**Electronic Supplementary Information (ESI)** 

# ZnO nanosheets with atomically thin ZnS overlayer for photocatalytic water splitting

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### **Supplementary Table**

#### Table S1. Photocatalytic H<sub>2</sub> production over SNS, ZnS, ZnO nanosheets

Photocatalyst	Morphology	Incident light [nm]	Reactant solution	Activity [ μ mol·g <sup>-1</sup> ·h <sup>-1</sup> ]	Stability	QY [%]	AQY [%]	Ref.	Light source
ZnO/ZnS	Nanorod Arrays (NRAs)	UV-Vis	glycerol	384	12h	13.9	-	[1]	350W(Xe)
ZnS-ZnO	Nanowires (NWs)	>420	Na <sub>2</sub> S/Na <sub>2</sub> SO <sub>3</sub>	22	12h	-	-	[2]	300W(Xe)
CdS-ZnO	1D porous	>400	Na <sub>2</sub> S/Na <sub>2</sub> SO <sub>3</sub>	851	15h	-	3	[3]	300W(Xe)
Ce-doped ZnO/ZnS	Nanoparticles (NPs)	UV	Na <sub>2</sub> S/Na <sub>2</sub> SO <sub>3</sub>	1200	16h (85%)	6.69	-	[4]	300W(Xe)
Ag <sub>2</sub> S-coupled ZnO@ZnS	Nanorods (NRs)	Vis	Na <sub>2</sub> S/Na <sub>2</sub> SO <sub>3</sub>	168	3h	-	-	[5]	300W(Xe)
ZnO/RGO	NRs	320-1100	ethanol	610	4h	-	-	[6]	300W(Xe)
RGO/ZnO @Zn <sub>0.6</sub> Cd <sub>0.4</sub> S	NRs	UV-Vis	50% ethanol	1865	5h	22.6	-	[7]	300W(Xe)
		>420	50% ethanol	160	5h	-	-		300W(Xe)
SNS	NSs	UV-Vis	Na <sub>2</sub> S/Na <sub>2</sub> SO <sub>3</sub>	2080	20h	34.7	7.2	Our work	300W(Xe)
		>420	Na <sub>2</sub> S/Na <sub>2</sub> SO <sub>3</sub>	79.8	20h	4.8	0.05	Our work	300W(Xe)

and different samples.

#### References

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## **Supplementary Figures**



**Figure S1.** Characterization of ZnS/Zn/ZnS SNSs. (a) SEM image. (b) TEM image, (c) HAADF image and corresponding element mappings of Zn and S.



**Figure S2.** (a) AFM surface image of ZnS/Zn/ZnS SNSs and (b) corresponding profiles.



Figure S3. XRD pattern of ZnS/Zn/ZnS SNSs.



Figure S4. XPS spectra of ZnS/Zn/ZnS SNSs. (a) Zn 2p spectrum and (b) S 2p spectrum.



**Figure S5.** SEM images of ZnS/ZnO/ZnS SNSs at (a) low magnification image and (b) high magnification.



Figure S6. TEM images of ZnS/ZnO/ZnS SNSs. (a) TEM and (b) HRTEM images, the lower and upper insets in (b) show FFT and SAED patterns of a SNS, respectively.



Figure S7. Side-view HRTEM image of SNS NSs with a line scanning of S element.



Figure S8. XRD patterns of ZnS/ZnO/ZnS SNSs, ZnS and ZnO nanosheets.



**Figure S9.** XPS spectra of SNSs and ZnO NSs. (a) Survey scan spectra, (b) Zn 2p, (c) O 1s and (d) S 2p spectra.



Figure S10. AFM image of SNSs with obvious surface roughness.



**Figure S11.** Optical microscopy images of SNSs taken after different etching times. (a) 5 min. (b) 10 min (c) 20 min (d) 30 min. Uniform and rather homogeneous etching of the ZnO layer is observed.



**Figure S12.** XPS spectra of SNSs after chemical etching. (a) Survey scan. (b) Zn 2p, (c) S 2p, (d) O 1s narrow scan spectra.



Figure S13. TEM image of SNSs after chemical etching.



Figure S14. AFM images of SNSs after chemical etching.



**Figure S15.** (a) Side-view HRTEM image of SNSs. (b) Corresponding intensity profile along line 1. (c) Corresponding intensity profile along line 2.



**Figure S16.** (a, b) SEM images of ZnS NSs. (c, d) SEM images of SNSs. (e, f) SEM images of ZnO NSs.



Figure S17. AFM images of (a) SNSs, (b) ZnS NSs, and (c) ZnO NSs.



**Figure S18.** Nitrogen adsorption-desorption isotherm curves. (a) SNS NSs, (b) ZnO NSs, (c) ZnS NSs, (d) The specific surface area values of the above samples.



**Figure S19.** Photocatalytic H<sub>2</sub> production of different photocatalyst loaded SNS NSs under irradiation of simulated air mass 1.5 solar illumination in 0.25M Na<sub>2</sub>S/0.35M Na<sub>2</sub>SO<sub>3</sub>.



**Figure S20**. Photocatalytic H<sub>2</sub> production of SNSs, ZnS NSs, and ZnO NSs under ultraviolet light irradiation (320 nm  $< \lambda < 400$  nm).



**Figure S21**. Photocatalytic H<sub>2</sub> production of SNSs, ZnS NSs, and ZnO NSs in 0.5M  $Na_2SO_4$  without sacrificial agents ( $Na_2S$  and  $Na_2SO_3$ ) under irradiation of simulated air mass 1.5 solar illumination.



**Figure S22.** Photocatalytic H<sub>2</sub> production of SNSs, ZnS NSs, and ZnO NSs under irradiation of simulated air mass 1.5 solar illumination for four cycles.



Figure S23. AQE and QE values of SNSs and ZnO NSs. (Incident light intensity:  $5mW/cm^2$ )



**Figure S24.** (a) Side view of a supercell with 2 layers of ZnS and 8 layers of ZnO. (b) Top view of the supercell. (c) Primitive unit cell in (b).



**Figure S25.** (a) Side view of a supercell of layered ZnO bulk structure. (b) Side view of a supercell of layered ZnS bulk structure.



**Figure S26.** Electronic band structure of (a) bulk ZnO, (b) SNS and (c) ZnS computed using the HSE06 functional at the respective PBEsol-optimized geometries.



Figure S27. The equivalent circuit model of the Nyquist plots.



**Figure S28** Linear sweep voltammograms measured in 0.5M Na<sub>2</sub>SO<sub>4</sub> under 1 sun AM 1.5G illumination.



**Figure S29.** Linear sweep voltammograms measured in 0.25M Na<sub>2</sub>S/0.35M Na<sub>2</sub>SO<sub>3</sub> solution under 1 sun AM1.5G illumination.



Figure S30. SEM image of (a) ZnO-R NSs and (b) SNS-R NSs.



Figure S31. XRD patterns of SNS-R and ZnO-R NSs.



Figure S32. UV-vis diffuse reflectance spectra of SNS-R and ZnO-R NSs.



**Figure S33.** (a)TEM image of ZnO-R NSs, (b) HRTEM image of ZnO-R NSs, (c)TEM image of SNS-R NSs, (d) HRTEM image of SNS-R NSs.



**Figure S34.** Photocatalytic H<sub>2</sub> production rate of SNS-R and ZnO-R NSs in different concentration of Na<sub>2</sub>S with 0.25M Na<sub>2</sub>SO<sub>3</sub> under irradiation of simulated air mass 1.5 solar illumination.