Supporting Information

Ultra-thin Cu_2S nanosheets: effective cocatalyst for photocatalytic hydrogen production

Yixuan Zhou[a†], Yongpeng Lei[b†], Dingsheng Wang[a]*, Chen Chen[a], Qing Peng[a], Yadong Li[a]

[a.] Department of Chemistry and Collaborative Innovation Center for Nanomaterial Science and Engineering, Tsinghua University, Beijing 100084 (P. R. China)

[b.] College of Basic Education, National University of Defense Technology, Changsha 410074 (P. R. China)

† These authors contributed equally to this work

*E-mail: wangdingsheng@mail.tsinghua.edu.cn

Chemicals

All the reagents used in this work, including $CuCl_2 \cdot 6H_2O$, PVP, CTAC, CTAB, benzoic acid, benzyl alcohol, dodecanethiol, sulfur powder, thiourea, vulcanized polyisoprene were of analytical grade from the Beijing Chemical Factory of China and were used without further purification.

Preparation of Cu_2S nanoplates with the thicknesses from 1.2 nm to 45 nm

In a typical synthesis of Cu_2S nanoplates, 80 mg PVP (30000W), 300 mg benzoic acid, 50 mg $CuCl_2 \cdot 6H_2O$, 150 mg CTAB plus CTAC (the mole ratio varies from 150:0 to 0:150 to get the thickness from 1.2 nm to 45 nm), 10 ml benzyl alcohol were mixed in flask with vulcanized polyisoprene hanged over 1 cm above the solution. The reaction was allowed to proceed at 200°C for 24 h. After cooling down to room temperature, the product was collected by centrifugation at 10000 rpm for 8 min and washed three times with ethanol, then dried at 60°C for 12 h.

Preparation of Cu_2S NS/TiO_2 nanocomposites

In a typical synthesis of Cu_2S NS/TiO_2 nanocomposites, 190 mg TiO_2 were dispersed in ethanol with ultrasound for 1 h. After cooling to room temperature, 10 mg Cu_2S nanosheets were added and mixed. Then the slurry was stirred for 24 h and the product was obtained by filtration.

Characterization

The powder XRD patterns were recorded with a Bruker D8-advance X-ray powder diffractometer with Cu Kα radiation (λ = 1.5406 Å). The size and morphology of as-synthesized samples were determined by using Hitachi model H-800 transmission electron microscope and JEOL-2010F high-resolution transmission electron microscope. High-resolution transmission electron microscope (HRTEM) was performed on a FEI TecnaiG^{2}F20S-TWIN with an acceleration voltage of 200kV. Energy dispersive spectroscopy was recorded to determine the composition of the products. Scanning electron microscopy (SEM, JEOL JSM-6301F) was introduced to measure the size and morphology of the as-obtained products. The optical properties of the products were determined with a Varian Cary Bio50 UV-vis spectrometer. AFM analysis was performed in tapping mode in air with a Multimode NanoscopeIIIa SPA (Veeco Instruments, Bruker). Ultrasharp cantilevers with a diamond-like carbon tip (NSG01, NT-MDT, Russia) were used. The image was flattened using the NanoScope Analysis software (version 1.40). A silicon wafer with thermal oxide layer of 2.850 Å in thickness (Silicon Valley Microelectronics, Inc. USA) was used. A

300 W xenon arc lamp (250～1800nm，Changzhou Siyu Environmental Materials Co., Ltd.) was employed as a solar light source to perform the photocatalytic experiment. The distance between reactor and lamp was about 20 cm.

Photocatalytic Hydrogen Production

The photocatalytic hydrogen production experiments were carried out in a 100 mL quartz flask at room temperature. A 300 W xenon arc lamp (Changzhou Siyu Environmental Materials Co., Ltd.), 20 cm away from the reactor, was employed as light source to trigger the photocatalytic reaction. In a typical experiment, 20 mg of the catalysts were dispersed with constant stirring in 50 mL mixed solution containing 10 mL menthol and 40 mL water. Prior to irradiation, the system was bubbled with nitrogen for 30 min to eliminate any residual O_2. 1.0 mL sample of the evolved gas was collected and analyzed by gas chromatograph (SP6890, ShangdongLunanRuihong Chemical Instrument Co., Ltd., TCD detector, Ar as carrier gas and 5 Å molecular sieve column.

