In-situ Fabrication of Patterned Perovskite Quantum Dots for Display Applications

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ABSTRACT

Aiming to the integration into Micro-LED applications, patterning is usually one of the most critical steps. We report on the combination of in-situ fabrication with inject-printing and direct laser writing, which provides an efficient and simple scheme for patterning perovskite quantum dots during the formation process.

1. Introduction

Colloidal quantum dots (QDs) have received great attentions in display technology due to their color tunability, narrow emission, and high photoluminescence quantum yields (PLQYs) [1-3]. Perovskite quantum dots (PQDs) are emerging to overcome some of these difficulties because of their intrinsic ionic characteristics including ultra-low formation energy and defects tolerance [4,5]. These characteristics enable us to fabricate highly luminescent PQDs at low temperature (or even room temperature) without sophisticated control [5]. After about 6 years' efforts, PQDs are now very promising candidates to fit the industrial gap of QDs in some of applications. In the field of display technology, the use of PQDs in liquid crystal display (LCD) backlights approaches to the critical point of industrial applications [6,7]. Meanwhile, the electroluminescence (EL) devices based on PQDs (or perovskites quantum well) achieved a maximum external quantum efficiency (EQE) comparable with well-developed OLEDs, while the stability is still a severe issue [8]. Patterned PQDs are considered as red and green color converters for Micro-LED and OLED applications [9-11].

Patterning is usually one of the most critical steps to integrate PQDs into Micro-LED and QD-OLED applications. We report on the combination of in-situ fabrication with inject-printing and direct laser writing, which provides an efficient and simple scheme for patterning perovskite quantum dots during the formation process. The as-fabricated perovskite quantum dots patterns show bright photoluminescence emission with a quantum yield of 80-90%.

2. Materials

2.1 Key Merits of PQDs Toward Display Technology

Figure 1 provides a comparison of the key merits between conventional QDs (CdSe and InP) and PQDs including absorbance coefficient, full width of half maximum (FWHM), PLQYs or EQE, as well as the processibility, reliability, and Restriction of Hazardous Substances (RoHS) limitation. Compared with conventional CdSe and InP QDs, PQDs show attractive merits to fit the industrial requirements of QDs in these on-going display techniques. The features of easy fabrication and high absorbance coefficient are the most attractive merits for color converter applications. Therefore, the earlier works focus on the patterning technology.

Figure 1 | The key merits between conventional QDs (CdSe and InP) and PQDs including absorbance coefficient, FWHM, PLQYs or EQE, as well as the processibility, reliability, and RoHS limitation.

2.1 In-situ printing fabrication of Patterned PQDs

In comparison with the traditional inkjet printing methods, this strategy avoids the use of polymer containing inks, which increased the versatility for multiple polymers (PAN, PMMA, PS, PVC, PVDF, CA and PVDC). The process was accomplished by inkjet printing ink of perovskite precursor dissolved in N, N-dimethylformamide (DMF) or dimethyl sulfoxide (DMSO) onto polymer films on heated substrates. This process of forming a microdisk contain four steps: i) a string of vertical ink drops was generated by adjusting the voltage waveform and negative pressure of the printer; ii) the ink drop spread on the surface of polymer film when they contact; iii) the polymer below spreading ink drop was partially dissolved or swelled by the ink on a heated substrate and forms a colloidal microdisk with the solvent evaporation; iv) the microdisk gradually become luminescent because perovskite begin to crystallize to PQDs inside polymeric matrix with further drying. As pixels of the pattern, microdisks locate at specific position according to a printing program. Moreover, it is versatile to fabricate large area, bright

luminescent (PLQY up to 80%) and color tunable (400-750 nm) APbX3 (A = MA, FA, Cs, X = Cl, Br, I) PQDs patterns. The average pixel size of resulting microdisks can be varied by changing nozzles and/or adjusting the substrate temperature. Furthermore, the combination of superior photoluminescence properties, simple process and low cost makes the ISIP strategy very promising for patterning PQDs toward the applications of anti-counterfeiting and display.

