One-step synthesis of highly efficient three-dimensional Cd$_{1-x}$Zn$_x$S photocatalysts for visible light photocatalytic water splitting

Zuzhou Xiong$^1$, Maojun Zheng$^{1*}$, Changqing Zhu$^1$, Bin Zhang$^1$, Li Ma$^2$ and Wenzhong Shen$^1$

Abstract

Visible light accounts for about 43% of the solar spectrum, and developing highly efficient visible-light-driven photocatalyst is of special significance. In this work, highly efficient three-dimensional (3D) Cd$_{1-x}$Zn$_x$S photocatalysts for hydrogen generation under the irradiation of visible light were synthesized via one-step solvothermal pathway. Scanning electron microscope, X-ray diffractometer, Raman spectrometer, and X-ray photoelectron spectrometer were utilized to characterize the morphology, crystal structure, vibrational states, and surface composition of the obtained 3D Cd$_{1-x}$Zn$_x$S. UV-Vis spectra indicated that the as-synthesized Cd$_{1-x}$Zn$_x$S had appropriate bandgap and position of the conduction band that is beneficial for visible light absorption and photo-generated electron-hole pair separation. Moreover, the 3D structure offers a larger surface area thus supplying more surface reaction sites and better charge transport environment, and therefore, the efficiency of water splitting was improved further.

Keywords: Visible light photocatalytic; Water splitting; Cd$_{1-x}$Zn$_x$S; Solvothermal pathway; Solid solutions

Background

The efficient conversion of solar energy into fuel via photochemical reactions is of great importance for the next-generation energy source for its cleanable, renewable, and abundant properties [1,2]. Solar-hydrogen, the conversion of solar energy into hydrogen as chemical energy carrier, has been regarded as one of the most desirable ways in considering energy consumption, resource sustainability, and environmental issues [3,4].

Since the pioneering work of Fujishima and Honda in 1972 [5], tremendous research on semiconductor-based photocatalysis and photoelectrolysis has yielded a better understanding of the mechanisms involved in photocatalytic and photoelectrochemical water splitting [6-9]. However, most of semiconductor photocatalysts can only absorb ultraviolet light due to their wide gap. As it is well known, ultraviolet light occupies only 3% ~ 5% of the solar spectrum; so, the energy conversion efficiency of visible-light-responsive photocatalysts to make the best use of solar energy in visible light region, which accounts for about 43% of the solar spectrum, is particularly important [13,14]. In the past, developing and understanding of semiconductor electrodes or photocatalysts for photoelectrochemical or photocatalytic water splitting were mainly performed on simple binary systems (e.g., binary oxides [15,16] and chalcogenides [17,18]) and their composite structure [19]. Recently, the ternary system as potentially excellent photoelectrode or photocatalyst material has attracted more and more attention [20-22] because ternary system can offer more possibilities for bandgap and band position tuning.

Cadmium sulfide is an important visible-light response photocatalytic material, in which sulfide ions serve as electron donors. However, the sulfide ion is readily oxidized to sulfate by the photo-generated holes, with Cd$^{2+}$ ions escaping into the solution. A feasible way for enhancing the photocatalytic activity and stability of cadmium sulfide is to develop CdS-based composite materials. Zinc sulfide has the similar crystal structure as cadmium sulfide. It is a good host material for the development of a visible-light-driven photocatalyst without...
adding noble metals by forming Cd$_{1-x}$Zn$_x$S solid solutions with a narrow bandgap semiconductor, CdS [22,23]. The bandgap of the solid solutions formed between ZnS and CdS can be regulated by changing the compositions and therefore the photocatalytic properties can be varied [24,25].

In this article, we reported a highly efficient three-dimensional (3D) visible-light-active Cd$_{1-x}$Zn$_x$S photocatalysts synthesized via one-step solvothermal pathway. The obtained photocatalysts had good crystallinity and ordered structure and showed excellent photocatalytic activity under the irradiation of visible light.

