This article can be cited before page numbers have been issued, to do this please use: J. Huang, X. Li, X. Jin, L. Wang, Y. Deng, F. Su, P. K. Wong and L. Ye, Mater. Adv., 2020, DOI: 10.1039/D0MA00187B.

This is an Accepted Manuscript, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this Accepted Manuscript with the edited and formatted Advance Article as soon as it is available.

You can find more information about Accepted Manuscripts in the Information for Authors.

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal’s standard Terms & Conditions and the Ethical guidelines still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this Accepted Manuscript or any consequences arising from the use of any information it contains.
High-efficiency and Stable Photocatalytic Hydrogen Evolution of Rhenium Sulfide Co-catalyst on Zn$_{0.3}$Cd$_{0.7}$S

Jindi Huang,a Xin Li,a Xiaoli Jin,a Li Wang,a Yu Deng,b Fengyun Su,a Po Keung Wong,c Liqun Ye,a,b,*

a Engineering Technology Research Center of Henan Province for Solar Catalysis; College of Chemistry and Pharmaceutical Engineering, Nanyang Normal University, Nanyang 473061, P. R. China.

b College of Materials and Chemical Engineering, Key Laboratory of Inorganic Nonmetallic Crystalline and Energy Conversion Materials, China Three Gorges University, Yichang 443002, P. R. China.

c School of Life Sciences, The Chinese University of Hong Kong, Shatin, NT, Hong Kong SAR, P. R. China.

*Correspondence author:

E-mail: yeliquny@163.com; lqye@ctgu.edu.cn (L Ye)
ABSTRACT: Photocatalytic hydrogen evolution is an attractive technology to solve the growing energy crisis. The development of advanced photocatalysts is an attractive but challenging issue. For the first time, we use inorganic ReS$_2$ as a co-catalyst for Zn$_{0.3}$Cd$_{0.7}$S by solvent thermal method, which enables highly efficient and recyclable H$_2$ evolution. Zn$_{0.3}$Cd$_{0.7}$S/ReS$_2$ composite photocatalysts contain 4 wt% ReS$_2$ co-catalysts, and Na$_2$S-Na$_2$SO$_3$ is used as a sacrificial reagent. Compared with bare Zn$_{0.3}$Cd$_{0.7}$S, Zn$_{0.3}$Cd$_{0.7}$S/ReS$_2$ corresponds 101 fold enhancement with the highest photocatalytic H$_2$ evolution rates of 92.45 mmol h$^{-1}$ g$^{-1}$. And it still maintains high hydrogen production after the 30-hour cycle experiment. In this paper, the mechanism of photocatalytic enhancement is expounded by various of experimental methods. In situ Fourier Transform Infrared (FT-IR) spectra and online mass spectrometry were used to discover the source of hydrogen. The experiment results show that ReS$_2$ is a promising joint catalyst for obtaining high-gloss catalytic hydrogen from water under visible light.

Keyword: rhenium sulfide • Zn$_{0.3}$Cd$_{0.7}$S • hydrogen • photocatalysis • co-catalyst
1. Introduction

Hydrogen is considered to be a clean energy source, it will solve the problems including scarcity of the environment and fossil resources in the future. However, the use of renewable resources rather than fossil fuels to produce hydrogen is a fundamental technical challenge.\cite{1,2} Honda and Fujishima presented the concept of photoelectrochemical decomposition of water into H\textsubscript{2} and O\textsubscript{2}, which converts solar energy into chemical energy and/or electrical energy.\cite{3,4} In recent years, using photocatalytic reactions of semiconductors to generate hydrogen from water has attracted considerable interest. And many semiconductor photocatalysts have been discovered including sulfides, nitrides, metals/metal oxides, and so on.\cite{5-8} Among them, metal sulfides and their composites are regarded as good candidates for photocatalytic H\textsubscript{2} production because of their suitable band gap and catalytic functions. CdS is the most widely used metal sulfide photocatalytic material for photocatalytic hydrogen production. It has a band gap of 2.4 eV, absorbs visible light, and has a suitable redox potential. However, CdS particles are easily agglomerated into irregular large-sized particles, resulting in a reduction in specific surface area, a high degree of recombination of photogenerated electrons and holes, and prone to photocorrosion, which severely limits the photocatalytic efficiency. To solve the above problems, a variety of effective methods, such as element dopation, construction of heterogeneous knots, or the use of co-catalysts has been developed.\cite{9-11}

Compared with CdS, ZnS has better performance, but the band gap of ZnS is 3.6 eV, which allows it absorb only the energy of ultraviolet light. In order to give full play to their respective advantages, CdS and ZnS are combined to form Zn\textsubscript{x}Cd\textsubscript{1-x}S solid solution as a high-efficiency catalyst for light.\cite{12} For example, Xing et al. synthesized Zn\textsubscript{x}Cd\textsubscript{1-x}S solid solution by simple coprecipitation method and N\textsubscript{2} atmosphere heat treatment.\cite{13} By adjusting the ratio of Zn to Cd, the forbidden band width of Zn\textsubscript{x}Cd\textsubscript{1-x}S solid solution is between 2.20 eV and 3.12 eV. Although Zn\textsubscript{x}Cd\textsubscript{1-x}S solid solution exhibits higher photocatalytic activity than the
one-component ZnS and CdS [14-17], these solid solutions still exhibit lower photocatalytic efficiency. Therefore, finding new solutions is necessary.

