



Research Article


Highly fluorescent CsPbBr₃/TiO₂ core/shell perovskite nanocrystals with excellent stability



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Abstract

The poor stability of CsPbX₃ (X = Cl, Br, I) perovskite nanocrystals is the most impediment to its application in the field of photoelectrics. In this work, monodisperse CsPbBr₃/TiO₂ nanocrystals are successfully prepared by coating titanium precursor on the surface of colloidal CsPbBr₃ nanocrystals at room temperature. The CsPbBr₃/TiO₂ nanocomposites exhibit excellent stability, remaining the identical particle size (9.2 nm), crystal structures and optical properties. Time-resolved photoluminescence decay shows that the lifetime of CsPbBr₃/TiO₂ nanocrystals is about 4.04 ns and keeps great stability after lasting two months in the air. Results show that the coating of TiO₂ on CsPbBr₃ NCs greatly suppressed the anion exchange and photodegradation, which are the main reasons for dramatically improving their chemical stability and photostability. The results provide an effective method to solve the stability problem of perovskite nanostructures and are expected to have a promising application in optoelectronic fields

Article highlights

1. Prepared the all-inorganic CsPbBr₃/TiO₂ core/shell perovskite nanocrystals by an easy method.
2. Explored its essences of PL and lifetime of the synthesized CsPbBr₃/TiO₂ perovskite nanocrystals.
3. CsPbBr₃/TiO₂ nanocrystals show the great thermal stability after the post-annealing.
4. The CsPbBr₃/TiO₂ nanocrystals have a high PLQY and have a promising application in solar cells.

Keywords Perovskite nanocomposites · Photostability · Optical properties

1 Introduction

Owing to the high absorption coefficient, long carrier diffusion distance, tunable emission bandgap and high photoluminescence quantum yield, colloidal metal halide

perovskite nanocrystals have been intensively explored in laser, photodetector, light-emitting diode (LED) and solar cell [1–4]. Kojima et al. [5] prepared the earliest perovskite solar cells, selecting organic–inorganic hybrid perovskite materials CH₃NH₃PbX₃ (X = Br, I) as new photosensitizer to

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replace the dyes in traditional DSSCs. However, due to the large bandgap, the photoelectric conversion efficiency is only about 3.8%, which extremely obstructs their prelude as the light-absorbing material.

Recently, due to particular crystal structure, high energy conversion rate, low cost and mild conditions, organic–inorganic hybrid perovskite nanostructure have attracted much attention of the academic and industry community [6, 7]. Under ongoing efforts, the photoelectric conversion efficiency has rapidly increased to 22.1% [8]. Liu et al. [9] added iodide ions to the organic cation solution and realized the high-efficiency PSC film based on "lead halide perovskite" absorbent and achieved the 22.1% energy efficiency in small batteries. In 2018, École Polytechnique Fédérale de Lausanne (EPFL) refreshed the world efficiency record of CIGS perovskite solar cells to 23.3% [10]. Similarly, Chen et al. [11] designed an inorganic perovskite device by adjusting bandgap at different positions, which increased the film thickness and reduced the charge recombination, behaving 15.2% of the final photoelectric conversion efficiency. Recently, the ground-breaking cell produced by Oxford PV has been proven to convert 29.52% of solar energy into electricity. However, when exposed to moisture, humidity, glare and high temperature, the perovskite nanocrystals would decompose and decrease their environmental stability. These uncontrollable factors block the development of nanocrystals in practical applications [12, 13].

