Research Article

Controlled Growth of ZnSe Nanocrystals by Tuning Reactivity and Amount of Zinc Precursor

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Zinc selenide (ZnSe) nanocrystals were synthesized via a phosphine-free route using the highly reactive alkylamine-H_2Se complex as selenium precursor and zinc precursors with different reactivity. The reactivity of zinc precursor was tuned by using three kinds of zinc carboxylates with different alkyl chain lengths, including zinc acetate, zinc nonanoate, and zinc stearate. The effect of the reactivity and the amount of zinc precursor on nucleation and growth of ZnSe nanocrystals were investigated by ultraviolet-visible absorption and photoluminescence spectra. Result indicates that the growth and optical property of the resulting ZnSe nanocrystals are strongly dependent on the alkyl chain length and the amount of the zinc carboxylates and both shorter alkyl chain length, and more amount of zinc carboxylate will lead to faster growth of ZnSe nanocrystals. This allows that the controlled growth and excellent optical property of high-quality ZnSe nanocrystals can be achieved by combining the different reactivity and the used amount of zinc precursor, such as by using stoichiometric and reactive Zn precursor and Se precursor or by using larger amount of more unreactive Zn precursor relative to the highly reactive alkylamine-H_2Se complex precursor.

1. Introduction

Relative to cadmium chalcogenide, zinc chalcogenide is regarded as a "greener" luminescent semiconductor due to the absence of cadmium element, a very toxic heavy metal to human body and natural environment. In recent several years, great development has been made in the synthesis of high-quality zinc selenide nanocrystals (ZnSe NCs) [1–10]. High-quality ZnSe NCs were usually synthesized at high temperatures by using the stable tri-n-octylphosphine selenide (TOP-Se) or selenium dispersed/dissolved in 1-octadecene (ODE-Se) as selenium (Se) precursors to react with various kinds of zinc (Zn) precursors with the proper reactivity, such as the relatively inactive zinc stearate ($ZnSt_2$) and zinc oleate [1–4].

Very recently, we made our effort to synthesize high-quality metal selenide NCs by appropriately increasing the reactivity of Se precursor [11, 12]. The alkylamine-H_2Se complex, which was generated by adsorbing H_2Se gas with long-chain alkylamine and used as a more active Se precursor

than the traditional TOP-Se and ODE-Se, showed rather high reactivity to zinc nonanoate ($Zn(NA)_2$), which results in the formation of magic-sized and even regular ZnSe NCs at relatively low temperatures [12]. The nucleation and growth of ZnSe NCs have been demonstrated to be driven by the reaction thermodynamics and can be tuned successfully by changing the reaction temperature, and four families of ZnSe magic-sized NCs including F280, F291, F319, and F347 with the first excitonic absorption peaks at 280, 291, 319, and 347 nm, respectively and regular ZnSe NCs were observed in different reaction temperature stages. However, a new problem occurs, that is, whether the Zn precursor species used will also affect the synthesis and optical properties of the resulting ZnSe NCs when using the alkylamine-H_2Se complex as Se precursor, as can be found in those reaction systems using traditional TOP-Se or ODE-Se precursors [2–4].

In this paper, we investigated the effect of the reactivity and the amount of Zn precursor on nucleation and growth

of ZnSe NCs in order to obtain high-quality ZnSe NCs when using the alkylamine-H_2Se complex as an active Se precursor. Zn precursor species of the same type, that is, zinc carboxylates with different alkyl chain length, including zinc acetate ($ZnAc_2$), $Zn(NA)_2$, and $ZnSt_2$, were used for easy comparison and investigation, and the reactivity of Zn precursor was tuned by changing the alkyl chain length of its carboxylate ligand. In addition, in the previously reported synthesis of ZnSe NCs using alkylamine-H_2Se and $Zn(NA)_2$ as Se and Zn precursors, respectively, it has been found that 220°C may be a key critical temperature because at this temperature, the F347 magic-sized ZnSe NCs will begin to gradually transform into regular NCs [12]. Therefore, the reaction temperature in this work was selected at 220°C, and at this temperature the effect of different Zn precursors on the synthesis of ZnSe NCs may be monitored facilely by the ultraviolet-visible (UV-vis) absorption and photoluminescence (PL) spectra.

