A Stable Photoluminescence of Waste Derived Acrylic Plastics (PMMA) and MAPbBr$_3$ Composite Film

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Abstract. This paper reports the synthesis and characterization of a composite thin of waste-derived acrylic plastic (PMMA) and MAPbBr$_3$ perovskite nanocrystal that prepared by ligand assisted re-precipitation (LARP) method. The composite thin film prepared from MABr, PbBr$_2$, oleic acid and oleyl amine, N, N-dimethylformamide (DMF) as a precursor, toluene as a solvent, and waste-derived PMMA as polymer, and then deposited on glass substrate using a spin coater with different speed. As a result, the highest transmittance value was around 90% for the sample with a high spin speed (3000 rpm). The photoluminescence of MAPbBr$_3$ film, when illuminated by UV shows a bright green color with a peak at 536 nm wavelength and maximum luminescence found in the sample with the lower spin speed (1000 rpm). Thus, the fabricated perovskite composite thin film using recycled acrylic plastic has a good prospect to be applied in optoelectronic application.

1. Introduction

Recently, Perovskite halides have received extensive attention due to their high photoluminescence quantum yield (PLQY), broadband absorption, narrow emission band, and tunable emission wavelength[1,2]. These advantages lead them the ideal candidates for a wide variety of high-performance optoelectronic devices, including solar cells [3], optically pumped lasers [4], light-emitting diodes [5], and photodetectors[6]. Despite the remarkable advantages of the perovskite halides, there are still some problems such as suffer from poor stability under external stresses, especially moisture, heat and light that impede their practical applications [7,8]. In order to increase their stability, a surface passivation strategy of embedding perovskites halides either in polymer matrices such as PMMA or inorganic materials has been broadly pursued [9,10].

PMMA is an amorphous, environmentally friendly, and inexpensive polymer used in many applications. Many researchers report the passivation of PMMA in perovskite by filling pinholes and surface traps [11–13]. Zhu's and co-workers fabricated CsPbBr$_3$ @ PMMA and CsPb (Br / I) 3 @ PMMA which produced consecutive green and red luminescence. Perovskite PMMA composites produced showed good stability in water, with the intensity of PL emission relatively decreasing...
slowly, up to 90% from the original after 12 hours left in water [14]. The hydrophobic nature of PMMA protects the open-perovskite metal lead site of organic-inorganic hybrid halide from water, effectively slowing diffusion into perovskite nanocrystals [15].

PMMA, also known as Acrylic, is an economical material and is commonly used in a variety of applications, including lenses and lighting fixtures, outdoor signboards, store and display fixtures, lightweight pipes, windows and skylights, sculptures, and furniture. Because of this wide variety of applications, Acrylics PMMA contributes considerable waste to the environment [16].

In recent years, the environmental impact of plastic waste has attracted a lot of attention. Various solutions are being carried out to reduce this problem, such as new legislation, product development from recycled materials, and the implementation of appropriate methodologies for disposing of plastic and electronic waste [17]. Recycling is an outstanding choice that has been implemented and encouraged. Recycling plastic waste contributes to environmental preservation and reduces the extraction of non-renewable natural resources [18].

Herein we report a synthesis and characterization of a composite thin film of waste-derived acrylic plastic (PMMA) and MAPbBr₃ perovskite nanocrystal that prepared by ligand assisted re-precipitation (LARP) method and spin coating method. The resulting MAPbBr₃ / PMMA composite film exhibited the bright green light emission. The composites also performed good transference in visible light.

2. Experimental Method

MAPbBr₃ perovskites was prepared using ligand assisted re-precipitation (LARP) technique adopted from the method developed by Zhang et al [1]. A blend of 0.16 mmol CH₃NH₃Br (sigma Aldrich) and 0.2 mmol PbBr₂ (sigma Aldrich) was dissolved in 5 mL of DMF with 0.5 mL of oleic acid and 20 μL of n-octylamine (sigma Aldrich) to form a precursor solution. A milliliter of precursor solution was dropped into 5 mL of toluene with intense stirring.

To prepare a film, the prepared MAPbBr₃ was compose with waste derived acrylic plastics (PMMA). Acrylic plastic waste sheets are shaved in advance using a knife to obtain small acrylic flakes. 50 mg of small acrylic flakes (PMMA) mixed with 1 mL of toluene and stirred at 75 C until the PMMA was absolutely dissolved and the solution was transparent and colorless. The MAPbBr₃ solution and the PMMA solution were mixed using magnetic stirrer at 750 rpm under atmospheric condition. Subsequently, the MAPbBr₃/PMMA composite solutions was deposited on the surface of the glass substrate using a spin coating method to produce MAPbBr₃/PMMA-composite film in different rotational speed.

