Enhancing photoluminescence of 2D perovskite materials via the use of mixed phenylethylammonium halides

Khine Zin Swe[1], Atittaya Naikaew[1], Paphada Kaewurai[1], Pongsakorn Kanjanaboos[1, 2*]

[1]School of Materials Science and Innovation, Faculty of Science, Mahidol University, 999 Phutthamonthon Sai 4 Road, Salaya, Nakhon Pathom 73170, Thailand
[2]Center of Excellence for Innovation in Chemistry (PERCH-CIC), Ministry of Higher Education, Science, Research and Innovation, Bangkok 10400, Thailand
*E-mail: Pongsakorn.kan@mahidol.edu

In recent years, perovskite materials are developed for the optoelectronic applications such as solar cells, LEDs, and lasers. Perovskite materials are suitable for LED application due to its unique properties like direct band gap, high charge carrier mobility, high, photoluminescence quantum efficiency (PLQE), pure color emission, and low non-radiative recombination rate. Creating 2D perovskite materials by adding long aliphatic or aromatic chain such as butyl ammonium (BUA), benzyl ammonium (BA), and phenylethylammonium (PEA) can promote photoluminescence via enlarging exciton binding energy. Among those organic cations, the intercalation of PEA can improve the perovskite film by impeding crystal growths, causing smaller grains and better surface morphology. In this work, we investigated the effect of different large cations on perovskite thin films fabricated by spin coating method. 2D perovskite with only phenylethylammonium iodide (PEAI), having formula of PEA_2PbI_3, provided low PLQE of 0.5%. However, with phenylethylammonium bromide (PEABr) mixing, the PLQE was increased more than ten times. The thin films became smoother while retaining similar color profile. The use of mixed phenylethylammonium halides could significantly improve photoluminescence efficiency and morphology.

1. Introduction

In recent years, organic-inorganic perovskite has attracted attention from solar research community due to their excellent properties i.e. high absorption coefficient, long diffusion length, band gap tunability, high exciton generation, and good carrier mobility[1,2]. Perovskite materials can also be used in light emission applications such as laser and LEDs because of their special opotoelectric properties including wide color tunability, high color purity, and direct band gap[2,3]. Perovskite light emitting diodes (PeLEDs) are highly popular among the other types of LEDs such as organic light emitting diodes (OLEDs) and inorganic quantum dot LEDs, which have disadvantages relating to poor color purity, high cost, and complex synthesis[4]. On the other hand, PeLEDs can be synthesized by simple solution-processable method[5].

However, three dimensional perovskite materials have long diffusion length, resulting in low exciton binding energy and therefore less radiative recombination for PeLEDs[3,5]. To get the large exciton binding energy, low dimensional perovskite materials are created by adding some large organic cations to the 3D perovskite materials[5], which increases exciton binding energy and emission efficiency by quantum confinement effect[2,3,5–8]. Strongly bounded excitons are caused by the spatial quantum

confinement of the 2D perovskite because of large differences in the bandgap of inorganic and insulating organic layers as well as their dielectric constant ($\epsilon_{org < inorg}$) [9,10]. The general formulae of 2D perovskite is $(R)_2PbX_4$ where R is a long aliphatic or aromatic chain such as butyl ammonium, (BUA), benzyl ammonium (BA), propyl phenyl ammonium (PPA) and phenylethylammonium (PEA)[2,6,11].

Muyang *et.al* mentioned that creating 2D structure with PEA^+ cation could get homogenous and small grain size film that can improve photoluminescence quantum efficiency (PLQE) and high performance[3]. This grain size reduction can be attributed to the PEA^+ molecules hindering crystal growth during crystal pinning[3]. Paphada *et.al* found that the violet photoluminescence is enhanced by reducing grain size via doping PEG to the 2D perovskite film and fast sequential treatment called swift cation doping to generate more nucleation sites[2].

Min Wang *et.al* reported that using pure N,N dimethyl sulfoxide (DMSO) can cause an unwanted phase (adduct phase) on the perovskite film due to the reaction of solvent and different precursors[12]. So, in this work, mixed solvent of N,N dimethylformamide and N,N dimethyl sulfoxide (DMF:DMSO) was used to produce compact perovskite films with less defect [12].

Moreover, mixed halide perovskite has tunable band gap via substitution of I with Br ions, which is caused by a strong dependence of electronic energies on the effective exciton energy[13,14]. For the mixed halide perovskite, the mixed (I-Cl) perovskite is hard to fabricate with high content of Cl because Cl^- cations are quite hard to dissolve in polar solvent, as like as requiring high temperature[15]. However, the mixed (Br-I) perovskite can be prepared at room temperature[14,16]. In this work, we investigate 2D perovskite with mixed phenylethylammonium halides (PEABr and PEAI). Mixed halide 2D perovskite film can reach higher %PLQE compared to pure 2D perovskite from PEAI. The bandgap (Eg) of mixed halide perovskite is reduced while morphology becomes smoother.

