Research Article

A Large-Scale Synthesis and Characterization of Quaternary CuIn$_x$Ga$_{1-x}$S$_2$ Chalcopyrite Nanoparticles via Microwave Batch Reactions

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Various quaternary CuIn$_x$Ga$_{1-x}$S$_2$ (0 ≤ x ≤ 1) chalcopyrite nanoparticles have been prepared from molecular single-source precursors via microwave decomposition. We were able to control the nanoparticle size, phase, stoichiometry, and solubility. Depending on the choice of surface modifiers used, we were able to tune the solubility of the resulting nanoparticles. This method has been used to generate up to 5 g of nanoparticles and up to 150 g from multiple batch reactions with excellent reproducibility. Data from UV-Vis, photoluminescence, X-ray diffraction, TEM, DSC/TGA-MS, and ICP-OES analyses have shown high reproducibility in nanoparticle size, composition, and bandgap.

1. Introduction

For nearly three decades, chalcopyrite CuIn$_{0.7}$Ga$_{0.3}$Se$_2$ (CIGS) and related materials have attracted much interest due to their potential applications in photovoltaic and other optoelectric devices [1–5]. Many thin film PV devices of CIGS set respectable power conversion efficiency of about 20% [6, 7]. In recent years, there have been increasing reports on using colloidal I–III–VI nanoparticle suspensions, composites, and inks to prepare PV devices. Solution processing strategies such as spin coating [8–10] and ink printing [1, 2, 4] are being explored for large areas of CIGS while lowering the overall costs.

One of the key stoichiometric requirements is to consistently maintain In/Ga ratio to 0.7/0.3 from batch to batch. Previously, we reported the efficient syntheses of quaternary CuIn$_x$Ga$_{1-x}$S$_2$ (0 ≤ x ≤ 1) chalcopyrite nanoparticles with precise stoichiometric control by decomposition of a mixture of two I–III bimetallic single-source precursors (SSPs), (Ph$_3$P)$_2$Cu(μ-SeEt)$_2$In(SeEt)$_2$ (1), and (Ph$_3$P)$_2$Cu(μ-SeEt)$_2$Ga(SeEt)$_2$ (2), in the presence of 1,2-ethanethiol via microwave irradiation [11].

Use of SSPs in preparation of nanomaterials presents distinct advantages such as precise control of reaction conditions and stoichiometry as SSPs contain all necessary elements in a single molecule. Despite the obvious advantages of SSPs, to our knowledge, no studies have been conducted using combinations of SSPs to form soluble and insoluble ternary and quaternary chalcopyrite nanoparticles.

Microwave-assisted preparation of nanoparticles from SSPs offers advantages over traditional thermolysis as microwave provides rapid heating as well as greater homogeneity in the overall reaction temperature [12]. This usually allows for the preparation of nanoparticles with increased size control [13], dramatic decreases in reaction times, improved product purities, and reactions exhibiting good reproducibility and high yields [14, 15].
In our studies, the nanoparticles were produced using 1,2-ethanediol as surface stabilizer and cross-linker of SSPs. 1,2-Ethanediol undergoes thiolate ligand exchange reactions, which produce random copolymers of SSPs. This formation of random copolymers between SSPs 1 and 3 is a significant requirement for us to control In-Ga ratio in nanoparticles. 1,2-Ethanediol also cross-links nanoparticles, and the resulting organic-nanoparticle composite precipitates out of reaction solution as insoluble micron-sized clusters [14]. Although the resulting material exhibited excellent size, stoichiometry, and band gap control, these micron-sized clusters are not suitable for some solution-based thin film processing methods, which require highly soluble nanoparticles in common organic solvents. Therefore, the ability to modulate organic constituents in these CIGS nanoparticles whether to improve solubility or to add functionality through a hybrid composite is important. Judicious use of organic cross-linking agents in conjunction with other monothiols can control the solubility of resulting nanoparticles. The ability to modulate both physical and chemical properties could lead to future applications of these particles in organic-inorganic composites in photovoltaics.

The full realization of the potential of these nanoparticles will require synthetic strategies capable of consistently producing nanoparticles on a multigram scale. Despite the obvious needs, scales of tens of milligrams are typical for the production of CIS and CIGS nanoparticles [23–26]. Thus far, the production of these nanoparticles on a gram scale or larger has received limited attention [11, 14, 27–29]. In our studies, the nanoparticles were produced using 1,2-ethanediol (1.8 mL, 21.46 mmol) and (Ph3P)2Cu(μ-SET)2Ga(SET)2 (1), (Ph3P)2Cu(μ-SEt)2In(SET)2 (2), (Ph3P)2Cu(μ-SPh)2In(SPh)2 (3), and (Ph3P)2Cu(μ-SPh)2Ga(SPh)2 (4) were synthesized according to the literature [30–33].

