Improved Synthesis of Perovskite $\text{CsPbX}_3@\text{SiO}_2$ ($\text{X} = \text{Cl}, \text{Br}, \text{and I}$) Quantum Dots with Enhanced Stability and Excellent Optical Properties

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Halide perovskite quantum dots (QDs) have been considered to be an outstanding optoelectronic material. However, their poor stability caused by their large specific surface area and high sensitivity to moisture, greatly hinders their practical application. Here, a simple silica (SiO_2)-coating process is adopted to solve this problem without affecting their optical properties. Firstly, monodispersed CsPbX_3 ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) with cubic morphologies (~ 8 nm edge lengths) are successfully obtained using a modified hot-injection method, omitting the links of drying and degassing which can reduce energy consumption and save cost. Next, $\text{CsPbX}_3@\text{SiO}_2$ nanoparticles with spherical morphologies ($1.2 \mu\text{m}$) are obtained through a novel method based on the high hydrolytic rate of tetramethyl orthosilicate (TMOS) using CsPbX_3 as the precursor. Photostability tests indicate that the $\text{CsPbBr}_3@\text{SiO}_2$ QDs are markedly more stable than the pure CsPbBr_3 . The PL intensity of the $\text{CsPbBr}_3@\text{SiO}_2$ dispersed in a mixed solution of toluene and water retained 77 % of the initial value even after 12 h, which was much higher than the pure CsPbBr_3 . Similar experimental results are also observed when $\text{CsPbBr}_3@\text{SiO}_2$ and CsPbBr_3 were dispersed in toluene exposed to air. This material provides a novel platform for the application of perovskite quantum dots in light-emitting device applications.

Keywords: Halide perovskite quantum dots; $\text{CsPbBr}_3@\text{SiO}_2$; Enhanced stability; Optical property

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1. Introduction

As a new optical material, halide perovskite quantum dots (QDs) have attracted widespread interest owing to their excellent photoluminescent and electronic properties, such as long-range charge transport, wide emission spectrum range, high absorptivity and high quantum efficiency.¹⁻¹⁰

The development of halide perovskite quantum dots has enabled them to be widely used in solar cells^{11,12} and in the fields of lighting and displays.¹³⁻¹⁶ All-inorganic CsPbX_3 ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) quantum dots, which have tunable bandgap energies, were first prepared by L. Protesescu *et al.* was found to realize full chromatographic emission over the visible range of 410-700 nm.¹ However, this material suffers from poor stability owing to its large specific surface area and high sensitivity to moisture in the surrounding environment, which greatly hinders its commercial application.¹⁷⁻²⁰ Therefore, improving their stability to air and moisture in the environment are important factors to fabricate commercial perovskite-based optoelectronic devices.

It is widely believed that coating methods are an effective way to protect colloidal nanoparticles from the influence of moisture and improve their photostabilities.^{20,21} Silica (SiO_2), which is a traditional transparent inorganic coating material, can prevent the core material from the air and moisture, even when dispersed in water, and can be used directly in biological applications.²⁰⁻²⁴ In fact, SiO_2 -coated inorganic

QDs (such as CdSe ,²⁵ ZnSe ,²⁶ CdTe/CdS ,²⁷ CdSe/CdS ,²⁸ and CdSe/ZnS ²⁹) have been widely studied, and their water solubility and photostability have been shown to improve significantly after coating. At present, the coatings by silica mainly use tetraethyl orthosilicate (TEOS) as the precursor, a mixture of water and ethanol as the solvent, and aqueous ammonia as the catalytic agent, respectively.^{30,31} However, there is no success that have been achieved to improve the photostability or water solubility of silicon-coated perovskite QDs by using the traditional method.^{32,33} The main reason is that perovskite QDs are highly sensitive to the surrounding environment, and the presence of water, alcohols or amines during the formation of the silica on perovskite QDs surface could quench the emission of perovskite QD. Generally, the hydrolytic reaction of TEOS requires the assistance of water, but a large amount of water can decompose the perovskite QDs before the generation of SiO_2 . Therefore, the key problem in the formation of silica-coated perovskite QDs is to avoid the direct contact between the QDs and water.

