Colloidal synthesis and characterizations of wittichenite copper bismuth sulphide nanocrystals

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Electronic Supplementary Information

Experimental Details

Synthesis of Cu_3BiS_3 nanocrystals

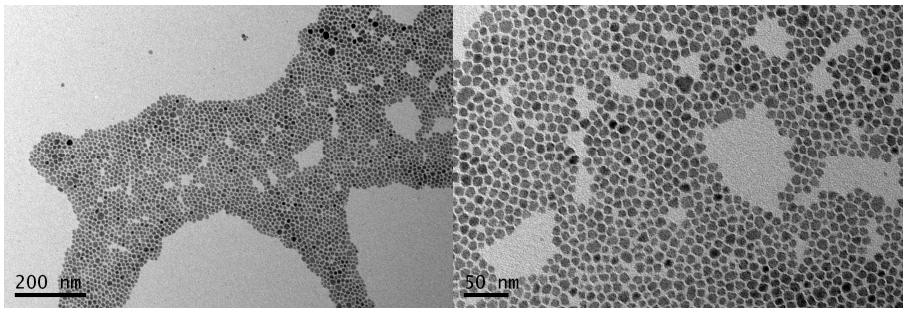
2.25 mmol copper (Ⅱ) acetylacetonate (97%, Aladdin), 0.75 mmol bismuch (Ⅲ) nitrate pentahydrate (99%), and 12 mL oleylamine (C-18 content 80%-90%, Aladdin) were added into a three-neck flask (100mL) connected to a Schlenk line (all chemicals are used as receives). Then the temperature raised up to around 140□ under vacuum and stirring, for degassing about an hour and purging with Ar 3 times. All reaction conditions were kept inert to prevent the formation of the oxide. Then, the flask was heated to 220□, where 2.5 mL of 1.2 M/L solution of sulfur in oleylamine were injected. After injection, the solution turns dark, and the temperature was held at 220□ for 30 minutes. After the reaction, the mixture was cooled to approximately 70□ by air quenching. Then, 10 mL of toluene and 30 mL of ethanol were added into the reaction mixture and the nanocrystals 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 20 mL toluene to form a stable ink solution. The Cu_3BiS_3 nanocrystals and the corresponding ink are stable at ambient condition for more than a month without decomposition and/or agglomeration.

Metal-semiconductor-metal device fabrication.

0.2-0.3mL ink (using a toluene solution of Cu_3BiS_3 nanocrystals) was drop-casted on a soda-lime glass(SLG) with area of 2.4 cm^2, then put the sample in the draught cupboard so that the solvent can evaporate naturally. Consequently, a dense Cu_3BiS_3 nanocrystal thin film was formed on the SLG. After that, two silver electrodes were made by dropping two silver paste on the surface of Cu_3BiS_3 nanocrystal thin film. The size of each silver electrode is approximate 3mm× 3mm, and the distance between the two silver electrodes is 7mm.

Materials characterizations

TEM samples were prepared by dropping the diluted Cu_3BiS_3 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 nanocrystal-ink. UV-vis-NIR spectra were collected for Cu_3BiS_3 nanocrystals using a Hitachi U-4100 spectrophotometer.



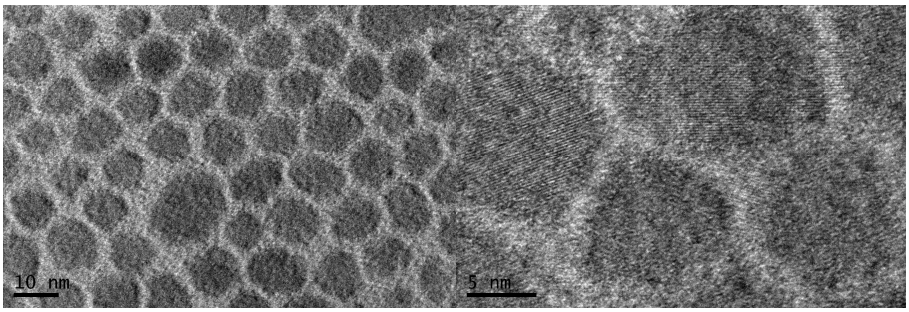


Fig. S1 Additional TEM images for as-synthesized Cu_3BiS_3 nanocrystals at different magnitude

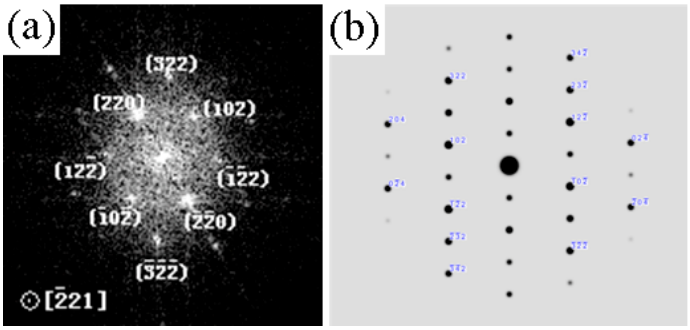


Fig. S2 (a) Fast Fourier transform (FFT) pattern of as-synthesized Cu_3BiS_3 nanocrystal. (b) simulated Cu_3BiS_3 single crystal electron diffraction data

The standard wittichenite (Cu_3BiS_3) structure data (lattice parameters, atoms coordinates) were obtained from American Mineralogist Crystal Structure Database.[1] The downloaded standard data match quite well with JCPDS card no. 71-2115 (Cu_3BiS_3). The given Cu_3BiS_3 single crystal electron diffraction data in Figure S2b were simulated by crystalmaker software and its SingleCrystal software packages using the standard wittichenite (Cu_3BiS_3) structural data.

