

## Supporting Information

### TiO<sub>2</sub>/CdS porous hollow microspheres rapidly synthesized by salt-assistant aerosol decomposition method for excellent photocatalytic hydrogen evolution performance

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#### Experimental section

##### Sample preparation

**Synthesis of TiO<sub>2</sub>/CdS solid spheres and dispersed particles.** TiO<sub>2</sub>/CdS solid spheres and dispersed particles were synthesized through a similar process. TiO<sub>2</sub>/CdS solid spheres were synthesized without adding NaCl and the other reaction conditions were the same with above synthesis of TiO<sub>2</sub>/CdS porous hollow spheres. TiO<sub>2</sub>/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 TiO<sub>2</sub>/CdS porous hollow spheres.

**Synthesis of simple CdS and simple TiO<sub>2</sub>.** Simple CdS were synthesized without adding TiCl<sub>4</sub> and the other reaction conditions were the same with above synthesis of TiO<sub>2</sub>/CdS porous hollow spheres. Simple TiO<sub>2</sub> were synthesized without adding Cd(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O and the other reaction conditions were the same with above synthesis of TiO<sub>2</sub>/CdS porous hollow spheres.

**The physical mixture of CdS with TiO<sub>2</sub>.** According to ICP of TiO<sub>2</sub>/CdS porous hollow spheres, simple CdS and simple TiO<sub>2</sub> was directly mix together as a reference photocatalyst.

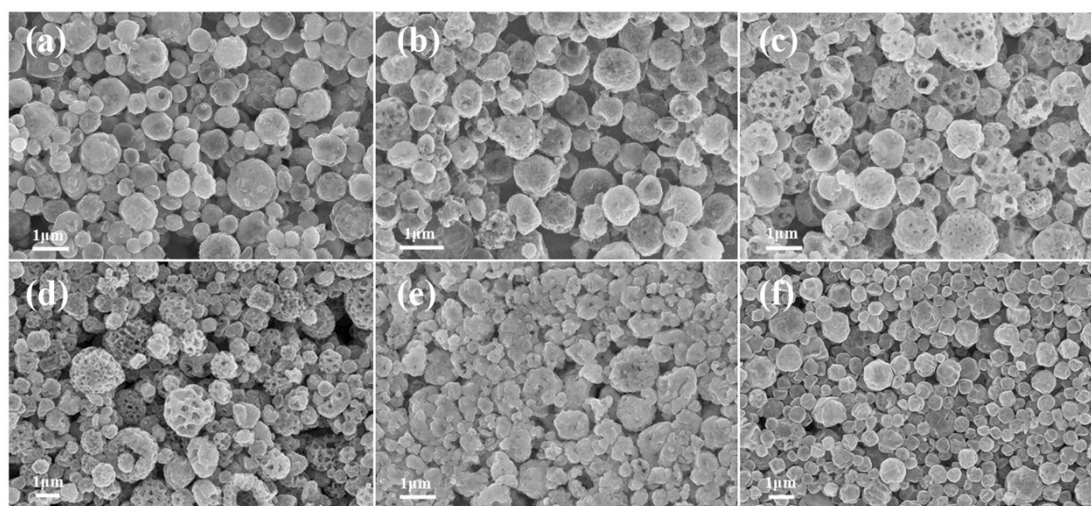
##### Characterization

The crystal structure of TiO<sub>2</sub>/CdS products was characterized by x-ray diffraction patterns (PANalytical X'Pert Powder PW3040/60, Holland) with Cu Kα1 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 (Quadrachrome Si, Quantachrome, America). The chemical composition of TiO<sub>2</sub>/CdS porous hollow spheres was analyzed by inductively coupled plasma mass spectrometry (ICP-MS, Agilent 7500C).