2. Materials and Methods

2.1. Chemicals. All commercial reagents were used without any purification. Selenium (Se) powder (99.5%) and 1-octadecene (ODE, 90%) were purchased from Alfa Aesar. Zinc acetate dehydrate ($ZnAc_2 \cdot 2H_2O$, AR), octylamine (OA, 99%), and sodium borohydride ($NaBH_4$, AR) were purchased from Beijing Chemical Plant. Zinc stearate ($ZnSt_2$, AR), *n*-nonanoic acid (NA, 98%), and oleylamine (OLA, 80–90%) were purchased from Aladdin Reagent Co., Ltd. Analytical-grade acetone and cyclohexane were supplied by Shantou Xilong Chemical Co. Ltd.

2.2. Synthesis of Zn and Se Precursors. Prior to synthesis of ZnSe NCs, Se precursor (alkylamine-H_2Se complex) solution and zinc nonanoate ($Zn(NA)_2$) were prepared according to our methods reported previously [12]. Briefly, Se precursor solution was obtained by using a mixture of OA (1 mL) and OLA (1 mL) to absorb H_2Se gas which was produced by reducing 0.5 mmol of Se powder with 1.5 mmol of $NaBH_4$ under acidic condition. The actual Se amount in the resulting Se precursor solution was estimated to be about 0.4 mmol by weighing the bottle before and after absorbing H_2Se gas. $Zn(NA)_2$ was synthesized by the reaction of $ZnAc_2$ with NA under reflux conditions.

2.3. Synthesis of ZnSe NCs. Synthesis of ZnSe NCs is detailed as follows. In a 50 mL three-neck flask, the mixture of 0.4 mmol or 0.6 mmol of Zn precursor, 2 mL of ODE, and 1 mL of OLA were heated at 220°C in argon atmosphere. Then, the freshly prepared Se precursor solution was injected rapidly into the hot reaction mixture under vigorous stirring. Finally, 0.1 mL aliquot of reaction solution was extracted at different time intervals, injected into 0.5 mL of acetone, and centrifugated at 4000 r/min for 10 min. The pale-yellow precipitation (ZnSe NCs) was obtained after removing the upper clear liquid, further redissolved by adding a small amount of cyclohexane, and purified repeatedly according to the previous procedure.

2.4. Characterization. Purified ZnSe NCs were dispersed into cyclohexane for ultraviolet-visible (UV-Vis) absorption and photoluminescence (PL) spectra measurements. The absorption spectrum was collected using Varian Cary-100 UV/Vis spectrophotometer in the wavelength range of 250–500 nm at the scanning speed of 600 nm/min with data interval of 1 nm. PL spectrum was collected using Shimadzu RF-5301 PC spectrofluorophotometer using excitation wavelength of 300 nm.

3. Results and Discussion

3.1. UV-Vis Absorption Spectrum. Figures 1(a)–1(c) shows the evolution of UV-Vis absorption spectra of ZnSe NCs using 0.4 mmol of $ZnAc_2$, $Zn(NA)_2$ and $ZnSt_2$ as Zn precursors, respectively. For these resulting ZnSe NCs, two sharp and characteristic absorption peaks at about 347 and 328 nm, respectively are generally believed to be the first and second excitonic absorption peaks of F347 magic-sized NCs, and the absorption at longer wavelength originates from the regular ZnSe NCs [7, 9, 12]. In the case using $ZnAc_2$ as Zn precursor, at first these two characteristic absorption peaks at 347 and 328 nm are observable during the relatively short reaction time and then disappear completely after 20 min, indicating the presence of a small amount of F347 magic-sized ZnSe NCs and their transformation into regular ZnSe NCs. However, when using $Zn(NA)_2$ or $ZnSt_2$ as Zn precursors, there are always the characteristic peaks of F347 magic-sized NCs within up to 120 min besides the continuous absorptions in the 350–400 nm. In addition, in the case using $ZnSt_2$, not only there remain two characteristic peaks of F347 magic-sized ZnSe NCs, but also the intensity ratio of the characteristic peak to the continuous absorption during 350–400 nm becomes higher than that in the case using $Zn(NA)_2$ with the same reaction time, indicating that these ZnSe NCs obtained using $ZnSt_2$ as Zn precursor correspondingly have higher ratio of F347 magic-sized ZnSe NCs to regular ZnSe NCs in the amount. This result should be related to different alkyl chain lengths of their carboxylate ligands of three kinds of Zn precursors [13]. Generally, the strong and large coordinating ligand will inhibit the growth of semiconductor NCs due to the steric effect. For these three kinds of zinc carboxylates, the order of the alkyl chain lengths of their carboxyl groups is as follows: $ZnAc_2 < Zn(NA)_2 < ZnSt_2$. Obviously, $ZnAc_2$ and $ZnSt_2$ have minimum and maximum steric hindrance effects, respectively. Therefore, there are the lowest and highest amount ratios of magic-sized to regular ZnSe NCs when using $ZnAc_2$ and $ZnSt_2$ as Zn precursors, respectively. The above results show that the Zn precursor species have very important effect on the nucleation and growth of ZnSe NCs and the used zinc carboxylate precursor with longer alkyl chain usually results in slower growth of ZnSe NCs.

