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Growth Kinetics and Optical Properties of CsPbBr$_3$ Perovskite Nanocrystals

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Abstract: We synthesized CsPbBr$_3$ perovskite nanocrystals (NCs) at different reaction temperatures and tracked their growth kinetics on the basis of their optical properties and estimated size. The energies of the absorption and fluorescence (FL) peaks with increasing reaction temperature for the CsPbBr$_3$ perovskite NCs were tuned within the regions of 2.429–2.570 eV and 2.391–2.469 eV, respectively, depending on size of the NCs (9.9–12.5 nm). The Stokes shifts of CsPbBr$_3$ perovskite NCs with increasing NC size decreased from 101 meV to 38 meV. The full-width at half-maximum of the FL peaks for the CdSe NCs decreased from 150 meV to 90 meV because of the improved size uniformity of the CsPbBr$_3$ perovskite NCs. The energy spacing of CsPbBr$_3$ perovskite NCs synthesized at various reaction temperatures was calculated from Tauc plots; this information is critical for determining the bandgap energy and enables the size of the CsPbBr$_3$ perovskite NCs to be estimated using the effective mass approximation.

Keywords: perovskite nanocrystals; CsPbBr$_3$; growth kinetics; energy spacing; effective mass approximation

1. Introduction

Lead halide perovskite nanocrystals (NCs) have inspired enormous interest in optoelectronics applications, such as light-emitting [1,2] and light-harvesting [3,4] devices and lasers [5], because of their tunable optical bandgaps through the precise engineering of halogen content and particle size [6]. In addition, nanostructured lead halide perovskites exhibit interesting optical properties, such as narrow photoluminescence (PL) linewidths and high PL quantum yields, enabling their potential application as high-performance optical materials [7]. In general, manipulating the defect concentration and size distribution of inorganic halide perovskite nanocrystals (IPNCs) is important for achieving narrow band emissions that improve color purity [8]. Because the high defect tolerance and self-passivating effect of IPNCs, the influence of defects on their optical properties is inconsequential compared with the influence of size homogeneity [9,10]. The surface-area-to-volume ratio of a material increases with decreasing particle size; below a certain particle size, surface ligands of a nanomaterial critically influence its photophysical properties, such as luminescence and carrier transport behavior [11]. During the synthesis of IPNCs, chemical agents that improve the dispersion stability and manipulate growth kinetics are added as fundamental components. Oleic acid and oleylamine are the most widely used surfactants in the ligand-assisted synthesis of CsPbBr$_3$ perovskite NCs [12]. Amines enhance the crystallization kinetics, potentially enabling the size tuning of perovskite NCs, whereas oleic acid plays a critical role in impeding NC aggregation and leads to stable NC colloids [13]. In the case of CsPbX$_3$, in particular, its bandgap cannot only be engineered through manipulation of its composition but also tuned via the reaction temperature. CsPbBr$_3$ perovskites are direct-bandgap structures with various crystal phases (e.g., orthorhombic, tetragonal, and
cubic crystal phases) [14]. However, only a few studies have focused on the temperature dependence of the photophysical properties of all-inorganic perovskites [15].

In this work, we investigated the growth kinetics and optical properties of CsPbBr$_3$ perovskite NCs with different reaction temperatures. CsPbBr$_3$ perovskite NCs synthesized at various reaction temperatures display size-tunability of their optical bandgap energies in the blue–green spectral range. The fluorescence (FL) of CsPbBr$_3$ perovskite NCs is characterized by narrow emission linewidths in the range of 90–150 meV. Moreover, from the physical parameters of CsPbBr$_3$, the radius of CsPbBr$_3$ perovskite NCs can be estimated on the basis of the effective mass approximation (EMA), which is used here to determine the energy spacing of the CsPbBr$_3$ perovskite NCs prepared at different reaction temperatures.

2. Materials and Methods

The CsPbBr$_3$ perovskite NCs were prepared at various reaction temperatures using a facile hot-injection method. Briefly, for the preparation of cesium oleate precursors, CsCO$_3$ (0.391 g, 1.2 mmol), oleic acid (1.27 mL, 4 mmol), and 1-octadecene (18.73 mL) were loaded into a 100 mL three-neck flask, dried at 120 °C for 1 h, and then heated under N$_2$ to 160 °C. After CsCO$_3$ was completely reacted with oleic acid, the mixture was preheated to 100 °C before injection. For the synthesis of CsPbBr$_3$ perovskite NCs, PbBr$_2$ (0.149 g, 0.4 mmol) and 1-octadecene (24 mL) were mixed in a 100 mL three-neck flask and dried for 1 h at 120 °C under vacuum. Oleic acid (1 mL) and oleylamine (3 mL) were injected at 120 °C under N$_2$. After the PbBr$_2$ salt was completely solubilized, the temperature was raised to the injection temperature (100–180 °C) to tune the size of the NCs and the pre-prepared Cs-oleate solution was quickly injected. After 5 s, CsPbBr$_3$ perovskite NCs were extracted and quickly cooled in an ice-water bath. The resultant NCs were precipitated by adding 5:1 (v:v) tert-butanol to a NC solution and centrifuging the mixture at 7000 rpm for 10 min; the supernatant was discarded, and the NCs were dispersed in toluene. The UV–vis absorption spectra and fluorescence spectra were recorded with a FLAME-S spectrometer (Ocean Optics Inc., Largo, FL, USA).