2D transition metal trihalides (TMDs), such as MoS$_2$ and WS$_2$, have large interlayer spaces and weak interlayer interactions, and have been widely studied as effective catalysts for hydrogen evolution. [18,19] Recently, it is confirmed that a new type of TMD Rhenium disulfide (ReS$_2$) has extraordinary photocatalytic properties due to its remarkable electron-hole separation, and is a promising photocatalyst for hydrogen production. [20-24] With this in mind, we expect ReS$_2$ to act as a cocatalyst to further enhance photocatalytic performance, which may provide new opportunities for photocatalytic H$_2$ evolution. [25-31] However, to the best of our knowledge, it has rarely been reported as a cocatalyst for photocatalytic hydrogen production.

In this work, ReS$_2$ was successfully loaded onto Zn$_x$Cd$_{1-x}$S nanorods by a simple two-step hydrothermal method. The Zn$_x$Cd$_{1-x}$S nanorods provide the substrate for the loading of ReS$_2$. The introduction of ReS$_2$ contributes to the transfer of photogenerated electrons, inhibits carrier recombination and improves the stability of Zn$_x$Cd$_{1-x}$S during photocatalytic reaction. Therefore, Zn$_x$Cd$_{1-x}$S with the ReS$_2$ which is cocatalyst exhibits higher hydrogen production performance and stability. The optimum performance is confirmed by adjusting the ratio of zinc/Cd and the amount of ReS$_2$ loaded. The results reveal that the ReS$_2$/Zn$_{0.3}$Cd$_{0.7}$S composite loaded with 4 wt% ReS$_2$ exhibits the highest hydrogen production rate of 92.45 mmol h$^{-1}$ g$^{-1}$, and it has stable hydrogen production for more than 30 hours when Na$_2$S-Na$_2$SO$_3$ is used as sacrificial reagents.

2. Experimental section

2.1 Materials preparation

Synthesis of Zn$_x$Cd$_{1-x}$S nanorods: In a typical synthesis of Zn$_x$Cd$_{1-x}$S nanorods ($x = 0, 0.1, 0.2, 0.3, 0.4, 0.5, 0.7$ and $1$), 2 mmol L-cysteine, zinc acetate and dihydrate cadmiumacetate amounting to a total of 1 mmol with various molar ratios were dissolved in 35 mL binary solution of ethanol amine. The reaction suspension was
stirred vigorously for 0.5 h until a homogeneous dispersion formed. Then the solution was transferred into a Teflon-lined autoclave and maintained at 180 °C for 24 h. After the autoclave was cooled to room temperature, Zn$_{0.3}$Cd$_{0.7}$S nanorods was washed with distilled water and absolute ethanol for several times, and then vacuum dried at 60°C overnight.

Synthesis of 10% ReS$_2$/Zn$_{0.3}$Cd$_{0.7}$S: 10.02 mg NH$_4$ReO$_4$, 5.62 mg thioacetamide (C$_2$H$_5$NS) and 400 mg CdS were dissolved in 40 ml H$_2$O. The reaction suspension was stirred vigorously for 30 min until a homogeneous dispersion formed. The reaction mixture was added to a Teflon-lined stainless steel autoclave and maintained at 220 °C for 48 h. After the autoclave was cooled to room temperature, 10% ReS$_2$/Zn$_{0.3}$Cd$_{0.7}$S was washed with distilled water and absolute ethanol for four times, and then vacuum dried at 60°C overnight.

2.2 Characterization

The phase and crystal structures of as-prepared samples were characterized by X-ray diffraction (XRD) on a Bruker D8 diffractometer using Cu Ka ($\lambda = 1.5406$) radiation in a 2θ range from 5° to 70°. X-ray photoelectron spectroscopy (XPS) data were obtained by Thermo ESCALAB 250XI X-ray photoelectron spectrometer (Al Ka, 150 W, C1s 284.8 eV). The high-resolution transmission electron microscopy (HRTEM) images and element mapping were obtained by a JEO LJEM-2100 F (UHR) field emission transmission electron microscopy. UV–vis diffuse reflectance spectroscopy (DRS) of samples was determined by a UV–vis spectrometer (Perkin Elmer, Lambda 850, BaSO$_4$ as a reference) and recorded in the range of 200–800 nm. Time-resolved photoluminescence (PL) spectra (380 nm excitation) was recorded on the FLS980 multifunctional steady-state and transient fluorescence spectrometer (Edinburgh Instruments, room temperature). The transient surface photovoltage data were recorded by a 500 MHz digital oscilloscope (TDS 3054C, Tektronix, Beaverton, OR, USA). Inductively coupled plasma (ICP) spectrometer (Shimadzu, ICPE-9820) was used.