The nucleation and growth process of ZnSe NCs were affected not only by the type of Zn precursor but also by the amount of these Zn precursors. Figures 1(d)–1(f) show UV-Vis absorption spectra of ZnSe NCs using 0.6 mmol of three kinds of Zn precursors when fixing other conditions including the amount of Se precursor. As described previously,
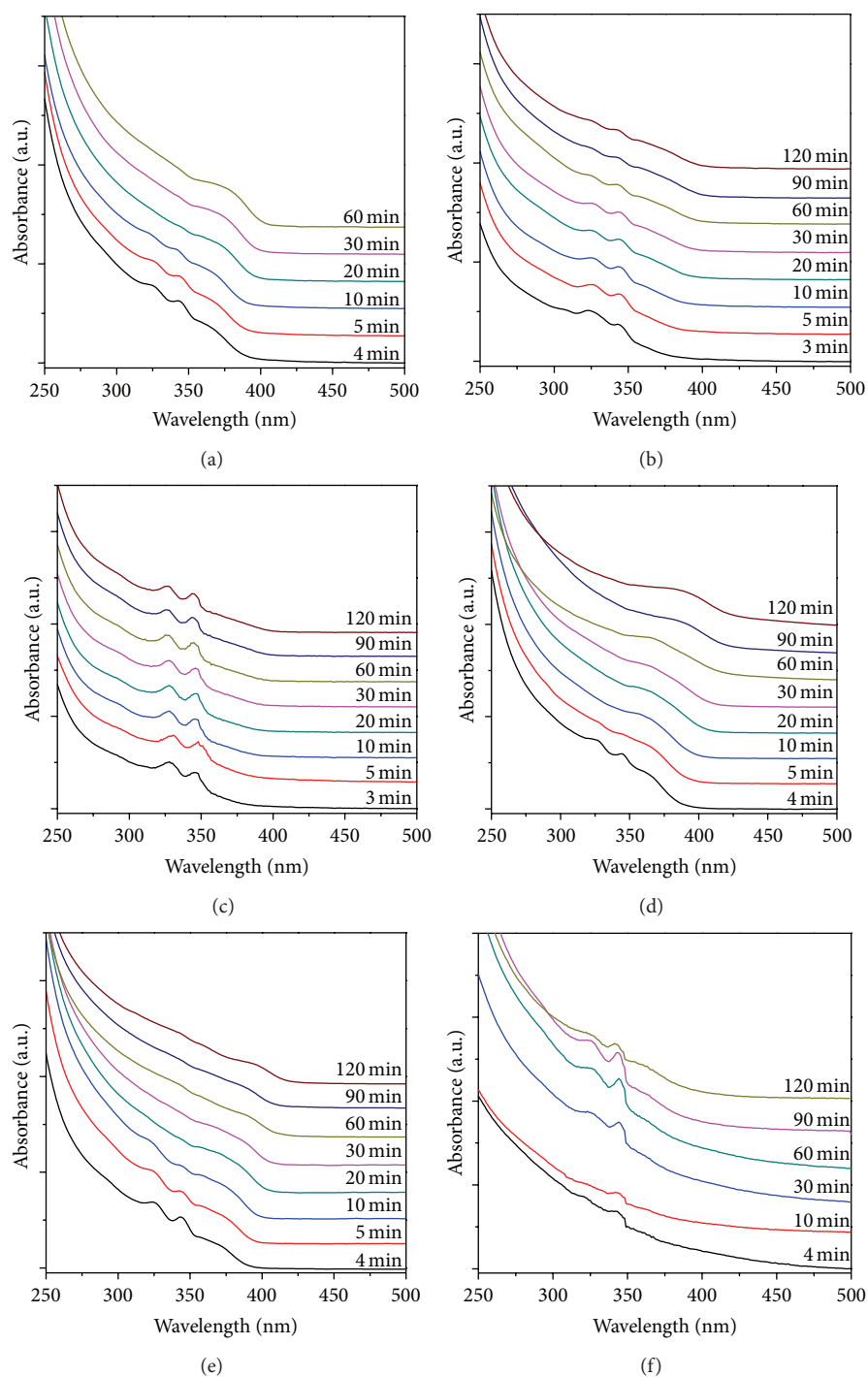
Figure 1: UV-Vis absorption spectra of ZnSe NCs synthesized at 220°C using different Zn precursors: (a) 0.4 mmol $ZnAc_2$, (b) 0.4 mmol $Zn(NA)_2$, (c) 0.4 mmol $ZnSt_2$, (d) 0.6 mmol $ZnAc_2$, (e) 0.6 mmol $Zn(NA)_2$, and (f) 0.6 mmol $ZnSt_2$.

