Accomplishing High Efficiency and High Durability Novel Perovskite Quantum Dots by the Low Carbon Green Technology

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ABSTRACT

Novel perovskite quantum dots were successfully synthesized by an eco-friendly (non-toxic precursors) and energy-saving (low temperature) process. A display panel was assembled with a blue LED chip, green QDs (530±5 nm, FWHM = 20 nm) and red-emission phosphor, shows almost 120% NTSC.

1 Introduction

Nanocrystals quantum dots (QDs), especially perovskite QDs, are one of the potential candidates for optoelectronic materials in the future. Perovskite QDs have many attractive optical properties, including the narrow full width at half maximum (FWHM), tunable color characteristics because of the components and quantum confinement effect, high photoluminescence quantum yields (PLQYs), and many more.

Metal halide perovskite with the general form of ABX₃, where A is a cation such as cesium (Cs⁺), methylammonium (CH₃NH₃⁺; MA⁺), guanidinium [C(NH₂)₃⁺; GA⁺], and formamidinium [CH(NH₂)₂⁺; FA⁺], B is divalent cations such as Pb²⁺ or Sn²⁺, X is a halide such as Cl⁻, Br⁻, or I⁻, have attracted extensive attentions because of the excellent optical properties described above, and the cadmium-free, lead-free possibility[1][2] also obey the Restriction of Hazardous Substances Directive (RoHS)[3], which adopted by an European Union. In this study, we focus on the synthesis and applications of organic-inorganic hybrid perovskite QDs (names CCL01 below) because their main peak is about 530±5 nm due to their natural size and almost satisfy the BT.2020 standard.

In the conventional synthesis method, a ligand-assisted re-precipitation (LARP)[4] approach or hot injection (HI)[5] method is commonly used to synthesize perovskite QDs. However, the high cost of ingredients and toxic solvent (e.g. dimethylformamide [DMF]) are necessary for the LARP method. Similarly, for the HI method, the high reaction temperature (usually > 100°C) is essential, and it will lead to the high energy consumption and more dangerous when products are fabricated in the factory. On the other hand, the method we propose in this work is a hot-injection-like approach. However, the moderate reaction temperature was adopted in our synthesis process. Hence, the novel method is energy-saving and eco-friendly (without using a toxic solvent or element like DMF and cadmium).

2 Experiment

2.1 Materials

All ingredients were commercially available and used directly without further purification process.

2.2 Synthesis of CCL01

The hot-injection-like method was created in this experiment. Initially, the precursors were added in an appropriate amount of 1-octadecene (ODE) and oleic acid (OA). After that, the mixture solution was vacuumed and raised to the proper temperature simultaneously to remove the moisture in the system.

When the mixture was observed to be homogeneous and transparent, the temperature was lowered to moderate condition. Then we quickly injected the bromide precursor into the mixture under vigorous stirring. After a while, the reaction was terminated by an ice bath.

Afterwards, proper anti-solvent was added before centrifuging at 20,000 rpm for 10 minutes. After discarding the supernatant, an amount of solvent was used to disperse QDs. Then the last centrifuge was set to 8,000 rpm for 8 minutes, and the supernatant was kept as the QDs solution.

2.3 Instrumental characterization

The crystal phase information of the sample was characterized by X-ray powder diffraction (XRD, D8
ADVANCE ECO, BRUKER) with the energy resolution of 380 eV @ 8 KeV, the models of Bragg 2D were collected 2D data with a divergent primary line beam with Cu radiation. The images of the transmission electron microscope (TEM) were obtained by Hitachi H7100 with an acceleration voltage of 75 kV. The optical properties of the QDs, such as emission, excitation, and absorbance, were obtained with a fluorescence spectrometer (FluroMax-4, HORIBA). Moreover, the absolute PLQY was measured by an integrating sphere with the fluorescence spectrometer.

3 Results

3.1 Crystallinity of CCL01
To decide the crystallinity of CCL01, XRD pattern of CCL01 is detected and shown in Fig. 1. By comparing with the open database, it is proved that our sample has a Pm3m cubic structure with the three main peaks that local for (001), (002), and (003) planes, respectively.

Fig. 1 XRD pattern of synthesized CCL01.

3.2 Morphology of CCL01
The TEM image of CCL01 QDs is described in Fig. 2. It exhibits a uniform size distribution with about 10~25 nm particle size and also shows a well-sharp morphology.

Fig. 2 TEM image of CCL01.

3.3 Optical properties of CCL01
The normalized absorption and emission spectra of CCL01 colloid are shown in Fig. 3. The broad absorption and sharp emission spectra are shown as a blue dash curve and red dash curve, respectively. Besides, a 450 nm emission light source was adopted as an excitation source, and the photoluminescence (PL) results exhibited 530 nm emission, 20.6 nm FWHM and almost ~96% PLQY. The actual compound is excited under UV light (inset).

