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Graphical Abstract:

A novel nanocomposite composed of graphene-like MoS$_2$ sheet and Zn$_x$Cd$_{1-x}$S nanoparticles was used for photocatalytic hydrogen under visible light.
Coupling Zn$_x$Cd$_{1-x}$S nanoparticles with graphene-like MoS$_2$: superior interfacial contact, low overpotential and enhanced photocatalytic activity under visible-light irradiation

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Abstract: A novel nanocomposite composed of two-dimensional graphene-like MoS$_2$ and Zn$_x$Cd$_{1-x}$S (0≤$x$≤0.5) nanoparticles has been synthesized by a simple exfoliation of bulk MoS$_2$ into single- or few-layer MoS$_2$ and then ultrasonic mixing Zn$_x$Cd$_{1-x}$S onto MoS$_2$ nanosheets. The samples were characterized by X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), high-resolution transmission electron microscopy (HRTEM), UV-visible diffuse reflectance spectroscopy (UV-vis DRS), photoelectrochemical experiment and photoluminescence. The results showed that the nanoparticles of Zn$_x$Cd$_{1-x}$S were well dispersed and anchored on the surface of the graphene-like MoS$_2$ nanosheets. The superior interfacial coupling between Zn$_x$Cd$_{1-x}$S and MoS$_2$ synergistically promoted the electron-holes transportation and separation. Upon visible-light irradiation (λ>420 nm), the composite consisted of Zn$_{0.3}$Cd$_{0.7}$S and ca. 0.6 wt% graphene-like MoS$_2$ gives the highest hydrogen evolution amount of 7179.1 µmol g$^{-1}$, which is ca. 7 times as high as that of Zn$_{0.3}$Cd$_{0.7}$S. This study displays a facile method to build a low-cost but effective photocatalyst for water reduction to produce hydrogen under solar light irradiation.

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1. Introduction

Due to the global energy crisis and environmental protection demand, hydrogen as an environmentally friendly and recyclable energy has attracted great attention. The photocatalytic water splitting to produce hydrogen has been considered as one of the most important technologies to solve the energy crisis and environmental issues.\(^1\)\(^-\)\(^3\) Since Fujishima and Honda reported H\(_2\) evolution from TiO\(_2\) electrode,\(^4\) many novel semiconductor-based photocatalytic hydrogen generation systems, including CdS,\(^5\)\(^-\)\(^9\) C\(_3\)N\(_4\),\(^10\)\(^-\)\(^14\) TaON,\(^15\)\(^-\)\(^16\) etc. have been developed. Various technologies such as forming solid solutions,\(^17\)\(^-\)\(^19\) semiconductor combination,\(^20\)\(^-\)\(^23\) co-catalyst loading,\(^24\)\(^-\)\(^26\) sensitization with organic dyes,\(^27\)\(^-\)\(^29\) and morphology controlling,\(^27\)\(^-\)\(^28\) have been adopted to improve the catalytic performance of the photocatalysts. For example, Wong’s group combined zinc cadmium sulphide with MoS\(_2\) using an in-situ photo-assisted deposition method. This novel composite photocatalyst showed enhanced photocatalytic activity for hydrogen evolution compared to sole zinc cadmium sulphide.\(^29\) Among the investigated semiconductors, CdS has excellent visible-light absorption ability with a sufficient narrow band gap (E\(_g\) ~ 2.4 eV). However, CdS without cocatalyst usually is low active for the photocatalytic hydrogen production from water because of its large H\(_2\) evolution overpotential. Another most investigated semiconductor ZnS is found to be an effective photocatalyst for H\(_2\) evolution even in the absence of noble metal co-catalysts since it has high conduction band potential.\(^30\)\(^-\)\(^32\) Unfortunately, ZnS is a wide band gap semiconductor (3.5 eV) and can only be active for H\(_2\) evolution under UV-light irradiation. Reber’s group first demonstrated that forming Zn\(_x\)Cd\(_{1-x}\)S solid solution between ZnS and CdS improved the photocatalytic activity.\(^3\)\(^-\)\(^4\) After this work, the Zn\(_x\)Cd\(_{1-x}\)S solid solution prepared in different method as a photocatalyst for water splitting in visible-light region has been investigated intensively.\(^17\)\(^-\)\(^18\),\(^33\)\(^-\)\(^35\) The results demonstrated that though Zn\(_x\)Cd\(_{1-x}\)S might be used as a visible-light active photocatalyst for reduction of water to produce hydrogen in the presence of sacrificial electron donors, the quantum efficiency was still relatively low. The hybridization of semiconductors with other materials to facilitate charge transfer and separation has been proved to be another powerful strategy to improve the photocatalytic activity.\(^26\)\(^-\)\(^29\) Various effective methods, including coupling the semiconductors with graphene or carbon tubes, have been developed. Coupling a semiconductor with graphene produces a kind of novel photocatalysts for hydrogen production since graphene can accommodate the photogenerated charges transfer and suppress charges recombination.\(^36\)\(^-\)\(^38\) Inspired by the outstanding properties of graphene, some graphene-like materials like molybdenum disulfide (MoS\(_2\)), have also attracted considerable attention. MoS\(_2\) with a layered structure consisting of sulfur layers with Mo ions in between can be exfoliated to single- or few-layer nanosheets similarly as what observed in graphene.\(^39\) It has also been reported that MoS\(_2\) demonstrated low overpotential for hydrogen evolution reaction.\(^40\) With these outstanding properties, graphene-like MoS\(_2\) sheet can act as an excellent supporting matrix and a non-noble metal co-catalyst.

