

Novel Direct Nanopatterning Approach to Fabricate Periodically Nanostructured Perovskite for Optoelectronic Applications

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While indirectly patterned organic–inorganic hybrid perovskite nanostructures have been extensively studied for use in perovskite optoelectronic devices, it is still challenging to directly pattern perovskite thin films because perovskite is very sensitive to polar solvents and high-temperature environments. Here, a simple and low-cost approach is proposed to directly pattern perovskite solid-state films into periodic nanostructures. The approach is basically perovskite recrystallization through phase transformation with the presence of a periodic mold on an as-prepared solid-state perovskite film. Interestingly, this study simultaneously achieves not only periodically patterned perovskite nanostructures but also better crystallized perovskites and improved optical properties, as compared to its thin film counterpart. The improved optical properties can be attributed to the light extraction and increased spontaneous emission rate of perovskite gratings. By fabricating light-emitting diodes using the periodic perovskite nanostructure as the emission layers, approximately twofold higher radiance and lower threshold than the reference planar devices are achieved. This work opens up a new and simple way to fabricate highly crystalline and large-area perovskite periodic nanostructures for low-cost production of high-performance optoelectronic devices.

1. Introduction

Organic–inorganic hybrid perovskite has attracted extensive attention in recent years for its wide applications in various optoelectronic devices such as solar cells,^[1] light-emitting diodes (LEDs),^[2] lasers,^[3] transistors,^[4] and photodetectors.^[5]

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Conventionally, optoelectronic devices adopt planar perovskite configurations. Compared with planar thin films, nanostructured semiconductors offer unique optical properties. In photovoltaics, semiconductor gratings integrated with metal electrodes have been utilized to excite surface plasmons^[6] and increase light path length^[7] within semiconductors for improving the power conversion efficiency of corresponding solar cells. In addition, periodic nanostructures have been incorporated in LEDs to enhance light extraction.^[8] Moreover, distributed feedback lasers^[9] and photonic crystal lasers^[10] have been realized through precisely designing semiconductor periodic nanostructures.

Recently, an indirect patterning approach has been adopted to prepare perovskite nanostructures. This approach starts with patterning substrates, such as glass,^[11] quartz,^[12] silicon,^[13] and Si₃N₄^[14] through electron-beam lithography or photolithography. Perovskite will then be fabricated on the patterned substrate. This indirect patterning approach typically requires relatively complicated processes and thus a higher fabrication cost.^[15] Alternatively, a direct patterning approach is likely to simplify the device fabrication process and reduce the cost.^[16] However, the difficulty of directly nanopatterning perovskite is that perovskite is very sensitive to polar solvents^[17] such as water, methanol, and acetone, as well as high-temperature environments.^[18] For instance, the direct patterning of perovskites through electron-beam lithography would lead to the unexpected phase transformation or defect of perovskite due to local heat induced by high-energy electrons.^[19] Gas-assisted focused-ion beam etching^[15] has been reported to eliminate the damage of perovskite during etching. Nevertheless, there is concern over the reduced photoluminescence (PL) of the patterned perovskite compared with the pristine planar one, which indicates that the film quality of the patterned perovskite is degraded. Consequently, it is still challenging to realize a simple and low-cost direct nanopatterning approach to fabricate periodic perovskite nanostructures with high crystal quality and good optical properties.

In this work, we demonstrate a simple and low-cost approach to directly pattern planar perovskites into periodic nanostructures, regardless of the substrate materials. The approach is basically perovskite recrystallization through phase transformation with the help of methylamine (MA) gas under ambient conditions. Our approach is completely different from traditional nanoimprinting techniques, which press the sample with a rigid stamp under high pressure. Simultaneously, the resultant perovskite shows higher crystal quality than its thin film counterpart. Using periodic perovskite nanostructures to fabricate LEDs, we achieve higher radiance and a lower threshold than the control planar perovskite LEDs due to the periodic nanostructure and improved crystallinity of the perovskite. This work opens up a new and simple way to fabricate highly crystalline and large-area periodic perovskite nanostructures for low-cost production of high-performance optoelectronic devices, such as solar cells, LEDs, laser diodes, and photodetectors.

2. Results and Discussion

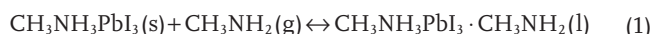
2.1. Fabrication of MAPbI₃ Periodic Nanostructures

The schematic image of a direct nanopatterning approach is shown in **Figure 1**. A solid-state MAPbI₃ thin film is first prepared by one of the conventional methods, such as the solvent engineering approach.^[20] A periodic PDMS mold^[21] is then placed on the solid-state perovskite film (see Figure 1A).

Second, the whole sample is put in a container filled with anhydrous MA vapor. The MA vapor penetrates into the MAPbI₃ film via the gaps between the PDMS mold and MAPbI₃, forming a transparent liquid-phase intermediate of

CH₃NH₃PbI₃·CH₃NH₂, as illustrated in Figure 1B. When the MAPbI₃ film becomes a liquid-phase intermediate, the PDMS mold goes down because of the gravitation and makes close physical contact with the liquid intermediate. This transformation approach is very different from the recently reported micropatterning approach,^[16] in which the mold was applied to a solution-based precursor of perovskite (not an as-prepared solid-state perovskite, as in our case) and an external pressure had to be applied on the mold during the process. As described below, our approach can form very good periodic perovskite nanostructures with improved crystallinity.

Third, the liquid intermediate returns back to solid perovskite after leaving the MA gas and is accompanied by a change of color from transparent to brown, as described in Equation (1)^[22] and illustrated in Figure 1C



Finally, after lifting off the PDMS mold an MAPbI₃ grating is obtained (Figure 1D). Due to the hydrophobic nature of the PDMS mold, no MAPbI₃ is attached to the PDMS mold during lift off. The PDMS mold therefore can be reused again. Details of the direct nanopatterning of perovskite are described in the Experimental Section. It is worth noting that the prepared MAPbI₃ grating can be converted into a HC(NH₂)₂PbI₃ (FAPbI₃) grating through ion exchange (Figures S8 and S9, Supporting Information).

