Supporting Information

Copper (I) Cysteine Complexes: Efficient Earth-Abundant Oxidation Co-catalysts for Visible Light-Driven Photocatalytic H_2 Production†

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Experimental Section

Synthesis of CdSe nanosheets.

CdSe nanosheets were prepared according to methods described in our previous report.[1] Typically, 110.96 mg SeO_2 and 266.53 mg $Cd(CH_3COO)_2$ were added into 40 mL diethylenetriamine in a beaker. The mixture was then heated to 55 °C in water bath and maintained at this temperature for about 30 min. The yellow turbid liquid obtained was transferred into a Teflon-lined autoclave and heated at 140 °C for 16 h. The final products were collected and washed with deionized water and ethanol for several times, and then dried under vacuum at 40 °C overnight.

Synthesis of $Sn_2Nb_2O_7$.

$Sn_2Nb_2O_7$ was prepared according to a literature procedure.[2] Typically, a mixture of 0.4 g Nb_2O_5 and 36 mL of 3 mol/L KOH solution was heated at 200 °C for 12 h in a sealed Teflon stainless autoclave. To 16 mL of the resulting clear solution, 0.38 g of $SnCl_2$ and 3 g of urea were added and ultrasonicated for 5 min. Then the solution was transferred into a 20 mL Teflon stainless autoclave. After that the sealed Teflon stainless autoclave was kept at 200 °C for 12 h, the final products were collected by filtration, washed with deionized water and absolute ethanol for several times, and dried under vacuum at 40 °C overnight.

Characterization.

Scanning electron microscopic (SEM) images were collected on a Hitachi S-4800 scanning electron microscope equipped with an Energy dispersive spectrometer (EDS). Cyclic voltammogram (CV) tests were carried out on a Chi660e instrument (Shanghai Chenhua). X-ray photoelectron spectroscopy (XPS) was obtained on a PHI Quantro SXM instrument. All binding energies were referenced to the C 1s peak (284.8 eV) arising from carbon impurities. High resolution electrospray ionization mass (HR-ESI-MS) data were obtained on an ApexIII (7.0 tesla) FTICR mass spectrometer (Bruker). ^{1}H NMR spectra were obtained on a Bruker AVNANCE 400 spectrometer. Electron spin resonance (ESR) experiments were performed on a Bruker E500 instrument. The amount of copper in Cu-cysteine complexes was measured by using inductively coupled plasma (ICP) optical emission spectroscopy on a Varian 710-OES instrument. Elemental analysis for C, N, and H was performed on a Vario EL III Element analyzer. Diffuse reflectance spectra (DRS) were measured using a Cary 5000 spectrophotometer with an integrating sphere scanning from 200-800 nm with $BaSO_4$ as the reference.

Preparation of Pt loaded $Sn_2Nb_2O_7$.

Pt loaded $Sn_2Nb_2O_7$ samples were prepared by a facile photodeposition method. 10 mg of $Sn_2Nb_2O_7$ powder was dispersed in a 60 mL quartz tube containing 20 mL of a 20 vol. % methanol aqueous solution. Then, 14 uL H_2PtCl_6 solution (18.49 mmol/L) was added. Subsequently, the quartz tube was deaerated with N_2 for at least 30 min and then sealed with a rubber septum. The suspension was irradiated with a 500 W high-pressure mercury lamp for 30 min under magnetic stirring (XPA-7 photochemical reactor, Nanjing Xujiang Machine-electronic Plant). The temperature of the suspension during irradiation was maintained at 298 K using a thermostatically controlled water bath. Pt loaded $Sn_2Nb_2O_7$ was isolated by centrifugation.

Photocatalytic H_2 evolution activity.