Recently, significant efforts have been committed to increasing the stability of perovskite nanocrystals, by embedding a protective semiconductor matrix, adulterating photocurable fluoropolymer or compounding to molecular sieve material with regular porous structure [14]. Employing a facile solution-phase method, Zhou et al. prepared CsPbX₃/ZnS nanocrystal heterodimer with a high quality and enhanced stability, which offers an interesting playground to design and fabricate novel perovskite heterostructures [15]. Zhang et al. [16] successfully prepared high-stability CsPbX₃/SiO₂ Janus nanoparticles, and the photoluminescence quantum yield reached 80%, and the luminescence lifetime achieved 19.8 ns. The implanting of Janus nanometers particles into the white light-emitting diode devices greatly improved the stability of CsPbX₃ (X = Cl, Br, I) nanocrystals in air, water and light environments. However, the stability of these perovskite composites could be only manifested in the short term, and the external protection layers are not uniform and fine. It is well known that the surface passivation could eliminate the defects and dangling bonds and therefore increase their stability. In 2016, Huang et al. proposed a new and efficient surface passivation method, in which a stable mixed-halide passivation layer was formed on the surface of nanocomposites by ion exchange between CsPbX₃ (X = Br, I) perovskite nanocrystals and lead selenide

quantum dots. Results show that it not only improved the fluorescence quantum yield, but also significantly increased the photoelectric conversion efficiency and air stability of perovskite solar cells [17]. Coincidentally, Dalal et al. firstly demonstrated that some p-type semiconductors could be used as high-efficient perovskite-defective passivation materials, and a passivation mechanism was proposed [18]. Although some new p-type semiconductor showed excellent perovskite depletion passivation effect, the exploration of those good stability passivation agent would be the focal point in the future. It could imagine that if we combining wider band-gap semiconductor materials with perovskite nanostructures and forming an external protective layer around the CsPbX₃ (X = Cl, Br, I), the more stable and efficient CsPbX₃ nanostructures could be expected to manufacture.

In our previous work, we prepared CsPbX₃ (X = Cl, Br, I) perovskite nanocrystals by the hot-injection method and studied their optical properties [19, 20]. By varying the amount of PbX₂ (X = Cl, Br, I), the prepared CsPbX₃ nanocrystals possess high photoluminescence quantum yield (PLQY, about 70%), narrow full width at half-maximum (FWHM) (4–17 nm), tunable band gap (407–680 nm), and highly strong photostability. In this paper, we coated titanium precursor on the outside of the colloidal CsPbBr₃ NCs at room temperature and formed perovskite CsPbBr₃/TiO₂ nanocomposites with high dispersion and high crystallinity. By forming a CsPbBr₃/TiO₂ nanocomposite, we are trying to improve its PLQY and thermal stability. The optical mechanism, containing microstructure, chemical state and time-resolved decay process, was comprehensively studied.

2 Experimental section

2.1 Synthesis of CsPbBr₃/TiO₂ nanocrystals

The preparation process of CsPbBr₃ has been introduced in our previous papers [19, 20]. To synthesize the CsPbBr₃/TiO₂ nanocrystals, 15 μL TBOT with 1 mL toluene was added into a 250-mL 3-neck flask containing 20 mL of CsPbBr₃ nanocrystal solution under stirring. The solution was placed in a glove box with 30% relative humidity (RH) at room temperature for hydrolysis. After stirring for 3 h, the crude solution was centrifuged at 6,500 rpm for 8 min, and the precipitate was dried in Ar atmosphere at 300 °C for 2 h to obtain CsPbBr₃/TiO₂ core/shell NCs.

2.2 Characterization

In the experiments, X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), FT-IR spectrometer (FTIR), micro-Raman Spectroscopy (Raman) and high-resolution transmission electron microscopy (HRTEM) were carried

out for microstructural characterization of the obtained samples. The absorption properties were conducted on a double UV–Vis absorption spectrophotometer model 727. Room-temperature photoluminescence (PL) spectra were taken on an Edinburgh (FLS920) fluorescence spectrophotometer.

