Continuous-flow synthesis of CsPbI₃/TiO₂ nanocomposites with enhanced water and thermal stability†

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The inherent poor stability of CsPbI₃ nanocrystals hinders the practical application of this material. Therefore, it is still a challenge to improve the stability of CsPbI₃ nanocrystals and realize their large-scale continuous preparation. In this work, we report the preparation of CsPbI₃/TiO₂ nanocomposites with high stability by a microfluidic method. After the combination of CsPbI₃ nanorods with TiO₂, the PL intensity increased by 1.3 times under excitation at 577 nm due to the passivating effect of TiO₂ on the surface of CsPbI₃ nanorods and its carrier transport characteristics. Meanwhile, due to the coating of TiO₂, the surface exposure area of CsPbI₃ nanorods is reduced, which blocks external environmental effects to some extent and effectively improves the stability of CsPbI₃ nanorods. Finally, an LED with a color gamut of 142% NTSC and a color temperature (CCT) of 3952 K was obtained by combining CsPbI₁.₅Br₁.₅/TiO₂ and CsPbBr₁/TiO₂ nanocomposites with a blue light chip (455 nm). This study shows that the continuous and controllable synthesis of all inorganic halide perovskite nanocrystals by a microfluidic method is of great significance in the fabrication of high-performance optoelectronic materials and display devices.

Introduction

All-inorganic lead halide perovskite nanocrystals (ALHP NCs) have been extensively investigated since they were synthesized by a simple thermal injection method.¹,² ALHP NCs exhibit significant potential for application in display devices and light-emitting diodes (LEDs) due to their exceptional optical properties, including inherently high charge carrier mobility, a long diffusion length, a high photoluminescence quantum yield (PLQY), facile bandgap tunability, and narrow full width at half maximum.³,⁴ Display technology can be categorized into two types based on the excitation mode: photoluminescence (PL) and electroluminescence (EL).⁵ The PL type employs blue light-emitting diodes (LEDs) in conjunction with down-conversion luminescent materials (phosphors/quantum dots) as the backlight source. The performance of display devices heavily relies on the luminescence materials, which necessitates high efficiency in luminescence, exceptional color purity, and outstanding stability to guarantee optimal display quality.⁶–⁸ Although ALHP NCs exhibit excellent optoelectronic properties, their practical application in display devices and LEDs is hindered by poor stability resulting from their ionic structures and efficiency loss caused by reabsorption. Consequently, perovskite NCs can undergo rapid material deterioration when exposed to moisture, oxygen, high temperature, or UV radiation.⁹,¹⁰

Compared to CsPbCl₃ and CsPbBr₃ NCs, CsPbI₃ NCs with the lowest bandgap are attractive materials for both photovoltaic and photodetector devices. CsPbI₃ NCs emit the deepest red light, contributing to the largest gamut in LED displays. Nevertheless, it is the most unstable member of the ALHP NC family.¹¹–¹³ Aside from the deterioration caused by external influences, which is common across the ALHP NC family, CsPbI₃ also experiences unfavorable inherent phase transitions during temperature fluctuations.¹⁴ Previous research has demonstrated that CsPbI₃ exists in four distinct stages, which may be categorized into two groups. The first group consists of perovskite-type materials that are fluorescently active. It includes three phases: α (α-cubic), β (β-tetragonal), and γ (γ-orthorhombic) phases. The three stages are generally referred to as “black” phases. While the second group, which is of the non-perovskite kind, is luminously inactive because it has an indirect bandgap. It contains one phase: δ (δ-non-perovskite) phase, and it is collectively denoted as the “yellow” phase.¹⁵–¹⁷ Due to the short radius of Cs⁺ ions, the tolerance factor (r) departs from the ideal range, causing CsPbI₃ to
spontaneously change from the perovskite “black” phase to the non-perovskite “yellow” phase (δ-CsPbI$_3$) at room temperature (RT). There are few reports on CsPbI$_3$ due to its intrinsic phase transition. Therefore, it is a great and fundamental challenge to improve the stability of CsPbI$_3$ NCs and their photoluminescence properties.\textsuperscript{18–21}

