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Kinetic analysis of the growth of semiconductor nanocrystals from the peak wavelength of photoluminescence

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Kinetic analysis of the growth of semiconductor nanocrystals from the peak wavelength of photoluminescence

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Abstract. Understanding the rate processes controlling the growth of semiconductor nanocrystals in liquid solutions is of great importance in tailoring the sizes of semiconductor nanocrystals for the applications in optoelectronics, bioimaging and biosensing. In this work, we establish a simple relationship between the photoluminescence (PL) peak wavelength and the growth time of semiconductor nanocrystals under the condition that the contribution of electrostatic interaction to the quantum confinement is negligible. Using this relationship and the data available in the literature for CdSe and CdSe/ZnS nanocrystals, we demonstrate the feasibility of using the PL peak wavelength to analyze the growth behavior of the CdSe and CdSe/ZnS nanocrystals in liquid solutions. The results reveal that the diffusion of monomers in the liquid solution is the dominant rate process for the growth of CdSe/ZnS nanocrystals, and the activation energy for the growth of CdSe nanocrystals in the liquid solution is ~ 9 kJ/mol. The feasibility to use this approach in the analysis of the thickness growth of core-shell nanocrystals with and without mechanical stress is also discussed. Such an approach opens a new avenue to in-situ monitor/examine the growth of semiconductor nanocrystals in liquid solutions.

1 Introduction

The successful syntheses of semiconductor nanocrystals, such as silicon [1–3], group II–VI compounds [4–6], inorganic perovskites [7–9] and hybrid organic-inorganic perovskites [10–12], have stimulated great interest for the applications in optoelectronics, bioimaging and biosensing. In the heart of the promise applications of semiconductor nanocrystals are the size-dependence and tunability of the optoelectronic characteristics of semiconductor nanocrystals.

The size-dependence of the peak wavelength of photoluminescence (PL) emission of a semiconductor nanocrystal of a in radius can be attributed to the quantum confinement as [13,14]

$$E(a) = E_0 + \frac{\pi^2 \hbar^2}{2\chi} \frac{1}{a^2} \quad (1)$$

with $E(a)$ and E_0 as the bandgaps of the semiconductor nanocrystal and the corresponding bulk phase at stress-free state, respectively, and $\hbar$ as the Planck constant. The parameter, χ , is a function of the effective masses of electron, m_e^* , and hole, m_h^* , as [15]

$$\chi = \begin{cases} m_e^* & \text{very small nanocrystal} \\ m_e^* + m_h^* & \text{weak confinement} \\ m_e^* m_h^* / (m_e^* + m_h^*) & \text{strong confinement} \end{cases} \quad (2)$$

Note that equation (1) assumes the negligible contribution of electrostatic interaction to the energy level of the particle with E_0 being a function of temperature.

Experimental results from PL measurements have supported the correlation of (1) for a variety of semiconductor nanocrystals, including nanoporous Si [16], Si nanocrystals [3], perovskite nanocrystals [9,12,17], and CdSe nanocrystals [18,19]. However, Ledoux et al. [2] found a power index of -1.39 for Si nanocrystals, and Yorikawa and Muramatsu [20] reported a power index of -1.25 for nanoporous Si. Their results still suggest the contribution of the quantum confinement to the shift of PL peaks of semiconductor nanocrystals, even though the power index for the semiconductor nanocrystals can deviate from the ideal one of -2 likely due to the contributions from other factors, such as the electrostatic interaction between charged particles and phonon-electron interaction. Here, we assume that the contributions of other factors are negligible and the bandgap change due to the quantum confinement can be described by equation (1).

There are two popular methods to characterize the sizes of nanoparticles and nanocrystals; one is transmission electron microscopy (TEM) [21,22], and the other is powder X-ray diffraction (XRD) [23,24]. Both methods generally require dry specimens and are not suitable for liquid solutions. Also, coarsening of nanocrystals can occur under e-beam and X-ray, which can lead to changes in the size distribution and average size of nanocrystals. Note that one can use liquid-cell TEM [25] to analyze the size evolution of nanoparticles and nanocrystals in a small liquid cell. However, such an approach is not cost-effective

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and limits the liquid solution in a confined space, in which nanocrystals and nanoparticles may exhibit different growth behaviors from that in a macroscopic space.

Dynamic light scattering has been used to analyze the size distribution of nanoparticles in liquid suspensions [26,27]. The principle of the dynamic light scattering technique is based on the analysis of the temporal evolution of the photon auto-correlation function. However, multiple scattering, fluorescence and small sizes of semiconductor nanocrystals under laser make it challenge to obtain the intrinsic size distribution and average size of semiconductor nanocrystals. One needs to use a near-infrared (NIR) laser to limit the fluorescent effect of semiconductor nanocrystals and mitigate the error from the signal dimmer associated with the nanoscales of semiconductor nanocrystals.

