Enhancing the Stability of Perovskite Quantum Dots by Encapsulation in Crosslinked Polystyrene Beads via a Swelling–Shrinking Strategy toward Superior Water Resistance

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Organic/inorganic hybrid lead halide perovskites are promising optoelectronic materials due to their unique structure, excellent properties, and fascinating potential applications in lighting, photovoltaic, etc. However, perovskite materials are very sensitive to moisture and polar solvent, which greatly hinders their practical applications. Here, highly luminescent perovskite–polystyrene composite beads with uniform morphology are prepared via a simple swelling–shrinking strategy. This process is carried out only in nonpolar toluene and hexane without the addition of any polar reagents. As a result, the as-prepared composite beads not only retain high luminescence but also exhibit superior water-resistant property. The composites emit strong luminescence after being immersed into water over nine months. Moreover, even in some harsh environments such as acid/alkali aqueous solution, phosphate buffer solution, and Dulbecco’s modified eagle medium biological buffers, they still preserve high luminescence. The applications in light-emitting diodes and cellular labeling agents are also carried out to demonstrate their ultrastability.

1. Introduction

Since the solar cells based on organometal lead halide perovskite were reported for the first time in 2009,[1] hybrid perovskite materials with excellent optoelectronic and photovoltaic properties have attracted plenty of attention in the scientific and industrial applications.[2–9] Their high photoluminescence quantum yield (PL QY) and narrow full width to half-maximum (FWHM) also indicate potential for light-emitting diode (LED) devices and display applications.[10,11] Additionally, the last few years have witnessed a burst of publications on all-inorganic CsPbX₃ (X = Cl, Br, I) perovskite quantum dots (PQDs) since a facile method developed by Protesescu et al.[12] The relative high quantum efficiency (CsPbBr₃ ≈90%), narrow emission, composition, and size-dependent luminescence covering the whole visible region (400–700 nm) make them the alternative candidates for LED or vivid color display devices.[13–18]

Suffering from the poor stability, the perovskite materials are sensitive to moisture, light, and temperature due to their low formation energy.[19,20] The highly dynamic ligand binding to the surface of nanocrystals results in the spontaneous growing or decomposition in polar solvent.[21–23] The fast anion-exchange reactions may occur in solution and even in the solid phase when mixing the PQDs with different halide components.[24–26] For instance, the red and green luminescence quickly shift to yellow when the green and red PQDs are mixed together.[27,28] Such chemical instability greatly limited the lighting applications of PQDs. Recently, many efforts have been devoted to stabilize PQDs or devices and a number of publications have reported this in different ways, but with limited success. Generally, mesoporous materials (such as TiO₂,[29] Al₂O₃,[30] and SiO₂[27,31–33]) were applied for stabilizing the perovskite. But, mesoporous materials will inevitable lead PQDs partially exposed in ambient air. Furthermore, fractional PQDs escape from the hole and lead to anion exchange when mixed two different PQDs during device fabrication. Crosslinking the perovskite nanocrystals (NCs) by incorporating organic ligands[34,35] or X-ray irradiation[36,37] is another effective method to enhance the stability. However, the progress in this direction is limited so far. Generally, the dense polymer matrices endow water-sensitive materials with water-proof characteristics. The method of embedding PQDs into polymer matrices can effectively improve the stability, especially water resistance.[38–42] For example, Wu, Dong et al. reported an in situ preparation of organic–inorganic
perovskite–polymer composite films through a simple microencapsulation strategy. Alivisatos and co-workers reported the encapsulation of perovskite nanocrystals into matched hydrophobic macroscopic polymer matrices by mixing the PQDs with presynthesized high-molecular-weight polymers. Despite some approaches based on embedding PQDs into polymer matrices have been reported recently, these approaches are suitable for preparing the luminescent films or bulk materials, but how to obtain a stable isolated PQD nanocomposite is still a challenge. Therefore, it is essential to explore an efficient method to protect PQDs in monodisperse nano/micron scale without fluorescence quenching.

