Supporting Information

CdS quantum dots and tungsten carbide supported on anatase-rutile composite TiO₂ for highly efficient visible-light-driven photocatalytic H₂ evolution from water

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Fig. S1 HRTEM image the water-soluble CdS QDs.





Fig. S3 Time-course H₂ evolution with (a) different amount of WC/TiO₂ (calcined at 800 °C, Ti/W molar ratio: 10/1) by fixing the amount of CdS QDs at 20 mg, (b) different molar ratio of Ti/W by fixing the amounts of WC/TiO₂ (calcined at 800 °C) and CdS QDs at 15 and 20 mg, respectively, (c) different calcination temperature by fixing the amounts of WC/TiO₂ (Ti/W molar ratio: 10/1) and CdS QDs at 15 and 20 mg, respectively, and (d) different metal oxide supports by fixing the amount of WC/oxide (15 mg) and CdS QDs (20 mg). Reaction conditions: 100 mL aqueous solution with 20 vol% lactic acid, 300 W Xe lamp ($\lambda > 420$ nm).



Fig. S4 (a) H₂ evolution rate on CdS/Pt/TiO₂ with different amount of Pt/TiO₂ (content of Pt: 2%) by fixing the amount of CdS QDs at 20 mg, and (b) H₂ evolution rate on CdS/Pt/TiO₂ with different content of Pt by fixing the amounts of CdS QDs and Pt/TiO₂ at 20 mg. Reaction conditions: 100 mL aqueous solution with 20 vol% lactic acid, 300 W Xe lamp ($\lambda > 420$ nm), irradiation time 6 h.



Fig. S5 XRD patterns of WC/TiO₂ calcined at different temperatures.

Table S1 Comparison of the photocatalytic H_2 evolution activity of CdS/WC/TiO₂ with those photocatalysts using Pt as the co-catalyst reported in the literatures.

Photocatalyst	Catalyst amount (mg); Reaction solution (mL)	Sacrificial reagent	Light source	H ₂ evolution rate (umol/h)	QE (%); wavelength (nm)	Ref.
CdS/WC/TiO ₂	35; 100	20 vol% lactic acid	300 W Xe, λ>420 nm	624.9	32.1%; 460 nm	This work
CdS/Pt/Ga ₂ O ₃	100; 100	20 vol% lactic acid	300 W Xe, λ>420 nm	995.8	43.6%; 460 nm	1
CdS/Pt/In ₂ O ₃				1032.2	45.3%; 460 nm	
CdS/Pt/TiO ₂				603.0	37.6%; 460 nm	
ZnO/Pt/CdS	20; 75	0.1M Na ₂ S, 0.1M Na ₂ SO ₃	450 W Xe, λ>420 nm	224	11.9% ^a	2
		benzyl alcohol		632	34.5% ^a	
Pt/CdS/TiO ₂	100; 100	0.1M Na ₂ S, 0.02M Na ₂ SO ₃	500 W, Hg-arc, λ>420 nm	~560	-	3
CdS/Al ₂ O ₃	100; 50	0.25M Na ₂ S, 0.35M Na ₂ SO ₃	500 W, tungsten- Hg λ>420 nm	724	11% ^a	4
CdS/ZnO				1008	15% ^a	
CdS/Pt/TiO ₂	40; 80	10 vol% lactic acid	350 W Xe arc, λ>420 nm	265	13.9%; 420 nm	5
CdS/Pt/ZnO	200; 300	0.1 M Na ₂ S, 0.1 M Na ₂ SO ₃	450 W Xe arc, λ>420 nm	774	3.2% ^a	6

^{*a*} No wavelength specified.



Fig. S6 Transient photocurrent responses of CdS/WC/Al₂O₃, CdS/WC/ZnO, CdS/WC/CeO₂, CdS/WC/MgO and CdS/WC/TiO₂ in 0.2 M Na₂SO₄ aqueous solution containing 20 vol% lactic acid under visible light irradiation ($\lambda > 420$ nm).

References

- 1 Y. X. Pan, H. Zhuang, J. Hong, Z. Fang, H. Liu, B. Liu, Y. Huang and R. Xu, *ChemSusChem*, 2014, 7, 2537-2544.
- 2 S. R. Lingampalli, U. K. Gautam and C. N. R. Rao, *Energy Environ. Sci.*, 2013, 6, 3589-3594.
- 3 J. S. Jang, S. H. Choi, H. G. Kim and J. S. Lee, J. Phys. Chem. C, 2008, 112, 17200–17205.
- 4 D. Barpuzary, Z. Khan, N. Vinothkumar, M. De and M. Qureshi, *J. Phys. Chem. C*, 2012, **116**, 150-156.
- 5 R. Marschall and L. Wang, *Catal. Today*, 2014, **115**, 111-135.
- 6 X. Wang, G. Liu, Z. G. Chen, F. Li, L. Wang, G. Q. Lu and H. M. Cheng, *Chem. Commun.*, 2009, 3452-3454.