

Supporting Information

Hybrid Metal-Cu₂S nanostructures as efficient co-catalysts for photocatalytic hydrogen generation

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Experimental details

1. Materials

All chemicals were used received. Copper(II) acetylacetonate (Cu(acac)₂, 99.99%), Platinum(IV) chloride (PtCl₄, 99.99%), Sodium borohydride (NaBH₄, 99%), Didodecyldimethylammonium bromide (DDAB, 98%), Tetrabutyl ammonium borohydride (TBAB, 98%), Iron pentacarbonyl (Fe(CO)₅, 99.999%), Platinum acetylacetonate (Pt(acac)₂, 98%), 1, 2-tetradecanediol (90%), dioctyl ether (99%), Oleic acid (OA, 90%), Oleylamine (OLA, 98%), Dodecanethiol (98%) were purchased from Sigma Alrich and used as received. TiO₂ nanoparticles were purchased from Degussa.

2. Synthesis of Pt NPs

In a typical synthesis of Pt NPs, 0.3 g of PtCl₄ and 0.1 g of DDAB were dissolved in 10 mL of toluene by sonication for 30 min, and a clear reddish brown color solution was obtained.¹ Then, 0.186 g of dodecylamine was added to the above solution and stirred for 1 h at room temperature followed by drop-wise addition of 0.2 mL of oleic acid and 0.035 g of NaBH₄ in 0.1 mL deionized water. Then, 0.026 g of TBAB in 1 mL of 100 mM DDAB aqueous solution was added and additionally stirred for 30 min. The product was precipitated by adding ethanol and collected by centrifugation. After three times washing with toluene-ethanol mixture, the NPs were re-dispersed in toluene (10 mL).

3. Synthesis of FePt NPs

Pt(acac)₂ (197 mg), 1, 2-tetradecanediol (345 mg) and dioctyl ether (20 mL) were mixed and heated to 100 °C under inert conditions.² At this temperature oleic acid (0.16 mL), oleylamine

(0.17 mL) and $\text{Fe}(\text{CO})_5$ (0.13 mL) were injected, and the mixture was further heated to reflux (295 °C). The refluxing was continued for another 30 min. Then the reaction mixture was cooled to room temperature, and the products were transferred into nitrogen filled glove-box. The black products were precipitated by adding toluene and ethanol and separated by centrifugation. The black precipitate was re-dispersed in toluene (10 mL) and stored in glove-box.

4. Synthesis of Cu_2S NPs

$\text{Cu}(\text{acac})_2$ (262 mg) was mixed with 30 mL of dodecanethiol and the mixture was heated to 70 °C under vacuum and maintained for 1 h. Then the temperature was raised to 200 °C and held at this temperature for 30 min. The obtained NPs were dispersed in hexane and centrifuged to remove any insoluble species. Then the NPs were precipitated by adding ethanol and collected by centrifugation. After three times washing with hexane-ethanol mixture, the NPs were re-dispersed in hexane (10 mL).

5. Synthesis of Metal- Cu_2S HNs

262 mg of $\text{Cu}(\text{acac})_2$ was mixed with 30 mL of dodecanethiol and the mixture was heated to 70 °C under vacuum and maintained for 1 h. The temperature was then raised to 100 °C under nitrogen flow, and 0.5 mL of metal nanoparticles (Pt or FePt) in toluene was injected into the reaction flask. The reaction flask held for 30mins under 200 °C followed by the removal of the heating mental and cooling down to room temperature using the water bath. Then the temperature was raised to 200 °C and held at this temperature for 30 min. The obtained NPs were dispersed in hexane and centrifuged to remove any insoluble species. Then the NPs were precipitated by adding ethanol and collected by centrifugation. After three times washing with the hexane-ethanol mixture, the NPs were re-dispersed in hexane (10 mL).

6. Material Characterization

Transmission electron microscopy (TEM) images were obtained using Hitachi HF-3300 operating at an acceleration voltage of 300 kV. Wide-angle powder X-ray diffraction patterns were collected using Empyrean HR-XRD with Cu K_α radiation source. The absorption spectra of the films were collected using a Cary 5000 UV-Vis-NIR spectrophotometer. The inductively coupled plasma optical emission spectrometer (ICP-OES) was analyzed amount of metal/ Cu_2S composition using thermo Scientific (iCAP7400) after dissolution in aqua regia.

7. Photocatalytic H_2 production

The photocatalysts were prepared by mixing 2 mL of toluene dispersions of above-prepared metal- Cu_2S HNs with 40 mg of TiO_2 NPs in 20 mL of dichloromethane and stirred for 24 h.