the characteristic absorption peaks of F347 magic-sized ZnSe NCs synthesized using 0.4 mmol of $ZnAc_2$ within 10 min can be observed clearly (Figure 1(a)), while the corresponding characteristic peaks only exist in the ZnSe NCs sample collected at 4 min when using 0.6 mmol of $ZnAc_2$; the excitonic absorption peak position after 60 min is also shifted from 375 nm in the 0.4 mmol of $ZnAc_2$ case to 390 nm in the 0.6 mmol of $ZnAc_2$ case (Figure 1(d)). The same results can

be obtained when using $Zn(NA)_2$ and $ZnSt_2$ as Zn precursors. When using 0.4 mmol of $Zn(NA)_2$, the characteristics peak of F347 magic-sized ZnSe NCs does not disappear completely up to 120 min, although the absorption in the range of 300–400 nm increases gradually, which means that some F347 magic-sized ZnSe NCs do not transform into regular ZnSe NCs. However, when adding 0.6 mmol $Zn(NA)_2$, the characteristics peaks of F347 magic-sized NCs can only be
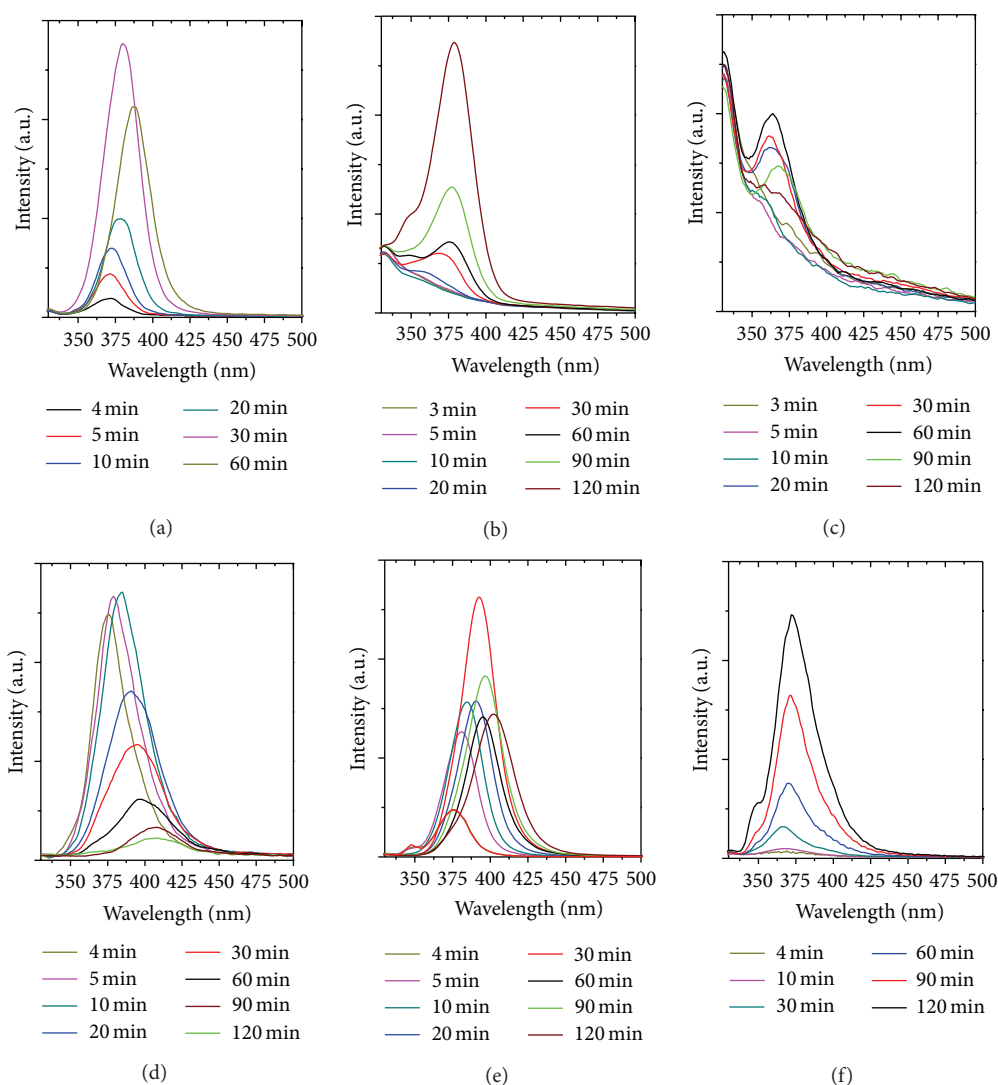
Figure 2: PL spectra of ZnSe NCs synthesized at 220°C using different Zn precursors: (a) 0.4 mmol $ZnAc_2$, (b) 0.4 mmol $Zn(NA)_2$, (c) 0.4 mmol $ZnSt_2$, (d) 0.6 mmol $ZnAc_2$, (e) 0.6 mmol $Zn(NA)_2$, and (f) 0.6 mmol $ZnSt_2$.