Figures and Scheme

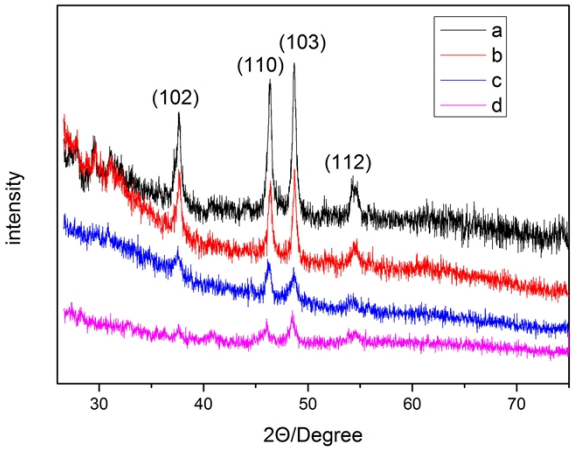
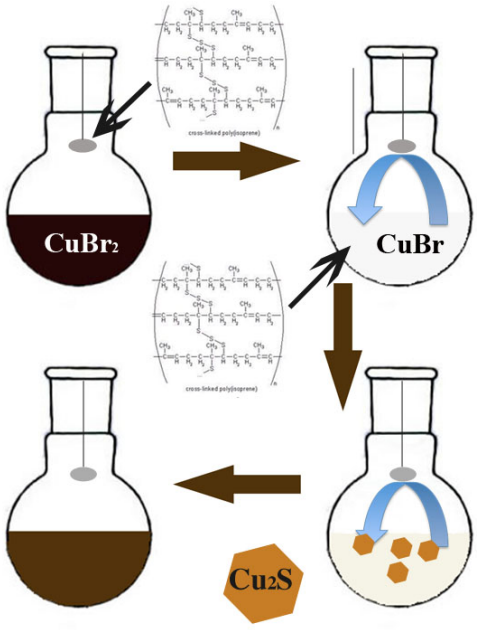


Figure S1. XRD patterns of Cu_2S nanoplates with different thicknesses: a) 45 nm; b) 30 nm; c) 5 nm; and d) 1.2 nm.



Scheme S1. Schematic diagram of the formation process of Cu_2S NS.

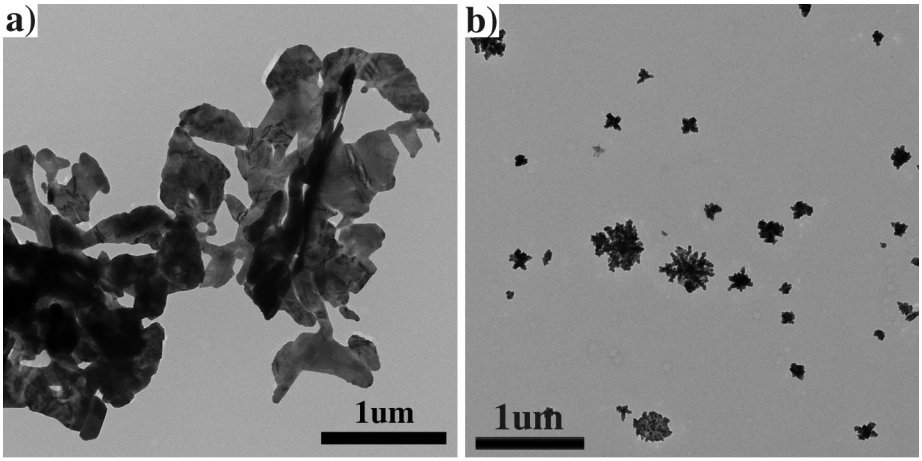


Figure S2. TEM images of Cu_2S synthesized with different precursors: a) sulfur powder; b) thiourea.

