Nanoscale

ROYAL SOCIETY OF CHEMISTRY

COMMUNICATION

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Cite this: *Nanoscale*, 2022, **14**, 5994

Received 28th February 2022,
Accepted 19th March 2022

DOI: 10.1039/d2nr01115h

rsc.li/nanoscale

Micropore filling fabrication of high resolution patterned PQDs with a pixel size less than 5 μm†

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PQDs are promising color converters for micro-LED applications. Here we report the micropore filling fabrication of high resolution patterned PQDs with a pixel size of 2 μm using a template with SU8 micropores.

Micro-LEDs are emerging as new generation display technology due to their high brightness, wide color gamut, high contrast, fast response time, high resolution, low power consumption, and long lifetime.[1,2] Although great success has been made in developing the massive transfer of RGB micro-LED chips, it is still a great challenge to achieve high resolution RGB micro-LED displays, in particular to meet the requirement of augmented reality (AR) display.[3–5] In addition, the low external quantum efficiency (EQE) of red micro LED chips also hinders the fabrication of micro-LED display panels.[6–8] Considering these challenges, high resolution quantum dot based color converters (QDCCs) with a high absorption coefficient are much preferred.[9] In addition, QDCCs can also serve as color conversion layers for OLED and LCD color filter replacement to improve the efficiency and color gamut.[10,11] Therefore, a number of efforts have been devoted to the development of patterning techniques for patterning quantum dots (QDs), resulting in different methodologies including inkjet printing,[12–15] photolithography,[16–18] microcontact printing[19–21] and selective electrophoretic deposition (SEPD).[22] To our knowledge, it is still a great challenge to achieve high resolution red and green patterned QDs with the pixel size less than 5 μm, which limits the development toward AR applications.[6]

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† Electronic supplementary information (ESI) available. See DOI: https://doi.org/10.1039/d2nr01115h

Perovskite-type quantum dots (PQDs) have been intensively investigated as promising color converters and successfully applied in LCD display backlights.[23,24] In addition, they are also suitable materials for fabricating high resolution patterned color converters for display applications due to their high absorption coefficient,[9] narrow band emission, high photoluminescence quantum yield (PLQYs), and easy processability.[25–28] In order to meet the requirements of micro-LED applications, it has been of great interest to develop fabrication techniques for patterning PQDs for integration and miniaturization.[29,30] Photolithography-assisted patterning has become the preferred manufacturing method for commercial products, thanks to the advantages of high resolution and large-scale fabrication of photolithography.[31,32] Because of the lack of suitable photoresists for PQDs, only a few works have achieved dual color QD patterns with the pixel size less than 10 μm for micro-LED based augmented reality (AR) display applications.[33,34]

In this work, a micropore filling method is proposed to fabricate patterned PQDs with a resolution of 2–100 μm. The fabrication was accomplished in two key steps including PQD filling and surface polishing. Benefitting from the photolithography fabrication of a SU-8 micropore mold, a super high-resolution pattern with a pixel size of 2 μm can be achieved.

As shown in Fig. 1(a), the micropore filling method includes three steps. First, a layer of the SU8 photoresist is spin-coated on a glass substrate, the required pixel pattern is made on the SU8 photoresist through the standard photoresist process (see the ESI† for detailed parameters of the photoresist process), and the SU8 micropore mold is made. The optical microscopy images of the SU8 micropore mold and the patterned perovskite quantum dots are shown in Fig. S1.† Subsequently, a fixed amount of preformed PQD gel (the fabrication details are provided in the ESI†) was dropped onto the SU8 micropore mold, and then the micropore mold was repeatedly scratched using a scraper, which enables the filling of PQDs into micropores and the removal of excess PQDs on the surface. Finally, the PQD gel in the SU8 micropore mold