Herein, we report the fabrication, characterization and photocatalysis of a novel nanocomposite composed of two-dimensional graphene-like MoS\(_2\) and Zn\(_x\)Cd\(_{1-x}\)S (0≤x≤0.5) solid solution. The nanocomposite was prepared by a simple exfoliation of bulk molybdenum disulfide into single- or few-layer MoS\(_2\) and then ultrasonic mixing Zn\(_x\)Cd\(_{1-x}\)S onto graphene-like MoS\(_2\) nanosheets. The as-prepared nanocomposite demonstrates a high photocatalytic activity for H\(_2\) evolution under visible-light irradiation without adding the noble-metal co-catalyst. The enhancement of photocatalytic activity may be attributed to the superior interfacial contacts between Zn\(_x\)Cd\(_{1-x}\)S and two-dimensional MoS\(_2\) nanosheets, which could synergistically promote the electron-holes transportation and separation. The structure, optical and photoelectrochemical properties of the composite have been fully investigated. Our work demonstrated a new prototype for constructing a low-cost but effective photocatalyst for water reduction to produce hydrogen under solar light irradiation.

2. Experimental

2.1. Materials and Syntheses

All chemicals were purchased from Sinopharm chemical reagent company and used without further purification. The Zn\(_x\)Cd\(_{1-x}\)S was synthesized by a hydrothermal treatment. In a typical experiment, zinc acetate (Zn(Ac)\(_2\)·2H\(_2\)O) and cadmium sulfate (3CdSO\(_4\)·8H\(_2\)O) in a total amount of 6 mmol with various molar ratios were dissolved in 40 mL of deionized water, then 20 mL of 0.45 M sodium sulfide (Na\(_2\)S·9H\(_2\)O) solution was added dropwise under magnetic stirring. The mixture was transferred to a 100 mL Teflon-lined autoclave and heated at 180 °C for 10 h. The solid was isolated by centrifugation, washed with deionized water for 3 times and dried at 70 °C. The resultant samples were stored in the darkness before further dealing with.

MoS\(_2\) was prepared following the reported method with some modifications.\(^41\)\(^-\)\(^42\) To a 100 mL Teflon-lined autoclave, 1.45 g (6 mmol) of Na\(_2\)MoO\(_4\)·2H\(_2\)O, 2.28 g (30 mmol) of thiourea and 60 mL of deionized water were added. The autoclave with the reactants was heated to 210 °C and kept at the temperature for 24 h. The autoclave was cooled to room temperature and the black precipitate was collected by centrifugation. The resulting solid was washed with deionized water for 3 times and then dried in an oven at 70 °C for 24 h. Single- or few-layered graphene-like MoS\(_2\) was prepared by exfoliation of MoS\(_2\) in an organic solvent.\(^43\) In a typical experiment, 750 mg of MoS\(_2\) was dispersed in 15 mL of methanol in a 100 mL flask. The mixture was sonicated for 2 h at room temperature, resulting in a dark brown suspension. The suspension was centrifuged for 10 min.
(2000 rpm) and the residue was removed by decantation. The concentration of as-prepared single- or few-layered graphene-like MoS$_2$ in the suspension was ca. 0.6 mg mL$^{-1}$.