3 Results and discussion

Figure 1 shows X-ray diffraction patterns of the as-prepared CsPbBr₃ and CsPbBr₃/TiO₂ nanocrystals. It can be seen that the diffraction peaks of CsPbBr₃ NCs are consistent with the standard data file (JCPDS No. 54–0752), which confirms the accuracy of the cubic phase [21]. Two samples exhibit eight obvious peaks at 15.27°, 21.58°, 26.50°, 30.55°, 34.44°, 37.67°, 43.86° and 46.71°, corresponding to (100), (110), (111), (200), (210), (211), (220) and (300) planes, respectively. For CsPbBr₃/TiO₂ NCs, two additional diffraction peaks at ~23.8° and ~46.5° can be observed, which are assigned to (101) and (200) planes for anatase TiO₂ (JCPDS No. 89-4921) [22]. Simultaneous appearance of characteristic peaks for TiO₂ and CsPbBr₃ nanocrystals represents that the TiO₂ has successfully deposited on the surface of CsPbBr₃ NCs. Compared with CsPbBr₃ and TiO₂ nanocrystals, CsPbBr₃/TiO₂ NCs exhibits two additional diffraction peaks at 41° and 56.5°, which may originate from the residue or incomplete existence of TiO₂ shell.

Figure 2 shows HRTEM images of the monodisperse CsPbBr₃/TiO₂ NCs. From Fig. 2a, it can be seen that cube-shaped CsPbBr₃ NCs arranged neatly in nonpolar solvent and exhibited a high degree of crystallinity and stability. The average size is about 8.8 nm. From Fig. 2b, c, one can see that the plurality of CsPbBr₃ NCs is wrapped by one core–shell TiO₂ structure, which caused by the incomplete hydrolysis of high-concentration TBOT on the surface of CsPbBr₃ NCs. Figure 2d is the lattice fringe pattern of CsPbBr₃/TiO₂ nanocomposites, which reflects the

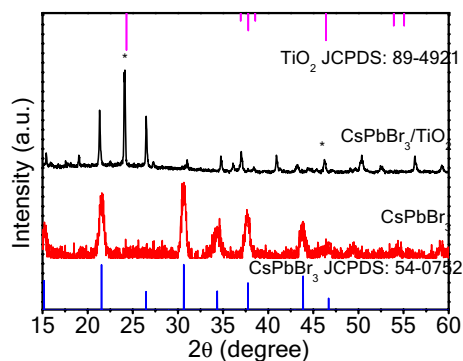


Fig. 1 XRD spectra acquired from CsPbBr₃ nanocrystals and CsPbBr₃/TiO₂ nanocomposites