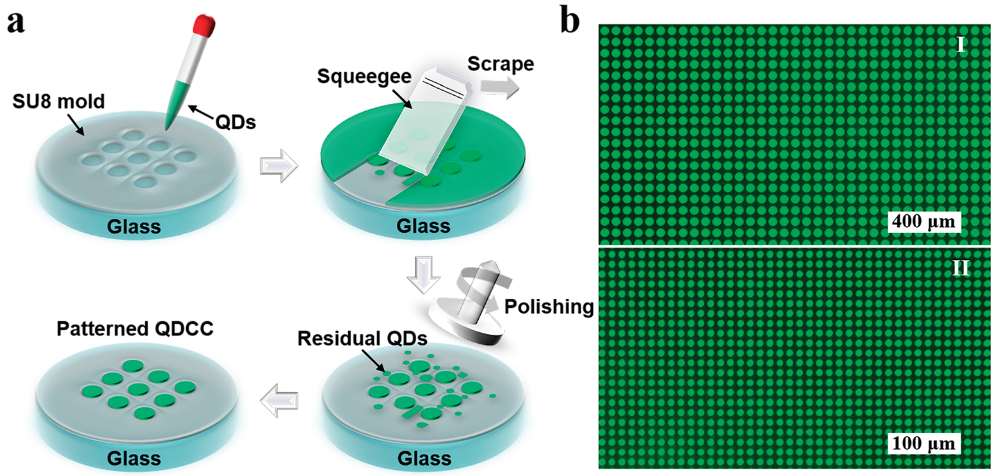

Fig. 1 (a) Brief process of making the QDCC by micropore filling. (b) Monochrome perovskite quantum dot color conversion arrays with pixel sizes of 40 μm and 6 μm circles under a fluorescence microscope.

underwent a solidification process and formed into pixels at 70 °C in 20 min. After that, the residual PQDs on the surface can be removed through a polishing process.

The micropore filling method is versatile in fabricating PQD patterns with different shapes and sizes and the thickness of a single pixel can also be easily varied by controlling the depth of the SU8 micropore mold. Fig. 1(b) shows the images of the green perovskite quantum dot color conversion arrays with pixel sizes of 40 μm and 6 μm circles under a fluorescence microscope (more patterned PQDs of different sizes are shown in Fig. S2†). Fig. 2(a and b) present the images of green and red perovskite films prepared on a 2-inch glass substrate excited under 365 nm UV light and their respective local magnified images. Fig. 2(c and d) show the emblem of our school formed with the patterned PQDs with a pixel density of 849 ppi and a fluorescence image of aligned markers. Based on this method, we successfully realized the rapid preparation of a high resolution quantum dot color conversion layer, and the minimum micropattern prepared is 2 μm (see ESI Fig. S2†). The "CAS" image and alignment markers of other shapes are presented in Fig. S3.† We believe that this method has the potential to produce higher resolution color conversion layers. All of the above images show that the prepared color conversion layer emits bright green and red light with high contrast and excellent luminescence uniformity, indicating that this method has excellent flexibility and repeatability.

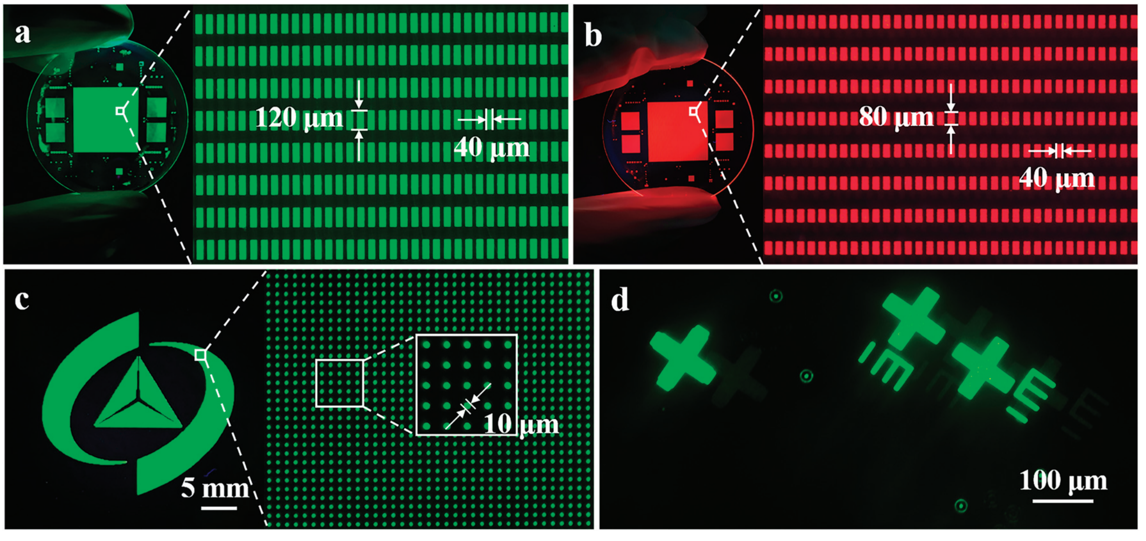

Fig. 2 (a) and (b) Optical images of the quantum dot color conversion layer on a two-inch glass sheet excited by UV light and their respective local magnifications. (c) Fluorescent photograph of the emblem of our school formed by the patterned PQDs and its local magnifications. (d) Fluorescent image of the aligned markers.