Here, an ultrastable and highly luminescent perovskite quantum dots@polystyrene (PQDs@PS) composite nano/micron beads via a swelling–shrinking strategy is reported. This process is performed only in toluene and hexane without the addition of water or any other polar solvent. So the PQDs embedded in polystyrene matrices still retain high quantum efficiency. PS is one of the hydrophobic, tough plastic, and provides good resistance to acids and alkali. So far there has been extensive research for monodisperse polystyrene microspheres applied in medicine, biotechnology, and nanotechnology. In comparison with the uncross-linked polymer matrices, crosslinked PS beads cannot swell in polar solvents that exhibit better stability, thermal resistance, and biocompatibility. PQDs@PS composite microspheres not only show high luminence, high color purity, but also present relative good stability even when immersing into water, acid aqueous solution, alkali aqueous solution, phosphate buffer solution (PBS), and Dulbecco’s modified eagle medium (DMEM), which has the potential applications as the LED lighting material and fluorescent biological probes.

2. Results and Discussion

It is widely known that crosslinked polymer swells in good solvent and shrinks in theta solvent. Compared with uncrosslinked polymer that totally dissolves into good solvent, crosslinked PS beads will swell several times in terms of volume without changing of morphology. Toluene and hexane are good and theta solvent for PS, respectively. The synthesized CsPbBr3 perovskite nanocrystals can be stored in such nonpolar solvents for a long period without obvious fluorescence quenching. After filling in toluene and shrinking in hexane, the sample of PQDs@PS can be obtained without inert gas or baking/heating operation. The compact encapsulation of PQDs by hydrophobic polymer chains protects nanocrystals from contacting with water, salt, and acid/alkali environment directly (Figure 1a).

The CsPbBr3 perovskite quantum dots were prepared following the published literature. Their size and shapes were examined by transmission electron microscopy (TEM) (Figure 1b). The X-ray diffraction (XRD) patterns of the as-prepared CsPbBr3 (a) and the standard data (c) for CsPbBr3 (JCPDS No. 54-0752) are shown in Figure 1c. According to the XRD data, the as-synthesized CsPbBr3 quantum dots are well crystallized, and the diffraction peaks are consistent with the cubic phase structure of CsPbBr3. The as-prepared PQDs were dispersed in toluene with addition of PS beads. After swelling in the good solvent, the solvent was removed by centrifugation at a high speed or vacuum evaporating at 50 °C (with the help of oil pumps). The shrinking process was carried out by stirring in hexane. Notably, an equal concentration of PQD hexane solution was performed in this shrinking process in the case of PQDs leaking from PS spheres during the process. The sample of CsPbBr3@PS composite beads can be separated by centrifugation at a low speed for more details please refer to the Supporting Information (Figure 1d). We also successfully embedded organic–inorganic hybrid perovskite quantum dots CH3NH3PbBr3 into polymer matrices according to a similar approach (described in the Supporting Information).

Apparently, the fluorescence intensity increases as the function of loading amount of CsPbBr3 NCs in PS microspheres. To optimize the luminescent intensity for single PS particle, a series of experiments were carried out. The influence of the concentration of PQDs, the size of as-prepared PS beads, the crosslinking degree, and the dosages of PS are discussed in the Supporting Information. Generally, PQDs@PS composite microspheres mentioned below were prepared by the protocol of adding 400 mg PS beads (3 µm, 12% crosslinking degree according to the feeding ratio) in the 50 mL (73 mmol L−1) of CsPbBr3 toluene solution for sufficient swelling and next shrinking in hexane, unless otherwise mentioned. This process was performed in nonpolar toluene and hexane without the addition of any polar reagents that might lead to fluorescence quenching. Therefore, the fluorescence was well preserved. The PL QY of obtained CsPbBr3@PS composites were 68%.

Figure 1e–g shows the scanning electron microscopy (SEM) images of pure polymer spheres (left) and PQDs@PS composites (right). The composite remains monodisperse and round-shape except for slight growth of diameter after impregnation of PQDs. In contrast, the uncrosslinked PS beads aggregate after the swelling–shrinking process and turn to disordered morphologies (Figure S5, Supporting Information). As shown in Figure 1c, the diffraction peaks coincide well with the pristine CsPbBr3 QDs and standard data (JCPDS No. 54-0752), which indicates the CsPbBr3 nanocrystals retained their cubic structure after the swelling and shrinking process.