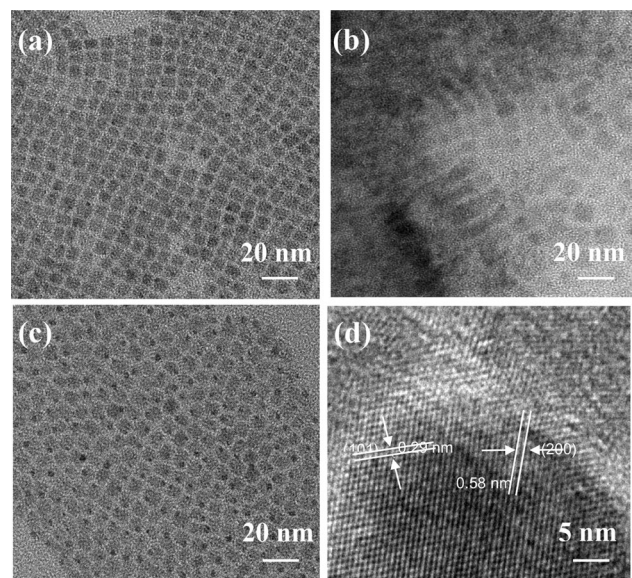


Fig. 2 HRTEM images of samples **a** CsPbBr₃ NCs, **b, c, d** CsPbBr₃/TiO₂ NCs

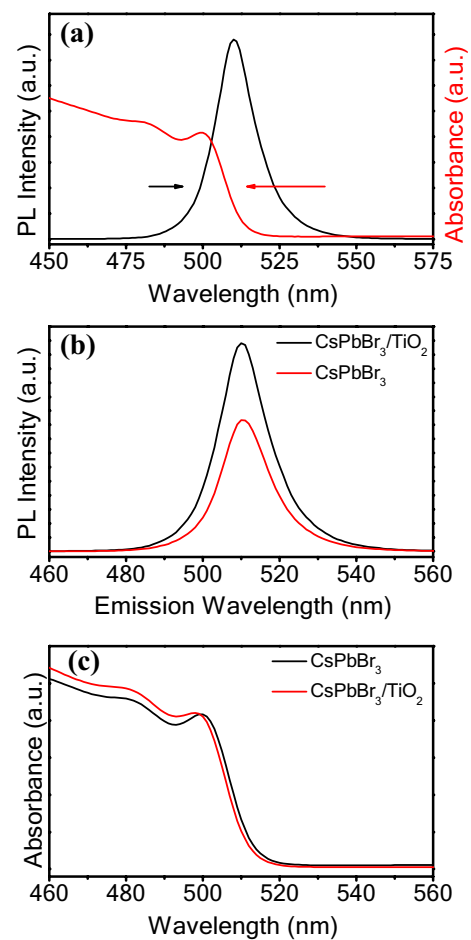


Fig. 3 **a** PL spectra and optical absorption spectra of CsPbBr₃/TiO₂ nanocomposites. **b** PL spectra of CsPbBr₃ and CsPbBr₃/TiO₂ NCs. **c** UV–visible absorption spectra of CsPbBr₃ and CsPbBr₃/TiO₂ NCs

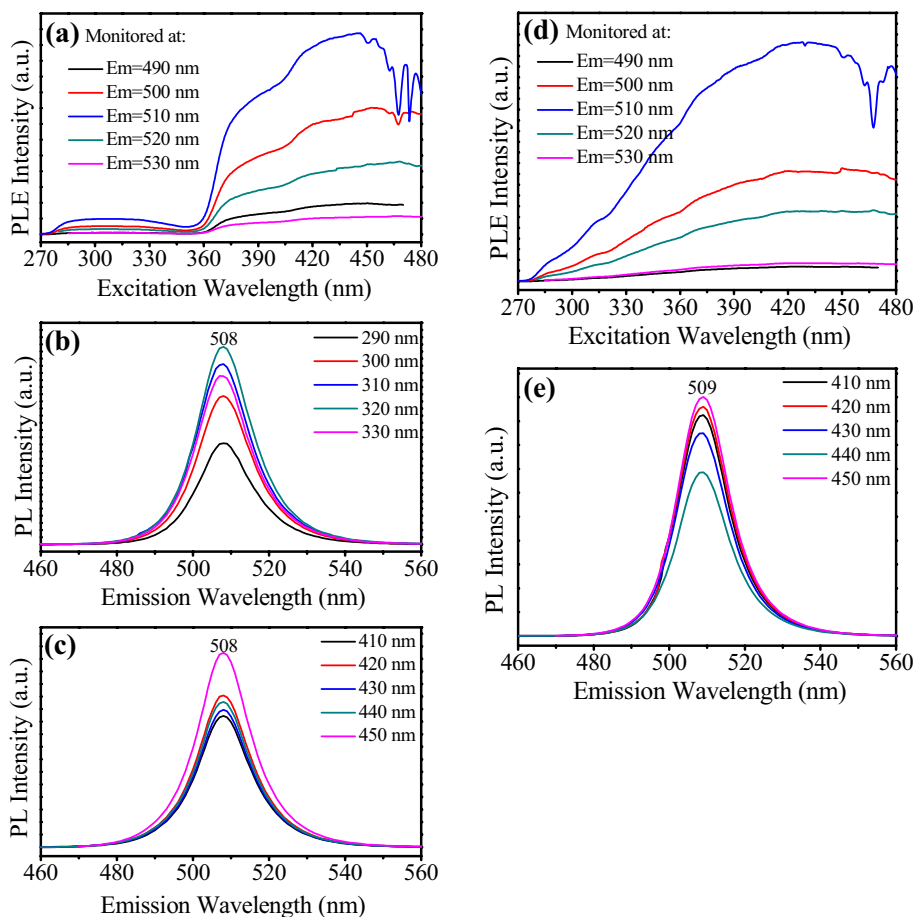
0.58 nm lattice fringe of CsPbBr₃ NCs and 0.29 nm of TiO₂ NCs, corresponding to the (200) and (101) planes, respectively. More importantly, there is a clearance exist between CsPbBr₃ and TiO₂, meaning that a tight interface is formed between CsPbBr₃ and TiO₂.

