Solution-based synthesis of chalcostibite ($CuSbS_2$) nanobricks for solar energy conversion.

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Electronic Supplementary Information

Experimental Details

Synthesis of $CuSbS_2$ brick-liked nanoparticles

1.5 mmol copper (Ⅱ) acetylacetonate (97%, Aladdin), 1.5 mmol antimony(Ⅲ) acetate (98%, Aladdin), and 12 mL oleylamine (C-18 content 80%-90%, Aladdin) were added into a three-neck flask (100mL) connected to a Schlenk line (all chemicals are used as receives). Then the temperature raised up to approximately 140°C under vacuum and stirring, for degassing about 60 minutes and purging with Ar 3 times. All reaction conditions were kept inert to prevent the formation of an oxide. The color of the mixture turns from blue into brown-red. After that, the flask was heated to 230°C, where 3 mL of 1M solution of sulfur in oleylamine were injected. After injection, the solution turns dark, and the temperature was held at 230°C for 60 minutes. During the reaction, aliquots were taken out at several of time to confirm the phase alternation of the product by XRD. The mixture was then cooled to approximately 70°C by air quenching. Then, 10 mL of toluene and 30 mL of ethanol were added into the reaction mixture and the nanobricks were collected using centrifuge (separated into eight 15 mL centrifuge tubes) at 8000 rpm for 10 minutes. The supernatant of the centrifuged mixture was discarded. And similar step of adding 10 mL of toluene and 30 mL of ethanol and centrifuge was repeated. The supernatant was decanted again. The final precipitant was dispersed in approximately 40 mL toluene to form a ink solution.

Materials characterizations

TEM samples were prepared by dropping the diluted $CuSbS_2$ ink solution directly to a carbon-coated copper TEM grids (200 mesh). TEM images were obtained on a JEM-2100F field-emission microscope at a working voltage of 200 kV. Energy Dispersive X-ray spectroscopy (EDX) data were collected as an ensemble measurement in an environment scanning electron microscope (ESEM, Quanta-200 at a 20 keV accelerating voltage). XRD was performed on a X-ray diffraction system (Rigaku3014) equipped with Cu Kα radiation (λ=1.54 Å) using a dried thin film sample prepared by drop-casting the nanobrick-ink. UV-vis-NIR spectra were collected for $CuSbS_2$ nanobricks using a Hitachi U-4100 spectrophotometer. FITR measurements were conducted using an Nicolet SI10 spectrometer. The thickness of the films were measured using a step profiler (Veeco Dektak 150)

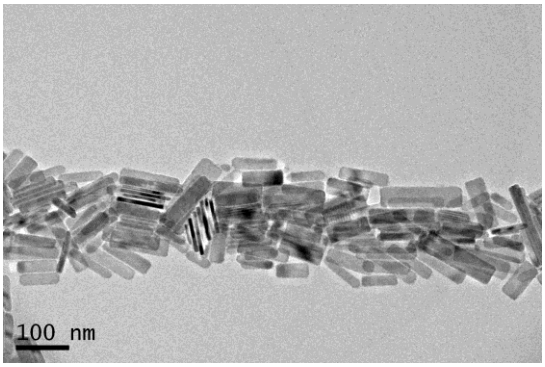


Fig. S1 A larger field of TEM view for $CuSbS_2$ nanobricks .

The yield of the synthesis of CuSbS2 nanobricks is approximately 0.166g per pot.

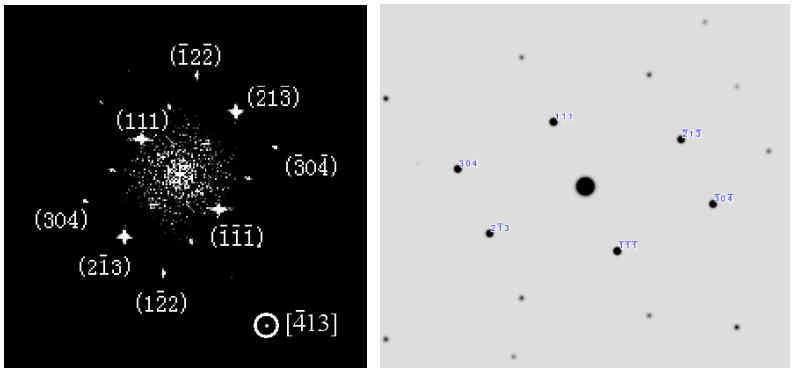


Fig. S2 (a) Fast Fourier transform (FFT) pattern of as-synthesized $CuSbS_2$ nanobrick. (b) simulated $CuSbS_2$ single crystal electron diffraction data.