Recently, considerable efforts have been made to solve the problem of instability of all-inorganic lead halide perovskite nanocrystals. Related studies have demonstrated that effective measures for improving the stability of ALHP NCs can be summarized into three types: (1) surface ligand modification;\textsuperscript{22–24} (2) matrix encapsulation;\textsuperscript{25–27} and (3) ion substitution.\textsuperscript{28,29} Matrix encapsulation is considered a widely used and effective approach for safeguarding perovskite NCs among these enhanced techniques.\textsuperscript{16,31} In current studies, matrix encapsulation mainly includes polymer coating and inorganic matrices. Although the water stability of ALHP NCs can be significantly enhanced through polymer packaging, most organic binders exhibit poor thermal stability and yellowing with age. At relatively higher temperatures, these binders decay along with the embedded perovskite nanocrystals, causing irreversible quenching of luminescence.\textsuperscript{14,32,13} Compared to polymer matrices, all-inorganic materials such as SiO$_2$,\textsuperscript{34,35} TiO$_2$,\textsuperscript{36–38} Al$_2$O$_3$,\textsuperscript{39,40} CaF$_2$,\textsuperscript{41,42} and ZrO$_2$\textsuperscript{43} with high transparency and robust thermal and chemical stability can improve the stability and maintain the optoelectronic properties of perovskite nanomaterials. TiO$_2$ has been utilized in the coating process for preserving CsPbX$_3$ NCs due to its chemical stability, optical transparency, and non-toxic nature. This technique effectively safeguards the NCs from degradation and enhances the transfer of charge carriers, enabling perovskite NCs to acquire additional innovative functionalities, such as photocatalysis.\textsuperscript{14} The TiO$_2$@CsPbBr$_3$ hybrid architectures were created using a mechanochemical method at room temperature in previous research. This architecture resulted in improved photoluminescence quantum yields and thermal stability due to the passivation of surface defects, a decrease in surface area, and effective energy transfer from CsPbBr$_3$ to TiO$_2$.\textsuperscript{45} CsPbBr$_3$/TiO$_2$ core/shell NCs were reported with high water stability that can be stable in water up to three months.\textsuperscript{10} However, because the stability of CsPbI$_3$ is the worst among all inorganic metal halides, there are relatively few studies on the luminescence properties of CsPbI$_3$ combined with TiO$_2$.

Traditionally, manual methods using flasks have been the main methodology for synthesizing, characterizing, and optimizing colloidal nanocrystals.\textsuperscript{4,46} Nevertheless, the characterization, assessment, and optimization of nanocrystals using a manual batch technique have inherent constraints in terms of sample rate, reagent quantity, and analysis time. In addition, when transitioning from batch synthesis to large-scale production of high-quality nanocrystals, the existing mixing inefficiencies and batch-to-batch variation are often magnified. It is still a challenge to scale up the manufacture of nanocrystals due to the limitations of batch reactors and low reactant concentrations.\textsuperscript{47–49} Therefore, there is an urgent requirement for a novel synthesis method that offers accurate control over the reaction duration and enhances the heat and mass transfer efficiency. This method should aim to elevate the reactant concentration, minimize ligand consumption, and enable the manufacture of nanocrystals on a large scale with high efficiency.\textsuperscript{50,51} Since microfluidic technology was first applied to biochemical detection and analysis in the 1990s, it has been widely used to improve the reaction and mixing efficiency due to its controllability, accuracy, low reactant inventory, and enhanced heat and mass transfer efficiency. So microfluidic technology is an effective method for large-scale preparation of nanocrystals.\textsuperscript{52,53}

Herein, we propose a method for continuous and efficient preparation of CsPbI$_3$/TiO$_2$ nanocomposites using the microfluidic method. TiO$_2$ was \textit{in situ} bonded to the surface of CsPbI$_3$ nanorods by microchannel reactions. Compared with CsPbI$_3$ nanocrystals, the water resistance and thermal stability of CsPbI$_3$ nanocomposites are significantly enhanced. In addition, the PL intensity increased by 1.3 times under excitation at 577 nm because the surface defects on CsPbI$_3$ nanorods were modified with nano-titanium dioxide. Finally, green CsPbBr$_3$/TiO$_2$ and CsPbI$_{1.5}$Br$_{1.5}$/TiO$_2$ nanocomposites prepared by the microfluidic method were combined with a blue light chip to prepare LEDs with a high color rendering index or wide color gamut, showing the broad prospects of CsPbX$_3$/TiO$_2$ nanocomposites in the field of lighting and display.

