

Supporting Information

TiO₂/CdS porous hollow microspheres rapidly synthesized by salt-assistant aerosol decomposition method for excellent photocatalytic hydrogen evolution performance

Yu Huang,^a Jun Chen,^{a,b,*} Wei Zou,^a Linxing Zhang,^a Lei Hu,^a Min He,^c Lin Gu,^c Jinxia Deng^a and Xianran Xing^{a,*}

^a Department of Physical Chemistry, University of Science and Technology Beijing, Beijing 100083, China.

^b Beijing Key Laboratory of Special Melting and Preparation of High-End Metal Materials, Beijing 100083, China.

^c Beijing Laboratory for Electron Microscopy, The Institute of Physics, Chinese Academy of Sciences, Beijing 100190, China.

Experimental section

Sample preparation

Synthesis of TiO₂/CdS solid spheres and dispersed particles. TiO₂/CdS solid spheres and dispersed particles were synthesized through a similar process. TiO₂/CdS solid spheres were synthesized without adding NaCl and the other reaction conditions were the same with above synthesis of TiO₂/CdS porous hollow spheres. TiO₂/CdS dispersed particles were synthesized with adding excess content of NaCl, (Ti + Cd): Na = 1:5. The other reaction conditions were the same with above synthesis of TiO₂/CdS porous hollow spheres.

Synthesis of simple CdS and simple TiO₂. Simple CdS were synthesized without adding TiCl₄ and the other reaction conditions were the same with above synthesis of TiO₂/CdS porous hollow spheres. Simple TiO₂ were synthesized without adding Cd(NO₃)₂·4H₂O and the other reaction conditions were the same with above synthesis of TiO₂/CdS porous hollow spheres.

The physical mixture of CdS with TiO₂. According to ICP of TiO₂/CdS porous hollow spheres, simple CdS and simple TiO₂ was directly mix together as a reference photocatalyst.

Characterization

The crystal structure of TiO₂/CdS products was characterized by x-ray diffraction patterns (PANalytical X'Pert Powder PW3040/60, Holland) with Cu K α 1 radiation. The microstructure and morphology were carried out by a scanning electron microscope (Supra 55; Zeiss, Oberkochen, Germany), and high-resolution transmission electron microscope (HRTEM, JEM-2010; JEOL, Ltd., Tokyo, Japan). A spectrophotometer (Carry 5000 UV-Vis-NIR, America) was used to record the UV/Vis spectra of various samples. The specific surface area was measured by nitrogen adsorption/desorption at 77 K using Brunauer–Emmett–Teller (BET) method (Quadasorb Si, Quantachrome, America). The chemical composition of TiO₂/CdS porous hollow spheres was analyzed by inductively coupled plasma mass spectrometry (ICP-MS, Agilent 7500C).

Photocatalytic H₂-production activity

Before reaction, Ru was deposition on photocatalyst by photodeposition method under visible light: photocatalyst was added in aqueous solution containing 1.5 wt% of RuCl₃·3H₂O and lighted for 20 minutes. The photocatalytic hydrogen evolution reactions were performed in Labsolar II system (Beijing Perfectlight Technology Co. Ltd.). 300 mL Pyrex reaction vessel is connected to a closed gas circulation and an evacuation system at 15 °C. The evolved gases were measured by an online gas chromatograph (GC 7900, Techcomp) equipped with a molecular sieve (5 Å pore size) and Ar carrier gas. Under continuous stirring, 50 mg photocatalysts were dispersed into 100 mL deionized water containing 0.35 M Na₂S·9H₂O and 0.25 M K₂SO₃ as sacrificial reagents by ultrasonication for 5 min (pH = 13.6). Prior to irradiation, the system was vacuumized for 30 min to remove the dissolved gases in water. A continuous magnetic stirrer was applied at the bottom of the reactor in order to keep the photocatalyst particles in suspension status during the whole experiment. A 300 W Xe lamp was used as a light source and 15 cm away from the reactor. A UV cut-off filter ($\lambda \geq 420$ nm) was used to be the visible light source for the photocatalytic hydrogen evolution reaction. The illumination intensity was 201 mW/cm² on the solution surface and the illumination area was 38.5 cm². The apparent quantum efficiency (AQE) was measured under the same conditions except that the 420 nm cut-off filter was changed to 420 nm band-pass filter (Figure S1). In the experiment, the irradiation intensity after the 420 nm band-pass filter was determined to be 9 mW/cm². The reaction solution was irradiated for 3h to calculate AQE according to the following equation:

$$\text{AQE} = \frac{\text{The number of reacted electrons}}{\text{The number of incident photons}} \times 100\%$$

$$= \frac{\text{The number of evolved H}_2 \text{ molecular} \times 2}{\text{The number of incident photons}} \times 100\%$$

