evaluated by the visible-light-driven hydrogen evolution reaction. As shown in Fig. 5a, blank $\text{Cd}_{0.8}\text{Zn}_{0.2}\text{S}$ shows very poor photocatalytic activity, with the hydrogen production rate of $46.6 \mu\text{mol h}^{-1} \text{ g}^{-1}$. When $\text{Cd}_{0.8}\text{Zn}_{0.2}\text{S}$ nanoparticles were hybridized with graphene, only moderately increased photocatalytic activity is achieved. Differently, the construction of composite photocatalysts with hollow-structured morphology shows an obvious impact on the performance of $\text{Cd}_{1-x}\text{Zn}_x\text{S}$, as $\text{Cd}_{0.8}\text{Zn}_{0.2}\text{S}/\text{MoS}_2$ hollow spheres exhibiting 21-fold increased activity. With the further introduction of graphene, $\text{Cd}_{0.8}\text{Zn}_{0.2}\text{S}/\text{MoS}_2/\text{graphene}$ hollow spheres present an unprecedentedly high hydrogen production rate of $2.97 \text{ mmol g}^{-1} \text{ h}^{-1}$, which is more than 64 times higher than that of $\text{Cd}_{0.8}\text{Zn}_{0.2}\text{S}$ nanoparticles. It proves the synergistic effect of defect-rich MoS_2 and graphene on the photocatalytic activity of $\text{Cd}_{1-x}\text{Zn}_x\text{S}$ for H_2 production.

The dependence of photoactivity on the amount of cocatalyst and the elemental composition of solid solution was studied.

Fig. 5 Visible-light-driven photocatalytic hydrogen evolution over (a) $\text{Cd}_{0.8}\text{Zn}_{0.2}\text{S}$, $\text{Cd}_{0.8}\text{Zn}_{0.2}\text{S}/\text{graphene}$, $\text{Cd}_{0.8}\text{Zn}_{0.2}\text{S}/\text{MoS}_2$ and $\text{Cd}_{0.8}\text{Zn}_{0.2}\text{S}/\text{MoS}_2/\text{graphene}$. (b) $\text{Cd}_{0.8}\text{Zn}_{0.2}\text{S}/\text{MoS}_2/\text{graphene}$ with different amounts of Mo precursors. (c) $\text{Cd}_{1-x}\text{Zn}_x\text{S}/\text{MoS}_2/\text{graphene}$ with different ratios of Cd/Zn. (d) $\text{Cd}_{0.8}\text{Zn}_{0.2}\text{S}/\text{MoS}_2/\text{graphene}$ and $\text{Cd}_{0.8}\text{Zn}_{0.2}\text{S}/\text{Pt}$.

In Fig. 5b, the photocatalytic performance is obviously facilitated even with a very small amount of MoS_2 , indicating the fascinating role of MoS_2 as an efficient cocatalyst for the water splitting reaction. With the increase of the amount of MoS_2 , the photocatalytic activity gradually increases and achieves the highest hydrogen yield in the presence of 0.2 mmol Mo precursors. The further increase of the Mo precursor to 0.3 mmol leads to the deduction of activity. The optimal composition of solid solution was determined by changing the ratio of Cd/Zn in $\text{Cd}_{1-x}\text{Zn}_x\text{S}$. As shown in Fig. 5c, the hydrogen evolution rate follows the order of $\text{Cd}_{0.8}\text{Zn}_{0.2}\text{S}/\text{MoS}_2/\text{graphene} > \text{CdS}/\text{MoS}_2/\text{graphene} > \text{Cd}_{0.5}\text{Zn}_{0.5}\text{S}/\text{MoS}_2/\text{graphene} > \text{Cd}_{0.2}\text{Zn}_{0.8}\text{S}/\text{MoS}_2/\text{graphene}$. Due to the synergistic effect of graphene and MoS_2 , $\text{Cd}_{0.8}\text{Zn}_{0.2}\text{S}/\text{MoS}_2/\text{graphene}$ hollow spheres also exhibit higher activity than Pt loaded $\text{Cd}_{0.8}\text{Zn}_{0.2}\text{S}$ (Fig. 5d) and several Cd-based sulfide/graphene photocatalysts reported in the literature.^{50–52}

The impact of a defect-mediated mechanism on the photocatalytic activity of hollow spheres was evaluated by the ESR analysis. Blank MoS_2 was firstly fabricated through a similar cysteine-assisted hydrothermal reaction, in order to find out the possible reasons for the formation of defect-rich cocatalysts. No apparent signal of defects is detected in the ESR spectrum of MoS_2 (Fig. 6a), excluding the possible influence of biomolecules on the formation of defective MoS_2 . The electronic structure of $\text{Cd}_{0.8}\text{Zn}_{0.2}\text{S}/\text{MoS}_2/\text{graphene}$ is further compared with $\text{CdS}/\text{MoS}_2/\text{graphene}$ hollow spheres. As shown in Fig. 6b, only the six hyperfine lines and the weak signal corresponding to Cd-vacancies are detected. The absence of Mo^{5+} signals indicates that the coupling of CdS with $\text{MoS}_2/\text{graphene}$ cocatalysts cannot induce the formation of defective nanostructures. However, the pristine Cd or Zn-vacancies in multicomponent solid solution shows significant influence on the formation of defect-rich MoS_2 . With the increase of the amount of Mo precursor, the signal corresponding to Mo^{5+} gradually increases accordingly (Fig. 6c). For $\text{Cd}_{0.8}\text{Zn}_{0.2}\text{S}/\text{MoS}_2/\text{graphene}$ fabricated from 0.2 mmol Mo precursor, the strongest ESR signal is observed, which is consistent

Fig. 6 ESR spectra of MoS₂ nanoparticles (a), CdS/MoS₂/graphene (b), Cd_{0.8}Zn_{0.2}S/MoS₂/graphene with different amounts of Mo precursor (c) and Cd_{0.8}Zn_{0.2}S/MoS₂/graphene with different ratios of Cd/Zn (d).

with its superior photocatalytic activity. It seems that the formation of defect-rich MoS₂ is facilitated by the presence of Cd_{0.8}Zn_{0.2}S, as much stronger ESR signals are detected compared to Cd_{0.2}Zn_{0.8}S and Cd_{0.5}Zn_{0.5}S (Fig. 6d). Therefore, hydrogen evolution over Cd_{0.8}Zn_{0.2}S/MoS₂/graphene composites can be significantly enhanced by controlling the defective structure of cocatalysts.