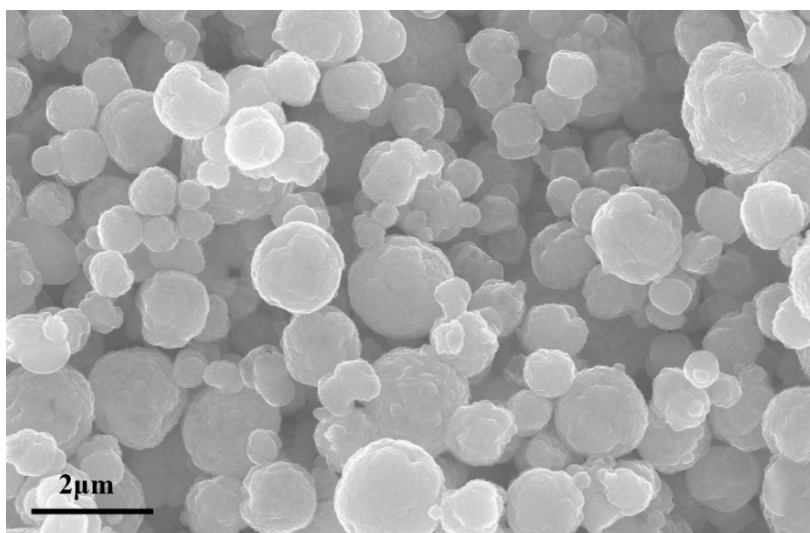
### Photocatalytic H<sub>2</sub>-production activity

Before reaction, Ru was deposition on photocatalyst by photodeposition method under visible light: photocatalyst was added in aqueous solution containing 1.5 wt% of RuCl<sub>3</sub>·3H<sub>2</sub>O 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 Na<sub>2</sub>S·9H<sub>2</sub>O and 0.25 M K<sub>2</sub>SO<sub>3</sub> 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/cm<sup>2</sup> on the solution surface and the illumination area was 38.5 cm<sup>2</sup>. 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/cm<sup>2</sup>. The reaction solution was irradiated for 3h to calculate AQE according to the following equation:

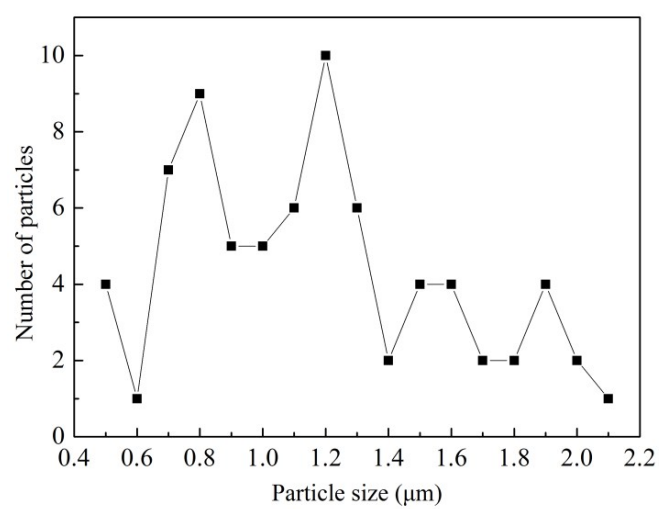
$$\text{AQE} = \frac{\text{The number of reacted electrons}}{\text{The number of incident photons}} \times 100\%$$
$$= \frac{\text{The number of evolved H}_2 \text{ molecular} \times 2}{\text{The number of incident photons}} \times 100\%$$



