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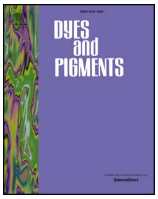

Synthesis of highly efficient and stable $CH_3NH_3PbBr_3$ perovskite nanocrystals within mesoporous silica through excess CH_3NH_3Br method

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ABSTRACT

Templated synthesis of $CH_3NH_3PbBr_3$ perovskite nanocrystals is facile, high-yield, ligand-free, and is another effective method aside from the colloidal method. However, the quantum yield (QY) is still inferior to that of the colloidal synthesized ones. In this report, we show that $CH_3NH_3PbBr_3$ nanocrystal within mesoporous silica with QY of 75% and full width at half-maximum (FWHM) of 22 nm are obtained through manipulating the molar ratio of CH_3NH_3Br versus $PbBr_2$ in precursor solution. It is found that excess CH_3NH_3Br can passivate the surface trap states, reduce nanocrystal size and narrow down the size distribution effectively. These features contribute to the rising of QY, blue-shifting of emission maximum and narrowing down of FWHM. The influence of excess CH_3NH_3Br can be interpreted in terms of enrichment on the interface of solvent/air because of amphipathy. Moreover, these $CH_3NH_3PbBr_3$ - mesoporous silica composites present good stability. They preserve 90% of its initial QY after a storage in wet weather with relative humidity of 70 ± 5% for 3 months. The synthesis method proposed in this research provides an effective way to achieve perovskite nanocrystals within mesoporous silica with high efficiency and stability.

1. Introduction

Organic–inorganic hybrid perovskites are denoted as ABX_3, wherein A is organic cation, B is metal cation (e.g., Pb^{2+}, Sn^{2+}), and X is halide anion (e.g., Cl^-, Br^-, I^-, pure or mixed) [1]. They possess favourable light absorption/emission and charge transfer properties and have been the research focus since 2009 [2]. The bandgap of ABX_3 can be tuned through utilizing appropriate A and/or X components [3,4]. For instance, replacement of bromide with iodide will reduce the bandgap, leading to a red shift of both absorption and emission [4]. Apart from this, ABX_3 nanocrystals have the advantage of high extinction coefficient, high quantum efficiency, high colour purity, and efficient charge injection/transport property [1,5,6]. Those merits collectively make it a promising candidate as light absorption and emission material in the field of photoelectric device, and have attracted tremendous research attentions [7–11]. Among these applications, quantum yield (QY) and colour purity of perovskites nanocrystals are two important parameters.

Perovskite nanocrystals are usually synthesized colloidally, which is of high QY and small FWHM [5,12–14]. In this method, perovskite nanocrystals are acquired via co-precipitation of several precursors with the aid of organic ligand, which consist of multiple steps and is low-yield [13,15]. On the other hand, template syntheses of perovskite nanocrystals, wherein crystallizations occur in confined region, also attract the interests of researchers since it is facile, high yield, and ligand-free [2,15–23]. The pioneering work is carried out by Kojima et al., who synthesize perovskite nanocrystals with the aid of mesoporous film of TiO_2 formed by sintering of TiO_2 nanocrystals [2]. Later on, Malgras et al. and Dirin et al. grow perovskite nanocrystals with regular size distributions within mesoporous silica of cylinder pore, with QY of 5.5% and 25% correspondingly [16,18]. However, QYs of perovskite nanocrystals synthesized within templates are low because of un-passivated surfaces, and an effective method to improve it is desired [23].

In addition, device stability is still a serious obstacle toward its practical application, which comes mainly from the degradation of perovskite materials, especially the moisture correlated degradation [24–27]. Recently, Arad-Vosk et al., Wang et al. and Lee et al. find that the thermal-, photo- and air-stability of perovskite nanocrystals inside template can be enhanced, benefiting from a prevention of structure rearrangement or/and surface energy related phase stabilization

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[19,28,29]. Nevertheless, the influence of silica wall upon the moisture stability of nanocrystals is still lacking, which is pivotal for its application in the optoelectrical devices.

In this work, we develop a simple and effective method for the synthesis of $CH_3NH_3PbBr_3$ nanocrystals with high quality inside mesoporous silica. The molar ratios of CH_3NH_3Br versus $PbBr_2$ in the precursor solution are manipulated in this method. Perovskite nanocrystals obtained are of high QY and small FWHM when CH_3NH_3Br is in large excess, which passivates surface trap states effectively and depresses the non-radiative recombination. In addition, we find that these nanocrystals are of high stability to resist moisture. We believe that results obtained here will provide valuable information for the future design and development of high QY and moisture-stable perovskite materials.

2. Experimental details

2.1. Chemicals

Lead bromide ($PbBr_2$, 98%, J&K Chemicals), methylamine solution in ethanol (33 wt%, Aldrich), hydrobromic acid (HBr, 48 wt%, Aldrich), cetyltrimethylammonium bromide (99%, J&K Chemicals), *N*,*N*-dimethylformamide (DMF, 99.8%, J&K Chemicals) are used as received. Mesoporous silica powders (meso-SiO_2) with pore size of 6 nm, 10 nm and 15 nm are purchased from Sigma-Aldrich.

2.2. Synthesis of methylammonium halides

CH_3NH_3Br is synthesized following the procedure reported in reference [4]. Firstly, 24 mL of a 33 wt% methylamine solution in absolute ethanol is added to 100 mL of ethanol (pre-cooled to 0 °C). Then 10 mL (8.6 mL) hydroiodic (hydrobromic) acid is added and the resulting mixture is stirred under inert atmosphere for 1 h. After that, water and ethanol are removed by rotary evaporation at 40 °C. Finally, the product is dissolved in ethanol, recrystallized in diethyl ether, and dried under vacuum at 40 °C for 14 h. Composition and phase purity are confirmed by powder XRD.

