SPECIAL ISSUE: Optical Gain Materials towards Enhanced Light-Matter Interactions

Continuous-flow synthesis of doped all-inorganic perovskite nanocrystals enabled by a microfluidic reactor for light-emitting diode application

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ABSTRACT All-inorganic perovskite nanocrystals (AIPNCs) possess the advantages of narrow emission spectrum, high quantum efficiency of luminescence and tunable luminescence position, which show a broad application prospect in the fields of optoelectronic materials and devices. Ion doping can tune their pristine crystal structures and luminescent properties or endow the AIPNCs with additional functionalities. Herein, a microfluidic reactor is designed to produce the Ce³⁺-doped AIPNCs based on the continuous-flow reaction. The mechanism of the flow synthesis of Ce³⁺-doped AIPNCs is the efficient physical mixing of the precursor ions in the confined micro-channel, the reaction nucleation of crystal seeds in the poor solvent and the crystal growth of the doped AIPNCs along the flow direction. The synthesis process can be on-line monitored by an optical fiber absorption spectrometer and an optical fiber fluorescence spectrometer. The doping concentration of Ce³⁺ can be facilely controlled by changing the flow parameters in the microfluidic reactor, and the highest value reaches 1%. The Ce³⁺ doping can improve the photoluminescence efficiency and the stability of the AIPNCs. The Ce³⁺-doped CsPbBr₃ AIPNCs can be used to manufacture green light-emitting diodes (LEDs) with a high color purity of 93.3% and white LEDs with correlated color temperature (CCT) of 10,436 K, CIE color coordinates of (0.261, 0.317) and color-rendering index (CRI) of 72.1. The continuous and controllable synthesis of AIPNCs by microfluidic reactor opens up new avenues for the application of the high-performance optoelectronic materials and devices.

Keywords: all-inorganic perovskite nanocrystals, microfluidics, ion doping, light-emitting diode

INTRODUCTION

In recent years, lead halide perovskites with excellent optoelectronic properties have become a kind of emerging luminescent materials [1–4]. Among them, all-inorganic perovskite nanocrystals (AIPNCs) CsPbX₃ (X=Cl, Br, I) possessing ultra-high photoluminescence quantum efficiency, narrow line width and wide color domain are expected to become a new generation of functional optical materials. Recent progress of AIPNC massive synthesis has promoted their advanced light-emitting diode (LED) applications [5,6]. AIPNC scintillators can be used to manufacture the flexible and highly sensitive X-ray detector with a detection limit of 13 nGy s⁻¹, which is 1/400 of the radiation dose of general medical imaging [7]. AIPNCs have been demonstrated as a new class of superior optical-gain materials towards low-threshold and ultra-stable lasing [8,9]. AIPNCs have been used to fabricate high-performance and low-cost image sensors and chemical sensors [10,11]. AIPNC-based photodetectors and temperature sensors have shown high sensitivity and considerable feasibility, respectively [12,13]. AIPNCs are novel photocatalysts to convert CO₂ into solar fuels, or to initiate the polymerization reaction [14,15]. AIPNCs can be combined with persistent phosphors to fabricate anti-counterfeiting materials [16].

Very recently, ion doping has been proposed as a chemical strategy to create the AIPNC homologues. The methodology for fabricating doped AIPNCs is partially or completely replacing the Pb²⁺ with main-group metal ions (Ag⁺, Bi³⁺, Al³⁺, In³⁺, Ba²⁺, Sr²⁺, Ca²⁺, Li⁺, K⁺), transition

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metal ions (Zn^{2+} , Cu^{2+} , Ni^{2+} , Mn^{2+}) or rare-earth metal ions (Ce^{3+} , Tb^{3+} , Eu^{3+} , Yb^{3+}). The heteroion doping of AIPNCs can realize the crystal growth control, structural stability control, light conversion control or optoelectronic performance control [17–20]. For instance, the Mn^{2+} -doped AIPNCs present both high-energy band gap emission and low-energy down-converted emission of Mn^{2+} [21]. The Ba^{2+} doping can adjust the lattice microstructure, band structure, surface potential, electron affinity, dielectric properties and other electrical properties of AIPNCs towards high-performance nano-generators [22]. Ni^{2+} doping of AIPNCs can significantly tune their optical properties, introduce magnetic functionality and improve their chemical and photochemical stabilities [23]. The Bi^{3+} -doped AIPNCs demonstrate broadened light absorption within the whole visible light region and excellent photostriction performances [24]. Doping Al^{3+} into the AIPNCs can extend the band gap and improve the stability of blue photoluminescence [25]. Li^{+} doping can cause a lattice expansion and improve the electron injection efficiency in the AIPNC LED devices [26].