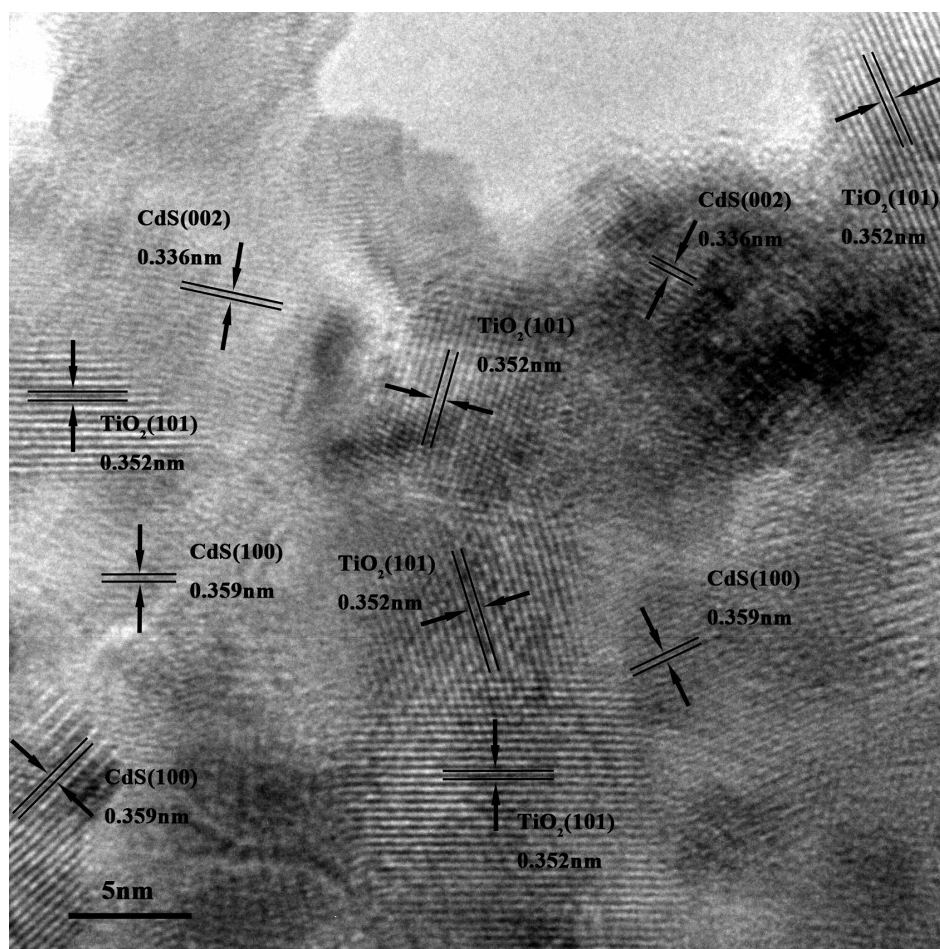
**Figure S1.** Microstructure of TiO<sub>2</sub>/CdS prepared by adding different NaCl salt content, simple CdS and simple TiO<sub>2</sub>: (a) (Ti + Cd): Na = 1:1; (b) (Ti + Cd): Na = 1:2; (c) (Ti + Cd): Na = 1:2.5; (d) (Ti + Cd): Na = 1:4; (e) simple CdS; (f) simple TiO<sub>2</sub>.