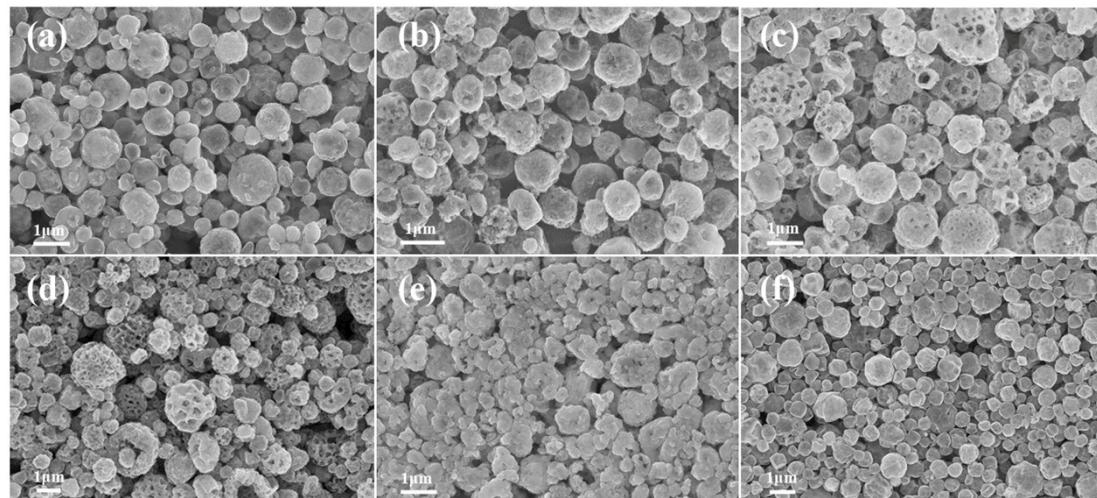


Figure S1. Microstructure of TiO₂/CdS prepared by adding different NaCl salt content, simple CdS and simple TiO₂: (a) (Ti + Cd): Na = 1:1; (b) (Ti + Cd): Na = 1:2; (c) (Ti + Cd): Na = 1:2.5; (d) (Ti + Cd): Na = 1:4; (e) simple CdS; (f) simple TiO₂.

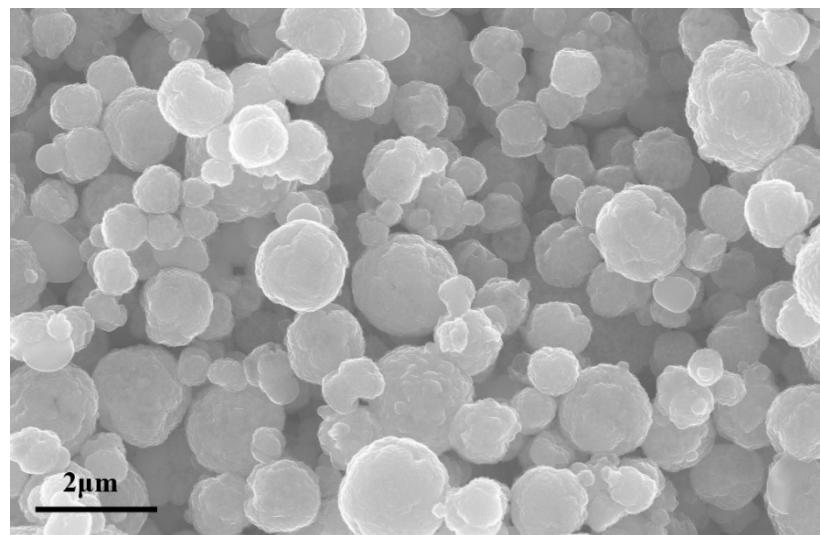


Figure S2. The SEM of TiO_2/CdS porous hollow microspheres before washing with water.

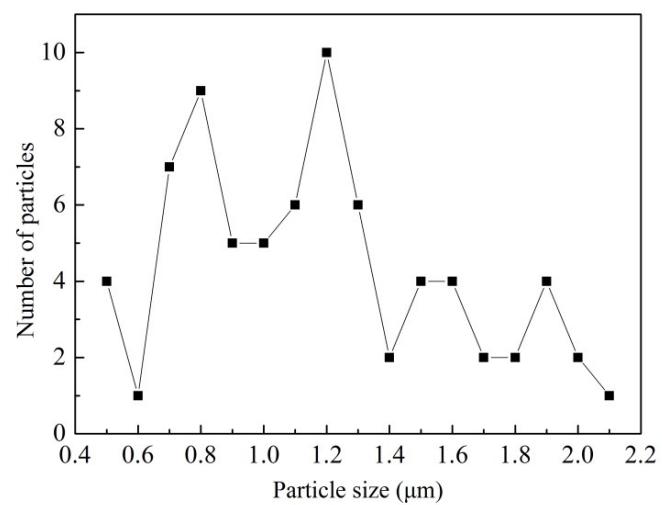


Figure S3. Particle size distribution of TiO_2/CdS porous hollow microspheres.