2.3 Photocatalytic H$_2$ production
The photocatalytic hydrogen tests were conducted in a Labsolar-III AG closed gas circulation and exhaust system (Beijing Perfect Light Technology Co., Ltd China) maintaining the photo-reaction temperature at 5°C with a low-temperature thermostat bath (Poly Science, USA). In the photo-reaction system, 20 mg ReS2/CdS was suspended in 50 ml of DI water containing 2.1 g Na2S and 0.8 g Na2SO3. A 300 W Xenon lamp (PLS-SXE-300UV, Beijing Trusttech Co. Ltd., China) with a UV-cutoff filter (providing visible light λ ≥ 420 nm) served as the visible-light source to trigger the water splitting reactions. To identify and quantify the gases produced, a volume of 1.5 ml of gas was hourly sampled and measured by a gas chromatograph (GC9790II, Zhejiang Fuli Analytical Instrument Co., Ltd. China) equipped with a thermal conductivity detector (TCD) and a 5 Å molecular sieve column, where argon (Ar) was used as a carrier gas. The quantification of the H2 yield was based on a calibration curve.

2.4 Apparent quantum efficiencies (AQE) calculations

The apparent quantum efficiency (AQE) was measured under the same photocatalytic reaction condition, except for the wavelength of the incident light. The H2 yields of 1 h photoreaction under monochromatic light. AQE was calculated by the following equation:

\[ \text{AQE} = \frac{N_{\text{H}_2}}{N_p} = \frac{\text{number of reacted electrons}}{\text{number of incident photons}} \times 100\% \]

\[ = \frac{2 \times \text{the number of evolved } \text{H}_2 \text{ molecules}}{\text{number of incident photons}} \times 100\% \]

2.5 Photoelectrochemical measurements

Photocurrent response, linear sweep voltammetry and electrochemical impedance of the catalysts were measured on an electrochemical workstation (CHI 630e) in a three-electrode quartz reactor using 0.5 M Na2SO4 solution and a mixed solution of 0.1 M K3[Fe(CN)6] and K4[Fe(CN)6]·3H2O, respectively, as the electrolyte solutions. Linear sweep voltammetry (LSV) was carried out at a scan rate of 10 mV/s from 0.4 to -0.6 V. Working electrodes for samples were prepared applying the
doctor-blading method. Then, 0.01 g ethyl cellulose was dissolved in 15 ml ethanol with 0.1 g catalyst. Subsequently, a glass stick was applied to FTO with a layer of high-temperature adhesive tape on the edge. Finally, dried it in air and activated it at 120 °C for 2 h. All tests were conducted under visible light irradiation.

2.6 In-situ fourier transform infrared spectrometer (FT-IR) analysis

Fourier transform infrared spectrometer (Nicolet IS-50) was used for in-situ FT-IR measurement. The sample was filled into the in-situ IR cell, and Ar and H2O gases were introduced into the cell and fibre source (FX300, Beijing Perfect light Technology Co., Ltd China) through the CaF2 window of the cell. Before the measurement, the sample was degassed at 423 K for 4 h. The baseline was obtained after adsorption equilibrium on the sample for 1 h. 1%ReS2/ Zn0.3Cd0.7S was used after treatment by Na2S-Na2SO3.

2.7 On-line mass spectrometry analysis

10ml H2O/D2O with 10 mg photocatalyst, 2.1 g–0.8 g Na2S-Na2SO3 was added to the closed quartz reactor (Beijing Perfect light Technology Co., Ltd., China). One end of the reactor was continuously fed into Ar and the other end was fed into the sampling port of the mass spectrometer (HPR-20 R&D, Beijing Hiden Analytical Technology Co., Ltd., China). H2 and D2 were detected simultaneously in MID mode of SEM detector. After the MS baseline was stable, 300 W high pressure xenon lamp (PLS-SXE300, Beijing Perfect light Technology Co., Ltd., China) was used to illuminate the gas products in the reactor on-line.

3. Results and discussions
Fig. 1. Composition and morphological characterizations of ReS$_2$/Zn$_{0.3}$Cd$_{0.7}$S. (a, b) XRD pattern, (c) Zn$_{0.3}$Cd$_{0.7}$S TEM image, (d) ReS$_2$/Zn$_{0.3}$Cd$_{0.7}$S TEM image, (e-g) HRTEM image, (f) Zn$_{0.3}$Cd$_{0.7}$S HRTEM image, (g) ReS$_2$/Zn$_{0.3}$Cd$_{0.7}$S HRTEM image, (h-l) EDS elemental mapping, and (m–o) XPS analysis of ReS$_2$/Zn$_{0.3}$Cd$_{0.7}$S.

