Supporting Information

Solution-based Synthesis of Quaternary Cu-In-Zn-S Nanobelts with Tunable Composition and Band Gap

Chao Zou,* Lijie Zhang, Lanlan Zhai, Deshang Lin, Jinming Gao, Qiang Li, Yun Yang, Xi’an Chen and Shaoming Huang*

Nanomaterials and Chemistry Key Laboratory, College of Chemistry and Materials Engineering, Wenzhou University, Wenzhou 325027, P. R. China

Email: zouchao@wzu.edu.cn, smhuang@wzu.edu.cn

Experimental Section

I. Materials. Copper nitrate (Cu(NO$_3$)$_2$, 99.9%), indium nitrate (In(NO$_3$)$_3$, 99.9%), zinc nitrate (Zn(NO$_3$)$_2$, 99.9%), n-dodecanethiol (DT, 98%) and sodium diethyldithiocarbamate (dedc) (NaS$_2$CNEt$_2$, 99%) were purchased from Aladdin. Oleylamine (OA, 97%) were purchased from TCI, Shanghai.

II. Synthesis of Cu(dedc)$_2$, In(dedc)$_3$ and Zn(dedc)$_2$ precursors. In a typical synthesis of Cu(dedc)$_2$, 2 mmol NaS$_2$CNEt$_2$ and 1 mmol Cu(NO$_3$)$_2$ were dissolved in 50ml ionized water, respectively. Then, Cu(NO$_3$)$_2$ aqueous solution was mixed with NaS$_2$CNEt$_2$ solution by drop adding, washed 3 times at least with ionized water and ethanol followed by drying. In(dedc)$_3$ and Zn(dedc)$_2$ were prepared as the same procedure, In(NO$_3$)$_3$ and Zn(NO$_3$)$_2$ instead of Cu(NO$_3$)$_2$ used, respectively.

III. Synthesis of Cu$_x$In$_x$Zn$_2$(1-x)S$_2$ nanobelts. In a typical synthesis of Cu$_x$In$_x$Zn$_2$(1-x)S$_2$ nanobelts, 0.04 mmol Cu(dedc)$_2$, 0.04 mmol In(dedc)$_3$, 0.12 mmol Zn(dedc)$_2$, 16.5 mmol DT were loaded into a 50 ml flask. After the flask was put into oil-bath heated to 180°C, the color of solution become straw yellow in few minutes. 12.2 mmol OA was swiftly injected into the flask under gentle magnetic stirring. The color of the reaction changed red black quickly. After keeping the mixture at the reaction temperature for 30 minutes, the resulting solution was cooled to room temperature and the as-synthesized nanobelts were precipitated with ethanol followed by further centrifugation and decantation. The purified nanobelts were re-dispersed in hexane for X-ray diffraction (XRD) and transmission electron microscopy (TEM) measurements. The whole experiments were carried out under atmosphere without inert gas protection. Quaternary nanobelts with tunable compositions can be achieved by varying the relative molar ratio of precursors in the source materials.

IV. Characterization. The obtained crystalline phases were identified using powder X-ray diffraction (XRD) (Bruker, D8 advance, Cu Ka radiation using a curved graphite receiving monochromate), with a step of 0.02° at a speed of 4°/min. Morphologies and structural analysis were undertaken using scanning transmission electron microscopy (STEM, FEI Nova NanoSEM 200) and transmission electron microscopy (TEM, JEOL 2100, accelerating voltage 200 kV). STEM-EDS were measured on Tecnai G2 F30 S-Twin microscope at accelerating voltage of 300kV. The samples for STEM and TEM were collected by placing a drop of dilute solution of sample in hexane onto carbon-film-supported molybdenum grids. Composition analysis was performed by Energy dispersive spectroscopy (EDS, oxford INCA). The binding energy of Cu$_x$In$_x$Zn$_2$(1-x)S$_2$ nanobelts was examined by X-ray photoelectron spectroscopy (XPS, ESCALAB MKII), and all the peaks were calibrated by using C1s at 284.60 eV as the reference. UV-Vis absorption spectra were recorded on a Unioco 482H spectrometer with a resolution of 1.0 nm. The photoluminescence spectrum (PL) was measured at room temperature on a FLuoromax-4 spectrofluorometer (HORIBA Jobin Yvon, Inc) equipped with a 150 W xenon lamp as the excitation source.
Figure S1. EDS spectrum of Cu$_x$In$_{1-x}$Zn$_{2(1-x)}$S$_2$ (x=0.8) nanobelts, collected from every point of the boxed area in Fig. 1e.

Figure S2. Energy dispersive X-ray spectroscopy (EDS, taken in the SEM) of quaternary Cu$_x$In$_{1-x}$Zn$_{2(1-x)}$S$_2$ nanobelts. The Al element is attributed to aluminum specimen mount.

