Simultaneous phase and size control in the synthesis of Cu_2SnS_3 and Cu_2ZnSnS_4 nanocrystals

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Experimental Section

I. Materials

Copper acetylacetonate ($Cu(acac)_2$, 99.99%), zinc acetylacetonate hydrate($Zn(acac)_2$), tin acetylacetonate ($Sn(acac)_2$, 99.9%), elemental sulfur (powder, 99.98%), 1-dodecanethiol (DDT, 98%), oleic acid and oleylamine (OLA, 70%) were purchased from Sigma-Aldrich. All chemicals were used without further purification.

II. Synthesis of Cu_2ZnSnS_4 and Cu_2SnS_3

The typical preparation of CZTS was followed. $Cu(acac)_2$ (0.6 mmol), $Zn(acac)_2$ (0.3 mmol), $Sn(acac)_2$ (0.3 mmol), sulfur precursor(elemental sulfur or DDT, 2.7 mmol), oleic acid (3.6 mmol) were dissolved in OLA(9 ml) and heated to 60 ^oC (for elemental sulfur) or 110 ^oC (for DDT) under vacuum for degassing. Then the mixture was purged with nitrogen gas, and heated to 100 ^oC (for sulfur powder) or around 240 ^oC (for DDT) within 20 min. When desire temperature reached, the reaction solution changed to a brown and the heating source was removed and the solution was cooled to room temperature. For purification, the Cu_2ZnSnS_4 particles was precipitated by adding excess methanol, collected by centrifugation, and redispersed in hexanes. Cu_2SnS_3 were prepared by a similar procedure, except $Zn(acac)_2$. To size control, oleic acid amount were increased to obtain smaller nanocrystals.

III. Charaterization

TEM images were recorded using a JEOL JEM-1011 microscope. X-ray diffraction patterns of the products were characterized by a Rigaku, D/Max-2500/PC using Cu-Kα radiation (λ = 1.5418 Å). Absorption spectrums were obtained using an Agilent 8453 UV-visible spectrophotometer. Raman spectra were collected on a Witech

Alpha 300R Raman microscopy with a 532 nm laser (0.5 mW). XPS was performed by an ESCALAB 220 instrument using a source of Mg Ka radiation. Chemical composition analysis of the as-synthesized CZTS crystals was determined by energy dispersive spectroscopy performed in scanning electron microscopy (JEOL JSM-7401F). The Cu K, Zn K, Sn L and S K lines were used for quantification.

