CsPbBr$_3$@CsPbBr$_{3-x}$Cl$_x$ Perovskite Core–Shell Heterojunction Nanowires via a Postsynthetic Method with HCl Gas

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ABSTRACT: CsPbX$_3$ (X = Cl, Br, I) perovskite nanocrystals (NCs) are promising materials due to their excellent optoelectronic properties. This work shows a successful anion exchange reaction in CsPbBr$_3$ nanowire (NW) systems with HCl gas, resulting in a blue-green light-emitting CsPbBr$_3$@CsPbBr$_{3-x}$Cl$_x$ core–shell heterojunction. By adjusting the reaction time and the reaction temperature, the structure and light emission of the NWs can be adjusted. The core–shell heterojunction NCs are stably luminescent in 24 h. The rational mechanism of anion exchange in perovskite NCs is also investigated. The work highlights the feasibility of NWs heterogeneous prepared under the HCl gas atmosphere, which provides a new strategy for studying the two- and multicolor luminescent perovskite NCs.

1. INTRODUCTION

All-inorganic halide perovskite materials have attracted extensive attention due to their unique optical properties in recent years.\textsuperscript{1–4} CsPbX$_3$ nanocrystals have become excellent photon and photoelectric materials due to their large absorption cross section, effective and adjustable photoluminescence, ultrahigh quantum yield of photoluminescence, narrow band emission, and low trap density of state.\textsuperscript{5–8} Their important applications in optoelectronic devices such as laser\textsuperscript{9,10} and LED\textsuperscript{5,11,12} were reported, and most of these reports are based on the realization of low threshold and high PLQY monochromatic CsPbX$_3$ nanocrystals, including nanoparticles, nanoflakes, nanowires, etc.\textsuperscript{2,13–16} The emission of CsPbX$_3$ nanocrystals can be adjusted in the whole visible light range by adjusting the halide composition and morphology.\textsuperscript{17–20} The single halogenated perovskite nanocrystalline structure has obvious advantages in the application of color display, lighting, and optical communication. However, the mixture of different halogenated perovskite NCs is a problem due to their anion exchange process, which also leads to the luminescent stability issue.

Recently, bichromatic or polychromatic NCs, such as doping Mn\textsuperscript{20–23} building heterojunction\textsuperscript{24} were prepared and investigated. However, these methods involve multistep transfer or manufacturing, which is limited by the operation of instruments and cannot be put into practical application. The all-inorganic halide perovskite forms a highly dynamic crystal lattice due to its ionic bonding properties, which easily leads to fast ion exchange at solid–gas, solid–liquid, and liquid–liquid interface.\textsuperscript{17,24–27} Therefore, whether the built perovskite nanocrystal heterojunction is stable is still a problem needing to be solved. It has been reported that anion exchange is a dynamic process that occurs in solution between NCs.\textsuperscript{26} Therefore, by mixing solutions containing different halide perovskite NCs, anion exchange that occurs rapidly makes perovskite NCs homogenized.\textsuperscript{26} This argument is even more pronounced in one-dimensional perovskite nanocrystalline materials, one of which is represented by Peidong Yang’s group. In their report, nanowire heterojunctions can stably exist and have clear interfaces. However, in the report of Jin’s group, due to the extremely high diffusivity of the halide ions, the anions easily diffuse with each other on the perovskite heterojunction.\textsuperscript{28}

In this work, CsPbBr$_3$ NWs with a uniform scale and bright luminescence were synthesized. The heterojunction nanowires with a core–shell structure were prepared by a postsynthetic method with HCl gas on the basis of CsPbBr$_3$ NWs. The core–shell heterojunction is quite stable, and the luminous efficiency has no obvious decrease with time. In our previous work, various shapes of perovskite nanocrystals were prepared and their stability has been improved. Two-color emission of quantum dots was obtained by exchanging Mn\textsuperscript{21} with Pb\textsuperscript{24,20} To improve the luminescence stability of nanocrystals, CsPbBr$_3$ quantum dots with stable blue and green light emission were obtained with an improved single-step solid...
solution phase method. Nanocrystals with a Cs$_4$PbBr$_6$ and CsPbBr$_3$ structure were synthesized, which prevented the anion exchange process. The anion exchange process can be controlled by the reaction parameters, including the ratio of the reactant, reaction temperature, and so on. In these stable CsPbX$_3$ core−shell heterojunction NWs, it is proven that, except for the exchange time and temperature, the raw content of chlorine source HCl is important too for the stable heterojunction structure and light emission of the CsPbX$_3$ NWs. The preparation method of the CsPbX$_3$ nanowire heterostructure is simple and reliable, which is of importance to uncover the ion exchange mechanism and the ion dynamic processes in perovskite materials.