The photocatalytic reactions were carried out in a 60 mL quartz vessel sealed with a rubber septum. The photocatalyst powders were dispersed in a 20 mL aqueous solution with a given concentration of cysteine as the sacrificial agents. Then the pH was adjusted to ~5.2 with 0.1 M

NaOH. The suspension was dispersed by ultrasonic treatment for 10 min, following by adding a specific amount of copper nitrate, and then deaerated with N_2 for 30 min to remove O_2 and then sealed with a rubber septum. A 300 W Xenon lamp equipped with an ultraviolet cut-off filter ($\lambda >$ 400 nm) (PLS-SXE300C photochemical reactor, Perfect Light Ltd, Beijing) was used as the light source. The temperature of the reaction system was maintained at room temperature by a flow of water. The amount of evolved H_2 was determined by a Shimadzu GC-2014 gas chromatograph (N_2 carrier gas, molecular sieve 5 Å, TCD detector).

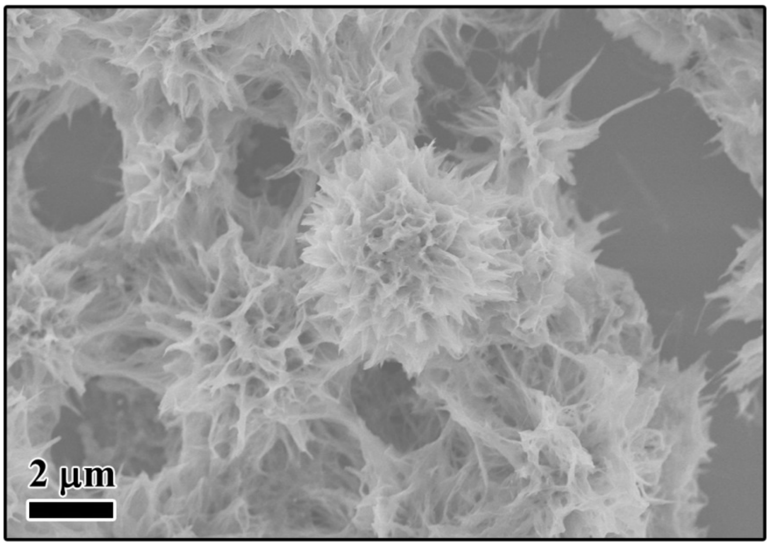

Fig. S1 SEM image of flower-like CdSe nanosheet assemblies.

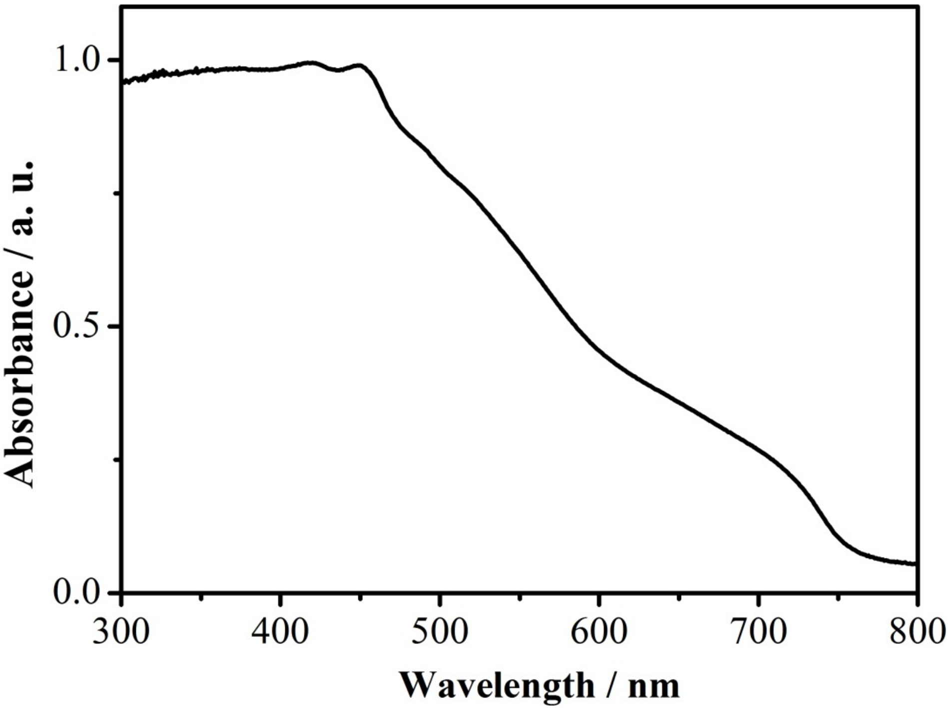

Fig. S2 UV-Vis DRS spectrum of flower-like CdSe nanosheet assemblies.