observed within 10 min; then the F347 magic-sized ZnSe NCs will grow up and form the relatively large regular ZnSe NCs with the first excitonic absorption peak above 400 nm at 120 min. For $ZnSt_2$ precursors, the characteristics peaks of F347 magic-sized ZnSe NCs are always apparent and strong when 0.4 mmol of $ZnSt_2$ is used, while the absorption in the range of 350–400 nm corresponding to regular ZnSe NCs will become much stronger when using the 0.6 mmol of $ZnSt_2$ as Zn precursor. All of the above results show that the more the added Zn precursors, the faster the resulting ZnSe NCs will grow. The fact that the addition of larger amount of Zn precursors facilitates faster growth of the resulting ZnSe NCs may be due to very high reactivity of our Se precursor (alkylamine-H_2Se complex). Thus, controlled and continuous growth of ZnSe NCs can be achieved not only by using highly reactive and stoichiometric Zn and Se precursors but also by using larger amount of more unreactive Zn precursor when the highly reactive alkylamine-H_2Se complex precursor was used as Se precursor.

3.2. PL Spectrum.
PL spectrum is also an important tool for characterizing the optical performance of luminescent semiconductor NCs, which is helpful for obtaining the best nucleation and growth conditions of high-quality ZnSe NCs [14]. Figure 2 shows the evolution of PL spectra of ZnSe NCs synthesized at 220°C using $ZnAc_2$, $Zn(NA)_2$, and $ZnSt_2$ as Zn precursors, respectively. By comparing Figure 1 with Figure 2, it can be found that these resulting ZnSe NCs emit band-edge fluorescence other than surface-defect fluorescence, and their corresponding full widths at half maximum (FWHM) are relatively narrow (usually about 25–30 nm). As shown in Figure 2(a), when 0.4 mmol of $ZnAc_2$ is used as Zn precursor, the resulting high-quality ZnSe NCs obtained at the shortest reaction time (4 min) emit the relatively strong band-edge fluorescence with the peak position at 372 nm, and the PL peak will gradually shift to 387 nm at 60 min. When 0.6 mmol of $ZnAc_2$ is used, the resulting ZnSe NCs will also emit the relatively strong band-edge fluorescence at 375 nm for 4 min, and the corresponding PL peak will shift to 396 nm for 60 min