To test the optoelectronic and electronic properties, the absorption and emission spectra of CsPbBr₃/TiO₂ nanocrystals were carried out, as shown in Fig. 3a. It exhibits an obvious slight of 9-nm Stokes shift between absorption edge and fluorescence peak, demonstrating the origin of direct band-gap bound exciton recombination, which could be attributed to the strong quantum confinement effect. After lasting in the air for one and two months, the photoluminescence and optical absorption spectra are measured to identify the stability of CsPbBr₃/TiO₂ nanocrystals, as shown in Fig. S1. Two patterns exhibit a similar small Stokes shift of 9 nm, showing high fluorescence and strong stability. Figure 3b shows the emission spectra of CsPbBr₃ and CsPbBr₃/TiO₂ NCs. Both of them show the analogous emission peak at about 510 nm, which demonstrate the similar size and uniform distribution, corresponding to the exhibition in Fig. 2. More precise observation reveals that the FWHM is about 15 nm, illustrating a favorable crystallinity and stability [23]. By

further comparison, it can be observed that there is an obvious increase in PL intensity of CsPbBr₃/TiO₂ nanocomposites. That means the as-prepared heterocomposites effectively inhibit the recombination of photogenerated charge carriers [24, 25]. From Fig. 3c, it can be seen that the absorption spectra of CsPbBr₃ NCs and CsPbBr₃/TiO₂ nanocomposites are broadcast. It can catch a strong sharp absorption peak at about 500 nm for CsPbBr₃ NCs and the absorption edge of the CsPbBr₃/TiO₂ nanocomposites blue-shifts to 498 nm for CsPbBr₃/TiO₂ NCs. In the range of 460 to 500 nm, the absorption capacity of CsPbBr₃/TiO₂ NCs is larger than that of CsPbBr₃, which is caused by the existence of amorphous TiO₂.

To explore the origin of emission for CsPbBr₃ and CsPbBr₃/TiO₂ nanocomposites, the PL and PLE spectra were carried out, as shown in Fig. 4. From the PLE spectra, as shown in Fig. 4a, a low-intensity broad peak at about 310 nm and a high-intensity broad peak at about 430 nm could be observed. Based on the PLE spectra, we measured the PL spectra under the center wavelength of 310 nm and 430 nm, as shown in Fig. 4b, c, respectively. Both of the two curves show a sharp peak at 508 nm, indicating that the emission at 508 nm is intrinsically linked with the excitation of 310 nm and 430 nm. To further research the

Fig. 4 **a** PLE spectra of CsPbBr₃ nanocrystals monitored at different wavelengths around 510 nm. **b** PL spectra of CsPbBr₃ nanocrystals taken under different excitation wavelengths around 310 nm. **c** PL spectra of CsPbBr₃ nanocrystals taken under different excitation wavelengths around 430 nm. **d** PLE spectra of CsPbBr₃/TiO₂ nanocrystals monitored at different wavelengths around 510 nm. **e** PL spectra of CsPbBr₃/TiO₂ nanocrystals taken under different excitation wavelengths around 430 nm