Fig. 3 Absorption (blue dash curve) and photoluminescence (red dash curve) spectra of CCL01.

3.4 Time-resolved PL spectra of CCL01
In addition, lifetime is one of an intrinsic characteristic that concerned for studying fast electronic deactivation processes. The lifetime signal of CCL01 was shown in Fig. 4. The raw data was fitted with bi-exponential decay function \( y = A_1 \exp(-x/\tau_1) + A_2 \exp(-x/\tau_2) + y_0 \). The short lifetime \( \tau_1 \) and the medium lifetime \( \tau_2 \) were been calculated, respectively. After that through the average lifetime formula \( \tau_{avg} = \frac{A_1 \tau_1^2 + A_2 \tau_2^2}{A_1 \tau_1 + A_2 \tau_2} \), the average lifetime \( \tau_{avg} = 24 \) ns was figure out to evaluate the defect of CCL01.

Fig. 4 TRPL spectrum of CCL01.
3.5 Stability of CCL01

Furthermore, the twice PL stability of CCL01 is shown in Fig. 5. We used Rhodamine 6G (R6G) as a standard to calibrate the intensity of the light source. The gray, green, and violet trends stand for R6G and CCL01 synthesis twice, respectively. The result indicates that CCL01 is good reliability and almost shows no decay after 336 hours by storing in normal conditions (room temperature and atmosphere).

![Fig. 5 Change for relative emission intensity of CCL01 stored in normal condition.](image)

3.6 Device and the corresponding color gamut

Eventually, we fabricated CCL01 into a thin film and assembled it with a backlight consisting of a blue LED chip and red-emission phosphors to manufacture the display panel. The device is shown in Fig. 6(a) to compare with commercial LCD display panels, as shown in Fig. 6(b). The display panel fabricated in this work exhibits excellent brightness and higher color saturation obviously. Additionally, the color gamut of the device is shown in Fig. 7, with around 120% NTSC and almost satisfies the standard of BT.2020.

![Fig. 6 The LCD display panel (a) with CCL01 film and (b) without CCL01 film.](image)

![Fig. 7 The color gamut of the LCD display device with CCL01 film in this work compared with NTSC standard.](image)

4 Discussion

Above all, we proposed a hot-injection-like method with moderate reaction temperature and used certain chemicals as precursors to precisely control the ABX\textsubscript{3} ratio. In the optimized temperature, we could ensure that QDs were all generated gradually, guaranteeing the crystal structure consistency and raising the yield of the effective QDs.

Importantly the synthetic process was not only cadmium-free and without toxic solvent (e.g., DMF) but also energy-saving (low reaction temperature) in this work. Hence, it obeys the RoHS regulation adopted by an European Union. Therefore, scaling up this method will reduce the enormous waste of energy and decrease the carbon discharge when mass production in the industry. Furthermore, the substantive benefits include saving cost, being eco-friendly, energy-saving, and assisting the enterprise in implementing the environmental, social, and governance (ESG) index.

Additionally, the well crystallinity and nanoscale of particle sizes are shown in Fig. 1 and Fig. 2, respectively. Moreover, the outstanding optical properties are shown in Fig. 3, the narrow FWHM (~20 nm) and high PLQY (>90%) corresponding to the high color saturation and excellent brightness of the device we fabricated. Furthermore, the lifetime of CCL01 was recorded in Fig. 4, and the result indicated the less defect at the surface of QDs. Besides, the stability of CCL01 was measured and depicted in Fig. 5, the result also further indicated that the CCL01 was successfully synthesis and was able to store for a long time. Finally, the more important that the device exhibited a more vivid performance compared with the commercial LCD display panel and almost
manifested 120% NTSC standard are shown in Fig. 6 and Fig. 7.

We will demonstrate detail the solution of CCL01 and the device fabricated in this work at International Display Workshops 2023.

5 Conclusions

In summary, this research successfully synthesized an organic-inorganic hybrid perovskite QDs that exhibited extraordinary optical properties. In fact, the value of this experiment is the feasibility of industrial production which is in line with the law required nowadays. For instance, RoHS is the most authoritative and demanding directive that strongly influences human society. Mediating technological progress and environmental sustainability are the primary issue we are concerned about.

To fit in with the commercial needs, the high performance of green emission in color gamut, color saturation and efficiency is the milestone that had been conquered. The success of assembling various advanced commercial products verifies that the CCL01 is the expected competitor to challenge those antiquated options.

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References