Methods
Synthesis of photocatalyst
Three-dimensional Cd$_{1-x}$Zn$_x$S nanowires were synthesized in a Teflon-lined stainless steel cylindrical closed chamber with a 100-mL capacity. All the chemicals were of analytical grade. Ethylenediamine (en; 60 ml) and H$_2$O (20 ml) were used as solvent. Thiourea [NH$_2$CSNH$_2$] (15 mmol) was added into the

![Figure 1 Typical SEM images of the obtained Cd$_{1-x}$Zn$_x$S photocatalysts. (a) Cd$_{0.98}$S, (b) Cd$_{0.9}$Zn$_{0.1}$S, (c) Cd$_{0.72}$Zn$_{0.26}$S, and (d) Cd$_{0.24}$Zn$_{0.75}$S.](image1)

![Figure 2 XRD patterns of the as-prepared Cd$_{1-x}$Zn$_x$S photocatalysts with different x values. (curve a) Cd$_{0.98}$S, (curve b) Cd$_{0.9}$Zn$_{0.1}$S, (curve c) Cd$_{0.72}$Zn$_{0.26}$S, (curve d) Cd$_{0.24}$Zn$_{0.75}$S, and (curve e) Zn$_{0.96}$S.](image2)
solvent as sulfur source, then 5-mmol mixture of cadmium acetate $[(\text{CH}_3\text{COO})_2\text{Cd} \cdot 2\text{H}_2\text{O}]$ and zinc acetate $[(\text{CH}_3\text{COO})_2\text{Zn} \cdot 2\text{H}_2\text{O}]$ was added into the mixed solution. After stirring for a few minutes, the closed chamber was placed inside a preheated oven at 160°C for 10 h and then cooled to room temperature. The obtained precipitates were filtered off and washed several times with water and ethanol, respectively. The final products were dried in vacuum at 45°C for a few hours.

**Characterization**

The morphology of the as-synthesized powder products were observed by field-emission scanning electron microscopy (Philips Sirion 200, Philips, Netherlands). The crystallographic structure was determined by X-ray diffraction (XRD, D8 DISCOVER X-ray diffractometer, Bruker, Karlsruhe, Germany) with Cu Kα radiation (1.54 Å). Surface composition of the sample was analyzed by X-ray photoelectron spectroscopy (XPS, AXIS ULTRA DLD, Kratos, Japan). The Raman spectrum was measured by the Jobin Yvon LabRam HR 800 UV system (Horiba, Kyoto, Japan) at room temperature. A laser wavelength of 514.5 nm was used as the excitation sources. Reflectance spectra of the obtained were collected using a UV/vis spectrometer (Lambda 20, Perkin Elmer, Inc., USA).

**Photocatalytic hydrogen evolution**

The photocatalytic performance of the synthesized 3D Cd$_{1-x}$Zn$_x$S photocatalysts were investigated in a gas-closed circulation system (Labsolar-III, Beijing Percablght Technology Co. Ltd., Beijing, China) with a top-window

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**Figure 3** Representative XPS spectra of typical sample Cd$_{0.72}$Zn$_{0.26}$S. (a) survey spectrum, (b) Cd 3d XPS spectrum, (c) Zn 2p XPS spectrum, and (d) S 2p XPS spectrum.

**Figure 4** Raman spectrum of the typical sample Cd$_{0.72}$Zn$_{0.26}$S.
Pyrex cell. A 300-W Xe lamp (SOLAREDGE700, Beijing Perfactlight Technology Co. Ltd., Beijing, China) was used as the light source, and UV light was removed by a cut-off filter ($\lambda > 420$ nm). Luminous power of the light source is about 40 W. The amount of H$_2$ evolved was analyzed by an online gas chromatography (GC7900, Techcomp Ltd., Beijing, China) equipped with a thermal conductivity detector, MS-5A column, and N$_2$ was used as carrier. In all experiments, 100 mL deionized water containing the mixed sacrificial agent which composed of 0.25 M Na$_2$SO$_3$ and 0.35 M Na$_2$S were added into the reaction cell. Then, these photocatalysts were directly placed into the electrolyte solution. The whole system was vacuumized with a vacuum pump before reaction to remove the dissolved air. The temperature for all photocatalytic reactions was kept at about 20°C.

