11-5-2013

Axial composition gradients and phase segregation regulate the aspect ratio of Cu2ZnSnS4 nanorods

Michelle J. Thompson
Iowa State University, mjl@iastate.edu

Thanthirige Purnima Anuththara Ruberu
Iowa State University, puruberu@iastate.edu

Kyle J. Blakeney
Iowa State University

Karen V. Torres
Iowa State University

Patrick Steven Dilsaver
Iowa State University, pdilsave@iastate.edu

See next page for additional authors

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Abstract
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Keywords
Composition control, CZTS, precursor loading, shape control

Disciplines
Chemistry

Comments

Authors
Michelle J. Thompson, Thanthirige Purnima Anuththara Ruberu, Kyle J. Blakeney, Karen V. Torres, Patrick Steven Dilsaver, and Javier Vela

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Axial Composition Gradients and Phase Segregation Regulate the Aspect Ratio of Cu₂ZnSnS₄ Nanorods

Michelle J. Thompson, T. Purnima A. Ruberu, Kyle J. Blakeney, Karen V. Torres, Patrick S. Dilsaver, and Javier Vela*

Department of Chemistry, Iowa State University, Ames, Iowa 50011, United States

Supporting Information

ABSTRACT: Cu₂ZnSnS₄ (CZTS) is a promising material for solar energy conversion, but synthesis of phase-pure, anisotropic CZTS nanocrystals remains a challenge. We demonstrate that the initial concentration (loading) of cationic precursors has a dramatic effect on the morphology (aspect ratio) and composition (internal architecture) of hexagonal wurtzite CZTS nanorods. Our experiments strongly indicate that Cu is the most reactive of the metal cations; Zn is next, and Sn is the least reactive. Using this reactivity series, we are able to purposely fine-tune the morphology (dots versus rods) and degree of axial phase segregation of CZTS nanocrystals. These results will improve our ability to fabricate CZTS nanostructures for photovoltaics and photocatalysis.

SECTION: Glasses, Colloids, Polymers, and Soft Matter

Cu₂ZnSnS₄ or “CZTS” is one of the most promising materials for solar energy harvesting. Modified slightly, this method uses the hot injection of 1-dodecylthiol (1-DDT, 3.7 mmol) to a mixture of Cu(acac)₂ (0.50 mmol), Zn(OAc)₂·2H₂O (0.25 mmol), Sn(OAc)₄ (0.25 mmol), trietylphosphine oxide (TOPO, 1.75 mmol), and 1-octadecene (ODE, 5 mL) under Ar at 120 °C for 30 min. This procedure typically yields CZTS nanorods with a mean length of 23.7 ± 4.1 nm, a mean diameter of 7.3 ± 1.4 nm, and a length-to-diameter “aspect” ratio of 3.3 ± 0.8. (Figure 1A and Table 1A). Unfortunately, simply repeating this procedure using different injection (nucleation) temperatures or reaction (growth) times, a common way to affect the anisotropy of chalcogenide nanocrystals, did not affect the nanorods’ original aspect ratio (see the Supporting Information).

We hypothesized that the reason behind the apparent lack of “plasticity” of CZTS nanorods might lie within their multielement composition. First-principles studies showed that this quaternary phase is stable only within a very small domain of chemical potentials. Slight deviations from optimal growth conditions result in spontaneous formation of undesired phases such as ZnS, SnS, SnS₂, CuS, and Cu₂SnS₃ rather than the desired CZTS phase. Critically, the first method of choice for distinguishing between possible nanocrystalline phases, powder X-ray diffraction (XRD), is of limited use here because CZTS and common impurities such as ZnS adopt very similar X-ray diffraction patterns. However, energy-dispersive X-ray spectroscopy (EDX) line scans on several nanorods prepared by the aforementioned procedure consistently showed marked axial composition gradients. Specifically, the amount of Cu increased, and the amount of Zn decreased from one side of the nanorods to the other (Figure 3).

We recently observed similar behavior in ternary CdS₁₋ₓSeₓ nanorods (0 ≤ x ≤ 1). After careful study, we learned that axial composition gradients could be purposely induced or

Received: September 23, 2013
Accepted: November 5, 2013
Published: November 5, 2013


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suppressed by fine-tuning the loading and/or reactivity of chemical precursors. Mismatched reactivities lead to sequential nucleation of phases and axial composition gradients, whereas purposely matched reactivities lead to concurrent nucleation and more complete alloying. We conjectured that the same principles could apply here to CZTS nanorods because preferential precursor reactivity would explain the observed axial composition gradients (Figure 3). However, the observation of opposing Cu-rich and Zn-rich tips alone was not enough to discern which cationic precursor (Cu, Zn, or Sn) was more or less reactive or which metal sulfide nucleated first. To sort out these differences, we purposely increased or decreased the loading (concentration) of the different cationic precursors in the original synthesis while keeping all other conditions constant (Table 1).

