MEET5-3
Invited

Patterning of Perovskite Quantum Dots Pixels Via In Situ Photopolymerization

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Keywords: Perovskite, Quantum Dots, In Situ Fabrication, Pattern, Photopolymerization.

ABSTRACT

Combining the photopolymerization reaction with the in-situ fabrication of PQDs, this report introduces a technical method for the patterning of PQDs pixels via in-situ photopolymerization.

1 Introduction

Micro-LED displays are emerging as one of the most important platforms for future display industry because of their outstanding advantages such as high resolution, high contrast, high brightness, etc. [1,2] However, due to the low luminous efficiency of red light chips and the difficulty of mass transfer of three-color chips, the full-color pixel is still the most important problem for micro-LED.[1, 2] Quantum dots color conversion (QDCC) technology is considered a facial and versatile way to achieve full-color Micro-LED display due to the wide color gamut performance and easy integration.[3-5] Compared with traditional CdSe and InP quantum dots, perovskite quantum dots (PQDs) exhibit a much higher absorption coefficient and can in situ fabricated directly on a substrate or in a matrix, becoming one of the important material systems for QDCC applications.[5-8]

In situ fabrication of PQDs directly into thin films or embedding them into solid matrix has become a major advantage in perovskite applications. The low formation enthalpy and high defect tolerance of perovskite allow for the in situ growth of high-quality PQDs directly on a substrate or in a matrix including polymer,[9] glass,[10] crystals,[11] or printed droplets,[12] where the in situ fabricated perovskite NC−polymer composite films have been successfully applied in TCL TV products. Despite these advances, for use in Micro-LED, in situ fabricated PQDs are still hindered by their limited patterned methods.

Using light to activate polymerization reaction not only leads to exquisite control over reaction dynamics, but also allows complex synthetic protocols to be easily achieved, offering more versatile methods for macromolecular synthesis.[13,14] Especially in recent years, a variety of novel approaches to converge additive manufacturing and advanced photopolymerization, moving from a wide range of photocuring materials to complex with functional materials. [15,16] Of them, colloidal quantum dots are photopolymerization was utilized to provide a robust and flexible host matrix for QDs patterns.[17,18] However, the incompatibility between QDs and polymers will result in the aggregation of QDs and further high optical scattering and losses.

Inspired by these achievements, here we present an in situ direct print photopolymerization method to fabricate PQDs pixels by combining the photopolymerization and in situ fabrication of PQDs during the manufacturing process. By using the inkjet printing strategy, the 20-micron PQDs microarrays exhibit 3D morphology with hemisphere shape as well as strong photoluminescence was fabricated, providing a new technical route for QDCC-based full-color Micro-LED. By photolithography, the 5-micron RGB PQDs pixels array with resolution as high as 2450 PPI was realized, which meets the needs of AR\VR display for high-resolution color conversion pixels.

2 Experiment

For in situ print photopolymerization: ITO substrate was first cleaned by ultrasonication successively in acetone, deionized water, and isopropyl alcohol, after being dried by using flowing nitrogen gas, the PDMS/UV curing resin was spin-coated on the blank substrate at a spinning rate of 2000 rpm for 45 s and then heat at 120 °C for 30 min. The inkjet printing on the polymer-modified substrate was accomplished by using a Sonoplot printer equipped with a 30 μm diameter piezoelectric driven inkjet nozzle. After printing, the precursor droplets were fully cured by illuminating 30 seconds with a 365 nm handheld UV lamp at a power of 5 W to model microarrays. After curing molding, the substrate with perovskite precursor microarrays were heated at 40-80 °C for 10-30 min to complete in situ crystallization of PQDs. All printing, curing and annealing were done in ambient conditions.

For in situ direct photolithography: all substrates were cleaned in an ultrasonic bath using deionized water, ethanol, acetone, ethanol, isopropanol for 15 min each and were blown dry with a nitrogen gun. VTMS (MPTS) modifying substrates were carried out with the vapor-deposition method: a small drop of VTMS (MPTS) was dropped onto the substrates, subsequently, these

substrates were heated to 80 (100) °C for 4 h. After casting 10 uL of PPR on the center of the substrate, the substrate was then bound between a black PMMA board and a patterned chrome mask. Then, a 20W 365 nm handheld-LED was put to expose above the mask for 3~10 s for green patterns, 5 ~ 12 s for blue patterns, and 4~8 min for red patterns. After exposure, the substrate was placed on a spin coater. The uncured zone was rinsed out by spin-washing with clean chloroform, yielding micropatterns. The substrate was then annealed at 80 °C for 3 min for green patterns, room temperature for blue patterns, and 130 °C for 5 min for red patterns to remove residual solvents and PQDs were in situ fabricated in the polymer matrix.