Results and discussions

The surface morphologies of the obtained Cd$_{1-x}$Zn$_x$S are shown in Figure 1. Figure 1a is the scanning electron microscopy (SEM) image of CdS; it presents porous flower-like 3D structure clearly, shorter nanowires appear at the periphery. As the value of $x$ increases, nanosheet emerges gradually, that is, the secondary structure builds up slowly. Figure 2 shows the XRD patterns of the as-prepared photocatalysts. CdS exhibits a Greenockite structure, while ZnS presents a Wurtzite polycrystalline structure, respectively. The diffraction peaks of the photocatalysts shift to a higher angle side as the value of $x$ increases. The successive shift of the XRD patterns means that the crystals obtained are Cd$_{1-x}$Zn$_x$S solid solution, not a simple mixture of ZnS and CdS [26].

The surface information is collected by XPS of the sample Cd$_{0.72}$Zn$_{0.26}$S (Figure 3). The survey scan spectrum (Figure 3a) indicates the existence of Cd, Zn, and S in the Cd$_{0.72}$Zn$_{0.26}$S sample. The two sharp peaks (Figure 3b) located at 404.3 and 411.2 eV are corresponding to the Cd 3d$_{5/2}$ and Cd 3d$_{3/2}$ level, respectively. The peaks of 1,020.8 and 1,043.7 eV can be assigned to the Zn 2p$_{3/2}$ and 2p$_{1/2}$ levels, respectively (Figure 3c). The single S 2p peak at 161.1 eV (Figure 3d) demonstrates that sulfur exists as a sulfur ion.

Raman scattering is a nondestructive technique for structural study of the material and a powerful probe to obtain the vibrational states of a solid. It is an inelastic process in which incoming photons exchange energy with the crystal vibrational mode. Figure 4 reveals the Raman spectrum of the as-obtained Cd$_{0.72}$Zn$_{0.26}$S sample. Bulk CdS has two characteristics of longitudinal-optical (LO) phonon peaks: (1) 1-LO (first harmonic (at 300/cm)) and (2) 2-LO (second harmonic (at 600/cm)) vibrations [27]. The two phonon peaks are also observed in the as-obtained Cd$_{0.72}$Zn$_{0.26}$S; they are located at 306.5 and 608.1/cm, respectively, and shift toward the higher energy side compared with that of the pure CdS. This can be ascribed to the Cd $\rightarrow$ Zn substitution in the obtained nanophotocatalysts. In addition, from Figure 4,
the Raman intensities of 1-LO and 2-LO are both relatively strong and narrow, which implies its good crystallinity and ordered structure [28].

Curves a, b, c, d, and e of Figure 5 show the UV-vis absorption spectra of the as-prepared Cd$_{0.98}$S, Cd$_{0.9}$Zn$_{0.1}$S, Cd$_{0.72}$Zn$_{0.28}$S, Cd$_{0.24}$Zn$_{0.76}$S, and Zn$_{0.98}$S, respectively. The absorption edge of Cd$_{1-x}$Zn$_x$S solid solutions are red-shifted relative to ZnS (Figure 5a), which can be attributed to the incorporation of Zn into the lattice of CdS or entered its interstitial sites (the radii of Zn$^{2+}$ ion (0.74 Å) is smaller than that of Cd$^{2+}$ (0.97 Å)). The bandgap of Cd$_{1-x}$Zn$_x$S can be acquired from plots of $(aE_{\text{photon}})^2$ versus the energy $(E_{\text{photon}})$ of absorbed light (α and $E_{\text{photon}}$ are the absorption coefficient and the discrete photon energy, respectively). The extrapolated value (a straight line to the x-axis) of $E_{\text{photon}}$ at α = 0 gives absorption edge energies corresponding to $E_p$. From Figure 5b, the bandgap of the synthesized Cd$_{1-x}$Zn$_x$S are 2.37 eV (curve a), 2.48 eV (curve b), 2.60 eV (curve c), 2.86 eV (curve d), and 3.67 eV (curve e), respectively. The bandgaps of Cd$_{1-x}$Zn$_x$S are beneficial to absorbing solar light to drive the water splitting reaction.

