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Supporting Information

In-situ synthesis of porous ZnO-embedded $Zn_{1-x}Cd_xS$/CdS heterostructure for the enhanced photocatalytic activity

Rong Chen, Kui Li, Xiao-Shu Zhu, Shuai-Lei Xie, Long-Zhang Dong, Shun-Li Li* and

Ya-Qian Lan *

Jiangsu Key Laboratory of Biofunctional Materials, School of Chemistry and
Materials Science
Nanjing Normal University, Nanjing 210023, P. R. China

*Address correspondence to yqlan@njnu.edu.cn, slli@njnu.edu.cn

The formation procedure of ZnO was concluded as follow:

The Zn^{2+} from the cation exchange reacted with the superfluous hydroxyl ion and produced $[Zn(OH)_4]^{2-}$, and immediately obtained ZnO.

$$Zn^{2+} + 2OH^{-} = Zn(OH)_2 \qquad (1)$$

$$Zn(OH)_2 + 2OH^{-} = [Zn(OH)_4]^{2-} \qquad (2)$$

$$[Zn(OH)_4]^{2-} = ZnO + H_2O + 2OH^{-} \qquad (3)$$

Supporting Figures:

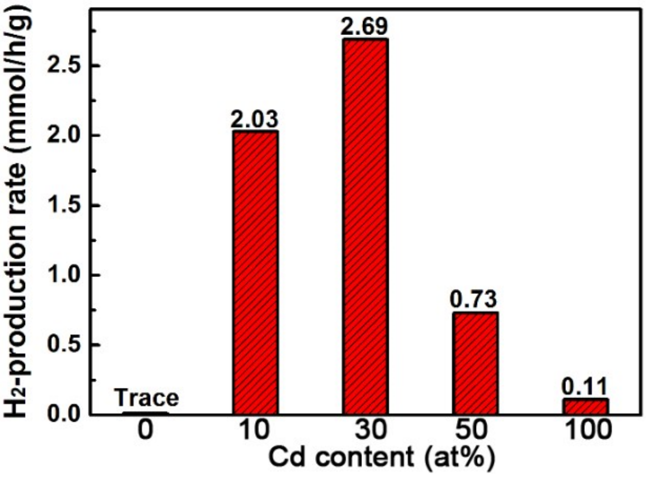

Fig. S1 The photocatalytic activity of the heterojunction samples with different concentrations of Cd^{2+} under visible-light. The ZnS shows the negligible visible light photocatalytic activity. The adoption of Cd^{2+} dramatically increases the photocatalytic H_2-production rate, and the heterostructure with 30 at% Cd shows the maximal H_2-production of 2.69 mmol/h/g (24 times higher than that of CdS).

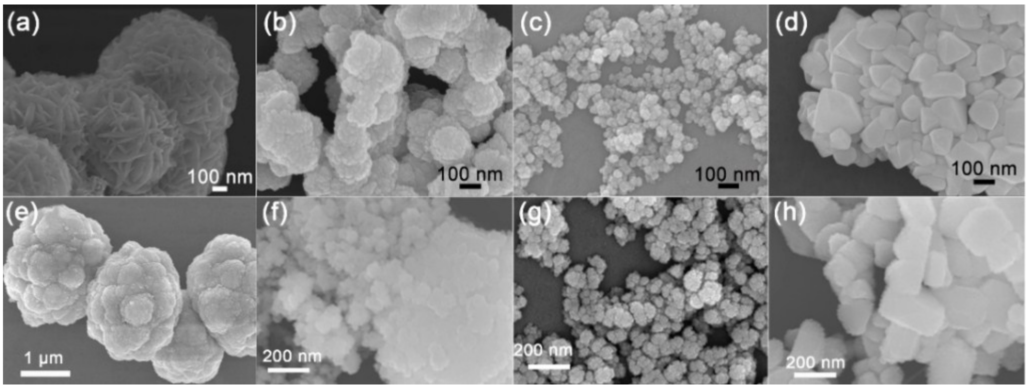

Fig. S2 The SEM images of ZnS precursors prepared with the NaOH/Zn ratio of (a) 0, (b) 1, (c) 4 and (d) 20. The (e-f) SEM morphology of the corresponding heterostructure samples. The NaOH shows dramatically effect on the particle size of the ZnS, and ZnS prepared with NaOH/Zn ratio of 4 shows the smallest particle size. Notably, the corresponding heterostructure shows the similar particle morphology, and the smallest particle size was found in the heterostructure sample derived from ZnS with the smallest particle size (prepared with the NaOH/Zn molar ratio of 4).