The preparation that we originally used employs stoichiometric (2:1:1) amounts of three cationic precursors (Table 1A). Using only a third of the original amount of copper (Cu/3, 0.17 mmol) resulted in the formation of much more elongated CZTS nanorods having a mean length of 33.3 ± 6.7 nm, a mean diameter of 6.1 ± 1.1 nm, and an aspect ratio of 5.5 ± 1.5 (Figures 1B and 2B and Table 1B). This constitutes an increase of 41% in length and 67% in aspect ratio upon slashing the Cu loading to a third. In contrast, using three times the original amount of copper (3 × Cu, 1.50 mmol) resulted in the formation of Cu-rich dots (aspect ratio ≈ 1) having a mean diameter of 5.8 ± 0.5 nm (Figures 1C and 2C and Table 1C).

The type and initial concentrations (loadings) of the copper precursor are known to have an effect on the shape of CuS and CuInSe2 nanocrystals. In our case, the fact that the CZTS aspect ratio is so dependent on Cu loading, along with the aforementioned axial composition gradient, strongly indicates that the Cu precursor is more reactive than the Zn (and Sn) precursors. Selectivity for anisotropic growth and formation of composition gradients are closely related phenomena that result from sequential nucleation events. We interpret these results as follows: During a typical CZTS nanorod prep, the most reactive (Cu) precursor quickly reacts (with 1-DDT/t-DDT) to homogeneously nucleate Cu sulfide seeds; the less reactive Zn and Sn precursors subsequently react to heterogeneously nucleate Zn, Sn (and leftover Cu) sulfide along the unique c(z) axis of existing hexagonal wurtzite seeds, resulting in anisotropic growth (elongation). This series of events yields CZTS nanorods with composition gradients.

In comparison to the stoichiometric experiment, a lower initial concentration of Cu leads to a decrease in the rate of nucleation of Cu sulfide. Slower homogeneous nucleation produces fewer seeds; it also leaves more precursors in solution to grow longer rods. The three metal precursors can then heterogeneously nucleate at more comparable rates, producing
longer CZTS nanorods with smaller composition gradients. Indeed, EDX line scans on the copper-“starved” Cu/3 nanorods consistently revealed much less pronounced composition gradients (Figure 4). On the contrary, a higher initial concentration of Cu leads to a further increase in the rate of nucleation of Cu sulfide. At its most extreme, nucleation is so fast and produces so many seeds that it quickly results in CZTS nanocrystals with spherical morphology (Figure 1C).

In contrast to the Cu loading-dependent behavior, changing the Zn or Sn loading does not directly affect the nanorods’ aspect ratio. For example, using only a third of the original amount of Zn (Zn/3, 0.08 mmol) resulted in a mixture of two different types of particles with rod-like (11.8 ± 3 nm length, 5.9 ± 0.9 nm diameter, 2.0 ± 0.6 aspect ratio) and dot-like morphologies (9.3 ± 0.7 nm diameter) (Figures 1D and 2D and Table 1D). EDX elemental mapping in combination with ensemble XRD measurements showed that the rod-like particles are Zn-rich (mostly ZnS with some Cu and Sn), whereas the dot-like particles are Cu-rich (Cu31S16 with some Zn) (Figure 5a and b). Clearly, starving the reaction of Zn precursor causes almost complete phase segregation (Figure 5).

In turn, using three times the original amount of Zn (3 × Zn, 0.75 mmol) resulted in the formation of CZTS dots having a mean diameter of 5.8 ± 0.5 nm (Figures 1E and 2E and Table 1E).

