Synthesis of Mn-doped CsPbCl$_x$Br$_{3-x}$ perovskite nanocrystals using ultrasonic irradiation-promoted with decrease of reaction order

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Abstract

The incorporation of impurity cation as a way of introducing various novel functionalities provides an additional level of control over the electronic and optical properties of perovskite nanocrystals (NCs). However, the conventional post-synthetic cation exchange approaches suffer from large time and energy consumption. In this work, we developed a novel one-pot method to synthesize Mn-doped CsPbCl$_x$Br$_{3-x}$ NCs by merit of sonochemical technique, achieving dramatically rapid reduce of time and energy consumption. The localized hot spots with high transient temperature, pressure, and cooling rate, as well as an excellent stirring action of ultrasonic preparation facilitate the diffusion of Mn$^{2+}$ in perovskite lattice. Besides, further reaction kinetics investigation reveals an apparent decrease of reaction order from original method (2.4) to our ultrasound-assisted method (1.0).

Introduction

Lead halide perovskite materials have attracted more and more attention for their good optical properties and potential applications [1–4]. All-inorganic cesium lead halide (CsPbX$_3$) NCs with superb photo-physical properties and facile chemical tunability of the bandgap have shown great application potential in fields of high-efficiency solar cells, color-tunable light-emitting diodes (LEDs), laser and so on [5–10]. More papers make great efforts to control over the electronic and optical properties of CsPbX$_3$ NCs. Doping is a good way of introducing various novel functionalities [8, 11–18]. Charge-carrier dynamics of lead halide perovskite NCs and Mn-doped perovskite NCs have been investigated [19–22]. There are two methods to introduce impurity into CsPbX$_3$ NCs. The first one is added impurity and crude materials simultaneously. The second one is post-synthetic cation exchange method. Our group have reported the post-synthetic doping of Mn$^{2+}$ via a halide exchange-driven cation exchange process. Post-synthetic halide-exchange is a cushy part in preparation of perovskite NCs owing to their unique ionic property. Unlike to post-synthetic halide-exchange, post-synthetic cation exchange would not be nearly as easy as we anticipated because of the rigid octahedron structure of Pb cationic sub-lattice around by six halide anions ([PbX$_6$]$^{2-}$) [23]. The entire reaction requires extremely long time (40 h) for the previous post-synthetic doping of Mn$^{2+}$ via a halide exchange-driven cation exchange process, since the diffusion for large sized MnCl$_2$ molecules from NC surface to center is quite difficult. Enormous efforts have been devoted to optimizing this reaction process, such as higher reaction temperature (50°) which leads to accelerated reaction time (2 h). But it is still several orders of magnitude of time consumption more than that of post-synthetic halide-exchange procedure.

As mentioned above, preparing at room temperature has been demonstrated as an inefficiency means for post-synthetic cation exchange. For the high-temperature preparation, a large energy consumption would not be ignored. Sonochemical technique as a very promising methodology has been developed to be widely used for initiation or enhancement of catalytic reactions, in both homogeneous and heterogeneous cases [24]. When the ultrasonic wave propagates in the liquid, fierce collision occurs between liquid particles, generating localized hot
spots with high transient temperature (5000 K), pressure (1800 atm), and cooling rate (1010 K s⁻¹) [25]. Besides, the intense interaction between particles can also work as an excellent stirring action, inducing emulsification between two immiscible liquid, improving the dissolubility and dissolution rate of the reactant, thus accelerating the chemical reaction. Under this extreme condition, some reactions which are previously difficult to realize by other methods can proceed. By merit of sonochemical technique, we developed an ultrasonic irradiation-promoted method to synthesize Mn-doped CsPbClₓBr₃₋ₓ NCs with dramatically rapid reduce of time and energy consumption. In this way, the diffusion of MnCl₂ molecules in lattice is tremendously accelerated. And the dramatically change of reaction order is observed and studied. The as-prepared Mn-doped CsPbClₓBr₃₋ₓ NCs possess good emission properties, including tunable perovskite intrinsic emission (PLQY: 40%) from 512 nm to 430 nm as well as concentration-depended Mn-induced emission band (PLQY:16%) around 574 nm.

Results and discussion

As mentioned in Experimental Section, Mn-doped CsPbClₓBr₃₋ₓ NCs were prepared through two steps. The first one is synthesis of CsPbBr₃ NCs. The following one is doped Mn into CsPbBr₃ NCs by ultrasonic irradiation-promoted with post-synthetic ion exchange reaction. Typically, Cs-precursor and Pb-precursor are added dropwise into a 50 ml beaker containing oleic acid, n-octylamine, and n-hexane in sequence to form CsPbBr₃ NCs. After purification and re-dispersion in the toluene, 1 M MnCl₂ DMF solution was added quickly with vigorous stirring. Then, the beaker is placed in ultrasonic environment for a few minutes. Finally, the products are centrifuged and washed with hexane.