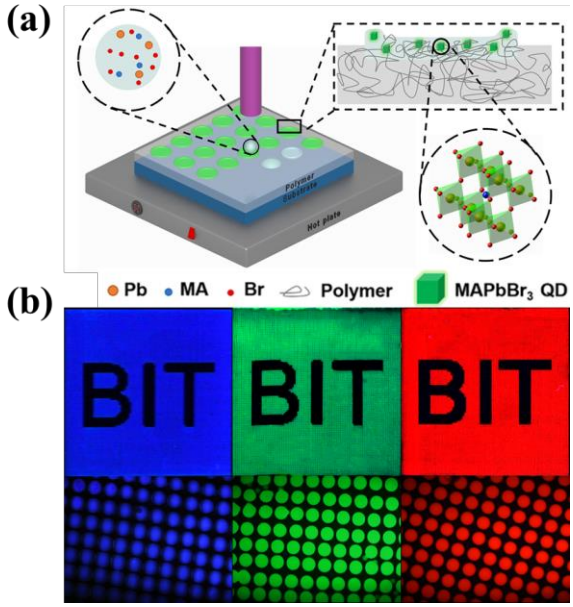

Fig. 2 (a) Schematic diagram of the in situ inkjet printing strategy. (b) The optical images and microscopic fluorescent images of printed PQDs patterns with red, green and blue colors under UV light illuminations.

2.1 In-situ Laser Direct Writing of Patterned PQDs

Figure 3a schematically illustrates the process of in-situ direct laser writing fabrication of patterned γ-CsPbI3 PQDs. Firstly, the preformed composite films with perovskite precursors were prepared by spinning coating a precursor solution in DMF with fixed amounts of CsI, PbI2, and PMMA (see the experimental details). Subsequently, a 405 nm nanosecond laser was used to write patterns on the preformed composite films with perovskite precursors. Upon the irradiation of a 405 nm focused pulse-laser beam with a 0.9 NA objective, the residual solvent of DMF can be further removed with the accumulation of heat. The illuminated region on the film began to nucleate and crystallize into PQDs. Bright red PL emission can be observed with the continuous laser illumination. Because PMMA has a low thermal conductivity of 0.14–0.2 W m−1 K−1,41 the laser induced crystallization can be precisely controlled to obtain higher resolution patterns.

As shown in Figure 3b, we fabricated a pattern of micro-disk array with bright PL emission under UV-365 nm irradiation, suggesting the formation of patterned PQDs after direct laser writing. Figure 3c show the cross-sectional transmission electron microscopy (TEM) image of a typical sample. It is noticed that the resulting PQDs are homogenously dispersed in polymeric matrix with an average size of 7.7 ± 0.4 nm. We further applied high-resolution TEM (HRTEM) measurements on the sample (see Figure 3d). The distance between adjacent crystal planes are 0.676 nm and 0.328 nm with an angle of 89º, which are consistent with the planes of (102) and (212) of γ-CsPbI3.

We further analyzed the influence of laser powers and scanning speeds on the direct laser writing of γ-CsPbI3 PQDs. The average size of the resulting samples slightly increased from 6.5 nm to 9.1 nm with the laser power increasing from 2.0 mW to 2.5 mW and the scanning speed decreasing from 30 mm^{-1} to 10 mm^{-1}.

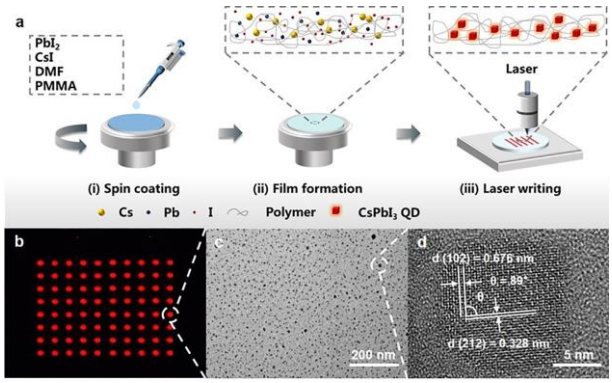

Fig. 3 In-situ direct laser writing fabrication of patterned γ-CsPbI3 PQDs. (a) Schematic illustration of the process direct laser writing. (b) The resulting patterned γ-CsPbI3 PQDs under UV-365 nm light illumination. (c) TEM image of resulting γ-CsPbI3 PQDs obtained from direct laser writing. (d) HRTEM image of single γ-CsPbI3 PQD.

3. Conclusions

In all, we here report on the combination of in-situ fabrication with inject-printing and direct laser writing, which provides an efficient and simple scheme for patterning perovskite quantum dots during the formation process. The as-fabricated perovskite quantum dots patterns show bright photoluminescence emission with a quantum yield of 80-90%. The pixel size of ink-jet printed perovskite quantum dots patterns can be varied from 30-150 m, while the perovskite quantum dots patterns fabricated by laser direct writing have a minimum size down to 900 nm. These reported approaches offer effective route for fabricating patterned perovskite quantum dots with designed structures for photonic applications including micro-LED display, anti-counterfeiting, and nano-lasers.

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