Zn$_x$Cd$_{1-x}$S functionalized graphene-like MoS$_2$ was prepared by an ultrasonic mixing method. An appropriate amount of the Zn$_x$Cd$_{1-x}$S sample was added in 50 mL of MoS$_2$ suspension (containing ca. 2 mg MoS$_2$) and the mixture was ultrasonicated for another 2 hours. After that, the solvent was removed on a rotary evaporator at 40 °C. The obtained lamellar solid was grinded into powders. The as-prepared sample labeled as Zn$_x$Cd$_{1-x}$S/MoS$_2$-$y$, where $y$ stands for weight percent of MoS$_2$ in the nanocomposite. All samples were stored in the darkness before used for the photocatalytic reactions.

### 2.2. Characterization

Powder X-ray diffraction (XRD) patterns were recorded on an X-ray diffractometer (X’ Pert-ProMPD) with Cu K$\alpha$ irradiation ($\lambda=1.5406$ Å). X-ray photoelectron spectroscopy (XPS) was performed on the Thermo Scientific ESCALA 250Xi X-ray Photoelectron Spectrometer. All the binding energies were calibrated by C 1s peak at 284.5 eV of the surface adventitious carbon. Transmission electron microscopy (TEM) studies were conducted on a transmission electron microscope (JEOL JEM-2100) operating at an accelerating voltage of 200 kV. The ultraviolet-visible diffuse reflectance spectra (DRS) were obtained on a UV-visible spectrophotometer (Shimadzu UV-3150). Photoluminescence (PL) spectra of the samples were recorded on an Edinburgh PLS920 fluorospectrophotometer.

### 2.3. Photoelectrochemical measurement

The photoelectrochemical behaviors of the samples were measured on a CHI660D potentiostat/galvanostat electrochemical analyzer in a three-electrode system consisting of a working electrode, a platinum wire as a counter electrode, and a saturated calomel electrode (SCE) as a reference electrode. The working electrode was prepared by coating the ethanol suspension of the sample onto a clean indium tin oxide (ITO) glass and was dried in vacuum at 70 °C. The electrodes were immersed in a supporting electrolyte solution of 0.5 M Na$_2$SO$_4$ containing 10 vol% lactic acid. Prior to the measurement, the solution was deaerated by bubbling Ar for 1 hour. The working electrode was irradiated with a GY-10 xenon lamp (150W) during the measurement. For the Mott-Schottky measurements, the supporting solution was 0.5 M Na$_2$SO$_4$ without adding lactic acid.

### 2.4 Photocatalytic reaction for hydrogen evolution

The photocatalytic reaction was carried out in a 70 mL quartz flask equipped with a flat optical entry window. The effective irradiation area for the cell is ca. 3 cm$^2$. In a typical photocatalytic experiment, 60 mL of 10 vol% lactic acid aqueous solution containing 50 mg of the fresh prepared catalyst were added into the quartz flask. Prior to irradiation, the system was sonicated for 3 min at room temperature. The system was deaerated by bubbling argon into the solution for 30 min before light irradiating. A 150 W Xe lamp equipped with a cut-off filter at 420 nm was used as a visible-light source. The lamp was positioned ca. 10 cm away from the optical entry window of the reactor. The produced hydrogen gas was analyzed with an online gas chromatograph (GC1650) equipped with a thermal conductivity detector (TCD) and 5 A molecular sieve columns using argon as carrier gas. The standard H$_2$/Ar gas mixtures of known concentrations were used for GC signal calibration.

