Preventing Anion Exchange between Perovskite Nanocrystals by Confinement in Porous SiO2 Nanobeads

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ABSTRACT: All-inorganic CsPbX3 (X = Cl, Br, I) perovskite nanocrystals (NCs) are highly attractive due to their outstanding optical and electrical properties. However, poor stability and easy anion exchanges between CsPbX3 nanocrystals with different halides limit their applications in light-emitting diodes (LEDs). To solve the problems, we developed an approach to in situ synthesize CsPbX3 NCs into porous silica colloidal spheres, which can effectively prevent anion exchange and increase photo stability. Based on our results, we first proved that the anion exchange between CsPbX3 nanocrystals is mainly driven by physical collision of the nanocrystals, not requiring a bridge such as a solvent. We subsequently used an optimized ratio of green, red, and blue SiO2/CsPbX3 composites as solid-state luminescent materials to fabricate single-layer white light-emitting diodes (WLEDs). No anion exchanges have been observed in the LED fabrication and lighting process.

1. INTRODUCTION

In recent years, CsPbX3 (X = Cl, Br, I) perovskite nanocrystals (NCs) have become attractive for their use in many fields such as photovoltaic cells,1−3 photodetectors,4−6 LED5,9 and lasers14−18 due to their outstanding optical and electrical properties. Particularly, CsPbX3 NCs are suitable for application in light-emitting diodes (LEDs) due to their wide color tunability (410−700 nm), narrow emission line widths of 12−42 nm, high photoluminescence quantum yields (PLQYs) of 50−90%, and short radiative lifetimes.19 Compared with traditional CdSe-based quantum dots (QDs), the synthesis of CsPbX3 NCs can be done with lower temperature and without extra treatment of surface shelling, making CsPbX3 NCs promising candidates in the applications of LEDs. However, the anion exchange between CsPbX3 nanocrystals (NCs) with different halides when mixed together obstructs their practical applications in WLEDs. It is reported that CsPbBr3 and CsPbI3 NCs can form mixed halide CsPb(Br/I)3 NCs as soon as they are dispersed together in the solvent, and this conversion can be accomplished in 2 min.20 This quick anion exchange makes it difficult to prepare white-emission materials just by simply mixing the CsPbX3 NCs with different halides in one layer. Normally, green, red, and blue layers with corresponding CsPbX3 NCs are prepared separated and then assembled on the UV LED for emitting white light, which definitely causes more complexities in emission layer preparation and LED assembly.21 On the other side, the mechanism study of the anion exchange between different NCs has been rarely reported. Recently, Alivisatos and co-workers have reported that the anion exchange between CsPbBr3 and I− presents a surface-reaction-limited mechanism in the nonpolar solvent.22 However, they mainly focus on the exchange between CsPbBr3 NCs and free I−, not the exchange directly between CsPbBr3 and CsPbI3 NCs. Whether the mechanism of these two exchanges is consistent remains to be further confirmed. Therefore, regardless of the application and mechanism, the study of anion exchange between CsPbX3 NCs with different halides is urgently required.

Here, we find that the confined CsPbX3 NCs in porous silica (SiO2/CsPbX3 composite) can efficiently prevent anion exchange between the NCs with different halides. Considering the structure of our as-prepared SiO2/CsPbX3 composite, the material exchange to the solution is not limited very much because of the relatively large silica porosity, while the direct collision between NCs is largely hindered. Therefore, we conclude that the anion exchange between different NCs is mainly based on the physical collision, not requiring a bridge of the solution. In a typical synthesis of SiO2/CsPbX3 composite spheres with good dispersion, we first prepared silica spheres by Stöber et al.’s method,23 and then the interior of the silica spheres was selectively etched to produce the desired porosity by removing the core etchant. Recently, Alivisatos et al.22 demonstrated that the use of CsPbBr3 and CsPbI3 NCs in different ratios could fabricate a white light-emitting diode (WLED) via physical blending. However, the anion exchange between CsPbX3 NCs with different halides is too fast, which results in poor stability of WLEDs. Therefore, we choose SiO2/CsPbX3 composite spheres as the new material to fabricate WLEDs.