Previously, the main reaction routes to synthesize doped AIPNCs are hot-injection at high temperature and postsynthetic ion exchange. For instance, Bi^{3+} -doped AIPNCs were synthesized by using a classic hot-injection method, and the incorporation concentration of Bi^{3+} into AIPNCs is 0.074% [27]. A halide exchange-driven cation exchange strategy was exploited to synthesize Mn^{2+} -doped $\text{CsPb}(\text{Cl}/\text{Br})_3$ nanocrystals *via* post-replacement of Pb^{2+} in the pre-synthesized AIPNCs [28]. Although the above-mentioned methods have been proved effective in synthesizing doped AIPNCs, the high reaction temperature, tedious reaction time, additional vacuum equipment, complex procedure, and discontinuous operation still remain to be optimized. In recent years, the microfluidic technique has been proposed as a versatile and robust method for the flow reactions and physical operations in liquid phases [29–31]. The key outcomes when using a microfluidic reactor instead of a batch reactor are the highly integrated reaction platform combining the reactant input, mechanical mixing, chemical nucleation, the online product monitoring and the dynamic control of product structures and properties. They are now widely used in nanomaterial synthesis, functional material assembly, drug release, biological analysis and so on [32–35]. Previously, the synthesis of doped AIPNC is generally conducted in the liquid phase with intense mechanical mixing. Therefore, the doped AIPNC synthesis by using microfluidic technique is practicable.

In this work, a multichannel co-flowing microfluidic reactor is put forward to synthesize the doped AIPNCs. The Ce^{3+} -doped AIPNC is selected as a typical example. The liquid sealed space in the microfluidic chip generates a self-contained closed environment to block the air and moisture. The high-speed mixing of the reactant fluids in the micro-reactor ensures the efficient collision and combination of reactive particles. The nucleation and crystallization of the doped AIPNCs are conducted based on the phase separation of the precursor ions in a poor solvent at room temperature. The synthesis process can be on-line monitored by an optical fiber absorption spectrometer and an optical fiber fluorescence spectrometer. The doping concentration of Ce^{3+} can be continuously tuned by changing the flow rates of Ce^{3+} source. Overall, the microfluidic reactor to synthesize the doped AIPNCs proposed in this work demonstrates significant advantages over the traditional hot-injection setup, including reduced reaction temperature, reduced reaction time, unnecessary external vacuum equipment, continuous synthesis, dynamic control of the reaction condition and real-time monitoring.

EXPERIMENTAL SECTION

Materials

Lead bromide (PbBr_2 , 99.5%, Aladdin), cesium bromide (CsBr , 99.9%, Alfa Aesar), cerium bromide (CeBr_3 , 99.5%, Aladdin), oleic acid (OA, 90%, Aladdin), oleamine (OAM, 90%, Alfa Aesar), *N,N*-dimethylformamide (DMF, analytical grade, Aladdin) and toluene (analytical grade, Aladdin) were directly used without further purifications. The blue phosphor ($\text{BaMgAl}_{10}\text{O}_{17}:\text{Eu}^{2+}$, 99%) and red phosphor ($\text{K}_2\text{SiF}_6:\text{Mn}^{4+}$, 99%) were purchased from Guangzhou Huakui Chemical Technology Co., Ltd. (China). The ultrapure water (18.2 M Ω cm) was provided by a pure water machine (Angel, China). The capillary tubes and glass slides to make the microfluidic reactor were purchased from the Sailing Company.