Recently, Li *et al.* reported that the CsPbBr_3 through incorporating them into a $\text{SiO}_2/\text{Al}_2\text{O}_3$ monolith using sol-gel reaction can improve the stability.³⁴ Loiudice *et al.* used the atomic layer deposition (ALD) method to synthesize a film of CsPbX_3 with an amorphous alumina matrix, and it can enhance their stability.³⁵ Huang *et al.* synthesized the water-resistant CsPbX_3 powders using polyhedral oligomeric silsesquioxane (POSS).³⁶ Sun *et al.* reported that the inorganic perovskite QDs capped with (3-aminopropyl) triethoxysilane (APTES) can improve their stability.³⁷ However, the improved stability of perovskite QDs just in air still limits their applications owing to the subsequent treatment and dissolution usually require a great amount of polar agents.

In this paper, we develop a new method of coating SiO_2 on all-inorganic perovskite QDs without destroying their luminescent properties in the presence of trace amounts of water. Toluene, as a nonpolar solvent, was selected as the solvent in the coating process

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because toluene contains very low content of water and is compatible with the all-inorganic perovskite QDs.³⁸ Additionally, we found that the hydrolytic rate of tetramethyl orthosilicate (TMOS) is much faster than that of TEOS.^{39,40} Therefore, TMOS can consume the majority of the water in a short period of time, thus reducing the damage caused by water to the all-inorganic perovskite QDs. However, the water content in toluene cannot completely hydrolyze the TMOS, which results in SiO₂ not being completely coated on the all-inorganic perovskite QDs. The solution is to add small amounts of water to the toluene such that the water can be consumed quickly by the TMOS. All-inorganic perovskite QDs coated by SiO₂ can be obtained successfully by using this method, which can provide a novel opportunity for photoelectric devices.

2. Experimental Section

2.1 Materials

The started chemicals used in this experiment mainly contain the cesium carbonate (Cs₂CO₃, 99.9%, Macklin), octadecene (ODE, 90%, Macklin), oleic acid (OA, 90%, Macklin), oleylamine (OLA, 80-90%, Macklin), lead chloride (PbCl₂, 99.9% Macklin), lead bromide (PbBr₂, 99%, Macklin), leaching iodide (PbI₂, 99.9%, Aladdin), toluene (99%, H₂O content 0.02%), tetramethyl orthosilicate (TMOS, 98%, Aladdin) and tetraethyl orthosilicate (TEOS, 99.99%, Macklin). All chemicals are directly required without further purification.

2.2 Preparation procedure

2.2.1 Preparation of Cs-oleate

Cs₂CO₃ (0.08g) was added into 50 mL 3-neck flask along with OA (0.25 mL) and ODE (3 mL). The mixture solution heated to 150 °C under nitrogen atmosphere with the heating rate of 3 °C/min until all the Cs₂CO₃ reacted with OA. It is worth noting that the Cs-oleate can precipitate out of ODE at room temperature, it has to keep the temperature at 120-150 °C before injection. The whole process was under nitrogen atmosphere.

2.2.2 Preparation of CsPbX₃ (X=Cl, Br, I) QDs

ODE (5 mL) and PbX₂ (0.188 mmol, X=Cl, Br, I or their mixtures) were added into 50 mL 3-neck flask and heated to 120 °C under nitrogen atmosphere with the heating rate of 3 °C/min. After 3 min, the OLA (0.5 mL) and OA (0.5 mL) were added quickly. When the PbX₂ salts were completely dissolved, the temperature was raised to 180 °C (the heating rate is 4 °C/min) and the Cs-oleate solution (0.4 mL) was quickly added. After 5 s, the crude solution was cooled down to room temperature by the ice-water bath and the CsPbX₃ nanoparticles were collected by centrifuging for 5 min at 12000 rpm. After centrifugation, the supernatant was discarded and the precipitate was redispersed in 4 mL toluene through the ultrasonic oscillation. Then, the solutions were centrifuged again at 12,000 rpm for 10 min, and the precipitate was dried under vacuum at 50 °C for 12 h. The dried CsPbX₃ nanoparticles were dispersed in 30 mL toluene to form the stable colloidal solutions for further experiment and characterization. For CsPbI₃, the heating rate is 6 °C/min when the temperature was raised from 120 to 180 °C.