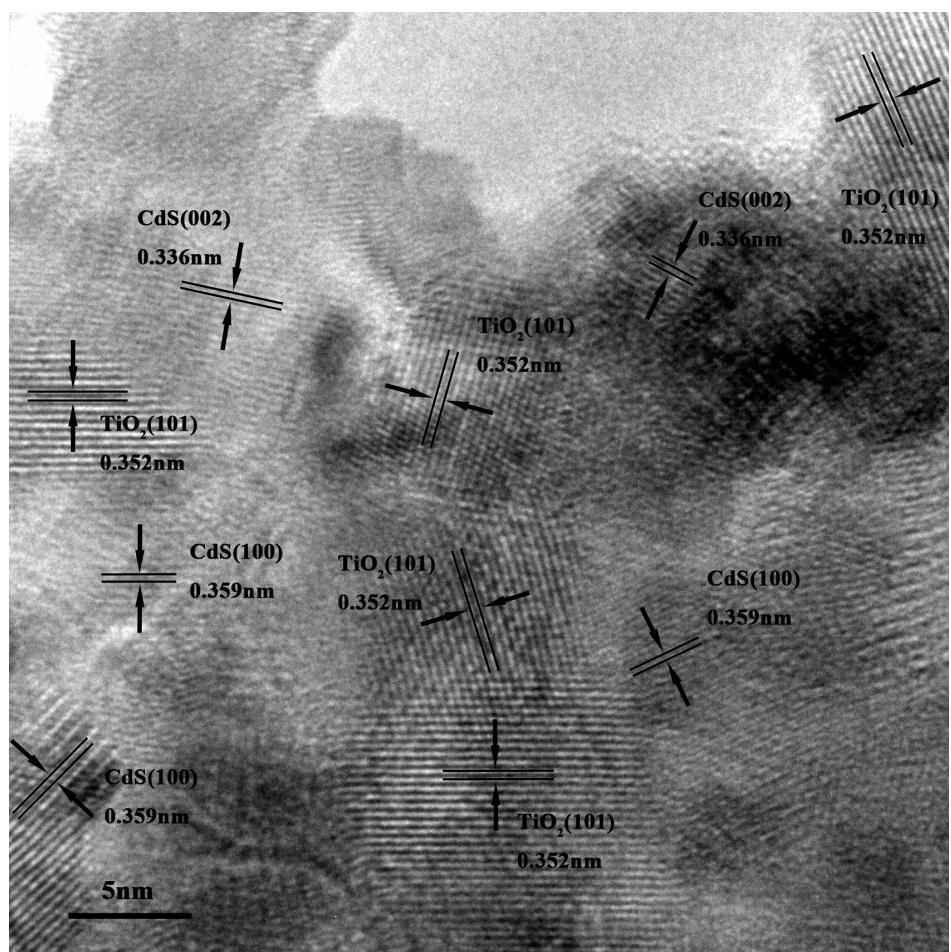


Figure S4. Higher scope HRTEM image of the TiO_2/CdS porous hollow spheres.

