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Improvement of Photoluminescence of Perovskite $CH_3NH_3PbI_3$ by Adding Additional CH_3NH_3I during Grinding

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The organic-inorganic hybrid perovskite $CH_3NH_3PbI_3$ has been a good candidate for many optoelectronic applications such as light-emitting diodes due to its unique properties. Optimizing the optical properties of the $CH_3NH_3PbI_3$ material to improve the device performance is a hot topic. Herein, a new strategy is proposed to enhance the light emission of $CH_3NH_3PbI_3$ phosphor effectively. By adding the reactant CH_3NH_3I powder in an appropriate proportion and simply grinding, the emission intensity of $CH_3NH_3PbI_3$ is greatly improved. The advantages of the proposed method are swiftness, simplicity and reproducibility, and no requirement for a complex organic ligand. The mechanism of this phenomenon is revealed by x-ray diffraction, scanning electron microscopy, energy dispersive spectroscopy, photoluminescence, and temperature-dependent photoluminescence. This study offers a unique insight for optimizing the optical properties of halide perovskite materials.

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Metal halide perovskite materials with unique optoelectronic properties, such as extremely high optical absorption coefficients, super-long photogenerated carrier lifetimes and bandgap tunability, have a wide range of applications in solar cells, lasers, light-emitting diodes (LEDs), photoelectric detectors and other fields.[1−5] Although a series of perovskite light emitters in the visible to near-infrared regions have already been fabricated by engineering perovskites' chemical composition and structure, the emission and quantum efficiency of the devices need to be further enhanced.[1,6−9] Therefore, optimizing the optical properties of halide perovskite materials to improve the device performance is essential.[9]

The ultra-long carrier diffusion length of organic-inorganic hybrid perovskites is ideal for applications in solar cells.[10,11] Instead, it is not good for radiation recombination of the materials.[1,12] To solve this problem and to improve the emission efficiency of halide perovskites, researchers have used a series of methods to limit the size of perovskite crystals.[13−16] The quantum limit effect is used to regulate the behavior of the carriers in nanoscale perovskites.[17,18] However, the methods that have been reported usually require a variety of organic ligands, and the process is complicated.[13,16] In addition, the photoelectric properties of halide perovskites are commonly limited by non-radiative losses.[19−21] Then core-shell structure was used to passivate the nonradiative defects that would otherwise be present in $CsPbBr_3$ films, boosting the photoluminescence quantum efficiency.[8] Therefore, it is of great significance to find a simple and repeatable method to improve the luminescence performance of a halide perovskite.

In this work, combined with the idea of crystal size control and passivation of nonradiative recombination defects, we greatly enhanced the emission of $CH_3NH_3PbI_3$ ($MAPbI_3$) in a very simple way.[22] A pre-synthesized $MAPbI_3$ perovskite was mixed with an MAI powder additive, and then the mixture was fully ground by the mechano-physical method, as shown in Fig. 1(a). Specifically, the effect of the adding amount of MAI powder on the photoluminescence (PL) properties of $MAPbI_3$ was studied.

$MAPbI_3$ crystals were synthesized by the following method. PbI_2 and MAI (1:1 molar ratio) were dissolved in dimethylformamide (DMF) in ambient atmosphere under continuous stirring, until no powder was observed. The precursor solution was coated on a clean glass substrate and annealed at 100℃ for about 12 h. As the solvent evaporated, crystals formed and grew. After cooling to room temperature, the perovskite crystals were collected from the substrate. Next, MAI powder was added to the prepared per-

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ovskite crystals in the ratio of 0 : 1, 2.5 : 1, 5 : 1, 7.5 : 1, 10 : 1, respectively, and they were ground carefully. The color of the sample was originally black in daylight. After grinding with MAI, the sample turned grayish brown. The produced samples were denoted as $MAPbI_3$, Mix-2.5, Mix-5.0, Mix-7.5, Mix-10, respectively.