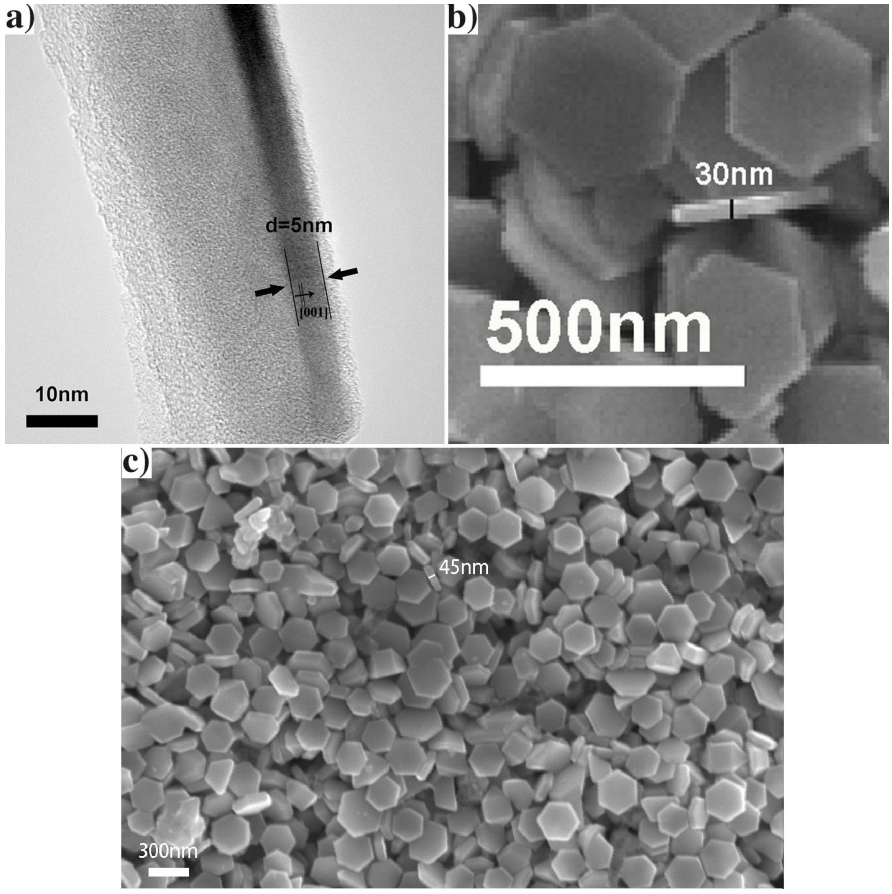


Figure S3. TEM and SEM images of Cu_2S nanoplates with different thicknesses: a) 5 nm; b) 30 nm; c) 45 nm.