Structures and compositions of ReS$_2$/Zn$_{0.3}$Cd$_{0.7}$S (4 wt% of ReS$_2$) are visualized in Fig. 1. Fig. 1a and Fig. 1b show the XRD patterns of CdS, ZnS, Zn$_{0.3}$Cd$_{0.7}$S, ReS$_2$/Zn$_{0.3}$Cd$_{0.7}$S, the standard diffraction patterns of ZnS (PDF#77-2100) and CdS (PDF#77-2306).

Compared with the standard diffraction peaks of ZnS and CdS, the diffraction peaks of Zn$_{0.3}$Cd$_{0.7}$S were shifted toward lower-angle and higher-angle side, respectively, indicating that the sample is not a compounds of ZnS and CdS, but a Zn$_{0.3}$Cd$_{0.7}$S solid solution. After the load of ReS$_2$ on the surface of Zn$_{0.3}$Cd$_{0.7}$S, the diffraction peaks of Zn$_{0.3}$Cd$_{0.7}$S were not shifted and no new peaks appeared. It indicates that the load of ReS$_2$ can’t affect the crystal structure of Zn$_{0.3}$Cd$_{0.7}$S. In addition, the value of full width at half maximum of the solid-soluble can be found to be very large, which can be attributed to the different thickness of the Zn$_{0.3}$Cd$_{0.7}$S and ReS$_2$/Zn$_{0.3}$Cd$_{0.7}$S samples. The load of ReS$_2$ onto Zn$_{0.3}$Cd$_{0.7}$S did not significantly
alter the nanorod morphology of Zn$_{0.3}$Cd$_{0.7}$S, but there were obvious interfaces formed between ReS$_2$ and Zn$_{0.3}$Cd$_{0.7}$S, indicating that ReS$_2$ is tightly bound to the Zn$_{0.3}$Cd$_{0.7}$S nanorod surface. This finding is further confirmed by transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) of ReS$_2$/Zn$_{0.3}$Cd$_{0.7}$S (Fig. 1c–g). HRTEM shows that the grid spacing of ReS$_2$/Zn$_{0.3}$Cd$_{0.7}$S is 0.33nm, which is consistent with the XRD test results (Fig. 1f). In addition, Element mapping of ReS$_2$/Zn$_{0.3}$Cd$_{0.7}$S corresponding to the area is marked in Fig. 1, confirming that elemental S is uniformly dispersed in the whole selected area, while Re, Cd and Zn are distributed separately, indicating that there is an intimate contact between ReS$_2$ and Zn$_{0.3}$Cd$_{0.7}$S. Effective interfacial contact can shorten the charge transfer distance and facilitate the electron transfer between CdS and Zn$_{0.3}$Cd$_{0.7}$S. To further characterize surface chemical composition and valence state, ReS$_2$/Zn$_{0.3}$Cd$_{0.7}$S was analyzed by X-ray photoelectron spectroscopy (XPS). As shown in Fig. 1m, n, the Cd 1s and Zn 2p XPS spectra exemplarily demonstrate the structural characteristics of Zn$_{0.3}$Cd$_{0.7}$S. Fig. 1o shows two distinct peaks at 41.4 and 43.8 eV, which can be assigned to the Re 4f 7/2 and Re 4f 5/2 states of Re$^{4+}$ in ReS$_2$. All the above results corroborate the successful deposition of ReS$_2$ on the Zn$_{0.3}$Cd$_{0.7}$S surface.
Fig. 2. Optical properties and charge carrier dynamics of 4% ReS$_2$/Zn$_{0.3}$Cd$_{0.7}$S and Zn$_{0.3}$Cd$_{0.7}$S. (a) UV-VIS, (b) $(ahv)^2$ vs. photon energy $(hv)$, (c) photocurrent responses, (d) electrochemical impedance plots, (e) PL spectra, (f) time-resolved PL spectra.

The effect of ReS$_2$ modification on the optical properties of Zn$_{0.3}$Cd$_{0.7}$S was studied by UV–Vis diffusion reflection spectroscopy (Fig. 2a). After ReS$_2$ was loaded, the light absorption of CdS and Zn$_{0.3}$Cd$_{0.7}$S in the visible light absorption area was significantly enhanced, while the light absorption of pure CdS and Zn$_{0.3}$Cd$_{0.7}$S was not very different, which indicates that the enhancement of visible light is due to the presence of ReS$_2$. This may be attributed to the inherent high visible light capture capability of black ReS$_2$ nanoparticles. According to the plot of $(ahv)^2$ versus energy $(hv)$, the band gap value of ReS$_2$/ Zn$_{0.3}$Cd$_{0.7}$S was significantly reduced, which is
more conductive to the excitation of visible light. Mott-Schottky plots (Fig.S5) and XPS price band spectrum (Fig.S6) also show that the price band of ReS$_2$/Zn$_{0.3}$Cd$_{0.7}$S is more negative, which can facilitate the reduction reaction.