### 3. Results and discussion

#### 3.1 Characterization of the photocatalysts

The XRD patterns of as-prepared samples are displayed in Fig. 1. The diffraction peaks at 26.5°, 43.8°, and 52.0° (Fig. 1, curve a) correspond to (111), (220), and (311) planes of the cubic structure of CdS (JCPDS card no. 10-0454); while the diffraction peaks at 28.6°, 48.6°, and 56.5° (Fig. 1, curve b) correspond to (111), (220), and (311) planes of the cubic structure of ZnS (JCPDS card no. 05-0566). The formation of Zn$_x$Cd$_{1-x}$S solid solution is confirmed by the diffraction peaks of CdS shifting to a higher degree (Fig. 1, curve c-f) as the molar ratio of Zn$^{2+}$ to Cd$^{2+}$ increased from 0.1 to 0.4. At higher molar ratio of Zn$^{2+}$ to Cd$^{2+}$ (e.g. $n_{Zn}/n_{Cd}=0.5:0.5$), ZnS appears as a separate phase in the sample (Fig. 1, curve g). For the MoS$_2$ modified sample, Zn$_x$Cd$_{1-x}$S/MoS$_2$-0.6, all diffraction peaks locate at ca. 27.0°, 44.8°, and 52.9° (Fig. 1 curve h), which are similar to the pristine Zn$_0.3$Cd$_{0.7}$S and there were no diffraction peaks attributable to MoS$_2$, which might be due to the low content and high distribution of the MoS$_2$ component. Fig. 2 depicts the XPS spectra of the sample Zn$_x$Cd$_{1-x}$S/MoS$_2$-0.6. The binding energies obtained were corrected for specimen charging by referencing carbon 1s to 284.5 eV. The survey XPS is shown in Fig. 2A. The peaks centred at 411.6 eV and 404.7 eV are attributed to Cd and the peaks at 1024.2 eV and 1047.7 eV are attributed to Zn.$^{43,44}$ The high-resolution XPS spectrum of Mo 3d (Fig. 2B) shows binding energy at 228.9 eV for Mo$^{4+}$ 3d$_{3/2}$ and 232.1 eV for Mo$^{4+}$ 3d$_{5/2}$, suggesting that Mo exist in the chemical states of Mo$^{4+}$. These values are close to those previously reported for MoS$_2$. In addition, as compared to the binding energy of Zn 2p reported for Zn$_x$Cd$_{1-x}$S, a higher binding energy shift was observed over the sample Zn$_x$Cd$_{1-x}$S/MoS$_2$-0.6. Such a shift to high binding energy may suggest an interaction between Zn$_x$Cd$_{1-x}$S and MoS$_2$. Fig. 1 XRD patterns of as-prepared Zn$_x$Cd$_{1-x}$S samples using the precipitate-hydrothermal method. Sample (a) CdS, (b) ZnS, (c) Zn$_0.1$Cd$_{0.9}$S, (d) Zn$_0.2$Cd$_{0.8}$S, (e) Zn$_0.3$Cd$_{0.7}$S, (f) Zn$_0.4$Cd$_{0.6}$S, (g) Zn$_0.5$Cd$_{0.5}$S, and (h) Zn$_0.6$Cd$_{0.4}$S/MoS$_2$-0.6.
The image of exfoliated MoS$_2$ region are observed for all Zn contents. The HRTEM image of Zn$_{0.3}$Cds$_{0.7}$S/MoS$_2$-0.6 exhibits fringes with the lattice spacing of ca. 0.32 nm and 0.62 nm, which correspond to the (101) plane of cubic Zn$_{0.3}$Cds$_{0.7}$S and the (002) plane of hexagonal MoS$_2$, respectively, indicating the two components coexist in the nanocomposite.

