Electronic Supplementary Information

Environment-benign synthesis of branched Bi_2O_3-Bi_2S_3 photocatalysts by an etching and re-growth method

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Details for preparation, characterization and evaluation of the photocatalysts:

All reagents were commercially available and of analytical grade. They were used without further purification.

Preparation of Bi_2O_3: Typically, 10 mmol of $Bi(NO_3)_3 \cdot 5H_2O$ was dissolved in 10 mL of nitric acid (1 mol/L). Then 47 mL of KOH (1 mol/L) was added to the above solution for pH adjustment, and there was the immediate formation of a white precipitant. Afterwards, the emulsion was transferred into a 100 mL Teflon-lined autoclave and maintained at 160 ºC for different durations (i.e. 1, 3 or 6 h). After the autoclave was cooled down to room temperature, Bi_2O_3 (hereinafter denoted as BO) in bright yellow was collected by filtration, and washed (de-ionized water and absolute ethanol) and dried at 80 ºC for 4 h in air.

Preparation of Bi_2O_3-Bi_2S_3 composites: In this process, BO that acted both as substrate and bismuth source was hydrothermally treated with sulfide sources. Typically, 0.932 g (2 mmol) of the as-synthesized BO was dispersed in 100 mL sulfide-containing solutions (sodium sulfide, thiourea or potassium thiocyanate, denoted herein as SS, TU or PT, respectively). Then the mixture was hydrothermally treated at 160 ºC for 6 h. The resulted Bi_2O_3-Bi_2S_3 composites (denoted as BO-BS) were collected by filtration, washed and dried as in the case of Bi_2O_3 preparation.

Characterization: The as-prepared BO and BO-BS samples in the form of crystals were collected and characterized by powder X-ray diffraction (XRD) on a Bruker Automatic Diffractometer (Bruker D8 Advance) with monochromatized CuKα radiation (λ=0.15406 nm) at a setting of 40 kV and 80 mA. The scanning rate was 0.02º (2θ)/s and the scanning range was 10-70º. The FT-IR spectra were collected on a Perkin-Elmer IR spectrophotometer using the KBr pellet technique. The surface composition and chemical states of as-synthesized samples were measured by X-ray photoelectron spectroscopy (XPS). The amount of Bi, S and O were analyzed using an X-ray Fluorescence Spectrometer (AXIOS Advanced). Field emission scanning electron microscope (FE-SEM) (Hitachi S-4800) was employed to observe the micro- and nano-structure as well as the morphology of as-prepared samples. Transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) images were taken over a JEM-3010F transmission electron microscope. UV-vis diffuse absorption spectra (UV-vis DRS) of samples were obtained over a UV-vis spectrophotometer (Cary 100) using $BaSO_4$ as reference. Photoluminescence spectra (PL) of the samples were obtained using a Varian Cary Eclipse Fluorescence spectrophotometer (at 425 nm excitation). Transient photocurrent responses for the as-prepared samples under the irradiation of visible light (500 W Xe lamp with a cutoff filter) were recorded over an electrochemical analyzer (CHI660D Instruments) in a standard three-electrode system using the prepared samples as working electrode (ITO as supporter), Pt wire as counter electrode, and saturated calomel electrode (SCE) as reference.

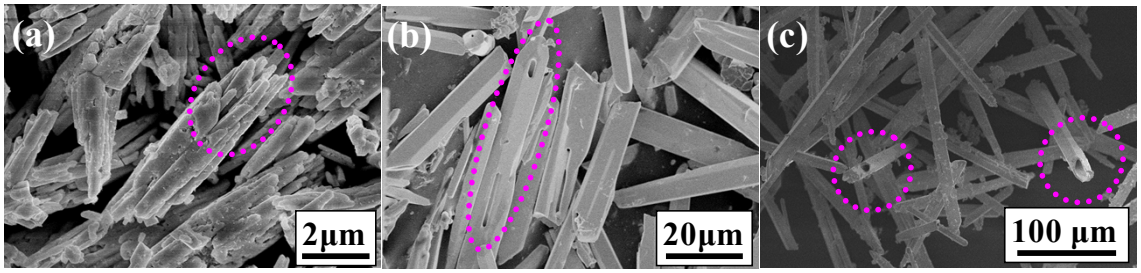

Figure S1. SEM images of Bi_2O_3 after hydrothermal treatment: (a) 1 h, (b) 3 h, and (c) 6 h at 160 ºC.