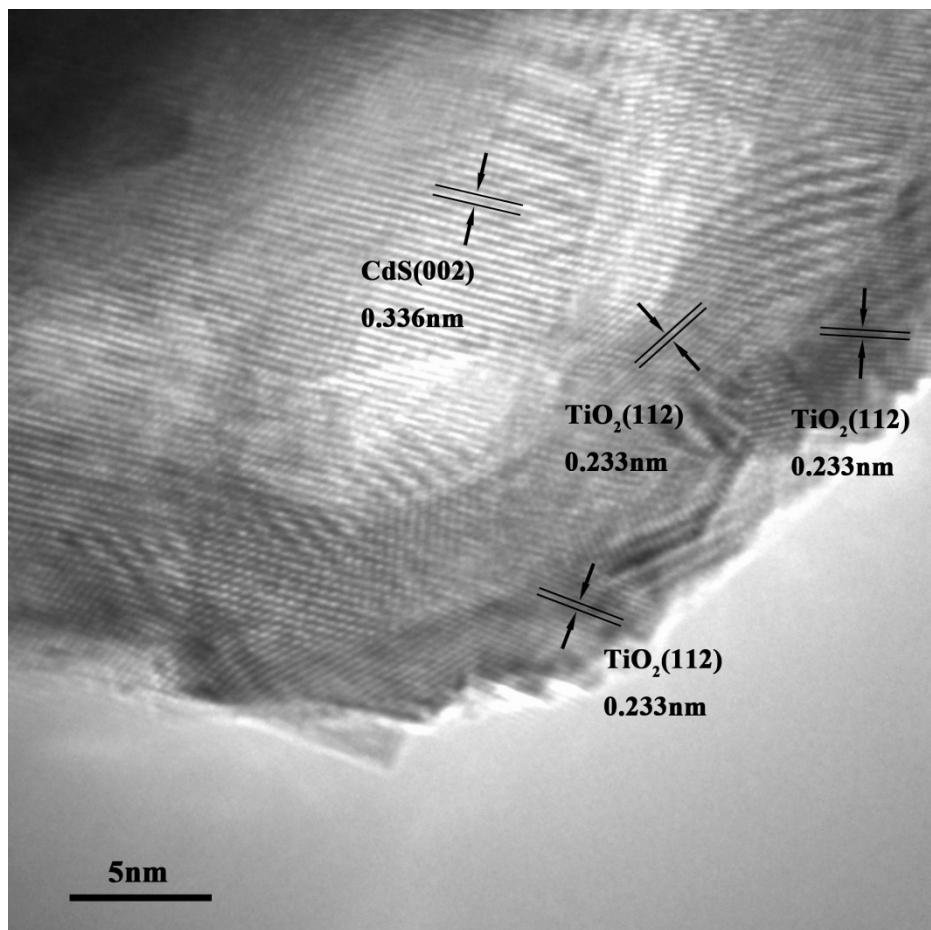


Figure S5. HRTEM image of the TiO₂/CdS dispersed particles.

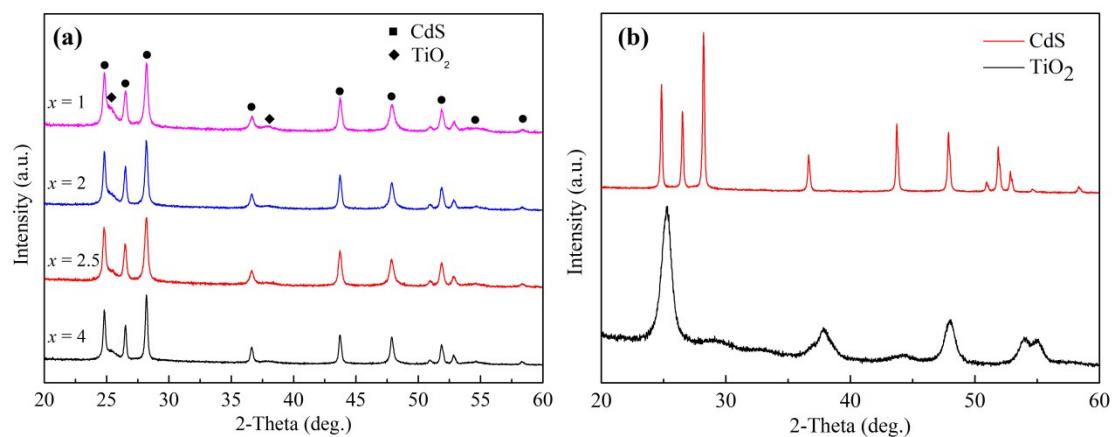


Figure S6. (a) XRD patterns of TiO₂/CdS prepared by adding different NaCl salt content into the precursor, (Ti + Cd): Na = x; (b) XRD spectra of simple TiO₂ and CdS.

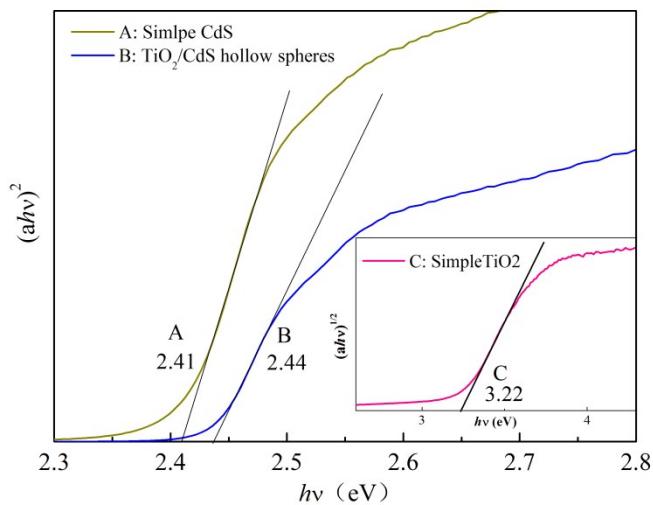


Figure S7. The plot of $(\alpha h\nu)^2$ and $(\alpha h\nu)^{1/2}$ (insets) versus $h\nu$.