2. Experimental Section

In this experiment, the main precursors are lead (II) iodide ($PbBr_2$, 99.95% purity), phenethylammonium iodide (PEAI), and phenethylammonium bromide (PEABr) which were purchased from Sigma-Aldrich. DMSO (anhydrous grade), and DMF (anhydrous grade) were also purchased from Sigma-Aldrich. Fluorine-doped tin oxide (FTO) was used.

The cleaning method of FTO was done in the following steps. All the substrates were placed into a tray with alconox soapy water, then sonicated at 60°C for an hour and rinsed for 3 times. Isopropanol was then used under sonication for 30 minutes. The substrates were dry with nitrogen blower. The substrates were always treated with UV ozone cleaner before experiment. To fabricate compact TiO_2, titanium isopropoxide (TTIP) and ethanol were mixed in an appropriate ratio. Those solution was stirred for whole night and small amount of solution was dropped on the substrate and spun for 30s. The detailed procedures of fabrication method can be found in our previous publication[17].

For 2D perovskite layer $(PEA)_2PbI_4$ as a control sample, PbI_2 and PEAI with the ratio of 1:2 was used with mixed solvent of 4:1 v/v (DMF: DMSO), having a concentration of 1 M. To get mixed halide system, different molar ratios of PEABr to PEAI were used (1:4, 2:3, 3:2, and 4:1). The solution was filtered using a 0.22 μm teflon filter and then coated onto TiO_2/FTO-glass substrate (2000 rpm for 20 s and 5000 rpm for 60 s)[2] without annealing. After spin coating, the crystallization process

occurred in the air.

For the characterization method, %PLQE was measured by a Horiba FluoroMax4+ equipped with Horiba K-Sphere Petite Integrating Sphere under 370 nm excitation. UV–Vis absorbance was characterized by using a spectrophotometer (Shimadzu UV-2600). Scanning electron microscope images are observed by HITASHI SU8010 (FE-SEM, 10 kV, SE). To analyze the perovskite structure, X-ray diffractometer (Aries) was used by detecting the scattering pattern from the beam.

3. Results and Discussion

The important characterization methods of perovskite thin films for LED application are PL intensity and %PLQE. PEA_2PbI_4 is 2D control with only I^-. For mixed phenylethylammonium halide perovskite, we mixed PEABr and PEAI to achieve $(PEA)_2PbI_{(4-x)}Br_{(x)}$. Figure 1 compares the PL spectra of perovskite films with different ratios of PEABr into $(PEA)_2PbI_4$. Control is the 2D perovskite with only PEAI. For the mixed phenylethylammonium halide films, the different ratios of PEABr and PEAI are utilized i.e. (1:4), (2:3), (3:2), and (4:1) to identify ideal composition. Among these ratios, 1:4 PEABr:PEAI and 2:3 PEABr:PEAI ratios are the optimized conditions in terms of optical properties and morphology.

Figure 2. (a-b-c) shows the morphology of perovskite films. The control sample has pinholes and poor surface morphology which leads to non-radiative recombination and therefore low %PLQE. From the SEM images of mixed phenylethylammonium halide samples, we can observe defect-free, smooth morphology with full coverage and smaller grain size, leading to high radiative recombination and PL emission by generating more binding excitons[3,5].
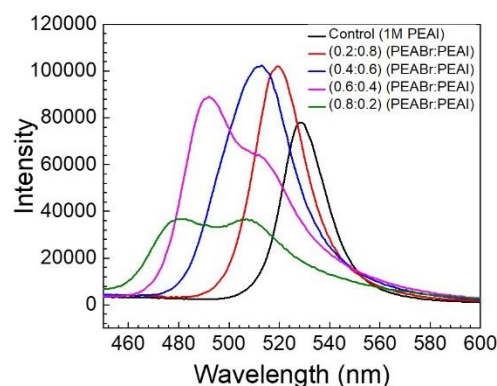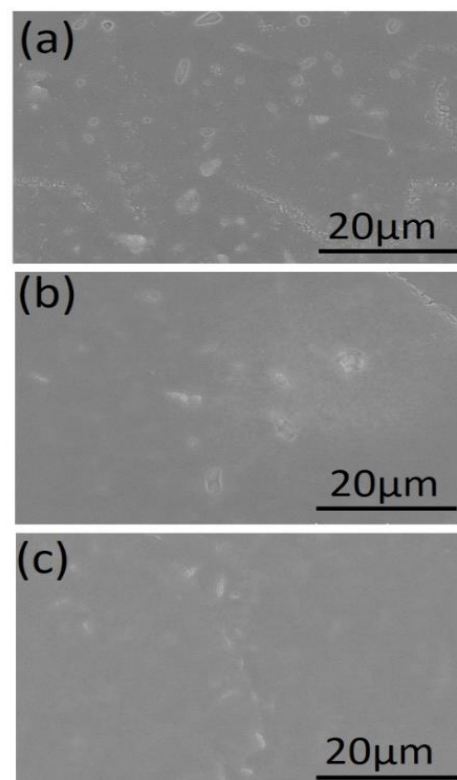

Figure 1. Identifying PL spectra of perovskite films with different PEABr:PEAI ratios.