2. RESULTS AND DISCUSSION

Figure 1a shows a schematic illustration of the preparation process of SiO2/CsPbBr3. Typically, the silica spheres were
first coated by PVP to prevent it from being completely dissolved by NaOH in the subsequent etching step for strong hydrogen bonds can form between the carbonyl groups of PVP and the hydroxyls on the silica surface. After refluxing for 3 h in an aqueous solution of PVP, silica spheres were etched by NaOH at 30 °C. The dried porous silica spheres were then transferred to TOP to form a good dispersion in toluene. In this process, the TOP molecules could intensively bond with the oxygen of the silanol groups and change the silica particle hydrophobic characteristics to ensure that the porous silica disperses well in the nonpolar solvent, such as toluene. Then, the dispersion was swiftly injected into the flask containing the PbBr₂ precursor at 150 °C to synthesize SiO₂/CsPbBr₃ composite spheres. The SEM image (Figure 1b) shows the spherical morphology and narrow size distribution of the composites. The first image is a conventional TEM image. The EDX spectrum of a single SiO₂/CsPbBr₃ composite sphere. (g) XRD pattern of CsPbBr₃ and SiO₂/CsPbBr₃ composites.

Figure 1. (a) Schematic illustration of the preparation process of SiO₂/CsPbBr₃. (b) SEM spectra of SiO₂/CsPbBr₃ composites. The inset table shows the element ratio of Si and Pb. (c) TEM image of the porous silica spheres etched by NaOH. (d) HAADF-STEM image of the SiO₂/CsPbBr₃ composite spheres. (e) Elemental mapping of Si, O, Cs, Pb, and Br against a typical SiO₂/CsPbBr₃ composite sphere through EDS. The first image is a conventional TEM image. (f) EDX spectrum of a single SiO₂/CsPbBr₃ composite sphere. (g) XRD pattern of CsPbBr₃ and SiO₂/CsPbBr₃ composites.

distributed evenly against composite spheres indicates that CsPbBr₃ NCs were successfully grown into the porous silica matrix. The EDS spectrum of a single SiO₂/CsPbBr₃ composite sphere displayed in Figure 1f further confirmed the composition of Si, O, Cs, Pb, and Br. Besides, the X-ray diffraction (XRD) of the SiO₂/CsPbBr₃ composites also indicated the existence of CsPbBr₃ NCs in the porous silica spheres (Figure 1g). According to the above measurements, we can confirm that the CsPbBr₃ NCs have been uniformly loaded to the pores of the SiO₂ spheres.

The optical properties of individual SiO₂/CsPbBr₃ composites were investigated by microspectroscopy analysis. The SiO₂/CsPbBr₃ composites in the nonpolar solvent were dispersed on the glass substrate through a spin-coating method. An optical image (Figure 2a) shows that the SiO₂/CsPbBr₃ submicron spheres can be well separated on the glass substrate. Figure 2b shows the PL microscopy image of SiO₂/CsPbBr₃ spheres under a pulsed excitation at 405 nm. As shown in Figure 2c, we measured the PL spectra of a single SiO₂/CsPbBr₃ composite on the substrate with a narrow green emission peak at 515 nm and full width at half-maximum (FWHM) of 20 nm, which demonstrates that the porous silica shell does not influence the CsPbBr₃ NCs crystal quality and optical properties.

The ease of anion exchange reactions occurring between green CsPbBr₃ NCs and red CsPb(Br/I)₃ NCs is demonstrated by the PL spectra shown in Figure 3a. After mixing the green and red NCs together, their PL spectra become broader and have a red and blue shift, respectively (sample denoted as 10s and 30s). After mixing for 1 min, the green and red PL peaks merge into a single yellow PL peak. After 2 min, the PL

Figure 2. (a) Optical image (bright field) of SiO₂/CsPbBr₃ composites. (b) PL microscopy image of SiO₂/CsPbBr₃ composites. (c) PL spectra of single SiO₂/CsPbBr₃ composite (red circle).

Figure 3. (a) PL spectra showing an intermediate stage formed during inter-NC anion exchange between CsPbBr₃ and CsPb(Br/I)₃. The insets show the photographs of CsPbBr₃, CsPb(Br/I)₃, and their 1:1 mol % mixture under UV light. (b) PL spectra showing an intermediate stage formed during inter-NC anion exchange between SiO₂/CsPbBr₃ and SiO₂/CsPb(Br/I)₃. The insets show the photographs of SiO₂/CsPbBr₃, SiO₂/CsPb(Br/I)₃, and their 1:1 mol % mixture under UV light.
spectra remain unchanged, which means anion exchange is completed. On the other hand, the SiO2 sphere confinement successfully slows down the anion exchange reaction between the green and red NCs. As shown in Figure 3b, after mixing for 30 min, no spectral shifting occurs, and the PL intensity and spectra of the two composites are completely preserved. After 60 min, their PL spectra begin to shift. The complete merger of the two PL peaks requires approximately three days, which is much longer than that without SiO2 confinement. This indicates that the isolation of the CsPbX3 NCs by porous SiO2 spheres can efficiently prevent the anion exchange between perovskite NCs with different halide ratios.