To confirm and better understand the enhanced migration and separation of photo-induced charge carriers of ReS$_2$/Zn$_{0.3}$Cd$_{0.7}$S, photoelectrochemical measurements were recorded. As expected, ReS$_2$/Zn$_{0.3}$Cd$_{0.7}$S showed a nearly 3 times higher photocurrent intensity than bare Zn$_{0.3}$Cd$_{0.7}$S, which infers that ReS$_2$ is an effective co-catalyst to promote the migration of photo-induced carriers (Fig. 2c). Meanwhile, the effect of ReS$_2$ deposition on the kinetics of charge migration was further studied by electrochemical impedance spectroscopy (EIS). In comparison with pure CdS, ReS$_2$/CdS, and Zn$_{0.3}$Cd$_{0.7}$S, the semicircle in the Nyquist plot of ReS$_2$/Zn$_{0.3}$Cd$_{0.7}$S has a smaller radius, it is indicative of an accelerated charge transport and improved charge separation during photocatalysis, which demonstrates the prominent role of ReS$_2$ nanoparticles as co-catalysts (Fig. 2d). Photoluminescence (PL) spectra (Fig. 2e) and time-resolved PL spectra (Fig. 2f) show that after the load of ReS$_2$ on Zn$_{0.3}$Cd$_{0.7}$S, more photocarriers can be produced, and the lifetimes are 0.361 ns (Zn$_{0.3}$Cd$_{0.7}$S) and 0.308 ns (ReS$_2$/Zn$_{0.3}$Cd$_{0.7}$S), indicating that the photogenerated carriers of ReS$_2$/Zn$_{0.3}$Cd$_{0.7}$S are more rapidly separated, and thus, hydrogen can be produced by driving a redox reaction.
Due to the unique characteristics of ReS$_2$ in promoting light absorption and charge separation, we studied the role of ReS$_2$ as a catalyst loaded on Zn$_x$Cd$_{1-x}$S in photocatalytic hydrogen production. Figure 3a shows the production of hydrogen for photocatalysts of solid-solubles with different Zn-Cd ratios in the condition of visible light irradiation and Na$_2$S-Na$_2$SO$_3$ as the expense of reagents. With the ratio of Zn and Cd in Zn$_x$Cd$_{1-x}$S being changed, the test results for comparing photocatalytic hydrogen production are shown in Figure 3a, and the optimal ratio product of Zn and Cd is Zn$_{0.3}$Cd$_{0.7}$S (0.91mmol g$^{-1}$ h$^{-1}$). By adjusting the amount of the load of ReS$_2$ (Figure 3b), it can be found that the load of 4 wt% ReS$_2$ on Zn$_{0.3}$Cd$_{0.7}$S has the highest hydrogen production (92.45mmol g$^{-1}$ h$^{-1}$), which is 101 times higher than
the pure Zn\textsubscript{0.3}Cd\textsubscript{0.7}S. It shows that the ReS\textsubscript{2} can greatly improve the photocatalytic hydrogen production of Zn\textsubscript{0.3}Cd\textsubscript{0.7}S. To understand the details of enhanced photocatalytic hydrogen evolution, the apparent quantum efficiency (AQY) of ReS\textsubscript{2} (4 wt%)/Zn\textsubscript{0.3}Cd\textsubscript{0.7}S was calculated at different irradiated wavelengths, as shown in Figure 3b. At wavelengths of 400, 420, and 500 nm, ReS\textsubscript{2} (4 wt%)/Zn\textsubscript{0.3}Cd\textsubscript{0.7}S AQY is 23.24%, 20.95% and 0.88%. The above results show that ReS\textsubscript{2} is a very promising candidate as a common catalyst for hydrogen evolution. To determine the photocorrosion properties of the CdS, we performed 30 hours of circulatory test of Zn\textsubscript{0.3}Cd\textsubscript{0.7}S and ReS\textsubscript{2}/Zn\textsubscript{0.3}Cd\textsubscript{0.7}S, as shown in Figures 3c and 3d. Every five hours is a group. The result shows that ReS\textsubscript{2}/Zn\textsubscript{0.3}Cd\textsubscript{0.7}S maintains high photocatalytic hydrogen production performance after 30 hours of light irradiation, with no significant reduction of the yield. The above results confirm that ReS\textsubscript{2}/Zn\textsubscript{0.3}Cd\textsubscript{0.7}S is a promising photocatalytic material with high photocatalytic activity and high cycle stability.