origins of emission of CsPbBr₃/TiO₂ nanocomposites, we also measured the PL and PLE spectra CsPbBr₃/TiO₂ at room temperature, as shown in Fig. 4d, e. It can be found that the PLE peak intensity increases with increasing the emission wavelength and reaches a maximum value when monitored at 510 nm. Additionally, the broad PLE band confirms that the perovskite nanocrystals can be excited under a broad wavelength. Compared with the PLE spectra of CsPbBr₃ and CsPbBr₃/TiO₂, they all show a peak at about 430 nm. However, the peak at 310 nm disappears for CsPbBr₃/TiO₂ nanocomposites, proving the successful compound of CsPbBr₃ with TiO₂. Combined with the above results, PL spectra of CsPbBr₃/TiO₂ nanocomposites under the excitation wavelength around 430 nm were implemented, as shown in Fig. 4e. One can see that all curves exhibit a sharp emission peak at 509 nm and do not shift with changing the excitation wavelengths, which exhibits the uniform size distribution of nanocrystals, matching the images in Fig. 2. With increasing the excitation wavelength, the PL intensity increases and shows the maximum value at 450 nm, illustrating that the emission at 509 nm is intrinsically linked with the excitation at 430 nm. The PLE spectra of CsPbBr₃/TiO₂ nanocrystals after lasting one and two months in the air by monitoring at 510 nm as center wavelength were carried out, as shown in Fig. S2 and Fig. S3. Both of them show a maximum absorption under monitoring at 510 nm, which exhibit the same behaviors with the original CsPbBr₃/TiO₂ nanocomposites. It is interesting that the curves measured after lasting in the air for a month present two saturation excitation peaks at 380 nm and 430 nm. The PLE curves show the fixed single emission peak at 508 nm, illustrating the excellent stability of CsPbBr₃/TiO₂ nanocrystals. Similarly, as shown in Fig. S3, the absorption peak shifts to 350 nm, which is caused by the surface passivation. The emission peak pinned at 508 nm, further demonstrating the excellent chemical stability and photostability of CsPbBr₃/TiO₂ nanocrystals.

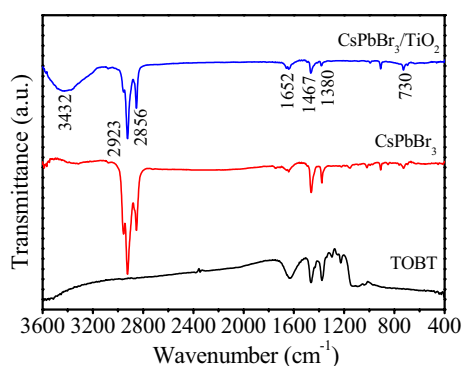


Fig. 5 FTIR absorption spectra of CsPbBr₃ nanocrystals and CsPbBr₃/TiO₂ nanocomposites

To explore the molecular structure and surface bonds of CsPbBr₃/TiO₂ nanocrystals, the FTIR spectroscopy for the samples was performed, as shown in Fig. 5. Compared with the CsPbBr₃ and CsPbBr₃/TiO₂ NCs, the decrease in two fundamental sharp peaks at 2923 and 2856 cm⁻¹ suggests the loss of carbonaceous residues and dehydroxylation process. The decrease in another two peaks at 1468 and 1380 cm⁻¹ indicates the losing of COO⁻ and -CH₃ groups. Besides, there is an increased intensity of surface-adsorbed water (H-O-H) at 3432 cm⁻¹ and hydroxyl groups (O-H) at 1652 cm⁻¹, plus a slight increase at about 730 cm⁻¹ for Ti-O-Ti bonds, stating the coating of titanium matrix on CsPbBr₃ nanocrystals.