The fabrication of microfluidic reactor

The co-flowing microfluidic reactor for the synthesis of Ce^{3+} -doped AIPNCs was fabricated by coaxially assembling four cylindrical capillaries (two left capillaries, one middle capillary and one right capillary) on a glass slide as shown in Fig. 1a. First, the middle capillary with an inner diameter of 500 μm and a length of 8 cm was tapered and sanded to have a 300- μm orifice. Then, two left capillaries with an inner diameter of 100 μm and a length of 8 cm were inserted into the tapered middle capillary

Figure 1 Continuous-flow synthesis of Ce^{3+} -doped AIPNCs enabled by a microfluidic reactor. (a) The schematic of experimental setup for the continuous synthesis of Ce^{3+} -doped AIPNCs based on the microfluidic reactor coupled with an optical fiber absorption spectrometer and an optical fiber fluorescence spectrometer. (b) The crystal structural model of the undoped CsPbBr_3 AIPNCs and Ce^{3+} -doped CsPbBr_3 AIPNCs. (c) Digital images of the undoped and doped AIPNCs when irradiated by UV light (365 nm), the flow rate ratios to prepare the samples from left to right are 0%, 10%, 20%, 30%, 40% and 50%. (d) The emblem of soft matter center of Guangdong University of Technology manufactured by screen printing of the Ce^{3+} -doped AIPNC ink on a black substrate.

side by side on a glass slide, and the depth of insertion is 4 cm. Lastly, both the left and middle capillaries were inserted into the right capillary with an inner diameter of 900 μm and a length of 15 cm, and the insertion depth of the middle capillary is 6 cm. The interstice between the left capillaries and the middle capillary was sealed by epoxy resin, while the interstice between the middle capillary and the right capillary remained open.

Synthesis of Ce^{3+} -doped AIPNCs in the microfluidic reactor

For the microfluidic synthesis of Ce^{3+} -doped AIPNCs, the micro-reaction system was based on the physical mixing and chemical reaction of fluids 1, 2 and 3 containing Cs^+ , Ce^{3+} , Pb^{2+} and Br^- as shown in Fig. 1a. Fluid 1 was prepared by dispersing PbBr_2 (0.4 mmol) and CsBr (0.4 mmol) in the mixture composed of DMF (10 mL), OA (1 mL) and OAM (0.5 mL) with the assistance of ultrasound. Fluid 2 was prepared by dispersing CeBr_3 (0.4 mmol) in the mixture composed of DMF (10 mL), OA (1 mL) and OAM (0.5 mL) with the assistance of ultrasound. Fluid 3 was toluene. Fluid 1 and fluid 2 were

independently injected into the two left capillaries, respectively. Fluid 3 was injected into the interstices between the right capillary and the middle capillary. The flow rate of fluid 1 was 20 $\mu\text{L min}^{-1}$. The flow rate of fluid 2 was set to be 0, 2, 4, 6, 8 and 10 $\mu\text{L min}^{-1}$, and the flow rate ratios between fluid 2 and fluid 1 are 0%, 10%, 20%, 30%, 40%, 50%. The flow rate of fluid 3 was 100 $\mu\text{L min}^{-1}$. The flow rates of these fluids were independently controlled by syringe pumps (Harvard Apparatus).

Fabrication of AIPNC-based green and white LEDs

The AIPNCs were firstly mixed with silicone to form uniform AIPNC dispersions with the assistance of the ultrasound, the concentrations of the undoped and doped AIPNCs in the dispersions were 1 wt%. Then, the AIPNC dispersions were placed on the surface of an ultraviolet (UV) LED chip of 370 nm and sealed by the epoxy resin under vacuum condition to obtain the AIPNC-based green LEDs. The blue phosphor ($\text{BaMgAl}_{10}\text{O}_{17}:\text{Eu}^{2+}$), green phosphor (Ce^{3+} -doped AIPNCs) and red phosphor ($\text{K}_2\text{SiF}_6:\text{Mn}^{4+}$) were dispersed in silicone and then deposited on the UV-LED chip of 370 nm from top to down

to assemble a three dimensional (3D)-layered white LED chip. The concentrations of the blue, green and red phosphors in the silicone were 1 wt%, 1 wt% and 2 wt%, respectively. The photoelectric properties of the AIPNC-based green and white LEDs were tested by an integrating sphere spectroradiometer system (LHS-1000, Everfine).