<table>
<thead>
<tr>
<th>Cu$<em>x$In$</em>{1-x}$Zn$_{2(1-x)}$S$_2$</th>
<th>Cu %</th>
<th>In %</th>
<th>Zn %</th>
<th>S %</th>
</tr>
</thead>
<tbody>
<tr>
<td>x=0.2</td>
<td>3.19</td>
<td>3.50</td>
<td>39.68</td>
<td>53.63</td>
</tr>
<tr>
<td>x=0.3</td>
<td>6.46</td>
<td>6.80</td>
<td>34.70</td>
<td>52.03</td>
</tr>
<tr>
<td>x=0.4</td>
<td>8.71</td>
<td>9.87</td>
<td>28.59</td>
<td>52.83</td>
</tr>
<tr>
<td>x=0.5</td>
<td>11.83</td>
<td>12.43</td>
<td>24.71</td>
<td>51.03</td>
</tr>
<tr>
<td>x=0.6</td>
<td>13.11</td>
<td>15.08</td>
<td>18.28</td>
<td>53.54</td>
</tr>
<tr>
<td>x=0.7</td>
<td>15.95</td>
<td>17.43</td>
<td>14.60</td>
<td>52.02</td>
</tr>
<tr>
<td>x=0.8</td>
<td>18.77</td>
<td>19.94</td>
<td>9.58</td>
<td>51.70</td>
</tr>
<tr>
<td>x=0.9</td>
<td>22.58</td>
<td>23.04</td>
<td>4.96</td>
<td>49.42</td>
</tr>
</tbody>
</table>

Table S1. Compositions (atomic percent) measured by EDS of quaternary Cu$_x$In$_{1-x}$Zn$_{2(1-x)}$S$_2$ nanobelts.
Figure S3. XPS survey spectra of Cu$_x$In$_x$Zn$_{2(1-x)}$S$_2$ nanobelts. Peaks assignable to core levels of Cu 2p, In 3d, Zn 2p, S 2p, O 1s, N 1s and C 1s are identified.

Figure S4. High-resolution of XPS analysis of Cu$_x$In$_x$Zn$_{2(1-x)}$S$_2$ nanobelts. In high-resolution spectrum of Cu 2p, two peaks at 931.8 and 951.5 eV appear, indicative of Cu(I) with a splitting of 19.7 eV, which is close consistent with standard separation of 19.8 eV. The In(III) is confirmed by a peak splitting of 7.6 eV, two peaks located at 444.6 and 452.2 eV, respectively. The zinc 2p peaks located at 1021.6 and 1044.6 eV, and a peak splitting of 23.0 eV indicates Zn(II). The two peaks of sulfur 2p are located at 161.4 and 162.6 eV, respectively, showing a peak separation of 1.1 eV, which are also consistent with the literature value in metal sulfide.
Figure S5. Photoluminescence (PL) spectra of quaternary Cu_{x}In_{x}Zn_{2(1-x)}S_{2} nanobelts. The excitation wavelength for PL emission was 350 nm. The emission spectra of nanobelts display several peaks, in which the peak located near the absorption edge is the excitonic emission and the peak located at a longer wavelength is the trap state emission. 1, 2, 3 The trap state emission peak, located fixedly at 823 nm, probably resulted from surface defects in quaternary Cu_{x}In_{x}Zn_{2(1-x)}S_{2} nanobelts, leading to nonradiative recombination of the electron and hole. The excitonic emission peak, substantial red shift with the increase of x values, suggests the tunable band gaps of quaternary Cu_{x}In_{x}Zn_{2(1-x)}S_{2} nanobelts.

Figure S6. STEM images of Cu_{x}In_{x}Zn_{2(1-x)}S_{2} (x=0.4) nanobelts prepared under different ratios of precursor/DT: (a) 1/20; (b) 1/80; (c) 1/160; (d) 1/320; (e) 1/480; (f) 1/640.
Figure S7. STEM images of samples prepared using different coordinating solvents instead of DT. (a) 3-mercaptopropionic acid; (b) oleic acid; (c) trioctylphosphine oxide.

Figure S8. EDS spectrum of tips of Cu$_x$In$_y$Zn$_{2(1-x)}$S$_2$ nanobelts (taken in the TEM) shown in Figure 3b. The Mo and C elements are attributed to molybdenum grids and carbon film, respectively.

Figure S9. XRD pattern of as-prepared sample derived from the control experiment that only Cu(dedc)$_2$ was used as precursor. The reaction continued 5 min. The standard reference represents Cu$_{1.75}$S (JCPDS No. 23-0958: monoclinic).
Figure S10. HRTEM images of Cu\textsubscript{1.75}S nanoplates derived from the control experiment that only Cu(dedc)\textsubscript{2} was used as precursor. The reaction continued 5 min.

References