Typically, the reaction between the MAPbI₃ and MA gas occurs immediately when they meet and it completes in several seconds.^[22] In this direct nanopatterning approach the PDMS mold reduces the reaction to a few minutes. The PDMS mold also suppresses back conversion of intermediates into perovskite. Different approaches have been investigated to convert the PDMS-covered intermediate into perovskite. Simply lifting off the PDMS mold from the liquid intermediate does not lead to fabrication of the perovskite grating. The reason is that the liquid intermediate becomes flat immediately after separating from PDMS mold and then converts back to solid perovskite. We therefore need to convert the intermediate into perovskite first and then lift off the PDMS mold. Room-temperature volatilization, 100 °C annealing, and vacuum treatment (at a pressure of 1 mbar) have been tried to convert the intermediate into perovskite. **Figure 2** shows the AFM image and height profile of a 735 nm period MAPbI₃ grating from different approaches. As can be seen from Figure 2B,E, 100 °C annealing contributes to the most uniform perovskite grating, followed by room-temperature volatilization. Vacuum treatment results in the worst perovskite grating. Additionally, we have discovered that the color change from transparent to brown completes in less than 1 min for 100 °C annealing, ≈5 min for room-temperature volatilization, and more than 10 min for

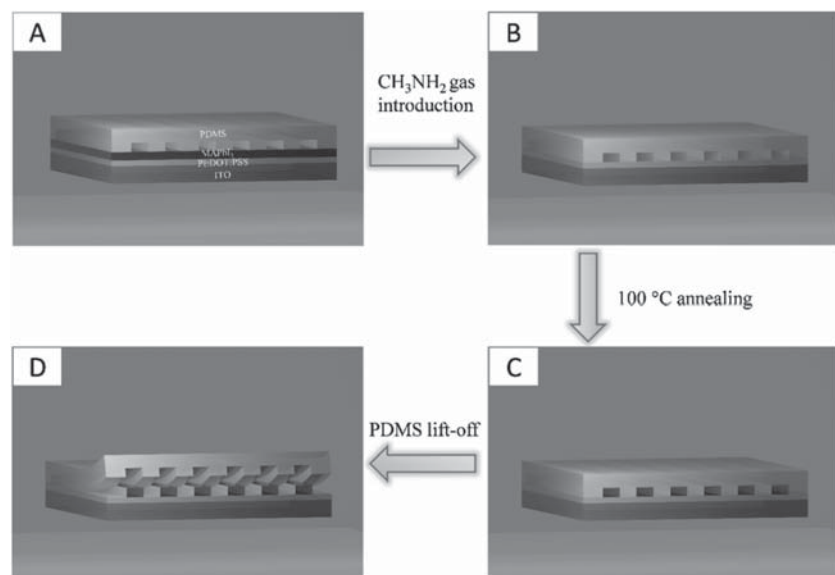


Figure 1. Schematic image of the direct nanopatterning approach for the fabrication of perovskite periodic nanostructures. A) As-prepared solid-state CH₃NH₃PbI₃ (MAPbI₃) thin film covered with a polydimethylsiloxane (PDMS) mold. B) Liquid phase transformation through the formation of a transparent intermediate of CH₃NH₃PbI₃·CH₃NH₂. C) Formation of solid-state perovskite periodic nanostructure through recrystallization. D) Resultant perovskite periodic nanostructure.

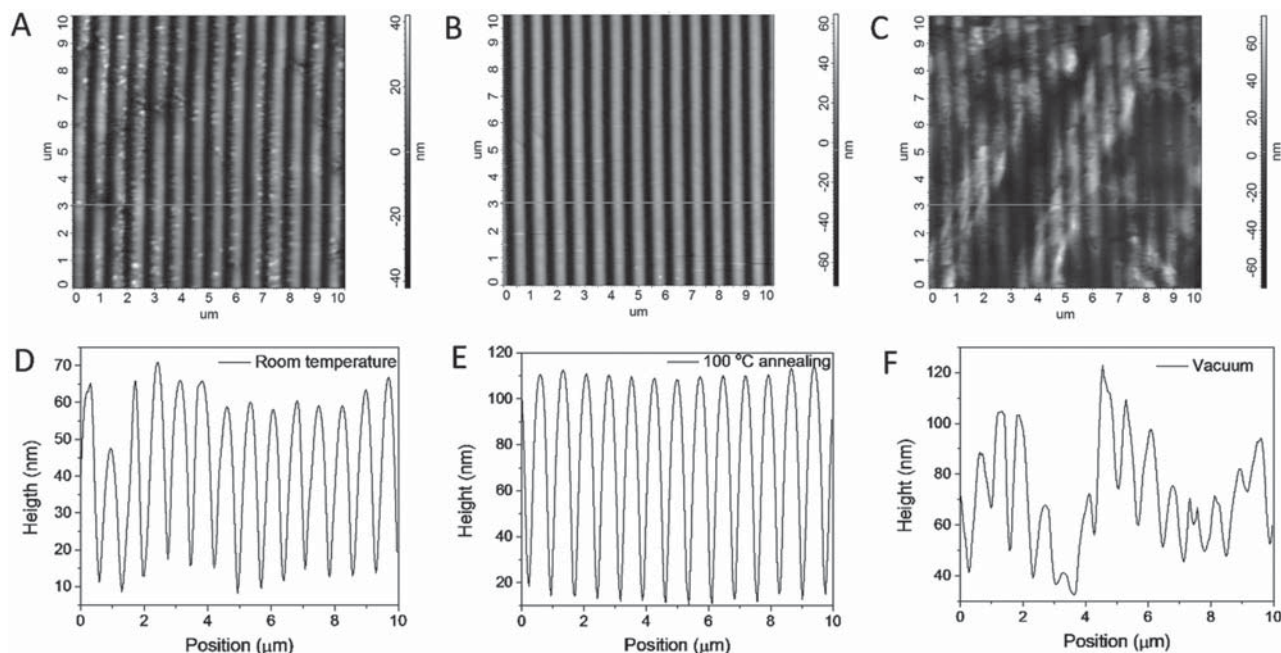


Figure 2. Atomic force microscopy (AFM) image and height profile of 735 nm period MAPbI_3 grating from different approaches for back conversion of intermediate into perovskite A,D) room-temperature volatilization, B,E) 100 °C annealing, and C,F) vacuum treatment.

vacuum treatment. It can be understood that the intermediate, $\text{CH}_3\text{NH}_3\text{PbI}_3 \cdot \text{CH}_3\text{NH}_2$, is more unstable under a higher temperature and thus easier to decompose into MAPbI_3 and MA gas. However, as for vacuum treatment, the vacuum-induced pressure on a soft PDMS mold creates close contact between the PDMS mold and the liquid intermediate. Accordingly, the intermediate is more difficult to decompose into perovskite and MA gas. These results conclude that faster back conversion of the intermediate into perovskite (quick removal of MA gas) is beneficial for formation of a high-quality perovskite grating.

