Halide Perovskite Quantum Dots: New Generation Materials for Display Applications

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ABSTRACT

Halide perovskite quantum dots exhibit desired photoluminescence properties with high quantum yields (60-90%), wide wavelength tunability (400-800 nm), and ultra-narrow emissions (< 30 nm), which are suitable for display technology. Here we describe the in-situ fabrication of perovskite quantum dots and their use in prototype devices and display system.

1. Introduction

Colloidal quantum dots (QDs) have received great attentions in display technology due to their color tunability, narrow emission, and high photoluminescence (PL) efficiency [1-4]. Ever since the first report of QDs based light emitting diodes (LEDs) were reported in 1994, the pursuit of higher luminescence efficiency and lower-cost emissive materials to enhance the device performance has never stopped. Based on PL mechanism, CdSe and InP based core-shell QDs have been successfully applied in the backlights for liquid crystal display (LCD) [5,6]. As efficient emissive materials, colloidal QDs have been applied electroluminescence (EL) devices that hold the potential as flexible display. However, the commercialized applications of these materials suffer from the lack of the lack of inexpensive and high-quality materials.

Along with the development of perovskite solar cells, halide perovskites are also emerging as potential candidates for display technology due to their color tunablity and narrow band emissions [7,8]. Especially, perovskite QDs with enhanced PL efficiency are more suitable for display technology [9,10]. Recently, we developed the room temperate reprecipitation synthesis of colloidal $CH_3NH_3PbX_3$ (X = Cl, Br, I) QDs with brightly luminescent and color-tunable emissions [9]. We further demonstrated two kinds of prototype devices for display applications. By integrating green emissive $CH_3NH_3PbBr_3$ QDs and red emissive rare-earth phosphor $K_2SiF_6:Mn^{4+}$ (KSF) with blue emissive GaInN chips, we fabricated wide color gamut white light emitting diodes. The optimized device shows improved luminous efficiency of 109 lm/W at 8190 K color temperature and more than 100% color reproducibility compared to the National Television Systems Committee (NTSC) standard in the Commission internationale de l'éclairage (CIE) 1931 color space [10,11]. Furthermore, a 32 inch LCD panel using perovskite QDs based backlight was successfully illustrated for the first time. In addtion, we also demonstrate the potential application in flexible EL devices.

2. Materials

2.1 Perovskite QDs

Well-developed CdSe or InP based core-shell QDs were usually synthesized at high temperature (200-300 ℃) through hot-injection technique with successive slow shell growth. Unlike these inorganic semiconductor QDs, perovskite QDs can be fabricated by adapting the reprecipitation synthesis at room temperature for organic nanocrystals. With using a pair of miscible toluene and N-dimethylformamide (DMF), we developed ligand-assisted reprecipitation (LARP) synthesis to fabricate the $CH_3NH_3PbX_3$ QDs at room temperature. Figure 1a shows typical samples of $CH_3NH_3PbX_3$ QDs with tunable emission from 400-700 nm.

To integrate these $CH_3NH_3PbX_3$ QDs toward display applications, we must carefully purify them from colloidal solution to remove excess precursors and surfactants, as these residues are detrimental to the PL efficiency and device performance. Unfortunately, $CH_3NH_3PbX_3$ QDs are unstable in many polar solvents such as DMF, methanol, and ethanol. The purification of these QDs using common reprecipitation technique encountered a challenge of finding a suitable pair of polar and non-polar solvents. To solve this problem, we developed non-aqueous emulsion synthesis by introducing an immiscible pair of DMF and hexane with oleic acid as surfactants[12]. This emulsion synthesis allows the purification of these QDs by precipitation from the colloidal solution and obtains solid-state powder which can be redissolved for thin film coating and device fabrication. The size of resulting $CH_3NH_3PbBr_3$ QDs can be tuned from 2 to 8 nm by varying the amount of demulsifier. The redispersed QDs solution show high PL efficiency of 80%, comparable with high quality core shell inorganic QDs. In addtion, we also illustrate the morphology transfermation from nanodots into

nanoplatelets vis self-organization process[13].