**Experimental**

**Materials**

Cesium carbonate (99.9%, Adamas), titanium dioxide (99%, particle size: 10–30 nm, XFNANO), lead iodide (99%, Adamas), 1-octadecene (>90%, Adamas), oleic acid (90%, Adamas), oleylamine (90%, Adamas), and n-hexane (≥97.0%, Greagent). All reagents were purchased without further purification.

**Microfluidic synthesis of CsPbI$_3$ nanorods and CsPbI$_3$/TiO$_2$ nanocomposites**

Detailed steps for preparing precursor 1 (Cs-oleate), precursor 2 (PbI$_2$), and precursor 3 (PbI$_2$/TiO$_2$) are described in the ESL.\textsuperscript{†}

Two kinds of continuous flow precursors were used for single-phase flow synthesis. A customized microchannel was used as the reaction device for perovskite nanocrystals, and the corresponding three-dimensional serpentine microchannel is 0.5 mm in width, 0.3 mm in depth, 205.22 mm in the preheating zone and 536.52 mm in the reaction zone. Because the surface of TiO$_2$ was fully modified with oleic acid, oleylamine and lead iodide in the precursor preparation process, and the contact probability of TiO$_2$ with Cs$^+$, Pb$^{2+}$ and I$^-$ was greatly increased due to the space limitation of microchannels, TiO$_2$ more easily combined with CsPbI$_3$ nanorods. Three kinds of microchannels were designed in the microfluidic reaction device, of which two kinds of microchannels were used as the preheating zone for two kinds of precursors, and one kind of microchannel was used as the reaction zone for perovskite nanocrystals. A custom fluorine rubber gasket can make the
microchannel into a liquid-sealed space, preventing the entry of air and water, and then the microfluidic reaction device was placed on a heating table to provide a heat source for synthesis.

Equal volumes of precursor 1 and precursor 2/precursor 3 were injected into the preheating zone using a precision injection pump (LSP-02B, Longer, China), respectively, and then the two precursors flowed into the reaction zone for nucleation and growth. Among them, TiO\(_2\) added in precursor 3 is anatase, and its surface is fully modified with oleic acid, oleylamine, 1-octadecene and PbI\(_2\), providing a favorable environment for the subsequent combination of CsPbI\(_3\) nanocrystals and TiO\(_2\). The Cs : Pb ratio of precursor 1 and precursor 2 (precursor 3) was controlled at 1 : 6. The temperature of the heating table was set at 150 °C and the flow rate of precursor 1 and precursor 2 (precursor 3) in the preheating zone is 500 μL min\(^{-1}\), so the flow rate in the reaction zone is 1000 μL min\(^{-1}\). The liquid volume within the reaction zone was 80.5 mm\(^3\). Through the calculation of the flow rate and liquid volume in the reaction zone, it is concluded that the reaction time of the mixed precursors in the reaction zone was 5 s. The reaction product was flowed into a 50 mL conical bottle through a polytetrafluoroethylene (PTFE) tube for the ice bath quenching reaction.

**Purification of CsPbI\(_3\) nanorods and CsPbI\(_3\)/TiO\(_2\) nanocomposites**

The crude solution resulting from the microfluidic reaction device was collected and centrifuged at a speed of 10 000 revolutions per minute for a duration of 5 minutes in order to remove the supernatant containing high concentrations of oleic acid and oleylamine. Then the precipitation was centrifuged at a speed of 10 000 revolutions per minute for 5 minutes after adding an appropriate amount of n-hexane. After discarding the supernatant containing unreacted substances, the precipitate was dispersed in an appropriate amount of n-hexane for related performance characterization.

**Manufacture of an LED**

The fabrication of an LED involved the utilization of CsPbI\(_{1.5}\)Br\(_{1.5}\)/TiO\(_2\) and CsPbBr\(_3\)/TiO\(_2\) nanocomposites, and a blue chip (455 nm). The LED was powered by a current of 10 mA and a voltage of 3 V, and the optical characteristics of the LED were automatically measured using an LED analyzer (admin HP9000).

