Freestanding nano-photoelectrode as highly efficient and visible-light-

driven photocatalyst for water-splitting

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Figure S1. (a) SEM image of pristine WS₂. (b) SEM image, (c) TEM image and SAED patterns (Insert) and (d) high magnification of TEM image of ZnO seeds/WS₂ sample.

Compared to bulk WS₂ (Figure S1a), WS₂ is exfoliated to be nanosheets after being ultrasonicated in ethanol in the presence of $Zn(OAc)_2 \cdot 2H_2O$ and LiOH (Figure S1b). The exfoliated nanosheets are also observed in the TEM image (Figure S1c). Two sets of diffraction spots are observed in corresponding SAED pattern (inset in Figure S1c), which are assigned to the WS₂ phase (JCPDS No. 08-0237) and ZnO phase (JCPDS No. 36-1451), suggesting the co-existence of ZnO and WS₂. ZnO nanoseeds with diameters around 5 nm were anchored on WS₂ nanosheets when observed in a high magnification TEM image (Figure S1d).



Figure S2. SEM image of C(0.6)/Z/W(10). Nanorod arrays grown on a 2D substrate are clearly distinguished.



Figure S3. XRD pattern of C(0.6)/Z/W(10). The peaks are well indexed to CdS (JCPDS NO. 77-2306), ZnO (JCPDS NO. 36-1451) and WS₂ (JCPDS NO. 08-0237).



Figure S4. (a) TEM image of C(0.6)/Z/W(10) and its EDX spectrum. Zn, O, Cd, S and W are detected, suggesting the existence of WS₂ in the structure.



Figure S5. HAADF images of C(0.6)/Z/W(10). Nanoarrays with hollow heads are clearly observed in the HAADF images.



Figure S6. EDX line scan profiles of Zn and Cd (b) along the line marked in (a).



Figure S7. HRTEM image of the solid core corresponding to Figure 2h. The fringes distance with 0.52 nm corresponds to the [001] direction of ZnO.



Figure S8. (a) TEM image of P(1.0)/C(0.6)/Z/W(10). (b) Raman spectra of PEDOT:PSS (blue), P(1.0)/C(0.6)/Z/W(10) (magenta)and C(0.6)/Z/W(10) (cyan).



Figure S9. Photocatalytic hydrogen evolution performance over samples with different amount of (a) CdS in C(x)/Z, (b) WS₂ in C(0.6)/Z/W(y) and (c) PEDOT:PSS in P(z)/C(0.6)/Z/W(10).



Figure S10. FT-IR spectrum of P(z)/C(0.6)/Z/W(10) after 60h long time test photocatalytic H₂ evolution test.



Figure S11. TRPL spectra of samples with different amount of (a) CdS in C(x)/Z, (b) WS₂ in C(0.6)/Z/W(y) and (c) PEDOT:PSS in P(z)/C(0.6)/Z/W(10).



Figure S12. UV-vis spectra of samples with different amount of (a) CdS in C(x)/Z, (b) CdS in $C(x)/Z/WS_2(10)$, (c) WS₂ in C(0.6)/Z/W(y) and (d) PEDOT:PSS in P(z)/C(0.6)/Z/W(10).



Figure S13. Linear sweep voltammagrams of (a) ZnO, (b) C(0.6)/Z, (c) C(0.6)/Z/W(10) and (d) P(1.0)/C(0.6)/Z/W(10)



Figure S14. (a) UV-vis spectrum and (b) Tauc plot of WS₂.



Figure S15. UV-vis spectrum of PEDOT:PSS.



Figure S16. Photocurrent density of samples under (a) $\lambda = 500$ nm, (b) $\lambda = 550$ nm, (c) $\lambda = 600$ nm and (d) $\lambda = 700$ nm.



Figure S17. Photocurrent density of WS₂ under $\lambda = 500$ nm (black), $\lambda=550$ nm (red), $\lambda=600$ nm (blue) and $\lambda = 700$ nm (magenta).



Figure S18. Spectra of the long wavelength light and their intensity. (a) $\lambda = 500$ nm, (b) $\lambda = 550$ nm, (c) $\lambda = 600$ nm and (d) $\lambda = 700$ nm.

Materials	Reaction conditions	H_2 evolution rate /µmol h ⁻¹ g ⁻¹	References
CdS/ZnO (Pt)	$0.1 \text{ M} \text{Na}_2\text{S}$ and $0.1 \text{ M} \text{Na}_2\text{SO}_3$,	3870	1
	300 W Xe lamp.		
CdS/Au/ZnO	$0.1\ M\ Na_2SO_3$ and $0.1\ M\ Na_2S$	608	2
	300 W Xe lamp.		
ZnO–CdS/RGO (Pt)	$0.1~M~Na_2S$ and $0.1~M~Na_2SO_3$	11000	3
	300 W Xe lamp.		
CdS/ZnO	$0.5\ M\ Na_2S$ and $0.5\ M\ Na_2SO_3$	851	4
	500 W Xe, λ> 400 nm		
ZnO/Pt/CdS	$0.1~M~Na_2S$ and $0.1~M~Na_2SO_3$	31600	5
	450 W Xe arc lamp (working at 400 W) fitted with water filter		
CdS/ZnO	$0.1 \text{ M} \text{ Na2S}$ and $0.04 \text{ M} \text{ Na}_2 \text{SO}_3$	~ 360	6
	500W Xe lamp, λ> 420 nm		
CdS/ZnO/WS ₂	$0.2~M~Na_2S$ and $0.3~M~Na_2SO_3$	33733	Present work
	300 W Xe lamp equipped with an AM 1.5G filter (100 mW·cm ⁻²).		
PEDOT:PSS/CdS/ZnO/WS2	$0.2\ M\ Na_2S$ and $0.3\ M\ Na_2SO_3$	68533	Present work
	300 W Xe lamp equipped with an AM 1.5G filter (100 mW·cm ⁻²).		

Table S1 Comparison of reported CdS/ZnO based photocatalysts and the samples from this work.

	ZnO	C(0.6)/Z	C(0.6)/Z/W(10)	P(1.0)/C(0.6)/Z/W(10)
$R_{s}(\Omega)$	14.7	14.3	14.9	14.5
$R_{ct}(\Omega)$	1742	938.7	704.2	532.9

Table S2. Fitting parameters of the ESI plots in Figure 3f.

References

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