2. RESULTS AND DISCUSSION

First, the monodispersed CsPbBr$_3$ NWs were prepared. The photoluminescence (PL) and absorption (ABS) spectra of the CsPbBr$_3$ nanowires are measured, as shown in Figure 1a. The absorption spectrum has an obvious exciton absorption band edge at 519 nm (2.39 eV). Correspondingly, a sharp PL emission was detected at a peak of 525 nm (2.36 eV) with a narrow full width at the half-maximum (FWHM) of 24 nm. The PL peak of CsPbBr$_3$ nanowires is basically the same as the PL spectrum of CsPbBr$_3$ quantum dots reported in the literature. To analyze the phase structure, X-ray diffraction (XRD) was characterized, as shown in Figure 1b, and coincided with the standard XRD patterns of monoclinic CsPbBr$_3$ (PDF-18-0366). The strong diffraction peak (30.4°) that was detected corresponds to the facet (002) compared with the standard XRD pattern. The strong diffraction peak shows that the growth direction of nanowires is facet (002). To further analyze the morphology, transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) were characterized, as shown in Figure 1c,d, respectively. The morphology of the NWs is uniform and monodispersed with diameters of approximately 200 nm, as shown in Figure 1c. The HRTEM image shown in Figure 1d reveals that the NWs have a clear lattice fringe with an interplanar spacing of 0.31 nm, which agrees with the facet (002) of monoclinic CsPbBr$_3$.

When the CsPbBr$_3$ nanowires were put in the environment of Cl$^-$ ions, an anion exchange reaction occurs rapidly from the surface to all the nanowire materials, which leads to the formation of the CsPbBr$_3$−Cl$_x$ homogeneous alloy, not heterojunction. However, CsPbX$_3$ core−shell heterojunction NWs can be obtained after a 30 s anion exchange of CsPbBr$_3$ nanowires in the HCl atmosphere, as shown in Figure 2a. The PL spectrum of the heterojunction nanowire under an excitation of 365 nm is shown in Figure 2b. It can be seen that there are two separate emission peaks. The core CsPbBr$_3$ barely changes after the anion exchange process. The emission peak at approximately 452 nm (2.74 eV) appears...
after the anion exchange process, which is consistent with the position of the emission peak of CsPbBr$_{3-x}$Cl$_x$ nanocrystals. This shows that Cl$^-$ in the HCl molecule enters the nanowires through anion exchange with Br$^-$ ions in the HCl vapor atmosphere. To determine the distribution of Cl and Br in nanowires, the HRTEM was characterized, as shown in Figure

