Electronic Supplementary Material (ESI)

Stacking design in photocatalysis: Synergizing cocatalyst roles and anti-corrosion functions of metallic MoS_2 and graphene for remarkable hydrogen evolution over CdS

Qian Liu,[a] Shihong Wang,[a] Qinhao Ren,[a] Tianyu Li,[a] Gaomei Tu,[c] Shuxian Zhong,[b] Yuling Zhao,[a]* Song Bai[a]*

[a] Key Laboratory of the Ministry of Education for Advanced Catalysis Materials, College of Chemistry and Life Sciences, Zhejiang Normal University, Jinhua, Zhejiang 321004, P. R. China.

[b] College of Geography and Environmental Sciences, Zhejiang Normal University, Jinhua, Zhejiang, 321004, P. R. China.

[c] Institute of Advanced Fluorine-Containing Materials, Zhejiang Normal University, Jinhua 321004, P. R. China.

E-mail: songbai@zjnu.edu.cn; yulingzhao@zjnu.edu.cn

Additional experimental

Preparation of graphite oxide

Graphite oxide was synthesized from natural graphite flakes by a modified Hummers method.[S1] In a typical procedure, 2.0 g of graphite powder was added to concentrated H_2SO_4 (80 mL) in a 500 mL flask in an ice bath. Under vigorous stirring, $KMnO_4$ (10.0 g) and $NaNO_3$ (4.0 g) were gradually added, while the temperature of the mixture was maintained below 10 °C for 4 h. Subsequently, the reaction mixture was stirred at 35 °C for another 4 h until it became pasty and green. The mixture was then diluted with water (200 mL), after which its color became brownish. The addition of water was performed in an ice bath to maintain the temperature below 100 °C. The mixture was then stirred for 30 min, and 15 mL of 30 wt% H_2O_2 was slowly added to the mixture to reduce the residual $KMnO_4$, after which the color of the mixture changed to brilliant yellow. The mixture was re-dispersed in water and was then dialyzed for one week to remove residual salts and acids. The resulting solid was centrifuged and dried at 45 °C for 12 h.

Preparation of CdS nanospheres

In a typical synthesis,[S2] 1.6 mmol of $Cd(CH_3COO)_2·2H_2O$ and 40 mmol of thiourea were dissolved in 40 mL of deionized water to form a clear solution after stirring for 30 min at room temperature. The solution was then transferred into a 50 mL Teflon-lined stainless-steel autoclave and maintained at 140 °C for 2 h. After cooling down to room temperature, the yellow precipitate was harvested by centrifugation, washed several times with deionized water and ethanol to remove possible remaining cations and anions, and dried at 45 °C in a vaccum.

Synthesis of CdS@MoS_2

570.0 mg of CdS was re-dispersed in 3.6 mL of water and then added into the solution containing 3.6 mL of water and 5 mL of absolute ethanol, followed by stirring for 1 h. Next, 0.0807 g of $Na_2MoO_4·2H_2O$ was added to the above mixture and stirred to form the suspension. Besides, another solution was prepared by dissolving 0.0214 g of S power in 2.5 mL of 85% $N_2H_4 \cdot H_2O$ at 50 °C by stirring, which was then dropwise injected to the first suspension. Finally, the mixture was transferred into 20 mL Teflon-lined stainless-steel autoclave and kept at 200 °C for 10 h. After cooling down to room temperature, the resultant product was separated by centrifugation, washed several times with deionized water and ethanol to remove possible remaining cations and anions, and dried at 45 °C in a vaccum.

