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Supplementary Information

Efficient visible-light photocatalytic H_2 evolution with heterostructured Ag_2S modified CdS nanowires

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Characterization section

The morphology of the samples was observed by field emission scanning electron microscopy (SEM, Zeiss Sigma300) and transmission electron microscopy (TEM, JEOL JEM-2010F). The X-ray diffractometer (XRD, Rigaku D/Max 2400) using Cu K radiation in the 2θ ranging from 20° to 90° at a scan rate of 4°/min. X-ray photoelectron spectroscopy (XPS, Thermo 163 Fisher ESCALAB 250Xi) were employed using a Thermo Scientific ESCA Lab250 spectrometer, and all of the binding energies were calibrated by the C 1s peak at 284.6 eV. The UV−Vis absorption spectroscopy was recorded using a UV-Vis diffuse reflectance spectrometer (DRS, Shimadzu UV-3600PLUS spectrophotometer), in which $BaSO_4$ was employed as the internal reflectance standard. The specific surface areas were measured by BET method utilizing nitrogen adsorption-desorption apparatus (Quantachrome Instruments U.S., PoreMaster). The pore volume and distribution were determined by the Barrett, Joyner, and Halenda (BJH) method. The photoluminescence (PL) and time-resolved photoluminescence (TRPL) spectra for samples were investigated on an Edinburgh FL and FS900 spectrophotometer with an excitation wavelength of 400 nm and 525nm, respectively.

Photocatalytic hydrogen evolution

The photocatalytic hydrogen evolution was performed in a Pyrex reaction cell at room temperature. In a typical experiment, 50 mg of the photocatalyst was added to the reactor which involved 50 mL of aqueous solution containing 2 vol% lactic acids as sacrifice agent under constant stirring. Before the photocatalytic reaction, the above suspension was evacuated with vacuum pump for 30 min to exhaust the air. A 300 W Xe lamp with a UV cut-off filter ($\lambda \geq 420$ nm) was used as the light source to trigger the photocatalytic reaction. A constant magnetic stirrer was used at the bottom of the reaction cell in order to keep the photocatalyst in suspension status during the photocatalytic water splitting process. The temperature of the reaction solution was maintained at 6 °C by a flow of cooling water during the whole experiment. The H_2 product was periodically analyzed by online gas chromatography (GC-7920, China) equipped with a thermal conductivity detector (TCD). The whole photocatalytic reaction was continued for 3 h.

Photoelectrochemical measurements

10 mg of as-prepared sample was dispersed in a mixed solution containing isopropanol (1.0 mL) by sonication to obtain a homogenous suspension. 100 μL of the suspension was drop-casted onto a fluorine-tin oxide (FTO) glass substrate with an exposed area of 2 cm^2 (1 cm × 2 cm) and then

dried at room temperature under the dark condition to fabricate working electrode. The PEC experiments were performed on the CHI-660E electrochemical workstation (Shanghai Chenhua, China) under a 300 W Xe lamp irradiation with an ultraviolet cutoff filter ($\lambda \geq 420$ nm). Ag/AgCl, FTO glass coated with photocatalyst and Pt plate were used as the reference electrode, working electrode and counter electrode, respectively. 0.1 M Na_2SO_4 solution was used as the electrolyte. The surface area of the working electrode exposed to the electrolyte was about 1.20 cm^2. Transient photocurrent response was measured at 0.0 V during on-off cycling of the solar simulator. The cathodic polarization curves were obtained using the linear sweep voltammetry (LSV) technique with a scan rate of 10 mV/s. The electrochemical impedance spectra (EIS) were measured with an excitation signal of 5 mV amplitude and the frequency range was from 0.1 Hz to 10^5Hz. Moreover, to evaluate the flat-band potential (V_{fb}) of CdS, and Ag_2S/CdS samples Mott−Schottky plots at a frequency of 1 kHz in the same electrochemical configuration and electrolyte under the dark condition. The measured potentials *vs.* Ag/AgCl were converted to the normal hydrogen electrode (NHE) scale by $E_{NHE} = E_{Ag/AgCl} + 0.197$.

Computational Methods

All the density functional theory (DFT) calculations were performed with the aid of the Vienna ab initio simulation package (VASP) [1,2] based on the projected augmented wave (PAW) [3] pseudopotentials with an cut-off energy of 500 eV. The generalized gradient approximation (GGA) [4] with Perdew-Burke-Ernzerhof (PBE) [5] functional was employed to approximate the exchange and correlation effects during the relaxations. During structure optimizations, the convergence criteria of energy on each atom were set to 1.0×10^{-5} eV, while the force convergence threshold of each atom was set to and 0.01 eV·Å^{-1}. The PBE + U approach was employed to accurately describe the 4*d* electron states of Ag and Cd, and the U values were chosen to 3.0 eV and 4.0 eV for Ag 4*d* and Cd 4*d* state according to the previous reports [6,7], respectively. To investigate the potential energy changes in the interface of Ag_2S/CdS nanocomposites, the electrostatic potential energy was calculated with a Ag_2S/CdS heterojunction model, which was built with the CdS (102) slabs (2 × 4 supercell) and Ag_2S (103) slabs (1 × 3 supercell). Considering the large number of atoms in the built model (including 96 Ag atoms, 64 Cd atoms and 112 S atoms), the corresponding Monkhorst-Pack grids of the slab model was chosen as 1 × 1 × 1. In addition, a vacuum spacing of 15 Å were used during the model simulating.

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