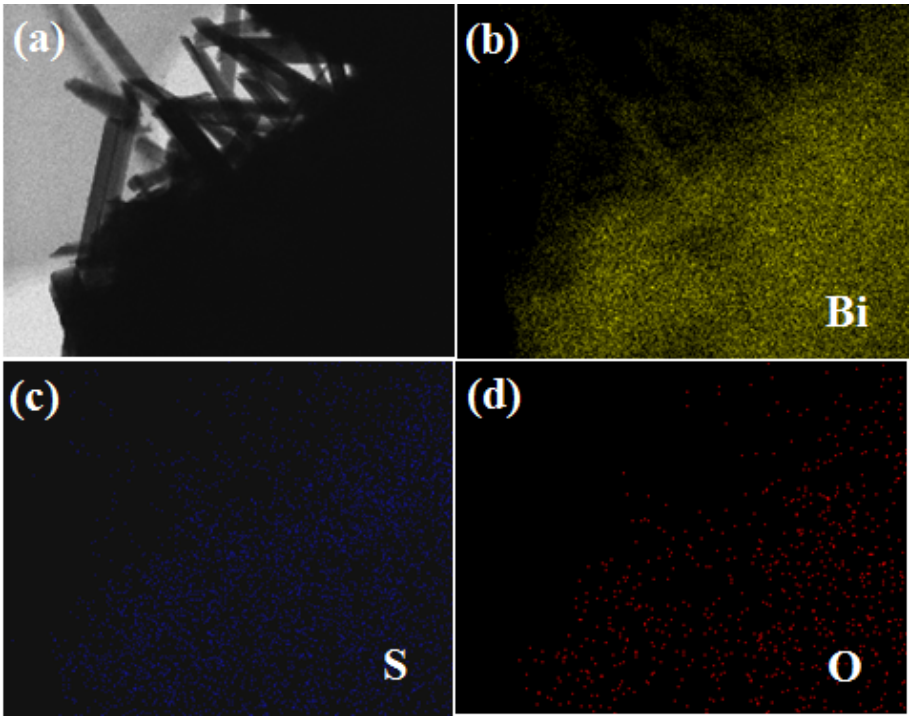

Figure S2. STEM images of (a) the Bi_2O_3-Bi_2S_3 composite, and the corresponding (b) Bi, (c) S, and (d) O elemental mappings.

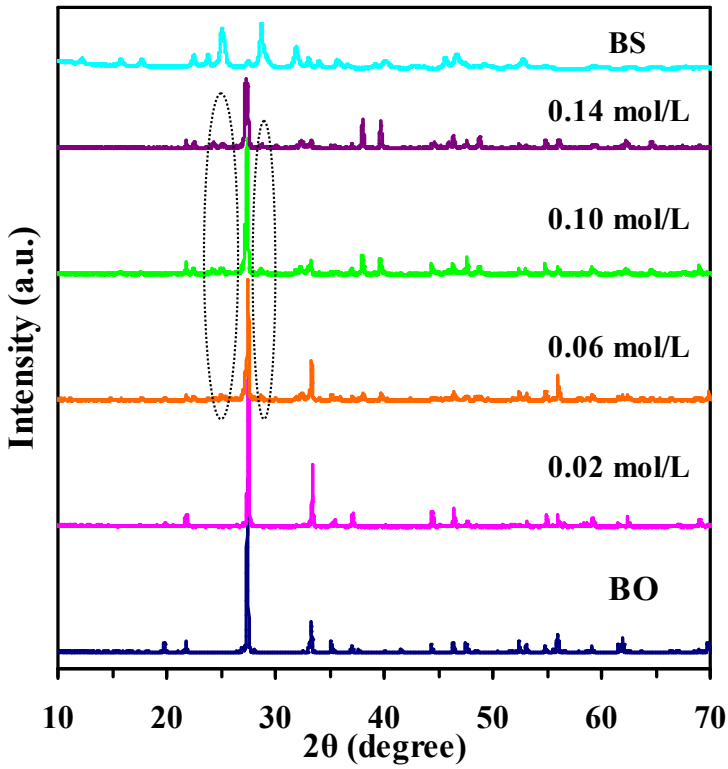

Figure S3. XRD patterns of BO (Bi_2O_3), BS (Bi_2S_3) and BO-BS (Bi_2O_3-Bi_2S_3) composites prepared using SS (sodium sulfide) sources of different concentrations.