We also sought to confirm the above results by performing time evolution experiments. Briefly, aliquots were taken out of the reaction mixture during the synthesis of CZTS nanorods and analyzed by optical spectroscopy, TEM, and EDX. Using a stoichiometric mixture of cationic precursors, the nanocrystals C/Z/T/S composition was 2:0:0.04:0.2:4 after 5 min and 3:4:1:5 after 30 min reaction (Table 2). Thus, only after the full 30 min reaction time were Zn and Sn incorporated into the particles, which is supported by previous observations on thin films.5,46 Similarly, using a third of the Cu loading (Cu/3), the nanocrystals’ C/Z/T/S composition was 2:1:0:06:4 after 5 min and 3:4:1:5 after 30 min reaction (Table 2 and Figure 6). In addition, the nanorods’ aspect ratio nearly doubled from 5.2 ± 1.1 after 5 min to 3.0 ± 1.3 after 30 min. The biggest contribution was a change in nanorod length from 16.3 ± 6 nm after 5 min to 32.2 nm ± 7 nm after 30 min. Nanorod diameters remained statistically similar at 5.5 ± 0.5 nm after 5 min and 6.2 nm ± 0.7 nm after 30 min (Figure 6).
Thus, time evolution experiments confirmed that (1) the reactivity order of the cationic precursors used here (and with it, the rate of nucleation of their binary sulfides) decreases in the order Cu (most reactive) > Zn > Sn (least reactive); (2) decreasing the loading of the most reactive (Cu) precursor increases the nanorods’ aspect ratio by lowering the rate of nucleation of seed particles; and (3) nanorods continue to elongate over time (5–30 min) via heterogeneous nucleation on existing seeds.

In summary, we have demonstrated that wurtzite CZTS nanorods synthesized using stoichiometric amounts of commercially available cationic precursors contain marked composition gradients along their axes. These hexagonal CZTS nanorods are characterized by a Cu-rich end, an opposite Zn-rich end, and low Sn content throughout. Nonstoichiometric syntheses, in which we varied the loading of the cationic precursors, along with time evolution experiments showed that the reactivity of the three cationic precursors and relative rate of nucleation of the corresponding metal sulfides decrease as Cu (most reactive) > Zn > Sn (least reactive). Under stoichiometric conditions, these reactivity differences lead to sequential nucleation events and axial composition gradients. Seeds made of Cu sulfides quickly form first by homogeneous nucleation, followed by heterogeneous (epitaxial) nucleation of Zn and Sn sulfides. Decreasing the loading of the most reactive (Cu) precursor increases the nanorods’ aspect ratio by lowering the rate of nucleation of Cu sulfides. This allows the three metal precursors to nucleate at more comparable rates, producing significantly longer CZTS nanorods with a more constant elemental composition along their axes. In contrast, increasing the loading of Cu precursor or changing the loading of Zn or Sn precursors either leads to a low aspect ratio (dots) and/or phase-segregated nanocrystals. Thus, we have shown that

Table 2. Evolution of CZTS Nanorod Composition over Time

<table>
<thead>
<tr>
<th>loading</th>
<th>time/min</th>
<th>Cu</th>
<th>Zn</th>
<th>Sn</th>
<th>S</th>
</tr>
</thead>
<tbody>
<tr>
<td>stoich.</td>
<td>5</td>
<td>60 ± 2</td>
<td>1.0 ± 0.9</td>
<td>1.0 ± 1.0</td>
<td>38 ± 1</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>29 ± 1</td>
<td>13 ± 1</td>
<td>2.0 ± 0.6</td>
<td>56 ± 1</td>
</tr>
<tr>
<td>Cu/3</td>
<td>5</td>
<td>31 ± 3</td>
<td>15 ± 2</td>
<td>1.0 ± 1.0</td>
<td>53 ± 2</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>24 ± 1</td>
<td>31 ± 1</td>
<td>7.0 ± 0.4</td>
<td>38.0 ± 0.3</td>
</tr>
</tbody>
</table>

\[\text{[Cu]}_T = 48 \text{ mM}, \text{[Zn]}_T = 24 \text{ mM}, \text{[Sn]}_T = 24 \text{ mM}, \text{and [S]}_T = 0.40 \text{ M (see text).} \]
cationic precursor loading predictably affects the morphology (dots versus rods) and degree of axial phase segregation of anisotropic CZTS nanocrystals. These discoveries will improve our ability to fabricate CZTS nanostructures for photocatalysis. More generally, they will aid our understanding of and ability to control phase segregation in complex compound semiconductors such as quaternary CZTS.

**ASSOCIATED CONTENT**

Supporting Information

Additional experimental synthetic and characterization data, including TEM images and EDX area scan data, powder X-ray diffraction data, absorption spectra, band gaps of several semiconductors, TEM size histograms, EDX line scans, and time evolution studies. This material is available free of charge via the Internet at http://pubs.acs.org.

**AUTHOR INFORMATION**

Corresponding Author

*E-mail: vela@iastate.edu.

Notes

The authors declare no competing financial interest.

**ACKNOWLEDGMENTS**

J.V. gratefully acknowledges the National Science Foundation for funding of this work through the Division of Materials Research, Solid State and Materials Chemistry program (NSF-DMR-1309510). T.P.A.R. thanks ISU for a Graduate Research Excellence Award.

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