Instruments and characterizations

The powder X-ray diffraction (XRD) patterns of the undoped and doped AIPNCs synthesized in the microfluidic reactors were recorded by a powder X-ray diffractometer (Empyrean, PANalytical). The transmission electron microscopy (TEM) image and the high-resolution TEM images of the undoped and doped AIPNCs were obtained by a JEOL JEM 2100 transmission electron microscope. The high-angle annular dark-field scanning TEM (HAADF-STEM) images coupled with the energy dispersive spectrometer (EDS) element mapping for the Ce^{3+} -doped AIPNCs were obtained by utilizing a Talos F200X STEM microscope (200 kV), FEI. The ultraviolet-visible (UV-Vis) absorption spectra were recorded by using a UV-Vis optical fiber absorption spectrometer (ocean optics USB2000+, USA). The photoluminescence (PL) emission spectra were recorded by an optical fiber fluorescence spectrometer (ocean optics STS, USA). The efficient Ce^{3+} doping concentration in the AIPNCs was determined by using a PerkinElmer Optima inductively coupled plasma-optical emission spectrometer (ICP-OES). The absolute quantum yield measurements of the undoped and doped AIPNCs were conducted by a Varian FLR025 spectrometer. The PL images were recorded by a fluorescence microscope equipped with a 365 nm UV LED (Mingmei QS1, China). The temperature in the experiment was controlled by a temperature controller (INSTECH, HCS402-STC 200).

RESULTS AND DISCUSSION

In this work, a continuous-flow synthesis of doped AIPNCs in liquid phase is proposed by designing and constructing a microfluidic reactor. The complete experimental setup is composed of a multichannel co-flowing microfluidic chip, an on-line optical fiber UV-Vis absorption spectrometer and an optical fiber PL spectrometer as illustrated in Fig. 1a. The detailed size parameters of the micro-reactor are listed in the experimental section. The microfluidic reactor provides a confined and sealed space for the physical mixing, reaction nucleation and crystal growth in the multifluids. The on-line spectrometers are introduced to monitor the real-time reaction state by recording the UV-Vis absorption spectra

and the PL emission spectra of the flowing AIPNC colloids at the end of the microfluidic reactor. The liquid-sealed space in the microfluidic reactor generates a self-contained closed environment to block the air and moisture, which avoids the utilization of additional vacuum equipment required in the traditional hot-injection synthesis. Fluid 1 is the main fluid containing the dissociated Cs^+ , Pb^{2+} , Br^- , OA, OAM and DMF. Fluid 2 is the doping fluid containing the dissociated Ce^{3+} , Br^- , OA, OAM and DMF. Fluid 3 is the poor solvent toluene. The dissociated Cs^+ , Pb^{2+} , Br^- and Ce^{3+} in the main fluid and the doping fluid are stabilized by OA and OAM, thus ensuring the homogeneity of the injected reactants. It is noteworthy that the elongated tip of the middle capillary in the co-flowing microfluidic reactor provides more contact and collision for the physical mixing of the reaction precursor ions (Cs^+ , Pb^{2+} , Br^- and Ce^{3+}) in fluid 1 and fluid 2 due to the increased linear velocity along the cone area. Then, the mixed reaction precursors flow into fluid 3 containing the poor solvent toluene. The high-speed mixing of the precursor ions with fluid 3 ensures the efficient collision and combination of reactant particles to trigger the nucleation process and to generate the crystal seeds. Afterwards, the crystal seeds grow into the mature AIPNCs in the micro-reactor. Furthermore, the flowing DMF/toluene solvent can transfer the newborn AIPNCs from the reaction area to the external collection bottle, demonstrating a mini physical mixing-reaction nucleation-crystal growth route along the flow direction as shown in Fig. 1a. The nucleation and crystallization of the Ce^{3+} -doped AIPNCs proceed based on the phase separation in a poor solvent as shown in Reaction (1) (x is the doping concentration). The corresponding structural models of the undoped and Ce^{3+} -doped CsPbBr_3 AIPNCs are illustrated in Fig. 1b, indicating the substitution of Pb^{2+} by Ce^{3+} in the lattice. The flow rate of the poor solvent ($Q_3=100 \mu\text{L min}^{-1}$) is controlled, far larger than those of the main fluid and the doping fluid, to provide a nonpolar liquid environment and to strengthen the mixing of the reactive fluids. The doping concentration of Ce^{3+} can be easily tuned by changing the flow rate ratios (Q_2/Q_1) between the main fluid and the doping fluid. The Q_2/Q_1 ratios are 0%, 10%, 20%, 30%, 40% and 50% in this work. The resulting undoped/doped AIPNCs are collected by centrifugation, washed by toluene, and redispersed in toluene as shown in Fig. 1c. Both the undoped and doped AIPNCs can emit intensive green fluorescence when irradiated by UV light. The dispersion stability of the AIPNCs is basically decreased with the increase of Q_2/Q_1 as the fluorescence location in the bottles gradually

moves down. The accelerated aggregation of the doped AIPNCs in toluene is probably caused by the weakened ligand stabilization or the decreased charge repulsion between adjacent AIPNCs. The highly luminous Ce^{3+} -doped AIPNC colloids can be used as photonic ink. Fig. 1d shows the emblem of the soft matter center of Guangdong University of Technology manufactured by screen printing of the Ce^{3+} -doped AIPNC ink on a black

substrate.