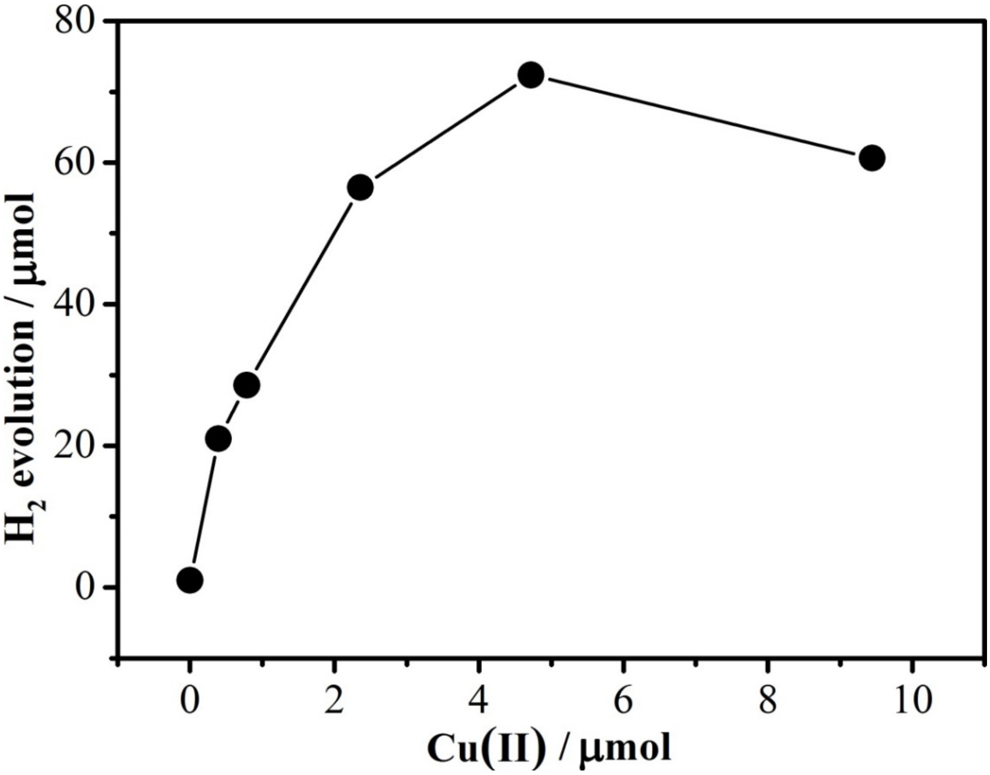

Fig. S3 Photocatalytic H_2 evolution rates with different amounts of Cu(II).