2.2. Synthesis of Single-Source Precursors (SSPs) [30–33]. (Ph3P)2Cu(μ-SET)2In(SET)2 (1), (Ph3P)2Cu(μ-SEt)2Ga(SET)2 (2), (Ph3P)2Cu(μ-SPh)2In(SPh)2 (3), and (Ph3P)2Cu(μ-SPh)2Ga(SPh)2 (4) were synthesized according to the literature [30–33].

2.3. General Procedure for the Preparation of CuInxGa1−xS2 (0 ≤ x ≤ 1) Chalcopyrite Nanoparticles [31]. For the general reaction, in a dry Milestone microwave vessel, (Ph3P)2Cu(μ-SEt)2In(SET)2 (SSP 1, 1.500 g, 1.583 mmol) and (Ph3P)2Cu(μ-SET)2Ga(SET)2 (SSP 2, 1.429 g, 1.583 mmol) were dissolved in 18 mL of dry benzyl acetate followed by addition of 1,2-ethanediethiol (1.8 mL, 21.46 mmol). The reaction mixture was stirred at room temperature for 5 min and heated at set temperatures for 1 hour via microwave irradiation. Upon completion, the reaction was cooled to room temperature, and CuIn0.5Ga0.5S2 nanoparticles were recovered by serial precipitation, centrifugation, and washing in CH3OH to provide yellow to black powder.

2.4. Preparation of Highly Cross-Linked Quaternary CuInxGa1−xS2 Chalcopyrite Nanoparticles from SSPs 3 and 4. For the general reaction, in a dry Milestone microwave vessel, (Ph3P)2Cu(μ-SPh)2In(SPh)2 (3, 13.61 g, 11.95 mmol),...
(Ph3P)2Cu(μ-SPh)2Ga(SPh)2 (4, 6.43 g, 5.87 mmol), and 1,2-ethanedithiol (9.72 mL, 115.9 mmol) were dissolved in 88.0 mL of benzyl acetate. The reaction was heated at reaction temperatures 160, 180, or 200°C for 1 hr. Upon completion, the reaction was cooled to room temperature, and CuIn0.5Ga0.5S2 nanoparticles were recovered by serial precipitation, centrifugation, and washing with CH3OH to provide black powder. This method has been successfully adapted to prepare up to 5 g of nanoparticles in a single vessel (Figure 2).

2.5. Preparation of Organic Soluble Quaternary CuInxGa1-xS2 (0 ≤ x ≤ 1) Chalcopyrite Nanoparticles. (Ph3P)2Cu(μ-SPh)2Ga(SPh)2 (1, 6.00 grams, 6.33 millimoles) and (Ph3P)2Cu(μ-SPh)2Ga(SPh)2 (2, 5.71 grams, 6.33 millimoles) were dissolved in 60 mL of benzene, and 1,2-ethanedithiol (1.06 mL, 12.66 millimoles) was added to afford random polymer of 1 and 2. After stirring at room temperature for 1 hr, the solvent and ethanethiol were removed to afford white solid. The resulting solid was redissolved in benzyl acetate (20 mL) followed by addition of 1-hexanethiol (2.00 mL). The reaction was heated at reaction temperatures between 160 and 200°C for 1 hr. Upon completion, the reaction was cooled to room temperature, and CuInxGa1-xS2 (0 ≤ x ≤ 1) nanoparticles were recovered by serial precipitation, centrifugation, and washing in CH3OH to provide red to red-black powder.

2.6. Preparation of Organic Soluble Quaternary CuIn0.5Ga0.5S2 Chalcopyrite Nanoparticles. Following general reaction, a combination of two SSPs, (Ph3P)2Cu(μ-SEt)2In(SEt)2 (SSP 1, 13.00 g, 13.72 mmol) and (Ph3P)2Cu(μ-SEt)2Ga(SeEt)2 (SSP 2, 6.67 g, 7.39 mmol), dissolved in 100 mL of benzyl acetate in the presence of 1,2-ethanethiol (2.4 mL, 28.50 mmol) and 1-hexanethiol (20 mL, 142.1 mmol). The reaction was heated at 195°C for 1 hr. Upon completion, the reaction was cooled to room temperature, and CuIn0.5Ga0.5S2 nanoparticles were recovered by serial precipitation, centrifugation, and washing in CH3OH to provide red-black powder. This method has been successfully adapted to prepare up to 25 g of nanoparticles in a single vessel.