3. Results and Discussion

Figure 1a shows a schematic illustration of the hot injection method used to synthesize CsPbBr$_3$ perovskite NCs and an energy band diagram of different-sized NCs with increasing reaction temperature. This method is useful in colloidal synthesis strategy and can be adapted to synthesize various compound, semiconductor NCs. The growth kinetics of CsPbBr$_3$ perovskite NCs by the hot injection method follows the LaMer nucleation and growth mechanism [8]. The larger-sized perovskite NCs synthesized at the higher reaction temperature, which is a crucial factor to determine the morphology in the procedure of nucleation and growth of perovskite NCs, exhibit a smaller bandgap energy than that of the smaller-sized perovskite NCs [15]. Figure 1b shows the FL and absorption spectra of CsPbBr$_3$ perovskite NCs prepared at various reaction temperatures (100–180 °C) and at a reaction time of 5 s. The absorption and FL peaks of the CsPbBr$_3$ perovskite NCs show a band-edge red shift with increasing reaction temperature from 100 °C to 180 °C. Prior to quantitative analysis of emission spectra, the FL spectra measured in a wavelength scale are converted to an energy scale by using the Jacobian transformation [16]. The FL peaks of the as-obtained CsPbBr$_3$ perovskite NCs prepared at 100 °C, 120 °C, 140 °C, 160 °C, and 180 °C were located at 2.469 eV (502.3 nm), 2.440 eV (508.2 nm), 2.427 eV (510.9 nm), 2.405 eV (515.5 nm), and 2.391 eV (518.6 nm), respectively. When the synthesis temperature was greater than 120 °C, the first excitonic absorption peak broadened because of the formation of a population of larger particles [17]. In the spectrum of the sample prepared at the lowest reaction temperature (100 °C), the FL peak is asymmetric because of incomplete chemical reaction [17]. This behavior is attributed to the presence of a pool of monomers resulting from dissolution of particles with a radius less than the critical radius [18].
Figure 1. Synthesis and the optical properties of CsPbBr$_3$ perovskite nanocrystals (NCs): (a) Schematic illustration of the hot injection method and band diagram within different-sized CsPbBr$_3$ NCs; (b) absorption and fluorescence spectra for the CsPbBr$_3$ perovskite NCs prepared at different reaction temperatures.

Figure 2a shows the absorption and FL peak positions of CsPbBr$_3$ perovskite NCs prepared at different reaction temperatures. The absorption and FL peaks of the CsPbBr$_3$ perovskite NCs could be tuned in the regions of 2.429–2.570 eV and 2.391–2.469 eV, respectively. The absorption and FL peak positions for the perovskite NCs decreased with increasing reaction temperature because of an increase in the NC size [1,19,20]. In the plots of peak positions for the absorption and FL spectra, the reaction’s temperature-dependent Stokes shift is observed due to the different size of synthesized CsPbBr$_3$ perovskite NCs. The Stokes shifts decreased from 101 meV to 38 meV with increasing NC size. The occurrence of the Stokes shifts is related to the crystal phase, NC size, and defect type [21]. Figure 2b shows the full-width at half-maximum (FWHM) of the FL peaks of the CsPbBr$_3$ perovskite NCs prepared at different temperatures. The FWHM of the FL peaks decreased from 150 meV to 90 meV with increasing reaction temperature because higher temperatures result in a narrower size distribution [18]. Thus, high reaction temperatures lead to rapid diffusion of the monomers and enabled the synthesis of high-quality CsPbBr$_3$ perovskite NCs with good size uniformity [2,12,18]. Figure 2c shows the photoluminescence quantum yield (PLQY) of CsPbBr$_3$ perovskite NCs as a function of reaction temperature. The relative PLQYs of the CsPbBr$_3$ perovskite NCs prepared at different reaction temperatures were determined by comparing the integrated emission of the NC samples with a standard fluorescence dye (Coumarin 500 in ethanol, QY = 47%). The highest PLQY of 56% was obtained for NCs prepared at the reaction temperature (140 °C).

Figure 3 shows Tauc plots for the CsPbBr$_3$ perovskite NCs prepared at different temperatures. The shape of the absorption edge in the absorption spectra of the CsPbBr$_3$ perovskite NCs is related to electronic transitions in the band-edge region [22]. The optical bandgap of the CsPbBr$_3$ perovskite NCs was calculated from the Tauc plots, which are valuable for determining the bandgap energy. The absorption coefficient ($\alpha$), which is directly proportional to the optical density and incident photon energy ($h\nu$), can be used to determine the optical bandgap by extrapolating the straight-line portion of the plot of the quantity ($\alpha h\nu$)$^2$ vs. photon energy [22]. The authors of a previous study reported that the calculated bandgap of perovskite materials from the Tauc plot compares with the discrete Fourier transform computed bandgaps [23]. In addition, the bandgap can be estimated...
using the Tauc plot without considering the exciton binding energy, and the results were in good agreement with the energy levels (conduction/valence band) derived from the photoelectron spectroscopy measurement [24]. The CsPbBr$_3$ perovskite NCs prepared under different reaction temperatures had an optical bandgap of 2.383–2.462 eV, and their optical bandgap decreased with increasing reaction temperature.