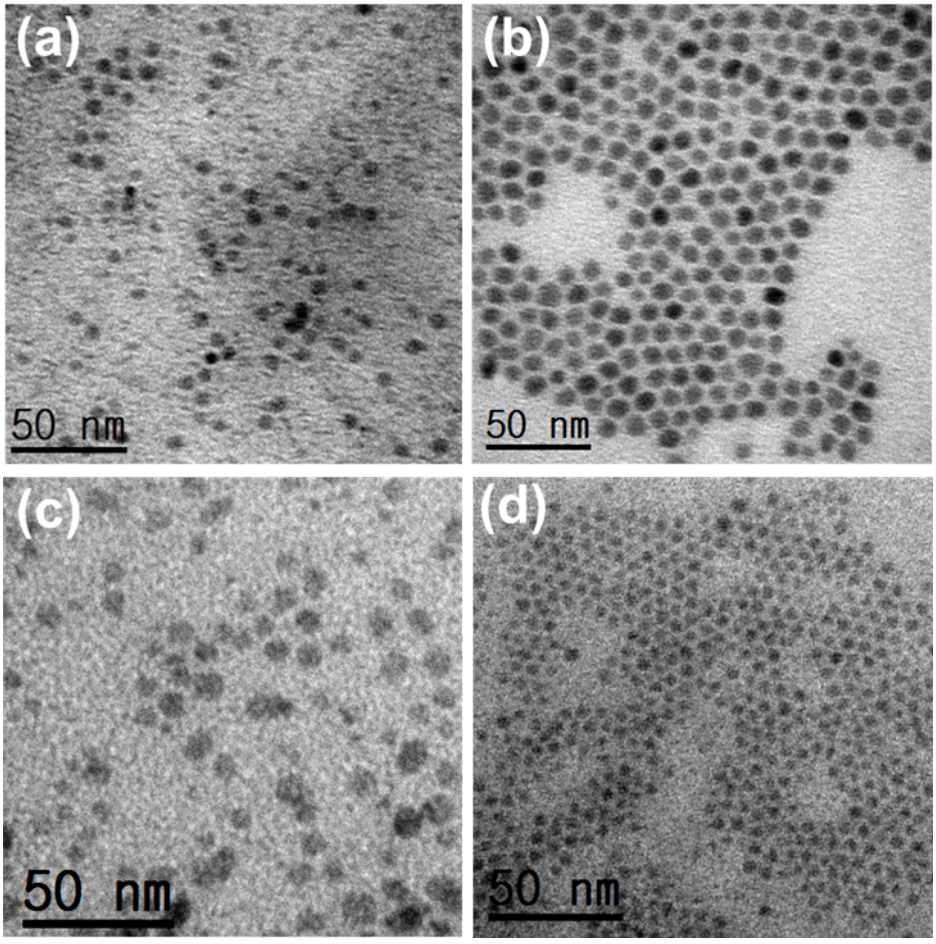

Figure S1. TEM images of CTS NCs synthesized by using elemental sulfur (a) or using 1-dodecanethiol (b) and CZTS NCs synthesized using elemental sulphur (c) or using 1-dodecanethiol (d) as the sulphur precursor. Scale bar: 50 nm.

Crystal formula	Crystal system	Space group	Crystal parameter
Cu_2SnS_3	Zinc Blende	*F*-43 m	a = b = c = 5.3466 Å
	Wurtzite	$P6_3mc$	a = b = 3.8424 Å c = 6.3311 Å
Cu_2ZnSnS_4	Kesterite	$I\bar{4}2m$	a = b = 5.3614 Å c = 10.6772 Å
	Wurtzite	$P6_3mc$	a = b = 3.8195 Å c = 6.2620 Å

Figure S2. Crystal parameters of synthesized zinc blende CTS, wurtzite CTS, kesterite CZTS and wurtztie CZTS nanocrystals.

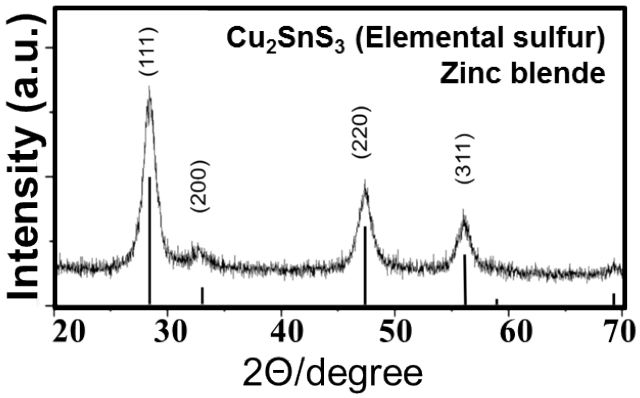

Figure S3. X-ray Diffraction (XRD) pattern of Cu_2SnS_3 nanoctystals using elemental sulfur with 300 ^oC reaction temperature.

Crystal formula	Crystal system	Cu %	Zn %	Sn %	Cu : (Zn) : Sn	Cu/((Zn)+Sn)
Cu_2SnS_3	Zinc Blende	21.57	-	17.53	2 : 1.62	1.23
	Wurtzite	36.95	-	20.55	2 : 1.11	1.80
Cu_2ZnSnS_4	Kesterite	29.45	7.52	12.12	2 : 0.51 : 0.82	1.50
	Wurtzite	21.35	8.38	21.77	2 : 0.79 : 2.04	0.71

Figure S4. Composition of synthesized zinc blende CTS, wurtzite CTS, kesterite CZTS and wurtztie CZTS nanocrystals.