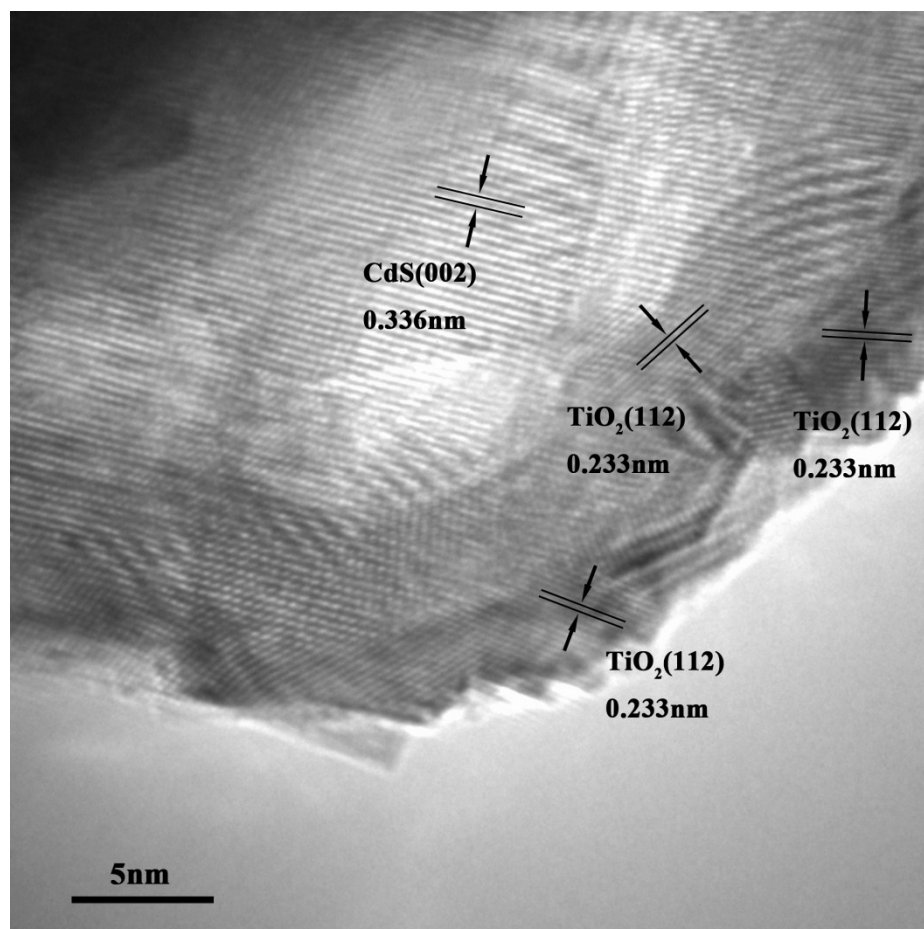
**Figure S2.** The SEM of TiO<sub>2</sub>/CdS porous hollow microspheres before washing with water.



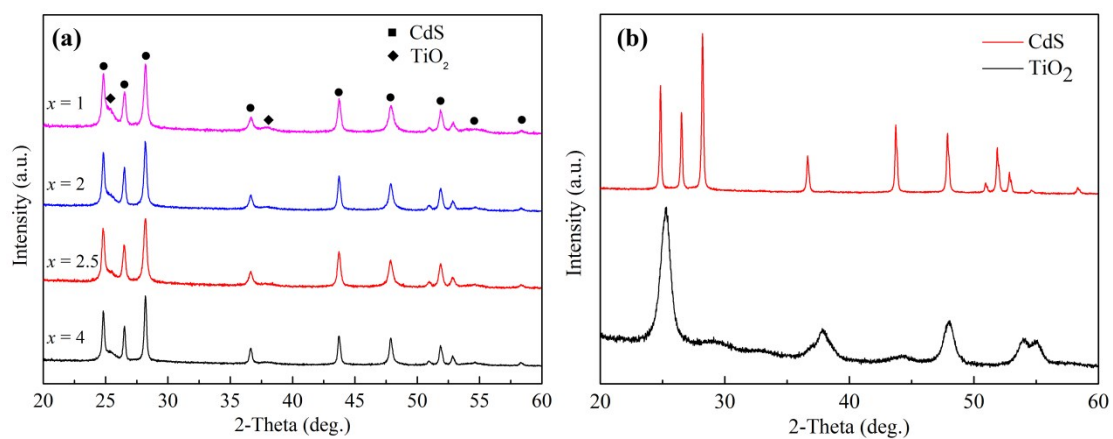
**Figure S3.** Particle size distribution of TiO<sub>2</sub>/CdS porous hollow microspheres.



