

Electronic Supplementary Information (ESI)

In-situ preparation of Bi₂S₃ nanoribbon-anchored BiVO₄ nanoscroll heterostructures for the catalysis of Cr(VI) photoreduction

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1. Reagents and Sample Synthesis

Bismuth nitrate pentahydrate (AR 99%) were obtained from Aladdin Industrial corporation. Ammonium metavanadate (AR), sodium hydroxide (AR) and ethanol absolute (AR) were purchased from Sinopharm Chemical Reagent Co., Ltd. Analytical grade sodium dodecylbenzenesulfonate(SDBS) and nitric acid were purchased from Chengdu Kolong Chemical Reagent Co., Ltd and Nanjing Chemical Reagent Co., Ltd, respectively. Analytical grade sodium dimethyldithiocarbamate were obtained from Chengdu Aikeda Chemical Reagent Co., Ltd. All chemicals were used as received, unless otherwise stated. Deionized water was prepared with a Milli-Q puritiesystem (18.2 MΩ). Bismuth (III) dimethyldithiocarbamate was synthesized by dissolving bismuth nitrate pentahydrate in 200 mL ethanol solvent for 30min. and then adding 16.0g sodium dimethyldithiocarbamate. After stirring the solution for 1 hr, the product was collected and dried at 100 °C vacuum for 12 hrs. The thus obtained solid was determined to be Bismuth (III) dimethyldithiocarbamate ($\text{Bi}(\text{dedc})_3$).

Synthesis of Bi_2S_3 nanoribbon-anchored BiVO_4 nanoscroll heterostructures

The synthesis of BiVO_4 nanoscroll (noted as S-0) adopted our previous method.²³ The Bi_2S_3 nanoribbon-anchored BiVO_4 nanoscroll heterostructures were synthesized via a facile solvothermal route. Typically, 0.2g of S-0 and a certain amount of $\text{Bi}(\text{dedc})_3$ were added to a mixture of ethylene glycol (20 mL) and deionized water (10 mL). After 30 min of continuous stirring, the above solution was transferred into a 50 mL, Teflon-lined stainless autoclave and maintained at 180°C for 5 hrs. After natural

cooling to room temperature, the resulting sample was collected via centrifugation, washed with alcohol and ultrapure water several times, and then dried at 60°C under vacuum for 12 hrs. To investigate the effect of Bi(dedc)₃ amount on the formation of BiVO₄/Bi₂S₃ heterostructures, the different Bi(dedc)₃ amounts (0.01, 0.03, 0.05 and 0.07g) were used during the solvothermal process, and the calculated weight ratio (R) of BiVO₄: Bi₂S₃, R is selected as 44.4, 14.8, 8.9 and 6.4, and the corresponding samples were noted as S-1, S-2, S-3 and S-4, respectively.

Synthesis of pure Bi₂S₃ nanoribbons

Pure Bi₂S₃ nanoribbons were prepared using an approach similar to that for Bi₂S₃ nanoribbon-anchored BiVO₄ nanoscroll heterostructures except adding 0.2g of Bi(dedc)₃ as the reactant.

2. Characterizations.

X-ray diffraction (XRD) was conducted on a Bruker D8 Advance diffractometer using Cu K α radiation ($\lambda = 0.15406$ nm), where the data was collected in the 2θ range of 20–80° at a step size of 0.02°. SEM images of solid products were measured on a Nova Nanosem 200 system operated at an acceleration voltage of 15 kV. Both transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) were performed on JEOL-3010 instrument. XPS was performed on a spectrometer from Kratos Axis Ultradld, using Mono Al K α (1486.71eV) radiation at a power of 120 W (8 mA, 15 kV). All binding energies were referenced to the C 1s peak (284.6 eV) arising from adventitious carbon. UV-vis diffuse reflectance spectra were obtained using a UV-vis spectrophotometer (UV-2550, Shimadzu, Japan), where fine BaSO₄ powder was used as a reflectance standard.

The Brunauer–Emmett–Teller (BET) surface areas of the samples were measured by nitrogen adsorption using a Micromeritics ASAP 2020 nitrogen adsorption apparatus (USA).