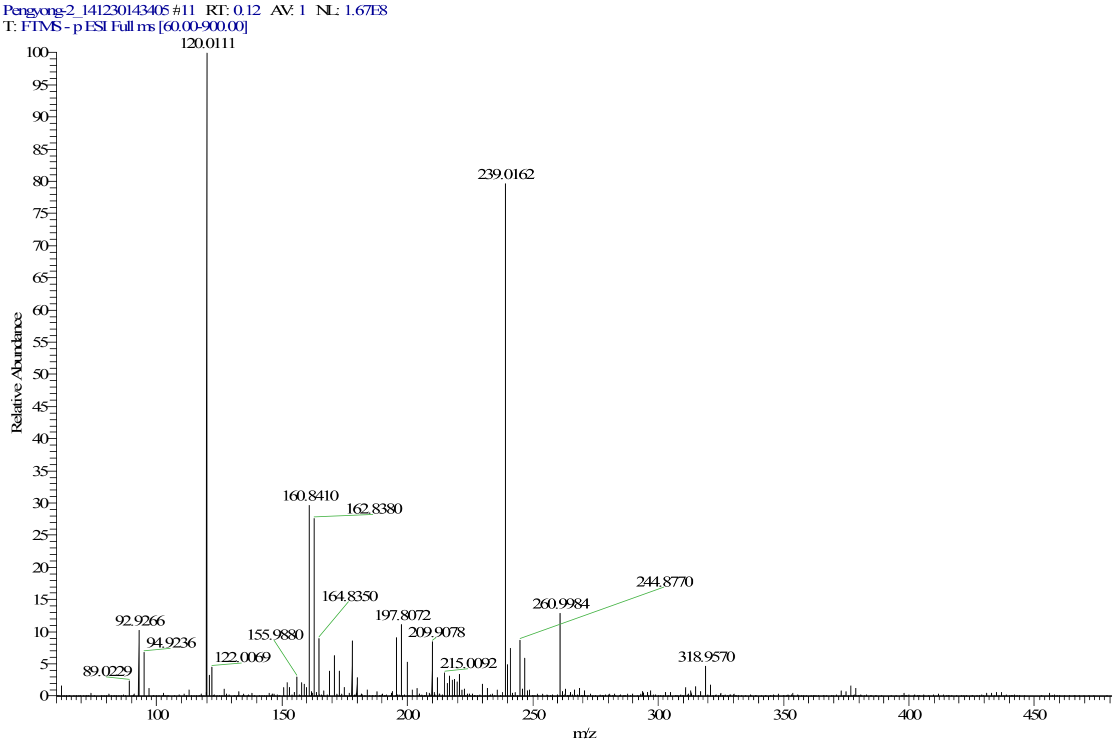

Fig. S4 HR-ESI-MS spectrum of the product obtained from the filtrate of the photocatalytic system containing CdSe, cysteine and Cu(I)-cysteine complex after irradiation for 1 h.

