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Fabricating efficient CdSe–CdS photocatalyst systems by spatially resetting water splitting sites

Zhijian Wang,‡[ab] Junmei Wang,‡[ac] Li Li,[a] Jianfeng Zheng,[a] Suping Jia,[a] Jiazang Chen,*[a] Bin Liu*[b] and Zhenping Zhu[a]

[a] State Key Laboratory of Coal Conversion, Institute of Coal Chemistry, Chinese Academy of Sciences, Taiyuan, 030001, China.*E-mail: chenjiazang@sxicc.ac.cn.
[b] School of Chemical and Biomedical Engineering, Nanyang Technological University, Singapore, 637459. *E-mail: liubin@ntu.edu.sg
[c] University of Chinese Academy of Sciences, Beijing, 100049, P. R. China.
‡ The two authors contribute the same.

Experimental section

Materials

TiO_2(Degussa) Chloroplatinic acid hexahydrate ($H_2PtCl_6\cdot 6H_2O$, Pt basis 10mg/ mL) $CdCl_2$, $CdSO_4$, $N(CH_2COONa)_3$, Se, $NH_3\cdot H_2O$, NH_4Cl, NH_2CSNH_2, FTO/glass substrates (12Ω/sq). A standard Pt-P25 paste was prepared by adding 0.1 g Pt-P25 powder (with diameter of 20nm) into 2 mL isopropanol with stirring for 2days to form homogeneous slurry.

Synthesis of TiO_2-Pt

The platinized 2% TiO_2-Pt was synthesized by photoreduced deposition method. The procedure was carried out by dispersing 2g TiO_2 in 200 mL methanolic solution containing $H_2PtCl_6\cdot 6H_2O$ (equal to 4 mg Pt) under irradiation of 300 W Hg lamp for 1 h. The TiO_2-Pt was collected as powder.

Synthesis of FTO/ TiO_2-Pt film

The FTO/TiO_2-Pt film were prepared by coating the TiO_2-Pt paste onto the cleaned FTO substrate(1.5cm × 1.5cm) using a spin coating method, the TiO_2-Pt coated FTO was dried for several minutes at room temperature and then sintered at 450 for 30min in air according to a described procedure [1].

Synthesis of CdSe-CdS-m-TiO_2-Pt film

CdS and CdSe QDs were assembled onto TiO_2-Pt film in sequence by chemical bath deposition(CBD) method as described in a previous paper[2].The deposition experiment were carried out using 80mM $CdCl_2$ 264mM NH_4Cl 560mM thiourea and 920mM ammonia in 40mL solution for 2h. Subsequently, after washing with water, putting into 30 mL aqueous solution containing 104 mM $CdSO_4$ 160 mM $N(CH_2COONa)_3$ and 104 mM Na_2SeO_3 for about 4h. The resulting CdSe-CdS-m-TiO_2-Pt film was then washed with DI water and dried overnight at room temperature.

Synthesis of CdS-CdSe quantum dots

CdS QDs were synthesized at room temperature using 80 mM $CdCl_2$ 264 mM NH_4Cl 560 mM thiourea and 920 mM ammonia in 40 mL solution stirred for 2h. Then the CdS QDs was centrifuged, washed and dispersed in 30 mL solution containing 104 mM $CdSO_4$ 160 mM $N(CH_2COONa)_3$ and 104 mM Na_2SeO_3 for about 4h. Subsequently, CdS/CdSe QDs was centrifuged washed and dried at 333k in vacuum for 12h.

Synthesis of CdSe-CdS-p-TiO_2-Pt

As-prepared Pt-P25 was put into 40 mL aqueous solution containing 80mM $CdCl_2$ 264mM NH_4Cl 560mM thiourea and 920mM ammonia for about 2 h. The Pt-P25/ CdS was washed with water. Subsequently, the obtained Pt-P25 /CdS was composited with CdSe in 30 mL aqueous solution containing 104 mM CdSO4 160 mM $N(CH_2COONa)_3$ and 104 mM Na_2SeO_3 for about 4h. The Pt-P25/ CdS/CdSe were centrifuged washed and dried at 333k in vacuum for 12h.