2.2.3 Synthesis of CsPbX₃-QDs@SiO₂

TMOS (100 μL) was added into 50 mL single-mouth flask which contains 20 mL of the stable colloidal CsPbX₃ QDs toluene solutions (0.08 mg/mL) with sealing plugs. The mixture solution was stirred for 5 min at the room temperature. After that, the deionized water (DI water) (70 μL) was added quickly. The sealed single-mouth flask was placed in a light-shielded environment at room temperature, and stirring

continuously for 48 h. The precipitations were collected through centrifugation at 4500 rpm for 5 min, washed repeatedly with toluene, and dried under vacuum at 60 °C for 12 h. For CsPbI₃@SiO₂, the powders were prepared following the same procedures by adding the mixture of TMOS (30 μL) and TEOS (70 μL), and DI water (10 μL) into CsPbI₃ (20 mL) toluene solution with the stirring time of 36 h.

2.3 Characterization

The X-ray diffraction (XRD) patterns for phase evolution were obtained through the nickel-filtered Cu Kα radiation in the 2θ range 10-50° at a scan speed of 4.0° 2θ/min (Model D8 ADVANCE, BRUKER Co., Germany). The UV/vis absorption spectra were measured by using a UV/vis spectrophotometer (UV-3600, Shimadzu Corporation). The microstructure of the samples was investigated by the HR-Transmission Electron Microscope (HR-TEM) (JEM-2100F, JEOL, Japan). The femtosecond pump-probe time-resolved spectrum was measured by the pump detection system (FemPum-A, Suzhou Guangda Sitong Instrument Technology Co., Ltd., China). The photoluminescence (PL) spectra of samples were performed using the Fluorescence Spectrophotometer (FP-6500, JASCO Co., Japan) at room temperature equipped with a Φ60-mm integrating sphere (ISF-513, JASCO, Tokyo, Japan) and using a 150-W Xe-lamp as the excitation source.

3. Results and discussion

Highly monodisperse CsPbBr₃ perovskite QDs are obtained by using the improved hot-injection method. In a typical synthesis, the preparation of Cs-oleate and the dissolution of PbX₂ are carried out at the same time in two 3-neck flask under nitrogen atmosphere. In the process, the links of drying and degassing (vacuum treatment) can be omitted compared with the traditional hot-injection method, which can reduce the energy consumption and save the cost. As shown in Fig. 1a, highly monodisperse CsPbBr₃ perovskite QDs with cubic morphology are obtained in high yield. From the size distribution histogram (inset of Fig. 1a), the average particle size is approximately 8.4±0.8 nm, and the microstructures of the other perovskite QDs samples are identical to those of CsPbBr₃. In addition, the substitution of the halogen element has no obvious effect on the morphologies and particle sizes of the CsPbX₃ perovskite QDs. The sample possesses a highly single-crystalline nature (Fig. 1b), and two typical interplanar distances of 0.563 and 0.397 nm, corresponding to the (100) and (110) planes of the cubic perovskite phase, can be observed (inset of Fig. 1b). The crystal structure of perovskite QDs are investigated by XRD (Fig. 1c). It is clearly revealed that all the perovskite QDs exhibit similar XRD patterns, which are well crystallized in the cubic phase (JCPDS No. 54-0752).⁴¹ This result arises from the combined effects of the higher synthetic temperature and surface energy contributions. The positions of the major peaks are found to blueshifted with the halogen atom doping changing from Cl, Br to I, owing to the ionic radii increasing (Cl<Br<I).⁴² These results are similar to those of perovskite QDs synthesized by the traditional hot-injection method.

