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Supporting Information

Quaternary semiconductor Cu_2FeSnS_4 nanoparticles as an alternative to Pt catalyst

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Synthesis of Cu_2FeSnS_4

When synthesizing CFTS nanoparticles with the stannite structure, 1.5 mmol copper(II) acetylacetonate (97%, Aldrich), 0.5 mmol iron(II) acetylacetonate (98%, Aldrich), 0.75 mmol of tin(II) chloride (99%, Aldrich), and 10 ml oleylamine (Aldrich) were added into a three neck flask (100 ml) connected to a Schlenk line. The temperature rose to approximately 130 ^{o}C under vacuum and stirring, during degassing about 30 min and purged with Ar 3times. The mixture then turned into a brown-red colored solution. Then it was heated to 280 ^{o}C, where 4 ml of 1 M solution of sulfur in oleylamine was injected. After injection, the solution darkened and eventually turned black when the temperature was held at 280 ^{o}C for 1.5 hr. The mixture was then cooled down to approximately 70 ^{o}C by air quenching. Then, 5 ml of toluene and 40 ml of isopropanol were added into the reactant solution and the nanoparticles were collected using a centrifuge at 8000 rpm for 15 min. The supernatant in the solution after centrifuging was decanted. This step was followed by adding 5 ml of toluene and 40 ml of isopropanol; the centrifuging was repeated and decanted. This process was done three times to obtain a high-purity product. The supernatant was decanted again, and the final precipitate was dispersed in approximately 40 ml toluene to form a well suspended solution[1].

Cell fabrication

The fabrication procedure is as follows. FTO glass (TEC-8, Pilkington) was cleaned by sonicating in ethanol, acetone, and isopropanol for 5 min, each and UV exposure for 15 min. Pre $TiCl_4$ treatment as a thin TiO_2 blocking layer was carried out by placing the sample in 40 mM $TiCl_4$ aqueous solution at 80 ^{o}C for 40 min. Then, a screen printing process was applied to evenly coat TiO_2 paste (homemade SS-7, 20 nm) on cleaned FTO glass with a thickness of about 9 µm which was followed by coating a scattering layer of 6 µm thick 500 nm TiO_2 (ENB Korea), and the sample was subsequently annealed at 325 ^{o}C for 5 min, 375 ^{o}C for 5 min, 450 ^{o}C for 5 min, and 500 ^{o}C for 30 min. Post $TiCl_4$ treatment was carried out again at the same conditions as above and annealed at 500 ^{o}C for 30 min. Dye coating was performed in 0.5 mM of N719 solution in acetonitrile/t-butanol (1:1 in volume ratio) for 20 hr. The counter electrode (CE) was prepared with the following materials. For a reference, CE with Pt was prepared by drop casting (10 µl, twice) 10 mM H_2PtCl_6 solution in ethanol on FTO glass and annealing at 200 ^{o}C for 20 min and 450 ^{o}C for 10min. For the CFTS nanoparticles, the materials were dispersed in nonpolar solvent such as toluene, and sonicated for 10 min. The solution was loaded on FTO glass by spin coating (1000 rpm for 20 s, 7 times) and annealed at 400 ^{o}C for 15 min under Ar atmosphere. Finally, the electrodes were assembled, and an electrolyte

was added through a pre-drilled hole. The hole was sealed with Surlyn and a piece of thin glass. The composition of the electrolyte was 0.5 M 1-butyl-3-methylimidazolium iodide (>99.5 %, Merck), 0.05 M iodine (ACS reagent, Aldrich), 0.5 M 4-tert-butylpyridine (Aldrich), and 0.1 M guanidine thiocyanate (Aldrich) in acetonitrile.