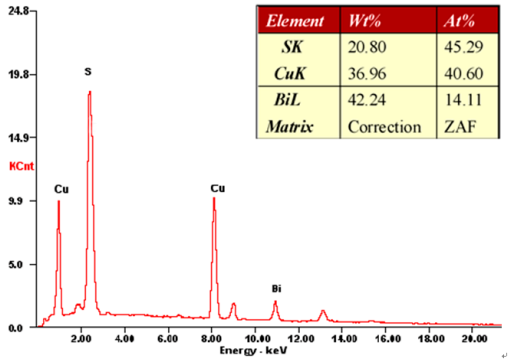


Fig. S3 Representative energy dispersive X-ray spectroscopy spectrum for Cu_3BiS_3 nanocrystals and the quantitative analysis

The sample used for determining the elemental composition of Cu_3BiS_3 film by EDX was prepared by dropping the concentrated dispersion of Cu_3BiS_3 nanocrystal-ink onto the soda-lime glass substrate. In order to get average composition of as-synthesized nanocrystals, 10 different area nanocrystal film were examined. The average composition of as-synthesized nanocrystal is $Cu_{2.88}BiS_{3.21}$.

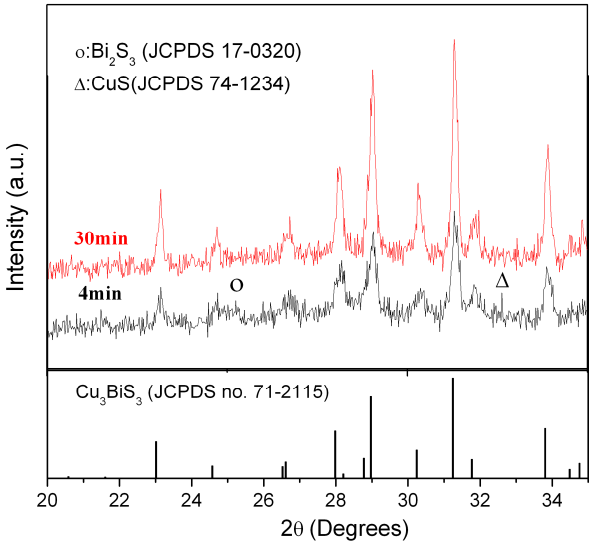


Fig. S4 XRD patterns for as-synthesized Cu_3BiS_3 at different reaction time. In the initial stage CuS (Covellite JCPDS no. 74-1234) and Bi_2S_3 (bismuthinite JCPDS no. 17-0320) were detected.

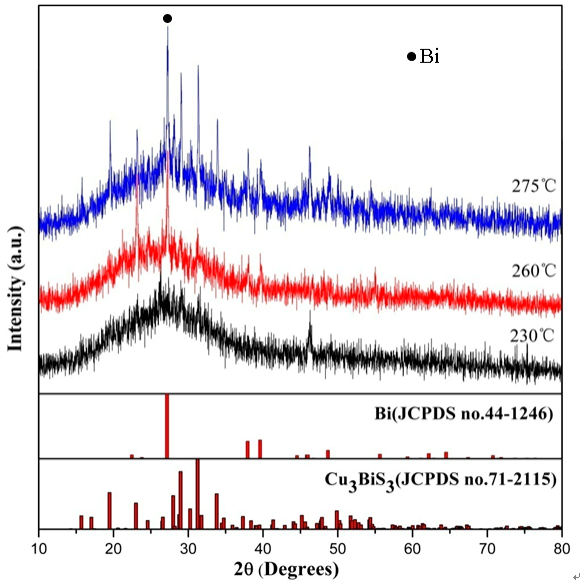


Fig. S5 XRD patterns for as-synthesized product when bismuth trichloride was utilized as Bi source at different reaction temperature

As can be seen from the XRD data in Fig. S5, when bismuth trichloride was utilized as the bismuth precursor, the product contains significant amount of elementary Bi at the reaction temperature ranged from 230℃ to 275℃. However, if the bismuth precursor change to bismuch (Ⅲ) nitrate pentahydrate, the reaction yields phase pure Cu_3BiS_3.

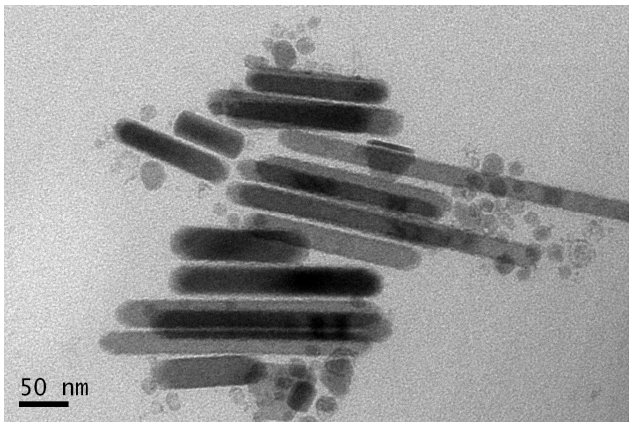


Fig. S6 TEM image for as-synthesized product at 290℃. Some of the products demonstrate the bar shape.

Reference

1. American Mineralogist Crystal Structure Database.URL: http://rruff.geo.arizona.edu/AMS/download.php?id=10072.amc&down=amc. Last access Date 9/10/2012.