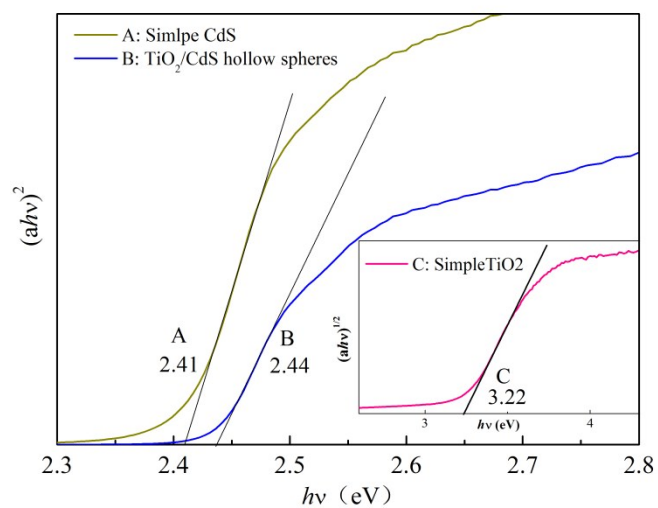
**Figure S4.** Higher scope HRTEM image of the TiO<sub>2</sub>/CdS porous hollow spheres.



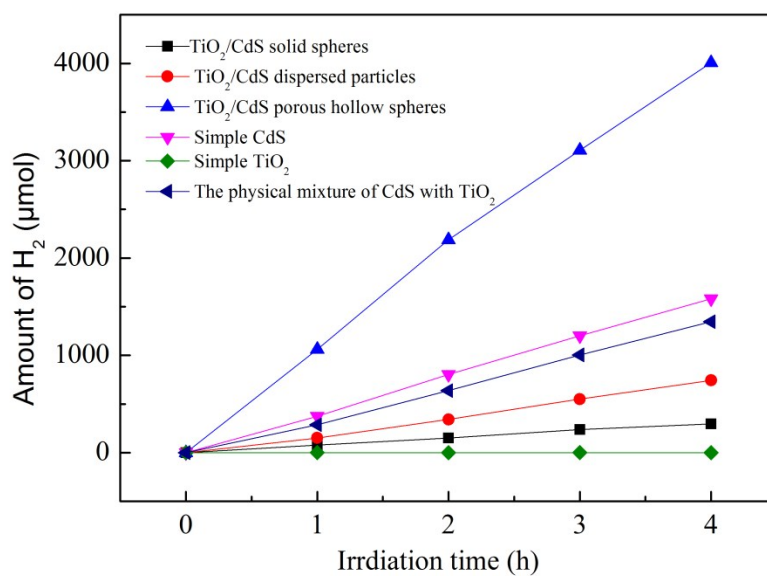
**Figure S5.** HRTEM image of the  $\text{TiO}_2/\text{CdS}$  dispersed particles.



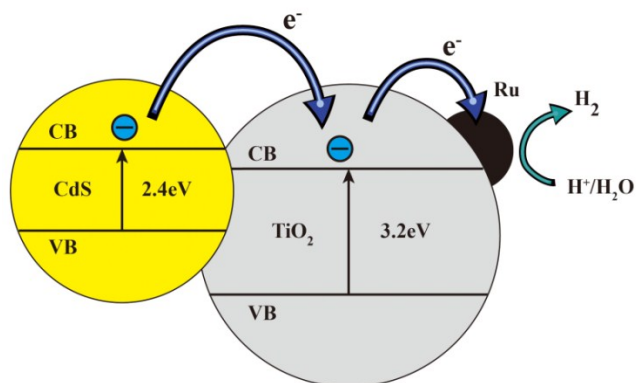
**Figure S6.** (a) XRD patterns of  $\text{TiO}_2/\text{CdS}$  prepared by adding different NaCl salt content into the precursor,  $(\text{Ti} + \text{Cd}): \text{Na} = x$ ; (b) XRD spectra of simple  $\text{TiO}_2$  and CdS.