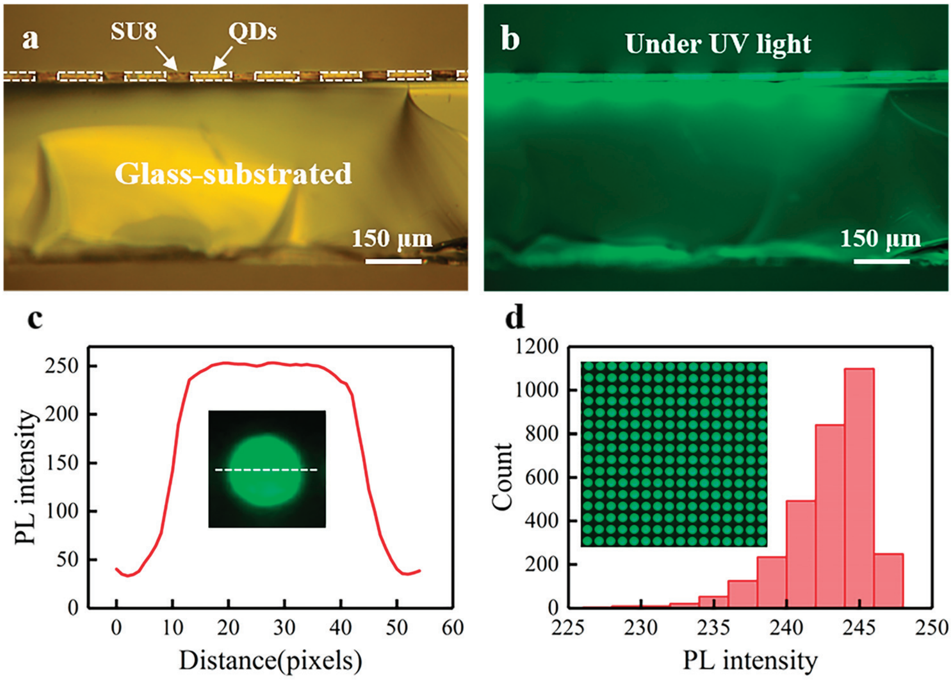

Fig. 3 (a) A cross-sectional optical microscopy image of the film and (b) an optical microscopy image of green fluorescence under UV light excitation. (c) Fluorescence intensity distribution of a single pixel. (d) Histogram of the average fluorescence intensity of all pixels in the array.

It is very important to study the morphology of the devices, which is an important factor affecting their performance. The cross-sectional view of the device was characterized using an optical microscope. Fig. 3(a and b) show the cross-sectional view of the device and the cross-sectional view under UV light. The depth of the SU8 micropore is about 20 μm. It can be seen that the SU8 micropores are fully filled with PQDs without obvious voids. We further characterized the uniformity of PQD patterns using a fluorescence microscope. Fig. 3(c) shows the fluorescence intensity distribution of PQD patterns with a