Synthesis of rGO@MoS_2-CdS

32.0 mg of graphite oxide was dispersed in 3.6 mL of water to form a GO aqueous suspension via probe sonication (Scientz-IID, China) for 1 h, which is then added to the solution containing 3.6 mL of water and 5 mL of absolute ethanol, followed by stirring for 1 h and ultrasonication for another 2 h. Next, 0.0807 g of $Na_2MoO_4 \cdot 2H_2O$ was added to the above mixture and stirred to form the suspension. Besides, another solution was prepared by dissolving 0.0214 g of S power in 2.5 mL of 85% $N_2H_4 \cdot H_2O$ at 50 °C by stirring, which was then dropwise injected to the first suspension. The mixture was transferred into 20 mL Teflon-lined stainless-steel autoclave and kept at 200 °C for 10 h. After cooling down to room temperature, the resultant product was separated by centrifugation, washed several times with deionized water and ethanol to remove possible remaining cations and anions, and re-dispersed in 125 mL water. Then 5.0 mmol of $Cd(CH_3COO)_2 \cdot 2H_2O$ and 125.0 mmol of thiourea were dissolved in the as-obtained rGO@MoS_2 aqueous suspension after stirring for 30 min at room temperature. The solution was then transferred into Teflon-lined stainless-steel autoclaves and maintained at 140 °C for 2 h. After cooling down to room temperature, the resultant product was separated by centrifugation, washed several times with deionized water and ethanol to remove possible remaining cations and anions, and dried at 45 °C in a vaccum.

Sample characterizations

Transmission electron microscopy (TEM), high-resolution TEM (HRTEM), selected-area electron diffraction (SAED), scanning TEM (STEM) and energy dispersive spectroscopy (EDS) mapping profiles were taken on a JEOL JEM-2100F field-emission high-resolution transmission electron microscope operated at 200 kV. Powder X-ray powder diffraction (XRD) patterns were collected on a D8 Advance X-ray diffractometer with Non-monochromated Cu-Kα X-Ray. X-ray photoelectron spectra (XPS) were collected on an ESCALab 250 X-ray photoelectron spectrometer, using nonmonochromatized Al-Kα X-ray as the excitation source. The Raman measurement was carried out on a Renishaw in ViaRefles under excitation wavelength of 532 nm. UV-vis diffuse reflectance data were recorded in the spectral region of 200-800 nm with a Cary-7000 eries UV-vis-NIR spectrophotometer. Photoluminescence (PL) spectra were examined using a HITACHI F-7000 Spectrofluorometer. The composition analyses and Cd^{2+} concentration measurements were performed through a Thermo Scientific PlasmaQuad 3 inductively-coupled plasma mass spectrometry (ICP-MS).

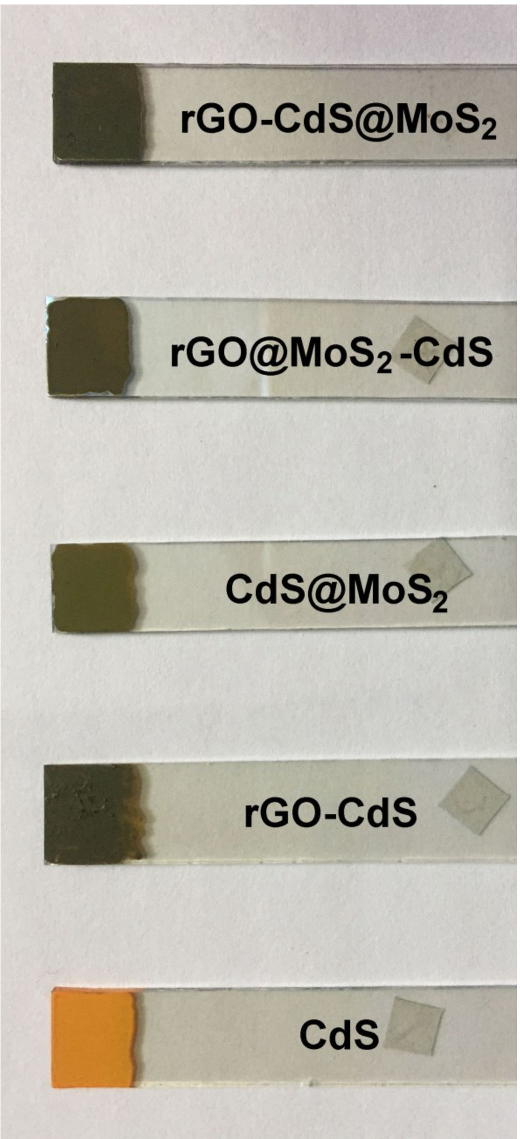


Fig. S1 Photograph of CdS based samples coated FTO glass.