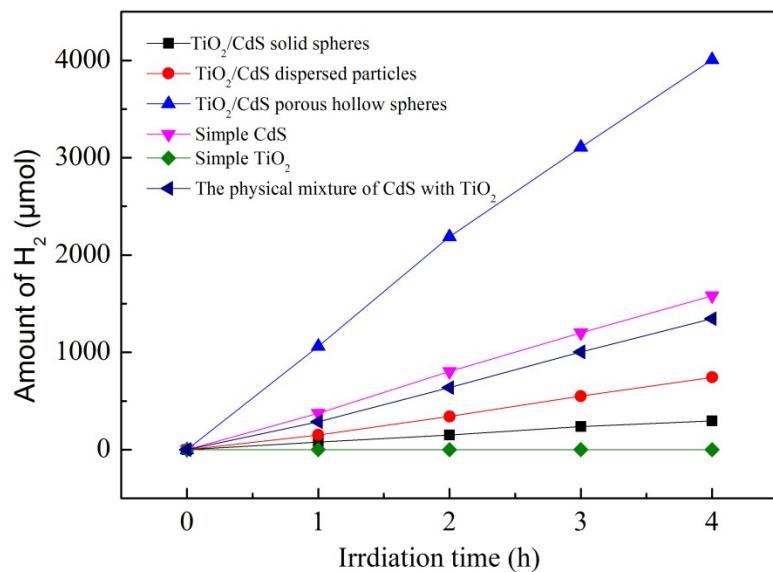


Figure S8. The time courses of hydrogen production in 4 hours.

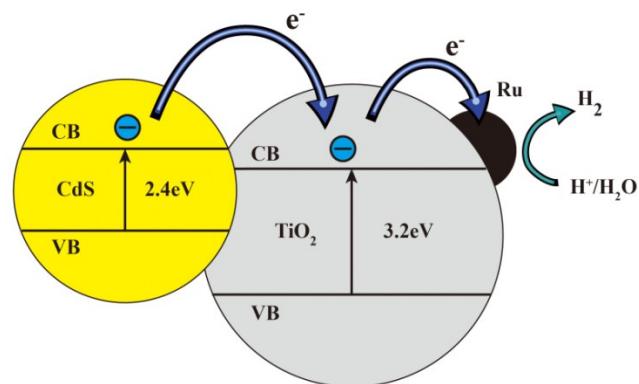


Figure S9. The illustration of electron transfer between CdS and TiO₂.

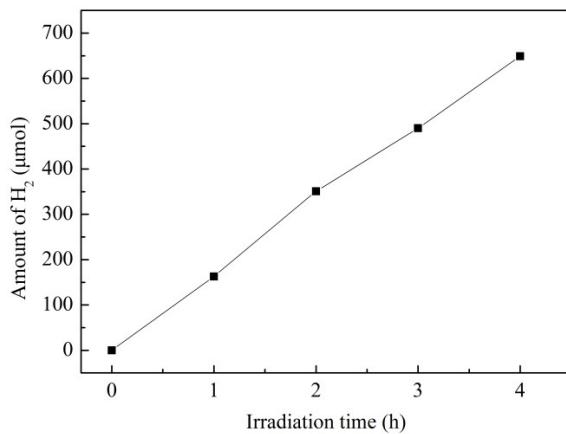


Figure S10. Photocatalytic hydrogen evolution amounts of TiO_2/CdS porous hollow spheres in 4 hours without loaded Ru co-catalyst.

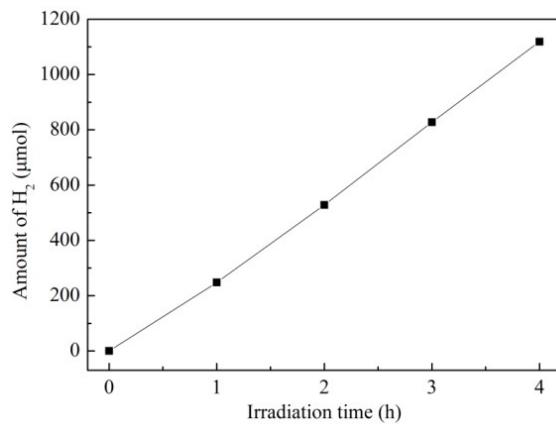


Figure S11. Photocatalytic hydrogen evolution amounts of TiO_2/CdS porous hollow spheres in 4 hours after adding the 420 nm band-pass filter.