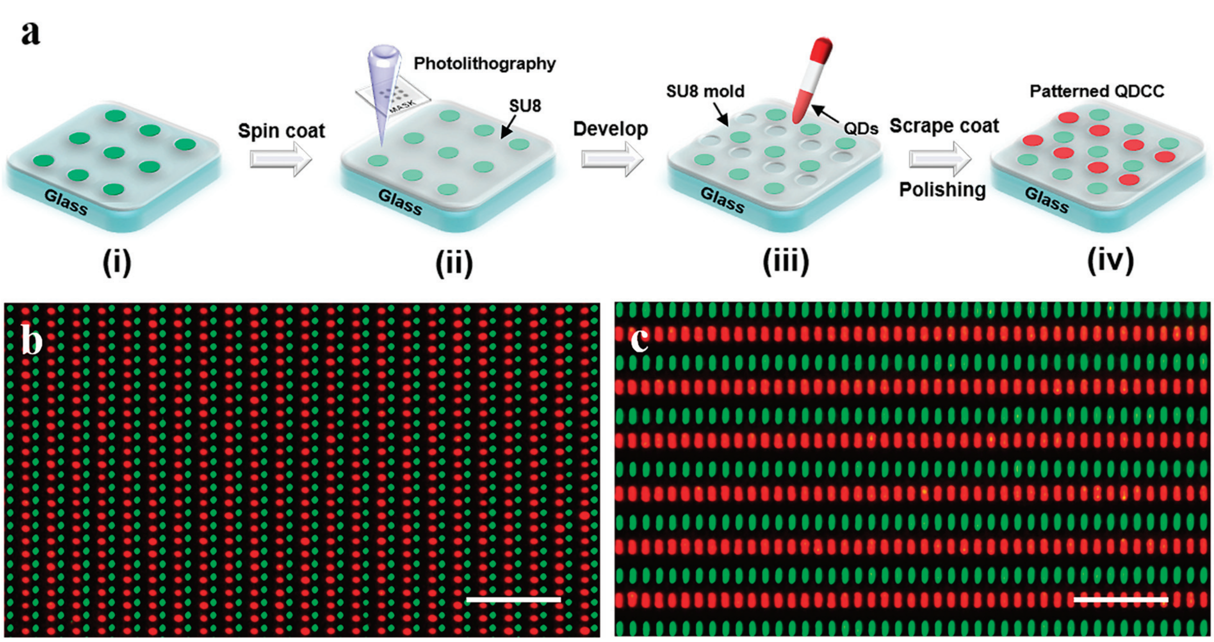

Fig. 4 (a) Preparation process of a dual-color QDCC by the overlay method; (b) QDCC fluorescence image with a single pixel size of 10 μm. (c) QDCC fluorescence image with a single pixel size of 30 × 10 μm; the scale is 200 μm.

pixel size of 60 μm under UV 365 nm excitation. Fig. 3(d) shows a statistical histogram of the fluorescence intensity of 3136 pixels. Please refer to the calculation method in the National Standard of the People's Republic of China "Measure methods of light emitting diode (LED) displays" (please refer to the ESI† for specific calculation methods); the uniformity is calculated to be 3.22% ± 0.61%, which meets the Class C standard of the brightness uniformity of the light-emitting diode display of the People's Republic of China. It is further proved that the device prepared by this method has better luminescence uniformity and has the potential to be used as a micro-LED light conversion device.

As shown in Fig. 4(a), we further fabricated high resolution dual-color PQD patterns by reproducing the micropore filling fabrication using green and red emissive PQDs. Fig. 4(b and c) show the fluorescence images of the dual-color PQD patterns with an average pixel size of 10 μm and 30 × 10 μm. More fluorescence images of the QDCC with different sizes are shown in Fig. S4.† Fig. S5† shows the images of dual-color PQD patterns and monochromatic patterns excited by UV light under an optical microscope.

By scraping and coating the PQDs repeatedly, the micropores can be fully filled with the PQDs, and polishing can effectively remove the residual PQDs outside the micropores. There are several advantages of this approach: (1) it can rapidly fabricate large-area patterned PQDs. (2) The physical method of polishing is used to remove perovskite residual PQDs, which is simple and easy to implement, and the process is mature. At the same time, this removal process does not require any solvent, thereby avoiding the incompatibility between PQDs and traditional lithography. (3) Squeegee coating can recycle some of the unfilled PQDs, thus reducing the material waste.

Conclusions

In summary, we developed a micropore filling fabrication method that combines micropore filling and polishing for fabricating high resolution PQD patterns. During processing, the residual PQDs can be easily removed without any complicated methods or contact with any chemical solvents. Based on this method, we successfully prepared PQD based color conversion layers with a tunable pixel size with a minimum size of 2 μm. The high resolution patterned PQDs with a pixel size of 60 μm have the advantages of a high uniformity of 3.22% ± 0.61%. Furthermore, we also fabricated dual-color PQD patterns with potential applications to achieve full-color micro-LED displays. The micropore filling fabrication provides a flexible and versatile method to fabricate PQD patterns with potential advantages of a low production cost and fast processing speed.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

This work was supported by the National Key Research and Development Program of China (2018YFB1801902, 2018YFB1801901); the National Natural Science Foundation of China (62004195, 51902022); the Jilin Scientific and Technological Development Program (20200401056GX).

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