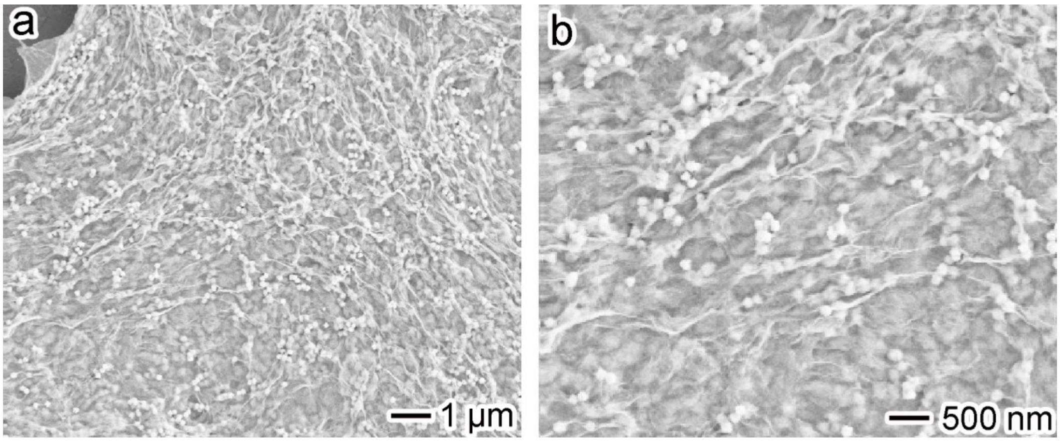


Fig. S2 SEM images of rGO-CdS@MoS_2.