The standard chalcostibite ($CuSbS_2$) structure data (lattice parameters, atoms coordinates) were obtained from American Mineralogist Crystal Structure Database.[1] The gained standard data match quite well with JCPDS card no. 88-0822 ($CuSbS_2$). The given $CuSbS_2$ single crystal electron diffraction data in Figure S1 b were simulated by crystalmaker software and its SingleCrystal software packages using the standard chalcostibite ($CuSbS_2$) structure data.

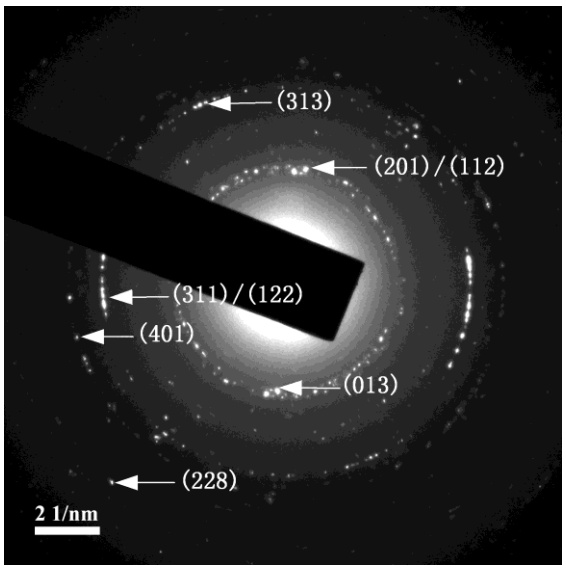
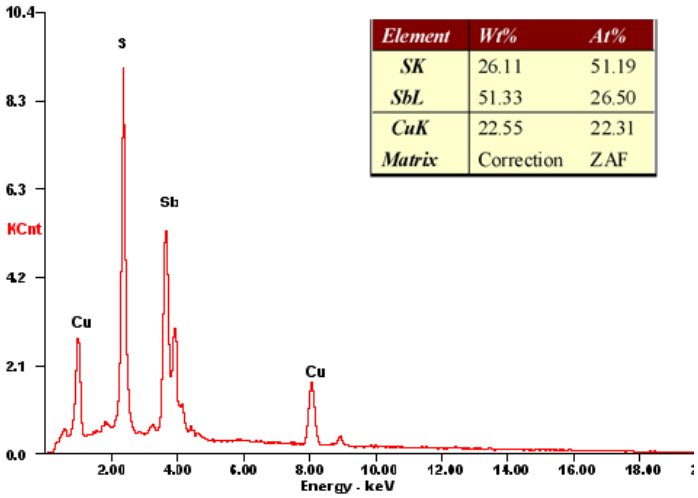


Fig. S3 Selected area electron diffraction pattern for as-synthesized $CuSbS_2$.
The marked diffraction spots correspond to (313), (201)/(112), (311)/(122), (401), (012), (228) planes of $CuSbS_2$



Element	Wt%	At%
SK	26.11	51.19
SbL	51.33	26.50
CuK	22.55	22.31
Matrix	Correction	ZAF

Fig. S4 Representative spectrum of the energy dispersive X-ray spectroscopy for $CuSbS_2$ nanobricks and the quantitative analysis

The sample used for determining the quantitative composition of $CuSbS_2$ film by EDX was prepared by dropping the concentrated dispersion of $CuSbS_2$ nanobricks onto the soda-lime glass substrate. In order to get average composition of as-synthesized nanocrystals, 10 different area nanocrystal films were examined. The average composition of as-synthesized nanobricks is $Cu_{0.86}Sb_{1.05}S_2$.