The PL emission spectra of the above five samples are shown in Fig. 1(b). All samples were prepared and tested under the same conditions and the excitation wavelength was 370 nm. It can be seen that the emission peak of each sample is mainly between 650 nm and 850 nm. Interestingly, with the increase of the proportion of MAI, the emission intensity of the sample first increases and then decreases, and reaches its maximum intensity when the proportion of $MAPbI_3$ vs MAI is 1 : 5. The emission photograph of Mix-5.0 is shown in the inset of Fig. 1(b). The maximum emission integral intensity is about 8 times that of pure $MAPbI_3$ powder. Furthermore, the emission peaks of the mixed powder samples show a slight blue shift compared with the pure $MAPbI_3$, that is, from 785 nm to 765 nm. Therefore, we can conclude that the adding amount of MAI powder affects the luminescence properties of the perovskite powder.

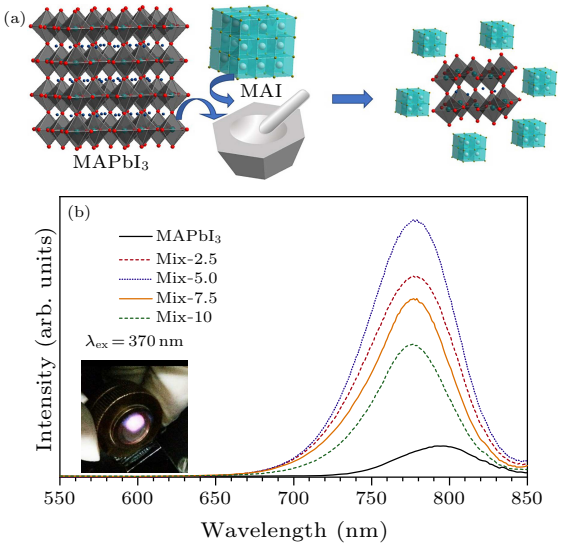

Fig. 1. (a) Schematic diagram of the material modification process. A pre-synthesized $MAPbI_3$ perovskite was mixed with MAI powder additive, and then the mixture was fully ground by the mechano-physical method. (b) PL emission spectra of $MAPbI_3$ with different adding amounts of MAI powder. The inset is the luminescence photo of Mix-5.0, which has the maximum emission intensity.

We put our insight into the mechanism of this phenomenon subsequently. A range of powder characterization studies were carried out to investigate the reason for the improvement of luminous performance of the perovskite phosphors.

To investigate the crystal structure of the perovskite powder added with MAI, the x-ray diffraction (XRD) patterns of the samples are shown in Fig. 2. It can be found that the XRD pattern of pure $MAPbI_3$ powder is completely consistent with the standard PDF file (ICSD card No.250739). The XRD peaks assigned to the (110), (220) and (330) diffraction at about 14°, 28.5° and 43°, respectively, confirming the formation of a tetragonal perovskite structure.[23] Extra diffraction peaks can be clearly seen in the samples doped with MAI, which apparently belong to the MAI lattice. The powder-XRD data reveals that the incorporation of MAI into $MAPbI_3$ does not change the matrix, and no new compound formed.[24]

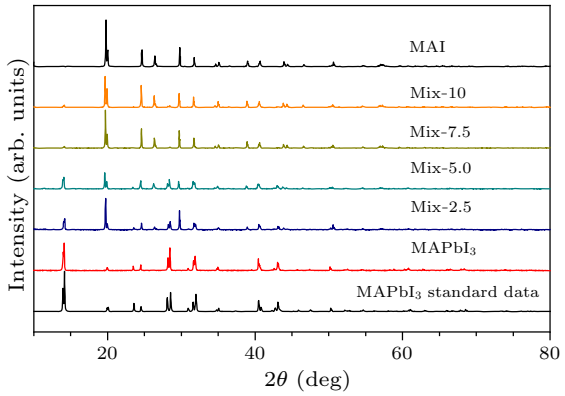

Fig. 2. XRD patterns of $MAPbI_3$ with different adding amounts of MAI powder, where it seems that the diffraction peaks of the mixture overlay the peaks from $MAPbI_3$ and MAI.

