Surpporting Information

Preparation of Monodispersed CuInS₂ Nanopompons and Nanoflake Films and Applications in Dye-sensitized Solar Cells

Yufeng Liu^a, Yian Xie^a, Houlei Cui^a, Wei Zhao^a, Chongyin Yang^a, Yaoming Wang^a, Fuqiang Huang^{*a,b}, Ning Dai^c

 ^aCAS Key Laboratory of Materials for Energy Conversion and State Key Laboratory of High Performance Ceramics and Superfine Microstructure, Shanghai Institute of Ceramics, Chinese Academy of Sciences, Shanghai 200050, P. R. China, E-mail: <u>huangfq@mail.sic.ac.cn</u>
^bBeijing National Laboratory for Molecular Sciences and State Key Laboratory of Rare Earth Materials Chemistry and Applications, College of Chemistry and Molecular Engineering, Peking University, Beijing 100871, China

^cNational Laboratory for Infrared Physics, Shanghai Institute of Technical Physics, Chinese Academy of Sciences, Shanghai 200083, P. R. China

Experimental

Synthesis of CuInS₂ nanopompons: In a typical synthesis of CuInS₂ nanopompons, 0.2 mmol of Cu₂O, 0.4 mmol of In(OH)₃ and 2 ml of thioaceticacid (CH₃COSH) were in turn added into a 25 ml vial to form a black mixture under stirring. Then 1 ml of ammonia aqueous solution was added drop by drop into the vial to form a clear red solution, following 16 ml of anhydrous ethanol and 0.8 mmol of polyvinylpyrrolidone (PVP) added into the solution under stirring for 5 minutes. Finally, the mixture was transferred and sealed into a 30 ml Teflon-line stainless autoclave to keep in an electric oven at 150 °C for 6 hours. The production was taken out and poured into 40 ml of acetone, and centrifuged at 13000 rmp for 5 minutes.

The precipitates were collected and re-dispersed in ethanol to form a stable solution.

Synthesis of CuInS₂ nanoflake films: In a typical synthesis of CuInS₂ nanoflake films, 0.8 mmol of Cu₂O, 1.6 mmol of In(OH)₃ and 4 ml of CH₃COSH were added in turn into a 25 ml vial to form a black mixture under stirring. Then 2 ml of ammonia aqueous solution was added to form a clear red solution, following 16 ml of anhydrous ethanol added into the solution. The mixture was transferred into a 30 ml Teflon-line stainless autoclave. Finally, one piece of molybdenum on soda lime glass (1 cm \times 2 cm) was put into the Teflon and sealed into a heating furnace at 150 °C for 6 hours.

Fabrication of Dye-sensitized solar cells: Firstly, 12 μ m thick transparent films of 20 nm-sized TiO₂ particles were screen printed on FTO substrates. The electrodes were sintered in dry air at 450 °C for 30 min. Subsequently, the electrodes were immersed in 40 mM of TiCl₄ aqueous solution at 70 °C for 30 min. After sintered in dry air at 450 °C for 30 min again, the electrodes were immersed into a 0.3 mM solution of ruthenium dye N719 in anhydrous ethanol overnight. Furthermore, Pt sputtered on FTO substrate and CuInS₂ nanoflake films on molybdenum substrate were used as counter electrodes. The electrolyte used consisted of 0.1 M LiI, 0.05 M I₂, 0.3 M 1,2-dimethyl-3-propylimidazolium iodine, and 0.5 M tert-butylpyridine in 3-methoxypropionitrile. Finally, the photoanode and the counter electrode were assembled and clipped in a sandwich type arrangement with the electrolyte solution placed in between. The active area was 0.25 cm².

Characterization: Field emission scanning electron microscopy (FESEM) images were acquired using FEI Sirion 200 with an energy dispersive X-ray (EDS) analysis. Low and high resolution transmission electron microscopy (TEM) images were taken on JEOL JEM-2100F at an accelerating voltage of 200 kV. TEM samples were prepared by dip-casting CIS nanopompons dispersed in ethanol onto carbon-coated copper TEM grids. X-ray diffraction (XRD) patterns was collected on a Bruker D8 Focus X-ray diffractometer equipped with a monochromatized source of CuKa radiation (λ = 0.15406 nm) at 1.6 kW (40 kV, 40 mA). The pattern was recorded in a slow-scanning mode with 20 from 10° to 80° with a scan-rate of 6°/min. UV-vis

absorbance spectrum were recorded on a Hitachi U-3010 spectrophotometer with an scanning velocity of 240 nm/min. X-ray photoelectron spectroscopy (XPS) data was obtained using ESCAlab250 X-ray Photoelectron Spectroscopy for surface analysis. Raman spectroscopy was performed on a Renishaw inVia Raman microscope using green laser (λ = 532 nm) excitation. Photocurrent density–voltage (*J*–*V*) characteristics were measured using a Keithley Model 2440 source meter under AM 1.5 illumination. A 1000 W Oriel solar simulator was used as a light source and the power of the light was calibrated to one sun light intensity by using a NREL-calibrated Si cell (Oriel 91150). Cyclic voltammetry (C-V) measurements were performed using a Pt wire as auxiliary electrode, an Ag/AgCl electrode as reference electrode, and CIS nanoflake films as working electrode on a CHI 660 electrochemistry workstation with the scanning rate of 50 mV/s.



Fig. S1 UV-vis absorbance spectroscopy of CIS nanopompons.



Fig. S2 (a) Overview XPS of CIS nanoflake film. (b) Cu 2p: bonding energy at 931.7eV and 951.6 eV with a peak split of 19.9 eV from Cu(I). (c) In 3d: bonding energy at 445.4 eV and 452.9 eV with a peak split of 7.5 eV from In(III). (d) S 2p: bonding energy at 161.9 eV and 163.1 eV from S in sulfide phases in CIS film.



Fig. S3 (a) SAED pattern of one CIS nanopompon. (b) SAED pattern of nanoflake in nanopompon.



Fig. S4 (a) HRTEM image of CIS nanoflake scratched from films. (b) SAED pattern of the nanoflake.



Fig. S5 (a) Linear sweep voltammetry of CIS nanoflake film as electrode under illumination and in the dark. (b) Periodic on/off photocurrent response of CIS nanoflake films as electrode in the mixture of 0.35 M Na₂SO₃ and 0.25 M Na₂S aqueous solution with 0.2 V bias relative to Ag/AgCl.