Figure 2. SEM surface morphology of (a) control sample $(PEA)_2PbI_4$, (b) $(PEA)_2$

$PbI_{3.8}Br_{0.2}$ and (c) $(PEA)_2PbI_{3.6}Br_{0.4}$.

The crystallinity of $(PEA)_2PbI_4$ films can be determined by X-ray diffraction (XRD) shown in figure 3.(a).

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The characteristic peaks are (002), (004), (006), (008), (0010), (0012) at 5.4º, 10.8º, 16.2º, 21.8º and 32.8º, respectively. To compare with the control sample, mixed cation films have lower crystallinity due to smaller grains. Figure 3. (b) shows the optical images, illustrating smooth and green emission for mixed phenylethylammonium halide samples.
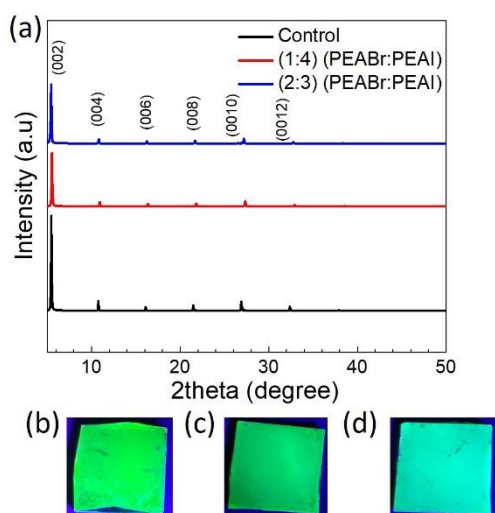

Figure 3. (a) XRD patterns of control and mixed phenylethylammonium halide samples and optical images of (b) control sample $(PEA)_2PbI_4$, (c) $(PEA)_2PbI_{3.8}Br_{0.2}$, and (d) $(PEA)_2PbI_{3.6}Br_{0.4}$.

Figure 4. (a) shows the PL spectra of control and mixed phenylethylammonium halide samples. Mixed samples show the highest PL intensity at the peak of 515nm. The PL peak is blue-shifted with higher PEABr content. As control is already the 2D perovskite film, the blue shift in PL spectra of mixed halide perovskite is mainly caused by Br-I substitution as the radius of Br is smaller than I along with the distribution of smaller average crystallite size[5,9]. Moreover, shifting PL spectra trend is consistent with the shift of absorbance and E_g. Furthermore, mixed phenylethylammonium halides enable

different sizes and excitonic states[9]. Figure 4. (b) shows the %PLQEs for those samples. Mixed-halide films provides no defect and smooth morphology with small grain size, leading to reduced diffusion length (L_D) for excitons and more phonons from recombination[18].
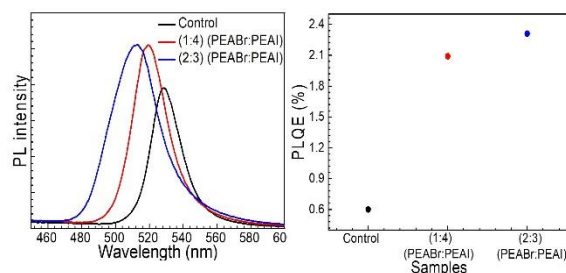

Figure 4. Comparing optical properties of mixed phenylethylammonium halide perovskite films by analyzing (a) PL spectra and (b) %PLQEs.

Figure 5. (a) shows the absorption spectra of control and mixed phenylethylammonium halide samples. The $(PEA)_2PbI_4$ film shows an absorption peak with wavelength near 510 nm while mixed phenylethylammonium halide samples peak near the wavelength of 490 nm, observing similar blue shift as seen in PL spectra. E_g of perovskite films are calculated through Tauc plot[19] and and shown in Figure 5. (b). The E_g of the films shrinks from 2.91eV to 2.86eV with PEABr mixing, consistent with other results.
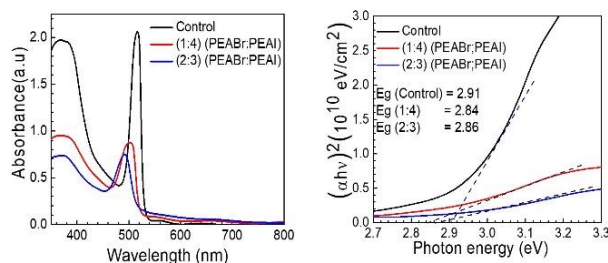

Figure 5. (a) The absorption spectra and (b) energy band gap of control and mixed phenylethylammonium halide perovskite films.

4. Conclusions

The 2D layered perovskite $(PEA)_2PbI_4$ has poor morphology with defects, leading to the high non-radiative recombination and low emission. With application of mixed phenylethylammonium halides to the 2D perovskite, the band gap becomes smaller with higher surface coverage, better surface morphology, and smaller grain. Those improved characteristics, which lead to better photoluminescence properties, are very beneficial for PeLED application.

Acknowledgments

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