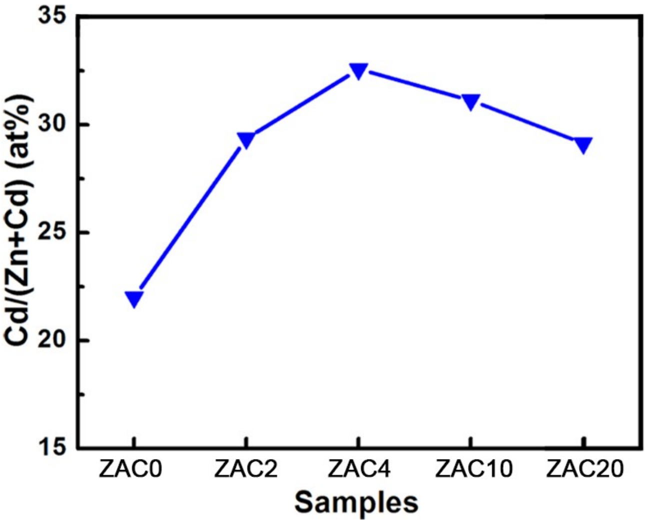

Fig. S3 The electron dispersive X-ray spectrum (EDX) results of the heterostructure samples derived from ZnS precursors with varied particle size. It can be found that the heterostructure sample with smaller particle size shows the larger Cd content, which may be attributed to the larger content of heterostructure active sites in the heterostructure sample resulting from the smaller particle size of ZnS.

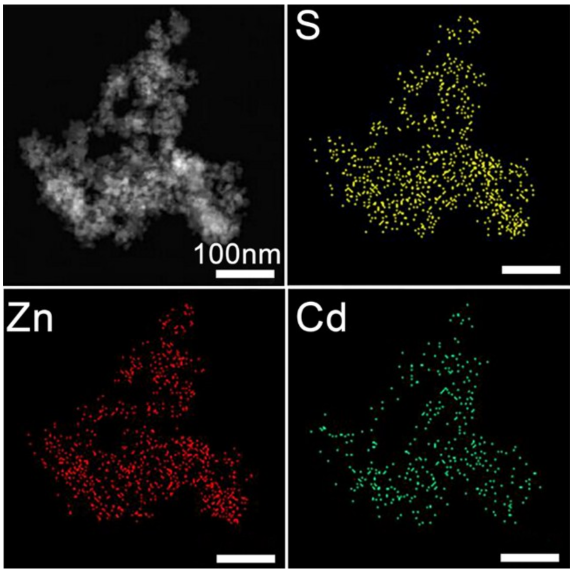

Fig. S4 The mapping of the $Zn_{1-x}Cd_xS$/CdS heterostructure with the smallest nanoparticle size. The elements of S, Zn and Cd are distributed uniformly in the whole skeleton.