The photoluminescence (PL) of perovskite QDs are measured by the Fluorescence Spectrophotometer at room temperature. As shown in Figs. 2a and 2b (Fig. 2a shows a digital photo of the QDs under 365 nm excitation from a hand-held UV lamp), it can be observed that a color-tunable emission can be obtained over the whole visible spectral region through adjusting the content ratio of the halogens in PbX₂ or by their mixture (X=Cl, Br, I, or Cl_xBr_yI_{1-x-y}, where 0 ≤ x, y ≤ 1) with the emission peaks shift to longer wavelengths, from near ultraviolet light (~ 412 nm) to infrared light (~ 700 nm), as the halide species and

Fig. 1 (a) Typical TEM images of the CsPbBr₃ QDs, the inset is the size distribution histogram; (b) the HRTEM micrograph of an individual CsPbBr₃ nanoparticle, the inset is the SAED pattern; (c) the XRD patterns of CsPbX₃ (X=Cl, Br, I) nanoparticles.

Fig. 2 (a) Digital images of the CsPbX₃ QDs under 365 nm excitation from a handheld UV lamp; (b) the representative PL spectra of CsPbX₃ QDs (λ_{ex} = 400 nm for all but 350 nm for CsPbCl₃ QDs); (c) the typical of optical absorption and PL spectra of the colloidal CsPbX₃ QDs; (d) the CIE chromaticity diagram for the emission of CsPbX₃ QDs under UV excitation (black data points) and compared to most common NTSC TV color standards (solid white triangle); (e) the time-resolved fluorescence decay curves of colloidal CsPbX₃ QDs.

Fig. 3 (a) The transient absorption spectra of the CsPbBr₃ QDs, excited by a femtosecond-pulsed laser at 400 nm with a pump-light intensity of 2.4 mW; (b) the variation curve of the optical density versus the delay time at the probe wavelength of 480 nm, for pump light powers of 1.2 and 2.4 mW; and (c) the instantaneous absorption curve of the CsPbBr₃ QDs over the 460-560 nm band, the excitation light is the pump light at a wavelength of 400 nm and a power of 1.2 mW.

content changes. The emission peaks are narrow and symmetrical, and the full width at half-maximum (FWHM) of the samples were 12 - 34 nm (Fig. S1). This phenomenon can be attributed to the forbidden bandwidth, where the addition of Cl ions can increase the forbidden bandwidth and thus a blueshift of the emission peak are observed. While increasing the I ions concentration can reduce the forbidden bandwidth such that the position of the emission peak will redshift.^{43,44} Furthermore, the emission spectra of the colloidal CsPbX₃ perovskite QDs are Stokes shifted compared to their corresponding optical absorption spectra (Fig. 2c). CsPbX₃ QDs with smaller Stokes shifts can be distinguished from the fluorescent dyes and the background fluorescence. In practical applications, the background fluorescence can be eliminated to improve the sensitivity by adjusting the excitation wavelength or using appropriate filters. In addition, effective control of the emission spectrum over a small wavelength range can be achieved by controlling the reaction temperature (140-200 °C) (Figs. S4 and S5). The reaction temperature had no obvious effect on the phase and morphology of the samples (Figs. S2 and S3). However, the particle size increased slightly with increasing reaction temperature due to the crystal growth rate increases with increasing reaction temperature.

Perovskite QDs typically have higher quantum efficiencies and narrower PL spectra compared with those of traditional rare earth phosphors or other fluorescent dyes, and their emission peaks can be fine tuned to produce saturated colors⁴⁵ based on the Commission International de L'Eclairage (CIE) chromaticity coordinates, which can compare the quality of colors by drawing hue and saturation comparisons that are visible to the human eye. Fig. 2d shows the CIE chromaticity coordinates for the emissions of the CsPbX₃ QDs under UV excitation. It can be seen that the QDs represent a wide range of pure colors. The selected green, red and blue emitting areas, indicated by triangles, encompass 139% of the NTSC TV color standard (introduced in 1951 by the National Television System Committee)^{1,46}, mainly extending into the green and red regions. It is further demonstrated that the CsPbX₃ QDs have a wide range of luminescent colors in the visible range, which can be used to produce Q-LEDs displaying with strong color reducibility and excellent color rendering. The luminescence decay curves of the CsPbX₃ QDs can be fitted with two-exponent exponential decay functions, as shown in Fig. 2e. The luminescent lifetimes are in the range of 2-18 ns, which is similar to the 1-29 ns reported in a previous paper and reveals a high ratio of radiative to nonradiative transitions.¹