Except for the 735 nm period PDMS mold, a planar PDMS mold, 1500 nm period PDMS mold, and no PDMS cover have been utilized to investigate the morphology change of perovskite after MA gas treatment, as shown in **Figure 3**. All of the samples are treated with dry MA gas under the same condition. The bare perovskite without a PDMS mold first changes its color from brown to transparent, followed by a 1500 nm period and planar PDMS mold. The bare perovskite without a PDMS mold becomes much smoother with an RMS of 1.76 nm, in comparison to the pristine planar perovskite thin film (an RMS of 4.10 nm) from solvent engineering. Perovskite covered with

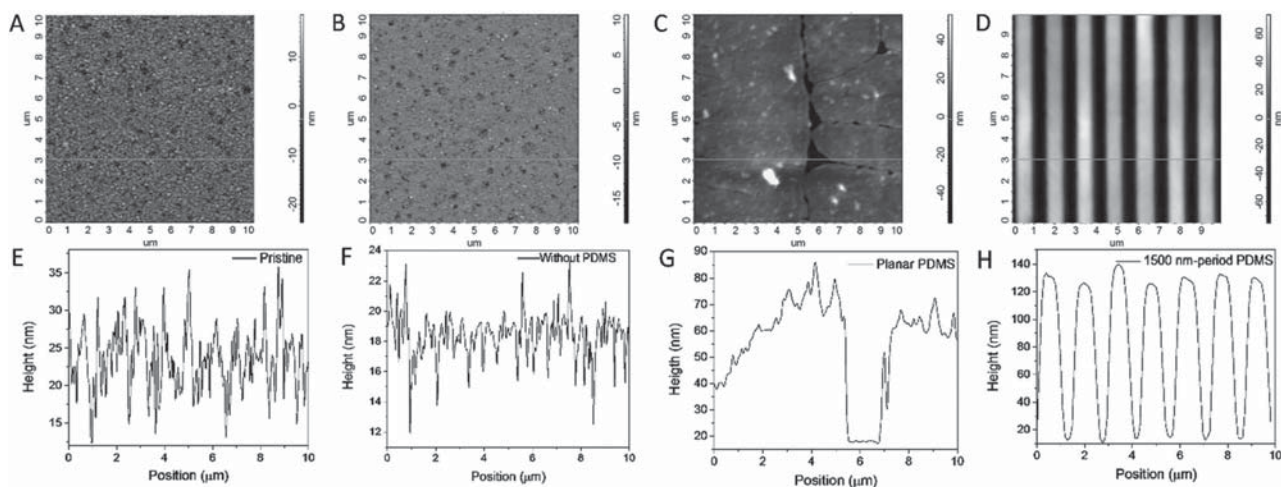


Figure 3. AFM image and height profile of A,E) (a root mean square (RMS) of 4.10 nm) pristine planar MAPbI_3 thin film, B,F) (an RMS of 1.76 nm) bare MAPbI_3 without PDMS cover treated with MA gas, C,G) (an RMS of 11.1 nm) MAPbI_3 covered with planar PDMS and treated with MA gas, D,H) MAPbI_3 covered with 1500 nm period PDMS and treated with MA gas.

a 1500 nm period PDMS results in a 1500 nm period perovskite grating, as shown in Figure 3D. However, unexpectedly, a planar PDMS mold does not produce a smooth planar perovskite thin film. The perovskite that is obtained has obvious pinholes that are surrounded by tens to hundreds of grains. Regarding this result, we have proposed the following understanding. For a PDMS 1D grating, the MA gas could easily leave along the groove of the grating during annealing. That is to say, the grating provides a channel for MA gas to leave and thus contributes to a high-quality grating structure. However, no such channel is provided in a planar PDMS for MA gas to leave. In particular, random escape of MA gas in the central part results in pinholes in the perovskite thin film.

2.2. Physical Properties of MAPbI₃ Periodic Nanostructures

To obtain deeper understanding of perovskite thin films and perovskite gratings, we have conducted scanning electron microscopy (SEM) and AFM measurements to characterize the morphology of planar MAPbI₃ thin film and prepared MAPbI₃ gratings. As can be seen from Figure 4A,D,G, both SEM and AFM images show that the planar MAPbI₃ thin film from the solvent engineering approach is quite smooth. After direct nanopatterning of the planar MAPbI₃ film, uniform periodic MAPbI₃ nanostructures with periods of 735 and 1500 nm are prepared, as shown in Figure 4B,E,H,C,F,I. The period of the perovskite grating is almost the same as that of the PDMS mold. This accurate replication of perovskite from the PDMS mold should attribute to the close contact of the liquid-phase intermediate with the PDMS mold.

Interestingly, the large amount of grain boundaries in the planar thin film (Figure 4D) are eliminated in the perovskite periodic nanostructures (Figure 4E,F) after the direct nanopatterning approach. The eliminated grain boundaries in the grating leads to a uniform Kelvin probe force microscopy (KPFM) image, as shown in Figure S4 (Supporting Information). This elimination of grain boundaries indicates better crystallinity of the perovskite grating. In addition, we have found that the depth of MAPbI₃ changes from 60–80 nm in the planar thin film to 100–120 nm after forming the gratings, as shown in Figure 4H,I. This is simply because the volume of the MAPbI₃ thin film is confined into the grating nanostructure during the phase transformation, which leads to increased depth in the perovskite grating. Furthermore, our direct nanopatterning approach is suitable for fabrication of large-area perovskite periodic nanostructures. As a conceptual demonstration, Figure 4K,L shows real images of the perovskite grating with periods of 735 and 1500 nm, respectively. The device area is 17 mm × 17 mm.