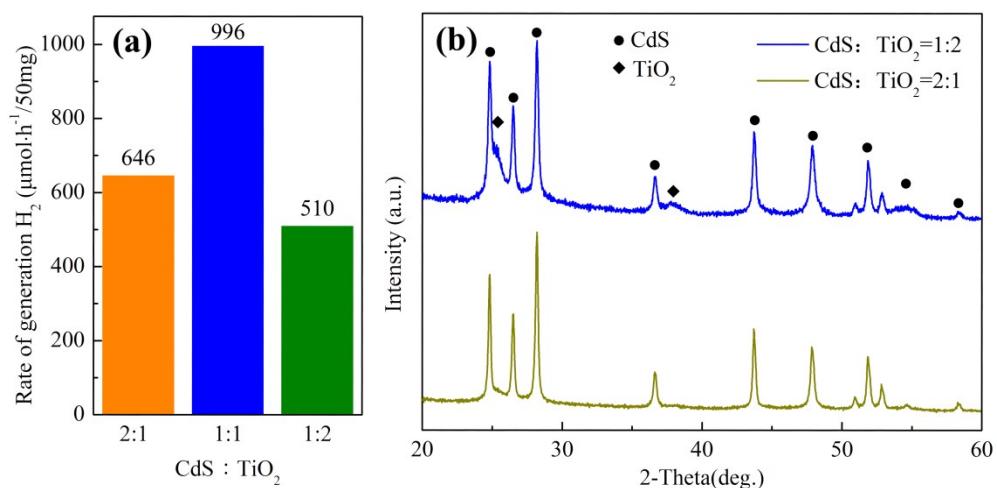


Figure S12. (a) Photocatalytic hydrogen evolution amounts of TiO_2/CdS with different Ti: Cd mole ratio; (b) The XRD patterns of TiO_2/CdS with different Ti: Cd mole ratio.

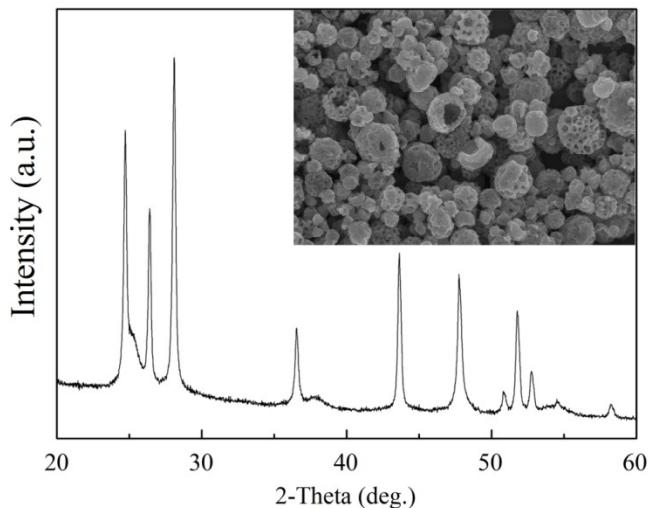


Figure S13. The XRD and SEM (insets) image of TiO_2/CdS porous hollow spheres with Ru-loaded after 20 hours photocatalytic hydrogen evolution reaction.

Table S1. Photocatalytic hydrogen evolution amounts of TiO_2/CdS porous hollow spheres synthesized with four times.

1	2	3	4	Average
980 $\mu\text{mol h}^{-1}$	994 $\mu\text{mol h}^{-1}$	1007 $\mu\text{mol h}^{-1}$	1002 $\mu\text{mol h}^{-1}$	996 $\mu\text{mol h}^{-1}$

Table S2. The details for the comparison of the performance of the present photocatalyst TiO_2/CdS porous hollow microspheres with other materials.

Photocatalyst	Co-catalyst	Light source	Reactant Solution	QY(420 nm)	H ₂ evolution	
					$\mu\text{mol h}^{-1}$	$\mu\text{mol h}^{-1} \text{g}^{-1}$
TiO_2/CdS porous hollow spheres (0.05g) (Present work)	Ru(1.5 wt%)	300 W Xe lamp ($\lambda \geq 420$ nm)	K_2SO_3 (0.25 M) Na_2S (0.35 M) aqueous solution	12.8%	996	19920
$\text{CdS}(\text{NW})/\text{TiO}_2$ (0.1g) [1]	Pt(1 wt%)	450 W Hg lamp ($\lambda \geq 420$ nm)	Na_2SO_3 (0.02 M) Na_2S (0.1 M) aqueous solution		11	110
Pt/ La^{3+} / $\text{TiO}_2\text{-CdS}$ (0.1g) [2]	Pt(1 wt%)	400 W Hg lamp ($\lambda \geq 420$ nm)	Na_2SO_3 (0.02 M) Na_2S (0.1 M) aqueous solution	10.8%	226	2260
$\text{CdS}/(\text{Pt-TiO}_2)$ (0.0125g) [3]	Pt	450 W Xe lamp ($\lambda \geq 420$ nm)	Na_2SO_3 (0.04 M) Na_2S (0.04 M) aqueous solution	4.5%		6700