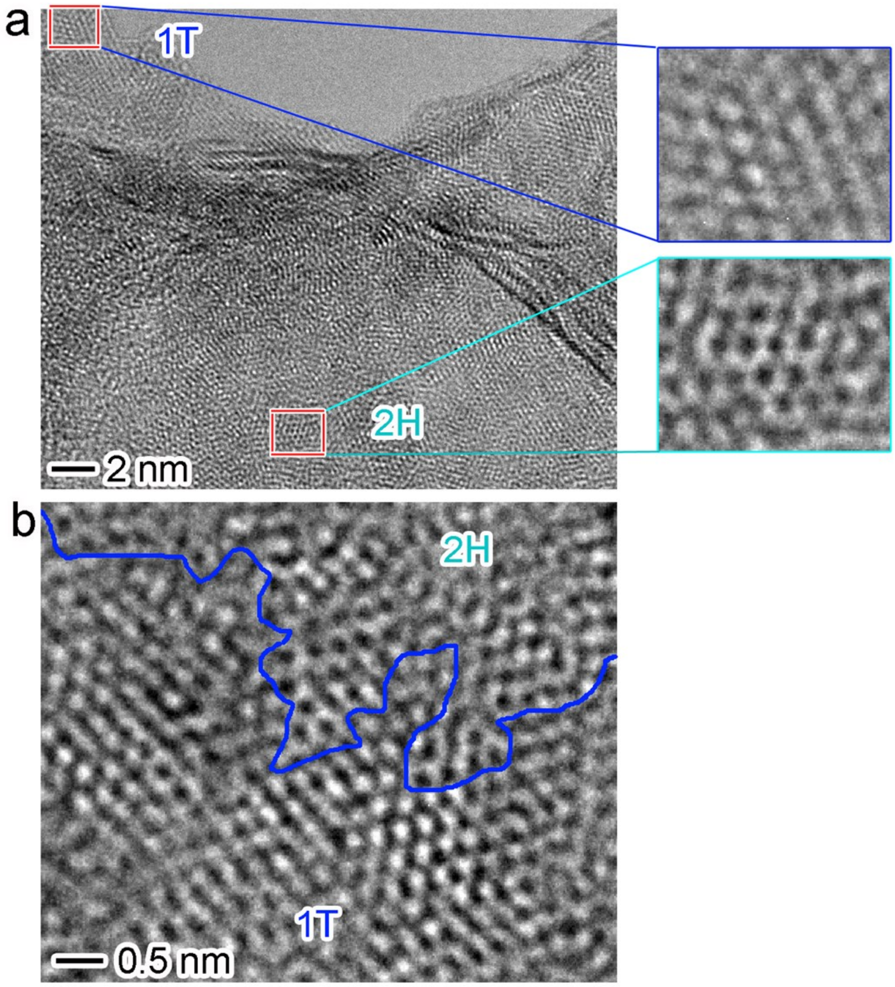


Fig. S3 Detailed HRTEM images of MoS_2 in rGO-CdS@MoS_2.

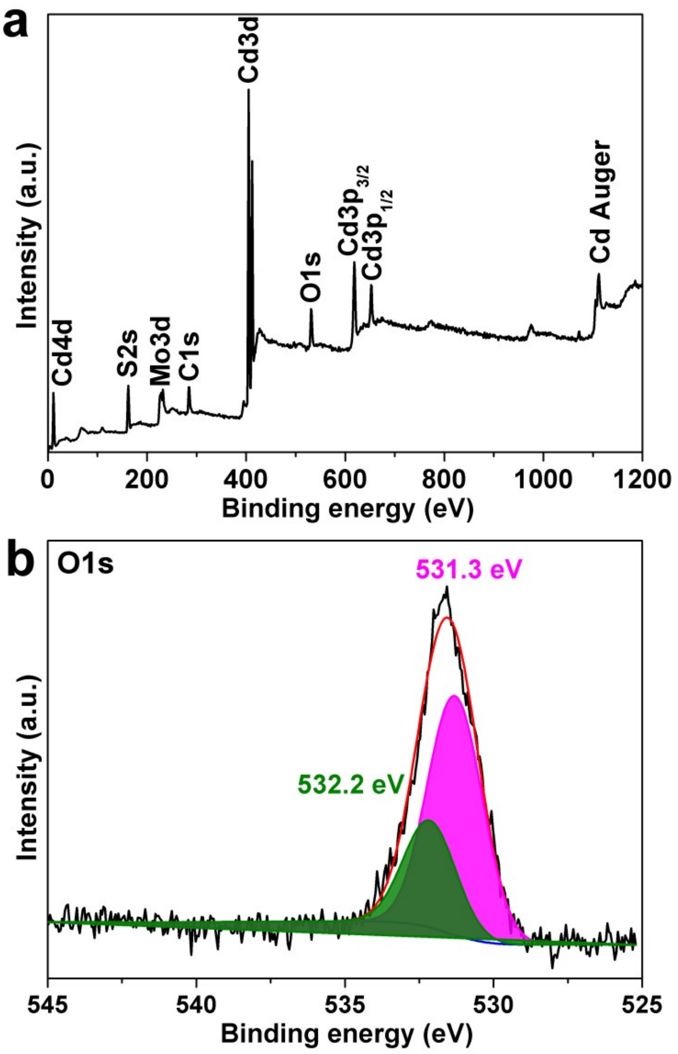


Fig. S4 (a) Survey and (b) high-resolution O1s XPS spectra of rGO-CdS@MoS_2.

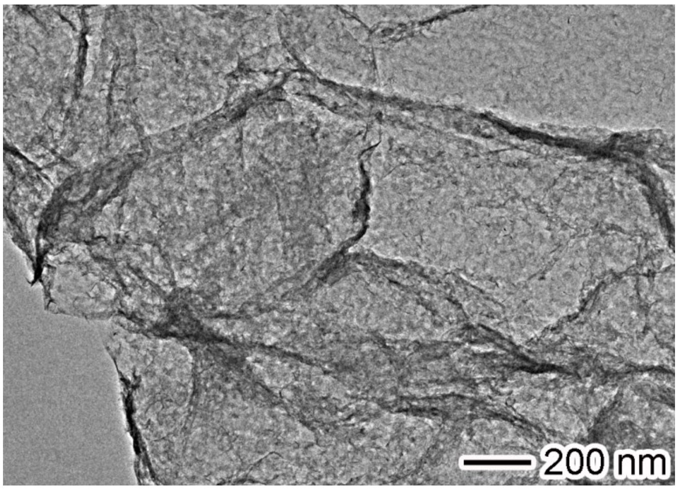


Fig. S5 TEM image of rGO@MoS_2 nanosheets.