To get insight into the reason of this phenomenon, the microstructure of the samples was characterized. The scanning electron microscope (SEM) images of $MAPbI_3$, Mix-5.0 and MAI are shown in Figs. 3(a)–3(c). It can be observed from Fig. 3(a) that the surface of $MAPbI_3$ powder is relatively smooth. Figure 3(b) shows the gully topography of MAI. Figure 3(c) indicates that the microstructure of the Mix-5.0 sample contains two kinds of distinct configurations. The one is "smooth surface", as shown in area 1, and the other is "nuclear-shell structure", as shown in area 2. It can be obtained from Fig. 3(c) that as the local area is enlarged, the "nuclear-shell" structure is more like a nanocluster whose surface is oxidized. The oxidized surface is the "shell", and the middle nanocluster is the "nucleus". Compared to Figs. 3(a) and 3(b), it can be inferred preliminarily that the the nuclear-shell structure is similar to the microstructure of MAI powder and the smooth surface belongs to $MAPbI_3$ powder. To obtain more information about the microstructure of the samples, the samples were analyzed by energy dispersive spectroscopy (EDS), as shown in Figs. 3(d)–3(i). Figures 3(d) and 3(e) are the SEM image and EDS detection map of $MAPbI_3$. Figures 3(f), 3(g) and 3(h), 3(i) belong to the smooth surface and the nuclear-shell structure of Mix-5.0, respectively. Fig-

ure 3(e) indicates that the ratio of I:Pb element in $MAPbI_3$ powder is about 7 : 1, while the theoretical molar ratio of I:Pb should be 3 : 1, so there is only qualitative discussion for the EDS test results rather than precise quantitative discussion. Figure 3(g) shows that the molar ratio of I:Pb in the smooth surface region is about 7 : 1, which is similar to the result of $MAPbI_3$. The ratio of I:Pb in Fig. 3(i) is close to 80 : 1, which means the amount of Pb element in the nuclear-shell structure is very small. Then it can be concluded that the composition of the nuclear-shell structure is almost entirely MAI powder, and the smooth surface is $MAPbI_3$ powder. The above results verify that the addition of MAI into $MAPbI_3$ by grinding does not have a large effect on its matrix, but enhance the PL of $MAPbI_3$ remarkably.

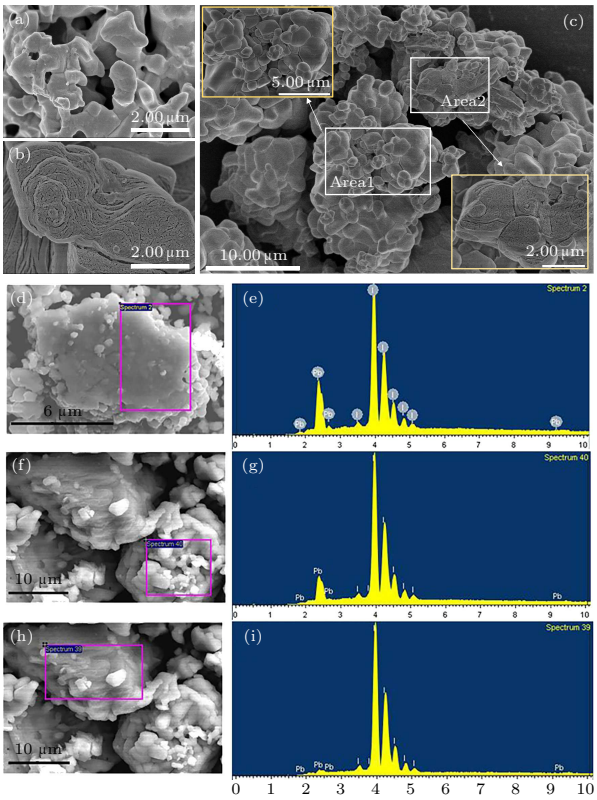

Fig. 3. SEM images of $MAPbI_3$ (a), MAI (b), and Mix-5.0 (c). The inset in the top left corner of (c) is the enlarged image of area 1, which has smooth surface and is similar to (a). The inset in the lower right corner of (c) is the enlarged image of area 2, which has a nuclear-shell structure and is similar to (b). SEM image and EDS detection map of $MAPbI_3$ [(d), (e)], the smooth surface [(f), (g)] and the nuclear-shell structure [(h), (i)] of Mix-5.0, respectively.