3 Results

3.1 in situ print photopolymerization

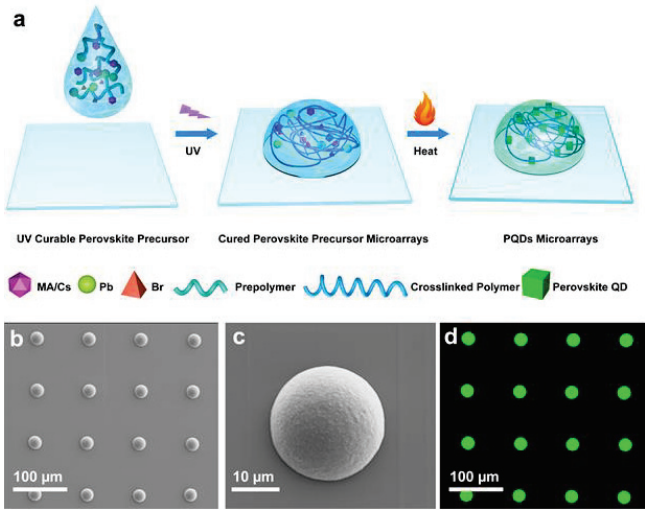

Fig. 1 In situ direct print photopolymerization fabrication of perovskite quantum dots pixels.

The fabrication process of PQDs microarrays via in situ direct print photopolymerization technique is illustrated in Figure 1a.[19] Prior to inkjet printing, PDMS mixed with curing agent was spin-coated onto the quartz glass substrate, pre-curing for about 30 min at 120 °C to form a solid hydrophobic polymer film. Such surface modification is critical for the successful inkjet printing of microarrays. After that, the inkjet printing process was conducted by continuously ejecting the perovskite precursor ink droplets onto the modified substrate from a piezoelectric nozzle. The precursor ink was obtained by mixing methylamine hydrobromide (MABr), lead bromide ($PbBr_2$), and UV curing resin in dimethyl sulfoxide (DMSO). Each droplet can form an individual pixel after being completely cured, the size of these microarrays can be controlled by adjusting the printing parameters including printing distance, release voltage, and time, as well as the size of the nozzle. Once the droplet reached the PDMS substrate, a spherical cap will shape immediately, with the perovskite precursor and UV curing resin randomly distributed. After the patterned microarrays were fabricated by continuous inkjet printing, UV light was irradiated to the substrate, curing the fluid convex and forming regular microarrays patterns. Subsequently, with the removal of residual DMSO in the droplet at a certain temperature, the concentration of MAPbBr3 reaches its critical value and then nucleation, PQDs microarrays were formed.

Figure 1b and 1c show the corresponding scanning electron microscope (SEM) images of the PQDs microarrays, demonstrating their great size homogeneity and conforming their 3D dome-shaped patterns, thanks to the well-controlled droplet shape in the printing process. In addition, cross-sectional transmission electron microscopy (TEM) measurement was performed to clearly demonstrate the QD structure of in situ crystallized MAPbBr3 perovskites, as shown in Figure S2 in Supporting Information. Figure 1d shows the fluorescence image of PQDs microarrays under laser scanning confocal microscope, the printed microarrays emit bright and uniform green fluorescence under UV irradiation. The fluorescence image of an individual PQDs microarray was further enlarged (Figure S3), from which we can see more clearly that the brightness in the center and the edge is almost the same as in other sections, demonstrating the highly uniform distribution of PQDs in these microarrays where normally coffee ring effect is missing.

