

Supporting Information for Synthesis and Characterisation of Famatinite Copper Antimony Sulfide Nanocrystals

Materials: Copper(I) chloride ($\geq 99\%$), Antimony(III) chloride (99%), 1-octadecene (90%), oleylamine (70%), oleic acid (90%), Bis(trimethylsilyl) sulfide (synthesis grade), and tetrachloroethylene ($\geq 99\%$) were purchased from Sigma Aldrich. AR grade chloroform, acetone, and methanol were purchased from Pacific Laboratory Products. All chemicals and solvents were used as received.

Purification: To effectively purify the nanocrystals it is necessary to first separate the unreacted salts. To accomplish this the mother liquor (2 mL), was dispersed in hexane (5 mL) and acetone (0.3 mL) was then added. The mixture was then centrifuged at 2500 rpm for 30 mins. After centrifugation the excess salt precipitated as a white powder. The supernatant was then isolated and methanol (5 mL) and acetone (2 mL) was added and then the dispersion was centrifuged at 3200 rpm for 10 mins to precipitate the NCs. The semi pure plug could then be purified by several precipitation/dispersion cycles using chloroform/methanol/acetone (1:1:2 v/v).

X-Ray Photoelectron spectroscopy: The spectral regions specific to Cu, Sb and S are shown in the bottom panels. Copper shows a 2p doublet at 932.1 and 951.9 ($2p_{3/2}$ and $2p_{1/2}$) with a separation of 19.8 eV. The positions and separation of the copper 2p peaks are consistent with Cu(I)¹, as expected for famatinite CAS. The presence of Cu(II) can be ruled out from the absence of peaks at 936 eV and 942 eV (satellite) ($\text{Cu}2p_{3/2}$) and 955 and 965 eV (satellite) ($\text{Cu}2p_{1/2}$)². The broad hump extending to lower binding energies (see arrow) might be due to inelastic electron scattering from the sample or to "shake-up" effects. Interestingly, this phenomenon does not appear for bulk CAS samples¹. However, it has been observed previously for quaternary Cu-Zn-Sn-S nanocrystals³, which is suggestive of effects arising from lower co-ordination number copper atoms at the NC surface. The antimony lines fit excellently to a 3d doublet at 529.8 and 539.1 ($3d_{5/2}$ and $3d_{3/2}$) with a separation of 9.3 eV. Interestingly, the $\text{Sb}3d_{3/2}$ spectral line position is somewhat more consistent with Sb(III) than the expected Sb(V) present in famatinite⁴, which typically has a peak closer to 940 eV⁵. Although it is possible that Sb(III) exists on the surface of the NCs in this case we would expect to see a broader spectral line consisting of two overlapping peaks for both surface Sb(III) and bulk Sb(V), which is not the case here. As such, this small shift (~ 1 eV) to lower binding energies is likely a consequence of the specific bonding environment of antimony within the CAS NCs. The sulfur 2p line is asymmetric due to spin-orbit splitting. The $\text{S}2p$ line fit well to a doublet at 161.7 and 162.9 eV ($2p_{3/2}$ and $2p_{1/2}$) with a separation of 1.2 eV. The positions, separations, and relative intensities of the doublet peaks (2:1, from their degeneracy) is consistent with sulfur in the sulfide chemical state (2^- oxidation state)^{2,6}. Oxidation of the NC surface could be ruled out as no sulfates were detected between 167-171 eV².

The elemental composition was analysed and it was subsequently found that the as-prepared CAS NCs have a stoichiometry of $\text{Cu}_{2.52}\text{Sb}_{1.46}\text{S}_{4.02}$. This indicates slightly copper-deficient and antimony-rich particles. From analysis of both the XRD and the lattice spacings from the HRTEM and SAED data it is highly unlikely that Sb atoms have replaced Cu atoms in the bulk lattice. Given the surface sensitivity of XPS and the fact that as-prepared NCs rarely have stoichiometric surfaces it is far more likely that we have a composition relative to copper of $\text{Cu}_3\text{Sb}_{1.74}\text{S}_{4.79}$, which (ignoring volumetric contributions) gives a surface that is approximately 75% and 20% rich in antimony and sulfur compared to the bulk stoichiometry respectively. The fact that that NC surface is terminated largely by antimony and sulfur atoms is not surprising given the three-fold excess of antimony and the slight excess of sulfur used in the synthesis, which may adsorb on the NC surface towards the end of the reaction.