Characterization

J-V characterization was carried out under 1 Sun condition with an Oriel SOL2A solar simulator by obtaining open circuit voltage (V_{oc}), short circuit current (J_{sc}), fill factor (*FF*), and power conversion efficiency (η). Cyclic voltammetry (CV) was completed with IVIUM stat electrochemical interface. For CV, Ag/AgCl and Pt mesh were used as a reference electrode and counter electrode, respectively. The electrolyte for CV was prepared with 1 mM I_2, 10 mM LiI, and 100 mM $LiClO_4$ in N_2 purged acetonitrile, and the scan rate was 100 mV/s. The impedance was measured using an impedance analyser (Autolab, Metrohm). The impedance spectra were analyzed by an equivalent circuit model for interpreting the characteristics of the DSSC. Morphology of the samples was analyzed by scanning electron microscope (SEM) using a Tescan VEGA II LSU microscope operating at 10 kV, whereas internal structures were visualized by transmission electron microscope (TEM) images using a transmission electron microscope (FEI Tecnai G2-20 S-Twin) at an accelerating voltage of 200 kV. X-ray diffraction (XRD) patterns of the samples were measured with a Rigaku D/MAX-2200V equipped with a Cu K_α source at 40 kV and 30 mA.

Notes and references

1. C. Yan, C. Huang, J. Yang, F. Liu, J. Liu, Y. Lai, J. Li and Y. Liu, *Chem. Commun.*, 2012, **48**, 2603-2605.

$$D = \frac{0.9\,\lambda}{B \cdot cos\,\theta_B} \qquad (1)$$

Where λ is the X-ray wavelength, B is the full-width at half maximum and θ_B represents the diffraction angle at a certain crystal plane.

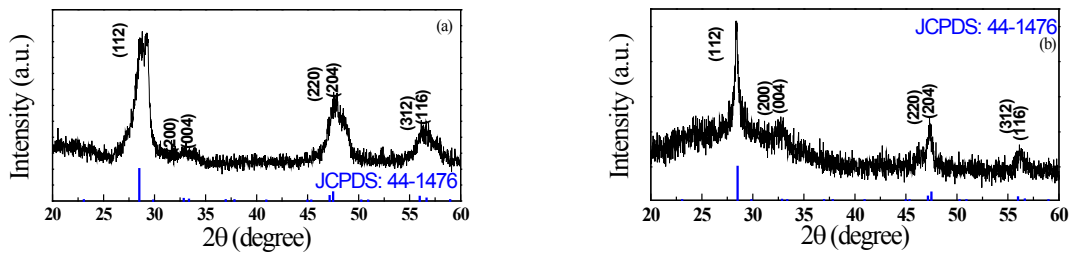

Fig. S1 (a) XRD pattern of as-prepared CFTS nanoparticles. (b) XRD pattern of CFTS thin film on FTO glass

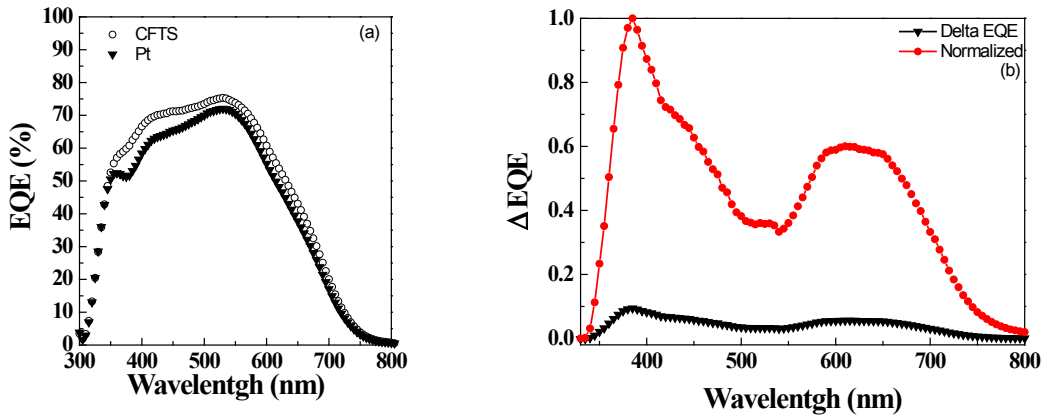

Fig. S2 (a) IPCE spectra of CFTS and Pt using Iodine electrolyte (b) the difference of IPCE value between CFTS and Pt