Figure 2. Optical analysis of CsPbBr$_3$ perovskite NCs as a function of reaction temperature: (a) Fluorescence and first excitonic absorption peak positions; (b) full-width at half-maximums (FWHMs); (c) photoluminescence quantum yield (PLQYs).

Figure 3. Optical bandgap of CsPbBr$_3$ perovskite NCs prepared at different reaction temperatures. Dashed lines indicate optical bandgaps determined from Tauc plots.

Figure 4 shows the calculated radius of the CsPbBr$_3$ perovskite NCs prepared at different temperatures, as determined using the EMA. The digital photographs of CsPbBr$_3$ perovskite NCs at different temperatures (100 °C, 140 °C, and 180 °C) under a single 365 nm UV light source are shown in the inset of Figure 4. In this EMA, an exciton is considered to be confined to a spherical crystallite and the mass of the electron and hole is substituted as the effective mass to define the wave function [25]. Equation (1) indicates the energy spacing ($\Delta E$) of the CsPbBr$_3$ perovskite NCs prepared at different temperatures, as determined using the EMA [3,6]:

$$\Delta E = E_g - E_{\text{bulk}} = \frac{\hbar^2}{8\pi^2 m^* r^2} = \frac{\hbar^2}{8\pi^2} \left( \frac{1}{m_e^*} + \frac{1}{m_h^*} \right)$$  (1)
where $E_g$ is the bandgap energy obtained from the Tauc plot of the CsPbBr$_3$ perovskite NCs, $E_{\text{bulk}}$ is the bandgap energy of the bulk semiconductor, $m^*$ is the reduced mass of the exciton, $m_{e^*}$ is the effective mass of an excited electron, $m_{h^*}$ is the effective mass of an excited hole, $r$ is the NC radius, and $h$ is Planck’s constant. The fitting of the energy spacing as a function of the radius for the CsPbBr$_3$ perovskite NCs prepared at different temperatures was obtained using the following parameters: $E_{\text{bulk}} = 2.25$ eV, $m_{e^*} = 0.15$ eV, and $m_{h^*} = 0.14$ eV [6]. The bandgaps are considered to reflect a constant offset of ~0.2 eV with respect to values measured experimentally at room temperature [6]. For a colloidal semiconductor NC to exhibit quantum-dot-like behavior, the NC diameter must be similar to or less than that of the exciton Bohr diameter, $a_0$ [25]. This approximation provides an estimate for the shifts of the emission and first excitonic absorption peaks, which are in good agreement with the experimental observations.

The energy spacing of the CsPbBr$_3$ perovskite NCs was calculated from their Tauc plots, and their diameters were estimated using the EMA. Table 1 shows the values for the energy spacing and diameter of CsPbBr$_3$ perovskite NCs that yield the best fit of the experimental data to Equation (1); the fitted curve is included in Figure 4. The size of CsPbBr$_3$ perovskite NCs with increasing reaction temperature increased due to a decrease in the energy spacing resulting from a decrease in the optical bandgap of NCs. The diameter of the CsPbBr$_3$ perovskite NCs ranged from 9.9 nm to 12.5 nm. These results are in agreement with the transmission electron microscopy observations of CsPbBr$_3$ perovskite NCs reported by Protesescu et al. [6].

Table 1. Energy spacing and diameter for CsPbBr$_3$ perovskite NCs prepared at different reaction temperatures.

| Reaction Temperature (°C) | 100 | 120 | 140 | 160 | 180 |
|---------------------------|-----|-----|-----|-----|-----|
| Energy Spacing (eV)       | 0.21| 0.19| 0.16| 0.14| 0.13|
| Diameter (nm)             | 9.9 | 10.5| 11.3| 12.0| 12.5|

4. Conclusions

We characterized the size dependence of the optical properties and the energy spacing of CsPbBr$_3$ perovskite NCs prepared at various reaction temperatures. With increasing size
of the CsPbBr₃ perovskite NCs, band-edge red shifts occurred in their absorption and FL spectra. With increasing size of the CsPbBr₃ perovskite NCs, their Stokes shifts decreased from 101 meV to 38 meV. The FWHM of the FL peaks for the CsPbBr₃ perovskite NCs decreased from 150 meV to 90 meV because of the NCs’ narrower size distribution when prepared at higher temperatures. The size of the CsPbBr₃ perovskite NCs was estimated using Tauc plots and the EMA. The results presented here improve the understanding of the growth kinetics and photophysics of CsPbBr₃ perovskite NCs and help in the development of high-efficiency optoelectronic devices.

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