**Characterization**

The morphology was analyzed and characterized by field emission scanning electron microscopy (ZEISS Gemini SEM 300). X-ray diffraction (XRD Tongda TDM-20) analysis was performed with a monochromatic source of Cu Kα radiation (\(\lambda = 1.5405 \text{ Å}\)) at 30 kV and 20 mA (2θ = 5°–80°) in order to acquire the information on the phase purity and crystal structure of the products. Photoluminescence (PL) and absorption spectra were recorded with a Hitachi F-7000 and Hitachi UH-4150 spectrophotometer, respectively. X-ray photoelectron spectroscopy (AXIS SUPRA+) was utilized in order to acquire X-ray photoelectron spectroscopy (XPS) data specifically for the purpose of surface analysis. Fourier transform infrared spectra (FTIR) were recorded using a Nicolet NEXUS 670 spectrophotometer. A steady-state and transient-state fluorescence spectrometer (FS5, Edinburgh) was utilized to record the luminescence decay curve. The CsPbI\(_{1.5}\)Br\(_{1.5}\)/TiO\(_2\) nanocomposites were combined with CsPbBr\(_3\)/TiO\(_2\) nanocomposites on a blue chip (455 nm) and an LED analyzer (admin HP9000) was used to record the optical properties of the LED.

**Results and discussion**

The reaction device for preparing CsPbI\(_3\)/TiO\(_2\) nanocomposites and its design are shown in Fig. 1. In a typical synthesis, the heating table is used to regulate the temperature of the preheating zone and the reaction zone. Precursor 1 and precursor 2/precursor 3 were injected into the preheating zone using a precision injection pump, and the flow rate and reaction time of the precursors are adjusted through the injection pump. Then the two precursors were mixed, nucleated and continued to grow into nanorods in the reaction zone. Finally, the product was collected in the collection zone and the reaction is terminated through an ice bath, and by observing the obvious color change of the solution in the conical flask, the formation of the CsPbI\(_3\) nanocrystals or CsPbI\(_3\)/TiO\(_2\) nanocomposites is indicated.

The XRD results of CsPbI\(_3\) nanocrystals with different Cs and Pb ratios prepared by the microfluidic method were compared with standard powder diffraction cards (PDF#97-016-1481), as illustrated in Fig. S1.† It can be seen that when the ratio of Cs to Pb is 1 : 4–1 : 6, CsPbI\(_3\) nanocrystals exhibit a black luminescent phase, and strong diffraction peaks are at 14.070°, 19.949°, 28.358°, 34.915° and 40.536° corresponding to the (100), (110), (200), (211), and (220) planes. When the ratio of Cs and Pb is 1 : 6, the crystal diffraction peak is the strongest. Therefore, the ratio of Cs and Pb is controlled at 1 : 6 in the synthesis of CsPbI\(_3\) nanocrystals by the microfluidic method. As shown in Fig. S2,† the effects of different synthesis
temperatures and flow rates on the luminescence properties of CsPbI3/TiO2 nanocomposites were studied and characterized using emission spectra. When the reaction temperature of CsPbI3/TiO2 nanocomposites is 90–130 °C, the emission peak undergoes a redshift, indicating that the grain size of CsPbI3 nanocrystals gradually increases with the increase of reaction temperature. However, when the reaction temperature is 130–200 °C, the emission peak experiences a slight redshift, which shows that the nucleation growth of CsPbI3 nanocrystals is stable and the particle size changes little. At the same reaction temperature, when the flow rate of the injection pump is set to 100–1000 μL min⁻¹, the emission peak center of CsPbI3/TiO2 nanocomposites gradually decreases with the increase of flow rate and a slight blue shift occurs, indicating that the nucleation reaction of CsPbI3 nanocrystals is not complete with the decrease of reaction time. Therefore, the continuous preparation of CsPbI3 nanocrystals with a high luminous intensity and stable emission position through microchannels requires a higher temperature and suitable flow rate.