The photocatalysts were obtained by centrifugation of the above mixture. The photocatalytic H₂ production experiment was performed by dispersing the respective photocatalyst (4 mg) in distilled water (3.2 mL) with and 20% methanol (0.8 mL). A rectangular quartz reactor (volume: 4 mL) was modified to a head volume of 2.4 mL for analysis using the UV-visible spectrophotometer. A 300-W Xe arc lamp (Newport) with a 295-nm cutoff filter was placed 15 cm from the quartz reactor and N₂ gas was bubbled through the photocatalyst suspension for 30 min before irradiation. The produced H₂ in the reaction was detected every 30 min for 3 h using a gas chromatograph (GC, Agilent HP6890) equipped with a thermal conductivity detector (TCD).

8. Electrochemical characterization

The electrocatalytic hydrogen evolution reaction (HER) of hybrid metal-Cu₂S HNs catalysts were evaluated in a conventional three-electrode configuration using a rotating disk electrode (RDE), saturated calomel electrode (SCE) and a platinum wire as a working, reference and counter electrodes, respectively. Three milligrams (3 mg) of catalyst was dispersed in a solvent consisting of isopropyl alcohol (IPA, 150 μl), deionized water (30 μl) and 5% Nafion (10 μl) and the contents were sonicated for 30 minutes to make the uniform homogeneous catalyst ink. Then 2 μl of catalyst ink was loaded onto a RDE with a geometric surface area of 0.07 cm². The HER activity was carried using a linear sweep voltammetry technique with a scan rate of 5 mVs⁻¹ in 0.5M H₂SO₄ solution as an acidic medium. The electrochemical AC impedance measurement was carried out by using same cell configuration except the working electrode replaced to glassy carbon with a geometric surface area of 0.1025 cm², and the applied voltage of -0.32 V against rotating disk electrode (RHE) from 500 kHz to 50 Hz with an AC signal amplitude of 10mV. The electrochemical measurement was carried out using SCE as the reference electrode, while reporting we have calibrated to RHE by using $E_{\text{RHE}} = E_{\text{SCE}} + 0.241 \text{ V} + 0.059 \times \text{pH}$.³ All the potential reported in this manuscript are against RHE.

