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One-pot synthesis of gradient interface quaternary ZnCdSSe quantum dots

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ABSTRACT

Quantum dots (QDs) are capable of controlling the emission and absorption wavelength due to the bandgap widening effect of nanometer-sized particles. Many efforts have been made to increase the efficiency of QDs by using a core/shell structure. However, the conventional method of creating the core followed by shelling has the disadvantage of repeated processing. In this study, we synthesize composition gradient quaternary ZnCdSSe QDs of high efficiency (quantum yield = 88.96%, full width at half maximum = 28.20 nm) through one-pot synthesis. The X-ray diffraction peak for the (111) plane in ZnCdSSe QDs was shifted 2.64° compared to that for pure CdSe. From Cs-corrected STEM-EDS line scan results, it can be seen that the center of the QDs consists for more than 40% of Cd, clearly showing that a CdSe-rich core was formed, while the amount of Zn increases significantly toward the outer area. In addition, by using thermodynamics simulation, we propose a mechanism for formation of the composition gradient in QDs using one-pot synthesis and how this can be achieved with other compositions. Finally, we confirmed the chemical composition gradient inside a single quantum dot and proposed the formation behavior thereof using results of the thermodynamics simulation. The results herein may provide a way to identify the one-pot synthesis mechanism for quantum dots of various other composition gradients. This method greatly simplifies the procedure for synthesizing composition gradient ZnCdSSe QDs.

1. Introduction

Over the last few decades, quantum dots (QDs) have attracted significant attention because of their unique size dependent properties, including a high absorption coefficient and widely tunable emission [1–3], as well as for their potential applications in the fields of light-emitting diodes (LEDs) [4], solar cells [5], displays [6], and biological labels [7]. Furthermore, QDs can be easily processed using solution-based methods [8–10]. Among the various QDs, CdSe based QDs are the most widely studied. However, unmodified CdSe QDs suffer from low quantum yields (QYs) because of high surface trap states and surface photo-oxidation. To enhance the QY, additional process has been performed to passivate the surface of QDs with various organic molecules (e.g., oleylamine, octylamine) or an inorganic high band-gap shell (e.g., CdS [11], ZnSe [12], or ZnS [13]) material to reduce dangling bonds [14,15].

In recent years, synthetic studies using II–VI ternary- and quaternary-alloyed QDs have attracted attention [16,17]. Most of these QDs use ZnX (X = Se, S) shelling of alloyed QDs. On the other hand, there have also been examples of alloyed QDs directly synthesized as core/shell structures to induce an interfacial composition gradient. Methods were reported that achieved high efficiency (>80%) using one-pot Synthesis without further shelling [17,18]. In addition, QDs prepared with such alloyed structures have been reported to have improved stability [19,20]. However, opinions differ on whether the ternary and quaternary compound can be formed in a preferential order of elements, with a specific interfacial composition gradient.

We report the one-pot synthesis of ZnCdSSe QDs, with an interfacial composition gradient determined using thermodynamic calculations. The results herein may lead to the one-pot synthesis

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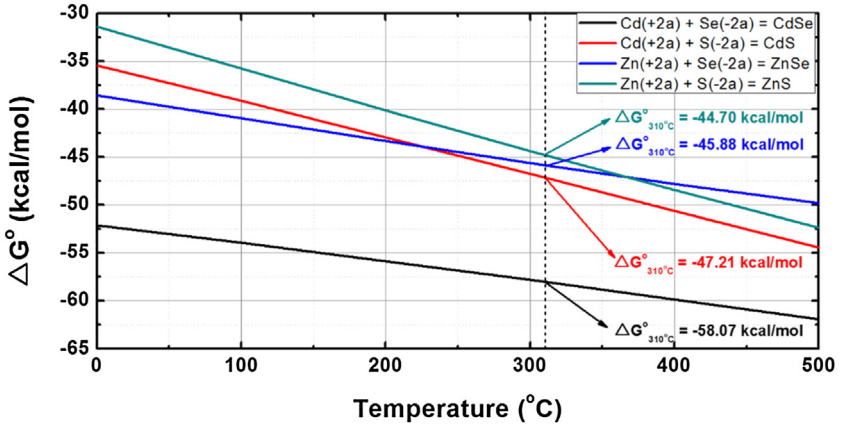

Fig. 1. Calculated Gibbs free energy (ΔG°) as a function of temperature for four reactions.

of ternary and quaternary Cd-based compounds with additional interfacial composition gradients.