The crystal quality of MAPbI₃ before and after the direct nanopatterning process is investigated by X-ray diffraction (XRD). As shown in Figure 5, the characteristic peaks of reported MAPbI₃^[23] are observed in our planar MAPbI₃ film at 13.95°, 28.38°, and 31.74°, which correspond to (110), (220), and (310) lattice phases, respectively. After nanopatterning, the perovskite gratings maintain the crystal characteristics of perovskite. It is interesting that the crystal intensity of perovskite gratings increases compared with the pristine planar one. The crystal

intensity at the lattice phase of (110) increases from 1728 in planar MAPbI₃ to 2223 in the 735 nm period grating and 2158 in the 1500 nm period grating. This increased intensity should attribute to better crystal quality of the MAPbI₃ grating. Nevertheless, the increased crystallinity of the perovskite grating is supported by evidence of the eliminated grain boundary (Figure 4) and the enhanced absorption spectrum in Figure 6A, which will be discussed below. In fact, the enhancement of crystal quality from the poor perovskite thin film (from spin-coating perovskite precursors in dimethylformamide (DMF) and subsequent annealing) is more significant. Figure S2 (Supporting Information) shows ≈2.5 times enhancement of crystal intensity at the lattice phase of (110) after making the planar MAPbI₃ thin film into a grating. Better crystal quality of the perovskite grating can be explained by the defect healing of MA to MAPbI₃^[22] during nanopatterning. Consequently, on top of forming periodic nanostructures, our direct nanopatterning approach can also improve the crystalline properties of the perovskites.

The optical properties of planar and nanostructured MAPbI₃ are shown in Figure 6. Figure 6A shows the absorption spectrum of the planar MAPbI₃ thin film, the 735 nm period MAPbI₃ grating, and the 1500 nm period MAPbI₃ grating, under the excitation of polarized light. The planar perovskite shows polarization-independent absorption properties. However, both the 735 nm period and 1500 nm period MAPbI₃ gratings exhibit differences under the transverse electric (TE) mode and transverse magnetic (TM) mode polarization due to the periodical nanostructures. For example, for the 735 nm period MAPbI₃ grating, a round trough at 550–600 nm in the absorption spectrum is observed under TM mode polarization. However, it was not the case under TE mode polarization. Moreover, the increased absorption from 550 to 800 nm of the perovskite grating, compared with the planar perovskite thin film, should attribute to the improved crystal quality (Figure 5) and the anti-reflection of incident light induced by the periodic nanostructure.^[24]

Furthermore, two enhancements are observed in the angular PL distributions for the MAPbI₃ grating nanostructure as compared to the planar one, as shown in Figure 6B. First, the overall emission intensity of both MAPbI₃ gratings is higher than that of the planar one. Second, the perovskite periodic nanostructure shows obvious enhancement of light emission at the directions around ±30° and 0°. The PL spectra of the planar and patterned perovskite under a detection angle of −30° are displayed in Figure 6C. The intensity improves obviously, without any clear shift in the peak wavelength and spectral shape. To investigate why the overall emission of perovskite grating is higher, we have conducted time-resolved photoluminescence. As seen in Figure 6D, the decay rate of MAPbI₃ gratings is much faster than that of the pristine planar MAPbI₃ thin film. The average lifetime of the grating (12.62 ns for the 735 nm period MAPbI₃ grating and 10.66 ns for the 1500 nm period MAPbI₃ grating) is considerably lower than that (51.44 ns) of the pristine planar MAPbI₃ thin film. Given the better grating morphology, higher XRD intensity, and improved PL signal, we attribute the shorter lifetime of our perovskite grating to the improved spontaneous emission rate by perovskite periodic nanostructures. From an optical physics' point of view, it is well