The femtosecond transient absorption spectrum is based on the pump-probe detection principle, and the time-resolved transmission or reflection spectra are measured by exciting the optical absorption processes within the material. At the same time, the time-decay information of the excited state can be obtained. We used a femtosecond-pulsed laser at 400 nm to excite the CsPbBr₃ QDs, and the sample produces nonequilibrium perturbations, which can cause the sample to enter the nonequilibrium state, that is, the sample is excited from the ground state to the excited state. The absorption intensity of the sample from the excited state to the ground state can be measured when the sample is irradiated by another quasi-continuous white light source (450-600 nm). Fig. 3a shows the transient absorption spectra of the CsPbBr₃ QDs. It can be seen that a strong photobleaching signal (PIB) is obtained within the wavelength range of 490 - 520 nm, which is caused by stimulated emission. In addition, two new photoabsorption signals can be seen. The variation curve of the optical density versus time at the probe wavelength of 480 nm was shown in Fig. 3b. It can be seen that increasing the excitation power does not affect the carrier lifetime and carrier transport velocity, indicating that the excitation

power has no effect on the performance of the quantum dots. Fig. 3c shows the instantaneous absorption curve of the CsPbBr_3 QDs for the 460 - 560 nm band. It can be seen that the absorption peak redshifts and decreases in intensity with increasing time delays. The main reason for this is that the photoabsorption lifetime at the short wavelength is short, and with the passage of time, only the excitation transient with a longer lifetime can absorb the probe signal. Through the femtosecond transient analysis of the CsPbBr_3 QDs, it can be seen that the optical gain of the sample is obvious and that a population inversion can be produced rapidly. The number of particles in the excited state with a low energy level is higher than that of particles in the ground state with a high vibrational energy level, and a typical four-level system is formed.

Based on the above analysis, CsPbX_3 QDs with good optical properties have been obtained by using the improved hot-injection method. However, these QDs suffer from low stability owing to their sensitivity to moisture.^{17, 20} To overcome the deficiency of stability, SiO_2 -coated inorganic CsPbX_3 perovskite QDs were successfully acquired to improve the stability. After a 48 h reaction, a large quantity of yellow-green gel powders (dried under vacuum at 60 °C for 12 h) were obtained (shown in the inset of Fig. 4a), which were easily collected at a relatively low centrifugal speed (4500 rpm/min). Fig. 4a shows the TEM images of the $\text{CsPbBr}_3/\text{SiO}_2$ powders. It can be seen that the resultant products exhibit a spherical morphology with an average size of $\sim 1.2 \mu\text{m}$, which is much larger than that of the pure QDs ($\sim 8 \text{ nm}$). After SiO_2 encapsulation, the production weight of the $\text{CsPbBr}_3/\text{SiO}_2$ increased from $\sim 1.6 \text{ mg}$ (the weight of the pure QDs) to $\sim 850 \text{ mg}$, indicating the successfully encapsulation by SiO_2 . Additionally, a large number of perovskite QDs may be coated in the silica sphere, which can be represented by a simple model (Fig. 4b). This simple model can be further confirmed by the HR-TEM images (Fig. 4c), which show that the $\text{CsPbBr}_3/\text{SiO}_2$ QDs have a core/shell structure. As shown in Fig. 4c, a large number of the cubic perovskite QDs are uniformly embedded inside the compact SiO_2 spheres, and very few QDs were attached to the outermost surface layers of the spheres. The XRD pattern of the $\text{CsPbBr}_3/\text{SiO}_2$ QDs exhibits a similar crystal structure as that of CsPbBr_3 , indicating that the growth of the SiO_2 shell does not affect the cubic crystal structure of the CsPbBr_3 core (Fig. S6). Additionally, Cs, Pb, Br, Si, and O elements are found in the EDX spectrum of the $\text{CsPbBr}_3/\text{SiO}_2$ QDs (Fig. S8), supporting the formation of silica-coated CsPbBr_3 .