Synthesis of TNTA array

The TiO_2 nanotube arrays (TNTA) were prepared according to previously reported process [3]. Briefly, a commercial Ti foil(purity>99.6%, 0.25mm thickness, 15mm × 15mm) was anodized at 60V for 1h in an electrolyte containing ethylene glycol 0.25 wt % NH_4F and 2 vol% deionized water. A Pt foil was used as the cathode in the anodic oxidation test setup. The oxidized surface films were removed by sonication in distilled water before the oxidized samples were dried under high purity N_2 stream at room temperature. Then the substrates were subsequently oxidized in the original electrolyte at 60V for 2h and repeated the first oxidation step. After electrochemical anodization, the amorphous TNTA were calcinated at 773K for 3h in a furnace to obtain crystalline phase.

Synthesis of CdSe-CdS-TNTA-Pt film

As-prepared TNTA was first platinized via photoreduced deposition method to form TNTA-Pt film. Then the Pt-TNTA film was put into an aqueous solution composition of 80mM $CdCl_2$ 264mM NH_4Cl 560mM thiourea and 920mM ammonia for about 2 h. The CdS deposited TNTA film was washed with water. Subsequently, the obtained CdS-TNTA was deposited by CdSe in 30 mL aqueous solution containing 104 mM $CdSO_4$ 160 mM $N(CH_2COONa)_3$ and 104 mM Na_2SeO_3 for about 4h. The CdSe-CdS coated TNTA were cooled to room temperature to obtain the CdSe-CdS-TNTA hierarchical ordered film.

Synthesis of carbon nanotube array (CNTA)

The vertically aligned multi-walled carbon nanotube array (CNTA) was prepared by chemical vapor deposition (CVD) method in a quartz tube furnace according to a described procedure [4] . Typically, a thin Al_2O_3 film (3nm) and Fe film (2nm) were sputtered on Si/SiO_2 substrate respectively as the catalyst for the growth of CNTs. A gas flow of C_2H_4 (20sccm), H_2 (40sccm), Ar (100sccm) were carried out as carbon source and carrier gas at 750 °C for 10min.

Synthesis of CdSe-CdS-CNTA-Pt film

CdSe-CdS-CNTA-Pt film were fabricated via the CBD approach resembles the procedure described in CdSe-CdS-TNTA-Pt film.

Characterization

The microstructure and arrangements of the hybrid materials were investigated using a field-emission SEM (JEOLJIB-4600F) and High-resolution transmission electron microscopy (JEM-2100, 200kV). Light absorption properties of the photocatalysts films are evaluated using a UV-vis spectrometer at room temperature. Photoluminescence recording was performed on a fluorescence spectrometer (F-7000, Hitachi, Japan).

Photocatalytic measurements

Photocatalytic reactions were carried out in a gas-closed circulation system. The deposited film catalyst (1.5 cm × 1.5cm) was placed inside a 100 mL quartz glass tube reactor and sealed with rubber plug. The composite film photocatalyst was placed in 50 mL aqueous solution containing 0.25M Na_2S/0.25M Na_2SO_3 as electron donors with the deposited catalyst film facing into a 300w Xenon arc light source after filtering the UV using a quartz water jacket filling with circulating cooling $NaNO_2$ (1M) solution system to pass only visible light ($\lambda \geq 400$nm, 5cm far away from the photocatalytic reactor)[5]. Recycling $NaNO_2$ solution was also utilized to maintain a constant reactor temperature at 289K. Prior to irradiation, the reactor was purged with Ar gas for 25min in order to replace air inside the solution. 1mL of gas was sampled intermittently through the rubber plug and the amount of H_2 evolved was analyzed by gas chromatography (Beifen-Ruili:SP-2100. MS-5A column. TCD. With Ar carrier).

Electrochemical measurements

Photocurrent measurements were performed on an electrochemical workstation(CHI 660D Shanghai, China) using a standard three-electrode system with prepared samples as working electrode, a foil as counter electrode and a standard calomel electrode in saturated KCl as reference electrode.