We propose two anion exchange routes between perovskite NCs with different halides. The first route is based on the physical collision, and anion exchange happens quickly at the solid state during the collision process (Figure 4a). Because of a high collision frequency of 10 nm nanoparticles dispersed in the solvent, together with a short diffusion path length and low active energy of CsPbX3 NCs, anion exchange can easily occur by collision. The second route is using a solvent as a bridge (Figure 4b). Typically, Br− is released from CsPbBr3 NCs to form a balance with free Br− in the solution and then exchange with I− anions in the CsPbI3 NCs. Considering the structure of as-synthesized SiO2/CsPbX3 composites, the porous silica sphere is highly permeable to the small molecules and ions, typically called nanoreactors in the reference, and having less influence in the balance of CsPbX3 NCs and free X− in the solution. However, direct collision of the different CsPbX3 NCs in the composite can be successfully prevented because of the steric hindrance of the SiO2 network. According to the significant difference of PL evolution with/without SiO2 protection, we can safely conclude that the major route of anion exchange between CsPbX3 NCs is through direct collision, not requiring a solvent as a bridge. As long as we prevent the direct collisions of different NCs in the dispersion, we can efficiently limit their ion exchanges.

The anion exchanges can result in undesirable light mixing when fabricating WLEDs by the direct combination of differently colored CsPbX3 NCs in a single emissive layer. As we discussed above, the SiO2/CsPbX3 composites are well protected against anion exchange reactions, so they can be employed to fabricate a single emitting layer for WLEDs. As depicted in Figure 5a, in LED packaging, an optimized amount of green, red, and blue SiO2/CsPbX3 composites were mixed with a transparent PMMA/toluene solution (10 wt %) and then coated on a UV LED. The WLED is operated at a current of 20 mA (the inset in Figure 5c). As shown in Figure 5b, the working WLED has a color coordinate of (0.33, 0.29), which is close to that of the standard white emission (0.33, 0.33). Figure 5c shows the spectra of the WLED at different lighting times. After the WLED has worked 8 h, there was no conspicuous change of its PL spectrum, demonstrating great photostability. With a prolonged working time, the intensity of the blue PL peak slightly dropped, while the green and red PL peaks were nearly unchanged. This indicates that the blue SiO2/CsPb(Br/Cl)3 composite is a little more sensitive to UV light than the other two. The great stability of WLEDs indicates the promising application of SiO2/CsPbX3 composites.

3. CONCLUSIONS

In summary, we in situ synthesized stable SiO2/CsPbX3 composites with a narrow size distribution and good dispersion in a nonpolar solvent. The SiO2/CsPbX3 composites possessed a narrow emission line width and great stability. More importantly, we found that the silica barrier can efficiently prevent anion exchange between two perovskite NCs with different halides, and we concluded that the major anion exchange route is based on the direct collision between the NCs. Based on the as-synthesized composite and understanding of the anion exchange of different NCs, a single-emission-layer WLED has been fabricated using green, red, and blue SiO2/CsPbX3 composites as solid-state luminophores, which showed excellent color purity and stability.

4. EXPERIMENTAL SECTION

4.1. Materials. Isopropanol (Sinopharm Chemical Reagent Co., Ltd., ≥99.7%, AR), NH3·H2O (Sinopharm Chemical Reagent Co., Ltd., 25–28%, AR), tetraethylorthosilicate (TEOS, Sinopharm Chemical Reagent Co., Ltd., ≥28.4%, AR), polyvinyl pyrrolidone (PVP, Aladdin, Mn ≈ 10,000), NaOH (Sinopharm Chemical Reagent Co., Ltd., ≥96%, AR), tri-n-octylphosphine (TOP, Aladdin, 90%), Cs2CO3 (Aladdin, 99%), 1-octadecene (ODE, Aladdin, 90%), oleic acid (OA, Aladdin, 90%), oleylamine (OAm, Aladdin, 80–90%), PbBr2 (Aladdin, 99.0%), PbI2 (Aladdin, 98.0%), PbCl2 (Aladdin, 99.0%), toluene (Sinopharm Chemical Reagent Co., Ltd., ≥99.0%, AR), acetone (Sinopharm Chemical Reagent Co.,