The photocatalytic hydrogen evolution of the obtained 3D Cd$_{1-x}$Zn$_x$S photocatalysts under the irradiation of visible light is given in Figure 6. All of the Cd$_{1-x}$Zn$_x$S photocatalysts show much higher photocatalytic H$_2$ evolution capacity than that of the sole CdS at visible light irradiation ($\lambda > 420$ nm). In addition, the photocatalytic activity of the Cd$_{1-x}$Zn$_x$S solid solutions is strongly dependent on the composition of the solid solutions. It is improved obviously with the increase of Zn content (x value). When the x value increases to 0.75, the 3D solid solutions photocatalyst has the highest photocatalytic activity. This is because ZnS has a high energy conversion efficiency, it is a good host material for the development of a visible-light-driven photocatalyst by forming solid solutions with a narrow bandgap semiconductor, CdS. The more negative reduction potential of the conduction band of solid solutions would allow for more efficient hydrogen generation than CdS. In addition, the large bandgap and wide valence bandwidth benefit the separation of the photo-generated electrons and holes, and the photocorrosion of the photocatalysts can be reduced effectively. The highest activity probably means that Cd$_{0.24}$Zn$_{0.75}$S has an optimum bandgap and a moderate position of the conduction band, beneficial for visible light absorption and photo-generated electron-hole pair separation. Moreover, the 3D structure offers a larger surface area, thus supplying more surface reaction sites and better charge transport environment. Therefore, the efficiency of water splitting is improved further. It is worth noting that no H$_2$ was detected for ZnS photocatalyst because its bandgap is too large to absorb the visible light.

**Conclusions**

We reported highly efficient three-dimensional Cd$_{1-x}$Zn$_x$S photocatalysts synthesized via one-step solvothermal pathway for photocatalytic H$_2$ evolution under the irradiation of visible light. The Raman spectrum implied the obtained Cd$_{1-x}$Zn$_x$S had good crystallinity and ordered structure. The XPS demonstrated that sulfur existed as a sulfur ion, while Cd and Zn are in 3d and 2p state, respectively. The bandgap of the synthesized Cd$_{1-x}$Zn$_x$S varied from 2.37 to 2.86 eV, which were suitable for the absorption of visible light. The photocatalytic activity of the obtained Cd$_{1-x}$Zn$_x$S photocatalysts were improved markedly compared with that of the sole CdS. This can be attributed to their appropriate bandgap and position of the conduction band that is beneficial for visible light absorption and photo-generated electron-hole pair separation, as well as 3D structure that offered a larger surface area, thus supplying more surface reaction sites and better charge transport environment.

**Abbreviations**

3D: Three-dimensional; XRD: X-ray diffraction; XPS: X-ray photoelectron spectrometer.

**Competing interests**

The authors declare that they have no competing interests.

**Authors’ contributions**

ZZX participated in the design of the study, carried out the experiments, and performed the statistical analysis, as well as drafted the manuscript. MIZ participated in the design of the study, provided the theoretical and experimental guidance, performed the statistical analysis, and revised the manuscript. CQZ and BZ helped in the experiments and data analysis. LM participated in the design of the experimental section and offered help in the experiments. WZS gave his help in using the experimental apparatus. All authors read and approved the final manuscript.

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**Author details**

1. Key Laboratory of Artificial Structures and Quantum Control (Ministry of Education), Department of Physics and Astronomy, Shanghai Jiao Tong University, Shanghai 200240, People’s Republic of China.
2. School of Chemistry and Chemical Technology, Shanghai Jiao Tong University, Shanghai 200240, People’s Republic of China.

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**References**

1. Haban G, Valdes-Solis T: Towards the hydrogen economy? Int J Hydrogen Energy 2007, 12:1625–1637.
2. Winter CJ: Hydrogen-energy-abundant, efficient, clean: a debate over the energy-system-of change. Int J Hydrogen Energy 2009, 34:51–552.
3. Lewis NS: Toward cost-effective solar energy issue. Science 2007, 315:798–801.
4. Andrews J, Shabani B: Re-envisioning the role of hydrogen in a sustainable energy economy. Int J Hydrogen Energy 2012, 37:1194–1203.
5. Fujishima A, Honda K: Electrochemical photolysis of water at a semiconductor electrode. Nature 1972, 238:37–38.
6. Bolton JR, Strickler SJ, Connolly JS: Limiting and realizable efficiencies of solar photolysis of water. Nature 1985, 316:495–500.
7. Rajeshwar K: Hydrogen generation at irradiated oxide semiconductor-solution interfaces. J Appl Electrochem 2007, 37:65–787.
8. Ohtani B: Photocatalysis A to Z-what we know and what we do not know in a scientific sense. J Photochem. and Photobiol. C: Photochem Rev 2010, 11:157–178.