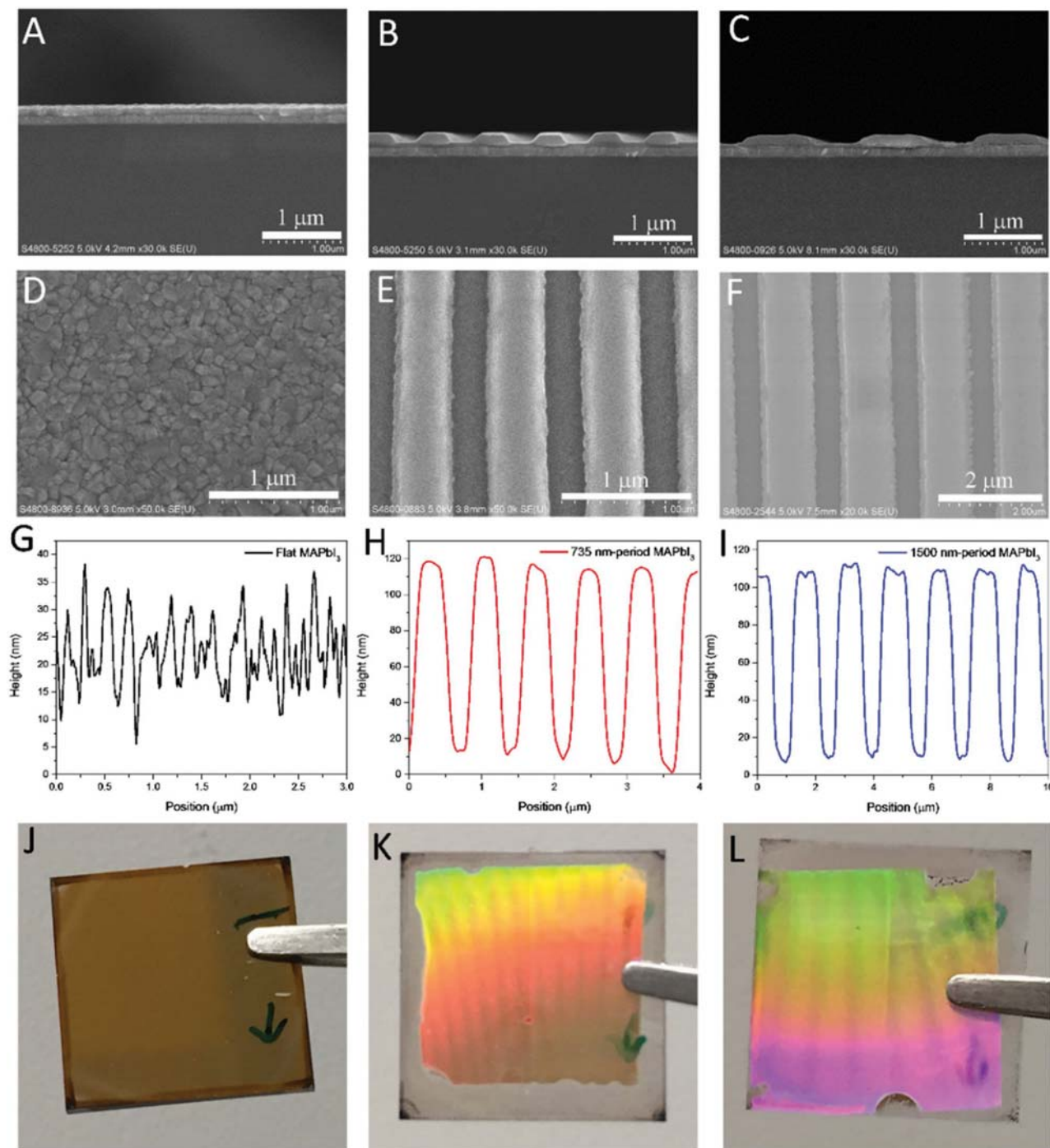


Figure 4. A) Cross-sectional SEM image, D) top-view SEM image, G) AFM height profile, and J) real image of a planar MAPbI₃ thin film on a PEDOT:PSS/ITO substrate. B) Cross-sectional SEM image, E) top-view SEM image, H) AFM height profile, and K) real image of MAPbI₃ grating with a period of 735 nm on PEDOT:PSS/ITO substrate. C) Cross-sectional SEM image, F) top-view SEM image, I) AFM height profile, and L) real image of MAPbI₃ grating with a period of 1500 nm on PEDOT:PSS/ITO substrate. The size of real devices in parts (J–L) is 17 mm × 17 mm.

known that the vacuum fluctuation of the electromagnetic (EM) field perturbs the atomic system and induces the spontaneous emission of photons. If the local EM environment is properly modified, which leads to the change of local density of states, spontaneous emission can be manipulated.^[25] In our case, the perovskite periodic nanostructure increases the spontaneous

emission rate and leads to higher overall emission. Regarding the angular PL properties of our grating patterned perovskite samples, the enhancement of perovskite gratings at the directions around $\pm 30^\circ$ and 0° can be understood by light extraction of the grating.^[26] For the planar perovskite structure, each point at the active layer can be regarded as a dipole source and thus

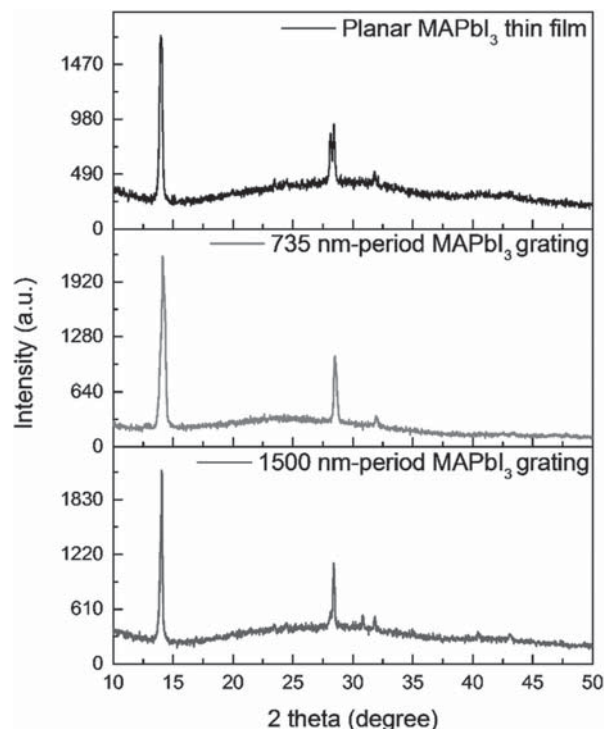


Figure 5. XRD spectrum of a planar MAPbI₃ thin film, a 735 nm period MAPbI₃ grating, and a 1500 nm period MAPbI₃ grating on PEDOT:PSS/ITO glass.

the guided modes are expected to be excited. The excited guided modes will lead to low out-coupling efficiency. After incorporating the grating structure, the guided mode can be coupled out of the perovskite layer with the help of Floquet (Bloch) mode. Using the eigenmode analysis,^[27] the planar structure only has two fundamental modes for S and P polarizations, with the propagation constants of $\beta = 0.016 - 0.0011i$ and $\beta = 0.0138 - 0.0004i$, respectively. The phase matching condition for the perovskite grating reads

$$k_0 \sin \Theta + m \cdot (2\pi/P) = k_\beta \quad (2)$$

where k_0 is the wavenumber in free space (air), Θ is the emission angle, m is the diffraction order, P is the periodicity, and k_β is the propagating constant of the grating incorporated structure, which can be approximated as the propagating constants of the planar structure. Here, we only consider the low-order Floquet (Bloch) mode with $|m| < 3$. For the P polarized mode, we get $|m| = 1$ for $P = 750$ nm and $|m| = 2$ for $P = 1500$ nm. For both periodicity cases, the emission angle Θ is around 30° , which agrees well with the experimental results. Regarding the fundamental S polarized mode, it will have an emission angle of 65° , which is less significant in experiments. There are two possible reasons. First, compared to the P polarized mode, the S polarized mode has a large radiation. It is well known that the S polarized mode is easy to leak out.^[28] Second, the emitters in the perovskite layer may have a bigger probability to be P polarized. To better understand the angular distribution, we have conducted a

full wave simulation using the finite-difference time-domain method,^[29] as shown in Figure 7. In the simulation, the planar MAPbI₃ film reveals a clear Lambertian radiation pattern (Figure 7A,D). Moreover, for the 735 nm period MAPbI₃ grating, two significant hot spots exist in the radiation pattern (Figure 7B,D). The hot spots locate at an emission angle of $\approx \pm 30^\circ$ and a wavelength of around 760 nm. These results agree well with the experimental results. For the 1500 nm period MAPbI₃ grating, similar enhancement occurs around angles of 0° and $\pm 30^\circ$ (Figure 7C,D), which matches with the measured radiation pattern, as shown in Figure 6B.