Realizing the challenge in in-situ measuring average size of semiconductor nanocrystals and the need to understand the growth behavior of semiconductor nanocrystals in liquid solutions, we explore the feasibility to use the PL peak wavelength to analyze the size evolution of semiconductor nanocrystals in liquid solutions. Such a method is based on the correlations between the bandgap and average size of semiconductor nanocrystals (Eq. (1)) and between the PL peak wavelength and the bandgap. The experimental data of CdSe nanocrystals and CdSe/ZnS core/shell nanocrystals given by Karim et al. [28] are used to illustrate the growth behavior of both CdSe nanocrystals and CdSe/ZnS core/shell nanocrystals.

2 Basic formulation

There are two rate processes contributing to the growth of semiconductor nanocrystals in a liquid solution [29–33]: one is the diffusion of monomers in the liquid solution, and the other is the reaction on the nanocrystal surface. Under isothermal growth, the temporal evolution of the size of a semiconductor nanocrystal can be expressed as

$$a^n = \beta t \quad (3)$$

with n as the growth exponent, β as a parameter proportional to the rate constant and t as the growth time. For diffusion-controlled growth of semiconductor nanocrystals in a non-confined space, we can solve the diffusion equation and have $n=2$. Note that Myers and Fanelli [34] suggested that there is an approximate-linear growth period for the early growth of CdSe nanocrystals and Pt nanocrystals [35] in a confined space, i.e. $n=1$. Yang [33] pointed out that such a linear growth behavior is likely due to the concentration change of monomers during the initial growth of the nanocrystals in the confined space.

Similar to the temperature dependence of diffusivity, the parameter β as a function of temperature follows the Arrhenius relation as

$$\beta = \beta_0 e^{-Q/RT} \quad (4)$$

with β_0 as a pre-factor, Q as the activation energy for the rate process, R as the gas constant and T as the absolute temperature. The relation between the bandgap of the

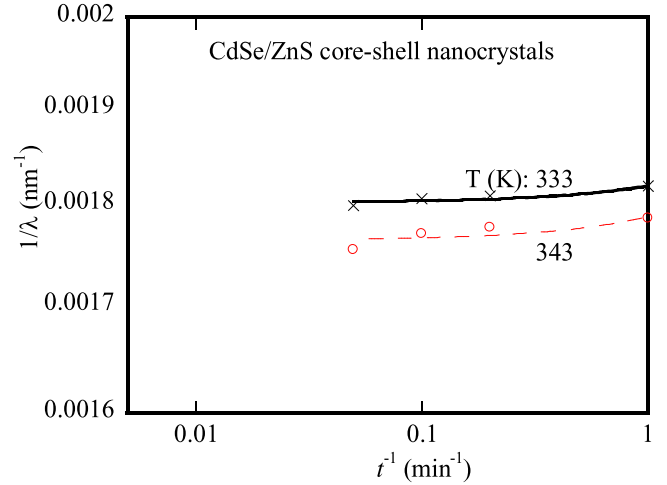


Fig. 1. Temporal evolution of the CdSe/ZnS core-shell nanocrystals at two different temperatures of 333 and 343 K.

semiconductor nanocrystal and the corresponding PL peak wavelength, λ , is

$$E(a) = \frac{hc}{\lambda} \quad (5)$$

with c as the light speed. Substituting equations (3)–(5) in equation (1) yields the temporal evolution of the PL peak wavelength of the semiconductor nanocrystals in a liquid solution as

$$\frac{hc}{\lambda} = E_0 + \frac{\pi^2 h^2}{2\chi} (\beta_0 t)^{-2/n} e^{2Q/nRT}. \quad (6)$$

For diffusion-controlled growth ($n=2$), equation (6) is simplified to as

$$\begin{aligned} \frac{hc}{\lambda} &= E_0 + \frac{\pi^2 h^2}{2\chi} (\beta_0 t)^{-1} e^{Q/RT} \\ &= \frac{hc}{\lambda_0} + \frac{\pi^2 h^2}{2\chi} (\beta_0 t)^{-1} e^{Q/RT} \end{aligned} \quad (7)$$

with λ_0 as the PL peak wavelength for the bulk phase at the same temperature. According to equations (6) and (7), there are two factors of temperature and time contributing to the temporal evolution of the PL peak wavelength of semiconductor nanocrystals in a liquid solution, as expected. It is expected that equation (7) can be used to analyze the growth behavior of semiconductor nanocrystals in a liquid solution.