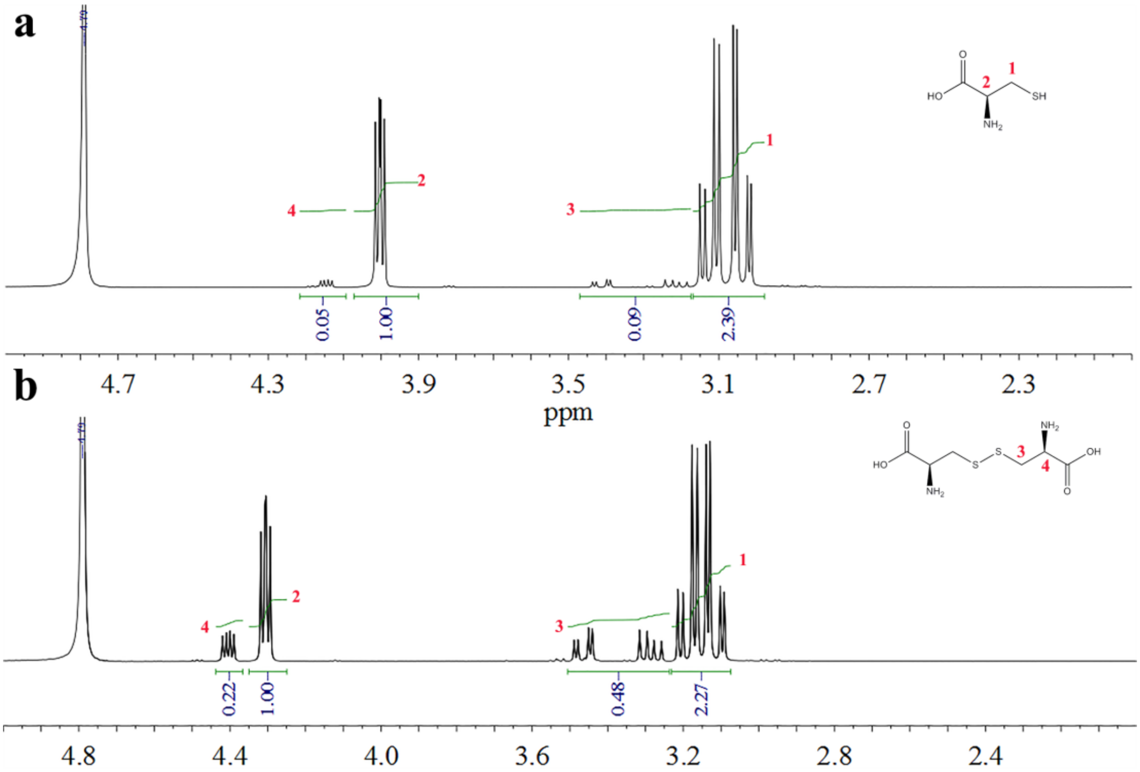

Fig. S5 ^{1}H NMR spectra of (a) pure cysteine and (b) the product obtained from the filtrate of the photocatalytic system containing CdSe, cysteine and Cu(I)-cysteine complex after irradiation for 1 h.

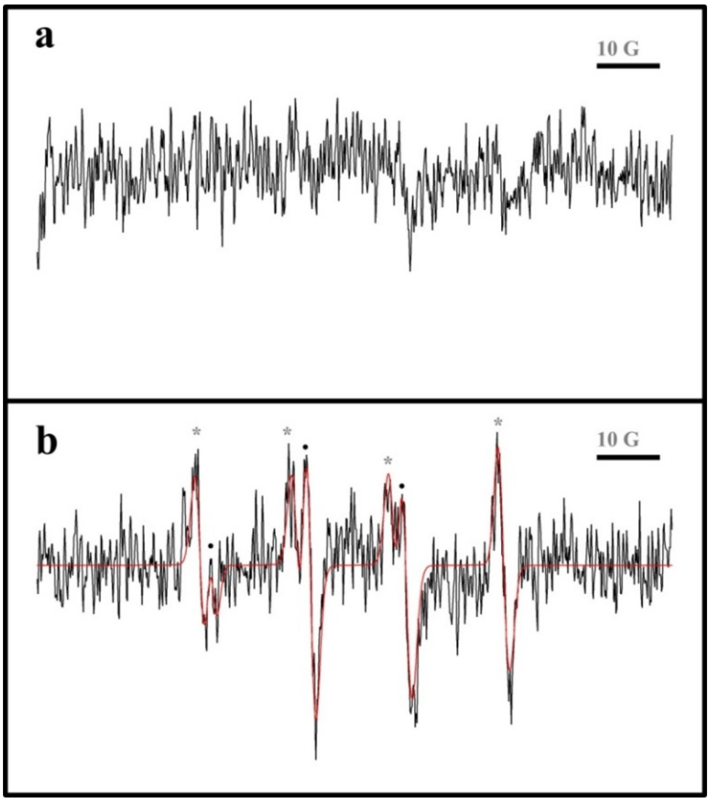

Fig. S6 ESR signals of an aqueous solution containing 0.1 mol cysteine, 1 mg CdSe, 6 wt. % Cu(II) ions and 0.02 M DMPO (a) before and (b) after visible light irradiation (λ >400 nm) (Red line, fitted curve). (* stands for the sulfenyl radical signals. • stands for the hydroxyl radical signals, which could originate from the reaction of holes with surface adsorbed water or hydroxyl groups)