3. Results and Discussions

We recently reported the efficient microwave syntheses of highly cross-linked quaternary CuInxGa1-xS2 (0 ≤ x ≤ 1) chalcopyrite nanoparticles in subgram scales. The method demonstrated high degrees of stoichiometric control by decomposing a mixture of two I–III bimetallic SSPs, (Ph3P)2Cu(μ-SEt)2In(SeEt)2 (1) and (Ph3P)2Cu(μ-SEt)2Ga(SeEt)2 (2), using 1,2-ethanethiol as a cross-linker. The resulting nanoparticles could be engineered to exhibit bandgaps ranging from 1.59 to 2.30 eV by varying the amount of Ga in CuInxGa1-xS2 nanoparticles [11].

These highly cross-linked quaternary nanoparticles are insoluble in common organic solvents but retain individual nanoparticle characteristics such as phase, size, and bandgap. As expected, XRD peaks associated with chalcopyrite phase shift toward narrower lattice spacing, as a function of increasing amount of Ga [11].

In order to increase reproducibility of large-scale reactions, we chose (Ph3P)2Cu(μ-SPh)2In(SPh)2 (SSP 3) and (Ph3P)2Cu(μ-SPh)2Ga(SPh)2 (SSP 4) to be used in place of SSPs 1 and 2. Due to their bulky and hydrophobic phenylthiolate ligands, SSPs 3 and 4 are more stable towards moisture and thermal decomposition compared to their ethylthiolate counterpart [33]. This allows for easier handling and greater reproducibility in larger reactions. The CuIn0.5Ga0.5S2 nanoparticles have been synthesized (29 separate reactions resulting in about 150 g of nearly uniform nanoparticles under the same reaction conditions) from decomposition of SSPs 3 and 4 via microwave irradiation in the presence of 1,2-ethanediethiol at 200°C with high reproducibility.

The analysis of CuIn0.5Ga0.5S2 nanoparticles by ICP-OES (Table 1) indicates that our method allows precise control of In/Ga ratio. The high level of control is likely due to the fact that 1,2-ethanediethiol acts as a bridging unit between two SSP units. This process produces cross-linked random polymers of SSPs, which undergo rapid decomposition to produce the resulting CuInxGa1-xS2 nanoparticles [14]. The ICP-OES data of CuIn0.5Ga0.5S2 nanoparticles also show evidence of little or no change in the atomic percent of Cu, In, and Ga for all 29 reactions, Table 1. These results exhibit high reproducibility, improved product purities, and indicate that different forms of precursors can be used. The target formula of CuIn0.5Ga0.5S2 was achieved by using 7:3 ratio of SSPs 3 and 4.

Figure 1: Single-source precursors 1 through 4.
Figure 2: Formation of soluble and insoluble CIGS nanoparticles from SSPs by controlling the ratio between 1,2-ethanedithiol and 1-hexanethiols.

Table 1: Representative sample compositions (from ICP-OES analysis) from 10 of 29 highly cross-linked CuIn$_{0.7}$Ga$_{0.3}$S$_2$ nanoparticle batches prepared at 200°C. *The standard deviation of all samples is 0.89 for Cu, 0.96 for In, and 0.35 for Ga.