3 Discussion

Using the data given by Karim et al. [28] in their study of the bandgap and size of CdSe and CdSe/ZnS nanocrystals, the temporal evolution of the average size of the CdSe/ZnS core-shell nanocrystals at two different temperatures of 333 and 343 K is shown in Figure 1 in a log-log plot. Using equation (7) to curve-fit the data in Figure 1, we obtain

$(E_0/hc, \pi^2 \hbar e^{Q/RT}/2c\chi\beta_0)$ in the unit of $(\text{nm}^{-1}, \text{min} \cdot \text{nm}^{-1})$ as $(1.80 \times 10^{-3}, 1.69 \times 10^{-5})$ and $(1.76 \times 10^{-3}, 2.36 \times 10^{-5})$ for the temperatures of 333 and 343 K, respectively. For comparison, the fitting curves are also included in Figure 1. It is evident that equation (7) can describe well the temporal evolution of the PL peak wavelength with $n=2$ for equation (6). This result suggests that the temporal evolution of the CdSe/ZnS core-shell nanocrystals follows the relation of $a^n = \beta t$ ($n=2$), indicating that the diffusion of monomers in the liquid solution is the dominant rate process controlling the growth of the CdSe/ZnS core-shell nanocrystals. Note that the size of the CdSe/ZnS core-shell nanocrystals consists of the contributions of the core size, a_c , and the shell thickness, a_s , as $a = a_c + a_s$. The results presented in Figure 1 represent the growth of the shell thickness of the CdSe/ZnS core-shell nanocrystals.

Comparing the numerical values of E_0/hc at two different temperatures, we note that E_0/hc at 333 K is larger than at 343 K. That is to say, the bandgap of the CdSe/ZnS core-shell nanocrystals at 333 K is larger than that at 343 K in consistence with that the higher the temperature, the smaller is the bandgap of a bulk semiconductor.

According to Varshini [36], the temperature dependence of the bandgap of a bulk semiconductor can be expressed as

$$E_0(T) = E_0(0) - \alpha T^2/(T + b) \quad (8)$$

with $\alpha = 4.09 \times 10^{-4}$ and $b = 187$ for bulk CdSe in the unit of eV [28]. Mei and Lemos [37] reported $E_0(300\text{K}) = 1.738$ eV for bulk CdSe. Substituting the numerical values of α , b and $E_0(300\text{K})$ in equation (8), we obtain $E_0(0\text{K}) = 1.814$ eV corresponding to a wavelength of 683.7 nm. Using the data given by Karim et al. [28] in their study of the bandgap and size of CdSe nanocrystals and equation (8) with the corresponding numerical values, the temperature dependence of the change of the PL peak wavelength from the corresponding bulk phase for the CdSe nanocrystals is presented in Figure 2 for two different growth times of 5 and 10 min. Equation (7) is used to fit the data in Figure 2, and the fitting curves are also included in Figure 2. It is evident that equation (7) describes well the temperature dependence of the change of the PL peak wavelength from the CdSe nanocrystals. From the curve fitting, we obtain an activation energy of ~ 9 kJ/mol for the rate process controlling the growth of CdSe nanocrystals in the liquid solution.

The above analyses demonstrate the feasibility to use the PL peak wavelength to investigate the growth kinetics of semiconductor nanocrystals in liquid solutions, which is based on the relation of (1) and (3). However, Ledoux et al. [2] found a power index of -1.39 for Si nanocrystals, and Yorikawa and Muramatsu [20] reported a power index of -1.25 for nanoporous Si. Their results suggest the contribution of the quantum confinement to the shift of PL peaks of semiconductor nanocrystals, while the power index for the semiconductor nanocrystals can be different from the ideal one of -2 . Such behavior suggests that the

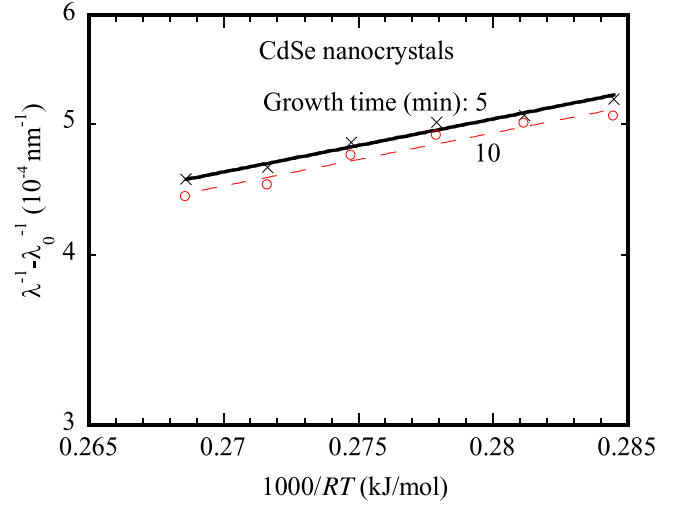


Fig. 2. Temperature dependence of the PL peak wavelength of the CdSe nanocrystals.