Instrumentation: Low resolution images were taken on a Philips CM120 BioTWIN Transmission Electron Microscope operating at 120 keV. High resolution TEM images and electron diffraction were performed on a Jeol 2100F TEM/STEM (2011) with X-ray detector, Gatan Image Filter operated at 200 keV. Strong carbon coated 300-mesh grids were employed and all grids were cast from NCs dispersed in chloroform. XPS was performed from drop-cast samples on a glass cover slip on a Thermo K-alpha X-ray Photoelectron Spectrometer. To compensate for sample charging effects during XPS data collection a low voltage electron flood gun was used throughout all experiments. EDAX was performed by loading a drop-cast sample on an aluminium stub on a FEI Nova NanoSEM (2007) with EDAX Si(Li)X-ray detector. Absorption measurements were conducted using a JASCO V-670 spectrophotometer. XRD was performed on a Bruker D8 Discover microdiffractometer fitted with a GADDS (General Area Detector Diffraction System). Data were collected at room temperature using Cu Ka radiation ($\lambda=1.54178\text{\AA}$) with a potential of 40 kV and a current of 40 mA, and filtered with a graphite monochromator in the parallel mode (175 mm collimator with 0.5 mm pinholes). The samples were mounted vertically, and aligned on an XYZ stage with the aid of a camera and laser guide.

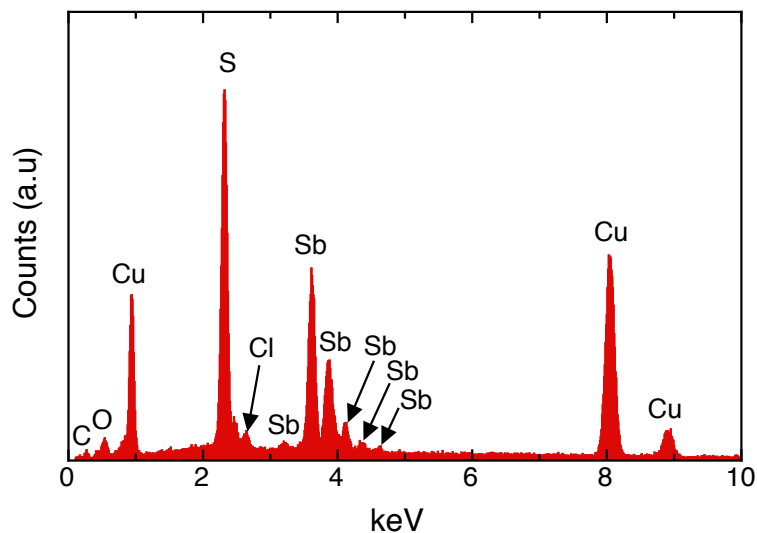


Figure 1 EDAX spectrum of Cu₃SbS₄.

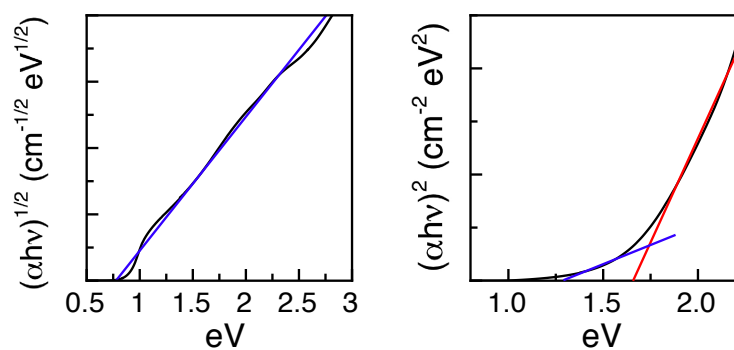


Figure 2 Tauc plots of Cu₃SbS₄ for both n=2 and 1/2.

References

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