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Controllable lasing performance in solution-processed organic-inorganic hybrid perovskites

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Solution-processed organic-inorganic perovskites are fascinating for their remarkable photo-conversion efficiency and great potentials in the cost-effective, versatile and large-scale manufacturing of optoelectronics devices. In this paper, we demonstrate that the perovskite nanocrystal sizes can be simply controlled by manipulating the precursor solution concentrations in a two-step sequential deposition process, thus achieving the feasible tunability of the excitonic properties and the lasing performance in the hybrid metal-halide perovskites. The lasing threshold is at around 230 μJ/cm² in this solution-processed organic-inorganic lead-halide material, which is comparable to the colloidal quantum dot lasers. The efficient stimulated emission originates from the multiple random scattering provided by the micro-meter scale rugged morphology and polycrystalline grain boundaries. Thus the excitonic properties in perovskites exhibit high correlation to the formed morphology of the perovskite nanocrystals. Compared to the conventional lasers normally served as a coherent light source, the perovskite random lasers are promising in making low-cost thin-film lasing devices for flexible and speckle-free imaging applications.

1. Introduction

Hybrid organic-inorganic metal-halide perovskites (CH₃NH₃PbxClₓ, Brₓ, or I) have attracted much recent attention due to their great solar energy conversion performance, which can be comparable to the light-absorbing semiconductor components in photovoltaic cells. Since Kojima et al. first proposed to replace the dye with a layer composed of the perovskite structures in dye-sensitized solar cells, the photo-conversion efficiency of proposed solar cell structures has been improved with an unprecedented growth among different photovoltaic technologies and has currently achieved a remarkable milestone of more than 20%. Moreover, advanced studies have shown that the photoluminescence (PL) quantum efficiencies of perovskites exceed 70% and the lasing behaviour in hybrid perovskite films exhibits an emission wavelength tunability at different halide compositions. These promising light emitting properties make the perovskites as alternative materials for the lighting applications such as the efficient on-chip coherent light sources and white-light light-emitting diodes.

Among the considerable research efforts made on the perovskite-based light emitters and lasing devices, the optical performances of the perovskites have been reported and can be controlled via different fabrication processes such as the low-temperature solution growth, chemical vapor deposition, and the two-step vapor synthesis. Other post-processing methods such as the insertion of a perovskite layer between a dielectric mirror and top evaporated gold mirrors or the conformal formation of a perovskite layer on SiO₂: spherical resonators via the atomic layered deposition (ALD) were also employed to enhance the photoluminescence efficiency of the perovskite-based devices. According to their results, the lasing thresholds reported in these works are in a wide range from hundreds nJ/cm² to hundred μJ/cm². Moreover, several studies have been conducted to investigate the specific material properties and excited-state dynamics in the perovskite crystalline structures, expecting to reveal the internal electron-photon interaction processes accompanied with established theoretical models.

In the halide crystalline structure, the heavy elements of the lead (Pb) and iodine (I) are the key factors in corresponding optoelectronic characteristics such as the polarizability and the effective charge carrier masses. Thus in this article, we employ the variation of the PbI₂ solution concentration in a relatively simple and low-cost two-step sequential deposition process of the perovskite synthesis and demonstrate that the excitonic properties and lasing performance of the perovskite nanocrystals can be manipulated. Via a series of corresponding PL measurements for the investigation of the excited-state dynamics and the random lasing behaviours, the results show the fascinating excitonic properties with large exciton binding energy in this organic-inorganic lead-halide material, suggesting that the perovskites can be one of the most promising high optical...
gain materials for the novel light-emitting devices operated at room temperature. The efficient stimulated emission may originate from the multiple random scattering provided by the micrometer scale rugged morphology and polycrystalline grain boundaries in the coexisting crystallographic phases. Comparing to the conventional lasers normally served as a coherent light source, the perovskite random lasers could be promising in making practical thin-film lasing devices for flexible and speckle-free imaging applications.