<table>
<thead>
<tr>
<th>Entry</th>
<th>[Cu]$^+$</th>
<th>[In]$^+$</th>
<th>[Ga]$^+$</th>
<th>In+Ga</th>
<th>In/In+Ga</th>
<th>Ga/In+Ga</th>
</tr>
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<tr>
<td>1</td>
<td>19.59</td>
<td>12.26</td>
<td>5.45</td>
<td>17.71</td>
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<td>0.31</td>
</tr>
<tr>
<td>2</td>
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<td>5.38</td>
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<td>0.30</td>
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<td>3</td>
<td>21.48</td>
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<td>5.14</td>
<td>20.52</td>
<td>0.70</td>
<td>0.30</td>
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<tr>
<td>4</td>
<td>20.17</td>
<td>13.14</td>
<td>6.29</td>
<td>19.43</td>
<td>0.68</td>
<td>0.32</td>
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<td>5</td>
<td>20.26</td>
<td>14.42</td>
<td>5.14</td>
<td>19.73</td>
<td>0.72</td>
<td>0.28</td>
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<tr>
<td>6</td>
<td>21.67</td>
<td>14.96</td>
<td>5.92</td>
<td>20.88</td>
<td>0.72</td>
<td>0.28</td>
</tr>
<tr>
<td>7</td>
<td>20.51</td>
<td>13.94</td>
<td>5.94</td>
<td>19.88</td>
<td>0.70</td>
<td>0.30</td>
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<td>13.28</td>
<td>5.72</td>
<td>19.00</td>
<td>0.70</td>
<td>0.30</td>
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<td>10</td>
<td>21.79</td>
<td>14.75</td>
<td>6.20</td>
<td>20.96</td>
<td>0.70</td>
<td>0.30</td>
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The estimated volume-weighted crystal diameters (employing Scherrer equation with a shape factor of 0.9) [34] of the CuIn$_{0.7}$Ga$_{0.3}$S$_2$ chalcopyrite nanoparticles samples are 4.4 ± 0.4 nm (Figure 3(a)). As shown in Figure 3(b), multiple batch samples exhibit almost identical absorption behavior with the average bandgap of 1.55 ± 0.05 eV.

Similar method can be used to prepare quaternary CuIn$_{0.7}$Ga$_{0.3}$S$_2$ chalcopyrite nanoparticles, which are soluble in common organic solvents such as hexanes, THF, and CH$_2$Cl$_2$. The increased solubility is attributed to the use of limited amount of 1,2-ethanedithiol in presence of excess 1-hexanethiol in the reaction mixture. Other monothiols with longer carbon chains and branched structures can also be used to modulate the resulting solubility.

From our previous experience, high-reaction temperature and/or the use of more than 2 equiv. of cross-linking agent is necessary to fully incorporate Ga to the crystalline structure. As shown in ICP-OES data (Table 2), Ga incorporation increases at higher reaction temperatures when 1:1 ratio of SSP 1 and 2 is used. However, the use of increasing amounts of 1,2-ethanedithiol leads to decreasing solubility, and the higher reaction temperatures result in larger particle sizes [11].

Thermogravimetric analyses (TGA/DSC-MS) of the soluble nanoparticles were performed at ambient pressure in alumina crucibles. The samples were heated at a rate of 10°C/min under an argon atmosphere. Weight loss was associated with decomposition of the passivation layers (Figure 4). Calculation of the derivative maximum rate of weight loss (MRW, %/°C) and step transition weight loss were used as a measure of relative stability. The TGA data show a smooth loss of mass over a temperature window of 250–400°C in two steps, accounting for a loss of 34.6%, 30.1%, and 28.4% for entries 11–13 (Table 2), respectively. The evolved gases were thermal decomposition products of 1,2-ethanedithiol and 1-hexanethiol as expected. These results are consistent with the ICP-OES analysis, a decrease in particle size results in a relative increase in the amount of organic material that makes up the passivation layer.

A bandgap range from 1.76 to 1.84 eV was obtained based on the absorption spectra. The estimated volume-weighted crystal diameters [34] of the CuIn$_x$Ga$_{1-x}$S$_2$ chalcopyrite nanoparticles samples based on the XRD spectra are from 3.7 to 3.9 nm (Figure 5(a)). The photoluminescence emission (PLE) maxima increases can also be directly related to the increase in bandgap with increased Ga content (Figure 5(b)).
Figure 3: (a) Representative of normalized XRD data of CuIn$_{0.7}$Ga$_{0.3}$S$_2$ nanoparticles prepared at 200$^\circ$C. (b) Normalized UV-Vis absorption spectra of typical CuIn$_{0.7}$Ga$_{0.3}$S$_2$ nanoparticles prepared at 200$^\circ$C.

Table 2: Composition (from ICP-OES analysis) of soluble CuIn$_{x}$Ga$_{1-x}$S$_2$ nanoparticles prepared at 160, 180, or 200$^\circ$C.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Temp. (°C)</th>
<th>Cu%</th>
<th>In%</th>
<th>Ga%</th>
<th>In+Ga</th>
<th>In/In+Ga</th>
<th>Ga/In+Ga</th>
<th>MRW (%)</th>
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<tr>
<td>11</td>
<td>160</td>
<td>18.73</td>
<td>13.00</td>
<td>3.69</td>
<td>16.69</td>
<td>0.78</td>
<td>0.22</td>
<td>34.6</td>
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<tr>
<td>12</td>
<td>180</td>
<td>19.81</td>
<td>12.61</td>
<td>5.95</td>
<td>18.56</td>
<td>0.68</td>
<td>0.32</td>
<td>30.1</td>
</tr>
<tr>
<td>13</td>
<td>200</td>
<td>20.48</td>
<td>11.57</td>
<td>7.38</td>
<td>18.94</td>
<td>0.61</td>
<td>0.39</td>
<td>28.4</td>
</tr>
</tbody>
</table>

Figure 4: DSC/TGA-MS data for entry 11.

