

Ultra-Stable Deep-Dyed Perovskite-Polymer Composites as Tunable Downconverters

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Abstract

We report a low cost, simple deep-dyeing method that can convert polyethylene terephthalate (PET) polymer matrix into ultra-stable luminescent perovskite-polymer composites (PPCs) which have excellent color tunability, color purity, and water-/photo-stability. The achieved PPCs can be utilized in displays, solid-state lighting or other applications.

Keywords

Perovskite, polymer, ultra-stable, downconverter, water stable, superior photostability.

1. Introduction

The request for large color gamut displays becomes urgent. As the color gamut evaluation metric gradually upgraded from sRGB (standard Red Green Blue), via NTSC (National Television Standards Committee), and now to Rec. 2020, the traditional phosphor converted-white light-emitting diodes (LEDs) cannot fulfill the demand for highly vivid colors. Meanwhile, in solid-state lighting (SSL) systems aiming at beyond energy saving, tailoring the spectra in terms of requirements becomes increasingly important [1]. Engineering the spectra according to the demands of different applications will maximize the effectiveness of the lighting by ensuring the presence of necessary components of the spectrum for specific lighting requirement, and in the meantime reducing or omitting unnecessary or even damaging portions of the spectrum [1, 2]. Working with blue LEDs, tunable downconverters with narrow emission peaks should provide the most cost-effective approach for fine spectral control. While quantum dot downconverter materials have shown promise for fine spectral tailoring and wide color gamut displays, their manufacturing cost remains to be lowered down and their stability needs to be further enhanced.

Metal halide perovskites (MHPs), particularly those with a chemical formula of $APbX_3$, where X is

generally a halide (F-, Cl-, Br-, I-) anion with larger organic or inorganic cations A such as Cs^+ , $CH_3NH_3^+$ (MA^+) or $CH(NH_2)_2^+$ (FA^+), have recently emerged as important low-cost solar photovoltaic or optoelectronic materials [3]. MHP nanoparticles have demonstrated high luminescence efficiency, excellent color purity and outstanding color tunability to cover a full range of visible emission spectra simply by varying cation or halide compositions.[4] Despite these progresses, instability under external stresses (heat, light and/or water or oxygen in ambient condition) remains one big challenge to be overcome [5].

In 2016, a swelling-deswelling microencapsulation (SDM) strategy has been developed by the authors' team to achieve well dispersed, intimately passivated perovskite nanoparticles inside polymer matrices and led to perovskite-polymer composite films with high PL efficiency, excellent color purity and unprecedented stability against heat and water exposure [6]. In this strategy, perovskite precursor solution is brought into the polymer matrices through solvent-induced swelling process, and high-quality, well-encapsulated nanoparticles formed during the polymer deswelling process upon solvent removal. The process is very simple and cost-effective. By tuning the halide compositions, perovskite-polymer composite (PPC) films of different colors can be obtained, covering the entire visible range, with narrow linewidths of 16 nm ~ 44 nm.

Although the previous results demonstrated bright green PPCs with excellent stability against moisture, oxygen and heat, the red ones were very dimmed and highly unstable to environmental stimuli, which is referred as perovskite "red wall" [7], and the green PPCs still need effort on further boosting their stability for practical applications. To tackle this issue, one may employ an even more stable polymer matrix to protect the vulnerable MHPs. For example, poly(ethylene terephthalate) (PET) has been widely used in the display industry due to its unique physical and mechanical properties.[8, 9] However, using the previously reported SDM strategy to convert PET into

PPCs is difficult because the swelling ratio is fairly low, as PET normally shows high crystallinity, tight structure, and a lack of reactive groups [9].

Here, we develop an improved process of SDM, termed deep-dyeing process, that leads to bright and ultra-stable red and green PPCs. Applying PET as the polymer matrix, the deep-dyed perovskite-polymer composites (DDPPCs) are achieved. Significantly, the as-synthesized DDPPCs offer widely-tunable highly-saturated colors and superior stability against external stimulus, which hold great promise to be adopted as a low-cost, high-quality replacement for the traditional, expensive downconverters in displays and beyond.

2. Results and Discussion

If the previously reported SDM is applied, the PET matrices will not be swelled by the solvent at room temperature. However, at a high-enough temperature, the PET matrices can be swelled. As schematically shown in **Figure 1a**, commercial PET matrices were immersed into the MHP precursor (CsX/MAX and PbX_2 , $\text{X} = \text{Cl}, \text{Br}, \text{I}$) solution and heated up to a relatively high temperature ($\sim 160^\circ\text{C}$). PET polymer chains will swell and expand under this condition, letting in solvents and solutes. Then, a deswelling process can be applied to drive out the solvent, for example, through annealing. During the deswelling process, the perovskite precursors starts to nucleate, and nanocrystals will form inside the polymer, the luminescent films can be achieved (**Figure 1b**).