2. Experimental

2.1 Materials

The solution-processed organic-inorganic halide perovskite thin films were prepared in a two-step sequential deposition process as the schematic diagram shown in Fig. 1(a). In the fabrication process, first the powdered lead iodide (PbI2, Sigma-Aldrich) was completely dissolved in N, N-dimethylformamide (DMF) and kept stirring overnight inside a nitrogen-filled glove box. Then the as-prepared PbI2 solution was spin-coated onto cleaned glass substrates and subsequently dried at 80 °C for 15 minutes, forming a yellow PbI2 film. Next, the PbI2 film was covered with a 1 wt% precursor solution of methylammonium iodide (MAI, Sigma-Aldrich) in 2-propanol (IPA) at room temperature. The IPA solution was gradually dried in 40 seconds and the sample was subject to a spin-coating process in order to remove the solvent completely. In order to drive the interdiffusion of the two precursors, the resulting films were annealed at 100 °C for 2 hours, finally generating dark-brown CH3NH3PbI3 perovskite layers.

2.2 Film morphology

In the two-step spin-coating deposition method, the perovskite film morphology can be manipulated by well controlling the PbI2 solution concentration, the thickness of PbI2 films and the adding process of the MAI solution.32,33 The top-view scanning electron microscope (SEM) images (Figs. 1(b) to 1(e)) show the corresponding morphology evolution of the perovskite layers fabricated with PbI2 solution concentration in a range changed from 10 wt% to 40 wt%. As presented in the images, more air-voids formed in the perovskite samples fabricated with lower PbI2 solution concentration, comprising inhomogeneous films with rugged surface and randomly distributed grain boundaries. This may result from the insufficient PbI2 component involved in the reaction process. The air-void occupation area is about half of the total area (58 %) as the PbI2 solution is prepared at 10 wt%. These air cavities would gradually shrink with an increase of the PbI2 solution concentration, generating a compact thin film with the air-void occupation ratio of 2 % at the PbI2 solution of 40 wt%.

2.3 Structural configurations

To characterize the structural configurations of the perovskites which were fabricated at different PbI2 solution concentrations, X-ray diffraction (XRD) measurements were conducted and the acquired XRD patterns are shown in Fig. 2(a). In the XRD spectra, the main diffraction peaks, assigned to the (110), (220) and (310) peaks at scattering angles 2θ of 14.07°, 28.42° and 31.92°, all can be clearly observed as the PbI2 solution concentration in perovskite fabrications higher than 30 wt%. These three major peaks indicate that the perovskite films fabricated with high PbI2 solution concentration are composed of the perovskite phase with tetragonal structures.34 With an increase of the metal-halide involved in the reaction process, a significant peak of the residual PbI2 crystals displays at the (001) plane. To confirm this peak position correlated to the PbI2 crystals, a lower concentration of the MAI precursor solution of 0.5 wt% was used to prepare the perovskite samples as a comparison counterpart. As a result, a higher PbI2 crystal peak intensity was obtained in the XRD spectra as the black curve shows, suggesting that more PbI2 crystals do not involve in the reaction and still remain in the perovskite samples.

Regarding the perovskites fabricated with lower PbI2 solution concentration, the three major peaks still remain but with relatively low intensity and slightly shift to the scattering angles at 14.07°, 28.32° and 31.72°. The subtle angle changes may refer to the orthorhombic phase generated in the composed perovskite films.35 In the fabrication process with lower PbI2 solution concentration, the incomplete transformation of MAI-PbI2-DMF may coexist within the perovskites, resulting in a diffraction peak occurred at 11.4° as the XRD patterns show in Fig. 2(a).36,37 Among these structural characterization results, we found that the perovskite compositions could be manipulated by changing the precursor solution concentrations in the reaction process and a high level of the structural purity could be obtained as the PbI2 solution was controlled at 30 wt%, giving an evident diffraction peak of perovskite crystalline structures at the (110) direction. In the process of forming perovskite crystals, the methylammonium cations (CH3NH3+) were embedded in the PbI2 octahedra, acting as the capping ligands.38 Thus, different ratios of the CH3NH3 and PbI2 solutions may affect the perovskite nanocrystals growth during the deposition process.
Also, the incomplete reaction may leave some unwanted composites in the prepared samples, further influencing their optical properties and light emission performance.