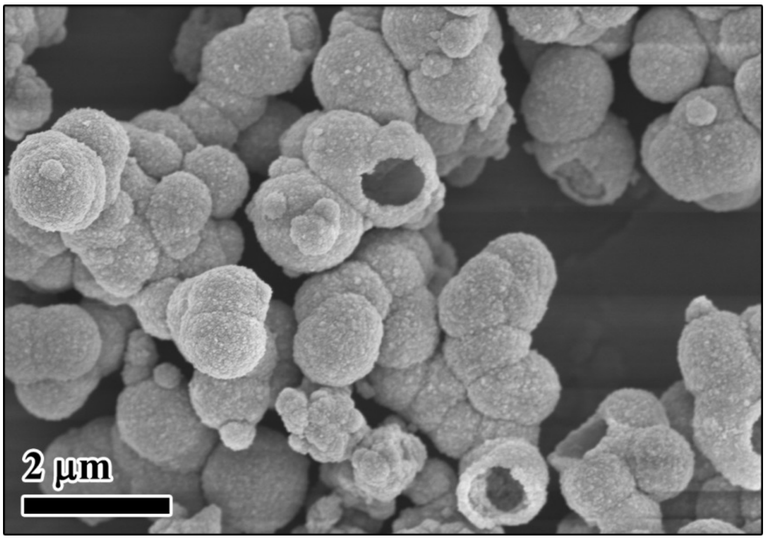

Fig. S7 SEM image of hollow $Sn_2Nb_2O_7$ spheres.

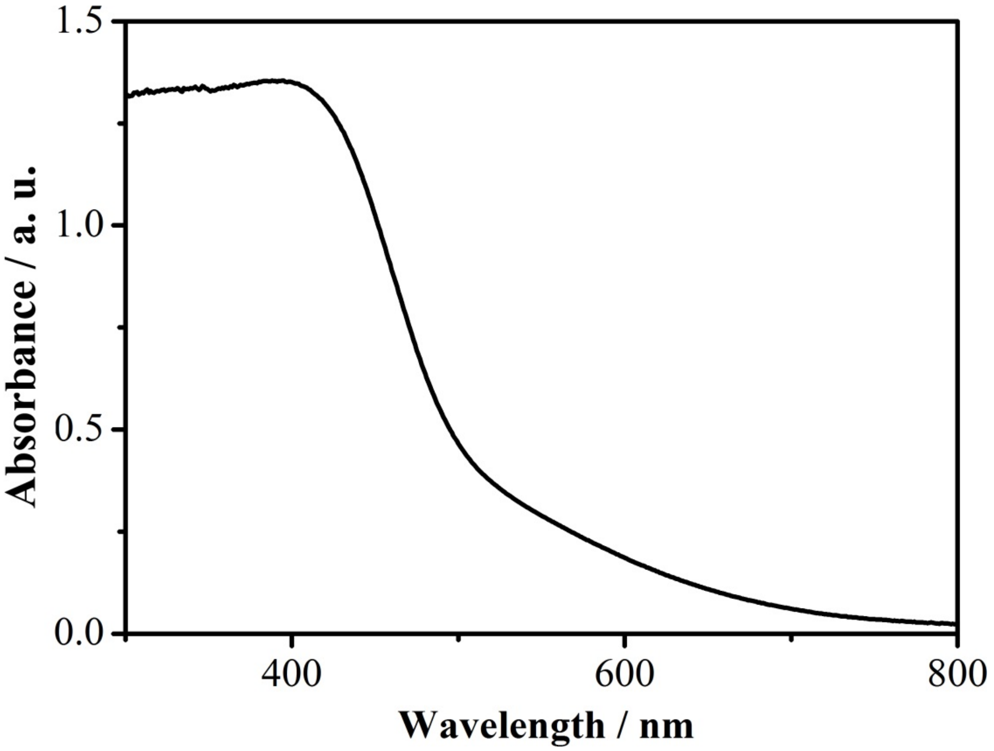

Fig. S8 UV-Vis DRS spectrum of hollow $Sn_2Nb_2O_7$ spheres.

1 Y. Peng, L. Shang, T. Bian, Y. Zhao, C. Zhou, H. Yu, L.-Z. Wu, C.-H. Tung and T. R. Zhang, *Chem. Commun.*, 2015, **51**, 4677-4680.

2 C. Zhou, Y. F. Zhao, T. Bian, L. Shang, H. J. Yu, L. Z. Wu, C. H. Tung and T. R. Zhang, *Chem. Commun.*, 2013, **49**, 9872-9874.