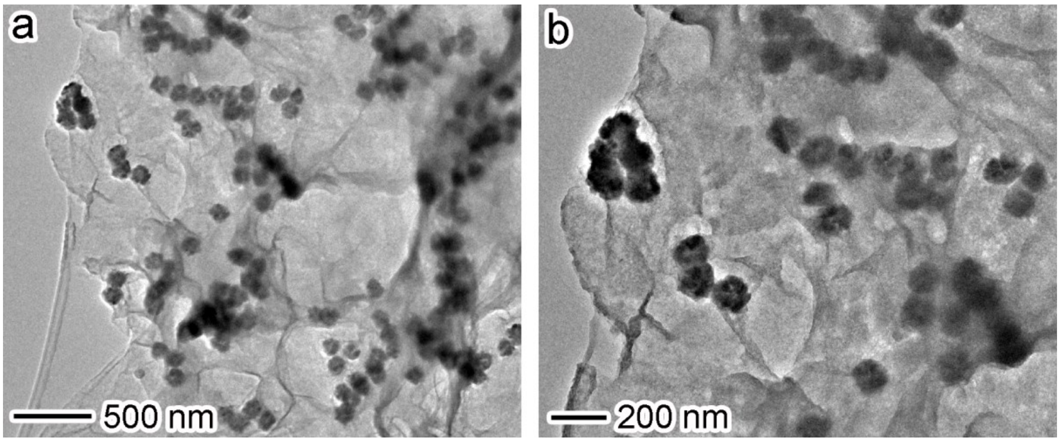


Fig. S6 TEM images of rGO-CdS@MoS_2 nanosheets after the photocatalytic cycles.

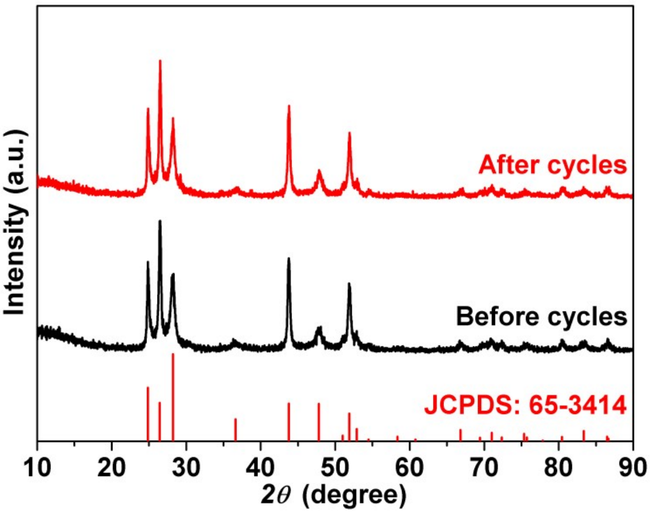


Fig. S7 XRD patterns of rGO-CdS@MoS_2 nanosheets before and after the photocatalytic cycles.