The electrolyte was an aqueous solution containin 0.25M Na_2S and 0.25M Na_2SO_3. The working electrode was the photocatalyst without Pt on FTO. Intensity-modulated photocurrent spectroscopy (IMPS) and photovoltage spectroscopy (IMVS) spectra were recorded on a Zahner IM6ex electrochemical workstation with a frequency-response analyzer under a 470 nm LED source supply. The disturbance light intensity was 2% of the base light intensity. The frequency range was set between 100 kHz and 0.1 Hz.

Preparation of working electrode: The TNTA were peeled from the Ti substrate by immersing in 5% H_2O_2 solution for 12h, and then dipped in the water to wash the H_2O_2 solution. The free standing TNT membranes were annealed at 450 ^oC for 2h in an oxygen ambient and then transferred to the fluorine-doped tin oxide (FTO) substrates that were spin coated with a layer of TiO_2(Degussa) nanoparticle paste. After being dried in the air, the TNT/FTO films were sintered at 450 ^oC for 30 min. The CdSe-CdS-TNTA/FTO was prepared similar with the procedure described in CdSe-CdS-m-TiO_2-Pt film. The CNTA was separated from the Si substrate by the process of ultrasonication. The free standing CNTA membranes were doctor-bladed onto FTO substrates with a layer of TiO_2(Degussa) nanoparticle paste. After being dried in the air, the CNT/FTO films were sintered at 80 ^oC for 3h. The CdSe-CdS-CNTA/FTO was prepared similar with the procedure described in CdSe-CdS-m-TiO_2-Pt film.