The process is generic and can be applied to CsPbX_3 or MAPbX_3 precursor solutions with different halide

compositions ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) to achieve widely tunable bandgaps. As depicted in **Figure 1c**, a series of CsPbX_3 -PET samples can be synthesized through

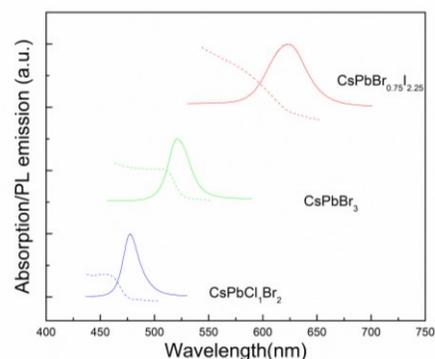


Figure 2. UV-vis(dotted line) and PL emission(solid line) for the CsPbX_3 DDPPC film spectra.

anion tuning, where vivid colors can be observed under UV exposure. As expected, the CsPbBr_3 sample exhibits pure green emission. By increasing the stoichiometric ratio of chloride and iodide precursors, the emission can be shifted to shorter and longer wavelengths, respectively, and the entire visible range can be covered.

Optical characterizations reveal the outstanding color purity and tunability of these DDPPCs. Photoluminescent (PL) spectra of the samples and their UV-vis absorption spectrums were plotted in **Figure 2**. The emission colors can be tuned from blue (477 nm) to red (645 nm) with a full width at half maxima (FWHM) ranging from 17.7 nm to 41.8 nm.

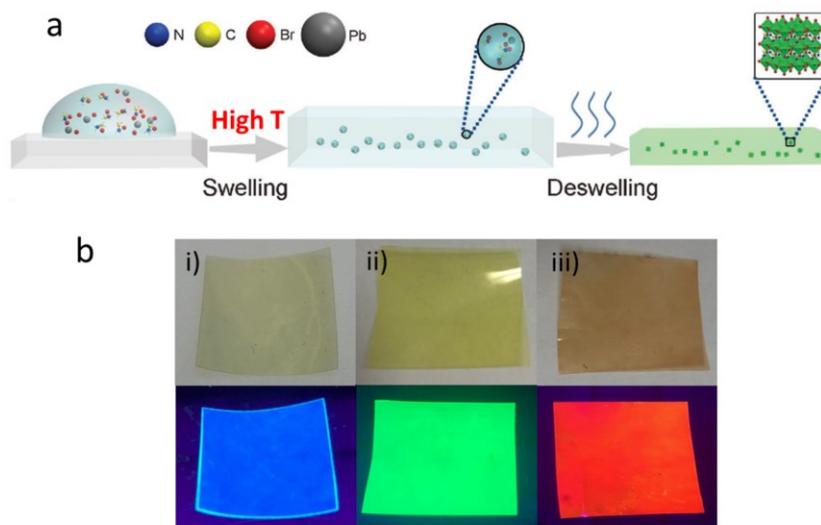


Figure 1. a) Scheme of ultrastable perovskite-polymer composite formation process through deep-dyeing swelling-deswelling microencapsulation strategy. b) Images of ultrastable perovskite-polymer composite films of different colors under ambient light (upper) and 395nm UV light (lower) excitation. Perovskite precursor compositions are i) $\text{CsPbCl}_1\text{Br}_2$, ii) CsPbBr_3 , iii) $\text{CsPbBr}_{0.75}\text{I}_{2.25}$.

Table 1. Emission peaks, FWHMs and PLQYs of selected ultrastable perovskite-polymer composite films.

Perovskite components	Emission peaks (nm)	FWHM (nm)	PLQY(%)
CsPbCl ₁ Br ₂	477	17.7	-
CsPbBr ₃	520	26.5	45.7
CsPbBr _{0.75} I _{2.25}	622	41.8	28.5
MAPbBr ₃	510	29.8	77.9

Among them, the pure green-emitting MAPbBr₃ manifests a high PL quantum yield of 77.9%, and other PL quantum yields were listed in **Table 1**.

Using PET as the polymer substrate, the corresponding DDPPCs exhibit much enhanced environmental stability even without barrier layer protection. Per our preliminary stability test, the DDPPC films remain brightly luminescent in water for over 2 years under ambient condition (**Figure 3a and 3b**). The red PPC films suffer from poor stability and very dimmed luminescence in the previous room-temperature SDM. Here, the DDPPCs can maintain their PL intensity in a homemade incubator with high temperature and high humidity (70°C and 90% RH) for 60 days (**Figure 3c**) without any decay. Moreover,

the DDPPC films also demonstrate excellent photostability. Under continuous excitation by a relatively intense blue laser (irradiance 100 mW/cm²) for 4 hours, the CsPbBr_{0.75}I_{2.25} DDPPCs still have 50.7% of its initial PL intensity, and can quickly recover (within 1 minute) to 90% of its initial intensity when the excitation is off. This improved SDM strategy not only works for the red ones, but also results in more stable MAPbBr₃-based green DDPPCs. In the same incubator, the MAPbBr₃-PET DDPPCs maintained 80% of their initial PL intensity after sixty days. Illuminating by the same blue laser continuously for 10 hours, the MAPbBr₃ green DDPPCs still have 87.8% of its initial PL intensity, and can fully recover to its initial PL intensity after the laser is turned off.

