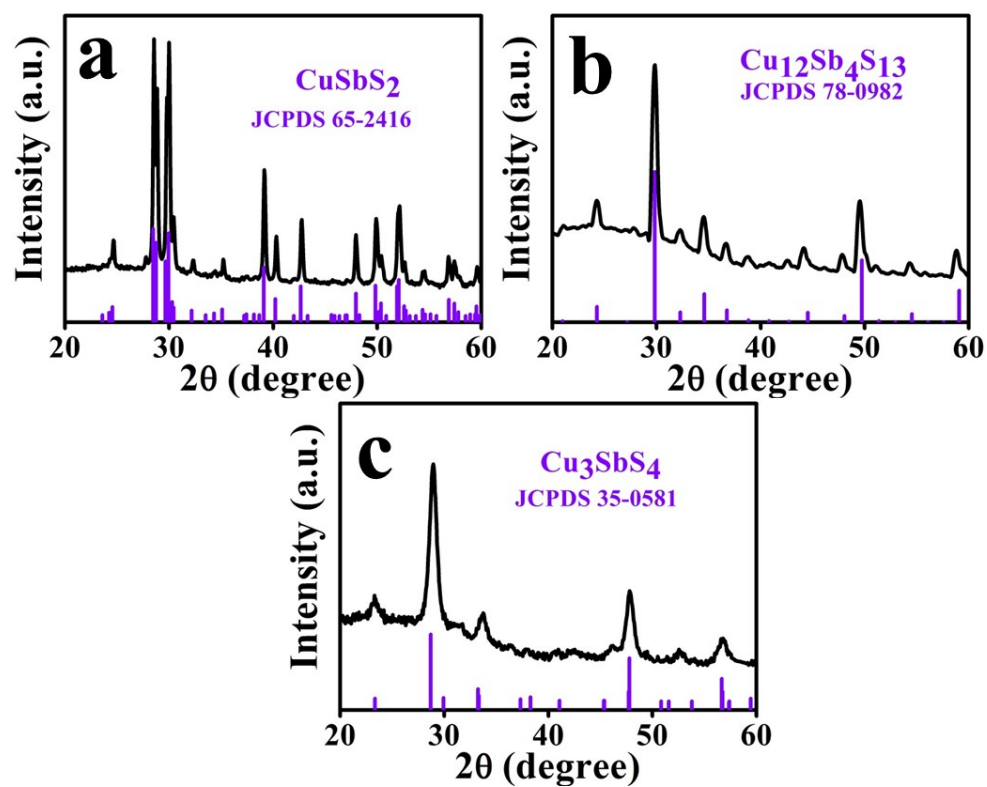


## Supporting Information



**Figure S1.** XRD patterns of CAS NCs of different phases prepared at 110 °C with heat treatment at 200 °C for 1 h.

<b>S:Sb (precursors)</b>	<b>Cu (at.%)</b>	<b>Sb (at.%)</b>	<b>S (at.%)</b>	<b>S:(Cu+Sb) (products)</b>
<b>2:1</b>	<b>25.14</b>	<b>24.52</b>	<b>50.34</b>	<b>1.01</b>
<b>2.5:1</b>	<b>24.91</b>	<b>24.47</b>	<b>50.62</b>	<b>1.03</b>
<b>3:1</b>	<b>24.58</b>	<b>24.25</b>	<b>51.17</b>	<b>1.05</b>
<b>3.5:1</b>	<b>24.33</b>	<b>24.16</b>	<b>51.51</b>	<b>1.06</b>
<b>4:1</b>	<b>24.29</b>	<b>24.11</b>	<b>51.60</b>	<b>1.07</b>