2.2 Perovskite QDs based composite films

Incorporation of QDs into polymer matrix is a critical step to process them into functional color converting films for the use in LCD backlights[11]. However, direct physical mixing of preformed QDs with polymeric matrix always bring serious aggregation and PL quenching. To overcome this problem, we developed an alternative *in-situ* fabrication strategy to achieve efficient perovskite QDs enhanced polymer composite films by controlling the crystallization process of polymer and perovskites through controlled vacuum evaporation[14]. The resultant composite films exhibit enhanced PL properties with an optimized PL efficiency up to 94.6±1% and improved stability against water and UV-radiation. The combination of large area, low cost, good uniformity and enhanced PL properties of these composite films makes them to be promising emissive materials in display systems.

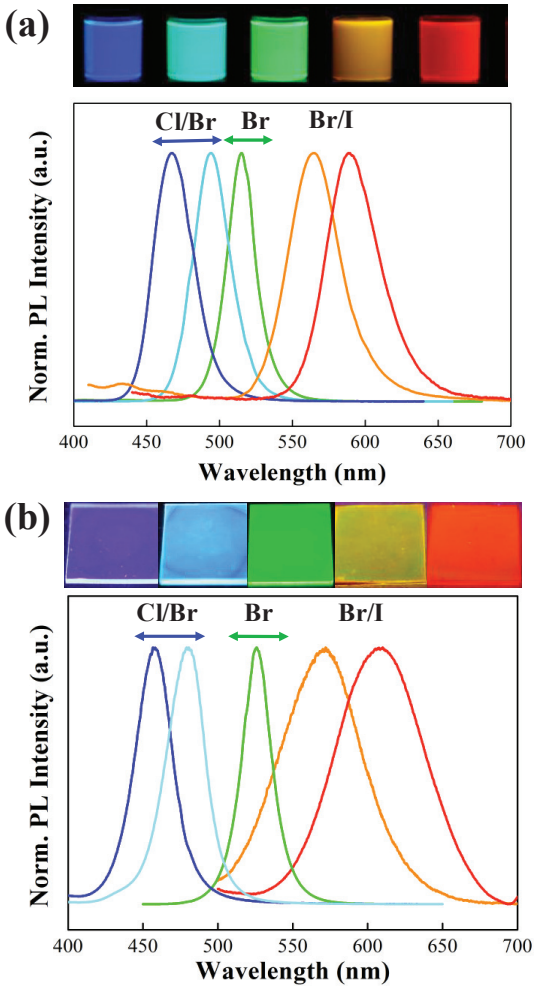

Fig. 1 (a) Optical images and emission spectra of $CH_3NH_3PbX_3$ QDs and (b) $CH_3NH_3PbX_3$/PVDF composite films under a 365 nm UV lamp.

3. Prototype Devices

3.1 Wide color gamut white light-emitting didoes

To illustrate the possible use of perovskite QDs in LCD backlights, we fabricated prototype device of phosphor-converted LED by encapsulating these composite films into UV cure adhesive with red emissive $K_2SiF_6:Mn^{4+}$. The configuration of the device is shown in Figure 2a and the corresponding EL spectrum is shown in Figure 2b. The optimized devices generate white light emission with a high luminous efficiency up to 109 lm/W and wide color gamut of 121% NTSC standard (with a matching rate of 100%) at 20 mA current. The color coordinates of obtained white LED is (0.272, 0.278), as shown in the CIE diagram of Figure 4d.