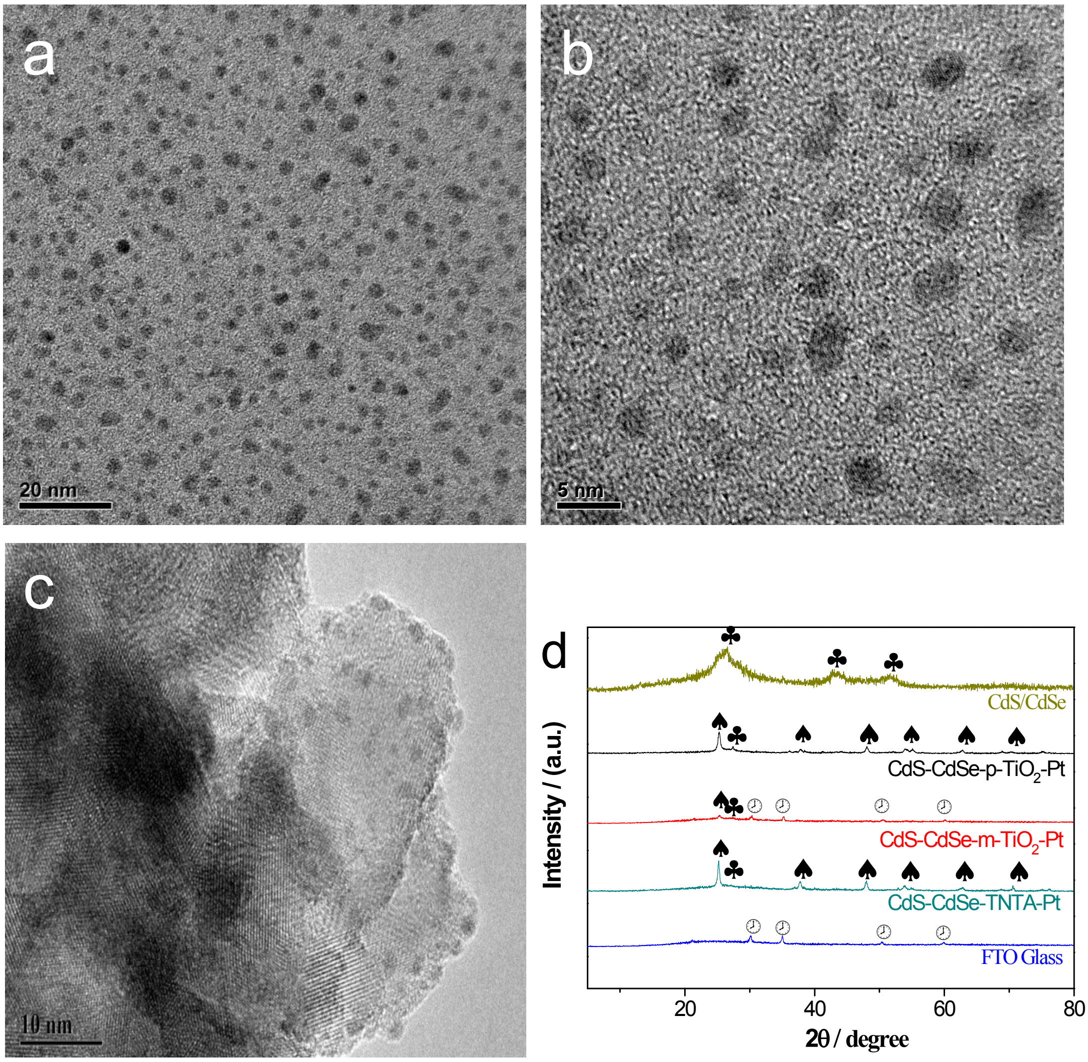

Fig. S1 TEM images of as-prepared CdSe-CdS QDs (a, b) and CdSe-CdS-p-TiO_2-Pt (c). XRD patterns (d) of CdSe-CdS QDs, CdSe-CdS-p-TiO_2-Pt, CdSe-CdS-m-TiO_2-Pt (on FTO galss), CdSe-CdS-TNTA-Pt and FTO Glass.

^{a} - corresponding to TiO_2, § -corresponding to CdS/CdSe, ■-corresponding to FTO Glass.