To achieve the surface states and compositions of the samples, the X-ray photoelectron spectrum XPS is conducted, as presented in Fig. 6. Compared with the CsPbBr₃, two additional peaks of Ti and O are observed in CsPbBr₃/TiO₂ NCs, indicating a successfully forming of CsPbBr₃/TiO₂ nanocomposites. The lower intensity of CsPbBr₃/TiO₂ NCs is caused by the existence of TiO₂ shell. Figure S4 is the fine XPS of CsPbBr₃/TiO₂ NCs. From Fig. S4a, it can be seen that there are only Cs, Pb, Br, Ti, N and O elements in the sample and no other elements are detected, showing good purity of as-prepared samples. The Cs, Pb and Br elements are contributed by the perovskite nanocrystals, while the N and part of O elements are related to the chemical adsorption of OA and OAm ligands [26]. From Fig. S4b, one can see two rough symmetrical peaks at 738.2 and 724.3 eV, corresponding to Cs 3d 5/2 and Cs 3d 3/2, respectively. Figure S4c shows the spin-orbit splitting energy of 4.8 eV from two sharp peaks at 138.2 and 143.0 eV for Pb 4f 7/2 and Pb 4f 5/2, respectively, which are characteristic for Pb²⁺ in CsPbBr₃/TiO₂ nanocrystals. Similarly, in Fig. S4e, the strong peak at 458.6 eV matches with Ti 2p 1/2, while the low peak at 464.2 eV matches with Ti 2p 3/2, which confirms the Ti⁴⁺ valence. In particular, Fig. S4d shows one single broad peak and can be deconvoluted into two

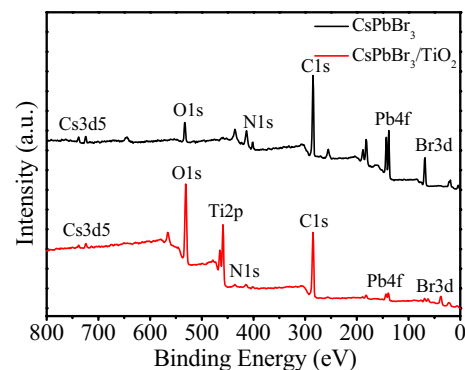


Fig. 6 XPS spectra of CsPbBr₃ nanocrystals and CsPbBr₃/TiO₂ nanocomposites

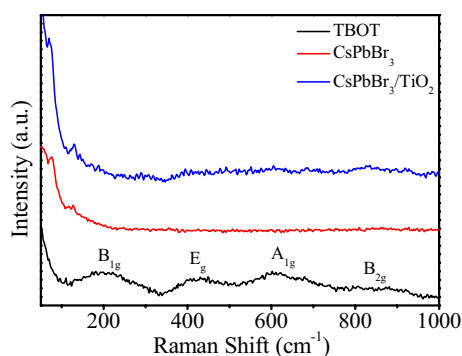


Fig. 7 Raman spectra acquired from TBOT, CsPbBr₃ and CsPbBr₃/TiO₂ nanocomposites

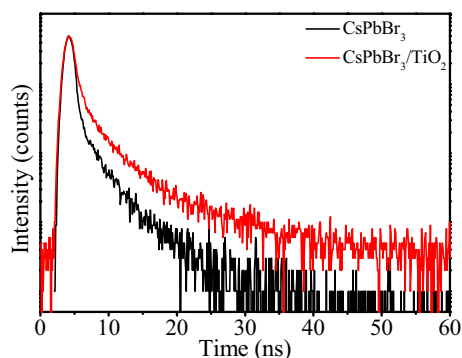


Fig. 8 Time-resolved PL decay curves obtained from CsPbBr₃ and CsPbBr₃/TiO₂ nanocomposites

subpeaks. The binding energy at 69.3 eV can be ascribed to the bromine in [PbBr₆]⁴⁻ octahedron, and the peak at 68.3 eV can be ascribed to the bromine in CsPbBr₃/TiO₂ NCs. Figure S4f is the O1s meticulous scan spectrum, which could be deconvoluted into two subpeaks. The main separation peak at 531.9 eV corresponds to lattice oxygen in the hydroxyl groups and another minor separation peak at 529.9 eV corresponding to adsorption oxygen in the Ti–O of TiO₂. Figure S5 and Fig. S6 are the XPS of samples lasting in the air for one and two months. Compared with the original samples, the similar phenomenon of the element meticulous scan spectrogram except oxygen is presented. By analyzing the characteristic profiles in Fig. S5(f) and S6(f), one can see that the main separation peak related to O–H functional groups decreases with lasing in the air, which is caused by the loss of hydroxyl groups for the dehydration with the time.