3.2 in situ direct photolithography

Figure 2 schematically describes the in situ direct photolithography method.[20] The patterning of PQDs can start from simply casting the photosensitive perovskite precursor resist directly onto the functionalized substrate. perovskite precursor resist is the key to the in situ direct photolithography, which is prepared by dissolving reagent salts, multifunctional thiol and ethenyl monomers in polar aprotic solvents. Unlike previous methods, in situ direct photolithography approach directly pattern original perovskite precursors instead of prepared QD inks, which often need extensive cleaning steps and PQDs can be destroyed under high-energy UV light in the presence of oxygen. Second, perovskite precursor film is exposed with UV light through a photomask. Upon UV irradiation, a photochemically activated reaction between TTMP and TAIC occurs, leading to the solidification of the PPR in the exposed area (Fig. 2b). Third, the unexposed PPR is removed by spin-washing with chloroform as a developer. Cured products on exposed areas can adhere to the substrate strongly during spin-washing because of the covalent interactions formed between functionalized substrates and TTMP or TAIC in perovskite precursor resist, making the developing process much easier. Finally, the prepared perovskite precursor patterns are

directly annealing in the ambient air to evaporate residual solvents, when the concentration reaches its critical value for in situ nucleation, luminescent perovskite patterns are formed (Fig. 2c).

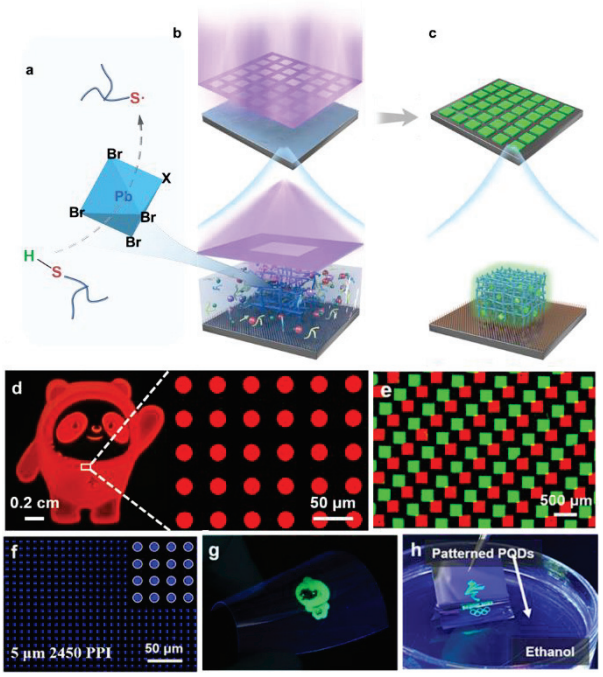

Fig. 2 In situ direct photolithography fabrication of perovskite quantum dots pixels.

Through in situ direct lithography method, we fabricated a series of micropatterns from mesoscale to microscale. Figure 2d shows the fluorescence microscope image cartoon composed of circle red pixels with a diameter and spacing of 20 μm, high contrast between the bright red and dark states showing clearly defined and sharp edges. The higher-resolution images were created, circle patterns with a diameter of 5 μm in Figure 2f, corresponding to the resolution of up to 2540 PPI, sufficiently enabling for the resolution of augmented reality (AR) and virtual reality (VR) display. We further evaluated the applicability of this method to various substrates, as shown in Figures 2g and 2h. Clear patterns were formed not only on rigid substrates, such as glasses and wafers, but also on flexible substrates like polyethylene terephthalate (PET), implying broader integration of the in situ direct photolithography method. What's more, the fabricated PQD patterns exhibited outstanding solvent resistivity and stability, which is highly important for further applications. As can be seen in Figures 2h, illustrating the robustness of the in situ direct photolithography method. Collectively, these results demonstrated that the in situ direct photolithography technology allows for high-resolution, full-color and patterned applications.

4 Discussion

For Micro-LED application, pixels are necessary. However, as the difficulty of mass transfer of three-color chips, full-color pixel is still the most important problem for large-scale application. QDCC technology provide a new route to achieve full-color Micro-LED. To fabricated patterned luminescent pixels, photopolymerization provide a powerful tool, enable in situ fabrication of PQDs directly into thin films or embedding them into solid matrix. By combinate photopolymerization and in situ fabrication of PQDs, high-quality fullcolor PQDs pixels can be achieved through both inject printing and photolithography approach, paving the way for the further fabrication of full-color QDCC micro-LED display.

5 Conclusions

Combining the photopolymerization reaction with the in-situ fabrication of PQDs, this report introduces a technical method for the patterning of PQDs pixels via in-situ photopolymerization. By using the inkjet printing strategy, the 20-micron PQDs microarrays exhibit 3D morphology with hemisphere shape as well as strong photoluminescence were fabricated. By in situ direct photolithography, the 5-micron RGB PQDs pixels arrays with resolution as high as 2450 PPI was realized, which meets the needs of AR\VR display for high-resolution color conversion pixels.

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