Electronic Supplementary Information for

Urchin-like Au@CdS/WO_3 Micro/Nano Heterostructure as a Visible-Light Driven Photocatalyst for Efficient Hydrogen Generation

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Experimental sections and characterizations

Experimental sections

Chemicals

Gold chloride, sodium sulfide, sodium sulfite and absolute ethanol were obtained from Sinopharm Chemical Reagent Beijing Co., Ltd. Sulfur, cadmium perchlorate hexahydrate, tungsten trioxide and tungsten hexachloride were obtained from Alfa Aesar, USA. All reagents were used directly without further purification. Ultrapure water with a resistivity of 18.2 MΩ cm, produced by a Milli-Q® Integral Water Purification System (Millipore), was used in all the experiments.

Preparation of Au/U-WO_3 and Au/C-WO_3

Urchin-like WO_3 was synthesized by a modified method.[1] In a typical synthesis, 2 g of WCl_6 was added into 100 mL absolute ethanol. The yellow solution was transferred into a Teflon-lined autoclave. The autoclave was sealed and heated in an oven at 160 °C for 24 h. After that, the blue floccule precipitates were collected by centrifugation, and rinsed with deionized water and ethanol. The blue powder was obtained after drying in a vacuum oven at 60 °C. Au/U-WO_3 was prepared by in-situ growing and loading Au nanocrystals on the prepared urchin-like WO_3. Specifically, 0.5 g of U-WO_3 powder was suspended into 100 mL of deionized water under strong stirring. 0.93 mL of 24.28 mM $HAuCl_4$ aqueous solution was added into the solution at the speed of 0.5 mL/min. The mixture was stirred for 4 h. 1.79 mL of 24.28 mM $HAuCl_4$ aqueous solution was then added into the solution under the irradiation of a 300 W Xenon lamp. The reaction and irradiation were kept for 2 min after the addition of $HAuCl_4$. The solid product was centrifuged, washed, and dried to obtain Au/U-WO_3. Au/C-WO_3 was prepared by the same procedure except for using C-WO_3 instead of U-WO_3 as the carrier.

Preparation of Au@CdS/U-WO_3, Au@CdS/C-WO_3, CdS/U-WO_3 and CdS

Au@CdS/U-WO_3 was prepared by a photodeposition method. 0.5 g of Au/U-WO_3 powder was suspended in 100 mL of ethanol/water solution ($V_{ethanol}$: V_{water} = 1:3) containing 51.2 mg of S_8 and 838.78 mg of $Cd(ClO_4)_2 \cdot 6H_2O$. The suspension was then bubbled with argon for 30 min in the dark, followed by the irradiation for 6 h with a 300 W Xenon lamp to achieve Au@CdS/U-WO_3. The product was washed with water and ethanol, and dried at 80 °C in vacuum oven. For comparison, Au/C-WO_3 and U-WO_3, instead of Au/U-WO_3, were used to synthesize Au@CdS/C-WO_3 and CdS/U-WO_3, respectively, by following exactly the same procedure. Pure

CdS were also synthesized using the same method as mentioned above except for no addition of any support.

Evaluation of Photocatalytic Activities

Photocatalytic H_2 evolution was performed in a Pyrex glass cell which had a flat, round upside-window with an irradiation area of 38 cm^2 for external light incidence. A 300 W Xenon arc lamp with a 420 nm cut-off filter (PLS-SEX 300, Beijing Trusttech Technology CO., Ltd) was used to simulate the visible light source. The spectrum range of the lamp without filter was shown in Fig. S2. The illumination intensity was adjusted to 100 mW cm^{-2}. The H_2-solar system (Beijing Trusttech Technology CO., Ltd) with a gas chromatogram (GC), equipped with a thermal conductivity detector (TCD), TDX-01 column and Ar carrier gas, was used to collect and on-line detect evolved H_2. 0.02 g of photocatalyst was suspended in a glass cell with 100 mL of deionized water containing 3.78 g Na_2SO_3 and 2.34 g Na_2S. The cell was kept at 5 ^oC by using a circulating water system. Before irradiation, the reaction system was pumped to vacuum. The H_2 evolution rate was determined by GC. The apparent quantum yield (Ø) was estimated by the following equation:

$$\text{Ø}(\%) = \frac{n_{e^-}}{n_p} \times 100 = \frac{2\mathrm{n}_{\mathrm{H}_2}}{n_p} \times 100$$

$$\mathrm{n_p} = \frac{\theta}{\mathrm{h\nu}} = \frac{\mathrm{I \times t \times S}}{\mathrm{h\nu}}$$

Where Ø is the apparent quantum yield, n_{e-} is the number of reacted electrons, n_p is the number of incident photos, n_{H2} is the number of evolved H_2 molecules, θ is the total energy of incident photos (J), h is the Planck constant (J s^{-1}), ν (6.34×10^{14} HZ) is the frequency of photo, I is the illumination intensity (W m^{-2}) determined with a ray virtual radiation actinometer, t is irradiation time (s), S is the irradiation area (m^2).