The powder X-ray diffraction (XRD) patterns confirm the crystalline structure of CsPbI3 nanorods and CsPbI3/TiO2 nanocomposites. Fig. 2a displays the anatase phase (PDF#00-021-1272) of TiO2, with distinct diffraction peaks at 25.28°, 36.95°, 37.80°, 38.58°, and 48.05°, which correspond to the (101), (103), (004), (112), and (200) planes, respectively. Meanwhile, the diffraction patterns of CsPbI3 nanocrystals (blue line) exhibit prominent peaks at 14.070°, 19.949°, 28.358°, 34.915°, and 40.536° corresponding to the (100), (110), (200), (211), and (220) crystallographic planes of a structure as indexed by PDF#97-016-1481. In the XRD analysis of CsPbI3/TiO2 nanocomposites (red line), two distinct peaks corresponding to TiO2 are observed at 25.28° and 48.05°, in addition to the diffraction peaks attributed to CsPbI3 nanocrystals. In order to study the binding form of CsPbI3 nanocrystals and TiO2, the morphologies of CsPbI3 nanorods and CsPbI3/TiO2 nanocomposites were presented by field emission scanning electron microscopy. As shown in Fig. S3 and S4, CsPbI3 nanocrystals and CsPbI3/TiO2 nanocomposites synthesized by the microfluidic method are uniformly distributed on the conductive adhesive with a rod-like morphology. The obvious difference is that the surface of CsPbI3 nanorods is very smooth [Fig. S5a†], while the surface of CsPbI3/TiO2 nanocomposites is wrapped by a large amount of TiO2 (Fig. 2b). Fig. S5b-d† and Fig. 2c–f show the elemental mapping of CsPbI3 nanorods and CsPbI3/TiO2 nanocomposites, respectively. As shown in Fig. 2c–f, Ti, Cs, Pb and I elements are uniformly dispersed in CsPbI3/TiO2 nanocomposites. Combined with the analysis of the SEM images of CsPbI3 nanorods and CsPbI3/TiO2 nanocomposites, TiO2 binds closely to the surface of CsPbI3 nanorods. The coating of TiO2 not only passivates the surface of CsPbI3 nanorods, but also reduces the exposure area of CsPbI3 nanorods in air and isolates oxygen and moisture in air to a certain extent, thus increasing the storage time of CsPbI3 nanorods.

To investigate the interaction between CsPbI3 nanorods and TiO2 in the nanocomposites, Fourier transform infrared spectroscopy (FTIR) was performed, as depicted in Fig. 3a. For discrete CsPbI3 nanorods and CsPbI3/TiO2 nanocomposites, the stretching vibrations of C–H at 2915, 2844, and 1404 cm⁻¹, the deformation vibrations of N–H at 1539 and 1464 cm⁻¹ and the deformation vibration of C=C at 1635 cm⁻¹ are observed, revealing the presence of surface capping ligands (i.e., oleic acid and oleylamine). The FTIR analysis of CsPbI3/TiO2 nanocomposites reveals a broad peak in the range of 1000–500 cm⁻¹, which corresponds to the Ti=O–Ti. This observation suggests the presence of TiO2 on the surface of CsPbI3 nanorods. Furthermore, X-ray photoelectron spectroscopy (XPS) is employed to validate the surface chemical compositions and ascertain the valence states of the structures. The pristine CsPbI3 nanorods and CsPbI3/TiO2 nanocomposites all exhibit peaks of Cs, Pb, and I as shown in Fig. 3b. In addition, two additional peaks are seen at 464.21 eV and 458.48 eV in the CsPbI3/TiO2 nanocomposite structures. These peaks match the binding energies of Ti 2p1/2 and 2p3/2 of Ti⁴⁺, respectively, as shown in Fig. 3c. This observation further confirms the successful binding of CsPbI3 nanorods and TiO2. From Fig. 3d–f, it can be seen that the binding energies of 738 eV and 724 eV represent Cs 3d (Fig. 3d), the binding energies of 143 eV and...
138 eV represent Pb 4f (Fig. 3e), and the binding energies of 630 eV and 618 eV represent I 3d (Fig. 3f). Furthermore, after CsPbI3 nanorods were combined with TiO2, the XPS peaks of Cs 3d, Pb 4f, and I 3d shift to a higher binding energy. This effect was particularly noticeable for the Cs 3d5/2 and Cs 3d3/2 peaks, as seen in Fig. 3d. Specifically, the Cs 3d5/2 peak shifted by 0.19 eV and the Cs 3d3/2 peak shifted by 0.26 eV. Correspondingly, similar phenomena were observed for the I 3d3/2 and I 3d5/2 peaks with a shift of 0.10 eV and 0.17 eV, respectively (Fig. 3f). According to the analysis results of XPS, after the combination of TiO2 with CsPbI3 nanorods, the chemical state of CsPbI3/TiO2 nanocomposites has changed compared to the CsPbI3 nanorods, indicating that charge transfer occurs between CsPbI3 nanorods and TiO2.