TEM results in Fig. 2a–f reveal that the as-prepared Ce^{3+} -doped CsPbBr_3 AIPNCs basically possess typical cubic morphologies, similar to the undoped CsPbBr_3 AIPNCs synthesized without injecting Ce^{3+} into the microfluidic reactor. The sizes of the CsPbBr_3 AIPNCs are

Figure 2 Crystal morphologies of the undoped and Ce^{3+} -doped AIPNCs. (a–f) TEM images of the undoped and Ce^{3+} -doped AIPNCs prepared by the microfluidic reactor. The Q_2/Q_1 ratios when producing the samples are 0%, 10%, 20%, 30%, 40% and 50%, respectively. (g–i) The magnified high-resolution TEM images of the representative samples, and the Q_2/Q_1 ratios when producing the samples are 0%, 30% and 50%, respectively. (j–n) The HAADF-STEM image of single randomly selected Ce^{3+} -doped AIPNC (the flow rate ratio is 30%) and its corresponding EDS elemental mapping images of Ce, Cs, Pb, and Br.

about 15 nm when the Q_2/Q_1 ratios are increased from 0% to 40%, implying that the Ce^{3+} doping does not influence the basic crystal growth of the $CsPbBr_3$ host and can avoid the change of optical properties caused by the size effect. However, the Ce^{3+} -doped $CsPbBr_3$ AIPNCs present sharply decreased size and irregular morphology when the flow rate ratio reaches 50%. This can be attributed to the formation of excess nuclei at a high flow rate of the doping fluid. Therefore, the maximum Q_2/Q_1 ratio in this work is 50%. The high-resolution TEM images in Fig. 2g–i demonstrate that both the doped and the undoped $CsPbBr_3$ AIPNCs possess single crystal structures and clear lattice fringes with a spacing distance of about 0.58 nm corresponding to the lattice space of (101) plane. The EDS mapping images of the Ce^{3+} -doped $CsPbBr_3$ AIPNCs ($Q_2/Q_1=30\%$) as shown in Fig. 2j–n demonstrate the existence of the Ce, Cs, Pb and Br in the hybrid nanocrystals. Fig. 3a illustrates that the powder XRD patterns of the as-synthesized doped and undoped $CsPbBr_3$ AIPNCs are almost the same and possess cubic crystalline structures according to the Powder Diffraction File No. 54-0752 (Joint Committee on Powder Diffraction Standards, 2001). This result demonstrates that the Ce^{3+} doping does not change the crystalline forms of $CsPbBr_3$ AIPNCs. However, as compared with the undoped

$CsPbBr_3$ AIPNCs, a slight shift of the diffraction peak at (200) around 30° toward larger angle is observed for the doped $CsPbBr_3$ AIPNCs (Fig. 3b), indicating the decreased cell parameters and the decreased lattice plane gap as the result of the replacement of Pb^{2+} by Ce^{3+} . The ICP-OES analysis reveals that the Ce/Pb atomic ratios in the Ce^{3+} -doped $CsPbBr_3$ AIPNCs synthesized at different Q_2/Q_1 ratios are quantified to be 0%, 0.23%, 0.4%, 0.55%, 1% and 0.5% as shown in Fig. 3c. It is convinced that controlling the ion doping concentration in AIPNCs by changing the flow parameters in the microfluidic reactor is an efficient and facile methodology. Furthermore, the optical properties of the doped and undoped $CsPbBr_3$ AIPNCs were analyzed by steady-state UV-Vis absorption spectroscopy and PL emission spectroscopy. From the UV-Vis absorption spectra shown in Fig. 3d, it can be clearly seen that the incorporation of Ce^{3+} heteroions into $CsPbBr_3$ AIPNCs induces a slight blue-shift of the characteristic absorption edge of $CsPbBr_3$ AIPNCs due to the electronic structure modulation of the Ce^{3+} -doped $CsPbBr_3$ AIPNCs. Importantly, upon incorporation of Ce^{3+} into the $CsPbBr_3$ AIPNCs, the PL emission wavelengths of the doped and undoped $CsPbBr_3$ AIPNCs are located at around 520 nm (Fig. 3e). The maximum fluctuation of the emission wavelengths is only 2 nm as