contribution from electrostatic interaction is not negligible in the analysis of the quantum confinement, i.e. the size dependence of the bandgap may include the contribution of electrostatic interaction as [38,39]

$$E(a) = E_0 + \frac{\pi^2 \hbar^2}{2} \frac{m_e^* + m_h^*}{m_e^* m_h^*} \frac{1}{a^2} - \frac{1.786e^2}{\epsilon_r a} + 0.284E_R \quad (9)$$

with e as the electron charge, ϵ_r as the relative dielectric constant, and E_R as the Rydberg energy of the bulk phase. Under such a case, one cannot follow the above procedure to analyze the growth behavior of semiconductor nanocrystals, since there are two terms associated with the average size of semiconductor nanocrystals in equation (9). However, one can use the PL peak wavelength to calculate the corresponding average size of semiconductor nanocrystals from equation (9) and correlate the variations of the average size with the growth time and temperature in the kinetic analysis of the growth behavior of the semiconductor nanocrystals in liquid solutions.

It should be pointed out that mechanical stress, such as mismatch stress for core-shell nanocrystals [40,41], interface stress/energy [42] and thermal stress [43], can cause the bandgap shift due to the dependence of the bandgap change on deformation [41–43]. According to the result given by Ünlü [43], the bandgap of a core-shell nanocrystal under a hydrostatic strain, $E(a, h)|_\epsilon$, can be expressed as

$$E(a_c, a_s)|_\epsilon = E_0 + \delta E|_{\epsilon=b} + E(a_c)|_{\epsilon=0} + \frac{\varpi}{a_s^2} \quad (10)$$

with ϵ being the hydrostatic strain, $\delta E|_{\epsilon=b}$ being the bandgap change of the corresponding bulk semiconductor under the hydrostatic strain, $E(a_c)|_{\epsilon=0}$ being the bandgap of the core at stress-free state and Ω being a constant dependent of the effective masses of electron and hole. It is evident that the bandgap of the core-shell nanocrystal is a

linear function of a_s^{-2} at the same stress state. The temporal evolution of the shell thickness also follows similar relation to equation (3) as

$$a_s^m = \mu_0 t e^{-Q_s/RT} \quad (11)$$

with m as the growth exponent for the shell, μ_0 as a pre-factor and Q_s as the activation energy for the rate process controlling the shell growth. Substituting equation (11) in equation (10) yields

$$E(a_c, a_s)|_\varepsilon = E_0 + \delta E|_{\varepsilon=b} + E(a_c)|_{\varepsilon=0} + \varpi(\mu_0 t e^{-Q_s/RT})^{-2/m} \quad (12)$$

which can be used to find the activation energy from the bandgap shift for the shell growth. Note that the results in Figure 1 suggests $m=1$ for the growth of the CdSe/ZnS core-shell nanocrystals. It is worth mentioning that equation (12) likely is not applicable to the scenarios, in which the stress state in a core-shell structure varies during growth and/or the growth is non-isothermal.

4 Summary

In summary, we have demonstrated the feasibility to use the PL characteristics of semiconductor nanocrystals in the analysis of the growth behavior of semiconductor nanocrystals in liquid solutions. Such an approach provides a unique method capable of in-situ monitoring/examining the average size of semiconductor nanocrystals and avoids the difficulty and challenge to use TEM and XRD in the characterization of the average size of semiconductor nanocrystals.

Using the experimental data (PL peak wavelength) available in the literature for the growth of CdSe and CdSe/ZnS nanocrystals, we have analyzed the growth behavior of the CdSe and CdSe/ZnS nanocrystals. The results reveal that the average size of the CdSe/ZnS nanocrystals is proportional to the square root of the growth time, suggesting that the diffusion of monomers in the liquid solution is the dominant rate process for the growth of the CdSe/ZnS nanocrystals. It also supports that the contribution of the electrostatic interaction to the bandgap change is negligible for both the CdSe and CdSe/ZnS nanocrystals. For the growth of the CdSe nanocrystals, we obtain an activation energy of ~ 9 kJ/mol.

It should be pointed out that such an approach is inapplicable to the growth analysis of the semiconductor nanocrystals with non-negligible contribution of the electrostatic interaction to the bandgap change. However, one can use the PL peak wavelength to calculate average size of semiconductor nanocrystals from equation (9) and analyze the variations of the average sizes with growth time and temperature in the growth analysis. This approach can also be extended to analyze the shell growth of core-shell

nanocrystals provided that the stress state in a core-shell structure remains unchanged during the growth and the growth is isothermal.

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