Characterization

Scanning electron microscopy (SEM) image was taken on a JSM-6701F (JEOL, Japan). Transmission electron microscopy images were obtained on a JEM 2100F (JEOL, Japan) operated at 200 KV. X-ray powder diffraction (XRD) was carried out on a Rigaku D/max-7000 using filtered Cu Kα irradiation. The UV-visible absorption spectra were recorded with a UV-visible spectrophotometer (UV-2550, Shimadzu, Japan). Brunauer-Emmett-Teller (BET) measurements were carried out on a Micromeritics's Tristar 3000. The Au and Cd content were measured using an inductively coupled plasma-atomic emission spectrometry (ICP-AES, ICPE-9000 Shimadzu).

Reference

1. G. C. Xi, J. H. Ye, Q. Ma, N. Su, H. Bai and C. Wang, *J. Am. Chem. Soc.*, 2012, **134**, 6508-6511.

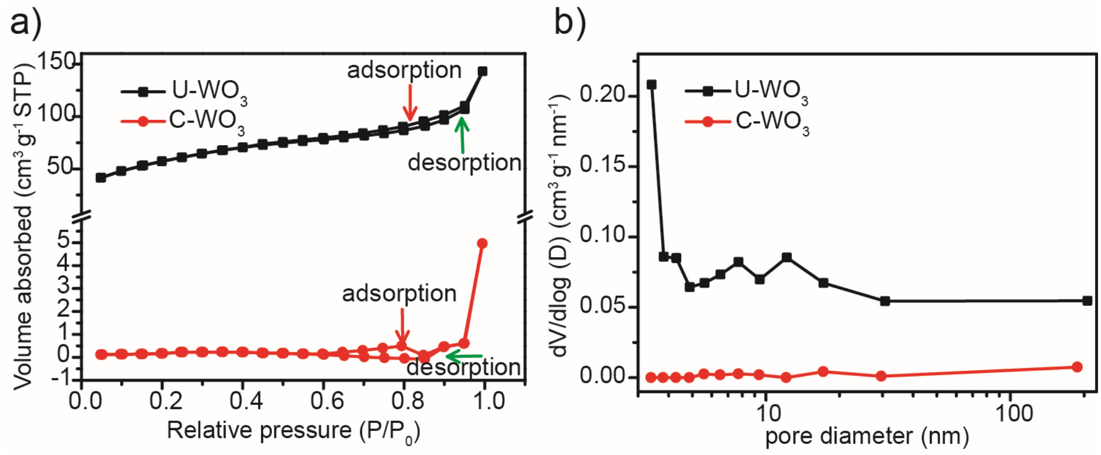

Fig. S1 (a) N_2 adsorption/desorption isotherms, and (b) the corresponding pore size distribution of U-WO_3 and C-WO_3.

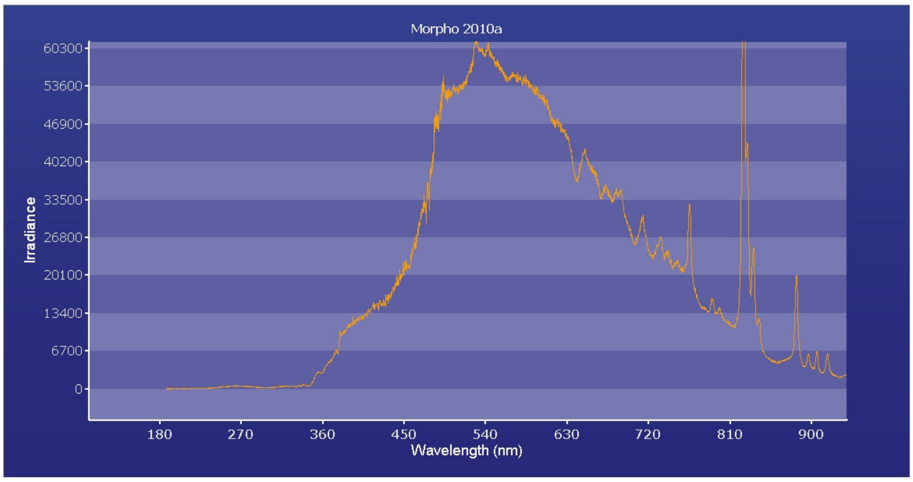

Fig. S2. The emission spectrum of Xenon lamp without a cut-off filter employed in all hydrogen evolution experiments.