9. Foley JM, Price MJ, Feldblum JJ, Maldonado S: Analysis of operation of thin nanowire photoelectrodes for solar energy conversion. Energy Environ Sci. 2012, 5:5203–5220.

10. Kim HG, Hwang DW, Kim J, Kim YG, Lee JS: Highly donor-doped (110) layered perovskite materials as novel photocatalysts for overall water splitting. Chem Commun 1999:1077–1078. doi:10.1039/A902892G.

11. Kim HG, Hwang DW, Bae SW, Jung JH, Lee JS: Photocatalytic water splitting over La0.9Ti0.1O2 synthesized by the polymerizable complex method. Catal Lett 2003, 91:193–198.

12. Kato H, Asakura K, Kudo A: Highly efficient water splitting into H2 and O2 over lanthanum-doped NaTaO3 photocatalysts with high crystallinity and surface nanostructure. J Am Chem Soc 2003, 125:3082–3089.

13. Silva LA, Ryu SY, Choi J, Choi W, Hoffmann MR: Photocatalytic H2 evolution under visible light over Pt-interlinked hybrid composites of cubic-phase and hexagonal-phase CdS. J Phys Chem C 2008, 112:12069–12073.

14. Kudo A: Development of photocatalyst materials for water splitting. Int. J Hydrogen Energy 2006, 31:197–202.

15. Chen X, Shen S, Guo L, Mao S: Semiconductor-based photocatalytic hydrogen generation. Chem Rev 2010, 110:6503–6570.

16. Masaaki K, Michikazu H: Heterogeneous photocatalytic cleavage of water. J Mater Chem 2010, 20:627–641.

17. Lan X, Jiang Y, Su H, Li S, Wu D, Liu X, Han T, Han L, Qin K, Zhang H, Meng X: Magnificent CdS three-dimensional nanostructure arrays: the synthesis of a novel nanostructure family for nanotechnology. Cryst Eng Comm 2011, 13:145–152.

18. Zong X, Yan H, Wu G, Ma G, Wen F, Wang L, Li C: 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. Li YX, Chen G, Zhou C, Sun JX: A simple template-free synthesis of nanoporous ZnS-In2S3-Ag2S solid solutions for highly efficient photocatalytic H2 evolution under visible light. Chem Commun 2009, 2020–2022. doi:10.1039/B819300B.

20. Osterloh FE, Parkinson BA: Recent developments in solar water-splitting photocatalysis. NRS Bull 2011, 36:17–22.

21. Berglund SP, Flaherty DW, Hahn NT, Bard AJ, Mullins CB: Photoelectrochemical oxidation of water using nanostructured BiVO4 films. J Phys Chem C 2011, 115:3794–3802.

22. Xing C, Zhang Y, Yan W, Guo L: Band structure-controlled solid solution of Cd1-xZnxS photocatalyst for hydrogen production by water splitting. Int. J Hydrogen Energy 2006, 31:2018–2024.

23. Zhang W, Xu R: Surface engineered active photocatalysts without noble metals: CuS–ZnS, CdS–S nanophases by one-step synthesis. Int. J Hydrogen Energy 2009, 34:8495–8503.

24. Wang L, Wang W, Shang M, Yin W, Sun S, Zhang L: Enhanced photocatalytic hydrogen evolution under visible light over Cd1-xZnxS solid solution with cubic zinc blend phase. Int. J Hydrogen Energy 2010, 35:19–25.

25. Wang DH, Wang L, Xu AW: Room-temperature synthesis of Zn2(1−x)S nanosolids with a high visible-light photocatalytic activity for hydrogen evolution. Nanoscale 2012, 4:2046–2053.

26. Tsuji I, Kato H, Kobayashi H, Kudo A: Photocatalytic H2 evolution reaction from aqueous solutions over band structure-controlled (AgIn)2Zn4S9 solid solution photocatalysts with visible-light response and their surface nanostructures. J Am Chem Soc 2004, 126:13406–13413.

27. Zeiri L, Patia I, Acharya S, Golan Y, Efrima S: Raman spectroscopy of ultranarrow CdS nanostructures. J Phys Chem C 2007, 111:1843.

28. Zhang YC, Chen W, Hu XY: Controllable synthesis and optical properties of Zn-doped CdS nanorods from single-source molecular precursors. Crystal Growth & Des 2007, 7:581–586.