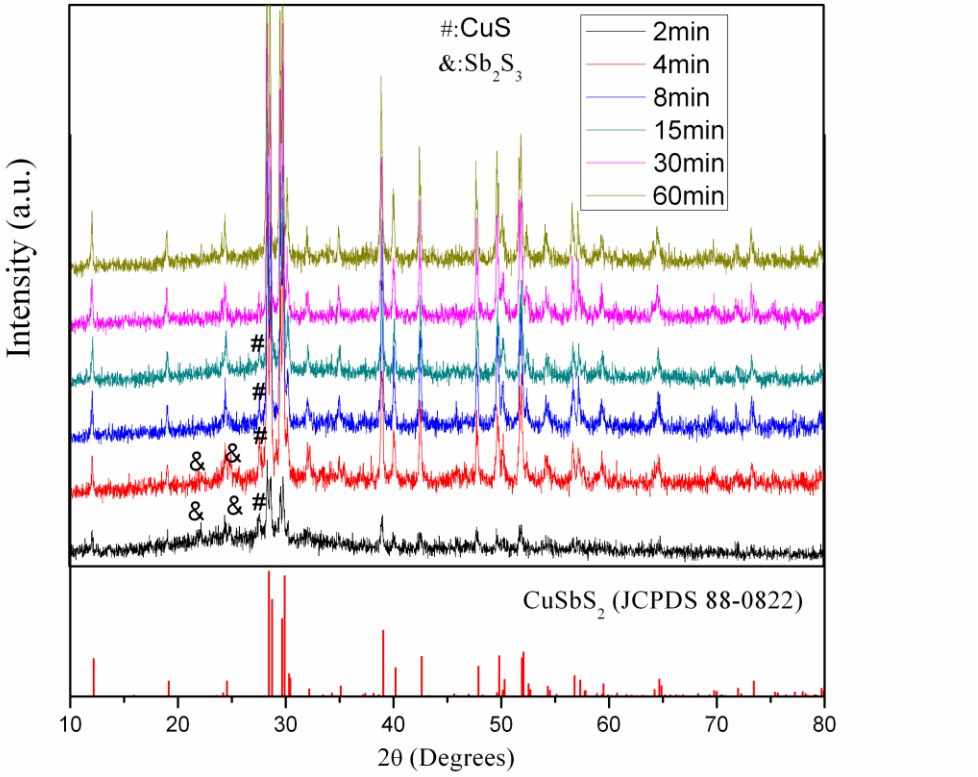


Fig. S5 XRD patterns for as-synthesized $CuSbS_2$. In the initial stage CuS (Covellite JCPDS no. 74-1234) and Sb_2S_3 (stibnite JCPDS no. 42-1393) were detected.

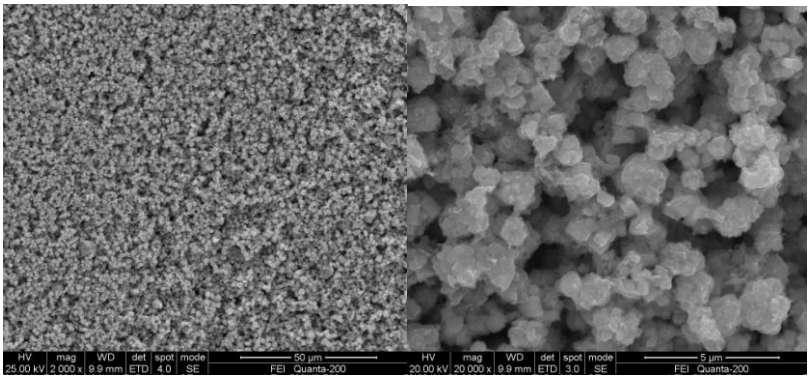


Fig. S6 SEM images of $CuSbS_2$ nanobricks film annealed at 350°C in Ar atmosphere. The film is loose and porous without cracks.

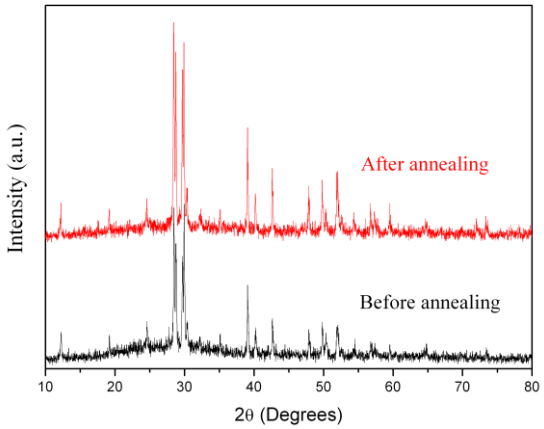


Fig. S7 XRD patterns of the $CuSbS_2$ film before and after annealing at 350°C in Ar atmosphere.