Fig. 2 Structural configurations and light emission performance of perovskite films prepared with different PbI$_2$ solution concentrations. (a) XRD patterns show that a high-level structural purity of the fabricated perovskites can be obtained as the PbI$_2$ solution controlled at 30 wt%._(b) PL emission peak positions of the perovskite layers fabricated at different PbI$_2$ solution concentrations. A clear peak position change occurs as the PbI$_2$ solution concentration exceeds 30 wt%, indicating that the material compositions may be altered with different ratios of the precursor solutions in the interdiffusion process. The insets (i) and (ii) show the lasing behaviour of the perovskite samples which were fabricated with 30 wt% and 40 wt% PbI$_2$ solution, respectively. The emission peak linewidths of the both perovskite samples drop down to below 3 nm from about ~16 nm. The nonlinear emission intensity and peak width variation indicate a typical fingerprint of lasing action.

3. Results and discussion
3.1 Light emission performance

A series of the power-dependent PL measurements was conducted to investigate the corresponding light emission properties using a third harmonic generation (THG) of a Nd:YVO$_4$ pulse laser as an optical excitation light source of 355 nm, while the pulse duration and the repetition rate were 0.5 ns and 1 kHz, respectively. More detailed PL experimental configuration is provided below in the method section. Figure 2(b) shows the light emission performance of the perovskite samples fabricated at different PbI$_2$ solution concentrations, while the results are extracted from the PL measurements which were conducted at 77K. From the results, a significant emission peak shift from 745 nm to 800 nm can be observed as the PbI$_2$ solution concentration exceeds 30 wt%. The emission peak difference may result from the perovskite phase states, material compositions or structural variations in the synthesized perovskites as interpreted in the XRD spectra, suggesting that the material properties and corresponding optical performance may be simply manipulated by different PbI$_2$ solution concentrations.

The insets in Fig. 2(b) show the lasing behaviours of the perovskites fabricated with 30 wt% and 40 wt% PbI$_2$ solution. The lasing peaks of the two perovskite samples occur at around 745 nm and 800 nm, while the peak linewidths at full width at half maximum (FWHM) both drop down from ~16 nm to about 3 nm with a gradually increased pumping power.

To have a closer look into the structural configuration of the perovskites fabricated at different metal-halide solution concentrations, the transmission electron microscopy (TEM) was employed and the corresponding crystalline structures of perovskite samples fabricated with 30 wt% and 40 wt% PbI$_2$ solution are demonstrated as the TEM images shown in Figs. 3(a) and 3(b), respectively. The perovskite nanocrystalline structures are densely distributed as inclusions in the fabricated thin films, while the perovskite nanocrystals grow in (110) crystal orientation direction. We also estimated the nanocrystal size and the size distribution of the perovskite samples fabricated with 30 wt% and 40 wt% PbI$_2$ solution concentrations as the results shown in Figs. 3(c) and 3(d). It is observed that the perovskite nanocrystals have the maximum size distributions in a range of 6-10 nm and 21-25 nm for the perovskite films fabricated with 30 wt% and 40 wt% PbI$_2$ solutions, respectively. Thus the packing densities of the fabricated perovskite films can be estimated to be around $2.26\times10^{11}$ and $6.45\times10^{10}$ particles/cm$^2$ for these two samples. Since the geometry of nanocrystalline structures would significantly influence the electro-optical properties, these structural configurations may provide us more information to further understand the excitonic properties of the perovskite films.

Fig. 3 Crystalline structure formation in synthesized perovskites. (a) and (b) represent the TEM images of the two perovskite samples. The perovskite nanocrystalline structures grow in (110) crystal orientation direction. (c) and (d) show the nanocrystal size distribution of the CH$_3$NH$_3$Pb$_x$ perovskite thin films fabricated with 30 wt% and 40 wt% PbI$_2$ solutions, respectively. The maximum size distribution of the crystalline perovskites is around 6-11 nm and 21-25 nm indicated in (c) and (d). The insets shown in (c) and (d) correspond to the fast Fourier transform in selected area circled in (a) and (b). The sharp diffraction peaks clearly indicate the single crystalline structures in perovskites.
3.2 Excitonic properties