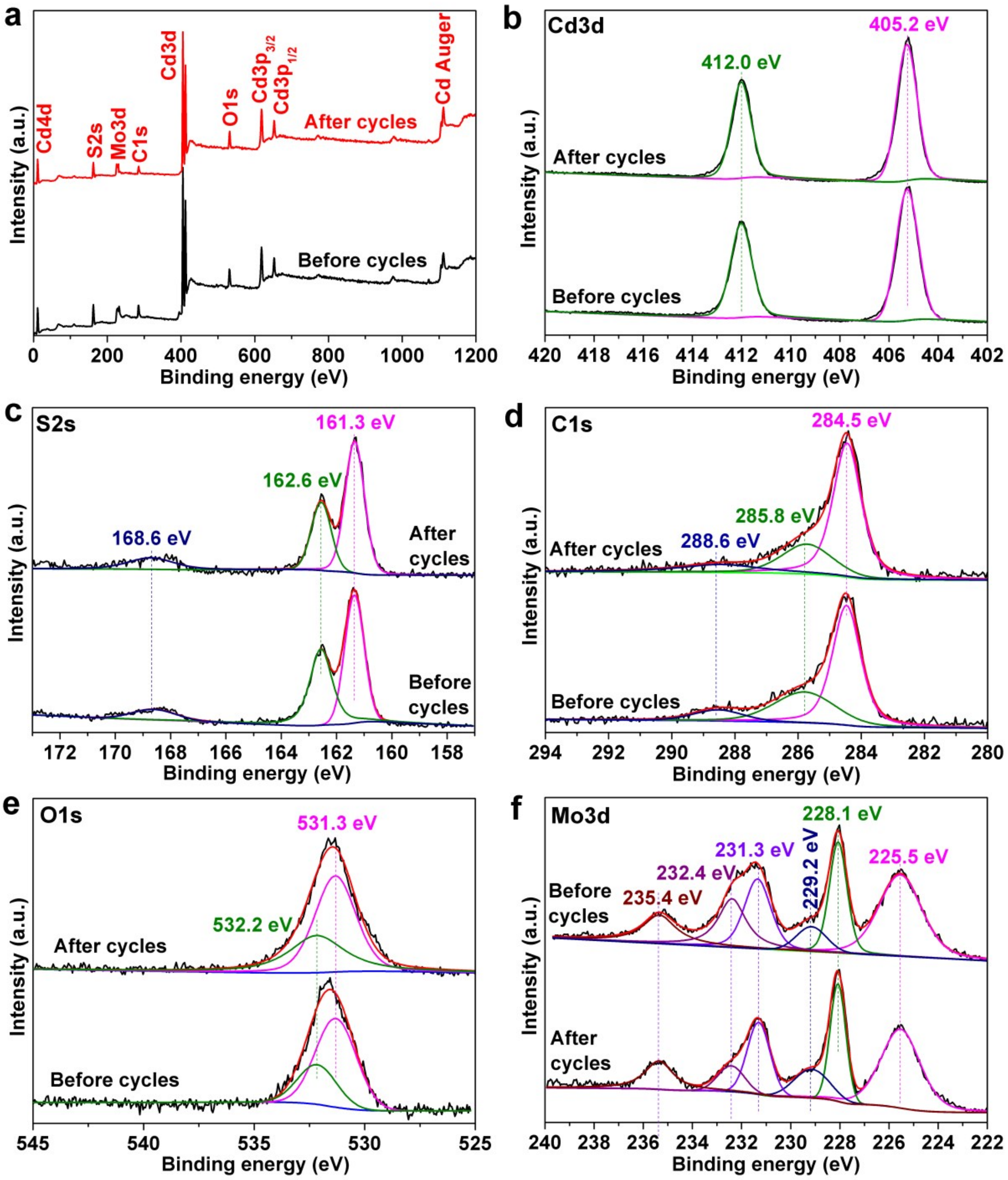


Fig. S8 XPS spectra of rGO-CdS@MoS_2 before and after the photocatalytic cycles: (a) survey spectra; (b) Cd3d; (c) S2s; (d) C1s; (e) O1s and (f) Mo3d.