All-inorganic $\text{CsPbBr}_3/\text{SiO}_2$ QDs were obtained based on the

above experimental analysis. To investigate the water solubilities and stabilities of the pure CsPbX_3 and $\text{CsPbX}_3/\text{SiO}_2$ QDs, they were both dispersed in two different solvents. One of the solvents was pure toluene (exposure to air, to verify the air stability); the other was a mixture of toluene and water (at a ratio of 4:1, seal). As shown in Fig. 5a (on the top), bright green emission can be obtained under a 365 nm hand-held UV lamp for all the solutions. Furthermore, a clear PL/liquid interface can be seen in the mixed solution of toluene and water (Fig. 5a, second from the top), indicating that the pure CsPbBr_3 QDs are completely insoluble in water. In contrast, there is no PL/liquid interface in the $\text{CsPbX}_3/\text{SiO}_2$ QD solution, which indicates that the $\text{CsPbX}_3/\text{SiO}_2$ QDs can be dispersed in water. The enhanced water solubility of the $\text{CsPbX}_3/\text{SiO}_2$ QDs has great potential for biological applications.

Stability is a very important issue for the all-inorganic CsPbBr_3 QDs. They are sensitive to polar solvents (such as water and alcohol), which can lead to the quenching of the QD photoluminescence. As shown in Fig. 5a, the strong green emission of the pure all-inorganic CsPbBr_3 QDs was substantially decreased after 20 h in the pure toluene (exposure to air) and completely disappeared after 12 h in the mixed solution of toluene and water (at a ratio of 4:1, seal). However, the $\text{CsPbBr}_3/\text{SiO}_2$ QDs maintained a bright green color in both solutions, which indicates that the SiO_2 -coated QD nanoparticles have ultrahigh air and water stabilities and are water dispersible. To further investigate the PL decay rate, PL spectra under 400 nm wavelength excitation over time were obtained. Figs. 5b and 5c show the PL spectra of the CsPbBr_3 and $\text{CsPbBr}_3/\text{SiO}_2$ QDs, respectively, which were dispersed in the pure toluene solution exposed to air. It can be seen that the PL spectra exhibits typical CsPbBr_3 green emission bands at $\sim 520 \text{ nm}$ (Fig. 5b) and $\sim 519 \text{ nm}$ (Fig. 5c), and the full-width at half-maximum (FWHM) values are 17–20 nm. Furthermore, the PL intensity of both materials decreased with increasing time (Fig. 5d). It can be seen that the $\text{CsPbBr}_3/\text{SiO}_2$ QDs show a slower decay rate compared to that of the CsPbBr_3 QDs, confirming that the presence of SiO_2 shell could significantly improve their air stability. After being exposed to air for 20 h, the PL intensity of the CsPbBr_3 QDs was reduced to 47% of their initial value, whereas the $\text{CsPbBr}_3/\text{SiO}_2$ QDs maintained a high PL intensity with a smaller decay rate, being reduced to 59% of their initial value. This indicates that the SiO_2 shell can effectively improve the air stability of the QDs. The PL spectra of the CsPbBr_3 and $\text{CsPbBr}_3/\text{SiO}_2$ QDs dispersed in the mixed solution of toluene and water are shown in Figs. 5e and 5f, respectively. The peak positions of the emission bands are located at $\sim$

Fig. 4 (a) TEM image of a silica sphere collecting CsPbBr_3 QDs, the inset is the digital images of the $\text{CsPbBr}_3/\text{SiO}_2$ powders under ambient daylight (left) and UV light (365 nm, right); (b) a diagrammatic sketch of the CsPbBr_3 QDs embedded in a silica sphere; and (c) a partially amplified TEM image of a single $\text{CsPbBr}_3/\text{SiO}_2$ sphere, the inset is the HR-TEM image of the $\text{CsPbBr}_3/\text{SiO}_2$ QDs.

