Supporting Information

Twins in Cd$_{1-x}$Zn$_x$S Solid Solution: Highly Efficient Photocatalyst for Hydrogen Generation from Water

Maochang Liu$^1$, Lianzhou Wang$^2$, Gaoqing (Max) Lu$^2$, Xiangdong Yao$^{2,3,*}$, Liejin Guo$^{1,*}$

$^1$ State Key Laboratory of Multiphase Flow in Power Engineering, Xi’an Jiaotong University, Xi’an 710049, China. $^2$ ARC Centre of Excellence for Functional Materials, The University of Queensland, St Lucia, QLD 4072, Australia. $^3$ Queensland Micro- and Nanotechnology Centre, Griffith University, Nathan Campus, Nathan, QLD 4111, Australia.

*Email: li-guo@mail.xjtu.edu.cn (L. Guo); x.yao@griffith.edu.au (X. Yao)

Estimation of depletion layer width of twin boundary in Cd$_{0.5}$Zn$_{0.5}$S-PH photocatalysts

Scheme S1. Twin boundary potential and depletion layer in photocatalysts.

\[
\begin{align*}
\frac{d^2V}{dx^2} &= -\frac{N_a e}{\varepsilon \varepsilon_0} \\
\omega &= \sqrt{\frac{2\varepsilon \varepsilon_0 V_B}{e N_a}}
\end{align*}
\]

for $0 \leq x \leq \omega$
The estimation the depletion layer width (2ω) is based on solving One Dimensional Poisson Equation (formulation (3)), where ε is the dielectric constant of the semiconductor and ε₀ is the permittivity of free space. N_d is the excess charge density at the depletion layer in the crystal. V_B is the potential at the boundary (x = 0), and at the edge of the depletion layer (x = w), the potential V = 0. Formulation (4) is the result [1]. The distribution of the boundary potential is schematically shown in Scheme S1.

Considering the crystal size of Cd_{0.5}Zn_{0.5}S-PH photocatalysts (assumed the volume of crystal of 100 nm × 100 nm × 100 nm), the average number of twin boundary in this crystal (about 10 ~ 20, here denoted as 10), and the captured charge density in (111) twin boundary (in the order of magnitude of 10^{15} m^{-2}) [2], we estimated the N_d ≈ 10^{23} m^{-3}. With V_B ≈ 0.05 V for (111) twin boundary determined by other researchers [2, 3], ε ≈ 8.6 (ε (CdS) = 8.9, ε (ZnS) = 8.3), ε₀ = 8.85 × 10^{-12} F m^{-1}, e = 1.6 × 10^{-19} C, we obtain ω ≈ 22 nm. Therefore, the half width of depletion layer is a little larger than the distance of the coherent twin boundaries, resulting in the complete separation of photogenerated electrons and holes.
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a) Absorption spectra of different compositions of\( \text{Cd}_x\text{Zn}_{1-x}\text{S} \) with varying x values.

b) Powder X-ray diffraction patterns of \( \text{Cd}_x\text{Zn}_{1-x}\text{S} \) for different x values.

c) Bar chart showing the average rate of \( \text{H}_2 \) evolution for different \( \text{Cd}_x\text{Zn}_{1-x}\text{S} \) compositions.

