One-Step Solution-Based Synthesis and Characterization of Kuramite Cu$_3$SnS$_4$ Nanocrystals

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Experimental

Materials. Copper acetylacetonate (>99,99%), Tin(II) chloride (>99,99%), sulfur (99.98%), oleylamine (technical grade, 70%), absolute ethanol and toluene were purchased from Aldrich. All chemicals were used directly without any further purification.

Synthesis of Cu$_3$SnS$_4$ nanocrystals.

In a typical synthesis, 2 mmol copper acetylacetonate, 1 mmol tin chloride, 3 mmol sulfur and 30 mL oleylamine were mixed in the three-neck flask in air. Then the flask was removed to a glove box filled with nitrogen and heated to 130 °C for 30 min. After that the mixture was heated to 250 °C and maintained at this temperature for 60 min to allow the growth of Cu$_3$SnS$_4$ (CTS) nanocrystals. After being cooled to room temperature by removing the heating mantle, the reaction mixture was precipitated with excess of ethanol, followed by centrifugation at 6000 rpm for 10 min. The supernatant was discarded, and the nanocrystals were dispersed in 10 ml toluene. The precipitation and dispersion steps were repeated one more time to remove excess oleylamine. Finally the nanocrystals were redispersed in 10 ml toluene and stored for further characterization.

Characterization.

Powder X-ray diffraction (PXRD) patterns were operated in the 2θ range from 10 to 90° on a Bruker D8-Advance X-ray diffractometer with Cu Kα1 radiation (λ=1.5406 Å) using a step size of 0.02° and step time of 0.3 second. TEM samples were prepared by dropping diluted nanocrystals solution onto a carbon film coated gold grids and a Philips CM12 transmission electron microscopy with 120 KV acceleration voltage was used to acquire TEM images of the nanocrystals. The optical properties of the as-prepared CTS nanocrystals were characterized by UV-visible absorption spectroscopy recorded on a Lambda 950 UV-Vis.
spectrometer. The X-ray photoelectron spectroscopy (XPS) measurements were carried out on a VG Clam IV analyzer using Mg Kα X-ray (200 W) as the excitation energy from a SPECS XR 50 source.

Fig. S1 PXRD patterns of CTS nanocrystals at different stages: (a) 5min, (b) 10min, (c) 30 min, and (d) 45 min.

Table S1 Chemical composition of CTS nanocrystals at different stages determined by EDX

<table>
<thead>
<tr>
<th></th>
<th>S at%</th>
<th>Cu at%</th>
<th>Sn at%</th>
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<tbody>
<tr>
<td>5 min</td>
<td>47.2</td>
<td>40.3</td>
<td>12.5</td>
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<tr>
<td>10 min</td>
<td>46.1</td>
<td>40.6</td>
<td>13.3</td>
</tr>
<tr>
<td>30 min</td>
<td>46.7</td>
<td>40.3</td>
<td>13.0</td>
</tr>
<tr>
<td>45 min</td>
<td>46.8</td>
<td>40.2</td>
<td>13.0</td>
</tr>
</tbody>
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Fig. S2 TEM images and corresponding size distribution histograms of CTS nanocrystals at different reaction stages: (a) and (b) 5min, (c) and (d) 10min, (e) and (f) 30 min, (g) and (h) 45 min.
Fig. S3 (a) TEM image and (b) corresponding size distribution histogram of contrast experimental sample.

Fig. S4 PXRD pattern of obtained nanocrystals from contrast experiment.