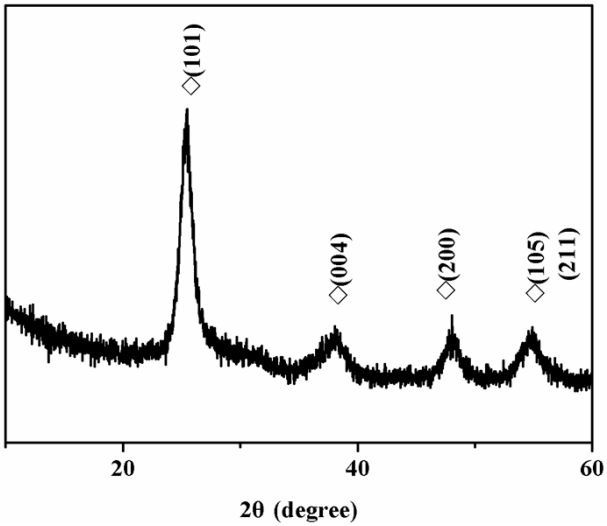


Figure S4. XRD pattern of TiO_2

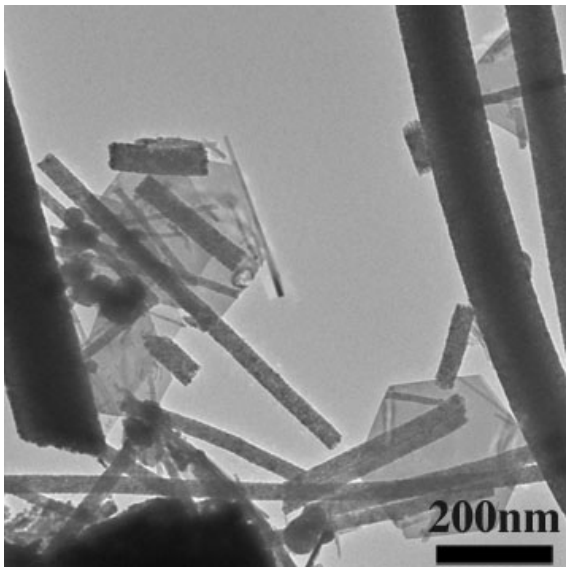


Figure S5. TEM image of Cu_2S NS/TiO_2

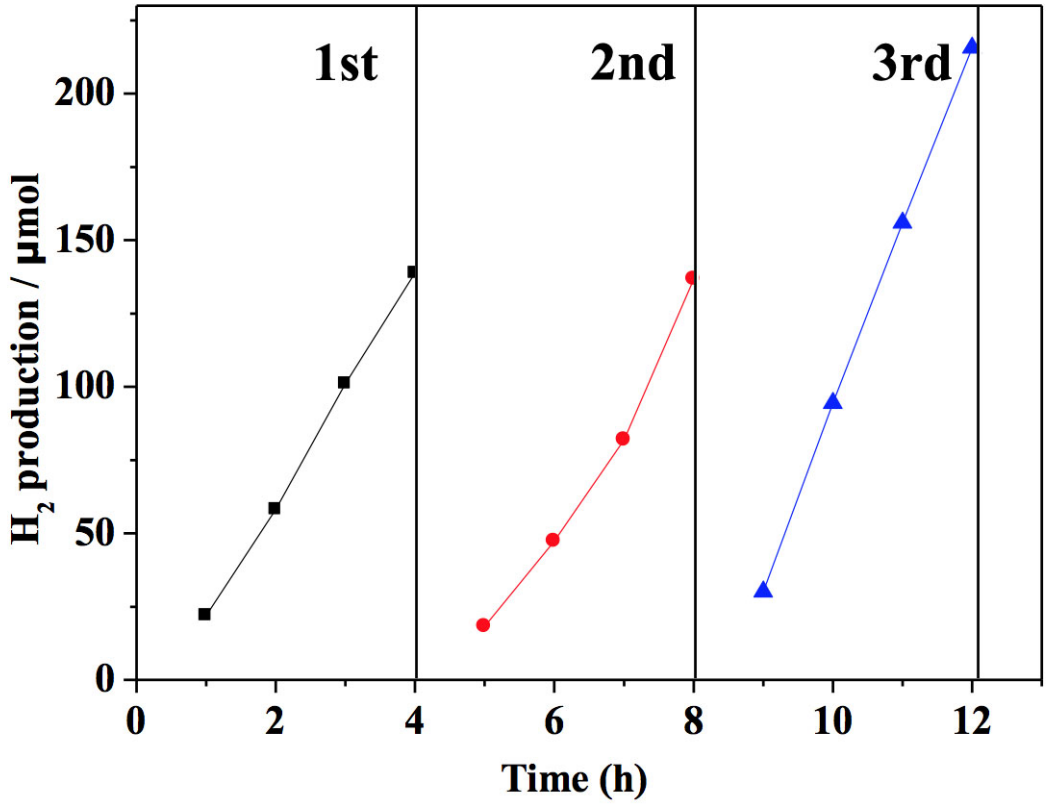


Figure S6. Time course of photocatalytic H_2 production over Cu_2S NS/TiO_2.