The XRD measurements were measured on X-Ray Diffraction Bruker D8 Advance, using a Cu Kα radiation source (wavelength at 1.5405 Å). UV–vis absorption spectra of film were measured on a UV-Vis spectroscopy (HR2000CGUV- NIR, Ocean Optic) equipped with a DH-2000-BAL deuterium halogen light source. PL spectra were taken using Cary Eclipse fluorescence spectrophotometer.

3. Result and discussion

XRD characterization was carried out to determine the structure of the MAPbBr₃ perovskite crystals synthesized using the LARP method. The XRD pattern in Figure 1 of as-prepared MAPbBr₃ indicates a cubic structure with space group Pm-3m. Diffraction peak positions measured at 15.0°, 21.21°, 26.04°, 30.12°, 33.78°, 37.15°, 43.18°, 45.93°, and 48.63° were converted to interplanar spacings which corresponds to the crystal planes (100), (110), (111), (200), (210), (211), (220), (300) and (310) respectively [19].
We use PMMA obtained from recycling acrylic plastic as shown by the inset in Figure 2. To analyze the PMMA that we obtained from recycling acrylic, we performed FTIR characterization. The FTIR spectrum indicates PMMA obtained from Acrylic glass is the same as PMMA in the reference [20]. The uptake at 1727 cm\(^{-1}\) shows the stretching vibrations of the carbonyl group (C = O), the other uptake was observed at 2995-2853 cm\(^{-1}\) (asymmetric and symmetrical stretching -CH), 1446 cm\(^{-1}\) and 1387 cm\(^{-1}\) (CH deformation), 1240 cm\(^{-1}\) (symmetric CCO strec), 986 cm\(^{-1}\) (O-CH3 rock), 844 cm\(^{-1}\) (rock CH2) and 750 cm\(^{-1}\) (stretch CC)[20,21].

Figure 2. FTIR spectrum of PMMA obtained from waste derived acrylic plastics and reference. Inset: waste derived acrylic plastics appearance.

Figure 3 shows the PL spectrum of the MAPbBr\(_3\) and MAPbBr\(_3\)/PMMA composite exited by 365 nm. From the inset in the Figure 3, it can be observed that the perovskite sample is dark yellow without UV illumination and bright green when irradiated to UV. The PL emission spectrum of both samples shows a peak position at 536 nm and 532 nm with respectively. Therefore, it can be observed that the location of the PL peak scantily shifted when MAPbBr\(_3\) solution was compose with PMMA solution. This means that the band structure of the MAPbBr\(_3\) not influenced by addition of the PMMA [15].
Figure 3. Photoluminescence spectrum of MAPbBr$_3$ and MAPbBr$_3$/PMMA composites. Inset: MAPbBr$_3$/PMMA composite photographs on daylight and UV light.

Figure 4 shows the photograph of MAPbBr$_3$/PMMA composite films fabricated using the spin coating method with different variations in speed. A sample with a spin coating speed of 1000 rpm was seen to be transparent. Moreover, the samples were seen to be increasingly transparent when the spin-coating speed was increased. The most transparent layer was found in the sample with the largest rotation speed 3000 rpm. When exposed to UV, the samples show a bright green luminescence with the most luminous emission in the sample with the slowest rotation speed 1000 rpm.

UV-Vis and PL characterization was used to further study the luminescence and transparency of the MAPbBr$_3$/PMMA composite films. The UV VIs characterization showed the highest transmittance value was around 95% for the sample with 3000 rpm, and the lowest was about 50% for samples with 1000 rpm. However, inversely proportional to the transmittance spectrum in Figure 5a, PL characterization in Figure 5b showed the maximum luminescence occurred in the sample with the lowest rotational speed of 1000 rpm. Therefore, this can be explained when the spin coating process with a low rotating speed will result in more MAPbBr$_3$/PMMA composite film being deposited in the
sample. So the transmittance value of the film will be small, but the light emission will be better.

![Transmittance spectrum (a) and photoluminescence spectrum (b) of MAPbBr3 + PMMA composite film composites.](image)

**Figure 5.** Transmittance spectrum (a) and photoluminescence spectrum (b) of MAPbBr3 + PMMA composite film composites.

**4. Conclusion**

MAPbBr3/PMMA composite film was successfully fabricated with source of PMMA is waste derived acrylic plastics. The method was using is LARP and continued with the spin coating method. The fabricated film has a bright green emission and high transmittance in the visible wavelength, which was up to 95%. The high spin speed on film fabrication process caused the increasing of film transference but decreasing the PL intensity.