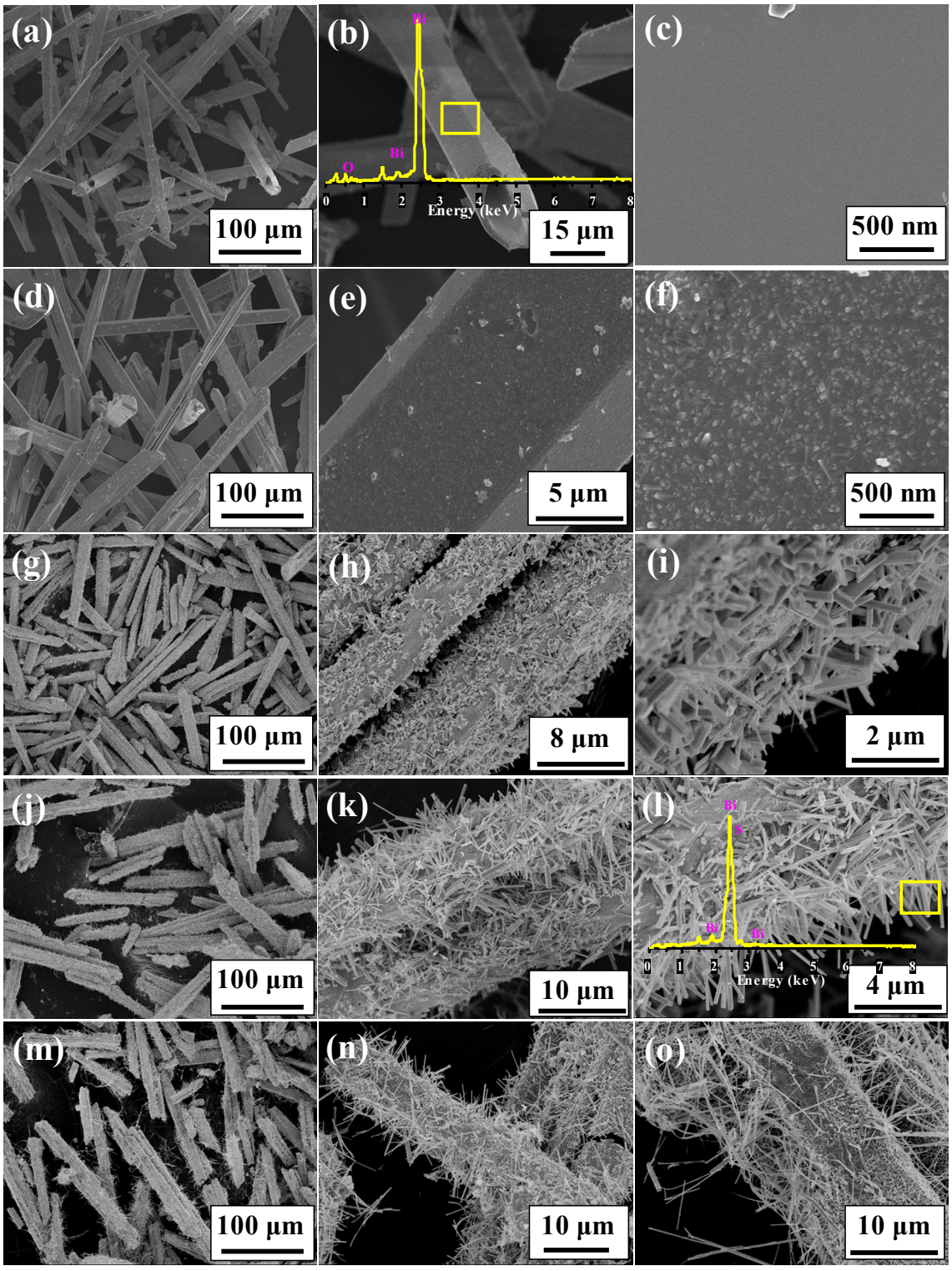

Figure S4. SEM images: Bi_2O_3, (a)-(c); Bi_2O_3-Bi_2S_3 composites crystallized at different SS (sodium sulfide) concentrations for 6 h: (d)-(f) 0.02 mol/L; (g)-(i) 0.06 mol/L; (j)-(l) 0.10 mol/L and (m)-(o) 0.14 mol/L.

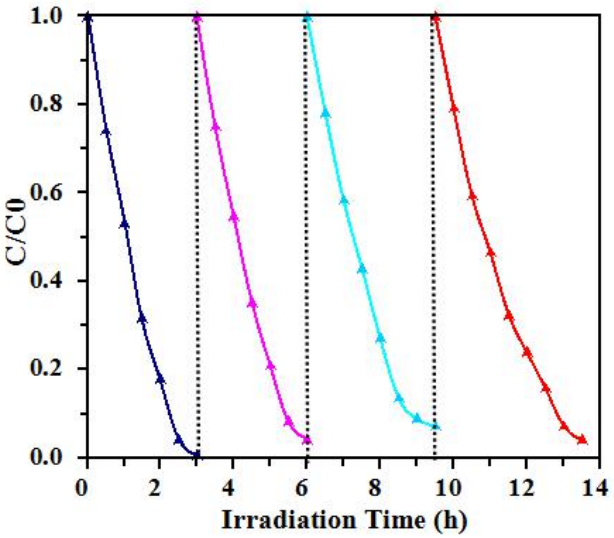

Figure S5. Recycling behavior of the Bi_2O_3-Bi_2S_3 composite (using thiourea as sulfur sources).