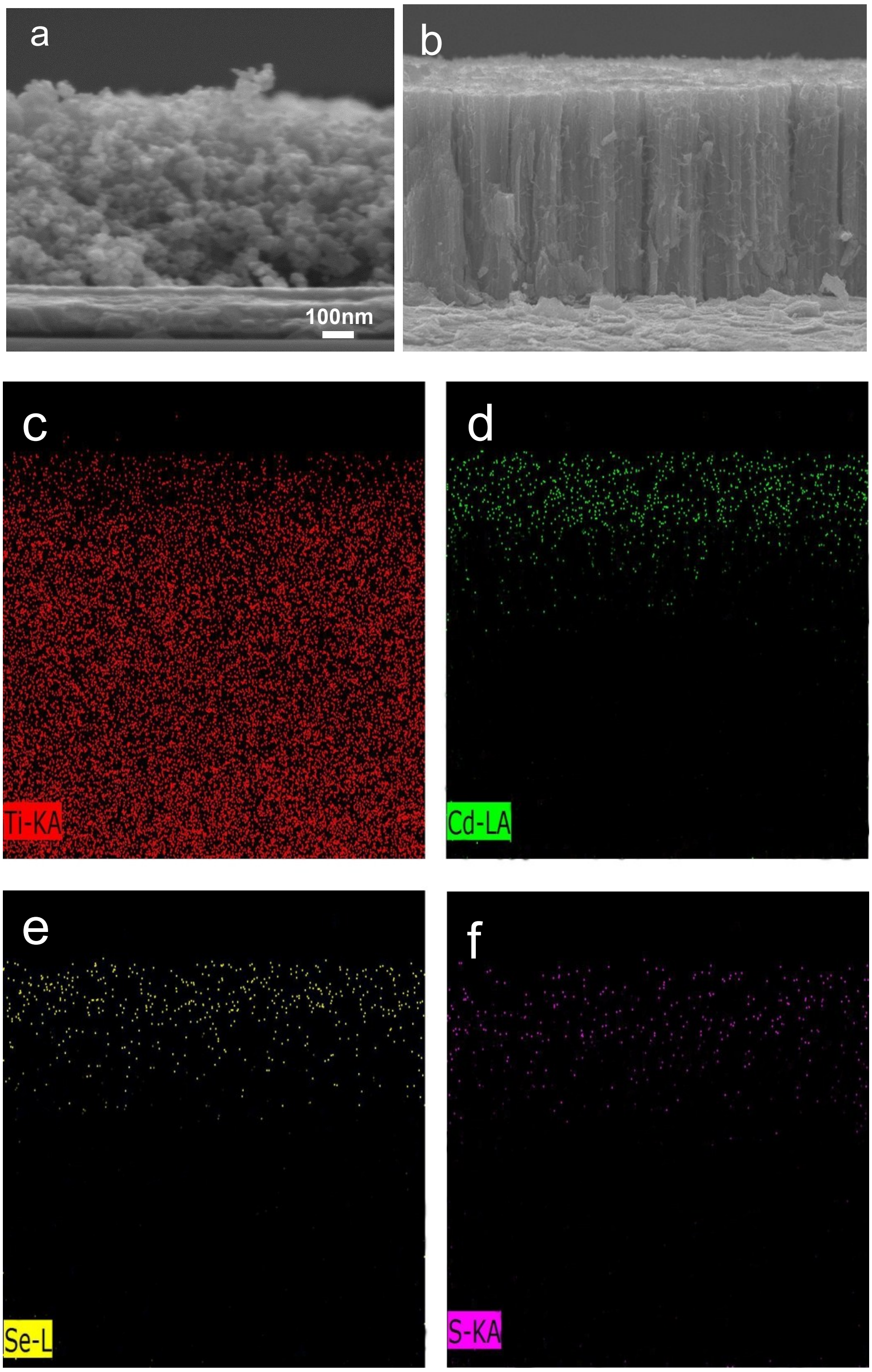

Fig. S2 SEM image of m-TiO$_2$-Pt (a) and CdSe-CdS-TNTA-Pt (b). Elemental mapping of Ti (c), Cd (d), S (e) and Se (f) by EDX spectroscopy for CdSe-CdS-TNTA-Pt.

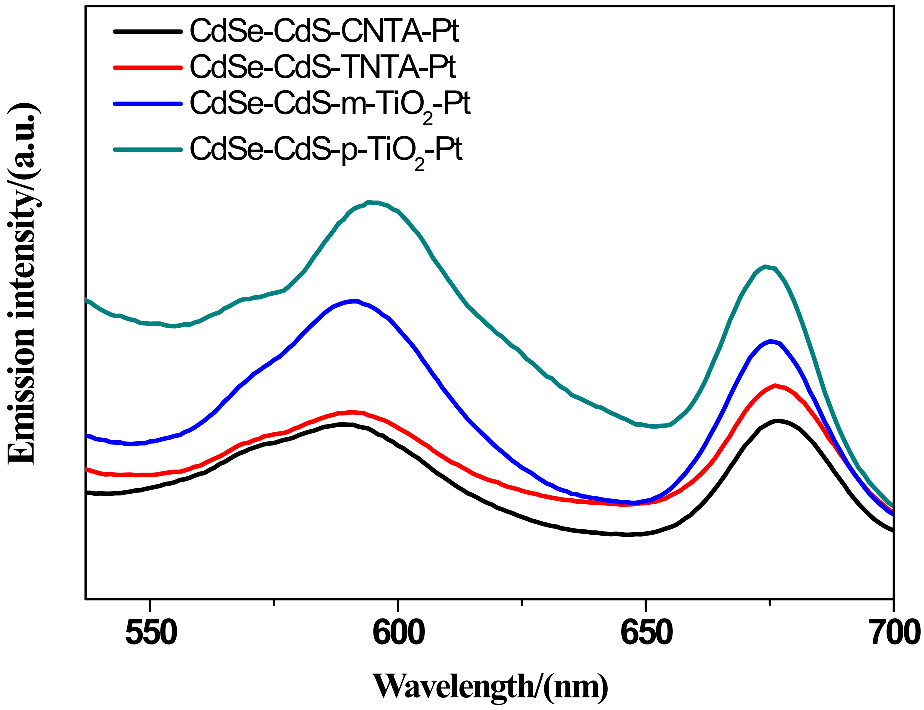

Fig. S3 PL spectrua of CdSe-CdS-p-TiO$_2$-Pt, CdSe-CdS-m-TiO$_2$-Pt, CdSe-CdS-TNTA-Pt and CdSe-CdS-TNTA-Pt.