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**References**

[1] Saparov B and Mitzi D B 2016 Organic–Inorganic Perovskites: Structural Versatility for Functional Materials Design Chem. Rev. 116 4558–96

[2] Stranks S D and Snaith H J 2015 Metal-halide perovskites for photovoltaic and light-emitting devices Nat. Nanotechnol. 10 391–402

[3] Lee M M, Teuscher J, Miyasaka T, Murakami T N and Snaith H J 2012 Efficient Hybrid Solar Cells Based on Meso-Superstructured Organometal Halide Perovskites Science (80-. ). 338 643–7

[4] Zhu H, Fu Y, Meng F, Wu X, Gong Z, Ding Q, Gustafsson M V., Trinh M T, Jin S and Zhu X-Y 2015 Lead halide perovskite nanowire lasers with low lasing thresholds and high quality factors Nat. Mater. 14 636–42

[5] Tan Z-K, Moghaddam R S, Lai M L, Docampo P, Higler R, Deschler F, Price M, Sadhanala A, Pazos L M, Credgington D, Hanusch F, Bein T, Snaith H J and Friend R H 2014 Bright light-emitting diodes based on organometal halide perovskite Nat. Nanotechnol. 9 687–92

[6] Fang Y, Dong Q, Shao Y, Yuan Y and Huang J 2015 Highly narrowband perovskite single-crystal photodetectors enabled by surface-charge recombination Nat. Photonics 9 679–86
[7] Wei Y, Audebert P, Galmiche L, Lauret J-S and Deleporte E 2014 Photostability of 2D Organic-Inorganic Hybrid Perovskites Materials (Basel). 7 4789–802

[8] Huang J, Tan S, Lund P D and Zhou H 2017 Impact of H 2 O on organic–inorganic hybrid perovskite solar cells Energy Environ. Sci. 10 2284–311

[9] Chen L-C, Tien C-H, Tseng Z-L, Dong Y-S and Yang S 2019 Influence of PMMA on All-Inorganic Halide Materials (Basel). 12 1–9

[10] Huang S, Li Z, Kong L, Zhu N, Shan A and Li L 2016 Enhancing the Stability of CH 3 NH 3 PbBr 3 Quantum Dots by Embedding in Silica Spheres Derived from Tetramethyl Orthosilicate in “Waterless” Toluene J. Am. Chem. Soc. 138 5749–52

[11] Awino C, Odari V, Dittrich T, Prajongtat P, Sakwa T and Rech B 2017 Investigation of Structural and Electronic Properties of CH 3 NH 3 PbI 3 Stabilized by Varying Concentrations of Poly(Methyl Methacrylate) (PMMA) coatings Artic. 115 1–12

[12] Kong W, Ding T, Bi G and Wu H 2016 Optical characterizations of the surface states in hybrid lead–halide perovskites Phys. Chem. Chem. Phys. 18 12626–32

[13] Wang F, Shimazaki A, Yang F, Kanahashi K, Matsuki K, Miyauchi Y, Takenobu T, Wakamiya A, Murata Y and Matsuda K 2017 Highly Efficient and Stable Perovskite Solar Cells by Interfacial Engineering Using Solution-Processed Polymer Layer J. Phys. Chem. C 121 1562–8

[14] Zhu J, Xie Z, Sun X, Zhang S, Pan G, Zhu Y, Dong B, Bai X, Zhang H and Song H 2019 Highly Efficient and Stable Inorganic Perovskite Quantum Dots by Embedding into a Polymer Matrix ChemNanoMat 5 346–51

[15] Li X, Xue Z, Luo D, Huang C, Liu L, Qiao X and Liu C 2018 A stable lead halide perovskite nanocrystals protected by PMMA Sci. China Mater. 61 363–70

[16] Owusu P A, Banadda N, Zziwa A, Seay J and Kiggundu N 2018 Reverse engineering of plastic waste into useful fuel products J. Anal. Appl. Pyrolysis 130 285–93

[17] Prado A R, Leal-Junior A G, Marques C, Leite S, de Sena G L, Machado L C, Frizera A, Ribeiro M R N and Pontes M J 2017 Poly(methyl methacrylate) (PMMA) recycling for the production of optical fiber sensor systems Opt. Express 25 30051

[18] Godiya C B, Gabrielli S, Materazzi S, Pianesi M S, Stefanini N and Marcantoni E 2019 Depolymerization of waste poly(methyl methacrylate) scraps and purification of depolymerized products J. Environ. Manage. 231 1012–20

[19] Wang K-H, Li L-C, Shellaiah M and Wen Sun K 2017 Structural and Photophysical Properties of Methylammonium Lead Tribromide (MAPbBr3) Single Crystals Sci. Rep. 7 13643

[20] Vijayakumari G, Selvakumar N, Jeyasubramanian K and Mala R 2013 Investigation on the Electrical Properties of Polymer metal Nanocomposites for Physiological Sensing Applications Phys. Procedia 49 67–78

[21] Ramesh S, Leen K H, Kumutha K and Arof A K 2007 FTIR studies of PVC/PMMA blend based polymer electrolytes Spectrochim. Acta Part A Mol. Biomol. Spectrosc. 66 1237–42