**4.2. Synthesis of Silica Spheres.** Silica spheres were prepared by Stöber et al.’s method.\(^\text{25,30}\) In a typical process, 5 mL of TEOS was injected into a mixture of 100 mL of isopropanol, 20 mL of deionized water, and 5 mL of NH\(_3\)·H\(_2\)O under magnetic stirring at room temperature. After reacting for 2 h, the silica spheres were collected by centrifugation and washed with water three times and then re-dispersed in 60 mL of deionized water.

**4.3. Etching Silica Spheres.** We etched silica spheres following previously reported procedures.\(^\text{24}\) In a typical process, 6 g of PVP was added to the abovementioned 60 mL SiO\(_2\) solution. The mixture was heated up to 100 °C and refluxed for 3 h to load PVP. After cooling to room temperature, 90 mL of 0.067 g mL\(^{-1}\) NaOH solution was added to selectively etch silica spheres under continuous stirring. The process was monitored by measuring transmittance of the solution by UV–vis spectrometry. The resulting porous silica spheres were collected by centrifugation and washed with water three times and then dried at room temperature.

**4.4. Growth of CsPbX\(_3\) within Porous Silica Spheres.** Porous silica (0.1 g) was added into 4 mL of TOP and then stirred at 90 °C until the silica spheres were dispersed well in the solution. A Cs-oleate solution was prepared via a reported approach developed by Protesescu et al.\(^\text{19}\) ODE (15 mL) and 0.75 mmol of PbX\(_2\) (0.28 g of PbBr\(_2\) for green CsPbBr\(_3\) QDs, 0.24 g of PbI\(_2\) and 0.08 g of PbBr\(_2\) for red CsPbBr\(_3\)QDs, and 0.10 g of PbCl\(_2\) and 0.14 g of PbBr\(_2\) for blue CsPb(Br\(_{0.5}\)Cl\(_{0.5}\))\(_3\) QDs) were loaded into 50 mL three-neck flasks along with 4 mL of oleylamine and 2 mL of oleic acid; then, the mixture was heated at 120 °C for 15 min. After complete solubilization of the PbX\(_2\) salt, 4 mL of the TOP solution of silica spheres was added. Then, the temperature was raised to 150 °C and the Cs-oleate solution (2 mL of stock solution prepared as described above) was swiftly injected, and 5 s later, the reaction mixture was cooled down by an ice-water bath. The resulting products were collected by centrifugation and washed with toluene three times.

**4.5. Fabrication of the Single-Layer WLED.** A certain amount of green, red, and blue SiO\(_2\)/CsPbX\(_3\) powders were mixed in a transparent PMMA/toluene solution (10 wt %). The obtained mixture was then coated onto a piece of quartz glass. The glass was cured at room temperature for 30 min. Finally, a single-layer WLED was obtained by putting the glass above a UV LED.

**4.6. Characterization.** The transmittance and photoluminescence (PL) emission spectra were measured by the Ocean Optics USB2000+ spectrometer. X-ray powder diffraction (XRD) measurements were employed a Bruker AXS D8 X-ray diffractometer equipped with monochromatized Cu K\(_\alpha\) radiation (\(\lambda = 1.5418 \times 10^{-10}\) m). Transmission electron microscopy (TEM) and energy-dispersive X-ray analysis (EDX) measurements were performed by Tecnai G\(_2\) F20, FEI. Scanning electron microscope (SEM) was measured by S-3400 N II, Hitachi. The photoluminescence (PL) emission spectra, CIE color coordinates, and color rendering index (CRI) of the LEDs were measured in an integrating sphere equipped with a high-accuracy array rapid spectroradiometer (Ocean Optics).

**ACKNOWLEDGMENTS**

This work was supported by the National Key R&D Program of China (no. 2016YFA0201100), Thousand Young Researchers Program for Young Researchers, National Natural Science Foundation of China (no. 21601083), and Fundamental Research Funds for the Central Universities. The authors acknowledge the Technical Center of Nano Fabrication and Characterization, Nanjing University, for the TEM characterization.

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