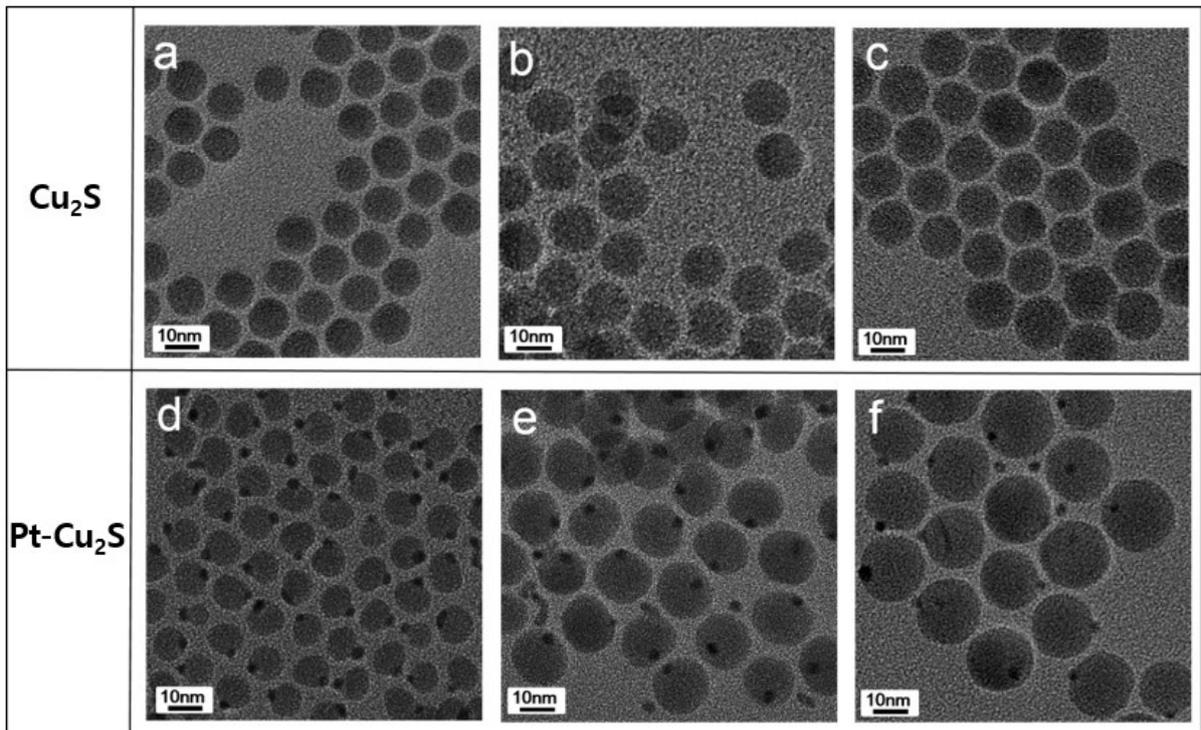


Figure S1. TEM images of Cu₂S and Pt-Cu₂S NPs synthesized at different growth time. Cu₂S NPs : (a) 5min, (b) 30min and (c) 1hr, Pt-Cu₂S NPs : (d) 5min, (e) 30min and (f) 1hr.

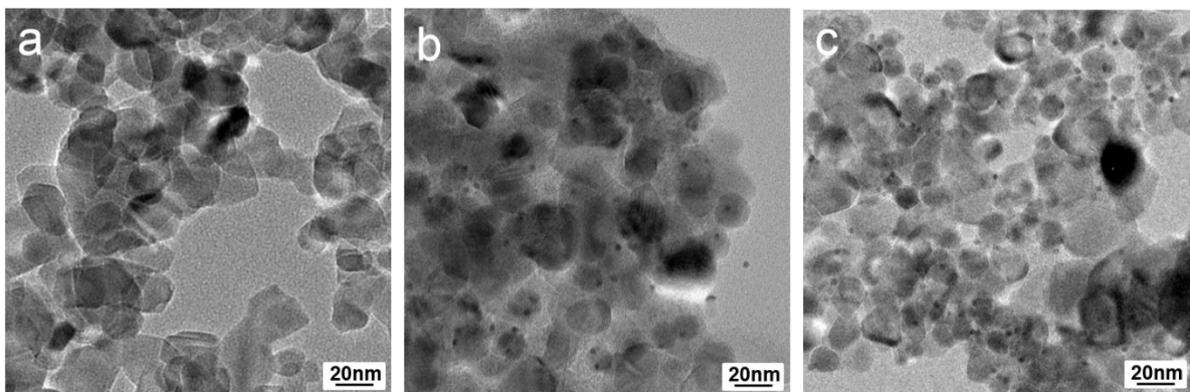


Figure S2. TEM images of (a) Cu₂S, (b) Pt-Cu₂S and (c) FePt-Cu₂S composited TiO₂ photocatalysts.

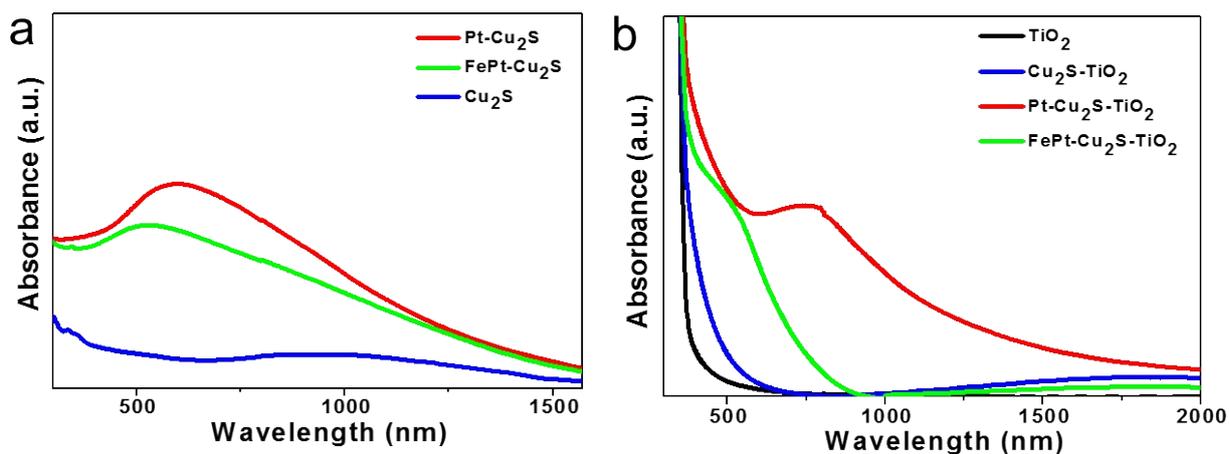


Figure S3. (a) UV-Vis absorption spectra of the Cu₂S and metal (Pt, FePt)-Cu₂S NPs in solution. (b) UV-Vis absorption spectra of the Cu₂S and metal (Pt, FePt)-Cu₂S composited with TiO₂ photocatalysts.