Figure 2. (a) Anion exchange schematic. (b) PL spectra. (c) HRTEM image and (d, e) FFT image of panel (c). (f) EDS pattern. (g) XRD pattern. (h) PL image (acquired at an excitation wavelength of 405 nm) of CsPbX$_3$ core–shell heterojunction NWs.
From Figure 2c, it can be seen that the surface and the interior of the nanowire correspond to two different crystal structures, respectively. Figure 2d,e presents the HRTEM images of CsPbX$_3$ NWs. They were selected for fast Fourier transform (FFT) measurements, and a series of twin points appeared. The diffraction images obtained by FFT measurements of the internal lattice and surface lattice of the nanowire are shown in Figure 2d,e, respectively. Each pair of twin points in the figure corresponds to a set of crystal faces, and the distance between the crystal faces can be calculated by the distance between the two points. If the distance between the two points is defined as "$I$", then the crystal plane spacing is defined as "$d$". The value of $d$ can be calculated by $I$ according to the function $d = 2/I$. The distances between each pair of twin points in Figure 2d are 2.45/\text{nm}, 3.69/\text{nm}, 3.26/\text{nm}, and 4.39/\text{nm}, respectively, corresponding to the (010), (−112), (002), and (102) crystal faces of the monoclinic CsPbBr$_3$ crystal. In Figure 2e, the distances between each pair of twin
points are 2.48/\text{nm}, 5.12/\text{nm}, 3.63/\text{nm}, 3.39/\text{nm}, and 4.42/\text{nm}, corresponding to the (101), (202), (200), (002), and (112) crystal faces of CsPbCl$_3$ crystals. Moreover, the (002) crystal plane of the CsPbBr$_3$ crystal with good crystallinity and the (101) crystal plane of the CsPbCl$_3$ crystal are marked in Figure 2g, which are in accordance with the XRD peaks observed at 30.3° for monoclinic CsPbBr$_3$ and 22.4° for tetragonal CsPbCl$_3$, as shown in Figure 2f. All the TEM images show perfect crystallization of all the samples. It is worth noting that the blue emission peak at 452 nm in the previous PL spectrum image corresponds to the emission peak of the CsPbBr$_{3-x}$Cl$_x$ (Cl-rich). The crystalline phase of CsPbCl$_3$ obtained in the HRTEM image and XRD pattern is due to the existence of a Cl-rich CsPbBr$_{3-x}$Cl$_x$ alloy, not pure CsPbCl$_3$. This indicates that the introduced Cl element exists not only on the surface of the NWs after exchange with Br$^-$ and forms a core–shell heterojunction with the Br-rich region inside the NWs. The elemental proportions of the CsPbX$_3$ core–shell heterojunction NWs were studied by EDS and plotted in Figure 2f. The elemental ratios of Cs, Pb, Br, and Cl are approximately 1:1:3:1, which is consistent with the CsPbX$_3$ (1:1:3) element ratio. The XRD spectra of CsPbX$_3$ core–shell heterojunction NWs are composed of peaks of both CsPbBr$_3$ and CsPbCl$_3$, which indicate the successful synthesis of CsPbX$_3$ core–shell heterojunction NWs. To further determine the NW light-emitting structure, the super-resolution confocal microscopic observation was measured, as shown in Figure 2h. The PL images show green emission in the core and blue emission on the surface along the lengths of the NWs. This is consistent with our previous analysis.

To investigate the anion exchange mechanism in the HCl gas atmosphere, the PL spectra of the nanowires placed in the HCl gas atmosphere for different times are shown in Figure 3a. The two luminescent images move to the middle and decrease in time to prevent the continued exchange of anions, a nanowire heterojunction with a core–shell structure is formed. The anion exchange will continue with HCl gas, resulting in the formation of alloy nanowires. To verify the stability of the CsPbX$_3$ core–shell heterojunction NW structure, the spectra of nanowires were measured in 24 h, as shown in Figure 3b,d. The CsPbX$_3$ core–shell heterojunction NWs show stable spectra, and more importantly, the emission peak does not shift in 24 h. This is significantly different from the anion exchange in solutions. Comparing Figure 3b,c, it can be seen that the heterojunction obtained with a reaction time of 30 s is more stable than the heterojunction obtained with a reaction time of 1 min. This may be due to the instability of the lattice structure due to the increase in the content of the Cl element. The CsPbBr$_3$ structure is more stable than the CsPbBr$_{3-x}$Cl$_x$ structure. To confirm this consideration, the decay curves of the exciton emission with different reaction times excited by a 339 nm pulse laser were measured, as shown in Figure 3e. With the increasing reaction time, the average lifetime decreases step by step due to the shorter lifetime of CsPbCl$_3$ than that of CsPbBr$_{3-x}$Cl$_x$.

In the process of ion exchange, the main factors affecting ion exchange are the catalyst, the ratio of the reactant, and temperature. The PL spectra were obtained by anion exchange at different anion temperatures, as shown in Figure 4a. When the reaction temperature is 20 °C, the emission spectrum has barely change. Two separate emission peaks appear when the temperature increases to 30 °C. When the reaction temperature increases to 40 or 50 °C, the emission peak at 450 nm disappears, while a wide emission appears at the band of the 520 nm emission peak. When the reaction time is 1 min, the same phenomenon also appears in the PL spectrum, as shown in Figure 4b. The phenomenon of double luminescence peaks appears only when the reaction temperature is 30 °C. The reason for this phenomenon is that we use HCl vapor to introduce the chlorine source instead of Cl$^-$ ions in solution, which results in the anion exchange reaction being slower and more controllable than that in solution. When the temperature reaches around 30 °C, the anion exchange starts with a layer of a Cl-rich structure formed on the surface of the perovskite NCs. As temperature increases, the exchange between Cl$^-$ and Br$^-$ in the nanowire becomes much easier and more rapid. The anion exchange occurs rapidly through all the perovskite nanowires. The Cl$^-$ is distributed not only on the surface of the nanowire but also inside the nanowires, which leads to CsPbBr$_{3-x}$Cl$_x$ alloy, not heterojunction.