An HRTEM image of CuIn$_{0.61}$Ga$_{0.39}$S$_2$ nanoparticles (Table 2, entry 13) is shown in Figure 6. Observed sizes of CuIn$_{0.61}$Ga$_{0.39}$S$_2$ nanoparticles are 3.9 nm from HRTEM images which is consistent with the XRD-calculated size (Figure 5).

In order to demonstrate the reproducibility of the method, we also tried a scale-up version of the previous synthesis five times on a 5 g scale in 5 different reaction vessels to produce 25 g of soluble CuIn$_{0.72}$Ga$_{0.28}$S$_2$ nanoparticles at one time.

The analysis of CuIn$_{x}$Ga$_{1-x}$S$_2$ nanoparticles by ICP-OES indicates that our method allows precise control of In and Ga ratio. The ICP-OES data of CuIn$_{0.72}$Ga$_{0.28}$S$_2$ nanoparticles also show evidence of little or no change in the atomic percent of Cu, In, and Ga for the reactions described in Table 3.

The average bandgap calculated from entries 14 through 18 is 1.78 ± 0.05 eV (Figure 7(b)). The estimated volume-weighted crystal diameters [29] of the CuIn$_{0.72}$Ga$_{0.28}$S$_2$ chalcopyrite nanoparticles samples are 4.1 ± 0.2 nm (Figure 7(a)).
Figure 5: (a) Normalized XRD data of typical CuIn\textsubscript{x}Ga\textsubscript{1−x}S\textsubscript{2} soluble nanoparticles prepared from 160 to 200°C. (b) Normalized photoluminescence spectra of typical CuIn\textsubscript{x}Ga\textsubscript{1−x}S\textsubscript{2} soluble nanoparticles prepared from 160 to 200°C.

Table 3: Composition (from ICP-OES analysis), optical bandgaps (E\textsubscript{g}) (from UV-Vis spectra), and sizes (from XRD) of soluble CuIn\textsubscript{0.72}Ga\textsubscript{0.28}S\textsubscript{2} nanoparticles prepared at 195°C.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Cu%</th>
<th>In%</th>
<th>Ga%</th>
<th>In+Ga</th>
<th>In/In+Ga</th>
<th>Ga/In+Ga</th>
<th>Eg (eV)</th>
<th>Size (nm)</th>
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<tr>
<td>14</td>
<td>21.77</td>
<td>14.85</td>
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<td>0.74</td>
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</table>

Figure 6: HRTEM image of CuIn\textsubscript{0.61}Ga\textsubscript{0.39}S\textsubscript{2} nanoparticles at 200°C.

4. Conclusion

The multigram scale synthesis of CIGS alloy nanoparticles is discussed. Potentially, these nanoparticles can be incorporated into next-generation quantum dot-based solar cells. The ability to prepare quaternary CuIn\textsubscript{x}Ga\textsubscript{1−x}S\textsubscript{2} (0 \leq x \leq 1) chalcopyrite nanoparticles with precise control of stoichiometry is important for controlling the bandgap and, therefore, the absorption behavior of the materials. The reaction temperatures are also critical for fine control of nanoparticle sizes and bandgaps. We have shown that by exploiting the microwave-assisted decomposition of two different SSPs in the presence of 1,2-ethanediithiol, we efficiently prepared CuIn\textsubscript{x}Ga\textsubscript{1−x}S\textsubscript{2} (0 \leq x \leq 1) nanoparticles. Short reaction times of less than 1 hour have been achieved for the preparation of these nanoparticles. Two major advantages of this approach are precise stoichiometric control of In and Ga ratio and controlling the size of nanoparticles by reaction temperatures. A wide range of bandgaps can be engineered through a combination of precise control of elemental composition and particle sizes. We are currently exploring the use of various related SSPs to prepare multinary nanoparticles that exhibit an even wider range of bandgaps and other unique optoelectric behaviors.
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