Figure S8 demonstrates the FTIR data for $CuSbS_2$ films before and after annealing. According to the figure, the wavenumber peaks of sample before annealing at about 2920cm^{-1} and 2850 cm^{-1} can be attributed to organic ligands (Oleylamine) [2,3]. Whereas, these peaks disappeared for sample after annealing. Therefore, we can conclude that organic ligands should be removed after annealing.

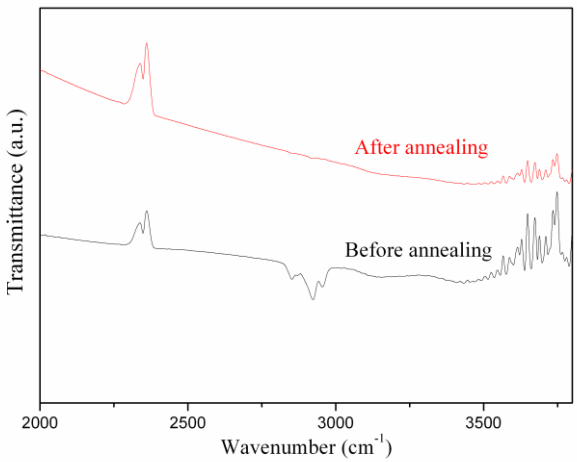


Fig. S8 FTIR spectrum for $CuSbS_2$ films before and after annealing.

The electrical properties of the samples before and after annealing were obtained using a Hall

measurement system. Accordingly, the carrier concentration, mobility, and conductivity of the samples were illustrated in Table S1.

After the heat treatment, the electrical conductivity of the sample has been increased notably owing to the increment of its carrier mobility caused by the elimination of the organic ligands.

Table. S1. The electrical properties of the obtained films before and after annealing

Sample	Carrier concentration (cm^{-3})	Mobility ($cm^2/(V\cdot s)$)	Conductivity $(\Omega\cdot cm)^{-1}$
CuSbS2-before annealing	4.75×10^{13}	3.52×10^{1}	1.07×10^{-4}
CuSbS2-after annealing	4.85×10^{13}	2.07×10^{2}	3.33×10^{-4}

The thickness of the $CuSbS_2$ thin film used for the photoelectrochemical characterization is around 4.2μm.

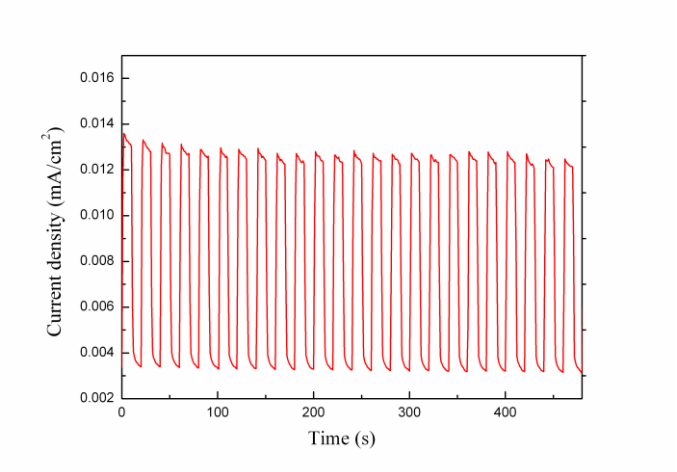


Fig. S9 The transient photocurrent spectrum for the obtained $CuSbS_2$ films at -0.2V vs. SCE

Reference

1. American Mineralogist Crystal Structure Database.URL: http://rruff.geo.arizona.edu/AMS/minerals/Chalcostibite. Last access Date 6/12/2012.

2. P. Zhang, Y. Wang, Y. Sui, C. Wang, B. Liu, G. Zou and B. Zou, *CrystEngComm*, 2012, **14**, 5937–5942.

3. M. Kar, R. Agrawal and H. W. Hillhouse *J. Am. Chem. Soc.*, 2011, **133**, 17239.