Kuramite Cu$_3$SnS$_4$ nanocrystals with tetragonal structure have been synthesized by a simple one-step solution-based process and characterized in detail by X-ray diffraction, transmission electron microscopy, energy dispersive X-ray spectroscopy and X-ray photoelectron spectroscopy. The nanocrystals show an optical band gap of 1.43 eV as estimated from the UV-vis-NIR spectrum.

Copper-based multinary chalcogenide semiconductor materials such as CuInS$_2$, Cu(In,Ga)S$_2$ and Cu$_2$ZnSnS$_4$$_2$ (CZTSSe) have attracted increasing attention due to their potential application in photovoltaic, thermoelectric and photocatalytic devices. Thin film solar cells based on CuInS$_2$ and Cu(In,Ga)S$_2$ have achieved efficiencies slightly over 20%. However, due to the scarcity of the indium constituent, the stannite group (I4/m) has attracted great attention due to its chemical compositions of samples at different reaction time, TEM image and PXRD pattern of controlled experiment. See DOI: 10.1039/c2ra21777e

**Fig. 1** PXRD patterns of as-synthesized CTS nanocrystals. For reference, the standard PXRD patterns of kuramite Cu$_3$SnS$_4$ is shown below.
the CTS nanocrystals which shows that the nanocrystals are slightly irregular shape. The corresponding size distribution histogram (Fig. 2(b)) reveals that the average size of the nanocrystals is 16.1 nm with a standard deviation of 2.9 nm. This value is in agreement with that estimated from PXRD by the Scherer equation. Fig. 2(c) shows the high resolution image of a single CTS nanocrystal, which displays clear lattice fringes throughout the whole particle indicating the high crystalline quality of the nanocrystals. The spacing of the lattice fringes was measured to be 0.313 nm, which matches the (112) plane of CTS. This result implies that the preferred orientation of CTS nanocrystals is (112), which is in accordance with the PXRD result. Fig. 2(d) shows a representative EDX spectrum of the nanocrystal samples. All elements, Cu, Sn, and S, were detected in the nanocrystals. Moreover, the inset table reveals the average ratio of Cu : Sn : S is 40.6 : 13.5 : 45.9 as determined by analysing five randomly selected areas. This value is close to the stoichiometry of Cu3SnS4 but slightly sulfur poor, providing further evidence that the obtained nanocrystals are kuramite CTS.

For profound understanding of the oxidation states of the elements in CTS nanocrystals, XPS measurements were performed on the CTS sample deposited on molybdenum coated glass substrate by drop casting. A survey spectrum, Fig. 3(a), identified the presence of Cu, Sn, S, O and C, which is in good agreement with the EDX results. The deposition process has been carried out in air and the nanocrystals were capped by oleylamine, which explains the content of O and C. The Cu2p3/2 core-level (Fig. 3(b)) is located at 932.3 eV binding energy. This value is close to the reported values for compounds with Cu(I), such as in Cu2S, and confirmed the existence of the Cu(I) state in the CTS samples. A weak shoulder and broadening of the Cu2p3/2 peak is observed. However, it can not be identified if this stems from a Cu(II) oxidation state in CTS or is a second component due to surface contamination. A satellite peak at higher binding energies, such as for CuO, is not observed.

Fig. 2 (a) Low resolution TEM image of as-synthesized CTS nanocrystals on a carbon film coated gold grids; (b) Corresponding histogram of particle size distribution; the average size of the nanocrystals is (16.1 ± 2.9) nm. (c) High resolution TEM image of a single CTS nanocrystal; (d) EDX spectrum of CTS nanocrystals. The inset shows the table of composition.

Fig. 3 XPS spectra of CTS nanocrystals: (a) typical survey spectrum, (b) Cu 3/2p core level, (c) Sn3d core level, and (d) S2p core level. Fig. 3(c) reveals the Sn3d5/2 peak centered at 486.5 eV, indicating the Sn(IV) state in the CTS samples.13,19 The S2p core-level spectrum (Fig. 3(d)) shows two peaks at 161.9 eV and 163.0 eV, which imply that S is in sulfide state.13,19 Note that a sulfate peak at around 169 eV was also observed during the measurement, which is not shown in the S2p spectrum. This suggests the oxidation of the samples due to exposure to air. Therefore, for an optimal XPS analysis, a further improvement of the deposition process is necessary to reduce the contamination.

We have studied the growth of the CTS nanocrystals by taking aliquots at different reaction times from the reaction vessel and analyzing them with PXRD, TEM and EDX. Fig. S1 shows the PXRD patterns of samples taken out at different reaction times. It can be seen that all samples show similar PXRD patterns with all the peaks matching with kuramite CTS very well, indicating that we can get kuramite CTS nanocrystals after reaction time of 5 min. Table S1 shows the average value of EDX analysis on five randomly selected areas in each sample. As can be seen, the composition of the nanocrystals is nearly stable by keeping the ratio of Cu : Sn : S close to the stoichiometry of Cu3SnS4. The results of PXRD and EDX analysis confirmed that the CTS nanocrystals can be synthesized in a short reaction time of 5 min. Fig. S2 shows the TEM images and the corresponding size distribution histogram. As the reaction time increased from 5 min to 45 min, the average size of the nanocrystals increased from 10.7 ± 4.1 nm to 16.4 ± 3.5 nm due to the Ostwald ripening of the nanocrystals. Generally, in a classic steady-state Ostwald ripening large particles grow larger and larger with the sacrifice of the smaller particles, resulting in increasing particle size and a broadening size distribution. However, there is a transient stage of Ostwald ripening before starting the classic steady-state Ostwald ripening according to Peng et al.20 who studied the growth of MnO nanocrystals and observed the transient stage during the
growth of the MnO nanocrystals. The feature of the transient stage is that the size of the nanocrystals increases slowly, as well as the decrease of the size distribution. In our reaction system, the slow growth of the nanocrystals can be explained by the experience of transient stage Ostwald ripening. It seems that a longer reaction time is needed in our CTS system in order to observe the classic steady-state Ostwald ripening.

To better understand the effect of reaction conditions on the final products, we performed several contrast experiments. For example, when the ratio of the precursors of Cu : Sn : S changed from 2 : 1 : 3 to 3 : 1 : 4, we found that nearly monodisperse nanocrystals with 13.4 ± 1.9 nm (Fig. S4f) can be obtained. However, PXRD (Fig. S4f) shows that Cu₁₋₀.₉₇S and Sn₃S₄ phases were also observed besides the CTS phase, indicating that precise control of the precursors ratio is important in order to acquire single phase CTS.

UV-vis absorption spectroscopy was used to evaluate the optical properties of the nanocrystals. Fig. 4 shows that the nanocrystals exhibit high absorption in the visible region. The optical band gap is 1.43 eV as estimated by extrapolating the linear part of the plot \((\text{d} / \text{d} h = 1)\) versus \(h_0\) (eV) for the nanocrystals.

In conclusion, we proposed a facile one-step solution-based approach for the synthesis of kuramite CTS nanocrystals with tetragonal structure. The kuramite CTS nanocrystals can be obtained in a short reaction time of 5 min. EDX and XPS analysis confirmed the existence of all three elements in the nanocrystals. The estimated band gap of the CTS nanocrystals is 1.43 eV, which is optimal for solar energy conversion. Further application of this material in photovoltaics is in progress.

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