3 Photoelectrochemical measurement

Photoelectrochemical properties were investigated in a three-electrode cell using an electrochemical analyzer (CHI-660C, Shanghai Chenhua). A 300 W Xe lamp was used as a light source for measurements. An aqueous solution of 0.5 M Na₂SO₄ (PH = 6.5) was employed as an electrolyte. The as-prepared BiVO₄ nanoscrolls or Bi₂S₃ nanoribbon-anchored BiVO₄ nanoscroll heterostructures was coated onto a slice of FTO glass with an area of 1×1 cm² and employed as the working electrode. A platinum wire and a saturated Ag/AgCl electrode were used as the counter and reference electrodes, respectively. Potentials of the working electrode were shifted on a RHE (reversible hydrogen potential) scale by the formula $V_{\text{RHE}} = V_{\text{Ag/AgCl}} + V_0 + 0.05916 \times \text{pH}$, where V_{RHE} was the potential vs. a reversible hydrogen potential, $V_{\text{Ag/AgCl}}$ was the potential vs. Ag/AgCl electrode, $V_0 = 0.1976$ V at 25 °C and pH was the pH value of electrolyte. The active area of the BiVO₄ sample was fixed to 0.28 cm² by using a black mask. The photocurrent of the sample was measured from the back side (electrolyte–substrate interface). A cyclic voltammetry method was adopted with a scan rate of 10 mV s⁻¹.

4. Photocatalytic test.

The photocatalytic activity of the as-prepared BiVO₄ nanoscrolls and Bi₂S₃ nanoribbon-anchored BiVO₄ nanoscroll heterostructures were evaluated by photocatalytic reduction of Cr(VI) with 300 W Xe lamp as the UV-visible-light source. The reactor was placed in a sealed black box with a window on the top. In a typical

process, 0.3 g of the as-prepared sample was added into 300 mL of Cr(VI) solution (50 mg L⁻¹, which was based on Cr in a dilute K₂Cr₂O₇ solution, and its pH=5.35). After the solution was stirred for 1 h in the dark to achieve adsorption equilibrium before being exposed to UV-visible-light irradiation. 4.0 mL of the suspension was taken out of the reactor every 30 min and separated by centrifugation. The Cr(VI) concentration was measured by a colorimetric method with diphenylcarbazide.¹

References

(S1) T. X. Wang, S. H. Xu and F. X. Yang, *Mater. Lett.*, 2012, **83**, 46.

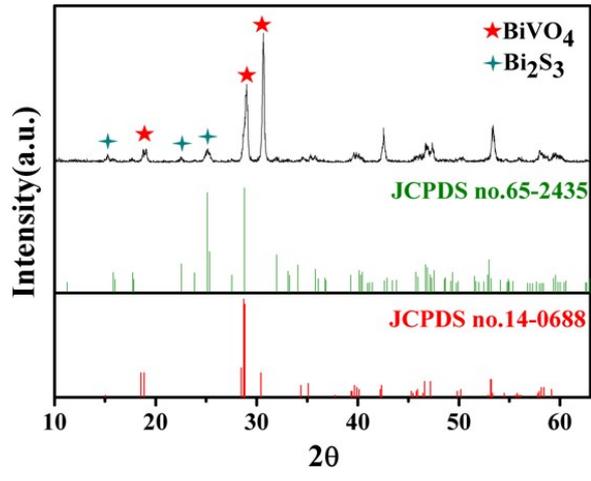


Fig. S1 XRD patterns of the S-2 sample.

