

Supporting information

Facile Synthesis of Hierarchical Bi₂S₃ Nanostructures for Photodetector and Gas Sensor

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Experiment section

All the reagents were analytically pure and used without further purification. In a typical procedure, 0.25 g of thiourea (Tu) was dissolved in 50 ml distilled water under constant stirring, then 0.61 g of Bi(NO₃)₃·5H₂O was added to the above solution. After being stirred at 60 °C for 10 min, the solution was transferred to a Teflon-lined autoclave. The autoclave was transferred into an oven and maintained at 120 °C for different times. After cooling down to room temperature naturally, the precipitates were collected and washed with distilled water and anhydrous ethanol for several times, then dried at 60 °C for 8 h.

The composition and phase of as-prepared products were identified by the powder X-ray diffraction (XRD, Bruker, D8 ADVANCE) with Cu K α radiation (λ = 1.5418 Å). The morphology and structure of the products were characterized by scanning electron microscope (SEM, Quanta 400), and transmission electron microscopy (TEM, JEM2010-HR). The optical properties of the products were measured with a UV-Vis-NIR Spectrophotometer (UV, Shimadzu UV-3150) and Laser Micro-Raman Spectrometer (Renishaw inVia) using a visible laser (λ = 514.5 nm) with an output laser power of 50 mW as the excitation wavelength at room temperature.

For photodetector and gas sensor devices fabrication, the standard photolithography technique followed by ITO evaporation and lift-off procedures were used to define the source and drain two ITO electrodes on a common glass. The spacing between these two ITO electrodes is 40 μ m, and the hierarchical Bi₂S₃ nanostructures were suspended in ethanol and then deposited into the spacing carefully. Two silver wires were fixed to the two ends of the Bi₂S₃ film with

silver paste, which were further fastened by coating with a thin PDMS film. The current–voltage and current-time characteristics were recorded by using an Autolab electrochemical station (PGSTAT 302N) under simulated AM 1.5 G illumination (100 mW cm^{-2}) provided by a solar simulator (91160, 1 kW Xe lamp, Oriel). The incident-light intensity was calibrated with a standard Si solar cell (91150V, Oriel). The gas sensing properties of Bi_2S_3 was measured by a synthesized function generator (Model DS345, STANFORD RESEARCH SYSTEMS, USA) and a low-noise current preamplifier (Model SR570, STANFORD RESEARCH SYSTEMS, USA). The methanol gas were provided by evaporating the methanol on a heating stage at 40°C .

The optical bandgap (E_g) of the semiconductor material can be calculated from the equation of $(\alpha h\nu)^n = A(h\nu - E_g)$, where $h\nu$ is the photon energy, α is the absorption coefficient, A is a constant for the material, and n is 2 for a direct transition or $1/2$ for an indirect transition.¹ As shown in Fig. S3, the calculated direct bandgap for the hierarchical Bi_2S_3 nanostructures is 1.67 eV.

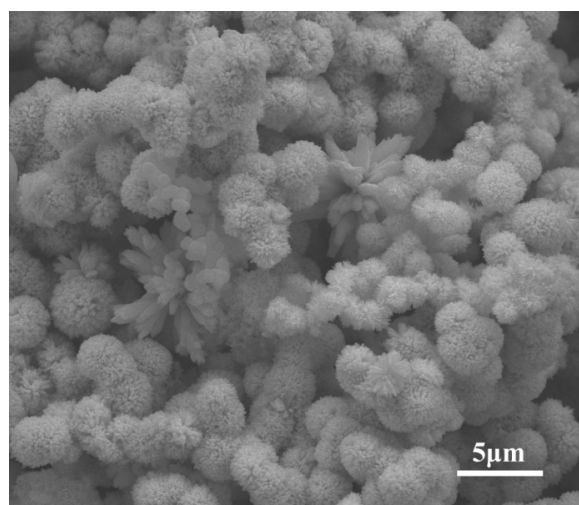


Fig. S1 SEM image of hierarchical Bi_2S_3 nanostructures obtained at 120°C .

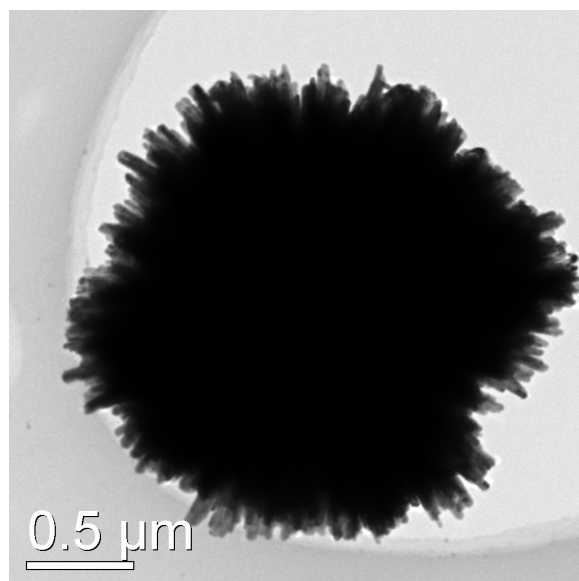


Fig. S2 TEM image of hierarchical Bi_2S_3 nanostructures obtained at 120 °C.

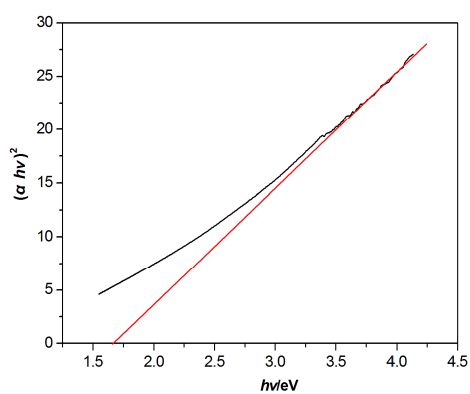


Fig. S3 $(\alpha h\nu)^2$ vs $h\nu$ curves for the hierarchical Bi_2S_3 nanostructures

Reference:

1. J. Y. Gan, X. H. Lu, T. Zhai, Y. F. Zhao, S. L. Xie, Y. C. Mao, Y. L. Zhang, Y. Y. Yang and Y. X. Tong, *J. Mater. Chem.*, 2011, **21**, 14685-14692.