

Polytritycene@CdS double shell hollow spheres with enhanced interfacial charge transfer for highly-efficient photocatalytic hydrogen evolution

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1. Experimental materials and methods

1.1 Characterization

The morphology of as-prepared sample was obtained with field-emission scanning electron microscopy (FESEM, Quanta 200F) and transmission electron microscopy (TEM, JEOL JEM 2100). The crystal phases of CdS@TCP HS were determined by Shimadzu XRD 6000 diffractometer equipped with Cu-K α radiation ($\lambda = 1.54 \text{ \AA}$). The ^{13}C CP/MAS NMR spectra were obtained using Bruker 400 M. Fourier transform infrared (FT-IR) spectra were obtained on an FTS-3000 spectrophotometer (American Digilab Company). Raman spectra were performing on a Thermo Scientific DXR Raman microscope with an excitation wavelength of 532 nm. The N_2 adsorption-desorption was detected using a Micromeritics ASAP 2000 at 77 K. UV-Vis diffused reflectance spectra (DRS) were performed using a Hitachi U-4100 spectrophotometer. Photoluminescence (PL) spectra were investigated on a Cary Eclipse fluorescence spectrophotometer. X-ray photoelectron spectra (XPS) were obtained with a ESCALAB 250Xi spectrometer using Al K α X-ray source.

1.2 Photocatalytic hydrogen evolution activity

The photocatalytic hydrogen evolution was carried out in a sealed quartz cylindrical vessel (100 mL) equipped with the flat window (effective irradiation area of 21.2 cm^2). 10 mg of sample was dispersed into 50 mL of distilled water containing Na_2S (0.1 M) and Na_2SO_3 (0.1 M) as the sacrificial agent under ultrasound for 30 min. Before reaction proceeding, the vessel was degassed to remove residual air by bubbling argon for 30 min under stirring. The 300 W Xenon lamp assembled with UV cut-off filter ($\lambda \geq 420 \text{ nm}$) was used as a visible-light source, which was 15 cm away from the vessel. The system temperature was kept at 20°C by circulating cooling water at 5°C . The amount of produced hydrogen was detected by gas chromatograph (GC 7900) equipped with a thermal conductivity detector (TCD). To investigate the photostability of the chalcogenides, the recycling tests were performed by a similar method using 10 mg sample for a total of 12 h with evacuation every 3 h.

1.3 Photoelectrochemical performance

Photoelectrochemical experiments were measured on a CHI660D electrochemical workstation, containing a conventional three-electrode cell with Pt as counter electrode, Ag/AgCl electrode as reference electrode and FTO glass as working electrode. 0.1 M Na₂SO₄ solution was used as the electrolyte. The working electrode was prepared by dispersing sample (10 mg) in ethanol (5 mL), and then the mixture was transferred onto the GC electrode and dried at 50°C for 2 h.

1.4 The experimental method of transient photovoltage (TPV)

The TPV measurements were conducted on films samples (1.5 cm × 4 cm) deposited on indium-tin oxide (ITO) glass substrates at room temperature. A 10 mg mL⁻¹ sample aqueous solution was dripped on the ITO substrate, and then dried in air to obtain the films samples. The working electrode (ITO glass modified with samples) and the counter electrode (Pt wire) were wetted with N₂ or O₂-saturated acetonitrile and N₂-saturated acetonitrile/water aqueous (0.5 vol%). Meanwhile, we also measured the powder samples, which were covered on the Pt network (1 cm × 1 cm). The samples were excited by a third-harmonic Nd: YAG laser (Polaris II, New Wave Research, Inc.) with a laser radiation pulse (wavelength 355 nm, pulse width 5 ns).