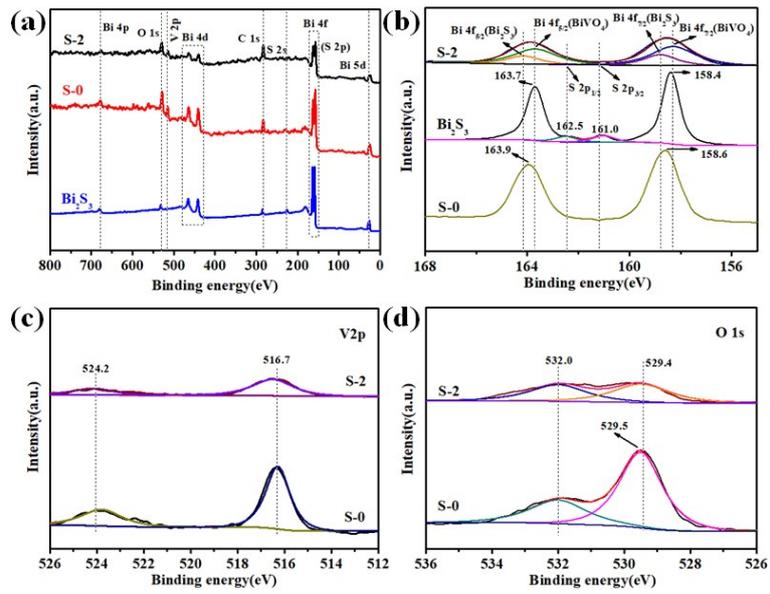


Fig. S2 Fully scanned XPS spectra (a), high-resolution XPS spectra of Bi 4f and S 2p (b) of the S-2, S-0 and Bi_2S_3 (pure Bi_2S_3 nanoribbons); High-resolution XPS spectra of V 2p (c), and O 1s (d) of S-2, and S-0.

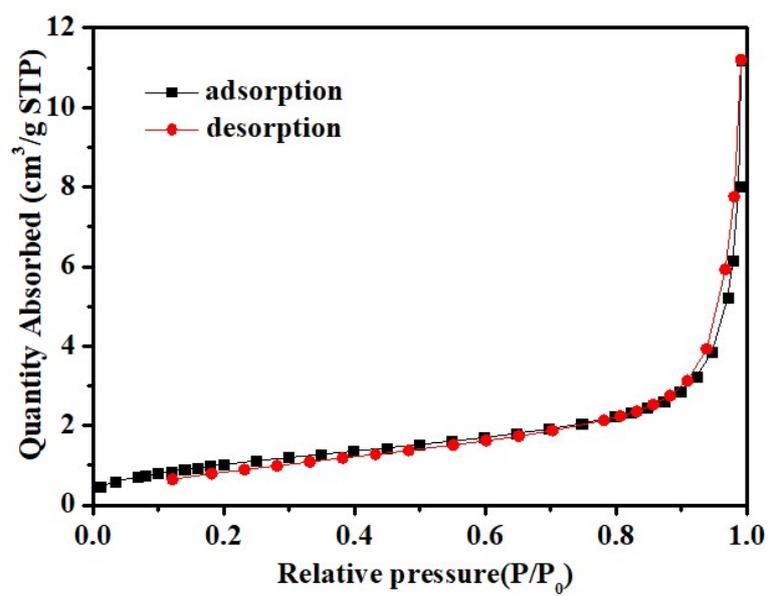


Fig. S3 Nitrogen adsorption-desorption isotherm curves of S-2.