2.3. Template-assisted synthesis of lead halide perovskite nanocrystals (NCs)

The silica was dried at 250 °C in ambient condition for 2 h before the experiment. Freshly prepared DMF solution of CH_3NH_3Br (0.5 M) and $PbBr_2$ (0.5 M) are mixed with volume ratio of 1-1, 3-1, 6-1, 10-1, 15-1. Then the mixture is added dropwise to the powders with an increment of 5 μL to reach a final concentration of 0.5 μL solution per milligram powder. To achieve homogeneous mixing, the impregnated powder is vortex mixed vigorously (2000 rpm) after each drop. Finally, impregnated powders are placed on a hot plate and dried at 90 °C for 60 min.

2.4. Characterization

2.4.1. Structural characterization

The wide-angle powder X-ray diffraction (XRD) measurement is conducted on Rigaku Smartlab coupled with a D/teX-Ultra detector. Data is acquired at 20 °C with radiation wavelength of 0.1541 nm. The composite is ground into small particles and then dispersed in hexane before the sample preparation. The high-resolution transmission electron microscope (HR-TEM) images are carried out by a Tecnai F30 operated at an accelerating voltage of 300 kV.

2.4.2. Measurement of optical properties

The UV-Vis-NIR reflectance data are acquired with a PerkinElmer LAMBDA 950 spectrophotometer equipped with an integrating sphere and a halogen lamp as a light source. The composite is laminated with two layers of adhesive tape and then is used for the photoluminescence (PL) and PL lifetime measurement. The PL measurement of composites is performed on a FluoroSENS-9000 photoluminescence spectrophotometer coupled with a 150 W Xenon lamp set at an excitation wavelength of 400 nm. The sample is mounted in an integrating sphere with a diameter of 120 mm, wherein the emitting light uniformly distributes across the sphere through multiple diffuse reflections, and the intensity is then measured accurately. To verify the accuracy of the system, Coumarin 6 (standard QY of 78%) and Rhodamine B (standard QY of 68%) are measured in ethanol, returning QY values of 78% and 66%, respectively. Time-resolved PL lifetime measurements are carried out using time-correlated single-photon counting (TCSPC, XH2162) lifetime spectroscopy system equipped with a picosecond pulsed diode laser ($\lambda_{em} = 325$ nm) and a fast-single photon counting detector ($\lambda_{em} = 525$ nm). The time-resolved PL decay curves are fitted with a biexponential function of time (t): $F(t) = f_1\exp(-t/\tau_1) + f_1\exp(-t/\tau_1)$, wherein $F(t)$ is normalized intensity value at time t, f_1 and f_2 are prefactors, τ_1 and τ_2 denote time constants for different recombination process. Average recombination lifetime (τ_{ave}) is estimated according to the following equation: $\tau_{ave} = (f_1\tau_1{}^2 + f_2\tau_2{}^2)/(f_1\tau_1 + f_2\tau_2)$.

3. Results and discussion

The dry mesoporous silica is impregnated by a concentrated precursor solution containing CH_3NH_3Br and $PbBr_2$. The mixtures are then vigorously vortexed to achieve homogeneous dispersion of precursors in the pores of silica. The composite powders of silica and $CH_3NH_3PbBr_3$ nanoparticles are finally obtained after the evaporation of solvent. To decrease trap density and increase QY, we vary the molar ratio of precursors and use an excess of CH_3NH_3Br, wherein the excess Br ions are expected to coordinate the metallic Pb ions [13] and passivate the trap states. Photographs of composite powders under different preparation conditions are given in Fig. 1. With the increase of CH_3NH_3Br:$PbBr_2$ ratio, the colour of composite under white light changes from orange to merdoie. Orange is observed when blue and

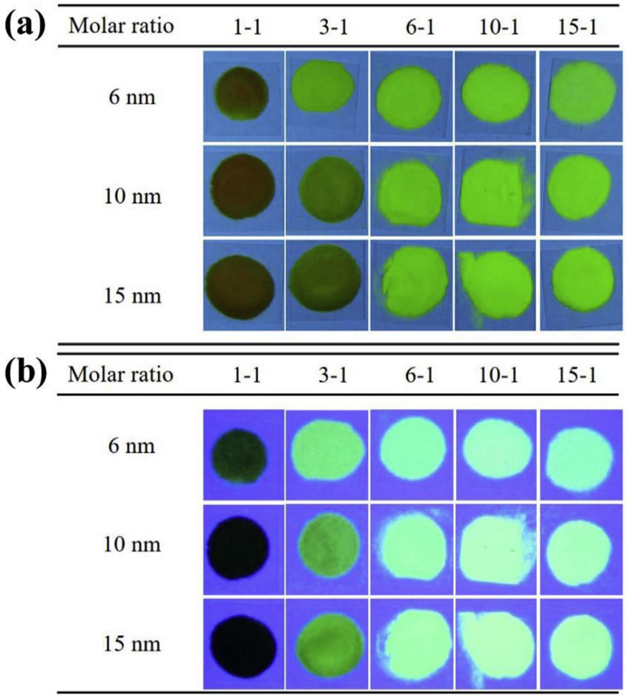

Fig. 1. Photographs of composite powders under the illumination of (a) white light and (b) UV light of 365 nm, respectively. The corresponding molar ratio of CH_3NH_3Br:$PbBr_2$ is indicated above the photograph while the pore size of mesoporous silica is shown in the left part.