To study the influence of sample granularity on the luminescence intensity, $MAPbI_3$ and Mix-5.0 samples were ground in different durations to get various particle sizes, and were further screened by sieves with different mesh sizes. Figure 4(a) is the PL spectra of samples Mix-5.0 and $MAPbI_3$ powder with different particle sizes. It can be seen that the PL intensity of $MAPbI_3$ in different particle size remains invariable, which means that simply grinding does not increase the luminescence of $MAPbI_3$. However, the PL intensity of Mix-5.0 is significantly enhanced with the sample particles decreasing. This indicates that the addition of MAI in the grinding process plays an important role in the luminescence improvement of $MAPbI_3$. The smaller $MAPbI_3$ particles need MAI as a matrix to space out. The longer the grinding duration, the smaller the crystal particles, and the larger the contact surface between $MAPbI_3$ and MAI, which is more favorable to light emission. The reason could be explained as follows: according to the reports from Babin[25] and Papavassiliou,[26] the luminescence of halide perovskites can be enhanced by using an organic ligand or a solid matrix to reduce the space size of perovskite crystals, which can limit the charge carrier, thus increasing the radiation recombination rate.[1,2,25,26] Thus, the PL intensity will be improved by sample grinding. However, more non-radiative defects will appear during this process, which will damage the luminescence of $MAPbI_3$. Then the emergence of MAI just made up for the loss from non-radiative defects. Wei *et al.* has reported that MABr can be used to passivate the non-radiative defects that would otherwise be present in $CsPbBr_3$ film in a $CsPbBr_3$/MABr quasi-core/shell structure.[8] To clarify if MAI in Mix-5.0 sample perform the same function, PL lifetimes were conducted by time-correlated

single-photon counting measurements [Fig. 4(d)]. The PL decay curves were fitted with a bi-exponential decay model, in which the PL lifetime is considered as the summation of fast- and slow-decay components that give a short lifetime τ_1 and a long lifetime τ_2, respectively. Obviously, Mix-5.0 decays faster. Johannes *et al.* have reported that photon recycling might lead to longer apparent recombination lifetimes in perovskite materials, accompanied by a drastic drop of the external yield.[14,27] Thus, the shorter lifetime of Mix-5.0 may be due to the fact that the additional MAI reduces the probability of photons being re-adsorbed by the neighboring $MAPbI_3$, and the reduced non-radiative loss leads to an increase in luminous intensity. Moreover, another possible reason for the enhanced emission could be due to the reduction of Pb metallic states while using excess MAI. Studies have shown that the presence of metallic Pb atoms can damage luminescence by increasing the non-radiative decay rate and decreasing the radiative decay rate.[28–30] Cho *et al.* prevented the formation of metallic Pb atoms by increasing the molar proportion of MABr in $MAPbBr_3$ solution, which leads to a substantial increase in steady-state photoluminescence intensity and efficiency of $MAPbBr_3$.[29] Therefore, grinding and MAI are two necessary conditions for the luminescence enhancement of $MAPbI_3$.

As mentioned above, the emission peaks of the mixed powder samples show a slight blue shift compared with the pure $MAPbI_3$ in Fig. 1(b). It is believed that the smaller $MAPbI_3$ particles were spaced out by the additional MAI during grinding, and the reduction in the size of the $MAPbI_3$ results in the blue shift.[14,25]