d) Plot showing the amount of \( \text{H}_2 \) evolution over time for different \( \text{Cd}_x\text{Zn}_{1-x}\text{S} \) compositions.
Figure S1 Characterizations of Cd\(_{1-x}\)Zn\(_x\)S-PH solid solutions. a, UV-Vis absorption spectra Cd\(_{1-x}\)Zn\(_x\)S-PH solid solutions which indicated the formation of the solid solutions of CdS and ZnS. b, XRD patterns of Cd\(_{1-x}\)Zn\(_x\)S-PH solid solution shows a transformed from hexagonal CdS to cubic ZnS. c, the rate of H\(_2\) evolution over Cd\(_{1-x}\)Zn\(_x\)S solid solution \(^{[6]}\), showing that Cd\(_{0.5}\)Zn\(_{0.5}\)S-PH has the highest photocatalytic activity, which is a result of the balance of light absorption and high conduction band level. d and e, Time course Photocatalytic hydrogen production from an aqueous Na\(_2\)S (0.35 M) and Na\(_2\)SO\(_3\) (0.25 M) solution under visible light from a PLS-SXE300/300UV Xe lamp with a 430 nm cutoff filter over Cd\(_{1-x}\)Zn\(_x\)S solid solutions prepared by precipitation-hydrothermal method. 5 hours tests to get a primary photocatalytic activity of these solid solutions. More than 20 hours test over Cd\(_{0.5}\)Zn\(_{0.5}\)S-PH photocatalyst to investigate its photocatalytic stability. As shown here, the photocatalyst is still active enough for hydrogen production over 20 hours. We choose to add the Na\(_2\)S sacrificial electron donors every 7 hours due to the great consumption of sacrificial reagents. The amount of Na\(_2\)S added to the initially reacting solution was equal to the molar amount of H\(_2\) evolution according to the photochemical reaction equations which were firstly and systematically investigated by Reber \(^{[4, 5, 6]}\). f, TEM images of Cd\(_{1-x}\)Zn\(_x\)S-PH solid solution show the nano-twin-modified Cd\(_{1-x}\)Zn\(_x\)S solid solution. As we discussed in the article, coherent twin boundaries greatly decrease the recombination probability of free carries inside the crystal, however, the separation of them on the surface is still due the high conduction band levels (without loading noble metal), which provide free election with more activity. Thus, the photocatalytic activity of CdS-PH and Cd\(_{0.5}\)Zn\(_{0.5}\)S-PH is not very high. The absorption of photons from visible light is another important factor. Therefore, the photocatalytic activity of Cd\(_{0.5}\)Zn\(_{0.5}\)S-PH, Cd\(_{0.1}\)Zn\(_{0.9}\)S-PH and ZnS is not high, too. The detailed discussion was given by Domen \(^{[7]}\). g, elemental mapping of C, S, Zn and Cd for (Cd\(_{0.5}\)Zn\(_{0.5}\)S-PH) by the energy-dispersive X-ray spectrometer (EDX) reveals that the distribution of all the ions is homogeneous. h and i, XRD patterns of Cd\(_{1-x}\)Zn\(_x\)S-PH solid solution before and after photocatalytic reaction, and HRTEM of Cd\(_{1-x}\)Zn\(_x\)S-PH after a 20 h photocatalytic reaction, confirms the structural stability of the nano twins. 

\(^{[a]}\) Catalyst: 0.1 g, 180 mL aqueous solution containing 0.35 M Na\(_2\)S and 0.25M Na\(_2\)SO\(_3\), side irradiation Pyrex cell, PLS-SXE300 /300UV Xe lamp.
Figure S2. Photocatalytic hydrogen production from an aqueous Na$_2$S (0.35 M) and Na$_2$SO$_3$ (0.25 M) solution under visible light from a PLS-SXE300/300UV Xe lamp with a 430 nm over Cd$_{0.5}$Zn$_{0.5}$S photocatalysts prepared by various methods.
Figure S3 Characterizations of variouse Cd$_{0.5}$Zn$_{0.5}$S photocatalysts. a, the XRD patterns of the various Cd$_{0.5}$Zn$_{0.5}$S photocatalysts shows both hexagonal phase and cubic phase can be obtained by different preparing methods, and also indicate that crystal phase was not the key factor for the extremely high photocatalytic activity of Cd$_{0.5}$Zn$_{0.5}$S-PH. b, SEM images with the BET specific surface areas inset. The crystals are all in nano sizes, but none of them were perfect, even some of them have a good crystallinity. As can be concluded from the pictures, the surface area was not an important factor for water splitting on the present photocatalytic system as usual.
a) The special nano-strips are only found in the Cd$_{0.5}$Zn$_{0.5}$S-PH photocatalysts. But not all of the crystals (denoted as non-twin crystals) in Cd$_{0.5}$Zn$_{0.5}$S-PH have this special nano-structure. These nano-strips are proved to be coherent twin boundaries.

b) HRTEM of Cd$_{0.5}$Zn$_{0.5}$S-PH over non-twin crystal

Figure S4 TEM images of the various Cd$_{0.5}$Zn$_{0.5}$S photocatalysts. a, the special nano-strips are only found in the Cd$_{0.5}$Zn$_{0.5}$S-PH photocatalysts. But not all of the crystals (denoted as non-twin crystals) in Cd$_{0.5}$Zn$_{0.5}$S-PH have this special nano-structure. These nano-strips are proved to be coherent twin boundaries. b, HRTEM of Cd$_{0.5}$Zn$_{0.5}$S-PH over non-twin crystal.
Figure S5 TEM images of Ru (wt. 0.44% in bulk)/Cd$_{0.5}$Zn$_{0.5}$S-PH and EDX spectra of it at different crystals (twin and non-twin crystals). a, Ru content in a big area was determined to be wt. 0.46%, which was very close to the Ru content in bulk (wt. 0.44%) determined by X-ray fluorescence spectrum (XRF). b, Ru contents on non-twin crystals were determined to be about wt. 0.14% and 0.14%. c, Ru contents on twin crystals were determined to be about wt. 0.68% and 0.76%. It was considered that Ru would like to be photodeposited at place where more free electrons were generated. Thus, it was concluded that more free electrons were photogenerated from the twin crystals. The contents’ difference indicated that photocatalytic activity of twin crystal was about 5 times of that non-twin crystal.
References