and to 408 nm for 120 min (Figure 2(d)). However, unlike $ZnAc_2$ as Zn precursor, there is not any obvious emission from ZnSe NCs synthesized using 0.4 mmol of $Zn(NA)_2$ or $ZnSt_2$ as Zn precursors during 10 min, and their emission at longer reaction time is also weaker than that corresponding to those obtained by using $ZnAc_2$ as Zn precursor (Figures 2(b) and 2(c)). These remarkably different PL phenomena may be due to their different steric effects when using different Zn precursors. In the synthesis of ZnSe NCs using $ZnAc_2$ precursor, acetate is a kind of carboxylate with very short alkyl chain and can be easily replaced by alkylamine because of the relative small steric effect of $ZnAc_2$. In comparison with $ZnAc_2$, both $Zn(NA)_2$ and $ZnSt_2$ have larger steric effect because of their longer carboxylate ligands. Generally, relative to the carboxylate ligand reported previously, alkylamine is more favorable to obtain excellent fluorescence performance such as high fluorescence efficiency and narrow fluorescence peak for ZnSe NCs [3, 7].

In addition, due to longer carboxylate ligands of $Zn(NA)_2$ and $ZnSt_2$ compared with $ZnAc_2$, the resultant stronger steric effects of $Zn(NA)_2$ and $ZnSt_2$ make them have lower reactivity than that of $ZnAc_2$. Therefore, in the synthesis using $Zn(NA)_2$ and $ZnSt_2$ precursors, Se precursor cannot be depleted completely, and the excess of Se precursor will adsorb at the surface of ZnSe NCs, which also quench fluorescence from ZnSe NCs. This result is further demonstrated by the fluorescence properties of ZnSe NCs synthesized using larger amount of $Zn(NA)_2$ and $ZnSt_2$ precursors, as shown in Figures 2(e) and 2(f). When the used $Zn(NA)_2$ or $ZnSt_2$ is added from 0.4 mmol to 0.6 mmol, the resulting high-quality ZnSe NCs will always emit relatively strong band-edge fluorescence with small FWHM comparable with that in the case of $ZnAc_2$, indicating excellent optical property that can be also achieved not only by using highly reactive Zn and Se precursors with stoichiometric ration but also by using larger amount of more unreactive Zn precursor than the highly reactive alkylamine-H_2Se complex precursor. In addition, when using larger amount of $Zn(NA)_2$ and $ZnSt_2$ precursors, the main PL peaks will gradually red-shift from 375 nm to 402 nm for $Zn(NA)_2$ case and from 361 nm to 372 nm for $ZnSt_2$ with the increase of reaction time during 120 min. Thus, for these three kinds of zinc precursors systems, the red-shift degrees of their fluorescence peaks, with the order of $ZnAc_2 > Zn(NA)_2 > ZnSt_2$, are obviously dependent on the alkyl chain length of their carboxyl groups, which will coincide with these results of UV-Vis absorption spectra shown in Figure 1. In addition, it is noteworthy that some shoulder peaks at about 347 nm from the emission of F347 magic-sized ZnSe NCs are also observed in the cases of 0.6 mmol of $Zn(NA)_2$ and $ZnSt_2$ precursors, consistent with the facts that a small amount of F347 magic-sized ZnSe NCs remain in these systems (Figures 1(e) and 1(f)).

4. Conclusions

Results of UV-Vis absorption and PL spectra studies on the ZnSe NCs indicate that the growth and optical property of the resulting ZnSe nanocrystals are strongly dependent on both the different alkyl chain length and the used amount of the zinc carboxylates. Zinc carboxylate of shorter alkyl chain length leads to faster growth of ZnSe nanocrystals than that of longer alkyl chain length, and for the three kinds of zinc precursors including $ZnAc_2$, $Zn(NA)_2$, and $ZnSt_2$, the order of the reactivity is as follows: $ZnAc_2 > Zn(NA)_2 > ZnSt_2$, and their corresponding growth rates of the resulting ZnSe NCs follow the same order. In addition, more amount of zinc precursor also leads to faster growth of ZnSe nanocrystals. These results allow us to tune the growth and optical property of ZnSe NCs by combining the different reactivity and the used amount of the zinc precursor when using the highly reactive alkylamine-H_2Se complex as Se precursor in the phosphine-free synthesis of high-quality ZnSe NCs. The controlled growth and excellent optical property of high-quality ZnSe NCs can be achieved by using reactivity of both Zn precursor and Se precursor with closeness to stoichiometric ratio or by using larger amount of unreactive Zn precursor relative to the highly reactive alkylamine-H_2Se complex precursor.

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