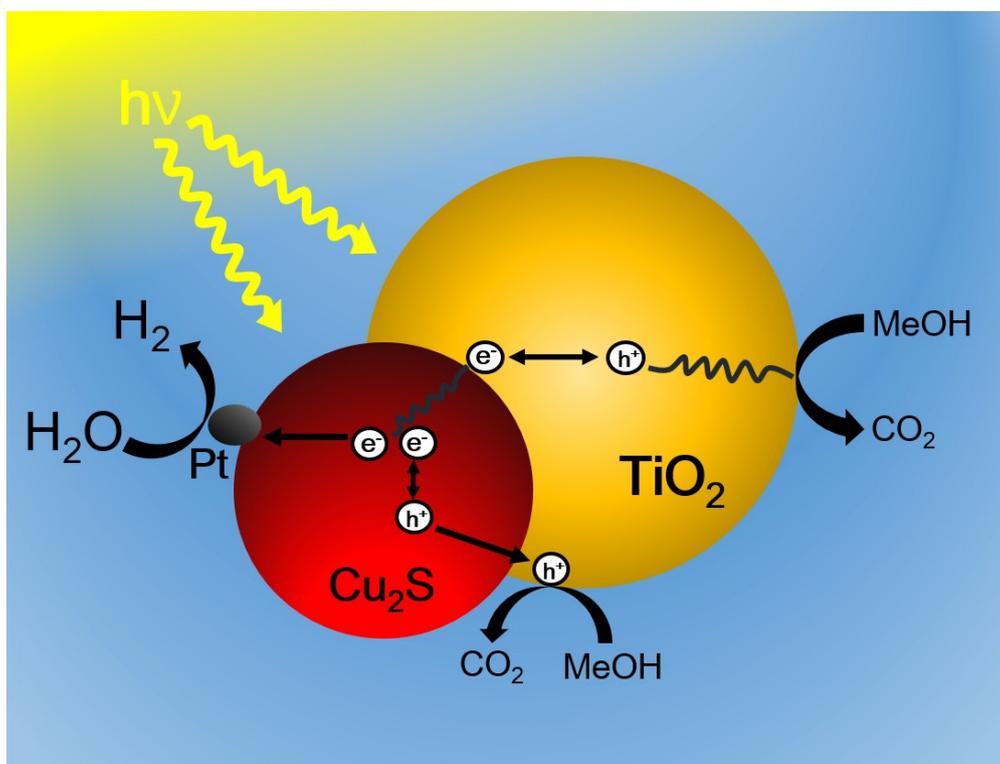


Figure S4. Schematic diagram of photocatalytic process for hydrogen generation using Pt-Cu₂S-TiO₂ photocatalyst.

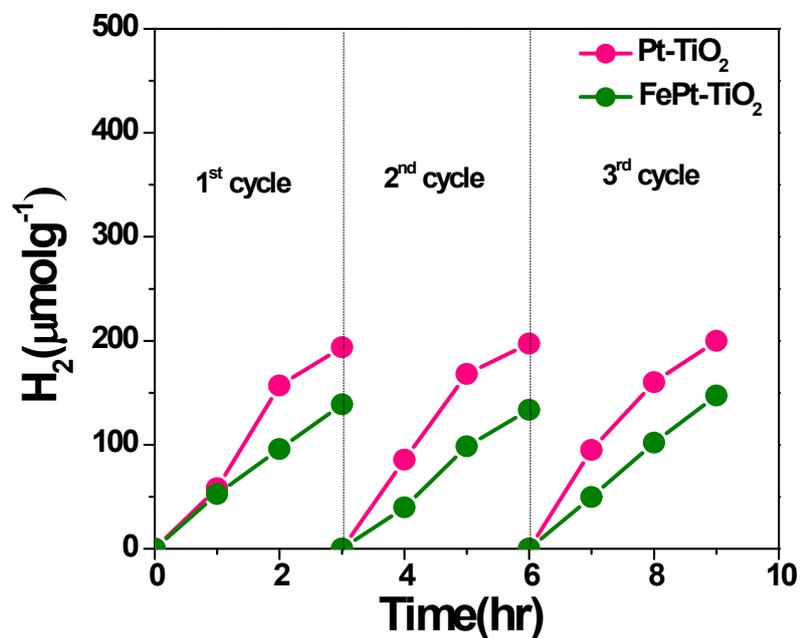


Figure S5. Hydrogen generation as a function of time with metal-TiO₂ samples under irradiation of UV-visible light

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