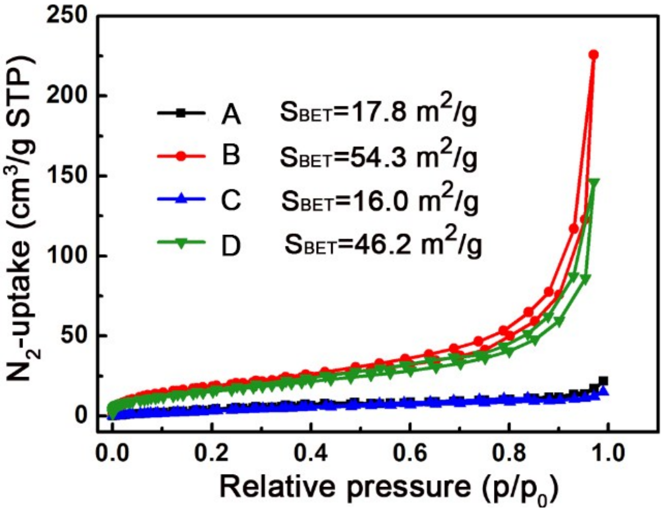

Fig. S5 Nitrogen adsorption/desorption isotherms of ZnS precursors and the corresponding heterostructure prepared with NaOH/Zn ratio of (A, C) 0 and (B, D) 4, respectively. The adoption of NaOH drastically improved the N_2-uptake, S_{BET} of the ZnS precursor and the corresponding heterostructure sample, and hence increased the content of exposed active sites.

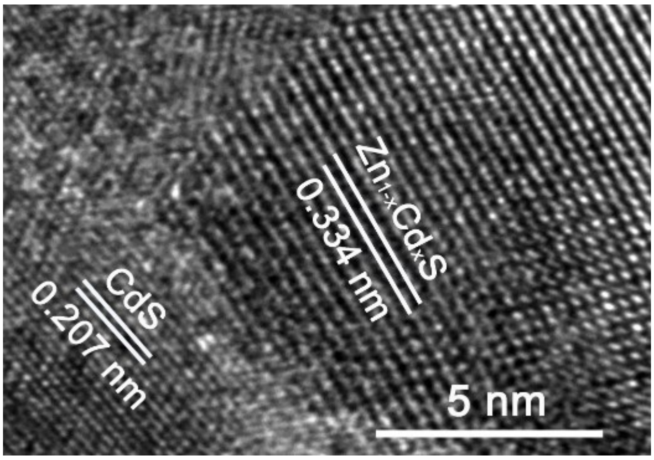

Fig. S6 The HRTEM image of the optimal heterostructure sample (ZAC4) with the smallest particle size derived from the ZnS prepared with NaOH/Zn ratio of 4. The lattice fringes (lattice constant of 0.334 nm and 0.207 nm) corresponding to $Zn_{1-x}Cd_xS$ and CdS could be observed.

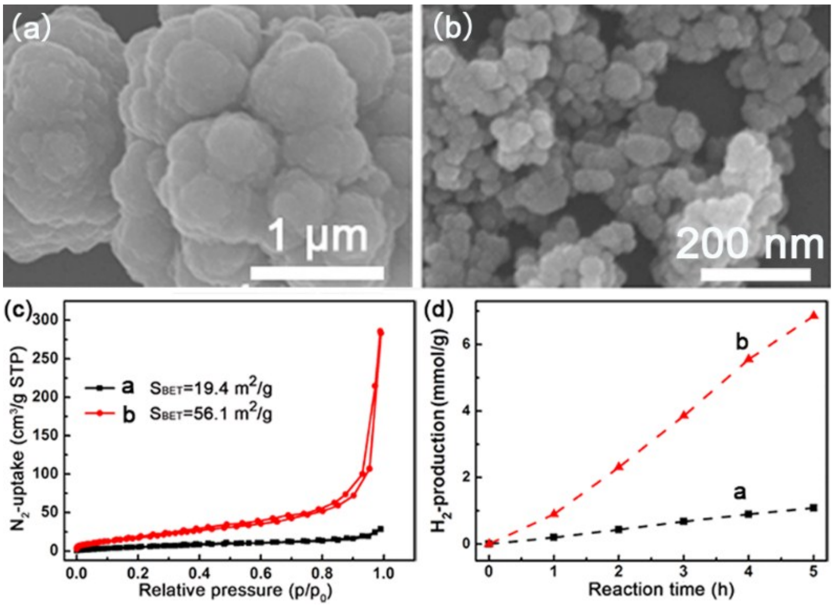

Fig. S7 The (a, b) SEM images, (c) nitrogen adsorption/desorption isotherms and (d) photocatalytic H_2-production of ZnS/CuS heterostructure derived from the ZnS with different particle sizes prepared with NaOH/Zn ratio of 0 (sample a) and 4 (sample b).

