

Microwave Initiated Nucleation for the Synthesis of High Quality Nanocrystalline Quantum Dot Materials

K.-J. Kim, C.-H. Chang, P.M. Haben, D.A. Peterson, T.E. Novet, D.M. Schut

ABSTRACT

The colloidal synthesis of quantum dots occurs through either a kinetically dominated process where nucleation proceeds rapidly followed by growth via coalescence of nucleates to form larger nanoparticles, or through a thermodynamically dominated process in which nucleation occurs at high temperatures followed by epitaxial growth of the nanoparticle at lower temperatures via step-wise addition of precursors to the surface of the nucleates. While either process may be utilized for the formation of binary quantum dots, problems arise when forming quantum dots of multinary compositions due to differences in thermodynamic or kinetic processes, or the rate of nucleation. We address this issue by using microwave irradiation to manipulate the reaction kinetics of the precursors in order to produce homogeneous materials.

1. INTRODUCTION

Nanocrystalline quantum dots (NQDs) are of interest because they are size-controlled, bandgap-tunable materials [1]. By controlling the size of the quantum dot, the bandgap can be controlled, which affects both the electronic and optical properties of the material. When compared to organic materials, quantum dots have several properties which make them preferable for consumer use, such as: narrow and symmetric emission spectra, tunable absorption, emission and emissivity, and superior photochemical stability. Additionally, when compared to bulk inorganic materials, quantum dots have increased optical absorption and reduced processing costs.

While not ubiquitous in practice, quantum dots have found use in many applications, including: light emitting diodes (LEDs) [2], photovoltaics [3], thermoelectrics [4], biosensing [5], and security applications [6]. However, their adoption into consumer applications has been severely limited because they can be highly toxic (for instance, CdX,

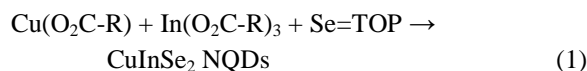
PbX where X = S, Se, Te; Hg_{1-x}Cd_xTe) [7] and because size control in large quantities has been difficult to obtain [8], especially when using multinary materials. The last issue arises from the fact that when synthesizing such materials, formation of nucleates may arise from different mechanisms, and even if the same mechanism of formation exists, form at different rates – resulting in inhomogeneous materials that have different optoelectronic properties.

Materials such as CIS (CuInSe₂), CIGS (CuIn_xGa_{1-x}Se₂) and PbS have been proposed for use as photovoltaic materials due to their high extinction coefficients and their ability to extend the absorption of light beyond 1100 nm where the cutoff for traditional Si exists [9]. However, in the case of CIS and CIGS, which are multinary materials, the synthesis of homogeneous nanocrystals are difficult because formation of the nucleate is dominated by fast reaction kinetics associated with the formation of CuSe (cubic) and Cu₂Se (hexagonal) nucleates. These nucleates lead to the formation, within the nanoparticle, of regions of copper rich areas and indium rich areas [10]. Furthermore, because of the fast kinetics associated with the reaction of the copper precursors (typically copper carboxylates) with the selenium precursors (typically Se=TOP, where TOP = trioctylphosphine), nanoparticles within the reaction solution can be copper rich, allowing InSe to nucleate at a slower rate to form In₂Se₃ nanoparticles within the same reaction solution.

To address this issue, we use microwave irradiation to increase the reaction kinetics of In-Se nucleate formation such that it is essentially the same as that of Cu-Se nucleate formation. By performing this step, the resultant product is the homogeneous formation (both within the nanoparticle and within the solution) of CuInSe₂.

2. DISCUSSION

Copper indium diselenide (CuInSe_2) quantum dots are formed from the reaction of copper(I) oleate ($\text{Cu}(\text{O}_2\text{C-R})$), indium(II) oleate ($\text{In}(\text{O}_2\text{C-R})_3$), and trioctylphosphine selenide (Se=TOP), as shown in Equation 1.



However, when this reaction is performed, a large distribution of nanoparticle sizes and shapes are obtained as shown in Figures 1 and 2.

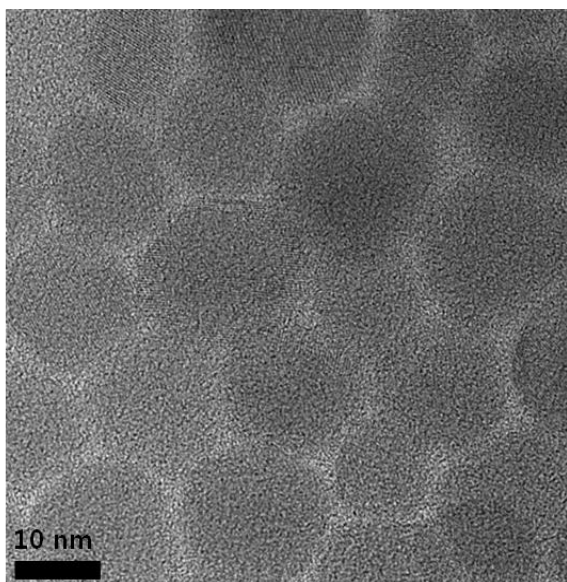


Figure 1: HR-TEM image of CuInSe_2 NQDs formed from reaction 1.

The large polydispersity observed in this reaction stems from the fact that Cu-Se nucleates faster than In-Se. Because of this difference in reactivity, Cu-Se nucleates form fast, allowing growth of larger nanoparticles that are Cu-rich. The smaller nanoparticles result from In-Se nucleates forming, and because most of the reaction material available has already been utilized in the formation of the Cu-rich nanoparticles, smaller nanoparticles that are In-rich are formed. Additionally, CuSe forms cubic nucleates, Cu_2Se forms hexagonal nucleates, and CuInSe_2 form tetrahedral nucleates (none of which are observed).