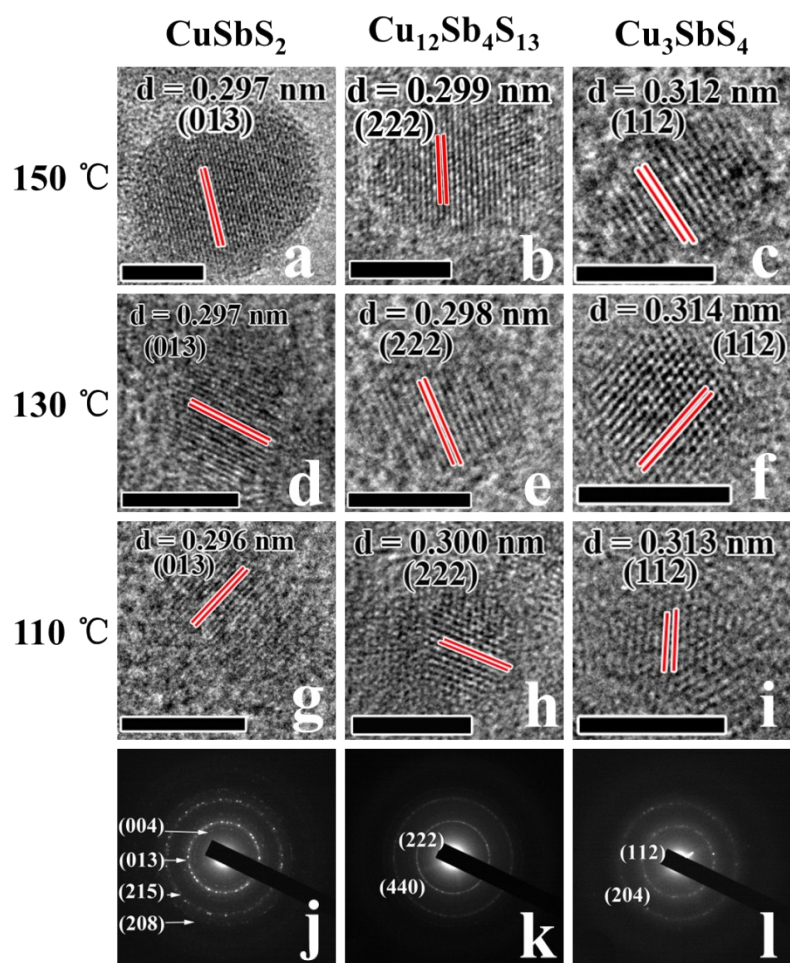
**Table S1.** EDX data of the products prepared at the standard reaction conditions for  $\text{CuSbS}_2$  but with variety precursors ratio of S:Sb. The results indicate that these samples should be  $\text{CuSbS}_2$ .

**Note:** Precursors ratio of Cu:Sb is set as 1:1.

S:Sb (precursors)	Cu (at.%)	Sb (at.%)	S (at.%)	S:Sb (products)
2.5:1	41.62	14.17	44.21	12.48:4
3:1	41.61	13.80	44.59	12.92:4
4:1	41.82	13.44	44.74	13.32:4
5:1	41.61	13.38	45.01	13.46:4
6:1	41.02	13.32	45.66	13.71:4
7:1	37.73	12.60	49.67	15.77:4
8:1	36.77	12.58	50.65	16.10:4

**Table S2.** EDX data of products prepared at the standard reaction conditions for  $\text{Cu}_{12}\text{Sb}_4\text{S}_{13}$  but with variety precursors ratio of S:Sb. The results indicate that the phase transformation has taken place when the precursors ratio of S:Sb reaches to 7:1.

**Note:** Precursors ratio of Cu:Sb is set as 3:1.



**Figure S2.** (a-i) HRTEM images of CAS NCs of different phases with tunable sizes prepared at various temperatures. The scale bars are 5 nm. (j-l) SAED patterns of CAS NCs of different phases.

<b>Phases</b>	<b>Size (nm)</b>	<b>Absorption band edge (nm)</b>	<b>Band gap (eV)</b>
<b>CuSbS<sub>2</sub></b>	<b>11.26</b>	<b>970</b>	<b>1.48</b>
	<b>6.12</b>	<b>910</b>	<b>1.66</b>
	<b>4.31</b>	<b>830</b>	<b>1.76</b>
<b>Cu<sub>12</sub>Sb<sub>4</sub>S<sub>13</sub></b>	<b>7.86</b>	<b>710</b>	<b>1.94</b>
	<b>5.76</b>	<b>690</b>	<b>2.10</b>
	<b>4.35</b>	<b>650</b>	<b>2.28</b>
<b>Cu<sub>3</sub>SbS<sub>4</sub></b>	<b>5.95</b>	<b>840</b>	<b>1.50</b>
	<b>4.81</b>	<b>810</b>	<b>1.58</b>
	<b>3.37</b>	<b>770</b>	<b>1.66</b>

**Table S3.** Absorption band edges and band gaps data of different phases with various sizes.