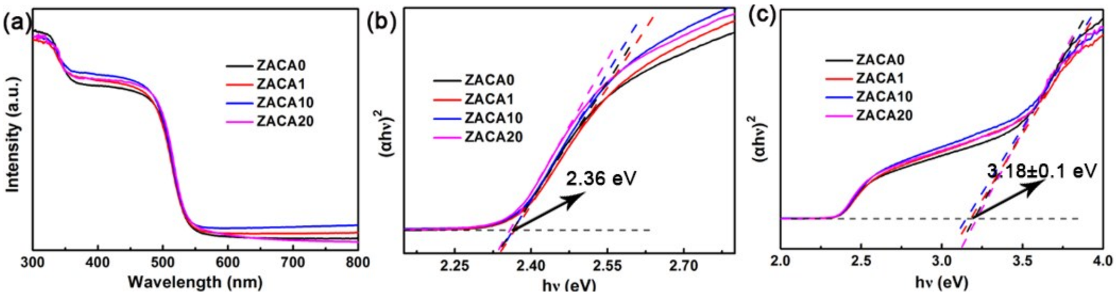

Fig. S8 Effect of the NaOH on the (a) UV-Vis diffuse reflection spectra, and the corresponding $(\alpha h\nu)^2$ versus hν curves in (b) visible and (c) UV regions of the heterostructure samples.

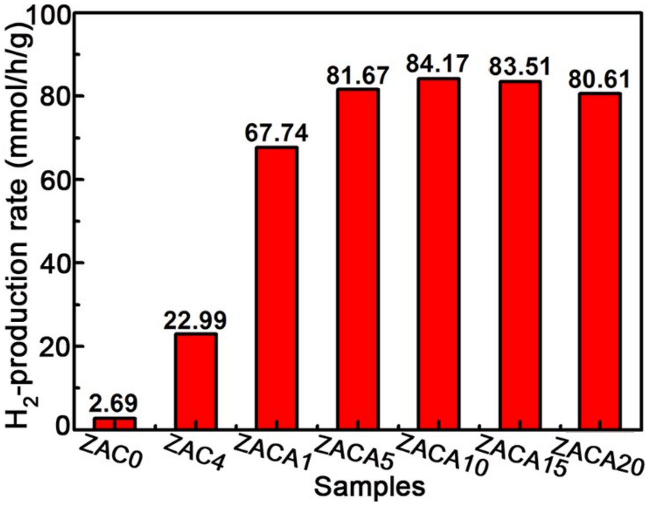

Fig. S9 Effects of the content of NaOH on the photocatalytic activity of the $Zn_{1-x}Cd_xS/CdS$ heterostructure samples.

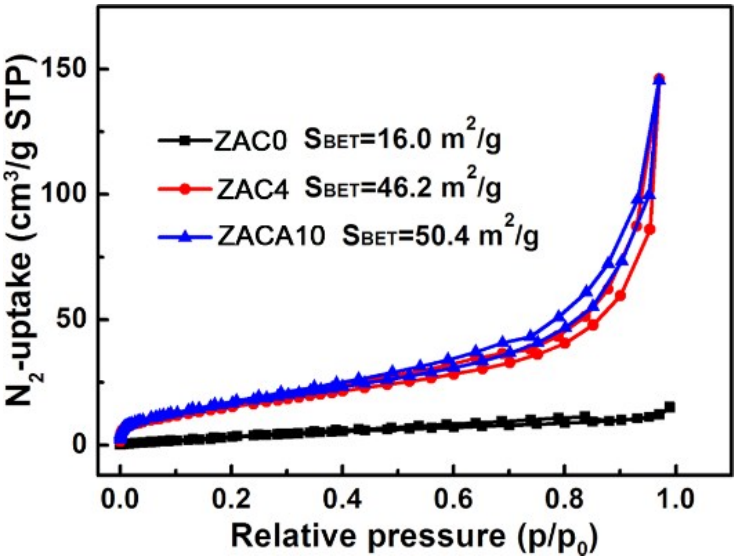

Fig. S10 Effect of the adoption of NaOH with the Cd^{2+} on the nitrogen adsorption/desorption isotherms and S_{BET}. The adoption of NaOH during the formation heterostructure show no effect on the nitrogen uptake and S_{BET} compared with that of the pristine ZAC4.