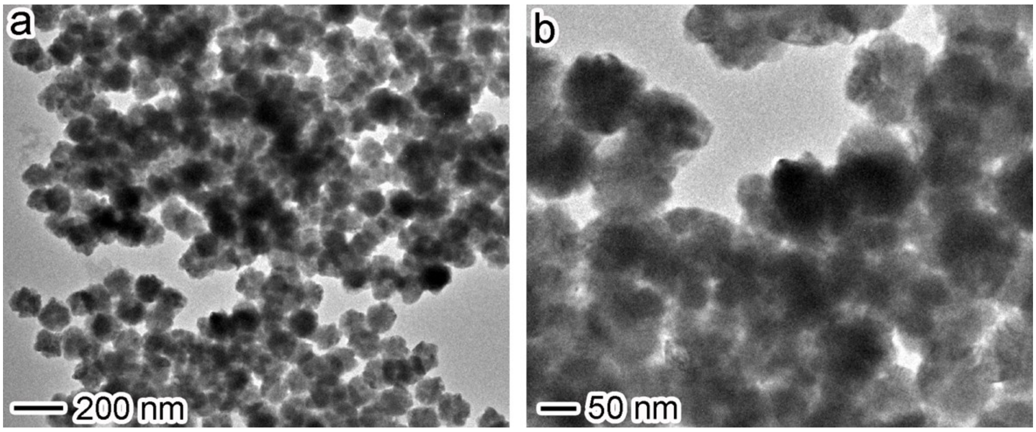


Fig. S9 TEM images of bare CdS after the photocatalytic cycles.

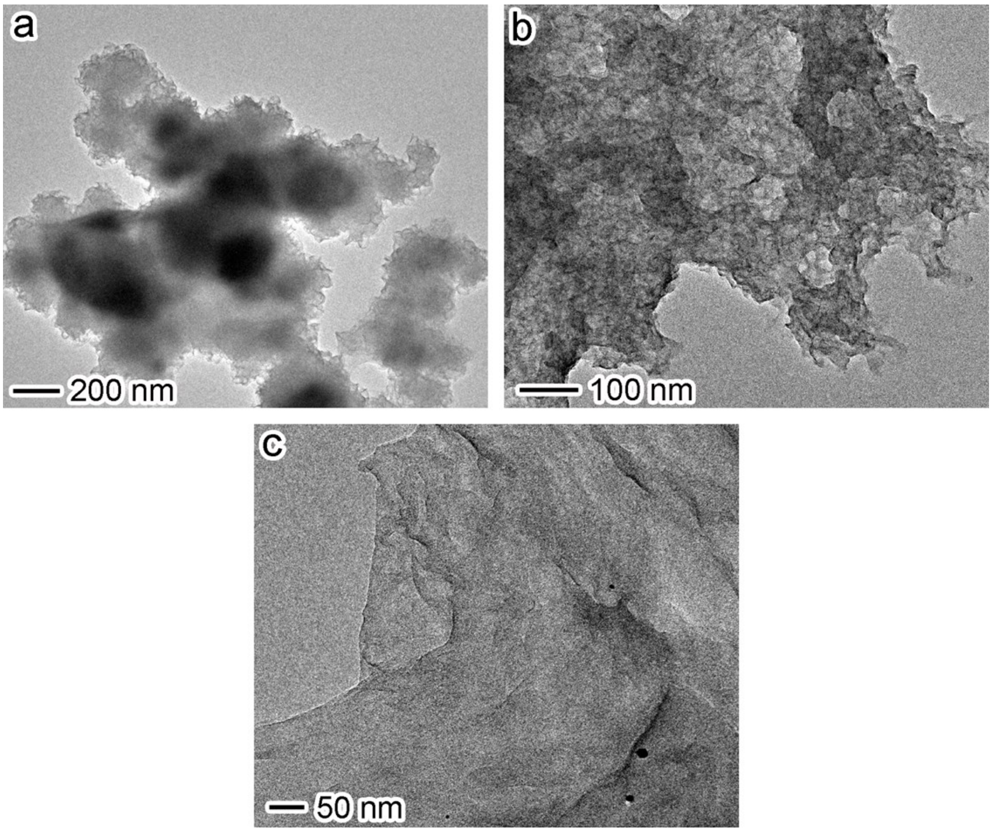


Fig. S10 TEM images of (a) 1T-MoS_2, (b) 2H-MoS_2 and (c) rGO nanosheets.