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

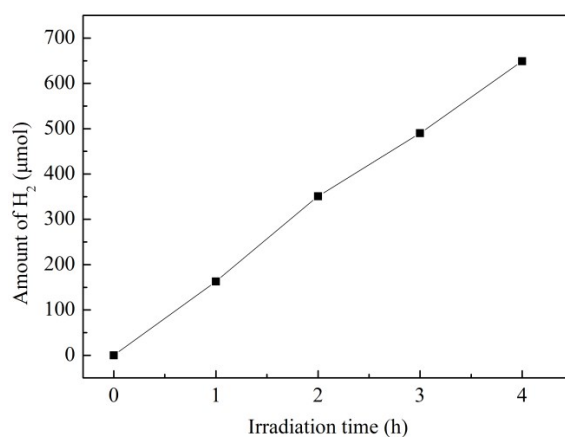


**Figure S8.** The time courses of hydrogen production in 4 hours.

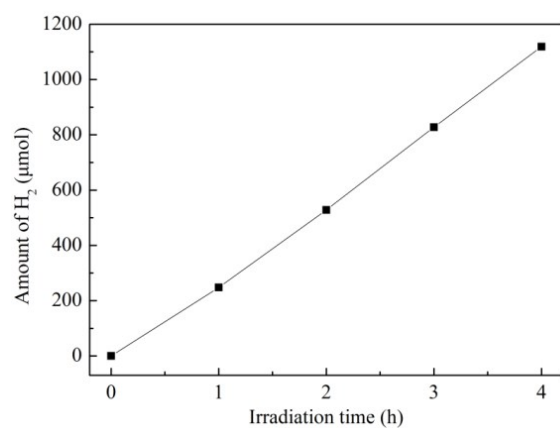


**Figure S9.** The illustration of electron transfer between CdS and TiO<sub>2</sub>.

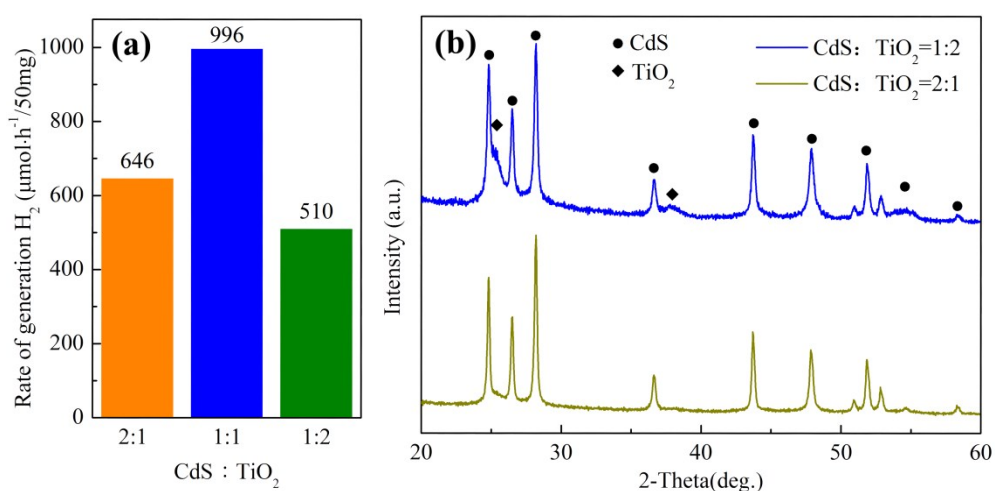




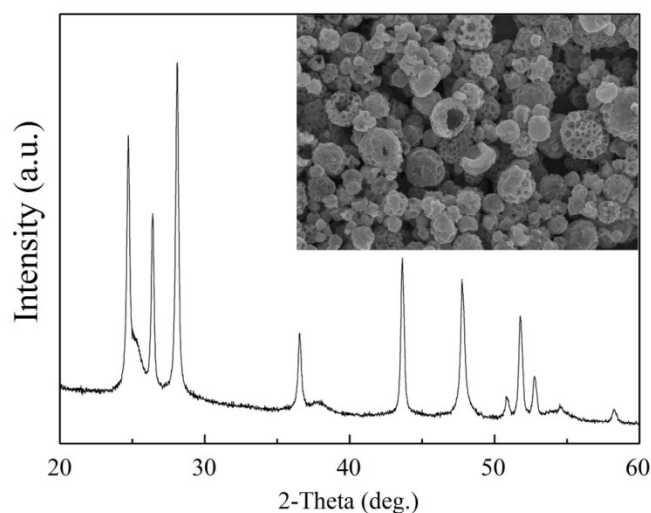
**Figure S10.** Photocatalytic hydrogen evolution amounts of TiO<sub>2</sub>/CdS porous hollow spheres in 4 hours without loaded Ru co-catalyst.