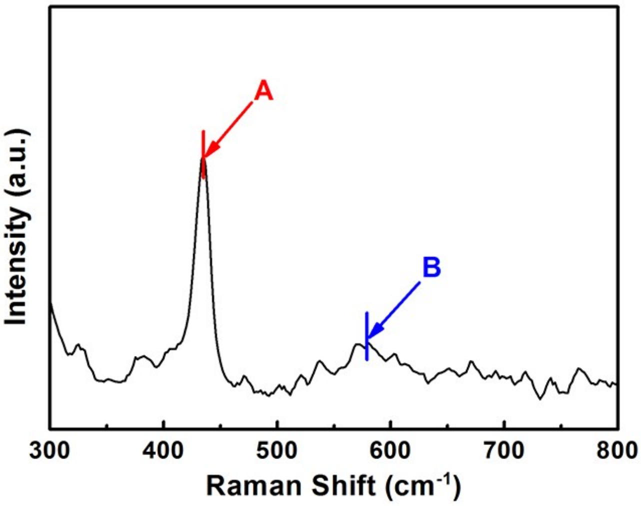

Fig. S11 Raman spectra of the ZnO prepared with the exactly same processing parameters to that of ZACA10. In the spectra, peak A at about 435 cm^{-1} was attributed to the stretching bond of Zn^{2+} – O^{2-}. Peak B at around 580 cm^{-1} was considered in connection with the oxygen vacancy in the ZnO crystal lattice.

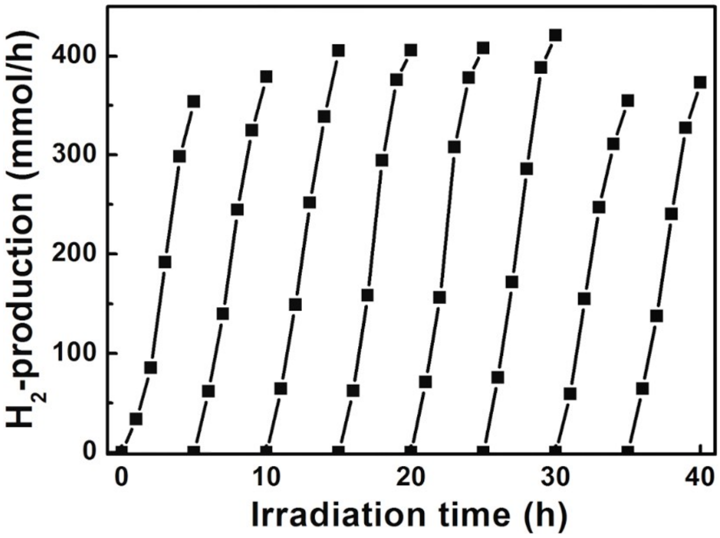

Fig. S12 The photocatalytic stability of ZACA10 over a period of 40 h in a mixed aqueous solution containing Na_2S (0.35 M) and Na_2SO_3 (0.25 M) without renewing sacrificial solution.