The excitonic properties of the perovskite nanocrystals synthesized with 30 wt% and 40 wt% PbI₂ solutions were investigated by conducting the temperature-dependent PL measurements, while the corresponding integrated PL intensities at different temperatures are represented in Fig. 4(a) and 4(b), respectively. To refrain the structural phase-transition in perovskite films during the temperature-increasing process, the temperature carried out in measurements was controlled to be changed in a range from 77 K to 180 K. As the results show in Fig. 4, the PL intensity integrated over an emission band from 710 nm to 810 nm changes as a function of the ambient temperature and may mainly attribute to the thermal dislocation of the exciton in the synthesized perovskite films. The exciton binding energy \( E_b \) can be estimated using the following equation,

\[
I(T) = R \left[ 1 - \exp \left( -\frac{E_b}{k_b T} \right) \right] + c.
\]

where \( R \) is the generated exciton density and \( k_b T \) is the thermal energy at different temperatures.\(^{15,19}\) Therefore, the exciton binding energy \( E_b \) for the perovskite samples fabricated with 30 wt% and 40 wt% PbI₂ solutions can be estimated ~92 meV and ~38 meV via the fitting process as shown in Figs. 4(a) and 4(b), respectively. The larger exciton binding energy \( E_b \) obtained in perovskite films fabricated with 30 wt% PbI₂ solution indicates that the lasing performance may be easier to be accomplished by using the perovskite thin films at a high structural purity, which is correspondent with the results demonstrated in the insets in Fig. 2(b).

![Fig. 4 Exciton properties of perovskite nanocrystals synthesized at different PbI₂ solution concentrations. (a) and (b) show the corresponding integrated PL intensities (solid spheres) extracted from a series of the temperature-dependent PL measurements of the perovskite films fabricated with 30 wt% and 40 wt% PbI₂ solutions, respectively. The temperatures are in a range from 77 K to 180 K, while the PL intensities are integrated over an emission band from 710 nm to 810 nm, covering the both emission peaks of the solution-processed perovskite films.](image)

3.3 Random lasing performance

Since there are no specifically defined laser cavities in the fabricated perovskite samples, it would be of interest to further investigate the lasing performance of the organic-inorganic metal-halide perovskites. First Fig. 5(a) shows the measured power-dependent PL emission spectra of the perovskite films fabricated with PbI₂ solution of 30 wt%. With gradually increased pumping powers, the emission intensity increases dramatically as the excitation power exceeds the threshold pumping power density of 230 μJ/cm², which is demonstrated by the log-scale light-light curve in the inset of Fig. 5(a). The nonlinear peak intensity increasing and a clear S-curve in the log-log plot strongly indicate the occurrence of lasing actions in the perovskites crossing over from the spontaneous emission and amplified spontaneous emission to the stimulated emission. The lasing thresholds of our perovskites are not comparable to the reported lowest threshold of 600 nJ/cm² in single crystalline perovskite nanowires; however, such a relatively easy solution-processed fabrication method still show its advantages in cost-effective and large-scale mass production.\(^{13}\) Furthermore, in our work, we demonstrated that the perovskite nanocrystal sizes and the corresponding emission wavelengths can be manipulated with the PbI₂ solution concentrations, instead of using the stoichiometry-dependent tunability. The inset in Fig. 5(a) shows the emission peak intensities extracted from the measured PL spectra at 77K as a function of the pumping powers. By dividing the slopes below and above the lasing threshold in the light-light curve, the spontaneous emission factor \( \beta \) of 5×10⁻³ can be estimated.

![Fig. 5 Lasing characteristics of the solution-processed CH₃NH₃PbI₃ perovskites at 77 K. (a) Power-dependent PL emission spectra of the perovskites fabricated with 30 wt% PbI₂ solution. The optical pumping density is gradually increased up to 0.7 mJ/cm², while a sharp emission peak occurs at 745 nm above the lasing threshold of about 230 μJ/cm². In the inset, the nonlinear peak intensity increasing as a function of the incident pumping densities indicates that the perovskite film is under stimulated emission operation. The dashed line represents the light-light fitting curve of the extracted data from the experimental results calculated using the modified rate equations. (b) Comparison of the extracted lasing thresholds from experimental data and the calculated threshold gains of the perovskites films fabricated with different PbI₂ solution concentrations. The inverse point appears at 30 wt% refers to the changing of morphology and the size of the crystalline structures. (c) The multiple PL emission peaks at high pumping power density of around 1.9 mJ/cm² may suggest the random lasing behaviour in perovskites which may result from the random scattering provided by the polycrystalline grain boundary at different sizes. (d) The ARPL measurements of the perovskite film fabricated at PbI₂ solution of 30 wt%.](image)
To understand the influence of the nanocrystals size effect on the optical properties, the lasing thresholds of perovskites fabricated at different PbI₂ solution concentrations are plotted in Fig. 5(b) with corresponding calculation results. The threshold pumping power density of perovskites decreases as the weight percentage of PbI₂ solution increases from 10 wt% to 30 wt%. This may originate from more nanocrystals generated in perovskites which may function as scattering centres, giving randomly distributed grain boundaries and also the increased volume fraction of the gain media. With an increase of the PbI₂ solution concentration to 40 wt% during the perovskite films fabrication, the threshold tendency of the thin film is reversed. This may result from the incomplete reaction process and the residual composites may reduce the random scattering. In addition, the larger size of the perovskite nanocrystals obtained after the material synthesis, the weaker exciton properties would affect the light emission properties.