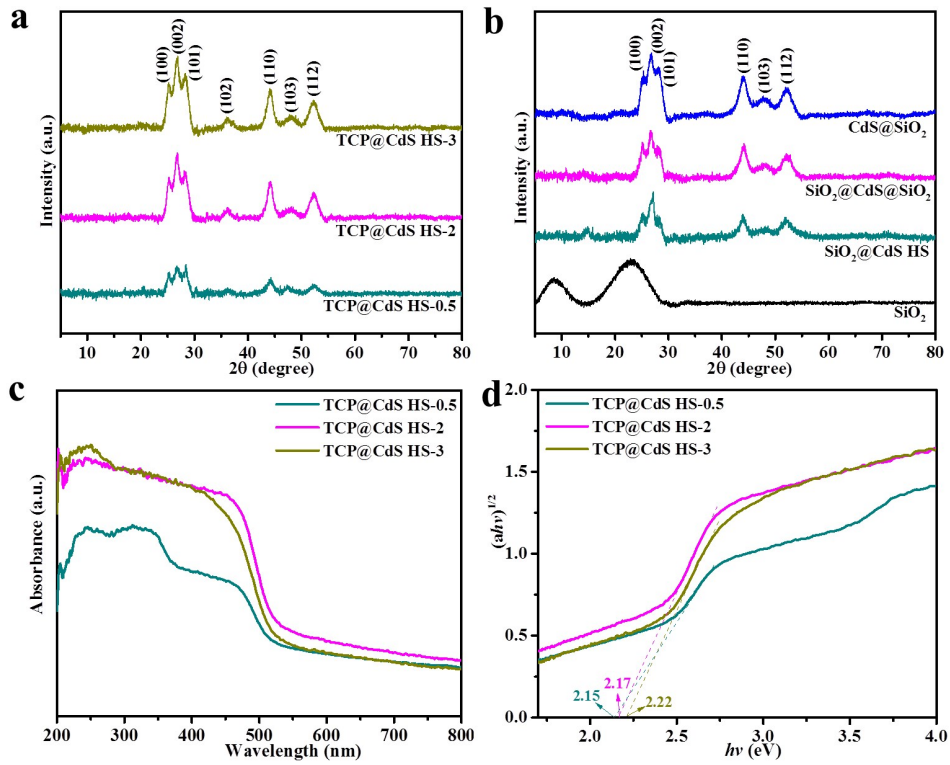


Figure S1. (a) XRD patterns of TCP@CdS HS-0.5, TCP@CdS HS-2, TCP@CdS HS-3. (b) XRD patterns of SiO₂, CdS@SiO₂, SiO₂@CdS@SiO₂ and SiO₂@CdS HS. (c) UV-vis DRS of TCP@CdS HS-0.5, TCP@CdS HS-2, TCP@CdS HS-3. (d) Tauc plots of TCP@CdS HS-0.5, TCP@CdS HS-2, TCP@CdS HS-3.