### 3.2 Optical and photoelectrochemical properties

Fig. 4A shows the UV-vis DRS spectra of the Zn$_x$Cd$_{1-x}$S samples. Intense absorption bands with the absorption edges in the visible region are observed for all Zn$_x$Cd$_{1-x}$S samples. The absorption edge shows a continuous blue shift as the Zn content in the Zn$_x$Cd$_{1-x}$S solid solution increases, indicating that the band gap becomes wider due to the increase of Zn concentration. However, the absorption edge of Zn$_{0.5}$Cd$_{0.5}$S shows a little red shift compared to that of the Zn$_{0.1}$Cd$_{0.9}$S sample. By the XRD results above, the Zn$_{0.5}$Cd$_{0.5}$S sample consists of both Zn$_{0.3}$Cds$_{0.7}$S solid solution and ZnS phase. This may be the reason for the discontinuous blue shift of the Zn$_{0.4}$Cd$_{0.6}$S sample. The colour of the Zn$_x$Cd$_{1-x}$S samples changes from orange to yellow as the Zn content in the solid solution increases (Fig. 4B). Fig. 4C shows the UV-vis DRS spectra of the Zn$_{0.5}$Cd$_{0.5}$S and Zn$_{0.3}$Cd$_{0.7}$S/MoS$_2$-0.6. The spectra of ZnS, CdS and physical mixture of ZnS and CdS are also demonstrated for comparison. From Fig. 4C we can see that the absorption edge of Zn$_{0.5}$Cd$_{0.5}$S lies between that of ZnS (curve a) and CdS (curve b). In addition, the absorption edge of Zn$_{0.3}$Cd$_{0.7}$S (curve c) is smooth, indicating that a real solid solution formed. The absorption of the physical mixture of ZnS and CdS in a molar ratio of 3/7 can be resolved into two segments (curve e): the absorption in the UV range of ZnS, and the absorption in the visible region of CdS. Similar absorption feature about mixed semiconductors was also reported. These results clearly indicate that homogeneous Zn$_{0.3}$Cd$_{0.7}$S solid solution is successfully prepared when $x$ is less than 0.3. It has been reported that MoS$_2$ has a small band gap of around 1.23 eV, corresponding to the absorption in the infrared range. However, the absorption spectrum of the Zn$_{0.5}$Cd$_{0.5}$S/MoS$_2$-0.6 sample (curve d) demonstrated obviously red shift and a tail-up phenomenon compared with that of Zn$_{0.1}$Cd$_{0.9}$S, showing an interaction between Zn$_{0.5}$Cd$_{0.5}$S and exfoliated MoS$_2$ sheets. The extrapolation of the Tauc plot on $x$ intercepts gives the band gaps of 2.28, 2.38 and 2.40 eV for Zn$_{0.1}$Cd$_{0.9}$S, Zn$_{0.2}$Cd$_{0.8}$S and Zn$_{0.3}$Cd$_{0.7}$S, respectively (insets of Fig. 4).

![Fig.2 XPS spectra of sample Zn$_{0.5}$Cd$_{0.5}$S/MoS$_2$-0.6: (A) the survey spectrum and (B) High-resolution XPS spectrum of Mo 3d.](image)

![Fig.3 The TEM image of exfoliated MoS$_2$ (A) and HRTEM images of Zn$_{0.3}$Cd$_{0.7}$S/MoS$_2$-0.6 photocatalyst (B) and (C).](image)

![Fig.4 A: UV-vis diffuse reflectance spectra and the band gap calculation of the samples (a) Zn$_{0.1}$Cd$_{0.9}$S, (b) Zn$_{0.2}$Cd$_{0.8}$S, (c) Zn$_{0.3}$Cd$_{0.7}$S, (d) Zn$_{0.4}$Cd$_{0.6}$S, (e) Zn$_{0.5}$Cd$_{0.5}$S. B: The photo images of the (a) Zn$_{0.1}$Cd$_{0.9}$S, (b) Zn$_{0.2}$Cd$_{0.8}$S, (c) Zn$_{0.3}$Cd$_{0.7}$S, (d) Zn$_{0.4}$Cd$_{0.6}$S, (e) Zn$_{0.5}$Cd$_{0.5}$S. C: UV–Vis diffuse reflectance spectra and the band gap calculation of the samples (a) ZnS, (b) CdS, (c) Zn$_{0.3}$Cd$_{0.7}$S, (d) Zn$_{0.5}$Cd$_{0.5}$S/MoS$_2$-0.6, (e) physical mixture of ZnS and CdS (mole ratio: 3:7). The band gap value of samples estimated by a related curve of (αhν)$^2$ versus photon energy plotted in the inset.](image)
Fig. 5 Fluorescence spectra of (a) Zn$_{0.3}$Cd$_{0.7}$S sample and (b) Zn$_{0.3}$Cd$_{0.7}$S/MoS$_2$-0.6 sample. Excited wavelength: 466 nm.

The photoluminescence spectra (PL) of the as-prepared samples are measured to reveal the photogenerated charge transfer process. As shown in Fig. 5, four emission peaks at 514 nm, 523 nm, 537 nm, and 547 nm can be observed for both Zn$_{0.3}$Cd$_{0.7}$S and Zn$_{0.3}$Cd$_{0.7}$S/MoS$_2$-0.6 at 466 nm excitation. The peaks at 514 nm and 523 nm correspond to the near-band emission of the zinc cadmium sulphide while the peaks at 537 nm and 547 nm commonly arise from the deep-level or trap-state emission of the zinc cadmium sulphide.

From Fig. 5, the PL intensity of Zn$_{0.3}$Cd$_{0.7}$S/MoS$_2$-0.6 decreased greatly compared with that of Zn$_{0.3}$Cd$_{0.7}$S. The calculated quenching efficiency at 514 nm for Zn$_{0.3}$Cd$_{0.7}$S/MoS$_2$-0.6 is 66.9%. This phenomenon is attributed to the efficient electron transfer from the Zn$_{0.3}$Cd$_{0.7}$S to the graphene-like MoS$_2$ sheets, leading to the spatial separation of the photogenerated electron and the hole.

The photocurrent-time experiments were conducted to investigate the photo-excited electron transfer in the as-prepared samples and the results are shown in Fig. 6A. Under UV-vis illumination, the photocurrent response of the Zn$_{0.3}$Cd$_{0.7}$S electrode was strong but not very steady. The average photocurrent density is ca. 340 µA cm$^{-2}$ for the five light-on and light-off cycles. An enhanced photocurrent response for Zn$_{0.3}$Cd$_{0.7}$S/MoS$_2$-0.6 electrode was observed under the similar experimental conditions and the photocurrent density reaches ca. 440 µA cm$^{-2}$. The photocurrent response for the Zn$_{0.3}$Cd$_{0.7}$S/MoS$_2$-0.6 electrode was prompt, steady, and reproducible during the light on/off illumination cycles. The enhancement and the stability of the photocurrent for the Zn$_{0.3}$Cd$_{0.7}$S/MoS$_2$-0.6 sample are owing to positive synergetic effect between Zn$_{0.3}$Cd$_{0.7}$S and MoS$_2$ in the nanocomposite.

Graphene-like MoS$_2$ in the nanocomposite may serve as an acceptor and a transporter for the excited electrons generated from Zn$_{0.3}$Cd$_{0.7}$S, thus, promotes the photoexcited $e^-/h^+$ pair separation and enhances the charge transfer from the nanocomposite to ITO.

The results of the linear sweep voltammetry of Zn$_{0.3}$Cd$_{0.7}$S and Zn$_{0.3}$Cd$_{0.7}$S/MoS$_2$-0.6 electrodes are shown in Fig. 6B. For Zn$_{0.3}$Cd$_{0.7}$S electrode, the proton reduction potential is ca. -1.09 V vs. SCE; while for Zn$_{0.3}$Cd$_{0.7}$S/MoS$_2$-0.6 electrode, the value changes to -1.03 V vs. SCE. The result demonstrates that the introduction of graphene-like MoS$_2$ sheet in the composite reduces the hydrogen evolution potential.

Fig. 6 (A) Transient photocurrent-time curves of blank ITO glass (blue line), Zn$_{0.3}$Cd$_{0.7}$S (black line) and Zn$_{0.3}$Cd$_{0.7}$S/MoS$_2$-0.6 (red line) in Na$_2$SO$_4$ solution (0.50 M) containing 10% volume lactic acid under visible-light irradiation in Ar. Initial voltage: 0.1 V; (B) The linear sweep voltammetry of Zn$_{0.3}$Cd$_{0.7}$S and Zn$_{0.3}$Cd$_{0.7}$S/MoS$_2$-0.6 electrodes in 0.50 mol/L Na$_2$SO$_4$ (10 vol% lactic acid). Hydrogen evolution potentials at 0.002 A were as follows: Zn$_{0.3}$Cd$_{0.7}$S, E=-1.09 V; Zn$_{0.3}$Cd$_{0.7}$S/MoS$_2$, E=-1.03 V. Inset: Mott-Schottky plot of the Zn$_{0.3}$Cd$_{0.7}$S and Zn$_{0.3}$Cd$_{0.7}$S/MoS$_2$-0.6 sample.
In order to further understand the function of graphene-like MoS$_2$ sheet in the nanocomposite, we measured flat band potentials of Zn$_{0.3}$Cd$_{0.7}$S and Zn$_{0.3}$Cd$_{0.7}$S/MoS$_2$$_{0.6}$. The flat band potential ($E_{fb}$) was determined by the onset potential of the Mott–Schottky plots and the results are shown in the inset of Fig. 6B. The positive slopes of the linear plots suggest n-type semiconductor features of Zn$_{0.3}$Cd$_{0.7}$S and Zn$_{0.3}$Cd$_{0.7}$S/MoS$_2$$_{0.6}$. $E_{fb}$ of Zn$_{0.3}$Cd$_{0.7}$S estimated from the $x$ intercepts of the linear region of the Mott–Schottky plot is ca. −0.4 V vs. SCE; while ca. −0.7 V vs. SCE for Zn$_{0.3}$Cd$_{0.7}$S/MoS$_2$$_{0.6}$ electrode. These results shows Zn$_{0.3}$Cd$_{0.7}$S/MoS$_2$$_{0.6}$ possesses a higher electron donor level than Zn$_{0.3}$Cd$_{0.7}$S, suggesting coupling Zn$_{0.3}$Cd$_{0.7}$S and graphene-like MoS$_2$ may produce a positive synergetic effect to shift the flat potential of the nanocomposite to a more negative position. This negative shift is certainly beneficial for the photocatalytic hydrogen evolution.