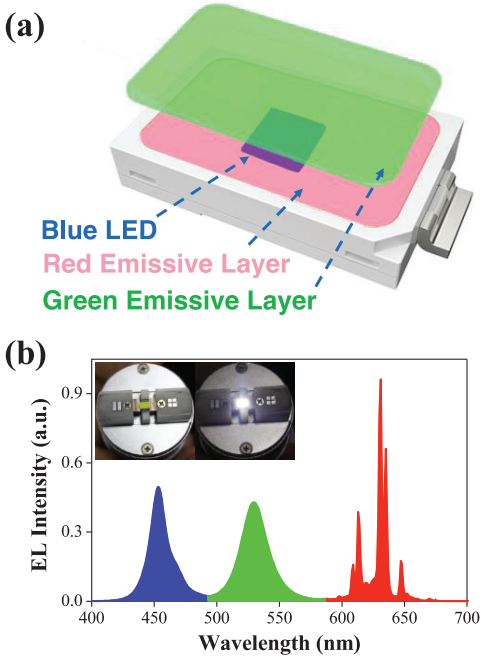

Fig. 2 (a) The device structure of $CH_3NH_3PbBr_3$/PVDF composite film based SMD LEDs; (b) EL spectra and photographs (shown in the inset) of as-fabricated SMD white LEDs.

3.2 Electroluminescence devices

The available high quality $CH_3NH_3PbBr_3$ QDs also provide alternative routes toward efficient electroluminescence devices. Green light-emitting diodes were fabricated by adapting a conventional device structure of ITO glass/PEDOT/QDs/TPBI/Al. The device comprising a spin-cast layer of the colloidal $CH_3NH_3PbBr_3$ QDs exhibited maximum current efficiency of 4.5 cd/A, power efficiency of 3.5 lm/W, and external quantum efficiency of 1.1%. With using Ag nanowire-polymer composite as electrode, we further illustrated highly flexible perovskites based light emitting diodes[15]. As shown in Fig. 3, the devices have been optimized by choosing suitable hole and electron transport layers. The optimized device has a current efficiency of 10.4 cd/A, luminous efficacy of 8.1 lm/W,

and external quantum efficiency of 2.6% at a brightness 1000 cd/m^2. The devices could be bent down to 2.5 mm and bent to 1000 cycles at radius of 4 mm without discernible performance degradation.

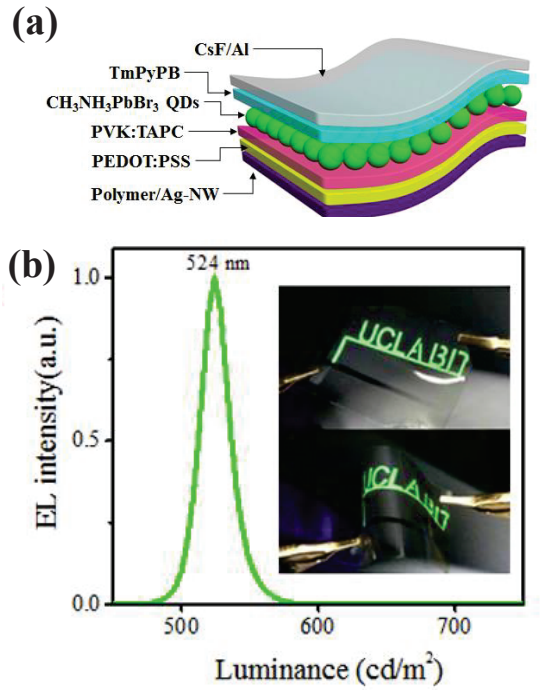

Fig. 3 (a) The device structure of flexible $CH_3NH_3PbBr_3$ QDs based LEDs; (b) EL spectra and images of the flexible CH_3NH_3PbBr3 QDs based LEDs and devices tailored with abbreviations of UCLA & BIT shown in the inset.

3.3 Patterned light conversion films

To incorporate perovskite quantum dots into display, anti-counterfeiting and optical chips applications, inkjet printing is a promising patterning technology. In this work, we develop an in situ inkjet printing strategy for fabricating PQDs patterns[16]. Figure 4a is the schematic diagram and Figure 4b show different colors patterns printed using this strategy. 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). 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.

