Silica addition effect on optical properties of halide perovskite-PMMA composite film

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Abstract. The effect of silica (SiO2) addition on optical properties of organometal halide perovskite PMMA composite film was studied. The organometal halide perovskite, MAPbBr3, was synthesized using ligand-assisted re-precipitation (LARP) method, and then was compose to PMMA and SiO2 directly to make composite films. The absorbances, transmittances, and photoluminescence (PL) spectrum of the samples were characterised using UV Vis and PL spectroscopy. The result shows that the addition of silica leads blueshift on photoluminescence and absorbance spectra. The blue shift reveals one-dimensional confinement effect in perovskite.

1. Introduction
The in recent years there has been extensive interest in perovskite halides. Perovskite halides have been identified as promising alternative optoelectronic devices because of their high-performance properties, such as high photoluminescence quantum yield (PLQY), narrow emission band, broadband absorption and tunable emission wavelength [1,2]. However, there are still some problems in this material, such as suffer from poor stability under external stresses, especially moisture light and heat [3,4]. Recently, several efforts have been made to enhance the stability such as using of high molecular polymer matrix or inorganic protective layer for encapsulation [5,6].

Passivation of PMMA in perovskite by filling pinholes and surface traps was reported [7–9]. Zhu's et all fabricated CsPbBr3 @ PMMA and CsPb (Br / I)3 @ PMMA which produced consecutive green and red luminescence. 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 [10]. In other hand, the addition of silica (SiO2) can also maintain the stability of perovskite. SiO2 is an inert material which estimated to be able to protect the core material from oxygen and moisture so as to increase the stability of perovskite. Wang was synthesizing CsPbX3-PQDs-SiO2 hybrid nanocomposites by filling perovskite on mesoporous silica particles with the usual mixing method [6].
In other studies, silica coated to the CsPbBr3 perovskite showed increased stability as well as being carried out by coating silica against Perovskite QDs CsPbBr3 show increased stability [11].

In this present work, we attempt to explore the effect of silica addition on optical properties of halide perovskite-PMMA composite film. Photoluminescent (PL) and UV-Vis characterization was used to investigate the optical properties of perovskite-SiO2-PMMA composite film.

2. Experimental method

2.1. Materials
Lead (II) bromide PbBr2 ≥98%, Methylammonium Bromide MABr 98%, Oleic acid C18H34O2, Oleylamine 70% were purchased from Sigma Aldrich. N, N-Dimethylformamide (CH3)2NC(O)H, Toluene C7H8 were purchased from Merck.

2.2. Synthesis of MAPbBr3
MAPbBr3 perovskites were prepared using ligand assisted re-precipitation (LARP) technique adopted from the method developed by Zhang et al.[12] a blend of 0.16 mmol MABr and 0.2 mmol PbBr2 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 in the glovebox. A millilitre of precursor solution was dropped into 5 mL of toluene with intense stirring. Finally, the crude solution was centrifuged at 4000 rpm to discard the precipitates, and a colloidal solution of MAPbBr3 quantum dots was obtained.

2.3. Preparation of MAPbBr3-SiO2-PMMA composite film
Fumed silica (SiO2) 0.18 mg and toluene (5 mL) mixed and stirred at 50°C for 30 minutes to form a silica solution. Furthermore, silica solution (1,375) ml and crude solution of MAPbBr3 (5,5 ml) mixed at ambient condition. Finally, the crude solution of MAPbBr3-SiO2 composite was centrifuged at 4000 rpm to discard the precipitates, and a and a colloidal solution of MAPbBr3-SiO2 composite was obtained. And then PMMA (100 mg) mixed with toluene (2 mL) and stirred at 75 OC until the PMMA was absolutely dissolved and the solution was transparent and colourless. The MAPbBr3/SiO2 solution and the PMMA solution were mixed using a magnetic stirrer at 750 rpm under atmospheric condition. Subsequently, the MAPbBr3-SiO2-PMMA composite solutions were deposited on the petri dish and dried up on a vacuum oven for 2 hours.

2.4. Characterizations
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. Results and discussion

![Image](image_url)

**Figure 1.** Free standing film of MAPbBr3 – PMMA composite ( ), and MAPbBr3 – SiO2 - PMMA composite ( ).
Photograph of MAPbBr$_3$-PMMA and MAPbBr$_3$–SiO$_2$-PMMA composite films shown by Figure 1. Both films show a yellow colour without UV illumination and bright green luminescence under UV illuminance. The PL emission spectrum of both samples in Figure 2 shows a peak position at 508 nm and 520 nm with respectively. Therefore, it can be observed that the location of the PL peak scantily blue-shifted on MAPbBr$_3$–SiO$_2$-PMMA composite film for the quantum confinement effect. This blueshift will be studied through further UV characterization. In addition, the luminescence intensity of the MAPbBr$_3$–SiO$_2$–PMMA composite film is smaller than MAPbBr$_3$–PMMA composite film. this is possible because of the fewer concentrations of MAPbBr$_3$ perovskite in the composite.

![Figure 2](image-url)  
**Figure 2.** Photoluminescence spectrums of MAPbBr$_3$–PMMA composite film, and MAPbBr$_3$–SiO$_2$-PMMA composite film.

![Figure 3](image-url)  
**Figure 3.** Absorbance spectrum (a) and transmittance spectrum (b) of MAPbBr$_3$–PMMA and MAPbBr$_3$–SiO$_2$-PMMA composite film.

Figure 3 show absorbance and transmittance spectra of MAPbBr$_3$–PMMA and MAPbBr$_3$–SiO$_2$-PMMA composite films. Multiple excitonic peaks on absorption and transmittance spectra in Figure 3 reveal a mixture of perovskite nanostructures with different morphologies including nanoscale particles and 2D nanoplatelets with a different number of unit cell layers, $n$ [13]. There are sharp absorptions peak at 390
nm, 435 nm, 480 nm, and 493 nm corresponding to nanoplatelets with n = 1, n=2, n=5 and n=6 respectively [14]. The absorption amplitude of 390 nm and 435 nm on each sample was different, constitute a different fraction of n=1 or n=2 of the sample. The absorption amplitude of 390 nm was stronger in PQDs-SiO2-PMMA composite film, illustrating nanoplatelets n = 1 dominate in quantity in the product perovskite film. Another striking difference is in the band edge at a wavelength of 493 nm for a sample of MAPbBr3- PMMA composite film and shifted to 480 for a sample MAPbBr3-SiO2- PMMA composite film. A blue shift on photoluminescence spectra in Figure 2 and absorption spectra in Figure 3 are attributed to quantum confinement effect. Thickness differences of the samples leads to a one-dimensional quantum confinement effect in the one direction [15].

Figure 4 shows the Tauc plot of the composite films. From this graph, it is known that there are multiple band gaps in the composite film. Each curve shows almost the same pattern, with the same bandgap 2.6 eV and 2.8 eV. The difference is that MAPbBr3- PMMA composite film has a 2.18 eV bandgap while MAPbBr3-SiO2-PMMA composite film has a larger band gap 2.24 eV. This result in line with quantum confinement effect in absorption and photoluominescent spectra.

![Tauc plot of MAPbBr3–SiO2-PMMA composite.](image)

4. Conclusion
This study demonstrated that SiO2 has an influence on the optical properties of halide perovskite-PMMA composite film. The addition of silica to the composite causes a blue shift in the PL and absorbance curve. This blue shift is possibly attributed to the one-dimensional quantum confinement effect in MAPbBr3 nanoplatelets.

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