3.3 Photoinduced hydrogen evolution

The photocatalytic performance for hydrogen production over Zn$_x$Cd$_{1-x}$S catalysts under visible-light irradiation ($\lambda > 420$ nm) is shown in Fig. 7A. The amount of hydrogen evolved from pure CdS is low (46.1 µmol g$^{-1}$) due to its large H$_2$ evolution overpotential and the absence of the cocatalyst.$^{58-60}$ Only trace amount of hydrogen can be detected from pure ZnS because it can’t absorb visible-light. However, the Zn$_x$Cd$_{1-x}$S solid solution catalyst demonstrated very nice photocatalytic performance for hydrogen production under visible-light irradiation. The total amount of hydrogen evolved over Zn$_{0.1}$Cd$_{0.9}$S is 833.1 µmol g$^{-1}$ under visible-light irradiation. The evident enhancement of the H$_2$ production from Zn$_{0.1}$Cd$_{0.9}$S owing to the suitable band gap and position of the Zn$_{0.1}$Cd$_{0.9}$S solid solution for the visible-light-driven photocatalytic hydrogen production from water.$^1$ Since both the band gap and position can be adjusted by varying the ratio of the compositions of the narrow and the wide band gap semiconductor in the solid solution, the optimized solid solution used as the photocatalyst was found to be Zn$_{0.3}$Cd$_{0.7}$S and the H$_2$ generation rate under visible-light irradiation reached 1061.8 µmol g$^{-1}$. However, the photocatalytic activity decreased with increasing ZnS content in the solid solution.

Fig. 7 The hydrogen production of the solid solution of Zn$_x$Cd$_{1-x}$S samples (A) and Zn$_{0.3}$Cd$_{0.7}$S/MoS$_2$ samples (B) in 6 hours. Reaction conditions: 50 mg photocatalyst, 6 mL lactic acid, 54 mL deionized water, 150 W Xe lamp equipped with a cut-off filter at 420 nm.

Fig. 8 The recycling experiment of the Zn$_{0.3}$Cd$_{0.7}$S (a) and Zn$_{0.3}$Cd$_{0.7}$S/MoS$_2$$_{0.6}$ (b). Reaction conditions: 50 mg photocatalyst, 6 mL lactic acid, 54 mL deionized water, 150 W Xe lamp equipped with a cut-off filter at 420 nm.
Fig. 7B shows the photocatalytic activity of Zn$_{0.3}$Cd$_{0.7}$S/MoS$_2$ photocatalysts with different amounts of MoS$_2$ in the nanocomposite. No H$_2$ was detected when MoS$_2$ was used as the photocatalyst, suggesting that MoS$_2$ itself was not active for photocatalytic H$_2$ evolution. Introduction of MoS$_2$ in the composite leads to a huge hydrogen production enhancement. Under visible-light irradiation, the total amount of hydrogen evolved over Zn$_{0.3}$Cd$_{0.7}$S/MoS$_2$-0.2 and Zn$_{0.3}$Cd$_{0.7}$S/MoS$_2$-0.6 were 4111.5 µmol g$^{-1}$ and 7179.1 µmol g$^{-1}$, which is ca. 4 times and 7 times as high as that of Zn$_{0.3}$Cd$_{0.7}$S respectively. The amount of H$_2$ evolved starts to decrease when the content of MoS$_2$ in the nanocomposite was above the optimized value, which is ~0.6 wt%. Since the MoS$_2$ itself was inactive for photocatalytic hydrogen evolution, excessive amount of MoS$_2$ in the nanocomposite may block the light-absorption and weaken the light intensity arriving at the surface of Zn$_{0.3}$Cd$_{0.7}$S, thus decreases the photocatalytic activity.