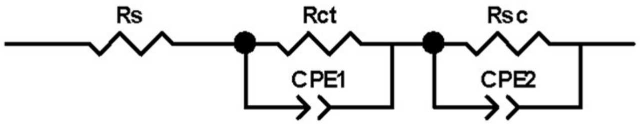
Table S1. Amounts of CdS, MoS_2 and rGO in the CdS based samples determined by the ICP-MS.

Photocatalyst	**CdS : rGO (mass ratio)**	**CdS : MoS_2 (mass ratio)**
rGO-CdS@MoS_2 (79 wt% CdS)	100.0 : 9.7	100.0 : 17.0
rGO-CdS@MoS_2 (85 wt% CdS)	100.0 : 6.6	100.0 : 11.6
rGO-CdS@MoS_2 (90 wt% CdS)	100.0 : 4.1	100.0 : 7.2
rGO-CdS@MoS_2 (94 wt% CdS)	100.0 : 2.1	100.0 : 3.8
rGO-CdS@MoS_2 (98 wt% CdS)	100.0 : 0.7	100.0 : 1.3
rGO-CdS	100.0 : 4.1	—
CdS@MoS_2	—	100.0 : 7.2
rGO@MoS_2-CdS	100 : 4.0	100.0 : 7.1

Table S2. Comparison of the photocatalytic performance of as-obtained rGO-CdS@MoS_2 in H_2 evolution with those of previous reported rGO-CdS-MoS_2 photocatalyst.

Photocatalyst	**Reaction conditions**		**Activity (mmol g_{cat}^{-1} h^{-1})**	**Stability**	**Ref.**
	Light source	Sacrificial reagent			
rGO-CdS-MoS_2	Xe (300 W, λ ＞ 420 nm)	lactic acid	9	No significant activity loss after 25 h	21
rGO-CdS-MoS_2	Xe (300 W, λ ＞ 400 nm)	lactic acid	1.9	—	38
rGO-CdS-MoS_2	UV (500 W, 280-320 nm)	lactic acid	6.8	—	49
rGO-CdS-MoS_2	Xe (350 W, λ ＞ 420 nm)	lactic acid	2.0	No significant activity loss after 20 h	50
rGO-CdS-MoS_2	Xe (300 W, λ ＞ 420 nm)	lactic acid	1.6	No significant activity loss after 30 h	51
rGO-CdS-MoS_2	Xe (300 W, λ ＞ 420 nm)	lactic acid	7.1	—	52
rGO-CdS-MoS_2	Xe (300 W, λ ＞ 420 nm)	lactic acid	12.8	Lower than 10% activity deterioration after 20 h	23
rGO-CdS-MoS_2	Xe (350 W, λ ＞ 420 nm)	lactic acid	12.4	—	53
rGO-CdS@MoS_2	Xe (300 W, λ ＞ 420 nm)	lactic acid	14.4	3.5% activity deterioration after 20 h	★

Table S3. Equivalent circuit of EIS plots and values of elements in equivalent circuit resulted from fitting the EIS data.



Sample	**CdS**[a]	**rGO-CdS**	**MoS_2@CdS**	**rGO@MoS_2-CdS**	**rGO-CdS@MoS_2**
R_s (Ω cm^{-2})	—	1.89	1.533	1.695	0.91534
R_{ct} (Ω cm^{-2})	—	45.51	55.15	38.56	25.84
R_{sc} (Ω cm^{-2})	—	719.5	373.1	241.6	123.7
CPE1-T	—	7.1011E-06	7.8127E-06	3.505E-06	8.0368E-06
CPE1-P	—	0.84646	0.87437	0.90129	0.89072
CPE2-T	—	0.0014943	0.0023809	0.002954	0.0064813
CPE2-P	—	0.81083	0.81283	0.87282	0.88387

[a] CdS is not fitted with the equivalent circuit in Fig. 5b.

References

S1 W. Hummers and R. Offeman, *J. Am. Chem. Soc.*, 1958, **80**, 1339.

S2 G. Lin, J. Zheng and R. Xu, *J. Phys. Chem. C*, 2008, **112**, 7363.