2. Experimental

2.1. Preparation of precursor solutions

Cadmium oxide (99.99%, Sigma-Aldrich), zinc acetate (99.99%, Sigma-Aldrich), selenium powder (99.99%, Sigma-Aldrich), sulfur powder (99.98%, Sigma-Aldrich), 1-octadecene (ODE, 90%, Sigma-Aldrich), oleic acid (90%, Sigma-Aldrich), and trioctylphosphine (TOP, 97%, Sigma-Aldrich) were commercially available and used without further purification. The Zn-Cd precursor solution was prepared by dissolving zinc acetate and cadmium oxide to concentrations of 0.14 mM and 0.014 mM, respectively, in a solution mixture of 16.63 g of oleic acid and 47.40 g of ODE. This mixture was heated to 160 °C for 30 min, the headspace filled with Ar gas, and further heated to 310 °C to form a clear Zn-Cd precursor solution. An S-Se precursor solution was prepared by dissolving Se and S at room temperature for 1 h to final concentrations of 0.014 mM and 0.14 mM, respectively, in 4.986 g of TOP.

2.2. One-pot synthesis of ZnCdSSe colloidal quantum dots

For the synthesis of ZnCdSSe QDs, the Zn-Cd precursor solution was maintained at 310 °C under continuous stirring in a 500 mL three-neck flask. The S-Se precursor solution was then rapidly injected into the reaction flask. Subsequently, the formed QDs were annealed at 300 °C for various reaction times under continuous stirring. Aliquots were then collected at various intervals such as S, 1, 2, 4, 6, 8, and 10 min after injection. (S = immediately after injection) in vials containing 5 mL cold hexane to quench further QD growth. The samples were purified by adding a solution of toluene and excess amount of ethanol, centrifugation and decanting the supernatant (3 times, 6000 rpm for 10 min at 10 °C); the QDs were then redispersed in hexane for further analysis.

2.3. Characterization of ZnCdSSe quantum dots

For the characterization of ZnCdSSe QDs, diluted QD solutions in hexane were placed in 1 cm^3 quartz cuvettes, and their absorption and corresponding fluorescence were measured. UV–vis absorption spectra were acquired on a double-beam UV–vis spectrometer (Optizen 3220UV, MECASYS, Daejeon, Korea). Photoluminescence (Maya2000-pro, Ocean optics, Dunedin, USA) QY measurements and the absorbance of QDs and the reference rhodamine 6G were adjusted to be comparable (optical density A = 0.08). A spherical aberration-corrected scanning transmission electron microscope (Cs corrected-STEM) (JEM-ARM 200F, JEOL, Tokyo, Japan) was used at 200 kV to obtain high-resolution images of individual QDs. The crystal phase of the QDs was confirmed by X-ray diffraction (XRD) (X'Pert-pro MRD, PANalytical, Almelo, Netherlands) using Cu Kα irradiation (λ = 1.5406 Å). The standard Gibbs free energy (ΔG°) at various temperatures for the four occurring reactions were calculated using HSC Chemistry (ver. 8.0).

3. Results and discussion

Fig. 1 shows the standard Gibbs free energy change for the formation of CdSe, CdS, ZnSe, and ZnS. The enthalpy and entropy values are available from databases. The Gibbs free energy change is defined by the following equation:

$$\Delta G = \Delta H - T\Delta S \quad (1)$$

The ΔG of each reaction at 310 °C, when the hot injection starts, was as follows:

$$Cd(+2a) + Se(-2a) \rightarrow CdSe,\ \Delta G^\circ_{310\,^\circ C} = -58.07\ \text{kcal/mol} \quad (2)$$

$$Cd(+2a) + S(-2a) \rightarrow CdS,\ \Delta G^\circ_{310\,^\circ C} = -47.21\ \text{kcal/mol} \quad (3)$$

$$Zn(+2a) + Se(-2a) \rightarrow ZnSe,\ \Delta G^\circ_{310\,^\circ C} = -45.88\ \text{kcal/mol} \quad (4)$$

$$Zn(+2a) + S(-2a) \rightarrow ZnS,\ \Delta G^\circ_{310\,^\circ C} = -44.70\ \text{kcal/mol} \quad (5)$$

As can be seen, CdSe has the most negative value of $\Delta G^\circ_{310\,^\circ C} = -58.07$ kcal/mol for a spontaneous reaction. This means that CdSe would be formed by preferential reactivity. In addition, since Cd and Se sources are consumed, the next reactions will result in the formation of Zn-based compounds. Thus, immediately after the hot injection, first a CdSe-rich phase is preferentially formed as a core. As Cd and Se are consumed, this is expected to be followed by the formation of small amounts of CdS and ZnSe, but mostly ZnS. Formation processes of similar structures have been reported by other researchers [16,17,20]. However, opinions differ on the formation of QDs with a preferential interfacial composition gradient depending on the order of the specific elements in the remained ternary and quaternary compound. Using the results of the above thermodynamic simulation may provide a way to identify the one-pot synthesis mechanism for quantum dots of various other compositions. For example, if the concentration of the Se precursor is increased, the formation of CdSe will not consume all the Se, so the ZnSe shell thickness would increase. Alternatively, if the concentration of the Cd precursor is increased, the formation of CdSe will not consume all the Cd, so the CdS shell thickness would increase.

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