Owing to the importance of the stability of a photocatalyst for its practical application, the photocatalytic stability of Zn$_{0.3}$Cd$_{0.7}$S/MoS$_2$-0.6 was further investigated by cycle photocatalytic experiments and the results are shown in Fig. 8. For comparison, the photocatalytic stability of Zn$_{0.3}$Cd$_{0.7}$S was also investigated in the same conditions. Under 6 h visible-light irradiation, Zn$_{0.3}$Cd$_{0.7}$S produced ca. 937.8 µmol g$^{-1}$ H$_2$ in the first run, and 706.2 µmol g$^{-1}$ H$_2$ in the second run. In the third run, the amount of evolved hydrogen decreased to 637.8 µmol g$^{-1}$. While Zn$_{0.3}$Cd$_{0.7}$S/MoS$_2$-0.6 in the first run produces ca. 7806.0 µmol g$^{-1}$ hydrogen under visible-light irradiation. In the second run, the photocatalytic activity of Zn$_{0.3}$Cd$_{0.7}$S/MoS$_2$-0.6 decreased ca. ten percent (7039.8 µmol g$^{-1}$). However, the amount H$_2$ evolved in the third run (7030.2 µmol g$^{-1}$) is almost the same as that of the second run. The results suggest that Zn$_{0.3}$Cd$_{0.7}$S/MoS$_2$-0.6 is much more stable than Zn$_{0.3}$Cd$_{0.7}$S under visible-light irradiation.

On the basis of above results, a possible mechanism for visible-light induced hydrogen production on the Zn$_{0.3}$Cd$_{0.7}$S/MoS$_2$ nanocomposite is shown in Fig. 9. Under visible-light irradiation, the electrons in the valence band of Zn$_{0.3}$Cd$_{0.7}$S are excited to the conduction band. Then, the excited electrons transfer from the conduction band of Zn$_{0.3}$Cd$_{0.7}$S to the MoS$_2$ nanosheets because of the low Fermi energy level of MoS$_2$ (ca. -0.1 eV) and the superior interfacial contacts between Zn$_{0.3}$Cd$_{0.7}$S and MoS$_2$, which enhances the charge separation and suppresses the recombination of e$^-$/h$^+$ pairs. H$^+$ ions in the solution accept the electrons from MoS$_2$ and forms H$_2$. Graphene-like MoS$_2$ here also acts as hydrogen evolution centres and reduces hydrogen evolution overpotential greatly. The holes remained on the surface of Zn$_{0.3}$Cd$_{0.7}$S nanoparticles are consumed by the lactic acid in the solution.
Conclusions

A novel nanocomposite composed of graphene-like MoS$_2$ and Zn$_x$Cd$_{1-x}$S solid solution as a photocatalyst has been synthesized. Zn$_x$Cd$_{1-x}$S nanoparticles well anchored on the two-dimensional graphene-like MoS$_2$ sheets of the nanocomposite, resulting in the excellent interfacial contacts between Zn$_x$Cd$_{1-x}$S and graphene-like MoS$_2$. Graphene-like MoS$_2$ in the nanocomposite serves not only as an excellent supporting matrix for anchoring Zn$_x$Cd$_{1-x}$S nanoparticles but also as a superior electron mediator to adjust electron transfer, and as the hydrogen evolution centres. It efficiently promotes the electron-hole separation, lengthens the charge lifetimes in the process of photocatalytic reaction, and reduces hydrogen evolution overpotential. The photocatalyst with the optimal composition showed much higher photocatalytic performance and superior stability for H$_2$ evolution under visible-light irradiation. This study demonstrates an efficient method to construct a low-cost but effective photocatalyst for water splitting to produce hydrogen under solar light irradiation.

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