A series of lead halide perovskite CsPbX3 (X = Cl, Br, I) nanocrystals were successfully packed into PS spheres by our protocol. The emission spectra of the composites and bare quantum dots are shown in Figure S6 (Supporting Information). The emission peaks of composites show some slight blue/redshift, and the FWHM is slightly boarder (described in Figure 2a) compared with the pristine CsPbBr3 QDs and standard data (JCPDS No. 54-0752), which indicates the CsPbBr3 nanocrystals retained their cubic structure after the swelling and shrinking process.

For the data shown in Figure S6a, the emission peaks of PQD@PS composite are redshifted compared to the pristine PQDs. The redshift between CsPbBr3@PS composites and pristine CsPbBr3 PQDs was ascribed to the aggregation effect of PQDs. While the blueshift was due to the fact that the halide-mixed NCs mixed-halide perovskites, CsPb(Cl0.5Br0.5)3 and CsPb(Br0.5I0.5)3, are unstable in comparison with CsPbBr3, and their composition (Br/I ratio or Cl/Br ratio) may be changed after 2 h stirring in ambient air. Based on the previous reports, red CsPbBr3(J10, J20), and CsPbI3 PQDs present higher air and moisture sensitivity. Similarly, we found that the vivid red solution (when x > 0.5) turned to yellow and the fluorescent emission strongly shifted to orange after 10 h stirring in ambient atmosphere. Ice bath can effectively avert this situation; however, the fluorescent intensity of the
obtained red composite such as CsPb(Br₀.₄I₀.₆)₃@PS was relatively low (results not shown here). The slow diffusion of nanocrystals and sluggish movement of polymer chains at low temperature which result in a lower efficacy of impregnation. The average PL lifetime of CsPbBr₃@PS composite is 56.8 ns, while that of the pristine CsPbBr₃ nanocrystal is 7.9 ns (Figure 2b), which implies that the nanocrystals were packed into PS matrices, and, simultaneously, the change of environment of...
PQDs led to the increasing of the fluorescence lifetime as well as better emitting property.\cite{41, 51–53} It is widely known that the surface quenching leads to the shorter lifetimes.\cite{54} Herein, the increased PL lifetimes could be the result of fewer surface traps. On the one hand, the crystal size increased. As mentioned above, the redshift between CsPbBr$_3$@PS composites and corresponding NCs is associated with spontaneous growth in the ambient air. A larger crystal size means less surface defect for each single nanocrystal. On the other hand, in comparison with the embedding PQDs into rigid silica matrices,\cite{31–34} silanol groups are not effectively passivated on the surfaces of NCs and thus cannot prevent nonradiative recombination through localized states, while the compact and flexible PS polymer chains can passivate the surfaces effectively.

As mentioned above, anion exchange reacted when different kinds of lead halide perovskites mixed. This phenomenon takes place in liquid and even solid phase, which impedes their applications in LED devices and liquid crystal display (LCD) backlights. As shown in Figure S7a (Supporting Information), blue and green luminescence shift to cyan within several seconds in toluene solution. While mixing the red and green PQD powders (Figure S7b, Supporting Information), their PL spectra become broader first, and then turned to be yellow sharp emission in the end after rapid anion-exchange process. As demonstrated in Figure 3a, packing PQDs into crosslinked PS spheres is an effective way to prevent the ion-exchange reaction. There is no spectral variation or shifts even after 24 h mixing of blue and green emitting PQDs@PS powders. Furthermore, the fluorescence microscopy can be used to visualize the isolated blue and green composites (inset of Figure 3a). The mixed composite microspheres still emit strong blue and green luminescence, respectively, after one-week storage. As previously described, ion-exchange reaction taken place in solid state reactions is much slower than in solution. Therefore, PQDs@PS composites were soaked in halide salts hexane solution for further test. 20 mg of CsPbBr$_3$@PS composite powders were dispersed in 2 mL of hexane, and different quantities of hexylamine chloride precursor solution (dispersed in 5 mL hexane, preparation details are described in the Supporting Information) were swiftly injected. To ensure the completion of ion-exchange reaction, each mixture was under vigorously stirred for 10 min. Then, the PL spectra were obtained as shown in Figure 3b. Obviously, both PL peak position and FWHM present little difference (within 2 nm) in comparison with pristine composites. All the results indicate that this approach is relatively efficient to protect PQDs against anion exchange and offers the possibility for the applications of white light-emitting diodes (WLEDs) and LCD backlights by simple mixing.