2.3. Nanopatterned MAPbI₃ as the Emission Layer of Light-Emitting Diodes

To investigate the optoelectronic applications of our MAPbI₃ gratings, we have fabricated them into an MAPbI₃ LED. The structure of MAPbI₃ LED is indium tin oxide (ITO)/poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) (30–40 nm)/MAPbI₃/phenyl-C61-butyric acid methyl ester (PC₆₁BM) (40–60 nm)/Ag (100 nm). The device performances of LEDs with nanopatterned MAPbI₃ and the planar perovskite as the emission layer are shown in Figure 8. The optimized planar perovskite LEDs have a radiance of $0.29 \text{ W (m}^2 \text{ sr)}^{-1}$. Interestingly, the radiance of 735 nm period perovskite LEDs reaches to $0.53 \text{ W (m}^2 \text{ sr)}^{-1}$, which is almost two times of that in the planar MAPbI₃ LED, as shown in Figure 8B. Additionally, the 1500 nm period perovskite LED shows radiance of more than 1.5 times that in the planar MAPbI₃ LED. The increased electroluminescence in the nanopatterned MAPbI₃ LED by addition of a grating agrees with the improved PL in the patterned MAPbI₃ nanostructure, when compared with that of planar perovskites, as shown in Figure 6C. The improvement attributes to the light out coupling and increased spontaneous emission by the nanostructured grating.^[26] Furthermore, as compared with the planar one, the patterned MAPbI₃ LEDs show a lower threshold current density and higher EQE.

3. Conclusions

In conclusion, we have successfully demonstrated a simple and low-cost approach to directly nanopatterned perovskite thin film in the nanoscale dimension. With the presence of a periodic mold on an as-prepared perovskite film, our approach converts the planar film into periodic nanostructures through perovskite recrystallization during phase transformation. Our results show that both periodically nanostructured and better crystallized perovskites have been achieved, which offer better optical properties than their thin film counterparts. By using the perovskite nanostructures as the emission layer of LEDs, we report a better emission radiance and lower threshold. Consequently, our work contributes to not only the evolution of fabricating large-area perovskite periodic nanostructures with any configurations, but also to the improvement of the device performances for the practical applications of perovskite LEDs.

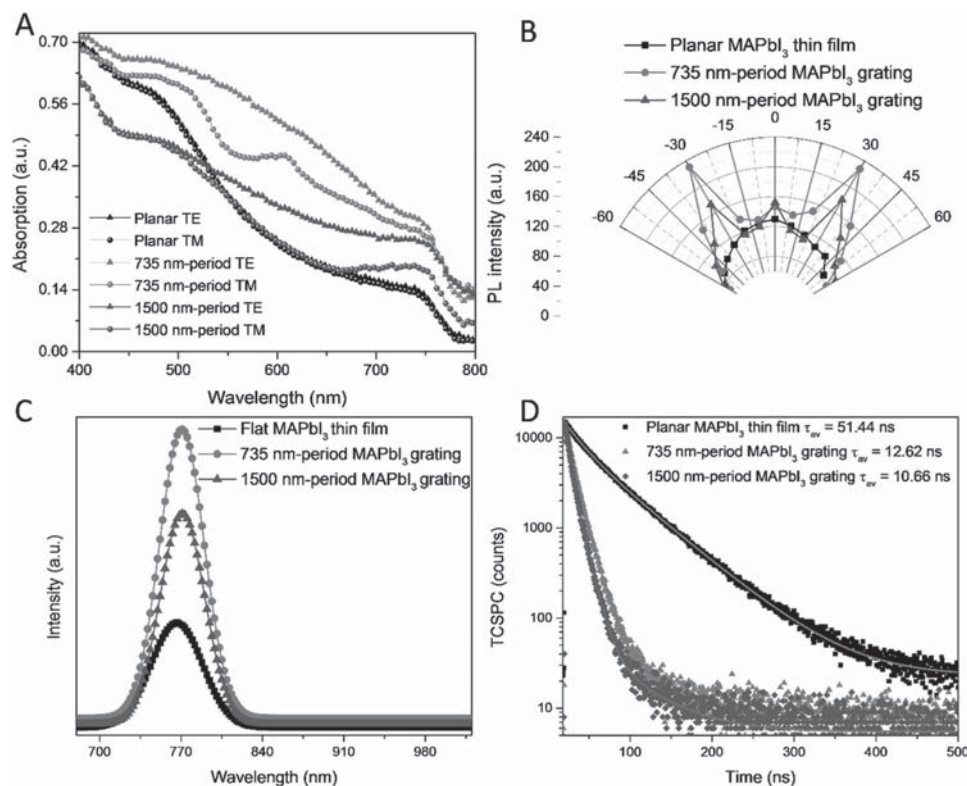


Figure 6. A) Absorption and B) angular PL distribution of the planar MAPbI₃ thin film, 735 nm period MAPbI₃ grating, and 1500 nm period MAPbI₃ grating on PEDOT:PSS/ITO substrate. C) PL spectrum of the planar MAPbI₃ thin film, 735 nm period MAPbI₃ grating, and 1500 nm period MAPbI₃ grating on PEDOT:PSS/ITO substrate at a detection angel of -30° . D) Time-resolved photoluminescence decay of the planar MAPbI₃ thin film, 735 nm period MAPbI₃ grating, and 1500 nm period MAPbI₃ grating on glass.

4. Experimental Section

Materials: PEDOT:PSS (P VP Al 4083) was purchased from Clevios. Lead (II) iodide (PbI₂, 99%) and 1,2-dichlorobenzene (DCB, anhydrous, 99%) were purchased from Sigma Aldrich. Dimethyl sulfoxide (DMSO, extra dry, 99%), dimethylformamide (DMF, extra dry, 99%), gamma-butyrolactone (GBL, extra dry, 99%), toluene (extra dry, 99.85%), calcium oxide (96%, extra pure), and methylamine (extra pure, 40 wt% in water) were bought from Acros Organics. Methylammonium iodide (MAI) and formamidinium iodide were purchased from Dyesol. PC₆₁BM was purchased from Solarmer Energy, Inc. Sylgard 184 Silicone Elastomer (base and curing agent) was purchased from Dow Corning.

