Supporting Information

A simple template-free synthesis of ultrathin Cu_2ZnSnS_4 nanosheets for highly stable photocatalytic H_2 evolution

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Experimental

Preparation of Cu_2ZnSnS_4: All the reagents were of analytical grade and used without further purification. In a typical synthesis, copper chloride dehydrate ($CuCl_2 \cdot 2H_2O$), zinc chloride ($ZnCl_2$), and tin chloride dehydrate ($SnCl_2 \cdot 2H_2O$) 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 ^oC for 6 h and at 120 ^oC for 12 h under vacuum, and then cooled to room temperature naturally. The resulting products were added in oleylamine and heated at 220 ^oC for 1 h under the N_2 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 Cu_2ZnSnS_4: 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 $10° \leq 2\theta \leq 80°$. 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 ^oC 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_2SO_3 and 0.35 M Na_2S 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.

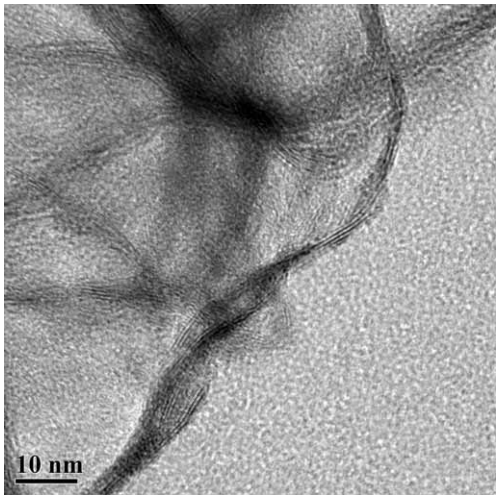

Figure S1. TEM image of Cu_2ZnSnS_4 with higher magnification

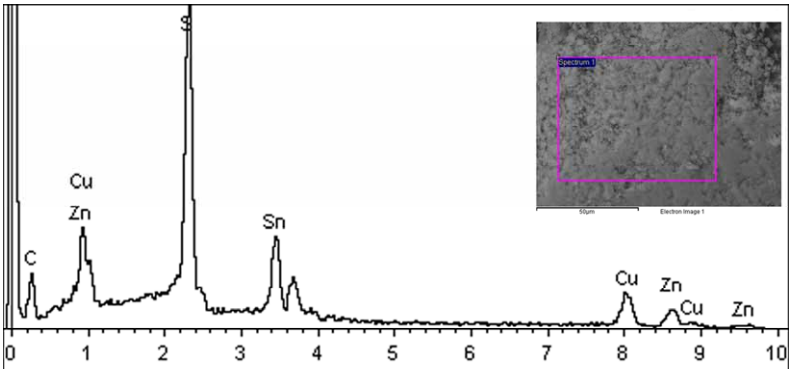

Figure S2. Energy dispersive X-ray spectrometer of Cu_2ZnSnS_4.

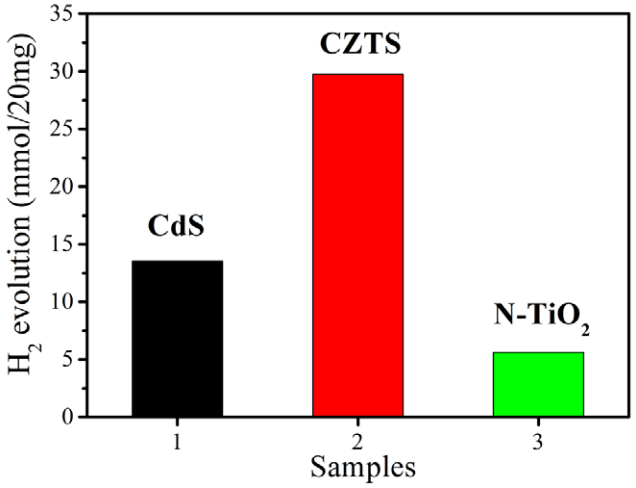

Figure S3. The comparison of photocatalytic H_2 evolution over different samples under the same condition.