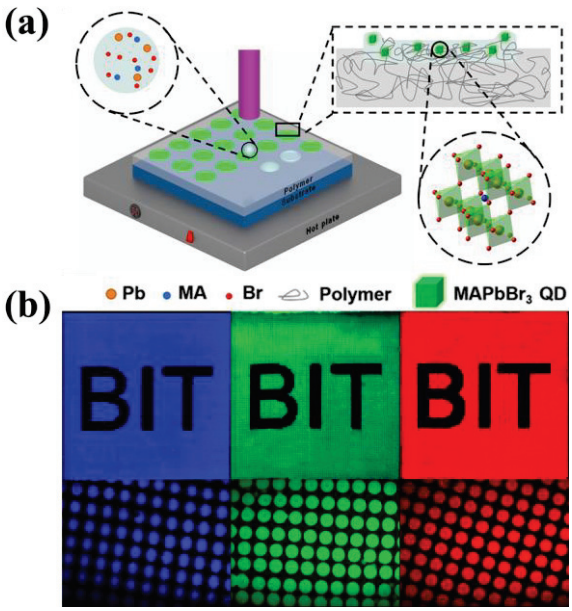

Fig. 4 (a) Schematic diagram of the in situ inkjet printing strategy. (b) The optical images and microscopic fluorescent images of printed PQDs patterns with red, green and blue colors under UV light illuminations

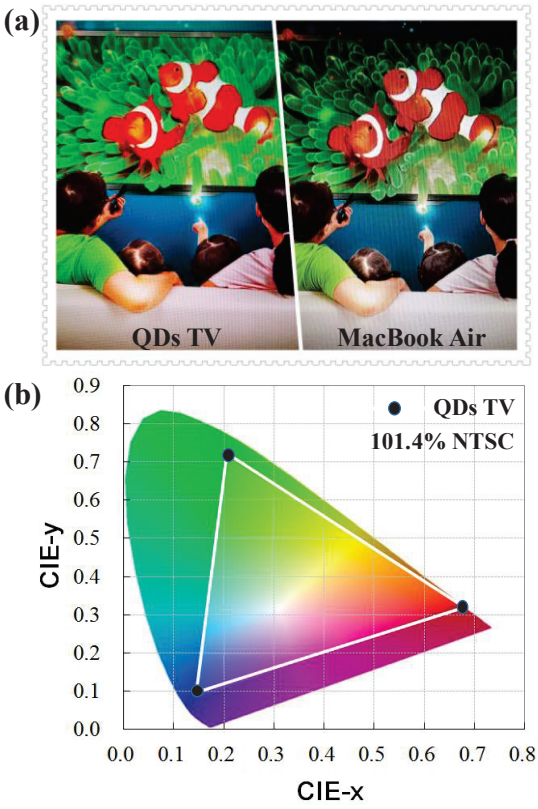

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Fig. 5 (a) A comparison between $CH_3NH_3PbBr_3$ QDs enhanced LCD screen (left) and MacBook LCD screen (right) (Image source from 3M website); (b) Color gamut triangle of $CH_3NH_3PbBr_3$ QDs enhanced LCD screen in CIE 1931 diagram.

4. Display system

Current LCD screens construct pictures by using thousands of pixels that made up of red, green and blue subpixels. The colorful pixels are displayed by filtering the white light that is produced from the LED backlight. With using white light emitting diodes with high color quality, we can achieve a wide color gamut with high brightness and high power efficiency. QDs can be integrated with blue chips to expand the color gamut and improve the brightness. Using $CH_3NH_3PbBr_3$ QDs based composite films and a LED with KSF red emissive phosphor, we firstly achieved a white LED backlight and integrate them into LCD panel, a wide color gamut of 101.4% NTSC and improved brightness of 120% commercialized LEDs was achieved for the LCD screen. Fig.5 shows the comprasion between perovskite QDs enhanced LCD screen (left) and MacBook LCD screen (right) as well the color gamut.

5. Conclusions

From the viewpoint of materials, these perovskite QDs can be prepared by classical hot-injection technique for inorganic semiconductor QDs, or the reprecipitation synthesis at room temperature for organic nanocrystals, or *in-situ* fabrication in the polymeric matrix. From the viewpoint of applications, these perovskite QDs show high PL quantum yields, wide wavelength tunability and ultra-narrow band emissions. The combination of these superior optical properties and low cost fabrication makes them to be suitable candidates for display technology. Motivated by the great progresses in the prototype devices, colloidal perovskite QDs will attract a great of industrial attentions and push forward the commercialized applications.

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