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Efficient light-emitting diodes based on *in-situ* self-assembled perovskite nanocrystals

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Abstract. We introduce a simple and low-cost approach—drop-coating method—for preparation of *in-situ* self-assembled perovskite nanocrystals for efficient light-emitting diodes (LEDs). The photoluminescence (PL) spectrum of the self-assembled NFPI₄ nanocrystals thin film prepared by the drop-coating method shows blue shift compared with that of the typical NFPI₄ thin film prepared by the spin-coating method. In addition, the PL spectra of these self-assembled nanocrystals are tuned from 765 to 725 nm by changing usage amounts of the perovskite precursor solution. More importantly, efficient LEDs with external quantum efficiencies up to 6.8% are achieved based on these self-assembled NFPI₄ nanocrystals. © 2018 Society of Photo-Optical Instrumentation Engineers (SPIE) [DOI: [10.1117/1.JPE.8.046002](https://doi.org/10.1117/1.JPE.8.046002)]

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1 Introduction

Metal halide perovskites have attracted enormous attention in recent years because of their promising photoelectric properties. These materials show exceptional properties, including suitable bandgaps, high absorption coefficients, low trap densities, and long carrier diffusion lengths, leading to a rapid progress in solar cells, of which high power conversion efficiency over 22% has been achieved.^{1–5} As promising semiconducting materials, these materials are also used in other optoelectronic applications, such as light-emitting diodes (LEDs), lasers, transistors, and photodetectors.^{6–10} Because of their outstanding light-emitting properties, such as high color purity, readily tunable emissions, and high photoluminescence (PL) quantum yields (PLQY), increasing efforts have been devoted to developing efficient perovskite LEDs (PeLEDs).^{11–20} Impressively, external quantum efficiencies (EQEs) of PeLEDs have been rapidly progressed from <1% to 14.4% within 4 years.^{6,21}

To realize high-efficiency PeLEDs, high-quality perovskite thin films are required, which are typically prepared via spin-coating from either perovskite precursor solutions or colloidal-nanocrystal solutions.^{22–24} With the efforts to colloidal growth of perovskite nanocrystals,²⁵ breakthroughs on PLQYs (>90%) make these materials promising candidates for light-emitting applications.²⁶ Colloidal perovskite nanocrystals are usually prepared through a direct, non-template method that makes use of organic ligands to disperse the nanocrystals into nonpolar solvents before being applied into thin films. Thus, these *ex-situ* perovskite nanocrystals require complex chemical synthetic processes. Moreover, their PLQYs remarkably decrease when the colloidal-nanocrystal solutions are processed into thin films, due to unavoidable aggregation of the materials.²⁷

In this work, we report preparation of *in-situ* self-assembled perovskite nanocrystals through a simple and low-cost method—drop-coating method for efficient PeLEDs. A perovskite [formamidinium lead iodide with 1-naphthylmethylamine iodide (NMAI), denoted as NFPI₄] is chosen to prepare the *in-situ* nanocrystals, of which the physical and electrical properties have been studied. We find that PL spectrum of the self-assembled NFPI₄ nanocrystals shows blue-shift of ~42 nm compared with that of the typical NFPI₄ thin film obtained through

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spin-coating. In addition, the PL spectra of the self-assembled NFPI₄ nanocrystals are tuned from 765 to 725 nm by changing usage amounts of the perovskite precursor solution. Finally, efficient PeLEDs with high EQEs up to 6.8% are realized based on these self-assembled NFPI₄ nanocrystals.

2 Result and Discussion

Figure 1(a) shows schematic illustrations of spin-coating and drop-coating methods. Spin-coating is a widely used processing technique for preparation of perovskite thin films. During the spin-coating process, the perovskite precursor solution is dropped on a substrate that is placed in a spin coater, immediately followed by spinning under certain speed and time, and, subsequently, thermally annealing to form the perovskite thin film. Comparatively, the drop-coating method is first used to prepare perovskite thin films. A small amount of perovskite precursor solution is dropped on a substrate, which has full coverage by the solution. The substrate is then dried under vacuum and finally thermally annealed to form the perovskite thin film. In this work, a perovskite, denoted as NFPI₄, is fabricated by the drop-coating method with that obtained by spin-coating as a control. As shown in Fig. 1(b), both of the two prepared perovskite films show black phase (P3m1) with domain (111) lattice plane (diffraction peak at 13.9 deg).²⁸ And a weak diffraction peak at 11.8 deg is observed in the XRD patterns of both two films, which can be assigned to the (010) lattice plane of its yellow phase (P3). This suggests that NFPI₄ films prepared by these two methods show almost the same perovskite crystal structures. Evaluated using the Scherrer equation [Eq. (1)], the mean crystal size of the drop-coated film is 19 nm, which is similar to that (23 nm) of the film prepared by spin-coating:

$$\tau = \frac{K\lambda}{\beta \cos \theta}, \quad (1)$$

Fig. 1 (a) Schematic illustrations of spin-coating and drop-coating methods. (b) XRD patterns of perovskite films. Top-view SEM images of (c) typical NFPI₄ thin film prepared by spin-coating and (d) *in-situ* self-assembled NFPI₄ nanocrystals prepared by drop-coating.

Fig. 2 Optical properties of perovskite films. (a) Normalized absorption and PL spectra. (b) PL spectra in log scale. (c) PL spectra of the *in-situ* self-assembled nanocrystals prepared using different volumes of perovskite precursor solution.

where τ is the mean size of the ordered (crystalline) domains; K is a dimensionless shape factor (~ 0.89); λ is the incident x-ray wavelength (0.1504 nm); β is the line broadening at half the maximum intensity (FWHM) in radians; and θ is the Bragg angle.

Figures 1(c) and 1(d) show scanning electron microscopy (SEM) images of these two films. Interestingly, morphologies of the NFPI₄ films fabricated by these two methods show obvious difference. The NFPI₄ film prepared by spin-coating is uniform and shows good coverage with few pin-holes [Fig. 1(c)], whereas the drop-coated film shows isolated *in-situ* perovskite nanocrystals [Fig. 1(d)]. The average diameter of the nanocrystals is around 40 nm. These *in-situ* perovskite nanocrystals are self-assembled during slow evaporation of the N,N-dimethylformamide (DMF) solvent.

Optical properties of the two films are also studied. Normalized absorption and PL spectra are shown in Fig. 2(a). The absorption spectrum of the NFPI₄ thin film prepared by spin-coating shows an obvious exciton absorption peak at 568 nm, indicating that it contains layered perovskite phase with $n = 2$.²⁹ The dominating peak of its PL spectrum is located at 788 nm. The semi-log-scale PL spectrum of the spin-coated NFPI₄ thin film reveals several weak emission peaks at 576 and 647 nm, which correspond to layered perovskite phases with $n = 2$ and 4, respectively [Fig. 2(b)]. In comparison, the absorption spectrum of the thin film consisting of *in-situ* self-assembled NFPI₄ nanocrystals shows more absorption peaks. In addition to the absorption peak at 578 nm, it shows an additional absorption peak at 518 nm, which corresponds to the $n = 1$ layered perovskite phase. However, the absorption bands (>650 nm) from large- n layered perovskite phases disappear. Its dominating PL peak locates at 746 nm, blue shifted by 42 nm compared with that of the spin-coated NFPI₄ thin film. Meanwhile, an additional peak at 625 nm in the semi-log-scale PL spectrum can be found, which corresponds to $n = 3$ layered perovskite phase [Fig. 2(b)]. In addition, the dominating PL peak of the self-assembled NFPI₄ nanocrystals is tuned from 765 to 725 nm by changing the usage amounts of the perovskite precursor [Fig. 2(c)], which can be considered as a result of more small- n layered perovskite formed. The power-dependent PLQYs of the two films are measured [Fig. 3(e)]. The perovskite film prepared by drop-coating method shows higher PLQYs and keeps relatively constant in the region of excitation intensity from 0.03 to 1000 mW cm^{-2} .

Finally, we fabricate PeLEDs based on these two kinds of thin films. The device structure is indium tin oxide (ITO)/PEIE-modified ZnO/perovskite/poly(9,9-dioctyl-fluorene-co-N-(4-butylphenyl)diphenylamine) (TFB)/MoO₃/Ag, where the perovskite layer is prepared through spin-coating and drop-coating, respectively. Because of the p-n junction formed between hole-blocking ZnO layer and electron-blocking TFB layer, leakage current in the devices is negligible. Figure 3(a) shows the current density-voltage-radiance curves of the two devices. The device based on the spin-coated perovskite film shows lower turn-on voltage of 1.3 V and higher radiance of 124 $\text{W m}^{-2} \text{sr}^{-1}$. These values are 1.4 V and 73 $\text{W m}^{-2} \text{sr}^{-1}$, respectively, for the device using *in-situ* self-assembled perovskite nanocrystals. Figure 3(b) shows EQE-current density plots of these two devices, suggesting high EQEs of 12.1% and 6.8% for the devices with the spin-coated film and drop-coated film, respectively. Both two devices show very small efficiency roll-off at high current densities. The EL peak of the PeLED with self-assembled

Fig. 3 Device performance of NFPI₄ based PeLEDs. (a) Current density-voltage-radiance and (b) EQE-current density curves. (c) EL spectra under 2 V. (d) Stability data of the device based on self-assembled nanocrystals. (e) Excitation-intensity-dependent PLQEs of the films under continuous-wave laser excitation. (f) Histograms of peak EQEs of the devices based on self-assembled nanocrystals.

NFPI₄ nanocrystals locates at 787 nm, blue-shifted by around 5 nm compared with that of the PeLED with the spin-coated film [Fig. 3(c)]. The EL spectra have the same blue shift tendency compared with the PL spectra. The operational stability of the device based on self-assembled nanocrystals under a constant current density (10 mA cm⁻²) is shown in Fig. 3(d). The EQE shows an increase within several minutes, and then decreases to 60% of its initial value after 38 min. Figure 3(f) shows histograms of peak EQEs from 27 devices based on the self-assembled NFPI₄ nanocrystals, presenting an average EQE of 4.6% with a max EQE of 6.8%. This demonstrates good reproducibility of the drop-coated devices.