MAPbI₃ Periodic Nanostructures Fabrication: First, the PEDOT:PSS/ITO substrate was fabricated via spin-coating of a PEDOT:PSS solution on ultraviolet ozone treated ITO glass at 3000 rpm and annealing at 130 °C for 10 min. Subsequently, the planar MAPbI₃ thin film was prepared on the PEDOT:PSS/ITO substrate according to the reported solvent engineering approach.^[20] More specifically, a 0.5 M precursor of PbI₂/CH₃NH₃I (molar ratio = 1:1) in a combinational solvent of DMSO/GBL (v/v = 3:7) was heated at 80 °C for 1 h and then spin coated on the PEDOT:PSS/ITO substrate with a speed of 1000 rpm for 10 s at first duration, and then 5000 rpm for 40 s at the second duration. Toluene was dripped on the spin-coating substrate at 17 s of the second duration (i.e., 27 s of the whole coating time). After spin coating, the substrate was baked at 100 °C for 10 min to crystallize the MAPbI₃ thin film. On the other hand, the planar, 735 nm period, and 1500 nm period PDMS molds were prepared via transferring from the grating by lithography.^[6,21] More specifically, the Sylgard 184 Silicone Elastomer base and curing agent (v/v = 10:1) were mixed uniformly and then poured on the patterned silicon grating or cleaned planar silicon. Annealing at 65 °C overnight led to the formation of a PDMS and silicon bilayer. Lift-off of

the PDMS from the silicon resulted in fabrication of the PDMS grating mold and PDMS planar mold. The PDMS mold was placed on a planar MAPbI₃ thin film. The above process was completed in a glove box. After covering with the PDMS mold, the MAPbI₃ device was put in a small container and then taken to an ambient environment. The container was filled with dry gaseous CH₃NH₂ (MA). The gas was prepared through heating aqueous MAI solution at 60 °C and drying twice with CaO powder. After several minutes of treatment with MA gas, the brown MAPbI₃ turned to transparent, indicating the formation of the liquid intermediate of CH₃NH₃PbI₃·CH₃NH₂. Subsequently, the container was transferred back to the glove box. The device in the container was taken out in the glove box. The back conversion of the intermediate to perovskite was performed using either room-temperature volatilization, annealing at 100 °C, or vacuum treatment (in the vacuum chamber at a pressure of 1 mbar). After a complete change of color from transparent to brown, the PDMS was lifted off, leading to the formation of MAPbI₃. Additionally, the prepared MAPbI₃ grating can be converted into an FAPbI₃ grating via ion exchange, as shown in Figures S8 and S9 (Supporting Information).

MAPbI₃ LED Fabrication: The structure of perovskite LED is ITO/PEDOT:PSS/MAPbI₃/PC₆₁BM/Ag. As for the planar perovskite LED, 20 mg mL⁻¹ PC₆₁BM in DCB was spin coated. The spin-coating rate of PC₆₁BM was optimized (500, 1000, and 2000 rpm), as shown in Figure S5 (Supporting Information). On the other hand, thicker PC₆₁BM was needed to fully cover the perovskite grating, so 30 mg mL⁻¹ PC₆₁BM was spin coated with a coating rate of 500 rpm. Finally, 100 nm Ag was deposited on PC₆₁BM via thermal evaporation under a vacuum of 10⁻⁴ Pa.

Characterization of the Perovskite Thin Film and LED: SEM (Hitachi S-4800 FEG) and AFM (NT-MDT NTEGRA Prima) were used to characterize the morphology of planar and patterned perovskite. The