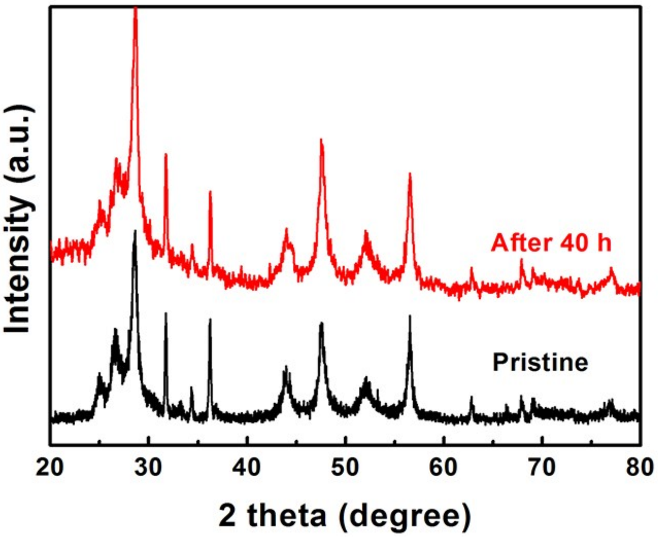

Fig. S13 The X-ray diffraction patterns of ZACA10 sample before and after the irradiation for 40 h, respectively.

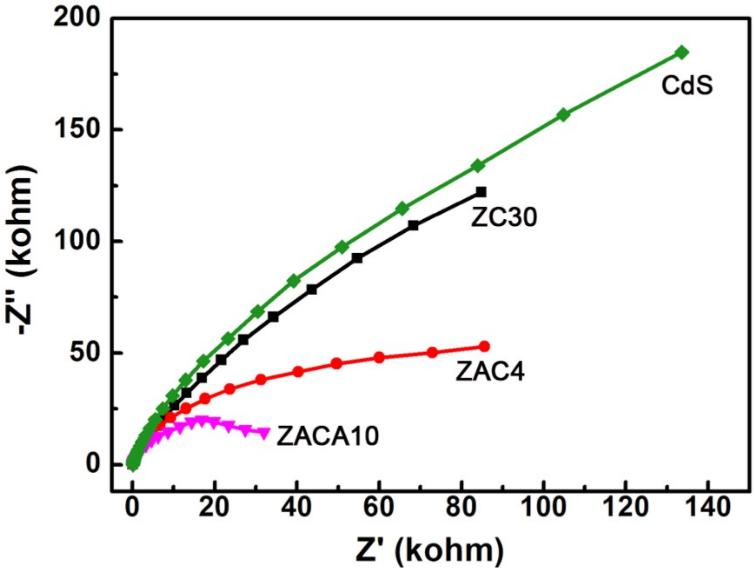

Fig. S14 The electrochemical impedance spectroscopy (EIS) of CdS, ZAC0 (ZC30), ZAC4 and ZACA10, respectively.

Table S1. The photocatalytic H_2-production activity of the ZnO-embedded $Zn_{1-x}Cd_xS$/CdS heterostructure and the previously reported CdS-based photocatalysts.

Photocatalyst	H_2 evolution			Ref.(year)
	Activity (mmol/h/g)	Improving multiple[a]	Stability (h)	
ZnO-embedded $Zn_{1-x}Cd_xS$/CdS	**84.17**	**765**	>40	**This work**
ZnS/$Zn_{1-x}Cd_xS$/CdS	**34.2**	**152**	≈20	[1](2015)
$Zn_{1-x}Cd_xS$/CdS	**2.13**	**53**	N/A	[2](2010)
CdS/ZnS	**0.792**	**56**	>60	[3](2014)
$Zn_{1-x}Cd_xS$	**7.42**	**24**	N/A	[4](2013)
Pt/CdS	**1.52**	**281.5**	15h	[5](2014)
CdS/MoS_2	**0.59**	**36**	N/A	[6](2008)
CdS/Cd	**11.687**	**7.012**	N/A	[7](2014)
1D-$Cd_{0.8}Zn_{0.2}S$	**N/A**	**3.01**	<12	[8](2015)
CdS/g-C_3N_4	**4.152**	**2.075**	N/A	[9](2013)
CdS/ZnS	**N/A**	**≈2**	N/A	[10](2013)

[a] Improving multiple=H_2-production rate of the optimal catalyst/H_2-production rate of CdS.

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