A perovskite WLED device was fabricated by mixing the green CsPbBr$_3$@PS and red CsPb(Br$_{0.4}$I$_{0.6}$)$_3$ on a blue emitting InGaN chip. The spectrum of the resulting device is shown in Figure 4, in which three individual emission peaks were observed, indicating that the ion-exchange reaction of perovskites was successfully averted. Both of the positions of the electroluminescence (EL) maximum and FWHM for the green CsPbBr$_3$@PS and red CsPb(Br$_{0.4}$I$_{0.6}$)$_3$ are in good correlation with the solid state PL spectra of the respective powders. The PL peak positions are 442, 524, and 614 nm for the primary colors, and 21, 22, and 44 nm for FWHM, respectively. The inset picture shows the...
color coordinates of three primary colors for the PQD-WLED at (0.16, 0.018), (0.14, 0.79), (0.64, 0.35), and (0.31, 0.30). The large covering area of color coordinates also indicates great potential application in vivid wide color gamut displays. Considering the photostability and thermostability are important for practical PL applications, we put PQDs@PS composites under continuous UV-light (emission: 365 nm; power: 16 W; window area: 4 cm × 19 cm; irradiation distance: 15 cm) irradiation for 15 d to test their photostability. Since the network density of polymer chains may affect the photostability, the crosslinking degree of 6%/12%/18% PS beads was tested in this experiment, respectively. From Figure S8 (Supporting Information) described above, all composites exhibit better photostability to some extent compared with bare PQDs. The thermal behavior of the composites was further studied by differential scanning calorimetry (DSC) and thermogravimetric (TG) techniques. As shown in Figure S9 (Supporting Information), the sharp endothermic peak on 135 °C was observed in the DSC curve (dashed line in blue) that attributed to the glass transition of pure crosslinking PS spheres. In comparison, the glass transition of CsPbBr3@PS composites got a relative broad temperature range from 100 to 190 °C (solid line in blue), which suggests that the interaction between PQDs and PS microspheres greatly influences the thermal movements of chain segments. Compared with the uncrosslinked PS latex got a glass transition temperature at about 100 °C and melting point of 270 °C,[55,56] the composites present high thermal resistant property owing to the fact that crosslinked PS are infusible. Despite numerous efforts in improving stability of perovskite, the highly luminescent nanohybrid PQDs still quenched most of their emission when being immersed into water.[28,42] In comparison with porous materials, polymer chains encompass the nanocrystals compactly, which endows the composite excellent water resistant property. We stirred the composite in water for 3 d. Then the composite was separated from water by a Büchner funnel and dried in a vacuum oven at room temperature. The absolute PL QYs of composites were 64.7%, while the luminescence of bare nanocrystals was completely quenched owing to irreversible degradation. It is very surprising that the PQDs@PS composites still emitted strong green luminescence even after nine-month storage in water. The photoluminescence spectra were measured to monitor the intensity of fluorescence. It is worth noting that in order to eliminate the instrumental error from spectrophotometer, a certain concentration of rhodamine B aqueous solution was used as reference (stored in dark) for each measurement. The sample of aqueous solution was sonicated for 10 min before testing to ensure the homogeneity. As shown in Figure 5a, the composite remains 20–30% intensity of fluorescence even after 30 d of stirring in water according to the different degree of crosslinking. The sample with 12% crosslinking degree exhibited the best performance for water resistance. It is surprising that the water resistance of PQDs@PS composites demonstrated a size-dependent effect. 400 and 800 nm PQDs@PS beads show rapid luminescence quenching in aqueous solution. This may be attributed to the distribution of PQDs in PS particles. It is reasonable to speculate a large proportion of nanocrystals located in periphery of small-size PS beads, which leads to poor waterproof property. In addition, increasing the dosage of PS making little difference with the loading amount of PQDs for PS spheres, their PL spectra (Figure S10, Supporting Information) also show similar water resistant property. Therefore, a large-scale production (about 6.2 g, Figure 6) with superior water resistant property can be obtained in one batch.

Figure 5. The water resistance test of CsPbBr3@PS composites: a) PL spectra of CsPbBr3 NCs packing into PS spheres with different degree of crosslinking (DCL) and different diameter. b) PL intensity of CsPbBr3@PS immersed into PBS, DMEM, alkali, and acid aqueous solution.

