Supplementary Information

Simulated-sunlight-driven Cr(VI) reduction on type-II heterostructured Sb₂S₃/CdS photocatalyst

Zhen-yu Zhu, Jia-yuan Li, Wei Li*, Xiao-yun Liu, Yan-yan Dang, Teng-hao Ma,

Chuan-yi Wang*b

^aCollege of Chemistry and Chemical Engineering, Shaanxi Key Laboratory of

Chemical Additives for Industry, Shaanxi University of Science & Technology, Xi'an,

Shaanxi 710021, China. E-mail: liweihg@sust.edu.cn

^bSchool of Environmental Sciences and Engineering, Shaanxi University of Science &

Technology, Xi'an, Shaanxi 710021, China. E-mail: wangchuanyi@sust.edu.cn

1. Methods

1.1. Reagents

Antimony trichloride (SbCl₃, A.R.), thiourea (H₂NCSNH₂, A.R.), sodium sulfide nonahydrate (NaS·9H₂O, A.R.), chromium acetate dihydrate (Cd(Ac)₂·2H₂O, A.R.), ethylene glycol (EG, A.R.), concentrated sulfuric acid (H₂SO₄, \geq 98%), diphenylcarbazide (DPC, A.R.), acetone (A.R.), potassium dichromate (K₂Cr₂O₇, A.R.) were purchased from Aladdin Chemical and used directly without any treatment.

1.2. Synthesis of Sb₂S₃ NRs

 Sb_2S_3 nanorods (NRs) were synthesized via a solvothermal method. Briefly, 0.724 g $SbCl_3$ was added in 80 mL ethylene glycol followed by a magnetic stirring for 1 hour, then 1.4 g thiourea was added in above solution and kept stirring to obtain a clear solution. Subsequently, the obtained solution was kept for 10 h at 180 °C in a closed steel autoclave. After reaching room temperature, the product was collected by centrifugation and rinsed several times with absolute ethanol and deionized water, then the black powder (Sb₂S₃ NRs) was gained after drying for 12 h at 80 °C.

1.3. Synthesis of CdS NPs

The CdS nanoparticles (NPs) were synthesized via a gel-hydrothermal method. Detailedly, $1.32g \operatorname{Na}_2 S \cdot 9H_2 O$ and $1.34 g \operatorname{Cd}(\operatorname{Ac})_2 \cdot 2H_2 O$ were respectively dissolved to 80 mL deionized water to obtain solution A and solution B. The solution A was added to solution B drop by drop with constant stirring, then the mixture was placed quietly for 12 h followed by a suction filtration. The collected sample was evenly dispersed in 80 mL deionized water and kept for 5 h at 180 °C in a 100 mL closed steel autoclave. After reaching room temperature, the product was collected by centrifugation and rinsed for several times with deionized water, then the yellow powder (CdS NPs) was obtained after freeze-drying.

1.4. Characterization

The microstructures of the samples were analyzed on laser microscopic Raman imaging spectrometer (DXRxi, U.S.), X-ray photoelectron spectroscopy (XPS, Axis Supra, U.K.) and X-ray diffractometer (XRD, Bruker D8 Advance, Germany). The morphologies of the samples were observed on field emission scanning electron microscope (FESEM, SU8100, Japan) and field emission transmission electron microscope (TEM, Talos F200X, U.S.). The optical properties of the samples were tested on UV-vis-NIR spectrometer (Agilent, Cary 5000, U.S.) and fluorescence spectrophotometer (Edinburgh, FS5, U.K.). The photo-electrochemical properties of the samples were analyzed on an electrochemical analyzer (CHI660E, CN).

1.5. Photo-electrochemical tests

The photo-electrochemical properties of the samples were tested in 0.2 M Na₂SO₄ or 0.2 M Fe[K₃(CN)₆] electrolyte by using a three-electrode system equipped with a Xenon light source (BBZM-I, 350 W, 803 μ W·cm⁻², CN). The Pt electrode, ITO glass coated by sample and Ag⁺/AgCl electrode were used as counter electrode, working electrode and reference electrode, respectively. The detailed testing parameters were given as bellows.

Linear sweep voltammetry (LSV) curves were tested in 0.2 M Fe[K₃(CN)₆] electrolyte under photo-irradiation. The initial potential, final potential, scan speed, sample interval, quiet time and sensitivity were set as -1 V, -0.5 V, 0.1 V/s, 0.01 V, 1 s, and 1×10^{-6} A/V, respectively.

Electrochemical impedance spectroscopy (EIS) spectra were tested in 0.2 M $Fe[K_3(CN)_6]$ electrolyte under photo-irradiation. The initial potential, high frequency, low frequency, amplitude and quiet time were set as 0 V, 100000 Hz, 0.01 V and 2 s, respectively.

Photocurrent-time (I-t) curves were tested in 0.2 M Na_2SO_4 electrolyte. The initial potential, sample interval, quiet time and sensitivity were set as -0.2 V, 0.1 s, 0 s and 1×10^{-6} A/V, respectively.

Mott-Schottky (M-S) plots was tested at different frequencies (1500 Hz and 2000 Hz) in 0.2 M Fe[K₃(CN)₆] electrolyte. The initial potential, final potential, incremental potential, amplitude and quiet time were set as 0 V, 0.5 V, 0.01 V, 0.01 V, 2 s, respectively.

1.6. Calculation of electrode potential conversion

$$E_{\rm RHE} = E_{\rm Ag/AgCl} + 0.197 + 0.059 \text{ pH}$$
(1)

 $E_{Ag/AgCl}$ is the Ag/AgCl electrode potential, and E_{RHE} is the reversible hydrogen

electrode potential.

2. Supplemented data



Fig.S1 Cr (VI) residual rates of the Sb_2S_3 .



Fig.S2 SEM images of SSCS-1 (a), SSCS-2 (b), SSCS-3 (c) and SSCS-4 (d).



Fig.S3 XPS spectra of the samples: (a) survey and (b) Sb 3d core-level.



Fig.S4 N_2 adsorption isotherms of the samples.



Fig.S5 UV-vis spectrograms of Cr(VI) solution treated different time by SSCS-3 composite.



Fig.S6 XPS survey spectra of the fresh and recycled SSCS-3 composite photocatalysts.



Fig.S7 XPS core-level spectra of the fresh and recycled SSCS-3 composite photocatalysts: (a) Sb 3d, (b) Cd 3d, (c) S 2p and (d) Cr 2p.

Fig.S8 UV-vis absorption spectrum of bare CdS NPs.