**Figure S11.** Photocatalytic hydrogen evolution amounts of TiO<sub>2</sub>/CdS porous hollow spheres in 4 hours after adding the 420 nm band-pass filter.



**Figure S12.** (a) Photocatalytic hydrogen evolution amounts of TiO<sub>2</sub>/CdS with different Ti: Cd mole ratio; (b) The XRD patterns of TiO<sub>2</sub>/CdS with different Ti: Cd mole ratio.



**Figure S13.** The XRD and SEM (insets) image of  $\text{TiO}_2/\text{CdS}$  porous hollow spheres with Ru-loaded after 20 hours photocatalytic hydrogen evolution reaction.

**Table S1.** Photocatalytic hydrogen evolution amounts of  $\text{TiO}_2/\text{CdS}$  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  $\text{TiO}_2/\text{CdS}$  porous hollow microspheres with other materials.

Photocatalyst	Co-catalyst	Light source	Reactant Solution	QY(420 nm)	H <sub>2</sub> evolution	
					$\mu\text{mol h}^{-1}$	$\mu\text{mol h}^{-1} \text{g}^{-1}$
$\text{TiO}_2/\text{CdS}$ porous hollow spheres (0.05g) (Present work)	Ru(1.5 wt%)	300 W Xe lamp ( $\lambda \geq 420 \text{ nm}$ )	$\text{K}_2\text{SO}_3$ (0.25 M) $\text{Na}_2\text{S}$ (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 ( $\lambda \geq 420 \text{ nm}$ )	$\text{Na}_2\text{SO}_3$ (0.02 M) $\text{Na}_2\text{S}$ (0.1 M) aqueous solution		11	110
$\text{Pt}/\text{La}^{3+}/\text{TiO}_2\text{-CdS}$ (0.1g) [2]	Pt(1 wt%)	400 W Hg lamp ( $\lambda \geq 420 \text{ nm}$ )	$\text{Na}_2\text{SO}_3$ (0.02 M) $\text{Na}_2\text{S}$ (0.1 M) aqueous solution	10.8%	226	2260
$\text{CdS}/(\text{Pt-TiO}_2)$ (0.0125g) [3]	Pt	450 W Xe lamp ( $\lambda \geq 420 \text{ nm}$ )	$\text{Na}_2\text{SO}_3$ (0.04 M) $\text{Na}_2\text{S}$ (0.04 M) aqueous solution	4.5%		6700