Figure 3 Crystal structures and optical properties of the undoped and Ce^{3+} -doped AIPNCs. (a, b) Powder XRD patterns and the enlarged powder XRD patterns of the undoped and Ce^{3+} -doped AIPNCs. (c) The Ce^{3+} doping concentrations in the Ce^{3+} -doped AIPNCs fabricated at different flow rate ratios by the ICP-OES analysis. (d) UV-Vis absorption spectra of the undoped and Ce^{3+} -doped AIPNCs. (e) The PL spectra of the undoped and Ce^{3+} -doped AIPNCs (excitation at 365 nm). (f) The central PL wavelengths and the corresponding normalized PL intensities of the undoped and Ce^{3+} -doped AIPNCs.

shown in Fig. 3f. However, the PL spectra show an obvious increase of the normalized PL intensity from 0.67 to 1 with the flow rate ratio increasing from 0% to 40% (Fig. 3e, f), indicating the enhancement effect of Ce^{3+} -doping on the PL of CsPbBr_3 AIPNCs. It should be noted that the PL intensity begins to decrease when the flow rate ratio reaches 50%, possibly resulting from the decreased crystallinity of the Ce^{3+} -doped CsPbBr_3 AIPNCs. The photoluminescence quantum yield (PLQY) analysis also present that the quantum yields of the undoped and doped AIPNCs are 67.5%, 71.5%, 75.2%, 81.8%, 86.7% and 79.5% with the flow rate ratio increasing from 0% to 50%.

The structure stability is a significant concern of AIPNCs as the results of the dissociation of the ionic bonds, the hydrolysis of the metal ions and the oxidation of the halogen ions. It is manifest that the optical stability of the doped AIPNCs depends on their structure stabilities under certain conditions. The pretreatment of the AIPNC materials in the process of device manufacture is inevitably conducted under ambient conditions containing oxygen and moisture. Therefore, the PL evolution of the 1% Ce^{3+} -doped CsPbBr_3 AIPNCs with the highest luminous efficiency is analyzed with the undoped

CsPbBr_3 AIPNC as the control sample. The testing samples in the form of thin films were prepared by vacuum drying the AIPNC inks on a quartz plate. Results show that both the undoped and doped CsPbBr_3 AIPNCs can emit bright green fluorescence under ambient conditions in the initial state as shown in Fig. 4a, b. The undoped CsPbBr_3 nanocrystal shows a slight discoloration without isolation from oxygen and moisture with the aging time of 10 d. Then, its green emission rapidly fades with the increase of aging time due to the dissociation effect of perovskite crystals to form mobile ions. The undoped CsPbBr_3 nanocrystals almost lose the green fluorescence after 30-d aging, while the doped CsPbBr_3 nanocrystals show a slower attenuation process. When the aging time is increased to 20 d, the PL intensity of the Ce^{3+} -doped CsPbBr_3 AIPNCs begins to decrease dramatically. When the aging time reaches 30 d, the doped CsPbBr_3 AIPNCs can still emit the green fluorescence. The normalized PL intensities in Fig. 4c also demonstrate a better stability of the Ce^{3+} -doped CsPbBr_3 AIPNCs under ambient conditions than that of the undoped sample, probably due to the enhanced ionic bonds in the perovskite lattice by replacing the Pb^{2+} with Ce^{3+} . When the CsPbBr_3 AIPNCs are sealed in an LED chip, the lu-

Figure 4 Optical stabilities of the undoped and Ce^{3+} -doped AIPNCs. (a, b) PL images of the undoped and 1% Ce^{3+} -doped AIPNCs after different aging times at ambient condition (excitation at 365 nm). (c) The normalized PL intensities of the undoped and 1% Ce^{3+} -doped AIPNCs after different aging times at ambient condition. (d, e) The normalized PL intensities of the undoped and 1% Ce^{3+} -doped AIPNCs at different temperatures in the heating-cooling cycle. The inserted images are the representative PL images (excitation at 365 nm).