Fig. 4. In situ FT-IR spectra and On-line mass spectrometry of photocatalytic hydrogen production on ReS\textsubscript{2}/Zn\textsubscript{0.3}Cd\textsubscript{0.7}S: (a) H\textsubscript{2}O solution of Na\textsubscript{2}S-Na\textsubscript{2}SO\textsubscript{3}; (b) D\textsubscript{2}O
solution of Na$_2$S-Na$_2$SO$_3$; (c) In situ FT-IR spectra of the H$_2$O reaction on ReS$_2$/Na$_2$S-Na$_2$SO$_3$ with Na$_2$S-Na$_2$SO$_3$ as sacrificial reagent.

In the field of photocatalytic hydrogen production, sacrifice reagents are often used to improve the hydrogen production activity, but there may be hydrogen sources in these reagents. To determine that water is indeed decomposed to hydrogen, isotope experiments were performed. When Na$_2$S-Na$_2$SO$_3$ was used as sacrificial reagent in H$_2$O solution, only H$_2$ was found and neither HD nor D$_2$ was detected (Fig. 4a). In D$_2$O solution, only D$_2$ and no H$_2$ or HD was detected (Fig. 4b). In addition, H$_2$ and D$_2$ were produced after light irradiation, and no signals of H$_2$ and D$_2$ were found in dark conditions, indicating that the hydrogen-producing reaction is performed under light-excited conditions and that the materials cannot produce hydrogen by themselves.

Fig. 4c shows the in situ FT-IR spectra of the H$_2$O reaction on ReS$_2$/Zn$_{0.3}$Cd$_{0.7}$S when Na$_2$S-Na$_2$SO$_3$ was used as sacrificial reagent. The spectrum shows the peak at 3407 cm$^{-1}$ can be attributed to the stretching vibration of adsorbed H$_2$O molecules. The two peaks at 1631 and 1340 cm$^{-1}$ can be assigned to the stretching vibration of adsorbed SO$_3^{2-}$. And the peak at 1243 cm$^{-1}$ can be assigned to the stretching vibration of SO$_4^{2-}$. After illumination for 60 min, IR peaks of H$_2$O and SO$_3^{2-}$ decreased with no obvious position change, while IR peaks of SO$_4^{2-}$ increased with the time of light illumination increasing. This result indicates that H$_2$O decomposition occurs during the photocatalytic hydrogen evolution, meanwhile, the SO$_3^{2-}$ as sacrificial reagent can be oxidized to SO$_4^{2-}$. The above results are also confirmed by the same online mass spectrometry explanation.

4. Conclusions

In summary, we successfully developed ReS$_2$ as a highly efficient cocatalyst on Zn$_{0.3}$Cd$_{0.7}$S nanorods for extraordinarily efficient photocatalytic hydrogen evolution. The optimal photocatalytic hydrogen evolution rate of ReS$_2$/Zn$_{0.3}$Cd$_{0.7}$S is 92.45 mmol h$^{-1}$ g$^{-1}$, and the best quantum efficiency is of 23.24% at 400 nm. What’s more,
there was no significant decrease in photocatalytic activity after the cycle of 30-hour photocatalytic reaction. Excellent catalytic activity is due to the interaction between Zn$_{0.3}$Cd$_{0.7}$S and ReS$_2$ that inhibits the compound of photogenic runners, when the Zn elements are addition to the CdS, the photo-corrosive effect can be inhibited and they may synergie with the surface ReS$_2$ to give it better photocatalytic properties. In addition, photocatalytic hydrogen evolution over ReS$_2$/Zn$_{0.3}$Cd$_{0.7}$S has been comprehensively elucidated at the molecular level using on-line mass spectrometry, and in situ FT-IR. It is anticipated that this work will promote the development of hydrogen production systems with advanced co-catalyst and provide extremely high photocatalytic activities.

Acknowledgments

This work was supported by the National Natural Science Foundation of China (No. 51872147), the 111 Project (D20015), the Program for Innovative Research Team of Science and Technology in the University of Henan Province (19IRTSTHN025).

References

[1] H. Kisch, Semiconductor Photocatalysis—Mechanistic and Synthetic Aspects, Angew. Chem. Int. Ed. 2013, 52, 812–847.

[2] J. Li, X. Gao, B. Liu, Q. Feng, X.B. Li, M.Y. Huang, Z. Liu, J. Zhang, C.H. Tung, L.Z. Wu, Graphdiyne: A Metal-Free Material as Hole Transfer Layer To Fabricate Quantum Dot-Sensitized Photocathodes for Hydrogen Production, J. Am. Chem. Soc. 2016, 138, 3954–3957.

[3] K. Honda and A. Fujishima, Electrochemical Photolysis of Water at a Semiconductor Electrode, Nature, 1972, 238, 37-38.

[4] X. B. Chen, S. H. Shen, L. J. Guo and S. S. Mao, Semiconductor-based photocatalytic hydrogen generation, Chem. Rev., 2010, 110, 6503-6570.

[5] X. Wang, K. Maeda, A. Thomas, K. Takanabe, G. Xin, J.M. Carlsson, K. Domen, M.
Antonietti, A metal-free polymeric photocatalyst for hydrogen production from water under visible light, Nat. Mater. 2009, 8, 76–80.