We believe the outstanding water and light stability should be ascribed to the protection effect of PET substrate. PET is a typical polymer that performs excellent barrier properties, which can prevent the small molecules such as oxygen, water and some organic molecules from penetrating into the polymer matrix.[10] Thus the lifetime of the perovskite nanocrystals that embedded inside of the polymer matrix could be significantly extended.

With the advantages of their process simplicity, extremely low cost, high stability, high luminescence efficiency and excellent color saturation, these PPCs hold great potential for many PL-related applications. The most immediate usage would be downconverters in the LCD backlights.[11] For concept demonstration, here we use the red CsPbBr_{0.75}I_{2.25} PPC film and green CsPbBr₃ PPC film as the downconverter pumped by a

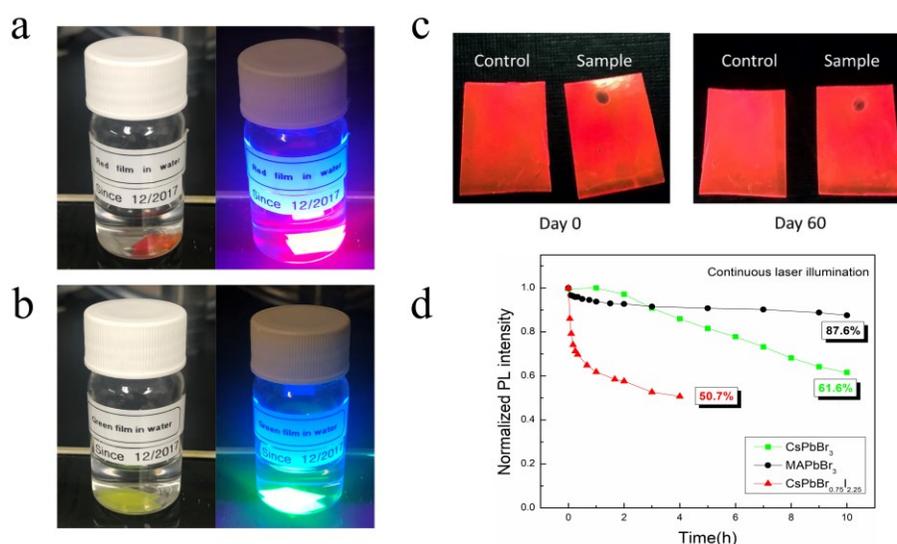


Figure 3. a) The red (CsPbBr_{0.75}I_{2.25}) DDPPC and b) the green(CsPbBr₃) DDPPC film (stored in water since 2017) synthesized by the deep-dyed strategy under ambient light and UV excitation. c) Pictures of the control and the sample during different stages of the stability test in a 70°C and 90% RH incubator. The control is stored in dark ambient air while the sample stays in the incubator. After 60 days, there is no visible PL decay of the red PPC sample. d) Normalized PL intensities of corresponding DDPPC films under continuous laser illumination.

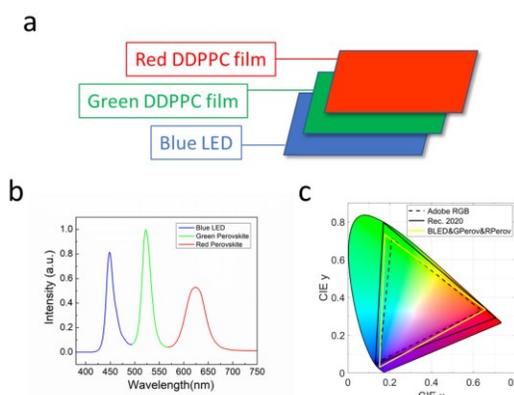


Figure 4. Application of the ultra-stable perovskite-polymer composite films as a) downconverting sheet in display backlighting. b) Emission spectra of a white LED system with green CsPbBr₃ DDPPC and red DDPPC films as downconverters for blue LEDs. c) Color gamut coverage of the white LED systems with Adobe RGB and Rec. 2020 standards for comparison in CIE 1931.

high power blue LED. Calculation indicates that the spectrum can match that of the CIE standard illuminant D65, as shown in **Figure 4b**, and can cover 99.8% of the adobe RGB color gamut and 81.83% of the Rec. 2020 color gamut. Hybridization of the PPC films with other state-of-the-art downconverters, such as quantum dots or narrow band phosphors will further enhance the color gamut coverage range [12]. This white light with narrow-band primary colors makes it ideal for LCD backlight.

3. Impacts

In conclusion, color-tunable DDPPCs are achieved through a simple, cost effective deep-dyeing process. The achieved DDPPCs demonstrate high efficiency, good color purity and excellent stability even without additional barrier layer. We believe our development of ultra-stable green and red DDPPCs can pave the way for perovskite downconverters to be utilized in practical display, lighting or other applications.

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