In order to explore the influence of CsPbI3 nanorods combined with TiO2 on their photoluminescence properties, the emission spectra, absorption spectra and time-resolved PL intensity of CsPbI3 nanorods and CsPbI3/TiO2 nanocomposites were compared as shown in Fig. 4. Compared with CsPbI3 nanorods, the PL intensity of CsPbI3/TiO2 nanocomposites increased by 1.3 times under 577 nm excitation (Fig. 4a) and by 1.19 times at their optimal excitation wavelengths (Fig. S6†), which is due to the passivation and enhanced light absorption resulting from the binding of TiO2 with the surface of CsPbI3 nanorods. Furthermore, the emission peak of CsPbI3/TiO2 nanocomposites is located at 688 nm, which shows a blue shift of 5 nm compared with the original CsPbI3 nanorods.

This is because when TiO2 particles are involved in the microchannel reaction, the free nucleation and growth space of CsPbI3 nanorods will be reduced to some extent. The smaller size causes a blue shift in the PL spectrum. At the same time, the absorption spectra of the CsPbI3/TiO2 nanocomposites showed a corresponding blue shift of 4 nm compared to the original CsPbI3 nanorods (Fig. 4b). In addition, in order to illustrate the advantages of preparing CsPbI3/TiO2 nanocomposites with microfluidic chips, the PL spectra of CsPbI3 nanorods, CsPbI3/TiO2 nanocomposites prepared by the microfluidic method (CsPbI3/TiO2-mic) and composites directly mixed with synthesized CsPbI3 nanorods and TiO2 (CsPbI3/TiO2-mix) were compared. As shown in Fig. S7,† only by preparing CsPbI3/TiO2 nanocomposites by the microfluidic method can the PL intensity be enhanced. Furthermore, as shown in the illustration in Fig. 4b, the color of CsPbI3 nanorods and CsPbI3/TiO2 nanocomposite powder is clearly different under natural light. The Tauc equation was employed to compute the bandgap of CsPbI3 nanorods and CsPbI3/TiO2 nanocomposites in order to investigate their bandgap fluctuation:57

\[(a\nu^2) = A(\nu - E_g)\]  

(1)

in which \(\nu\) represents the incident photon energy, \(A\) is the absorption coefficient, and \(A\) is a proportional constant.

It is well known that the band gap of TiO2 is 3.2 eV, and because of the carrier transport characteristics of TiO2, it is often used to improve the performance of perovskite materials.58,59 According to the illustration in Fig. 4b and the schematic diagram of the band gap distribution of TiO2 and CsPbI3 in Fig. 4c, the band gap of CsPbI3 nanorods is 1.73 eV, while that of CsPbI3/TiO2 nanocomposites is 1.78 eV and the heterojunction shows type II band arrangement. The coupling of electron states is advantageous for the charge separation of photogenerated electrons and holes. A portion of the excited electrons at the conduction band minimum (CBM) of CsPbI3 nanorods inject into the CBM of TiO2 before the radiative transition, resulting in a shortened fluorescence lifetime, as shown in the time-resolved luminescence decay curve (Fig. 4d). The time-resolved luminescence decay curves are fitted using a biexponential decay function, as illustrated by the subsequent equation:29,60

\[y = A_1 \times \exp\left(-\frac{t}{\tau_1}\right) + A_2 \times \exp\left(-\frac{t}{\tau_2}\right) + y_0\]  

(2)

\[\tau_{ave} = \frac{\sum_i \tau_i^2}{\sum_i \tau_i}\]  

(3)

where \(\tau_1\) and \(\tau_2\) are on behalf of the decay lifetimes of nanocrystals and the values of \(A_1\) and \(A_2\) represent the proportions of \(\tau_1\) and \(\tau_2\), respectively. The corresponding parameters are shown in Table S1.† Compared with CsPbI3 nanorods, heterojunctions formed in CsPbI3/TiO2 nanocomposites promote charge transfer. Eqn (2) states that TiO2, being a highly
effective electron acceptor, has a greater tendency to transfer electrons from the excited state of CsPbI\textsubscript{3} nanorods. This leads to a faster decrease in fluorescence intensity in CsPbI\textsubscript{3}/TiO\textsubscript{2} nanocomposites, with an average lifetime of 93.6 ns, compared to CsPbI\textsubscript{3} nanorods which have an average lifetime of 107.7 ns.

