Supporting Information

A simple template-free synthesis of ultrathin Cu₂ZnSnS₄ nanosheets for highly stable photocatalytic H₂ evolution

Lu Wang, Wenzhong Wang*, Songmei Sun

State Key Laboratory of High Performance Ceramics and Superfine Microstructure, Shanghai Institute of Ceramics, Chinese Academy of Sciences, 1295 Dingxi Road, Shanghai 200050, China

Experimental

Preparation of Cu₂ZnSnS₄: All the reagents were of analytical grade and used without further purification. In a typical synthesis, copper chloride dehydrate (CuCl₂·2H₂O), zinc chloride (ZnCl₂), and tin chloride dehydrate (SnCl₂·2H₂O) with molar ratio of 2:1:1 was added in 40 mL absolute alcohol, respectively. Then excessive thiourea was dissolved in the above white suspension. After stirring for 30 minutes, the as-obtained colorless transparent solution was heated at 50 °C for 6 h and at 120 °C for 12 h under vacuum, and then cooled to room temperature naturally. The resulting products were added in oleylamine and heated at 220 °C for 1 h under the N₂ atmosphere. The resulting suspension was cooled down to room temperature and separated by filtration, washed with absolute alcohol several times to obtain samples with dark brown color.

Characterization of Cu₂ZnSnS₄: The X-ray diffraction (XRD) patterns were measured with a D/Max 2250 V diffractometer (Rigaku, Japan) using Cu Kα (λ=1.5406 Å) radiation over the range of 10° ≤ 2θ ≤ 80°. The morphologies and microstructures of as-prepared sample were analyzed by the Scanning Electron Microscope (SEM) (JEOL JSM-6700F) and Transmission Electron Microscope (TEM) (JEOL JEM-2100F, accelerating voltage 200 kV). The accurate composition of the sample was obtained by using the Oxford INCA energy dispersive X-ray spectrometer (EDS) attachment of the JEOL JXA-8100 electron probe microanalyzer (EPMA). The optical diffuse reflectance spectrum was conducted on a
UV-Vis spectrophotometer (Hitachi U-3010) using BaSO$_4$ as the reference. Nitrogen adsorption-desorption measurements were conducted at 77.35K on a Micromeritics Tristar 3000 analyzer after samples were degassed at 150 °C for 6 h.

**Photocatalytic Reaction:** Photocatalytic reactions were conducted in a gas-closed circulation system. The photocatalyst powder (20 mg) was dispersed by a magnetic stirrer in an aqueous solution (200 ml) containing 0.25 M Na$_2$SO$_3$ and 0.35 M Na$_2$S as electron donors in a Pyrex cell with a top window. This suspension was irradiated under UV-visible light from a 500 W Xe lamp. The amount of H$_2$ evolved was determined with on-line gas chromatography equipped with a thermal conductivity detector (TCD). Nitrogen was purged through the cell before reaction to remove oxygen.

![Figure S1. TEM image of Cu$_2$ZnSnS$_4$ with higher magnification](image1)

**Figure S1.** TEM image of Cu$_2$ZnSnS$_4$ with higher magnification

![Figure S2. Energy dispersive X-ray spectrometer of Cu$_2$ZnSnS$_4$.](image2)

**Figure S2.** Energy dispersive X-ray spectrometer of Cu$_2$ZnSnS$_4$. 
Figure S3. The comparison of photocatalytic H₂ evolution over different samples under the same condition.