minescence performance of the LEDs can be affected by the surrounding heat generated by the LED working circuit. Therefore, the PL stability of the doped and undoped CsPbBr₃ AIPNCs against temperatures was also studied. The PL characteristics of the samples were recorded within a heat-cooling cycle. Results in Fig. 4d show that the green emission of the undoped CsPbBr₃ AIPNCs presents a continuous weakening in the heating process. The downward trend is approximately linear. The undoped CsPbBr₃ nanocrystals completely lose the green fluorescence when the temperature reaches 105°C. When the temperature is gradually back to 30°C, the green emission demonstrates a slow increase. However, the PL intensity of the undoped CsPbBr₃ AIPNCs only recovers ca. 62% due to the temperature-dependent deformation of the perovskite octahedral units [36]. On the contrary, the 1% Ce³⁺-doped CsPbBr₃ AIPNCs can reserve the green fluorescence when the temperature is below 60°C. The green fluorescence finally disappears when the temperature reaches 125°C, 20°C higher than the undoped CsPbBr₃ AIPNCs. When the temperature is gradually back to 30°C, the green emission demonstrates a fast increase. The PL intensity of the 1% Ce³⁺-doped CsPbBr₃ AIPNCs can recover ca. 90% as shown in Fig. 4e. Overall, the stability improvement of the Ce³⁺-doped CsPbBr₃ AIPNCs can be ascribed to the following mechanisms. One is that the incorporation of Ce³⁺ ions can enhance the formation energy, cause a slight lattice contraction, and hence stabilize the perovskite structures of the nanocrystals [18,37]. The other is that the Br-rich element can decrease the trap state and improve the stability of AIPNCs during the purification process and device fabrication [37,38].

In order to analyze the optical properties of the AIPNC-based LED device, both the undoped and doped AIPNCs were sealed in UV-pumped LED chips as shown in Fig. 5a. The as-prepared AIPNCs were firstly mixed with silicone to form uniform AIPNC dispersions with the assistance of the ultrasound, and the concentrations of the undoped and doped AIPNCs in the dispersions were 1 wt%. Then, the AIPNC dispersions were placed on the surface of a UV-LED chip of 370 nm and sealed by the epoxy resin under vacuum condition. The result in Fig. 5a shows that the AIPNC-based LED filled with 1% Ce³⁺-doped CsPbBr₃ nanocrystals can emit bright green fluorescence when the working voltage is set to be 3.2 V. The undoped and doped CsPbBr₃ nanocrystals as the green phosphors were sealed in six UV LED chips respectively. The fluorescence emission spectra of the AIPNC-based green LED chips were recorded by an op-

tical fiber fluorescent spectrometer. Results indicate that the central emission wavelengths of these LED chips are 537, 535, 536, 535, 535 and 534 nm, as shown in Fig. 5b–g, and the slightly blue shift of the PL emission wavelength can be ascribed to the edge blue-shift of the optical absorption as described in Fig. 3d. In the meantime, the color purity of the LED chip reaches a highest level of 93.3% when the flow ratio is 40% due to the efficient doping of Ce³⁺ in the crystalline lattice of AIPNCs. When the flow rate ratio is further increased to 50%, the color purity of the green LED chip is sharply decreased to 89.2% as the result of the decreased crystallinity of the doped AIPNCs.

The 0.1% Ce³⁺-doped AIPNC as the green phosphor was coupled with commercial blue phosphor (BaMgAl₁₀O₁₇:Eu²⁺) and red phosphor (K₂SiF₆:Mn⁴⁺) to assemble a 3D layered white LED chip. Fig. 5h, i show that the central emission wavelengths of the commercial red phosphor (K₂SiF₆:Mn⁴⁺) and blue phosphor (BaMgAl₁₀O₁₇:Eu²⁺) are 628 and 460 nm, respectively. The central emission wavelength of the green phosphor (1% Ce³⁺-doped AIPNCs) is 535 nm as shown in Fig. 5f. The green, red and blue phosphors (quantum yields of 86.7%, 72% and 85%) show strong emission under UV light excitation (Fig. 5a, h, i). The blue, green and red phosphors were uniformly dispersed in silicone and then deposited on the UV LED chip from top to down. Fig. 5j displays the schematic diagram of a 3D layered white LED with a combination of blue film outer layer, green film middle layer, and red film inner layer on top of a UV-LED chip of 370 nm. The PL spectrum of the white LED operated at 50 mA is shown in Fig. 5k. The 3D layered LED chip can emit bright white light as shown in the insert of Fig. 5k with correlated color temperature (CCT) of 10,436 K, CIE color coordinates of (0.261, 0.317) and color-rendering index (CRI) of 72.1, and achieve a luminous efficiency of 10.47 lm W⁻¹, which exhibits typical characteristics of cold white LEDs. The glowing characters “CHINA” in Fig. 5l show that the as-fabricated Ce³⁺-doped AIPNCs can be applied for the mass production of white LEDs, demonstrating the potential applications in lighting and display.