The charge transfer processes at the semiconductor/electrolyte interfaces were studied by electrochemical impedance spectra (EIS) measurements. In the Nyquist plots (Fig. S7, ESI†), Cd_{0.8}Zn_{0.2}S/MoS₂/graphene hollow spheres show a much smaller radius than that of blank Cd_{0.8}Zn_{0.2}S nanoparticles. Generally, the smaller arc radius in the Nyquist plot indicates an effective separation of the photogenerated electron-hole pairs and fast interfacial charge transfer to the electron donor or electron acceptor.⁵³ Based on the suggested equivalent circuits shown in the inset of Fig. S6 (ESI†), both curves can be fitted with the CPE model. In the high frequency region, although there is no obvious difference in the ohmic series resistances (R_u), the charge transfer resistance (R_p) of Cd_{0.8}Zn_{0.2}S/MoS₂/graphene decreased from 3.76×10^6 to 1.2×10^6 .⁵⁴ It proves that the existence of a MoS₂/graphene cocatalyst as an “electron reservoir” contributes to the separation of photo-generated electron-hole pairs and the charge transfer at the solid-liquid interface. As a result, the as-synthesized hollow spheres show improved photocatalytic activity.

The carrier transfer process in the composites was further investigated by photoluminescence (PL) spectra. As shown in Fig. 7a, the Cd_{0.8}Zn_{0.2}S nanoparticles showed an emission peak centered at 610 nm, which is ascribed to the band gap emission of Cd_{0.8}Zn_{0.2}S. Differently, Cd_{0.8}Zn_{0.2}S/MoS₂/graphene hollow spheres show remarkably decreased peak intensity. The photoluminescence quenching can be ascribed to the facilitated electron transfer between Cd_{0.8}Zn_{0.2}S and MoS₂/graphene cocatalysts, which suppressed the recombination of generated photogenerated charge carriers in Cd_{0.8}Zn_{0.2}S.⁵⁵

Fig. 7 (a) Photoluminescence spectra of the Cd_{0.8}Zn_{0.2}S nanoparticles and Cd_{0.8}Zn_{0.2}S/MoS₂/graphene hollow spheres. (b) Schematic photocatalytic mechanism of H₂ evolution over Cd_{0.8}Zn_{0.2}S/MoS₂/graphene hollow spheres.

Based on the above discussion, the mechanism of photocatalytic H₂ evolution over Cd_{0.8}Zn_{0.2}S/MoS₂/graphene hollow spheres is illustrated in Fig. 7b. Firstly, the unique hollow structure of graphene-based photocatalysts not only acted as photon trap-wells for enhanced light absorption by multiple reflections, but also provided 3-D reactors with large surface area and more reaction sites for photocatalytic hydrogen evolution. Secondly, defect-rich MoS₂ with lower activation potential and abundant unsaturated active S atoms is a promising low-cost co-catalyst for H₂ production.⁵⁶ The strategy of one-pot self-assembly synthesis resulted in the *in situ* formation of heterostructures loaded with MoS₂ for efficient interfacial separation of charge carriers. Thirdly, the utilization of 2-D graphene showed a significant impact on the photocatalytic property. On one hand, the graphene substrate with superior electron mobility offered great opportunity to overcome the poor conductivity of MoS₂ cocatalysts.⁵⁷ On the other hand, synergistic effects between graphene and MoS₂ could remarkably facilitate the transfer of photogenerated electrons to MoS₂, where they reacted with H⁺ to form H₂ under lower overpotential.⁵⁸ In particular, few-layer MoS₂ with active exposed edges could either directly accept electrons from CdS or through graphene as an electron transfer mediator. This electron transfer pathway was favorable for the separation of charge carriers and efficient electron transfer to the reactive sites.⁵⁹ Above all, the synergistic effect contributed to the significantly enhanced visible-light-driven activity of Cd_{0.8}Zn_{0.2}S/MoS₂/graphene hollow spheres for H₂ production without noble metals.

Conclusion

In summary, a biomolecule-assisted one-pot reaction was used to fabricate Cd_{1-x}Zn_xS/MoS₂/graphene hollow spheres. Through the strategy of defect engineering, we demonstrated the significant role of defect-rich MoS₂ as low-cost cocatalysts for highly efficient photocatalytic hydrogen evolution. Due to the unique hollow-shaped structure and improved charge separation ability, Cd_{0.8}Zn_{0.2}S/MoS₂/graphene hollow spheres exhibited an unprecedentedly high hydrogen production rate of $2.97 \text{ mmol g}^{-1} \text{ h}^{-1}$, which is more than 64 times higher than that of Cd_{0.8}Zn_{0.2}S nanoparticles and also even better than that of the Cd_{0.8}Zn_{0.2}S/Pt composite. This work provides a promising prospect to develop

multicomponent solid solutions as efficient non-noble metal photocatalysts for many promising applications in the field of clean energy.

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