CdS(bulk)/TiO <sub>2</sub> (0.1g) [4]	Pt(1 wt%)	500 W Hg lamp ( $\lambda \geq 420$ nm)	Na <sub>2</sub> SO <sub>3</sub> (0.02 M) Na <sub>2</sub> S(0.1 M) aqueous solution		422	4220
CdS/TiO <sub>2</sub> (0.1g) [5]	Pt(2 wt%)	500 W Hg lamp ( $\lambda \geq 420$ nm)	Na <sub>2</sub> SO <sub>3</sub> (0.02 M) Na <sub>2</sub> S(0.1 M) aqueous solution		560	5600
CdS(bulk)/TiO <sub>2</sub> (0.1g) [6]	Pt(0.75 wt%)	350 W Hg lamp ( $\lambda \geq 420$ nm)	Na <sub>2</sub> SO <sub>3</sub> (0.02 M) Na <sub>2</sub> S(0.1 M) aqueous solution		640	6400
CdS-Pt/TiO <sub>2</sub> (0.04g) [7]	Pt	350 W Xe lamp ( $\lambda \geq 420$ nm)	lactic acid aqueous solutions	13.9%	265	6400
CdS/TiO <sub>2</sub> NT (0.15g) [8]	Pt(1 wt%)	300 W Xe lamp ( $\lambda \geq 420$ nm)	Na <sub>2</sub> SO <sub>3</sub> (0.35 M) Na <sub>2</sub> 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 <sub>2</sub> SO <sub>3</sub> (0.1 M) Na <sub>2</sub> S(0.1 M) aqueous solution		138	4600
CdSe/CdS/Pt [10]	Pt	450 W Xe lamp ( $\lambda \geq 420$ nm)	Na <sub>2</sub> SO <sub>3</sub> (0.1 M) Na <sub>2</sub> 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 <sub>2</sub> SO <sub>3</sub> (0.1 M) Na <sub>2</sub> 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 <sub>2</sub> SO <sub>3</sub> (0.1 M) Na <sub>2</sub> S(0.1 M) aqueous solution		1920	19200
In <sub>2</sub> O <sub>3</sub> /Ta <sub>2</sub> O <sub>5</sub> (0.05g) [13]	Pt(1 wt%)	300 W Xe lamp ( $\lambda \geq 420$ nm)	20 vol.% methanol aqueous solution,			189
TiO <sub>2</sub> /MoS <sub>2</sub> /graphen e (0.08g) [14]	MoS <sub>2</sub> /graphene (0.5 wt%)	300 W Xe lamp (UV irradiation)	25 vol.% ethanol aqueous solution,	9.7%(36 5 nm)	165	2063
TiO <sub>2</sub> @MoS <sub>2</sub> [15]	without cocatalyst	visible light irradiation	Na <sub>2</sub> SO <sub>3</sub> (0.25 M) Na <sub>2</sub> S(0.35 M) aqueous solution			1600
MoS <sub>2</sub> /CdS (0.1g) [16]	MoS <sub>2</sub> (0.2 wt%)	300 W Xe lamp ( $\lambda \geq 420$ nm)	10 vol.% lactic aqueous solution		540	5400
TiO <sub>2</sub> /AgGaS <sub>2</sub> (0.1g) [17]	Pt(1 wt%)	450 W Hg lamp ( $\lambda \geq 420$ nm)	Na <sub>2</sub> SO <sub>3</sub> (0.02 M) Na <sub>2</sub> 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 <sub>2</sub> SO <sub>3</sub> (0.1 M) Na <sub>2</sub> S(0.1 M) aqueous solution	2.1%	273	5460
(AgIn) <sub>0.22</sub> Zn <sub>1.56</sub> S <sub>2</sub> (0.3 g) [19]	Pt(3 wt%)	300 W Xe lamp ( $\lambda \geq 420$ nm)	K <sub>2</sub> SO <sub>3</sub> (0.25 M) Na <sub>2</sub> S(0.35 M) aqueous solution	20%	944	3147
AgInZn <sub>7</sub> S <sub>9</sub> (0.3 g) [20]	Pt(3 wt%)	300 W Xe lamp ( $\lambda \geq 420$ nm)	K <sub>2</sub> SO <sub>3</sub> (0.25 M) Na <sub>2</sub> S(0.35 M) aqueous solution	15%	940	3133
GuGa <sub>2</sub> In <sub>3</sub> S <sub>8</sub> (0.3 g) [21]	Rh(1.5 wt%)	300 W Xe lamp ( $\lambda \geq 420$ nm)	K <sub>2</sub> SO <sub>3</sub> (0.5 M) Na <sub>2</sub> S(0.2 M) aqueous solution	15%	3200	10667
(CuIn) <sub>0.09</sub> Zn <sub>1.82</sub> S <sub>2</sub> (0.3 g) [22]	Ru(0.5 wt%)	300 W Xe lamp ( $\lambda \geq 420$ nm)	K <sub>2</sub> SO <sub>3</sub> (0.25 M) Na <sub>2</sub> S(0.35 M) aqueous solution	12.5%	1227	4090

## References of Table S2.

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