Figure 4. Photoluminescence spectra of (a) CsPbBr$_3$ NW reaction at different temperatures for 30 s and (b) CsPbBr$_3$ NW reaction at different temperatures for 1 min.
3. CONCLUSIONS

To sum up, the method of introducing a chlorine source into CsPbBr3 NWs through HCl gas at a reaction temperature of 30 °C for anion exchange can directly obtain CsPbX3 core−shell heterojunction NWs. During anion exchange, anion exchange time and reaction temperature play key roles in the formation of CsPbX3 core−shell heterojunction NWs. When the chlorine source was introduced, the bromine atoms in the outer layer of the CsPbBr3 NWs were replaced by chlorine atom. After the chloride source was cut off, the heterojunction structure and light emission of the CsPbX3 NWs tended to be stable. The introduction of anions through HCl gas and the anion exchange in perovskite nanowires are feasible, which is of great significance for the application of perovskite heterojunctions and polychromatic nanocrystals.

4. EXPERIMENTAL SECTION

4.1. Materials. Cesium carbonate (Cs2CO3; 99.9%), lead(II) bromide (PbBr2; 99.999%), oleic acid (OA; 90%), oleylamine (OLM; 70%), and octadecene (ODE; 90%) were purchased from Sigma-Aldrich. Hexane (99%) and HCl solution (36–38%) were obtained from Innochem. All chemicals were used without further purification.

4.2. Preparation of Cs-Oleate. The preparation of Cs-oleate is based on previous reports.14,33 ODE (15 mL), OA (1.2 mL), and Cs2CO3 (0.4 g) were added to a three-neck flask and dried for 1 h at 120 °C under flowing high-purity argon gas. The mixture was then heated to 150 °C for 30 min until Cs2CO3 was dissolved, and the mixture became clear.

4.3. Synthesis of CsPbBr3 NWs with Green Light Emission. ODE (6 mL) and PbBr2 (0.069 g) were loaded into a three-neck flask and dried for 1 h at 130 °C flowing high-purity argon gas. Dried OA and OLM (0.5 mL each of OLM and OA) were injected at 130 °C. After PbBr2 was completely dissolved, the temperature was increased to 160 °C and 0.6 mL of the Cs-oleate solution prepared above was injected rapidly. After heating the mixed solution to 220 °C, the reaction mixture was cooled by using an ice-water bath.

4.4. Synthesis of Blue-Green Core−Shell Nanowire Heterojunction. The nanowires obtained in step 2 were washed with ethyl acetate and dispersed in n-hexane. Take 1 mL of nanowire n-hexane solution, let it on a quartz plate, place the quartz plate in the atmosphere of HCl for 1 min, and then take it out. Among them, the HCl atmosphere mentioned is obtained by volatilization of concentrated hydrochloric acid. At this time, blue-green nanowires with a core−shell structure were obtained on the quartz plate.

4.5. Characterization. X-ray powder diffraction (XRD) was performed using a D/ max 2200 V X-ray powder diffractometer with Cu Kα radiation (wavelength = 1.540 A) to characterize the perovskite nanocrystal structure. A laser confocal microscope image was performed by Leica SP8 STED 3X in HC PL APO CS2 100×/1.40 OIL. The transmission electron microscopy (TEM) images were obtained using a JEOL JEM-1400 microscope equipped with a thermionic gun operated at an acceleration voltage of 100 kV. The high-resolution transmission electron microscopy (HRTEM) images were recorded using a JEM-2100F microscope operated at 200 kV. The steady-state PL emission spectra were recorded on a Hitachi F4500 fluorescence spectrophotometer with an Xe lamp coupled to a monochromator. The PL image was performed using HC PL APO CS2 100×/1.40 OIL by a super-resolution laser confocal microscope. All spectral measurements were performed at room temperature.

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Notes
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