Raman spectroscopy is a powerful technique to identify the molecular structure of perovskite nanocrystals. Figure 7 shows the Raman spectrum of TOBT, CsPbBr₃ and CsPbBr₃/TiO₂ NCs. From the figure, we can see that CsPbBr₃/TiO₂ NCs contain two sharp peaks in CsPbBr₃ NCs and four weak peaks in TOBT armamentarium. The

peaks at about 70 and 120 cm⁻¹ are ascribed to the vibrational mode of [PbX₆]⁴⁻ octahedron and motion of Cs⁺ cations, respectively [27]. The peaks at about 175, 420 and 620 cm⁻¹ are ascribed to the stress change of O–Ti–O variable angle vibration. Both of them indicate the formation of TiO₂ core/shell with an anatase-like structure.

Figure 8 and S7 reveals the time-resolved photoluminescence decay spectrum for CsPbBr₃ and CsPbBr₃/TiO₂ nanocomposites. A radiative emission decay with about 4.04 ns average lifetime of CsPbBr₃/TiO₂ NCs can be obtained. However, the radiative emission decay time of CsPbBr₃ NCs is about 2.52 ns, indicating that the energy transfer happens between CsPbBr₃ and TiO₂. After lasting months in the air, the lifetime of CsPbBr₃/TiO₂ NCs keeps at about 3.98 ns and 3.81 ns, meaning the high stability of perovskite nanocomposites after coating with the TiO₂. Deposition of TiO₂ shell reduces the surface defects of nanocrystals and increases the non-radiative transitions, thereby improving the lifetimes of CsPbBr₃/TiO₂ nanocrystals. The defect tolerance of CsPbBr₃ NCs offers a long lifetime and high PLQY, causing improved stability for CsPbBr₃/TiO₂ perovskite nanocomposites.

To further check the thermal stability of perovskite nanostructures, we tested CsPbBr₃/TiO₂ nanocrystals annealing at 80 °C, as shown in Fig. S8–S11. The XRD characteristic diffraction peaks after annealing were similar to the original sample, illustrating the stability of CsPbBr₃. In Fig. S9, there was a Stokes shift of 10 nm, demonstrating the emission originated from the exciton recombination. Figure S10 is the fluorescence spectroscopy of CsPbBr₃/TiO₂ NCs under different excitation wavelengths. One could see an excitation peak at about 400 nm and an emission peak at about 508 nm in PLE and PL spectra. Unchanged emission peaks present the uniform size distribution of nanocrystals and robust stability of the sample after annealing. Figure S11 is the time-resolved PL decay curves of CsPbBr₃/TiO₂ nanocrystals before and after post-annealing. The PL decaying time of about 3.13 ns indicates a high thermal stability of perovskite nanocrystals.

4 Conclusions

In summary, we successfully prepared monodispersed colloidal CsPbBr₃/TiO₂ core/shell nanocomposite. The CsPbBr₃/TiO₂ nanocomposite exhibits a uniform size distribution of about 9.2 nm. A narrow FWHM indicates good crystallinity and favorable stability. The time-resolved photoluminescence decay lifetime of CsPbBr₃/TiO₂ nanocrystals increases to 4.04 ns which that of CsPbBr₃ is 2.52 ns, which leads to a high PLQY. After a

post-annealing at 80 °C, it was found that the emission peak and fluorescence lifetime of CsPbBr₃/TiO₂ nanocrystals remained unchanged, indicating the prepared composite nanocrystals have a strong thermal stability. The results provide an effective method to improve the stability of perovskite nanostructures and are expected to have a practical application in optoelectronic fields.

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Declarations

Conflict of interest The authors declare that they have no conflict of interest.

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