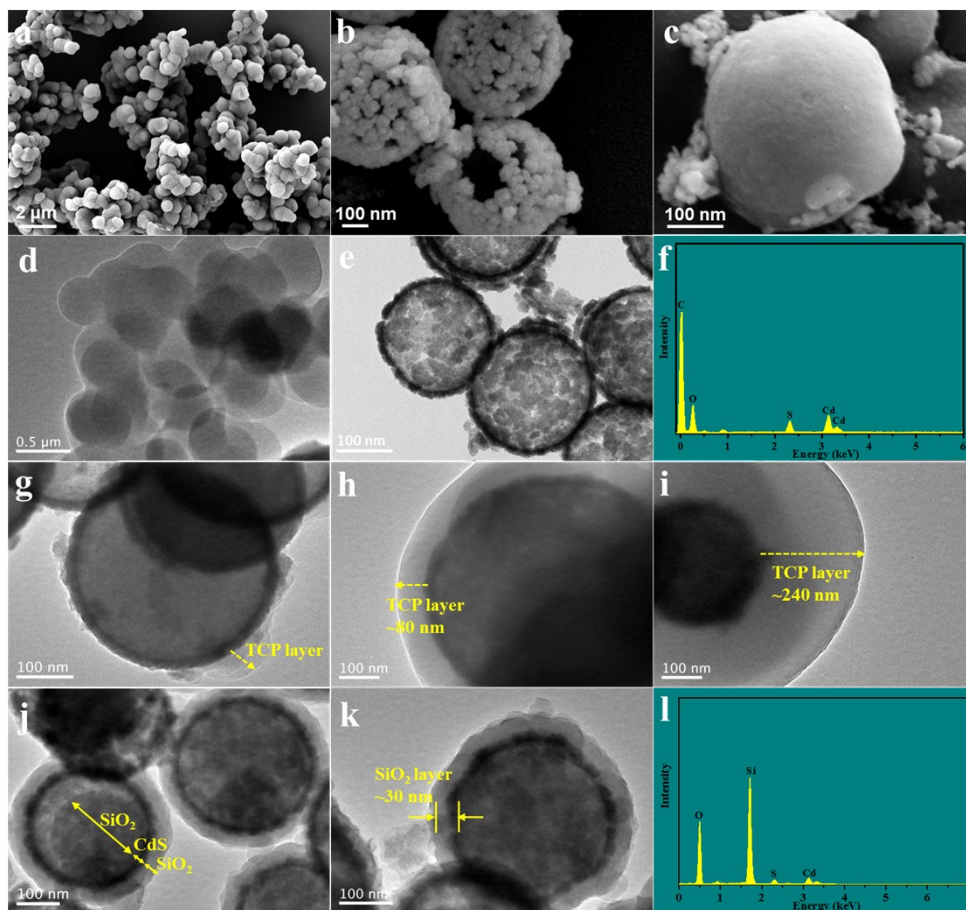


Figure S2. SEM images of (a) TCP, (b) CdS HS, (c) TCP@CdS HS-1. TEM images of (d) TCP, (e) CdS HS, (f) EDS spectrum of TCP@CdS HS-1, (g) TCP@CdS HS-3, (h) TCP@CdS HS-2, (i) TCP@CdS HS-0.5, (j) SiO₂@CdS@SiO₂, (k) SiO₂@CdS HS, (l) EDS mapping of SiO₂@CdS HS.

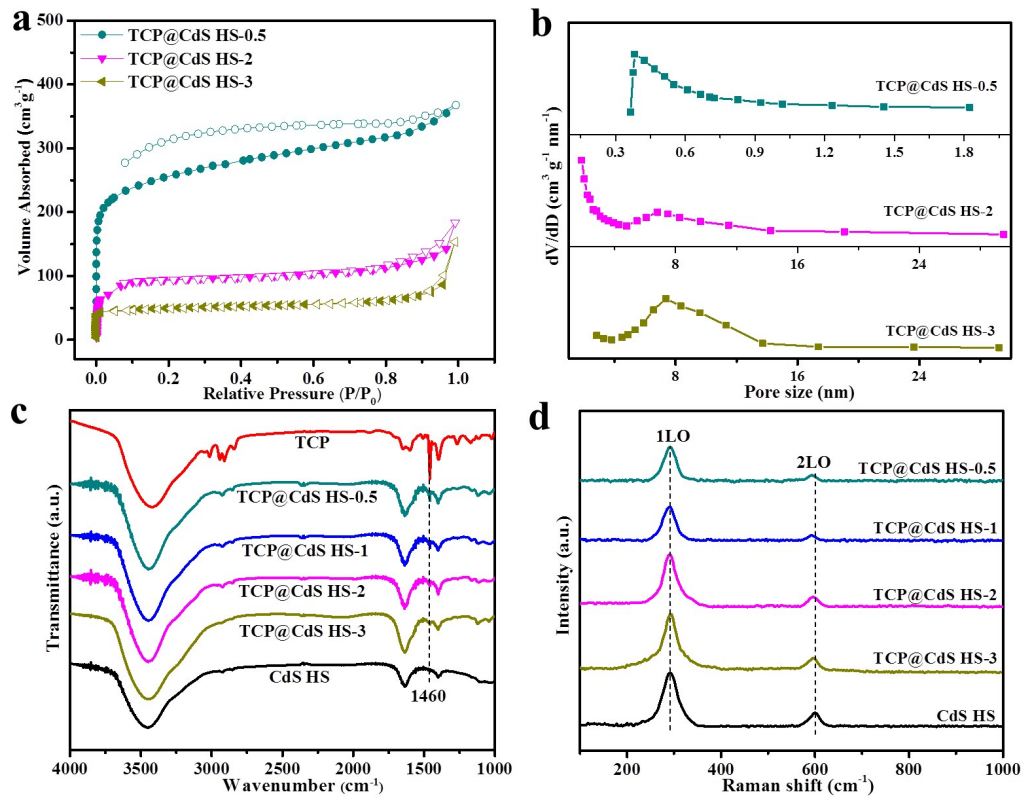


Figure S3. (a) Nitrogen adsorption-desorption isotherms of TCP@CdS HS-0.5, TCP@CdS HS-2, TCP@CdS HS-3. (b) Pore-size distribution of TCP@CdS HS-0.5, TCP@CdS HS-2, TCP@CdS HS-3. (c) FT-IR spectra of TCP, CdS HS and TCP@CdS HS composites. (d) Raman spectra of CdS HS and TCP@CdS HS composites.