[6] L. Cheng, Q. Xiang, Y. Liao, H. Zhang, CdS-based photocatalysts, Energy Environ. Sci. 2018, 11, 1362–1391.

[7] Y. J. Yuan, Z. T. Yu, D. Q. Chen, Z. G. Zou, Metal-complex chromophores for solar hydrogen generation, Chem. Soc. Rev. 2017, 46, 603–631.

[8] L. Jing, W. Zhou, G. Tian, H. Fu, Surface tuning for oxide-based nanomaterials as efficient photocatalysts, Chem. Soc. Rev. 2013, 42, 9509–9549.

[9] A. Nag, S. Sapra, C. Nagamani, A. Sharma, N. Pradhan, S.V. Bhat, D.D. Sarma, A Study of Mn$^{2+}$ Doping in CdS Nanocrystals, Chem. Mater. 2007, 19, 3252–3259.

[10] N. J. Borys, M. J. Walter, J. Huang, D. V. Talapin, J. M. Lupton, The role of particle morphology in interfacial energy transfer in CdSe/CdS heterostructure nanocrystals, Science. 2010, 330, 1371–1374.

[11] J. Yang, H. Yan, X. Wang, F. Wen, Z. Wang, D. Fan, J. Shi, C. Li, Roles of cocatalysts in Pt–PdS/CdS with exceptionally high quantum efficiency for photocatalytic hydrogen production, J. Catal. 2012, 290, 151–157.

[12] W. Zhang, R. Xu, Surface engineered active photocatalysts without noble metals: CuS–Zn$_x$Cd$_{1-x}$S nanospheres by one-step synthesis, Int. J. Hydrogen Energy. 2009, 34, 8495–8503.

[13] Xing C, Zhang Y, Yan W, Guo L., Nano-CdS confined within titanate nanotubes for efficient photocatalytic hydrogen production under visible light illumination, Nanotechnology. 2019, 25, 035603.

[14] Chan Chih-Chieh, Chung-Chieh Chang, Chia-HaoHsu, Yu-ChingWeng, Kew-Yu Chen, Hsiao-Han Lin, Wen-Chih Huang, Sheng-Fa Cheng, Efficient and stable photocatalytic hydrogen production from water splitting over Zn$_x$Cd$_{1-x}$S solid
solutions under visible light irradiation, International Journal of Hydrogen Energy, 2014, 39, 1630-1639.

[15] Y. Wang, J. Wu, J. Zheng, R. Jiang, R. Xu, Ni²⁺-doped ZnₓCd₁₋ₓS photocatalysts from single-source precursors for efficient solar hydrogen production under visible light irradiation, Catalysis Science & Technology 2011, 1, 940-947.

[16] J. D. Huang, J. Y. Liu, and K. L. Han., Hybrid functionals studies of structural and electronic properties of ZnₓCd₁₋ₓS and (ZnₓCd₁₋ₓ)(SeₓS₁₋ₓ) solid solution photocatalysts international journal of hydrogen energy, 2012, 37, 17870-17881.

[17] M. R. Gholipour, C. C. Nguyen, F. Béland, T.O. Do, Hollow microspheres consisting of uniform ZnₓCd₁₋ₓS nanoparticles with noble-metal-free co-catalysts for hydrogen evolution with high quantum efficiency under visible light, Journal of Photochemistry and Photobiology, A: Chemistry. 2018, 358, 1-9.

[18] X. Zong, H. Yan, G. Wu, G. Ma, F. Wen, L. Wang, C. Li, Enhancement of Photocatalytic H₂ Evolution on CdS by Loading MoS₂ as Cocatalyst under Visible Light Irradiation, J. Am. Chem. Soc. 2008, 130, 7176–7177.

[19] K. Chang, X. Hai, J. Ye, Transition Metal Disulfides as Noble-Metal-Alternative Co-Catalysts for Solar Hydrogen Production, Adv. Energy Mater. 2016, 6, 1502555.

[20] Q. Zhang, W. Wang, J. Zhang, X. Zhu, Q. Zhang, Z. Zhang Ren, S. Song, J. Wang, Z. Ying, R. Wang, X. Qiu, T. Peng, L. Fu, Highly Efficient Photocatalytic Hydrogen Evolution by ReS₂ via a Two-Electron Catalytic Reaction, Adv. Mater. 2018, 30, 1707123.

[21] Q. Zhang, W. Wang, J. Zhang, X. Zhu, L. Fu, Thermally Induced Bending of ReS₂ Nanowalls, Adv. Mater. 2018, 30, 1704585.
[22] H. Liu, B. Xu, J.M. Liu, J. Yin, F. Miao, C.G. Duan, X.G. Wan, Highly efficient and ultrastable visible-light photocatalytic water splitting over ReS$_2$, Phys. Chem. Chem. Phys. 2016, 18, 14222–14227.

[23] Q. Zhang, S. Tan, R.G. Mendes, Z. Sun, Y. Chen, X. Kong, Y. Xue, M.H. Rümmeli, X. Wu, S. Chen, L. Fu, Extremely Weak van der Waals Coupling in Vertical ReS$_2$ Nanowalls for High-Current-Density Lithium-Ion Batteries, Adv. Mater. 2016, 28, 2616–2623.

[24] M. Mao, C. Cui, M. Wu, M. Zhang, T. Gao, X. Fan, J. Chen, T. Wang, J. Ma, C. Wang, Flexible ReS$_2$ nanosheets/N-doped carbon nanofibers-based paper as a universal anode for alkali (Li, Na, K) ion battery, Nano Energy 2018, 45, 346–352.

[25] H. Li, Z. Liang, Q. Deng, M. T. Hu, N. Du, W. Hou, Facile Construction of Defect-rich Rhenium Disulfide/Graphite Carbon Nitride Heterojunction via Electrostatic Assembly for Fast Charge Separation and Photoactivity Enhancement, ChemCatChem 2019, 11, 1633-1642.

[26] H. M. Liu, B. Xu, J. M. Liu, J. Yin, F. Miao, C. G. Duan, X. G. Wan, Highly efficient and ultrastable visible-light photocatalytic water splitting over ReS$_2$, Physical Chemistry Chemical Physics 2016, 18, 14222-14227.

[27] J. A. Song, R. R. Sun, Y. L. Chen, D. J. Sun, X. Y. Li, L-Cysteine assisted synthesis of Zn$_{0.5}$Cd$_{0.5}$S solid solution with different morphology, crystal structure and performance for H$_2$ evolution, International Journal of Hydrogen Energy. 2018, 43, 18220-18231.

[28] Y. T. Lu, D. D. Wang, P. Yang, Y. K. Dua, C. Lu, 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, Catalysis Science & Technology. 2014, 4, 2650-2657.
[29] H. T. Zhao, R. R. Sun, X. Y. Li, X. Sun, Enhanced photocatalytic activity for hydrogen evolution from water by Zn$_{0.5}$Cd$_{0.5}$S/WS$_2$ heterostructure, Materials Science in Semiconductor Processing. 2017, 59, 68-75.

[30] J. A. Song, Y. L. Chen, D. J. Sun, X. Y. Li, Perylenetetracarboxylic diimide modified Zn$_{0.7}$Cd$_{0.3}$S hybrid photocatalyst for efficient hydrogen production from water under visible light irradiation, Inorganic Chemistry Communications. 2018, 92, 27-34.

[31] Q. Li, H. Meng, J. G. Yu, W. Xiao, Y. Q. Zheng, J. Wang, Enhanced Photocatalytic Hydrogen-Production Performance of Graphene–Zn$_x$Cd$_{1-x}$S Composites by Using an Organic S Source, Chemistry–A European Journal. 2014, 20, 1176-1185.

[32] Song J, Tian Q, Gao J, Wu H, Chen Y, Li X. Controlled preparation of CdS nanoparticle arrays in amphiphilic perylene tetracarboxylic diimides: organization, electrontransfer and semiconducting properties, Cryst. Eng. Comm 2014, 16, 1277-1286.

[33] Corbet C. M, McClellan C, Rai A, Sonde S. S, Tutuc E, Banerjee S. K, Field Effect Transistors with Current Saturation and Voltage Gain in Ultrathin ReS$_2$, ACS nano. 2015, 9, 363–370.

[34] F. Li, Q. Gu, Y. Niu, R. Wang, Y. Tong, S. Zhu, H. Zhang, Z. Zhang, X. Wang, Hydrogen evolution from aqueous-phase photocatalytic reforming of ethylene glycol over Pt/TiO$_2$ catalysts: role of Pt and product distribution, Appl. Sur. Sci. 2017, 391, 251–258.

[35] H. A. Al-Abadleh, V. H. Grassian, FT-IR study of water adsorption on aluminum oxide surfaces, Langmuir. 2003, 19, 341–347.

[36] E. Yoda, FT-IR Study of Dissociative Water Adsorption on 1-Butyl-3-methylimidazolium Exchanged Mordenite Zeolite, J. Phys. Chem. C. 2009, 113, 9851–9856.
[37] L. Li, R. Bennett, W. Conway, H. Yu, S. Clifford, M. Maeder, G. Puxty, Development and Evaluation of a Novel Method for Determining Absorbent Composition in Aqueous Ammonia-Based CO$_2$ and SO$_3^{2-}$ and SO$_4^{2-}$ Loaded Capture Process Solutions via FT-IR Spectroscopy, Energy Fuels. 2018, 32, 8563–8570.
High-efficiency and Stable Photocatalytic Hydrogen Evolution of Rhenium Sulfide Co-catalyst on Zn$_{0.3}$Cd$_{0.7}$S.