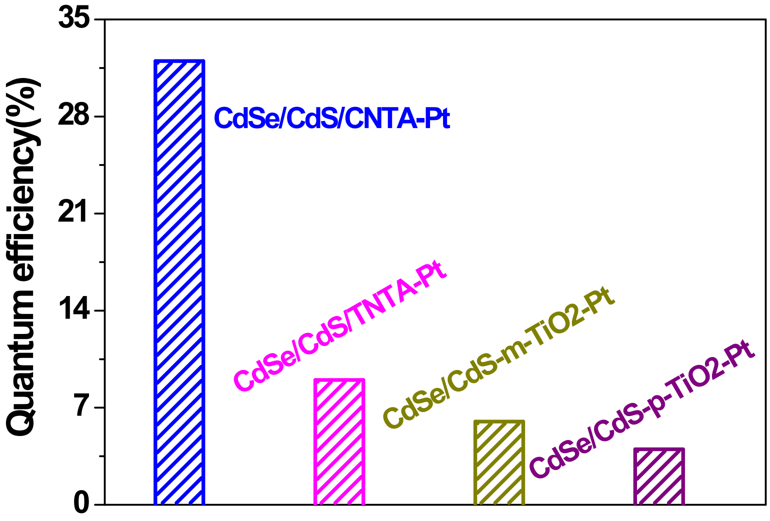

Fig. S4 Quantum efficiency values for CdSe-CdS-CNTA-Pt , CdSe-CdS-TNTA-Pt, CdSe-CdS-m-TiO$_2$-Pt and CdSe-CdS-p-TiO$_2$-Pt in 0.25M Na_2SO_3 + 0.25M Na_2S solution under 420nm irradiation.

Table S1 CdS based photocatalysts for photocatalytic hydrogen generation

Photocatalyst	Cocatalyst	Light source	Aqueous reaction solution	H_2 evolution activity (mmol g^{-1} h^{-1})	Quantum efficiency (%)	Reference
CdS	Pt	$\lambda \geq$ 420nm (Xe-lamp)	0.35M Na_2SO_3 + 0.25M Na_2S	27	60 (420nm)	6
CdS	NiS	$\lambda \geq$ 420nm (Xe-lamp)	Lactic acid	7	51 (420nm)	7
CdS/GO	Pt	$\lambda \geq$ 420nm (Xe-lamp)	Lactic acid	1	23 (420nm)	8
CdSe	Pt	$\lambda \geq$ 420nm (Xe-lamp)	0.35M Na_2SO_3 + 0.25M Na_2S	36	0.63 (454nm)	9
CdS/CdSe	Pt	Xe-lamp	Isopropanol	40	20 (450nm)	10
CdS/CdSe	MoS_3	450nm (Hg- Xe-lamp)	TEOA	100	10 (450nm)	11
CdS nanorods	Ni_2P	$\lambda \geq$ 420nm (Xe-lamp)	0.25M Na_2SO_3 + 0.25M Na_2S	1200	41 (450nm)	12
TiO_2/CdS	Pt	$\lambda \geq$ 420nm (Xe-lamp)	Lactic acid	14	7 (420nm)	13
ZnO/CdS	Pt	$\lambda \geq$ 420nm (Xe-lamp)	Benzyl alcohol	32	35(Visible light)	14
ZnS/CdS	Pt	$\lambda \geq$ 420nm (Xe-lamp)	0.1M Na_2SO_3 + 0.1M Na_2S	0.8	-	15
TiO_2/CdS QDs	Pt	$\lambda \geq$ 420nm (Xe-lamp)	Lactic acid	7	14 (420nm)	16
TNTA/CdS/CdSe	Pt	$\lambda \geq$ 400nm (Xe-lamp)	0.25M Na_2SO_3 + 0.25M Na_2S	44	15 (420nm)	Present work
CNTA/CdS/CdSe	Pt	$\lambda \geq$ 400nm (Xe-lamp)	0.25M Na_2SO_3 + 0.25M Na_2S	1270	21 (420nm)	Present work

Table S2 The electron transit time (τ_d) and electron lifetime (τ_n) of CdSe-CdS-p-TiO_2-Pt, CdSe-CdS-m-TiO_2-Pt, and CdSe-CdS-TNTA-Pt from IMPS or IMVS measurement.

Catalysts	Electron transit time (τ_d)	Electron lifetime (τ_n)
CdSe-CdS-p-TiO_2-Pt	17.0	18.6
CdSe-CdS-m-TiO_2-Pt	14.2	23.5
CdSe-CdS-TNTA-Pt	6.1	36.2

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