CONCLUSIONS

In conclusion, a microfluidic reactor is designed to produce the Ce³⁺-doped AIPNC based on the continuous-flow reaction. The mechanism of the flow synthesis of the Ce³⁺-doped AIPNCs is the efficient physical mixing of the precursor ions in the confined micro-channel, the reaction nucleation of crystal seeds in the poor solvent and

Figure 5 Fabrication and optical performance of the green and white LED devices based on the AIPNCs. (a) The fabrication procedure of the green LED devices, the right LED is filled with the 1% Ce^{3+} -doped CsPbBr_3 AIPNCs. (b–g) The PL spectra of the green LED devices (excitation at 370 nm), and the Q_2/Q_1 ratios when producing the AIPNCs are 0%, 10%, 20%, 30%, 40%, and 50%, respectively. (h) The PL spectrum of the red phosphor in the white LED devices (excitation at 370 nm). (i) The PL spectrum of the blue phosphor in the white LED devices (excitation at 370 nm). (j) The device structure of white LEDs, the blue, green and red phosphors from top to bottom are $\text{BaMgAl}_{10}\text{O}_{17}:\text{Eu}^{2+}$, 1% Ce^{3+} -doped CsPbBr_3 and $\text{K}_2\text{SiF}_6:\text{Mn}^{4+}$, respectively. (k) The PL spectra of the white LED devices (excitation at 370 nm). (l) The word CHINA lightened up by the white LED devices.

the crystal growth of the doped AIPNCs along the flow direction. The doping concentration of Ce^{3+} can be facilely controlled by changing the flow parameters in the microfluidic reactor, and the highest value reaches 1%. The Ce^{3+} doping can significantly improve the PL efficiency of the AIPNCs. The quantum yield can be increased from 67.5% to 86.7%. The PL stability of the AIPNCs at ambient condition and against high temperature also can be improved by Ce^{3+} doping. The Ce^{3+} -doped CsPbBr_3 AIPNCs can be used to manufacture the green LEDs with a high color purity of 93.3% and the white LEDs with CCT of 10,436 K, CIE color coordinates of (0.261, 0.317) and CRI of 72.1. Together, the continuous and controllable synthesis of AIPNCs by microfluidic reactor provides new avenues for the application of high-performance optoelectronic materials and devices.

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

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微流控反应器中连续流动合成掺杂型全无机钙钛矿纳米晶及其在发光二极管中的应用

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摘要 全无机钙钛矿纳米晶具有发射光谱窄、发光量子效率高和发光波长可调等优点, 在光电子材料和器件领域具有广阔的应用前景。离子掺杂可以调节其原始的晶体结构和发光性能, 或者赋予其额外的功能。本文设计了一种基于连续流动反应制备Ce³⁺掺杂的全无机钙钛矿纳米晶的微流控反应器。流动合成Ce³⁺掺杂全无机钙钛矿纳米晶的机理是前驱体离子在限域微通道中的有效物理混合、晶种在不良溶剂中的反应成核以及全无机钙钛矿纳米晶沿着流动方向的晶体生长。利用光纤式吸收光谱仪和光纤式荧光光谱仪可以对合成过程进行在线监测。通过改变微流控反应器的流动参数, 可以便捷地控制Ce³⁺的掺杂浓度, 最高可达1%。Ce³⁺掺杂可以提高全无机钙钛矿纳米晶的光致发光效率和稳定性。Ce³⁺掺杂的CsPbBr₃全无机钙钛矿纳米晶可用于制造色纯度高达93.3%的绿色发光二极管, 以及色温为10,436 K、CIE色坐标为(0.261, 0.317)、显色指数(CRI)为72.1的白色发光二极管。微流控反应器连续可控合成全无机钙钛矿纳米晶为高性能光电材料和器件的应用开辟了新途径。