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

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Experimental section

Materials

TiO$_2$(Degussa) Chloroplatinic acid hexahydrate (H$_2$PtCl$_6$·6H$_2$O, Pt basis 10mg/ mL) CdCl$_2$, CdSO$_4$, N(CH$_3$COONa)$_2$, Se, NH$_3$·H$_2$O, NH$_4$Cl, NH$_2$CSNH$_2$, 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$_2$PtCl$_6$·6H$_2$O (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$_4$Cl 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$_2$COONa)$_3$, and 104 mM Na$_2$SeO$_3$ 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$_4$Cl, 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$_2$COONa)$_3$, and 104 mM Na$_2$SeO$_3$ 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$_4$Cl, 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 CdSO$_4$, 160 mM N(CH$_2$COONa)$_3$, and 104 mM Na$_2$SeO$_3$ 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 $\times$ 15mm) was anodized at 60V for 1h in an electrolyte containing ethylene glycol 0.25 wt % NH$_4$F 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$_4$Cl, 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$_3$COONa)$_3$, and 104 mM Na$_2$SeO$_3$ 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$_2$O$_3$ 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$_2$H$_4$ (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$_2$S/0.25M Na$_2$SO$_3$ 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 (λ≥400nm, 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 containing 0.25M Na$_2$S and 0.25M Na$_2$SO$_3$. 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$_2$O$_2$ solution for 12h, and then dipped in the water to wash the H$_2$O$_2$ solution. The free standing TNT membranes were annealed at 450 °C 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 °C 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 °C 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 glass), CdSe-CdS-TNTA-Pt and FTO Glass.

$^*$ - 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 spectra 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$_2$SO$_3$ + 0.25M Na$_2$S solution under 420nm irradiation.
<table>
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<tr>
<th>Photocatalyst</th>
<th>Cocatalyst</th>
<th>Light source</th>
<th>Aqueous reaction solution</th>
<th>H₂ evolution activity (mmol g⁻¹ h⁻¹)</th>
<th>Quantum efficiency (%)</th>
<th>Reference</th>
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<tr>
<td>CdS</td>
<td>Pt</td>
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<td>NiS</td>
<td>λ ≥ 420nm (Xe-lamp)</td>
<td>Lactic acid</td>
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<td>51 (420nm)</td>
<td>7</td>
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<td>23 (420nm)</td>
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<td>CdSe</td>
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<td>0.63 (454nm)</td>
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<td>CdS/CdSe</td>
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<td>TEOA</td>
<td>100</td>
<td>10 (450nm)</td>
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<td>41 (450nm)</td>
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<td>Lactic acid</td>
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<td>7 (420nm)</td>
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<td>ZnO/CdS</td>
<td>Pt</td>
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<td>Benzyl alcohol</td>
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<td>35(Visible light)</td>
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<td>CNTA/CdS/CdSe</td>
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Table S2 The electron transit time ($\tau_d$) and electron lifetime ($\tau_n$) of CdSe-CdS-p-TiO$_2$-Pt, CdSe-CdS-m-TiO$_2$-Pt, and CdSe-CdS-TNTA-Pt from IMPS or IMVS measurement.

<table>
<thead>
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<th>Catalysts</th>
<th>Electron transit time ($\tau_d$)</th>
<th>Electron lifetime ($\tau_n$)</th>
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<td>CdSe-CdS-p-TiO$_2$-Pt</td>
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References: