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Enhanced emission from CH$_3$NH$_3$PbBr$_3$ perovskite films by graphene quantum dot modification

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Abstract

Organic–inorganic hybrid perovskites have emerged as promising emitters with the benefits of low cost and high color purity, but their low luminescence efficiency is a drawback for practical application on light emitting devices. Here we show that by incorporating proper amount of graphene quantum dots (GQDs) into perovskite precursor, dense CH$_3$NH$_3$PbBr$_3$ films with reduced grain size and well passivated grain boundaries could be obtained. This gives rise to enhanced emission from GQD modified perovskite films. Our work thus provides a viable way to prepare highly luminescent perovskite films for optoelectronic applications.

Introduction

Organic–inorganic hybrid perovskites have attracted significant interest in solution processed high-performance optoelectronic devices [1–18]. Besides the great success in photovoltaics, their unique optical and electrical properties make hybrid perovskites promising candidates for next generation light emitting diodes (LEDs) [19–26]. Many efforts have been made to enhance the luminescence from hybrid perovskites, such as passivating defects [27–31], constructing multiple quantum wells [30], utilizing plasmonic structures [31, 32], and so on. Among these methods, growth of dense and low-defect films is most essential [33, 34]. Additive-assisted growth method has been widely studied to modulate the morphology of hybrid perovskites [34–36]. For example, Himchan Cho et al introduced 2,2′,6′-(1,3,5-benzinetriyl)-tris(1-phenyl-1′-H-benzimidazole) (TPBi) into precursor to inhibit the growth of perovskite crystals [34]. Our previous report shows that n-butyl amine would terminate the grain surface and inhibit crystal growth [35]. Lewis base additives such as dimethyl sulfoxide (DMSO) could form adduct with PbI$_2$ and delay the crystallization of perovskites, promoting the formation of large grains [36]. Due to the low exciton binding energy in hybrid perovskites, small nanograins could help confine excitons and enhance radiative recombination, while large grains would facilitate dissociation of excitons [34]. In this regard, perovskite LEDs would favor films with small grains and well passivated grain boundaries.

As a kind of star materials with unique optoelectronic properties, two-dimensional (2D) materials have been used to improve the performance of perovskite optoelectronic devices, mostly as interfacial layers to enhance carrier transportation [37–39]. 2D material quantum dots have also been incorporated into iodide perovskite films to passivate grain boundaries and to improve photovoltaic performances [40, 41]. However, there are few reports about incorporation of 2D materials into bromide perovskites as well as its effect on optical properties. Here we introduce graphene quantum dots (GQDs) into the methylammonium lead bromide (MAPbBr$_3$) perovskite precursor and evaluate the effects of GQD addition on the film morphology and optical characteristics. We found that GQD incorporation could significantly increase the luminescence of MAPbBr$_3$ films.

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Experimental sections

Materials
Methylammonium bromide (MABr) and lead bromide (PbBr₂) were purchased from Xi’an Polymer Light Technology Corp. DMSO and dimethylformamide (DMF) were purchased from Sigma-Aldrich. Ethyl acetate was purchased from Aladdin. Graphene quantum dots were purchased from Nanjing XFNANO Materials Tech Co., Ltd. The GQDs were dissolved in DMF and the concentration was 1 mg ml⁻¹. All the materials were used as received without further purification.

Perovskite film fabrication
PbBr₂ and MABr (1:1 molar ratio) were dissolved in DMF/DMSO mixed solvent, and then different amount of GQD solution was added into precursor solution. The concentration of MAPbBr₃ in precursor was 40 wt%. The concentrations of GQDs normalized by the weight of MAPbBr₃ in precursor were 0 wt%, 0.03 wt%, 0.07 wt%, 0.1 wt%, and 0.2 wt%, respectively. The perovskite precursor was spin-coated at 300 rpm for 10 s and 3000 rpm.
for 60 s. Ethyl acetate as anti-solvent was dropped in the second step. Afterwards, the perovskite films were annealed at 120 °C for 10 min on a hotplate.

**Characterization**

Transmission electron microscope (TEM) images of GQDs were recorded on a JEM2100 (Japan). Field emission scanning electron microscope (FE-SEM) images of perovskite films were recorded on a Hitachi S4800 (Japan). X-ray diffraction (XRD) patterns were recorded on a Bruker D8 Advance x-ray diffractometer (Germany). Steady-state, time-resolved photoluminescence (PL) and PL quantum yield (PLQY) were recorded on an Edinburgh FLS920 spectrometer (United Kingdom), with a xenon lamp and a 405 nm pulsed laser diode as excitation source.

**Results and discussion**

Figure 1(a) shows the TEM images of GQDs. The size of GQDs is about 5 nm. Figures 1(b)–(f) show the SEM images of MAPbBr₃ films with different amounts of GQDs. For the control sample without GQDs, the crystals are large with a wide size distribution (figure S1 is available online at stacks.iop.org/MRX/7/016415/mmedia). The average grain size for the control sample is 383 nm. With the addition of GQDs, the grains become small with a narrower size distribution. The average grain size decreases continuously with the increase of GQD concentration, from 337 nm for the sample with 0.03 wt% GQDs to 138 nm for the sample with 0.1 wt% GQDs. All the films are dense without pinholes except for the sample with 0.2 wt% GQDs. Many pinholes emerge on that sample and the surface is fuzzy, making it difficult to extract the average grain size. We believe that GQDs act as either heterogeneous nucleation centers that accelerate the nucleation of perovskites, or terminators that inhibit the growth of perovskite crystals [40]. In each case, the grain size of perovskite films would decrease with the increase of GQD concentration.

Figure 2 shows the x-ray diffraction patterns of perovskite films with different amount of GQDs. The control sample have two XRD peaks at 15.0° and 30.2°, which correspond to (100) and (200) lattice planes of cubic structure for MAPbBr₃. With the addition of GQDs, the intensity of these peaks decreases and the full width at half maximum increases, consistent with the decrease of grain size. Moreover, new peaks emerge at 21.3°, 33.9°, 37.5°, which correspond to (011), (021), and (211) lattice planes of cubic structure. Notably, the (211) peak becomes more intense than the (100) peak in the sample with 0.2 wt% GQDs. This indicates that the incorporation of GQDs would affect the orientation of perovskite crystals, promoting a preferential orientation of (211) plane. Due to the low concentration of GQDs in the precursor, no XRD peaks corresponding to GQDs could be observed.

Figure 3(a) shows the PL spectra of MAPbBr₃ films with different amount of GQDs. All the spectra show similar shape with peaks at about 535 nm. The PL intensity increases with the increase of GQD concentration, peaking at 0.1 wt%. The PL intensity of the sample with 0.1 wt% GQDs is about 2.7 times that of the control sample. However, the PL intensity decreases when the GQD concentration exceeds 0.2 wt%. This might be due to increased nonradiative recombination in such a film with deteriorated morphology. To verify this hypothesis,

![Figure 2. XRD patterns of MAPbBr₃ films prepared by precursors with different amount of GQDs.](image-url)
we have conducted time-resolved PL spectra measurement, as shown in figure 3(b). The spectra are fitted with a bi-exponential decay function [34], which gives a short lifetime $\tau_1$ and a long lifetime $\tau_2$, as listed in table 1. The short lifetime $\tau_1$ is related to recombination at grain boundaries or surfaces, while the long lifetime $\tau_2$ is related to recombination inside the grains. Both $\tau_1$ and $\tau_2$ increase with the increase of GQD concentration until it reaches 0.1 wt%. After that, $\tau_1$ and $\tau_2$ start to decrease. The evolution of PL lifetime with GQD concentration is consistent with that of PL intensity. This indicates that GQDs could effectively passivate defects in MAPbBr₃ films and result in enhanced emission. On the other hand, GQD overload could deteriorate the morphology of MAPbBr₃ films, inducing defects and causing nonradiative recombination. The PLQY is 2.5%, 3.1%, 5.6%, 9.6%, and 0.9% for the sample with GQD concentration of 0 wt%, 0.03 wt%, 0.07 wt%, 0.1 wt%, and 0.2 wt%, respectively.

### Conclusion

In summary, GQD incorporation would decrease the average grain size of perovskite films and modify the preferential crystal orientation from (100) to (211). A proper amount of GQDs (0.1 wt%) could lead to dense film with well passivated grain boundaries, boosting the luminescence as well as PL lifetime. On the contrary, GQD overload would induce pinholes on the films, decreasing the luminescence. Our work clarifies the effect of GQD incorporation on the morphological, structural, and optical properties of MAPbBr₃ films, and would provide a feasible way to fabricate high-quality perovskite films for light emission.

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### Author contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.
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