Figure 5(c) shows the power-dependent PL emission spectra of the perovskite film fabricated with 30 wt% PbI₂ solution. Under low optical power excitation, only broad spontaneous emission spectra can be observed. With a gradually increased pumping fluence, the emission intensity increases dramatically as the pumping fluence exceeds the lasing threshold of 230 μJ/cm², while the emission peak appears at around 745 nm as represented in the inset (i) in Fig. 2(b). As the incident optical pumping density increases to around 1.9 mJ/cm², multiple emission peaks occur in the acquired PL emission spectra. The multiple PL emission peaks may suggest that the random lasing performance occurs in the fabricated perovskite films. Regarding the random lasing in perovskites, R. Dhanker, et al. has observed and demonstrated that random lasing actions in one-step solution-processed perovskite with microcrystal networks, which may result from the ballistic waveguiding in linear network segments. In their work, the lasing threshold decreased with increasing the illumination area and a low lasing threshold could be found to be slightly less than 200 μJ/cm². Different from their findings, we consider that the random lasing may originate from the multiple random scattering provided by the microscale rugged morphology and nanoscale grain boundaries in the coexisting crystallographic phases. The random lasing performance in perovskite films can be further characterized and examined by the angular-resolved PL (ARPL) measurements, while the result is shown in Fig. 5(d), showing that the light radiation from the planar perovskites is in a wide angle due to the contribution of random scattering.

Though lasers are normally thought of as a source of coherent light, they can also emit radiation in the regimes of temporally or spatially incoherent light emissions. The high power sources with spatially incoherent radiation might be useful in illumination and projection systems. Thus one of the most promising applications of random lasers may be in imaging apparatus. In terms of the optical imaging systems, highly coherent light sources such as conventional lasers suffer in some imaging and lighting applications from shifting patterns of bright and dark zones that appear when a laser beam passes through a scattering medium - speckles. Such speckles may result in the quality degradation of images recorded using laser radiation. Random lasers with low spatial coherence are very attractive for speckle-free imaging offering solutions alternative to low-brightness light-emitting diodes or incoherent lamps. A range of other potential applications of random lasers includes medical applications, compact light sources, spectroscopic monitoring devices, illumination materials and others. Therefore, the random lasing performance and relatively low lasing threshold properties of the solution-processed perovskite thin films may make the perovskites as potential materials for the efficient and cost-effective coherent light sources implementation in the near future.

4. Conclusions
In conclusion, the size effect of the perovskite nanocrystals can be simply manipulated by changing the precursor solution concentrations in a two-step sequential deposition process, achieving the tunable light emission wavelength with the lasing threshold of around 230 μJ/cm², which is comparable to the colloidal quantum dot lasers. From the morphology and optical characterizations, the efficient stimulated emission of the perovskites may originate from the multiple random scattering provided by the micron-meter scale rugged morphology and polycrystalline grain boundaries in the coexisting crystallographic phases. Thus, the high optical gain is manifested by the excitons generated in perovskite nanocrystals with large exciton binding energy. Comparing to the conventional lasers normally served as a coherent light source, the random cavity sources with spatially incoherent radiation might be useful in illumination, projection, and imaging systems while highly coherent sources suffer speckle problems, which result in the degradation of image quality. Therefore, a range of potential applications of this solution-processed perovskite random lasers including flexible and compact light sources, medical applications, spectroscopic monitoring devices, versatile illumination materials and others can be expected.

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Notes and references