In order to test the water resistance of the prepared CsPbI\textsubscript{3}/TiO\textsubscript{2} nanocomposites, CsPbI\textsubscript{3} nanorods prepared by the same method were evaluated. First, equal amounts of CsPbI\textsubscript{3} nanorods and CsPbI\textsubscript{3}/TiO\textsubscript{2} nanocomposites were dispersed in n-hexane and placed in a 5 mL transparent sample bottle with a 1:1 volume ratio of deionized water, as shown in Fig. 5b. In the absence of other interference, the PL intensity of the two groups of samples was tested every 5 minutes and photographed under natural light.

As shown in Fig. 5a and Fig. S8a and b, the PL intensity of CsPbI\textsubscript{3} nanorods and CsPbI\textsubscript{3}/TiO\textsubscript{2} nanocomposites gradually decreased and their spectra gradually shifted blue within 30 minutes. Among them, CsPbI\textsubscript{3} nanorods are quenched in 20 minutes, which revealed the rapid destruction and poor water resistance of naked CsPbI\textsubscript{3} nanorods. However, the CsPbI\textsubscript{3}/TiO\textsubscript{2} nanocomposites still maintained 38.3% of the original PL intensity at 30 minutes, and the stability was significantly enhanced, because after the TiO\textsubscript{2} coating on the surface of CsPbI\textsubscript{3} nanorods, the exposed surface area was reduced, and water erosion was isolated to a certain extent.

In addition, the thermal quenching properties of CsPbI\textsubscript{3} nanorods and CsPbI\textsubscript{3}/TiO\textsubscript{2} nanocomposites were studied, as shown in Fig. S8c and d. The PL spectra of CsPbI\textsubscript{3} nanorods and CsPbI\textsubscript{3}/TiO\textsubscript{2} nanocomposites blue shifted when the temperature was increased from 303 K to 383 K. When the temperature was increased at 383 K, the red emission of CsPbI\textsubscript{3} nanorods was quenched, while the PL intensity of CsPbI\textsubscript{3}/TiO\textsubscript{2} nanocomposites remained at 52% of the initial level (Fig. 5c).

The results show that TiO\textsubscript{2} has a certain protective effect on the luminescence of CsPbI\textsubscript{3} nanorods, which is due to the rapid transfer of charge carriers to transfer heat from CsPbI\textsubscript{3} nanorods to TiO\textsubscript{2}. In order to more directly observe the change of the thermal stability of CsPbI\textsubscript{3} nanocrystals after combining with TiO\textsubscript{2}, the powder of CsPbI\textsubscript{3} nanorods and CsPbI\textsubscript{3} nanocomposites was prepared into “squares” with a width of 2 cm, a length of 3 cm and a depth of 1 mm. The two “squares” were placed on the heating table, and gradually the temperature of the heating table was increased from 313 K to 383 K, and the degree of etching of the “squares” was observed. According to Fig. 5d, it can be observed that with the gradual increase of temperature, the “block” etching degree of CsPbI\textsubscript{3} nanorods is serious, while the “block” etching degree of CsPbI\textsubscript{3}/TiO\textsubscript{2} nanocomposites is relatively light, which reflects that TiO\textsubscript{2} has a certain protective effect on the luminescence of CsPbI\textsubscript{3} nanorods.