Fig. 5 (a) Optical images of the colloidal solutions of CsPbBr₃ and CsPbBr₃@SiO₂ QDs in solvents containing pure toluene and a mixture of toluene: water (4:1); the PL spectra of the CsPbBr₃ (b) and CsPbBr₃@SiO₂ (c) QDs dispersed in the pure toluene solution exposed to air as a function of the exposure time; (d) the air stabilities of the CsPbBr₃ and CsPbBr₃@SiO₂ QDs; the PL spectra of the CsPbBr₃ (e) and CsPbBr₃@SiO₂ (f) QDs, which were dispersed in the mixed solution of toluene and water, as a function of the time; and (g) the water stabilities of the CsPbBr₃ and CsPbBr₃@SiO₂ QDs.

520 nm and ~ 518 nm for CsPbBr_3 and $\text{CsPbBr}_3/\text{SiO}_2$ QDs, respectively, and the FWHM of both samples are approximately 17 nm. Similarly, the PL intensities of both samples decrease with increasing exposure time, but the decay rate of the CsPbBr_3 QDs was notably faster than that of the $\text{CsPbBr}_3/\text{SiO}_2$ QDs (Fig. 5g). It can be seen that after 12 h, the CsPbBr_3 QDs shows a degradation of nearly 74% in its initial value. However, only 23% decrease was observed for the $\text{CsPbBr}_3/\text{SiO}_2$ QDs. This suggests that the SiO_2 coating can effectively protect the CsPbBr_3 QDs from degradation owing to moisture exposure. The SiO_2 coating method can also be applied to the other CsPbX_3 QDs, as shown in Fig. 6. All the results are consistent with the CsPbBr_3 QDs. For CsPbCl_3 and $\text{CsPbCl}_3/\text{SiO}_2$ QDs which were dispersed in the mixed solutions of toluene and water, the PL intensity descend 84% and 68% in their initial values, respectively. Additionally, the PL intensities of $\text{CsPb}(\text{Cl},\text{Br})_3$ and $\text{CsPb}(\text{Cl},\text{Br})_3/\text{SiO}_2$ QDs decreased to 78% and 34% in their initial values, respectively. Combined with the above analysis, it can be seen that, through a simple coating process, a SiO_2 shell can effectively improve the stability and water solubility of QDs without affecting their optical properties by reducing the contact between the quantum dots and the environment.⁴⁷

4. Conclusions

In summary, we first synthesized CsPbX_3 ($X = \text{Cl}, \text{Br}, \text{I}$, and mixed Cl/Br and Br/I systems) nanoparticles with broadly tunable photoluminescence, spectrally narrow emissions, short fluorescence lifetimes and wide color range by using a modified hot-injection method which can reduce energy consumption and save cost. Next, we used pure CsPbX_3 nanoparticles as a precursor to embed completely into silica spheres. The synthetic process was very simple and was based on

the high hydrolytic rate of tetramethyl orthosilicate. Taking the $\text{CsPbBr}_3/\text{SiO}_2$ QDs as the example, the air and water stabilities and the water solubility of the CsPbBr_3 QDs coated with SiO_2 have been effectively improved compared to those of the uncoated QDs, without affecting their optical properties. These improvements in the stability properties are attributed to the SiO_2 layers reducing the contact of the quantum dots with the surrounding environment. Similar results were also obtained in the other CsPbX_3 QDs systems. We believe that these new $\text{CsPbBr}_3/\text{SiO}_2$ QDs with enhanced properties will be widely used in light-emitting device applications.

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Fig. 6 Air- (a) and water- (b) stabilities of the CsPbCl_3 and $\text{CsPbCl}_3/\text{SiO}_2$ QDs; the air- (c) and water- (d) stabilities of the $\text{CsPb}(\text{Br}/\text{Cl})_3$ and $\text{CsPb}(\text{Br}/\text{Cl})_3/\text{SiO}_2$ QDs.

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