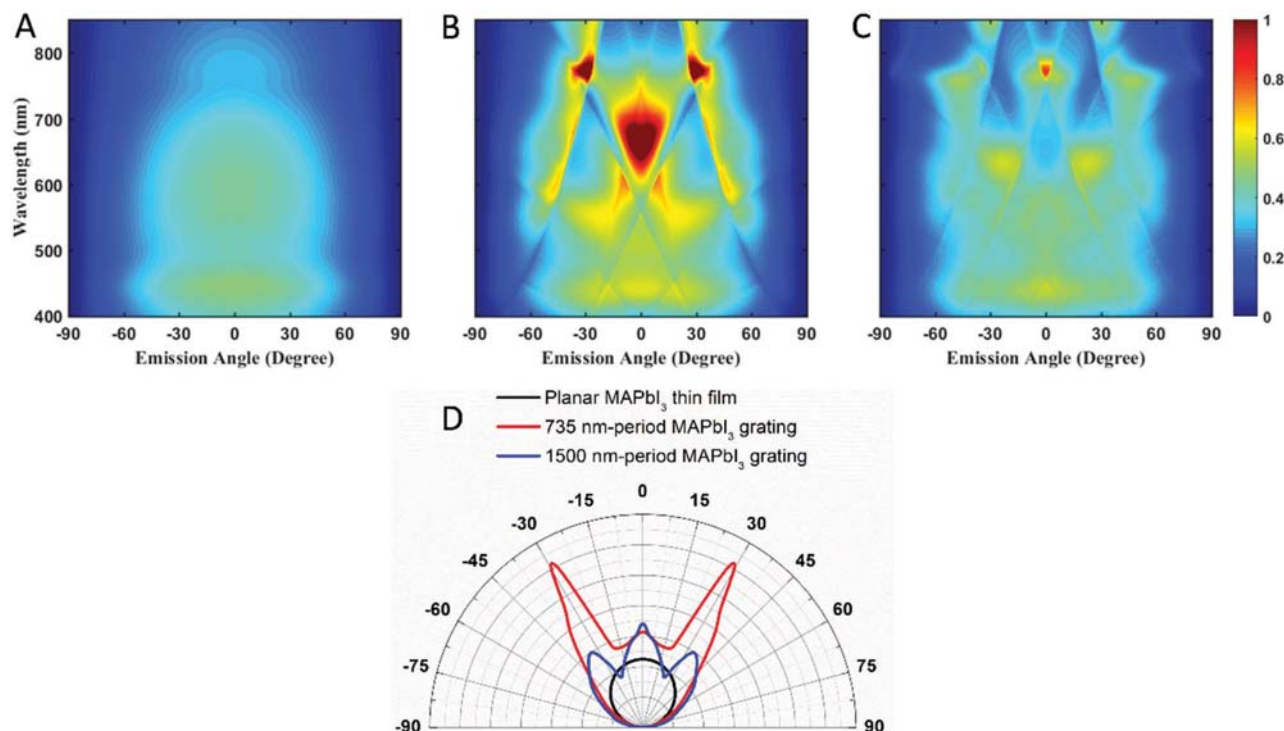


Figure 7. Angular- and wavelength-dependent radiation power of A) the planar MAPbI₃ film, B) the 735 nm period MAPbI₃ grating, C) the 1500 nm period MAPbI₃ grating on ITO (100 nm)/PEDOT:PSS (40 nm). D) Simulated angular distribution of the planar MAPbI₃ thin film, 735 nm period MAPbI₃ grating, and 1500 nm period MAPbI₃ grating after integrating wavelength from 700 to 800 nm. The simulated perovskite structure is glass/ITO (100 nm)/PEDOT:PSS (40 nm)/perovskite (60 nm depth for planar, 120 nm depth for grating).

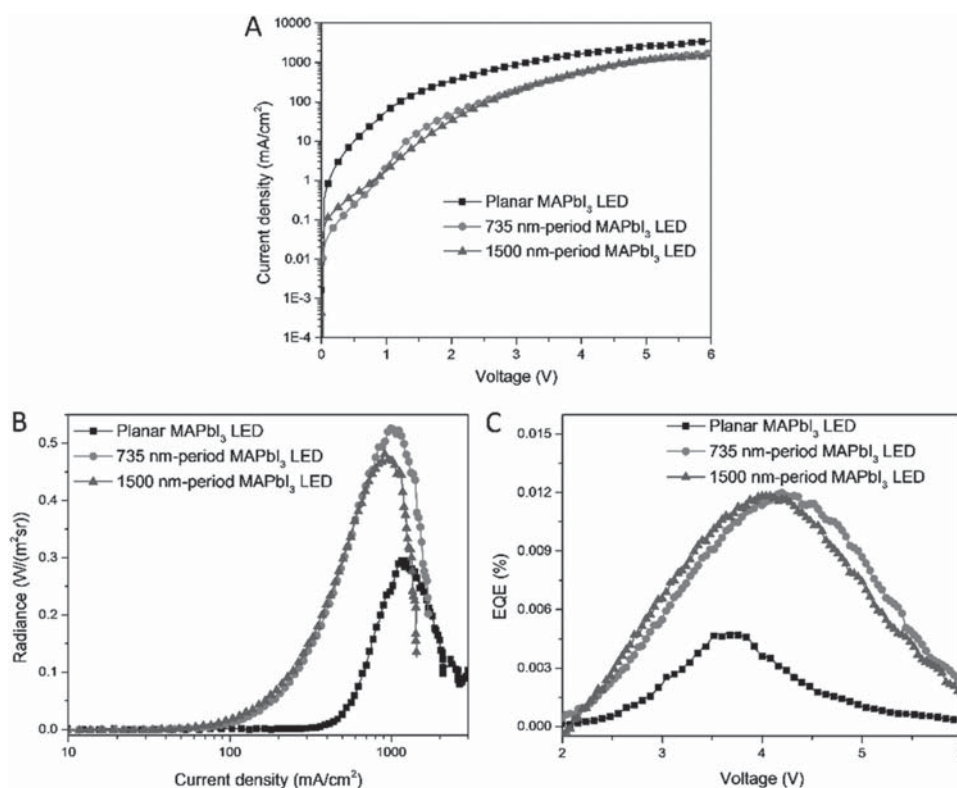


Figure 8. A) The plot of voltage–current density characteristics of the planar MAPbI₃ LED, 735 nm period MAPbI₃ LED, and 1500 nm period MAPbI₃ LED; B) the curve of current density–radiance characteristics of the planar MAPbI₃ LED, 735 nm period MAPbI₃ LED, and 1500 nm period MAPbI₃ LED; C) the curve of voltage–external quantum efficiency (EQE) of the MAPbI₃ LED, 735 nm period MAPbI₃ LED, and 1500 nm period MAPbI₃ LED.

SEM was performed under an acceleration voltage of 5 kV. The AFM was conducted under semicontact mold and a scan rate of 1 Hz. Probes HA_NC (NT-MDT) and VIT_P/Pt (NT-MDT) were used to measure AFM morphology and KPFM, respectively. The XRD spectrum was obtained using a Bruker D2 Phaser. The absorption spectrum was obtained from a home-build system with a xenon lamp as a light source and an integrated sphere associated with charge-coupled device (Ocean Optics QE Pro) as a detector. Polarized light was achieved after placing a polarizing prism (Thorlabs) between the light source and the sample. The light source for angular distribution of photoluminescence was a 325 nm pulse laser (6 ps, 100 Hz). The setup was shown in Figure S3 (Supporting Information). All of the samples were excited from normal direction at the same power intensity. The time-resolved photoluminescence of perovskite on glass was investigated using PicoQuanta FluoTime 300. A picosecond 375 nm pulse laser (LDH-P-C-375) with a pulse width of <40 ps and a repetition rate of 2 MHz was used to excite the perovskite. The time-resolved single was measured by a time-corrected single photon counting (TCSPC, PicoHarp 300E) module with photomultiplier (PMA-C 192-M) detector. The obtained data were fitted using either a bi-exponential function (for the pristine planar MAPbI₃ thin film and bare MAPbI₃ thin film treated with MA gas) or a triexponential function (for the MAPbI₃ thin film after being covered with flat PDMS and treated with MA gas, MAPbI₃ thin film after being covered with 735 nm period PDMS and treated with MA gas, and MAPbI₃ thin film after being covered with 1500 nm period PDMS and treated with MA gas)

$$I_{(t)} = \sum_{i=1}^i A_i e^{-\frac{t}{\tau_i}} \quad (3)$$

Perovskite LED was biased with a Keithley 2635 SourceMeter and the electroluminescence was recorded with Newport Model 818-UV.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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