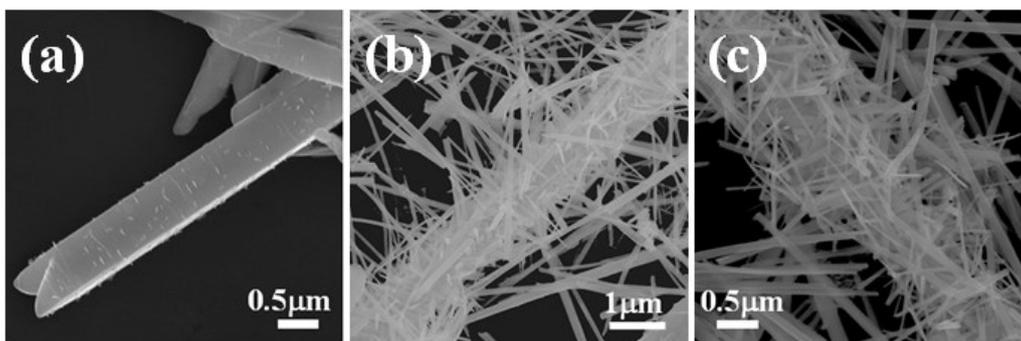


Fig. S4 SEM images of (a) S-1, (b) S-3 and (c) S-4

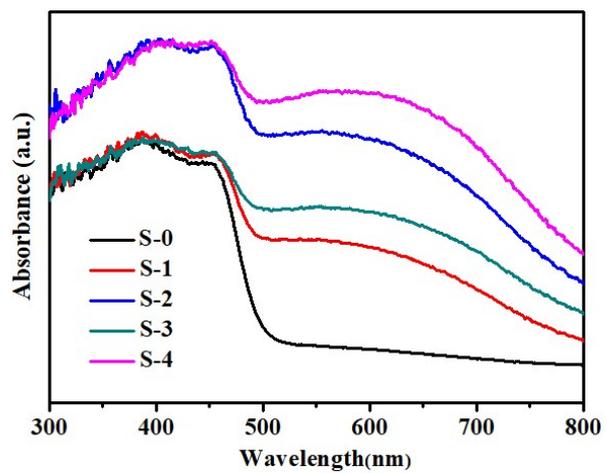


Fig. S5 UV-visible absorption spectra of S-0, S-1, S-2, S-3, and S-4.

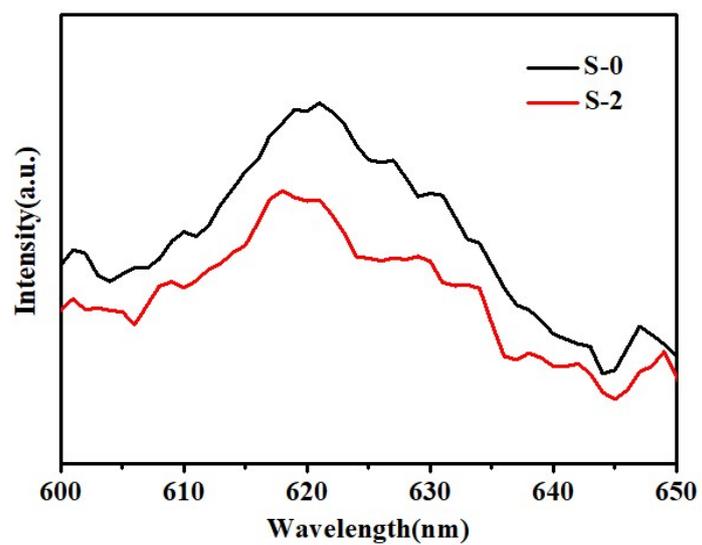


Fig. S6 PL emission spectra of S-0 and S-2 samples excited at 320 nm, at room temperature.

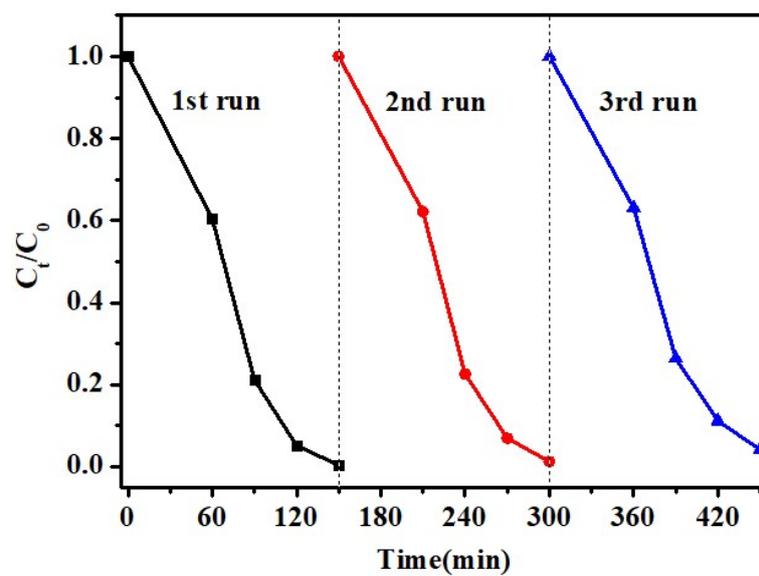


Fig. S7 Recyclability of the S-2 sample in the the photocatalytic reduction of Cr(VI) under UV-visible-light irradiation for 90 min.