Figure 6. a) Preparation of CsPbBr3@PS composites in large scale. The photographs of large-scale production under normal indoor light b) and UV light c) illumination.
Inspired by the superb water-resistant characteristic of this hybrid material, the stability of the composite was tested under harsher condition. The green luminescence of CsPbBr$_3$@PS composites still remained when the samples were stirred into the PBS, DMEM, alkali, and acid aqueous solution. All samples exhibit good stability except for the pH = 1 strong acid solution. The intensity of luminescence remains 53–69% after stirring for 96 h in different chemical environment (Figure 5b). These experiments verified that the hydrophobic PS network is very compact that can effectively prevent permeation of water molecules and even ions. Moreover, the crosslinked polystyrene-polyacrylic acid (PS-PAA) beads were prepared by adding a certain amount of hydrophilic acrylic acid monomer during polymerization. The integration of PAA to PS improves the hydrophilicity. The Zeta potential shows the evidence of hydrophilic PAA grafted on the sphere surface (inset of Figure S11, Supporting Information). As shown in Figure S12 (Supporting Information), similar to the situation of bare nanocrystals, the PQDs embedded into the PS-PAA matrices rapidly degraded and lost luminescence when immersed in water. This suggests that the hydrophobic PS network plays an important role in the preservation of water resistant property.

Despite high luminescence of CsPbBr$_3$ perovskite nanocrystals, the hypertoxic lead content and degradation in water enable their applications in biolabeling to be a
big challenge. However, the PS-encapsulated PQDs exhibit resistance for water, alkali, acid, and PBS buffer solutions, which provides opportunities for potential bioapplications. Therefore, standard 3-(4,5-dimethylthiazol-2-yl)-2,5-diphenyltetrazolium bromide (MTT) assay was carried out to prove our assumption. The MTT assay is a general tool to measure the cytotoxic effect. In this study, HeLa cells were seeded in 96-well plates and then blue CsPb(Br0.5Cl0.5)3@PS was added to the medium for 24 h co-incubation. As shown in Figure S12 (Supporting Information), the samples with 10 mL deionized water (the same concentration used in bioimaging experiment). After stirring for 24 h, the supernate was obtained by filtering the composite out via 0.45 nm filter for three times. Then the concentration of Pb²⁺ was measured by inductively coupled plasma-atomic emission spectrometry (ICP-AES). As a result, the concentration of Pb²⁺ was 1.931 ppm in the supernate. In comparison with the “drinking water quality standards” (10–15 ppm),[7] the result is rather low and safe, which also indicates the validity of encapsulation. Hence, the water resistant property of the composite and adequate encapsulation offers them opportunities for cellular labeling agent, which is difficult to realize based on the previous reports. As shown in Figure 7, after culturing together with PQDs@PS (1.67 mg mL⁻¹) at 37 °C for 1 h, the bright green luminescence was found from the HeLa cells. It is notable that the green luminescence is mainly concentrated on the edge of the cells. In addition, different from other cellular labeling agents, the intensities of luminescence were not obviously increased with time prolonging. These results may be attributed two reasons. On the one hand, the PS beads were hard to internalize into the cytoplasm owing to the relative large size. On the other hand, we speculate that the PS beads were detained in cell membrane due to the hydrophobic interaction between PS beads and phospholipid molecules. These interesting properties enable the PQDs@PS beads to be a special luminescence probe for cell membrane labeling. Additionally, one can see that the blue luminescence of 4,6-diamidino-2-phenylindole dihydrochloride (DAPI) for cell nucleus dye was significantly decreased after two-week storage in PBS buffer, while the PQD luminescence still presents high signal to noise ratio, which exhibits the high stability.

3. Conclusion

In summary, we have demonstrated that perovskite quantum dots can be packed into crosslinked polystyrene beads via a simple swelling–shrinking strategy in nonpolar toluene and hexane without the addition of any polar reagents. The PQDs in the polymer matrices not only retain strong luminescence, high color purity but also present high stability. The ion-exchange reaction of perovskite was successfully averted. A perovskite WLED device was fabricated by simply mixing the green CsPbBr3@PS and red CsPb(Br0.4I0.6)3 on a blue InGaN chip. The composite exhibits superior resistance to water, acid/alkali aqueous solution, and even biologic buffers such as PBS and DMEM. The superior stability makes the composite a cellular labeling agent possible, which is difficult to be realized before.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

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