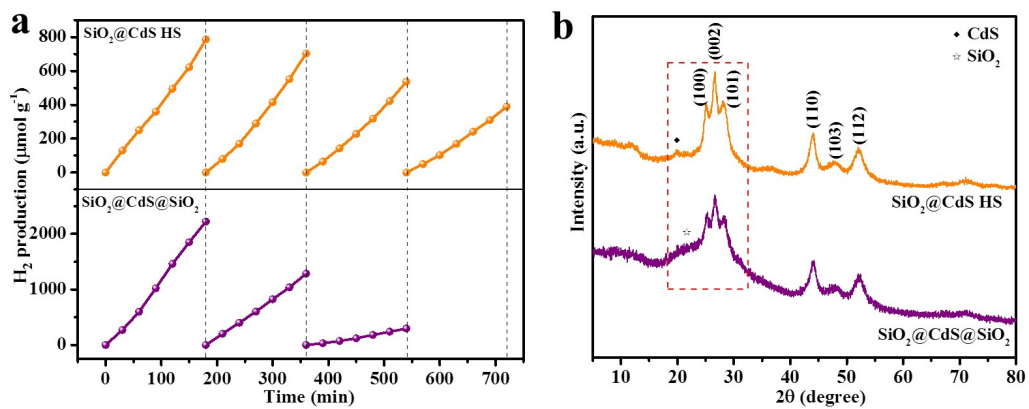


Figure S4. (a) Recycling experiments of SiO₂@CdS@SiO₂ and SiO₂@CdS HS. (b) XRD patterns of SiO₂@CdS@SiO₂ and SiO₂@CdS HS after reaction.

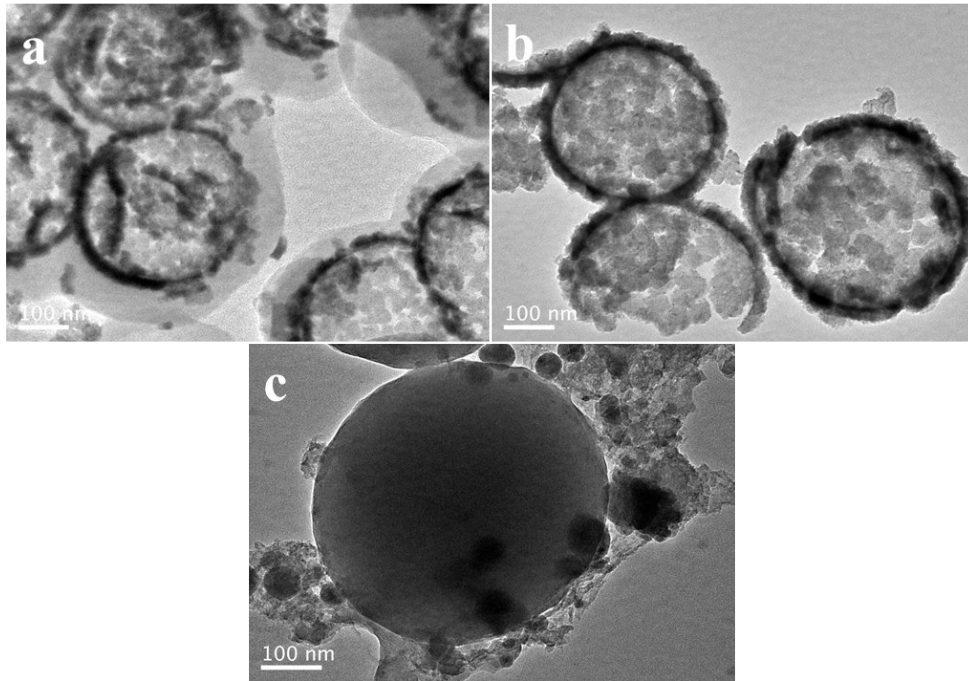


Figure S5. TEM images of (a) TCP@CdS HS-1, (b) SiO₂@CdS HS and (c) SiO₂@CdS@SiO₂ after reaction.

Table S1. Porous characteristics of as-prepared samples.

Sample	SBET (m ² g ⁻¹)	S _{Langmuir} (m ² g ⁻¹)	Pore volume (cm ³ g ⁻¹)
TCP	1452.3298	2561.7254	0.7281
TCP@CdS HS-0.5	659.2402	1223.8123	0.3159
TCP@CdS HS-1	402.6247	785.7812	0.17353
TCP@CdS HS-2	245.9532	432.2045	0.1208
TCP@CdS HS-3	187.7864	295.4877	0.0912
CdS HS	25.7125	52.5485	0.0327