CdS(bulk)/TiO ₂ (0.1g) [4]	Pt(1 wt%)	500 W Hg lamp ($\lambda \geq 420$ nm)	Na ₂ SO ₃ (0.02 M) Na ₂ S(0.1 M) aqueous solution		422	4220
CdS/TiO ₂ (0.1g) [5]	Pt(2 wt%)	500 W Hg lamp ($\lambda \geq 420$ nm)	Na ₂ SO ₃ (0.02 M) Na ₂ S(0.1 M) aqueous solution		560	5600
CdS(bulk)/TiO ₂ (0.1g) [6]	Pt(0.75 wt%)	350 W Hg lamp ($\lambda \geq 420$ nm)	Na ₂ SO ₃ (0.02 M) Na ₂ S(0.1 M) aqueous solution		640	6400
CdS-Pt/TiO ₂ (0.04g) [7]	Pt	350 W Xe lamp ($\lambda \geq 420$ nm)	lactic acid aqueous solutions	13.9%	265	6400
CdS/TiO ₂ NT (0.15g) [8]	Pt(1 wt%)	300 W Xe lamp ($\lambda \geq 420$ nm)	Na ₂ SO ₃ (0.35 M) Na ₂ S(0.25 M) aqueous solution	43.4%	402	2680
CdS (0.03g) [9]	Pt(10 wt%)	500 W Xe lamp ($\lambda \geq 420$ nm)	Na ₂ SO ₃ (0.1 M) Na ₂ S(0.1 M) aqueous solution		138	4600
CdSe/CdS/Pt [10]	Pt	450 W Xe lamp ($\lambda \geq 420$ nm)	Na ₂ SO ₃ (0.1 M) Na ₂ S(0.1 M) aqueous solution			434
Au/CdS/ZnO (0.1g) [11]	Au(1 wt%)	450 W Hg lamp ($\lambda \geq 420$ nm)	Na ₂ SO ₃ (0.1 M) Na ₂ S(0.1 M) aqueous solution		61	610
ZnO–CdS@Cd (0.1g) [12]	Pt(3 wt%)	300 W Xe lamp ($\lambda \geq 420$ nm)	Na ₂ SO ₃ (0.1 M) Na ₂ S(0.1 M) aqueous solution		1920	19200
In ₂ O ₃ /Ta ₂ O ₅ (0.05g) [13]	Pt(1 wt%)	300 W Xe lamp ($\lambda \geq 420$ nm)	20 vol.% methanol aqueous solution,			189
TiO ₂ /MoS ₂ /graphene (0.08g) [14]	MoS ₂ /graphene (0.5 wt%)	300 W Xe lamp (UV irradiation)	25 vol.% ethanol aqueous solution,	9.7%(36 5 nm)	165	2063
TiO ₂ @MoS ₂ [15]	without cocatalyst	visible light irradiation	Na ₂ SO ₃ (0.25 M) Na ₂ S(0.35 M) aqueous solution			1600
MoS ₂ /CdS (0.1g) [16]	MoS ₂ (0.2 wt%)	300 W Xe lamp ($\lambda \geq 420$ nm)	10 vol.% lactic aqueous solution		540	5400
TiO ₂ /AgGaS ₂ (0.1g) [17]	Pt(1 wt%)	450 W Hg lamp ($\lambda \geq 420$ nm)	Na ₂ SO ₃ (0.02 M) Na ₂ S(0.1 M) aqueous solution		420	4200

SiC/CdS (0.05) [18]	Pt(3 wt%)	300 W Xe lamp ($\lambda \geq 420$ nm)	Na ₂ SO ₃ (0.1 M) Na ₂ S(0.1 M) aqueous solution	2.1%	273	5460
(AgIn) _{0.22} Zn _{1.56} S ₂ (0.3 g) [19]	Pt(3 wt%)	300 W Xe lamp ($\lambda \geq 420$ nm)	K ₂ SO ₃ (0.25 M) Na ₂ S(0.35 M) aqueous solution	20%	944	3147
AgInZn ₇ S ₉ (0.3 g) [20]	Pt(3 wt%)	300 W Xe lamp ($\lambda \geq 420$ nm)	K ₂ SO ₃ (0.25 M) Na ₂ S(0.35 M) aqueous solution	15%	940	3133
GuGa ₂ In ₃ S ₈ (0.3 g) [21]	Rh(1.5 wt%)	300 W Xe lamp ($\lambda \geq 420$ nm)	K ₂ SO ₃ (0.5 M) Na ₂ S(0.2 M) aqueous solution	15%	3200	10667
(CuIn) _{0.09} Zn _{1.82} S ₂ (0.3 g) [22]	Ru(0.5 wt%)	300 W Xe lamp ($\lambda \geq 420$ nm)	K ₂ SO ₃ (0.25 M) Na ₂ S(0.35 M) aqueous solution	12.5%	1227	4090

References of Table S2.

[1] Jang J. S., Kim H. G., Joshi U. A., et al., Fabrication of CdS nanowires decorated with TiO₂ nanoparticles for photocatalytic hydrogen production under visible light irradiation. Int. J. Hydrogen. Energ. 33 (2008) 5975-5980.

[2] Peng S., Huang Y., Li Y., Rare earth doped TiO₂-CdS and TiO₂-CdS composites with improvement of photocatalytic hydrogen evolution under visible light irradiation. Mat. Sci. Semicon. Proc. 16 (2013) 62-69.

[3] Park H., Choi W., Hoffmann M. R., Effects of the preparation method of the ternary CdS/TiO₂/Pt hybrid photocatalysts on visible light-induced hydrogen production. J. Mater. Chem. 18 (2008) 2379-2385.

[4] Jang J. S., Li W., Oh S. H., et al., Fabrication of CdS/TiO₂ nano-bulk composite photocatalysts for hydrogen production from aqueous H₂ S solution under visible light. Chem. Phys. Lett. 425 (2006) 278-282.

[5] Jang J. S., Choi S. H., Kim H. G., et al., Location and state of Pt in platinized CdS/TiO₂ photocatalysts for hydrogen production from water under visible light. J. Phys. Chem. C 112 (2008) 17200-17205.

[6] Jang J. S., Ji S. M., Bae S. W., et al., Optimization of CdS/TiO₂ nano-bulk composite photocatalysts for hydrogen production from Na₂S/Na₂SO₃ aqueous electrolyte solution under visible light($\lambda \geq 420$ nm). J. Photoch. Photobio. A 118 (2007) 112-119.

[7] Qi L., Yu J., Jaroniec M., Preparation and enhanced visible-light photocatalytic H₂-production activity of CdS-sensitized Pt/TiO₂ nanosheets with exposed (001) facets. Phys. Chem. Chem. Phys. 13 (2011) 8915-8923.

[8] Li C., Yuan J., Han B., et al., TiO₂ nanotubes incorporated with CdS for photocatalytic hydrogen production from splitting water under visible light irradiation. Int. J. Hydrogen. Energ. 35 (2010) 7073-7079.

[9] Muruganandham M., Kusumoto Y., Okamoto C., et al., Mineralizer-assisted shape-controlled synthesis, characterization, and photocatalytic evaluation of CdS microcrystals. J. Phys. Chem. C 113 (2009) 19506-19517.

[10] Tongying P., Vietmeyer F., Aleksiuk D., et al., Double heterojunction nanowire photocatalysts for hydrogen generation. Nanoscale 6 (2014) 4117-4124.

[11] Yu Z. B., Xie Y. P., Liu G., et al., Self-assembled CdS/Au/ZnO heterostructure induced by surface polar charges for efficient photocatalytic hydrogen evolution. J. Mater. Chem. A 1 (2013) 2773-2776.

[12] Wang X., Liu G., Wang L., et al., ZnO-CdS@Cd heterostructure for effective photocatalytic hydrogen generation. Adv. Energy. Mater. 2 (2012) 42-46.

[13] Xu L., Guan J., Gao L., et al., Preparation of heterostructured mesoporous In₂O₃/Ta₂O₅

nanocomposites with enhanced photocatalytic activity for hydrogen evolution. *Cataly. Commun.* 12 (2011) 548-552.

[14] Xiang Q., Yu J., Jaroniec M., Synergetic effect of MoS₂ and graphene as cocatalysts for enhanced photocatalytic H₂ production activity of TiO₂ nanoparticles. *J. Am. Chem. Soc.* 134 (2012) 6575-6578.

[15] Zhou W., Yin Z., Du Y., et al., Synthesis of Few-Layer MoS₂ Nanosheet-Coated TiO₂ Nanobelt Heterostructures for Enhanced Photocatalytic Activities. *small* 9 (2013) 140-147.

[16] Zong X., Yan H., Wu G., et al., Enhancement of photocatalytic H₂ evolution on CdS by loading MoS₂ as cocatalyst under visible light irradiation. *J. Am. Chem. Soc.* 130 (2008) 7176-7177.

[17] Jang J. S., Hong S. J., Kim J. Y., et al., Heterojunction photocatalyst TiO₂/AgGaS₂ for hydrogen production from water under visible light. *Chem. Phys. Lett.* 475 (2009) 78-81.

[18] Peng Y., Guo Z., Yang J., et al., Enhanced photocatalytic H₂ evolution over micro-SiC by coupling with CdS under visible light irradiation. *J. Mater. Chem. A* 2 (2014) 6296-6300.

[19] Tsuji I., Kato H., Kobayashi H., et al., Photocatalytic H₂ Evolution Reaction from Aqueous Solutions over Band Structure-Controlled (AgIn)_xZn_{2(1-x)}S₂ Solid Solution Photocatalysts with Visible-Light Response and Their Surface Nanostructures. *J. Am. Chem. Soc.* 126 (2004) 13406-13413.

[20] Kudo A., Tsuji I., Kato H., AgInZn₇S₉ solid solution photocatalyst for H₂ evolution from aqueous solutions under visible light irradiation. *Chem. Commun.* 17 (2002) 1958-1959.

[21] Kaga H., Saito K., Kudo A., Solar hydrogen production over novel metal sulfide photocatalysts of AGa₂In₃S₈(A= Cu or Ag) with layered structures. *Chem. Commun.* 46 (2010) 3779-3781.

[22] Tsuji I., Kato H., Kobayashi H., et al., Photocatalytic H₂ Evolution under Visible-Light Irradiation over Band-Structure-Controlled (CuIn)_xZn_{2(1-x)}S₂ Solid Solutions. *J. Phys. Chem. B* 109 (2005) 7323-7329.