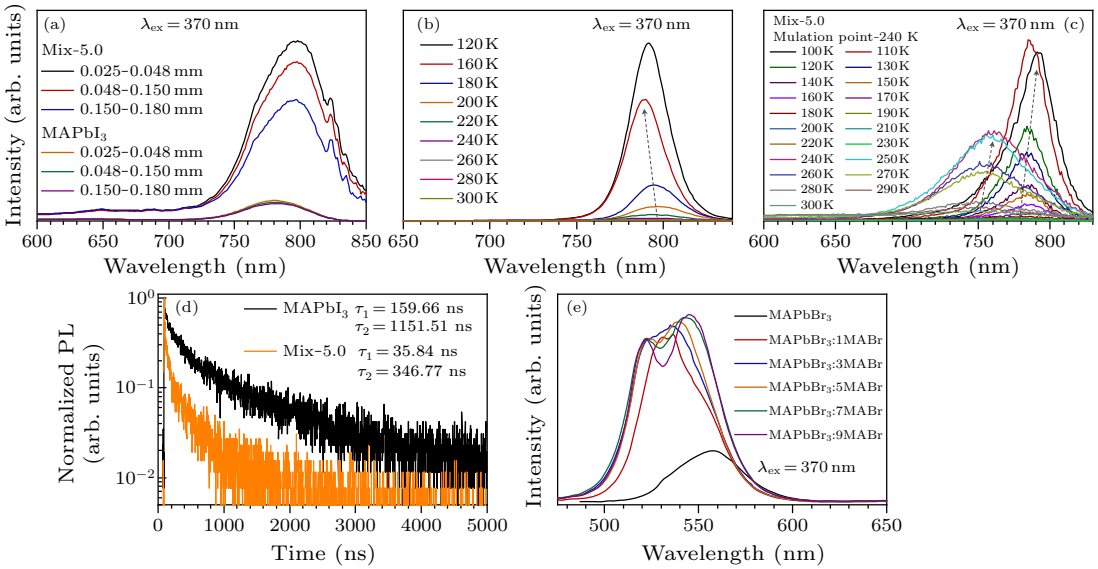

Fig. 4. (a) PL emission spectra of Mix-5.0 and $MAPbI_3$ powder samples with different particle sizes. Temperature-dependent PL spectra of $MAPbI_3$ (b) and Mix-5.0 (c). (d) PL lifetime of $MAPbI_3$ and Mix-5.0 (e) PL emission spectra of $MAPbBr_3$ with different adding amounts of MABr powder.

To further study their luminescence properties, temperature-dependent PL tests on samples $MAPbI_3$ and Mix-5.0 were performed respectively, as shown in Figs. 4(b) and 4(c). As the temperature decreases, the luminescence intensity of $MAPbI_3$ increases gradually [Fig. 4(b)]. It has been studied before and can be interpreted that the additional complexity induced by thermal effects is reduced, and the charge in semiconductor materials is mainly in the form of excitons at low temperature, which is better for radiative recombination.[23,31,32] As for the blue-shift with decreasing temperature, it is related to the interplay between the electron-phonon renormalization and thermal expansion, which have opposite effects on the bandgap of semiconductors.[23,32] It is obvious that the temperature-dependent PL spectra of the Mix-5.0 sample [Fig. 4(c)] is significantly different from that of $MAPbI_3$ in the range of 300–240 K, which proves that MAI does have an effect on carrier behavior in $MAPbI_3$ materials at room temperature. However, the effect of temperature on carrier behavior plays a major role in the range of 240–100 K.

Inspired by the above results, the luminescence of $MAPbBr_3$ is also improved with the same method by adding suitable amount of MABr, which means the reactant mixed grinding method may be a universal method to enhance the luminous intensity of perovskite luminescent materials. The relevant PL results are shown in Fig. 4(e). The explanation about the second peak at the PL band needs further research in the future.

In conclusion, we have proposed a simple method to improve the PL intensity of $MAPbI_3$ powder greatly. By adding an appropriate amount of MAI

reactant to $MAPbI_3$ and grinding, the PL intensity of $MAPbI_3$ powder has been improved eight times. This process does not introduce any impurities to the system. MAI can act as a solid matrix to disperse $MAPbI_3$ microcrystals by grinding, and the space size of $MAPbI_3$ is confined effectively. Thus there will be more excitons in $MAPbI_3$ for radiative recombination. Moreover, adding an appropriate amount of MAI can reduce the probability of photons reabsorption and the Pb metallic states, which is conductive to the improvement of luminescent intensity. The mechano-physical grinding method could be a convenient selection to optimize the optical properties of halide perovskite materials, which will promote the development in optoelectronic materials and devices.

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