In order to study the universality and potential application of continuous preparation of CsPbBr\textsubscript{x}/TiO\textsubscript{2} nanocomposites by the microfluidic method, CsPbBr\textsubscript{x}/TiO\textsubscript{2} nanocomposites with different emission colors were synthesized by changing the precursor composition. The photo of the CsPbBr\textsubscript{x}/TiO\textsubscript{2} nanocomposites uniformly dispersed in n-hexane and exposed to 365 nm UV light is shown in Fig. 6a. The PL spectrum of CsPbBr\textsubscript{x}/TiO\textsubscript{2} nanocomposites is shown in Fig. 6b, covering the entire visible spectral region from purple (408 nm) to dark red (692 nm), with a half-peak width of 13.2–34.4 nm, which is clearly to a narrow peak emission. By substituting Cl with Br and I, the emission peaks of the CsPbBr\textsubscript{x}/TiO\textsubscript{2} nanocomposites progressively more towards longer wavelengths. This shift is caused by the decreased bandgap energy of the nanocrystals. The wide emission peaks seen in CsPbI\textsubscript{3}/TiO\textsubscript{2} composites containing I ions can be attributed to the less-ordered organization of halides in the crystal lattice. This change in arrangement may be caused by the variation between Br and I ions. As shown in Fig. 6c, the emission position of CsPbI\textsubscript{3}/TiO\textsubscript{2} nanocomposites is at 692 nm, close to far-
red light, which is not suitable for display, while the emission position of CsPbI1.5Br1.5/TiO2 is at 630 nm, which is pure red light. Therefore, CsPbI1.5Br1.5/TiO2 nanocomposites are the most suitable to encapsulate LEDs as red light.

According to the above research, after combining with TiO2, CsPbI3 nanorods have better PL performance and higher stability, and CsPbX3/TiO2 nanocomposites can be continuously prepared by the microfluidic method. Since the emission position of CsPbI3/TiO2 nanocomposites is close to far-red light, while that of CsPbI1.5Br1.5/TiO2 nanocomposites is pure red light, in order to further explore the potential application of CsPbX3/TiO2 nanocomposites in lighting and display, the CsPbX3/TiO2 nanocomposite was deposited on a blue light chip (455 nm) to encapsulate the LED and evaluate the related performance. The PL maximum of the blue chip (455 nm) matched well with the PL peaks of the corresponding CsPbX3/TiO2 nanocomposites in lighting and display, the CsPbX3/TiO2 nanocomposite was deposited on a blue light chip (455 nm) to encapsulate the LED and evaluate the related performance. The PL maximum of the blue chip (455 nm) matched well with the PL peaks of the corresponding CsPbX3/TiO2 nanocomposites in lighting and display, the CsPbX3/TiO2 nanocomposite was deposited on a blue light chip (455 nm) to encapsulate the LED and evaluate the related performance.

Conclusions

In conclusion, this work proposes a microchannel reaction method for continuous and efficient preparation of CsPbI3/TiO2 nanocomposites. According to the results, TiO2 can be coated in situ on the surface of CsPbI3 nanorods by the microfluidic method and form a heterojunction. Compared with CsPbI3 nanorods, the PL intensity of CsPbI3/TiO2 nanocomposites is increased by 1.3 times under excitation at 577 nm, and the water resistance and thermal stability are significantly enhanced. When soaked in water for 30 minutes, the PL intensity of CsPbI3/TiO2 nanocomposites is 38.3% of the initial level, and when the temperature is 383 K, the PL intensity of CsPbI3/TiO2 nanocomposites is 52% of the initial level, but the fluorescence quenching of CsPbI3 nanorods occurs. Finally, full-spectrum CsPbX3/TiO2 nanocomposites can be continuously prepared by the microfluidic method. CsPbBr3/TiO2 and CsPbI1.5Br1.5/TiO2 nanocomposites deposited on a blue light chip (455 nm) can produce LEDs with a color rendering index of 86 (Ra = 86), a color temperature (CCT) of 4331 K and a color gamut covering 125% NTSC. In addition, green CsPbBr3/TiO2 nanocomposites and red CsPbI1.5Br1.5/TiO2 nanocomposites with emission positions of 527 nm and 645 nm were obtained by adjusting the reaction temperature and flow rate of the microfluidic method, which can encapsulate an LED with a color gamut of 142% NTSC. This study shows the great potential of CsPbX3/TiO2 nanocomposites in lighting and display. Additionally, this work also provides a feasible scheme for the continuous preparation of other perovskites by the microfluidic method.

Data availability

The data supporting this article have been included as part of the ESI.†

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

This work was financially supported by the National Natural Science Foundation of China (No. 52172150, 62275161, 52302188, U2141240), the Shanghai Rising-Star Program (No. 21QC1401100), the Shanghai Sailing Program (No. 23YF1446100) and the National Foreign Experts Program (No. G2023013005L).

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