3 Experimental Section

3.1 Materials

Colloidal ZnO nanocrystals were synthesized following the reported solution-precipitation process.²⁹ Formamidinium iodide (FAI) was obtained from Dyesol, and PbI₂ was obtained from TCL (≥98.0% purity). NMAI was synthesized through the following procedures: hydroiodic acid (4.34 g, 45 wt% in water) was added to a stirring solution of 1-naphthalene-methylamine (12.72 mmol) and ethanol (30 ml), which was then kept at 0°C for 2 h. The solution was then evaporated at 50°C to give the NMAI precipitates, which was washed three times with ethyl acetate and then dried under vacuum. Other chemicals were obtained from Sigma-Aldrich.

The NFPI₄ perovskite precursor solution was prepared by dissolving NMAI, FAI, and PbI₂ with a molar ratio of 1:1:1 in DMF (Sigma-Aldrich, anhydrous, 99.8%) solution and then the solution was put on hot plate and stirred at 50°C for 2 h.

3.2 Preparation of Thin Films

The ZnO layer was prepared by spin-coating the colloidal ZnO solution on ITO-coated glasses at 4000 rpm for 30 s. Then, the ZnO-based substrates were transferred into an N₂-filled glovebox. Polyethylenimine ethoxylated (PEIE) was diluted in isopropyl alcohol to be 0.05 wt%, and then

spin-coated on ZnO at 5000 rpm for 30 s and annealed at 100°C for 10 min. The spin-coated perovskite film was deposited by spin-coating the perovskite precursor (10 wt%, 30 μ L) on ZnO/PEIE sublayer at 4000 rpm for 30 s and annealed at 100°C for 10 min. The drop-coated perovskite film was prepared by dropping the perovskite precursor (0.05 wt%, 15 μ L, or specified volumes) on ZnO/PEIE sublayer, dried under vacuum for 10 min, and then annealed at 100°C for 10 min.

3.3 Device Fabrication and Characterization

The ZnO, PEIE, and perovskite layers were prepared following the above-mentioned methods. The TFB layer was deposited from a chlorobenzene solution (12 mg/mL) at 3000 rpm for 30 s. Then, the films were transferred into a vacuum deposition system, where MoO₃ and Ag were deposited at the rates of 0.4 and 3 Å/s, respectively. The emitting area of the PeLEDs is 0.0725 cm² defined by the overlapping area of the ITO pattern and the Ag electrode. Characterizations of the devices were carried out at room temperature in a nitrogen-filled glove-box. Current density-voltage ($J - V$) characteristics were recorded by Keithley 2400 source meter. Forward-viewing spectral radiant flux was collected by an integrating sphere coupled with a QE65 Pro spectrometer. The EQE and radiance were calculated with the assumption that the PeLEDs are ideal Lambertian emitters, which are isotropic, emitting with equal radiance into any solid angle within the forward-viewing hemisphere.

3.4 Characterization

The surface SEM images were taken on a Philips XL30 FEG SEM operated at 5 keV. X-ray diffraction patterns were obtained using an x-ray diffractometer (Panalytical X'Pert Pro) with an x-ray tube (Cu K α , $\lambda = 1.5406$ Å). Absorption spectra were measured with a PerkinElmer model Lambda 900. Steady-state PL spectra were recorded with excitation by a 450-nm laser and an Andor spectrometer (Shamrock sr-303i-B, coupled to a Newton EMCCD detector) at room temperature in air.

3.5 External Quantum Efficiency Calculation

The EQE was determined as the product of the number of emitted photons to the number of injected electrons. The EQE is calculated based on the following equation:

$$\text{EQE} = \frac{N_p}{N_c} = \frac{e}{h \cdot c \cdot I} \int \varphi_{(\lambda)} \cdot \lambda d\lambda,$$

where N_p represents the number of emitted photons collected by the photodiode, N_c represents the number of injected electrons, e is elementary charge, h is Planck's constant, c is the speed of light in a vacuum, I is the current passing through the device, and $\varphi_{(\lambda)}$ is the EL spectra collected by the photodiode.

4 Conclusion

In conclusion, we report a simple and low-cost method—drop-coating method—for preparation of *in-situ* self-assembled perovskite nanocrystals for efficient PeLEDs. The PL spectrum of the self-assembled NFPI₄ nanocrystals prepared by drop-coating shows blue shift compared with that of typical thin film prepared by spin-coating. In addition, the PL spectra of the self-assembled NFPI₄ nanocrystals are tuned from 765 to 725 nm by changing the volumes of the perovskite precursor solution, which is considered as a result of more small- n layered perovskite formed. A series of PeLEDs are fabricated with the *in-situ* self-assembled NFPI₄ nanocrystals as the light-emitting layer, of which a high EQE of 6.8% is realized with an average EQE of 4.6%, demonstrating good reproducibility.

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