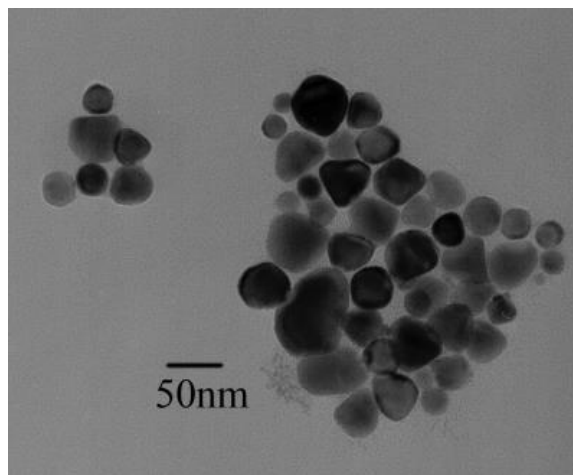


Figure 2: TEM image of several CuInSe_2 NQDs formed from reaction 1.

Because In^{3+} has a larger d-orbital system than Cu^+ , which allows for greater polarizability of the electrons within In^{3+} - and because microwaves interact more strongly with materials having larger dipoles, exposure of the reaction material shown in Equation (1) leads to greater absorption of the microwave energy by $\text{In}(\text{O}_2\text{C-R})_3$ than by $\text{Cu}(\text{O}_2\text{C-R})$. This greater absorbance of microwave energy increases the reactivity of the indium precursor. This is illustrated in Figure 3.

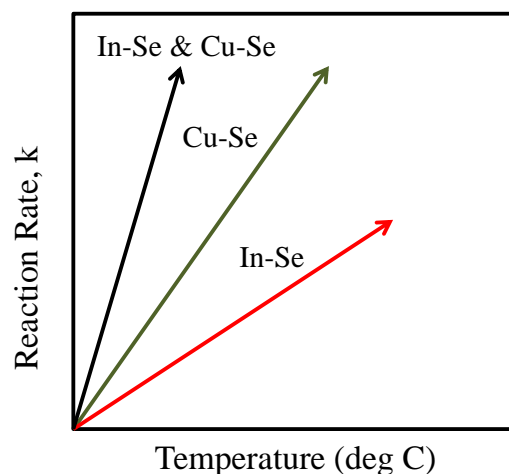


Figure 3: Graph illustrating the different reaction rates exhibited during standard reaction conditions and with microwave irradiation.

What Figure 3 shows is that Cu-Se (green line) and In-Se (red line) have different reaction rates during traditional processing. The Cu-Se nucleate formation is much faster than the In-Se nucleate formation and dominates the early steps of the reaction. However, upon irradiation of the reaction solution with microwave energy, the In-Se and Cu-Se nucleation reaction rates occur on the same time scale, allowing for the formation of homogeneous material as shown in Figures 4 and 5.

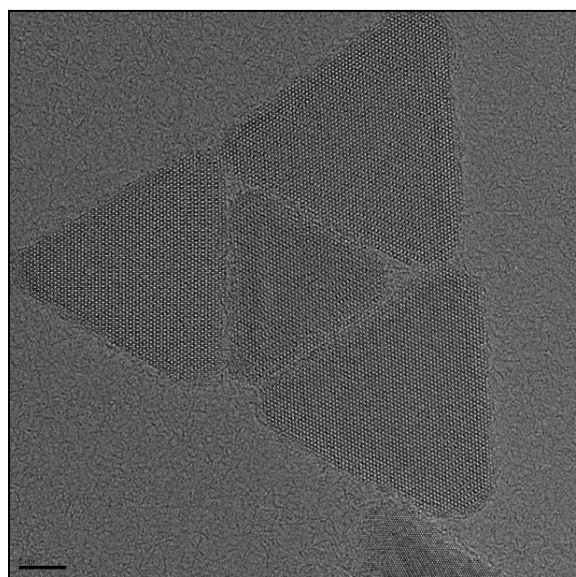


Figure 4: HR-TEM image of CuInSe₂ NQDs formed using reaction 1 while being irradiated by microwave energy.

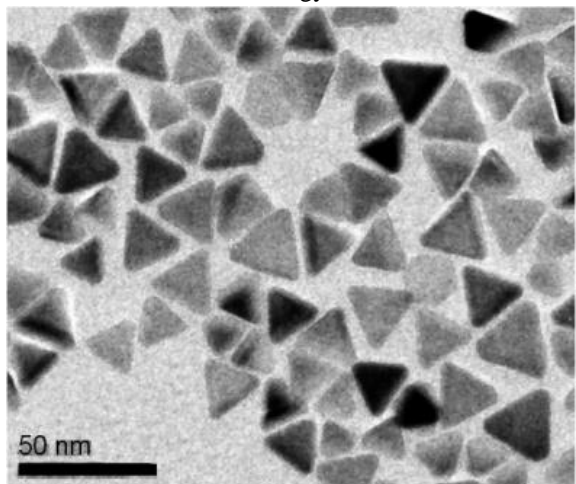


Figure 5: TEM image of several CuInSe₂ NQDs formed using microwave irradiation and showing a high degree of monodispersity.

When performing the reaction shown in Equation (1) using microwave irradiation, not only is the size distribution of the resultant material narrowed, but the NQDs generated are homogeneous in nature, as shown by the fact that only tetrahedral nanocrystals are formed (indicative of CuInSe₂).

CONCLUSION

We have shown that the use of microwaves in the synthesis of nanoparticles enhances the reaction product by producing material that has a smaller size distribution, and a high degree of homogeneity that is not otherwise observed. Furthermore, this practice is shown to work for multinary materials such as CuInSe₂.

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