The morphology and structure of as-prepared Mn-doped CsPbClₓBr₃₋ₓ NCs are shown in figure 1. From transmission electron microscopy (TEM) image, as-prepared NCs show a 2D anisotropic crystal growth with well-defined rectangular shapes as well as clear tetragonal phase structure. High resolution transmission electron microscopy (HRTEM) clearly shows legible crystal lattices with an inter-planar distance of 0.41 nm, assigning (101) facet of perovskite structure. Powder x-ray diffraction (XRD, figure 1(b)) further demonstrates that Mn-doped NCs possess highly crystalline structure of tetragonal bulk CsPbBr₃ (PDF #18-0364). It means the doping of Mn would not seriously change the crystalline structure of NCs. However, when MnCl₂ is doped into CsPbBr₃ NCs, part of Cl ion would replace Br ion and form Mn doped CsPbClₓBr₃₋ₓ NCs. For the lattice contraction, XRD of Mn doped CsPbClₓBr₃₋ₓ NCs has a little shift, compared with pure CsPbBr₃ NCs [26]. In figure 1(c), the appearance of the Mn emission beside the perovskite intrinsic emission together with the
decreased PL lifetime of perovskite NC intrinsic emission provide a solid proof for the successful doping of Mn in perovskite host. The decreased PL lifetime of Mn$^{2+}$ at 572 nm is about 0.67 ms in Mn-doped CsPbCl$_{3-x}$Br$_{x}$ NCs (figure 2(a)). The presence of Mn, Pb, Cs, Cl, Br in the doped NCs is further confirmed by Energy-dispersive x-ray spectroscopy (EDX) and showing atomic ratios at 1.7/15.25/18.79/49.59/15.25, which is also close to the typical stoichiometric ratio of all-inorganic perovskite (figure 1(d)).

Effect on time consumption
As shown in figure 3(a), without sonochemical treatment, post-synthetic ion exchange would maintain an extremely long reaction time, making it possible to observe mid-states as well as appearance of three emission peaks during exchange. The complete exchange from initial CsPbBr$_3$ NCs to final Mn doped CsPbCl$_{3-x}$Br$_x$ NCs requires at least 40 h as indicated by (i) the disappearance of CsPbBr$_3$ NC emission nearby 520 nm, (ii) the simultaneous appearance of Mn$^{2+}$ ligand-field transition emission from $^4T_1$ to $^6A_1$ centered at 572 nm, and (iii) the appearance of strong CsPbCl$_{3-x}$Br$_x$ NCs emission near 438 nm. Since halide exchange is quite fast, the long reaction time is caused not by ionic exchange but by the difficult diffusion of large sized MnCl$_2$ molecules into NC lattice as discussed below. When halide exchange occurs between MnCl$_2$ molecules and CsPbBr$_3$ NCs, the Mn atoms on MnCl$_2$ molecules have opportunity for replacing some of Pb in octahedron structure and resulting in Mn in ligand field of halide with strong Mn emission. Since the diffusion for large sized MnCl$_2$ molecules from NC surface to center is quite difficult, the reaction requires extremely long time (40 h).

By virtue of the generating localized acoustic energy, fasten molecular diffusion has been realized. Temporal evolution of PL spectra in figure 3(b) reveals that ultrasound has no obvious influence on the developed law of PL emission properties as mentioned above, yet drastically reduces the time consumption to $\sim$15 min. It indicates that the ion exchange process between CsPbBr$_3$ NCs and MnCl$_2$ molecules remains unchanged but radically accelerates. We ascribe this phenomenon to the rapid MnCl$_2$ molecular diffusion into the perovskite NCs with the collision of Mn-, Cs-, Pb-, and X- ions (Br- ions, Cl-ions) in one pot [24, 25]. According to the less reaction time, the optimized preparation economizes energy consumption in comparison with another method via higher reaction temperature (50°C) but at least 2 h used. Besides, temporal evolution of absorption spectra (figure 3(c)) of CsPbBr$_3$ NCs after adding MnCl$_2$ precursor are similar to that of pure CsPbBr$_3$ NCs, which shows that doping MnCl$_2$ precursor would not change the intrinsic band gap structure of perovskite. Moreover, doping MnCl$_2$ precursor would not change the stability of perovskite (figure 2(b)).

Effect on reaction order
Since ultrasonic treatment plays an important role in the promoted ion exchange, reaction kinetics was conducted on tracking the whole experimental procedure. And the change of reaction order between original and sonochemical reaction condition was dramatically observed.

In general, for an n order kinetics models, the following equation stands:

$$\frac{d\alpha}{d\tau} = k(1 - \alpha)^n$$

(1)

Where ‘$\alpha$’ is the conversion fraction, ‘n’ is the reaction order which is a constant independent of the temperature and conversion. ‘$d\alpha/d\tau$’ is the reaction rate, and ‘k’ is the apparent rate constant. When $n = 1$, the definite integral of differential expression of the reaction rate (equation (1)) can be represented by:
\[ \ln \left( \frac{1}{1 - \alpha} \right) = k\tau \]  

(2)

As for the condition of \( n \neq 1 \), the definite integral of differential expression of the reaction rate can be represented by:

\[ \frac{1}{(1 - \alpha)^{n-1}} - 1 = (n - 1)k\tau \]  

(3)

In order to obtain more experimental data relevant to the determination of the order of the ion exchange reaction, a few experiments were carried out at the identical temperature (20°, Nanjing) in which the initial concentrations of CsPbBr_3 NCs, and Mn-precursor were in strict conformity. The conversion (\( \alpha \)) data used to derive the reaction orders can be represented by the normalized intensity of Mn emission, since the fluorescence intensity is proportional to the concentration of fluorescent material in dilute solution.

Equations (2) and (3) was used to fit the experimental data of conversion (\( \alpha \)) versus reaction time (\( \tau \)). The fit for data obtained at ultrasonic environment or not was shown in figure 4. As a result, the kinetics model of original ion exchange without ultrasonic treatment shows a reaction order of 2.4, while the sonochemical treatment would change it to first-order reaction model.

**Conclusion**

In this work we developed an ultrasonic irradiation-promoted one-pot method to synthesize Mn-doped CsPbCl_{1-x}Br_3-x NCs. The ultrasound-assisted method can achieve dramatically rapid reduce of time and energy consumption by supplying localized hot spots and excellent stirring action. Reaction kinetics investigation
reveals an apparent decrease of reaction order from original method (2.4) to our ultrasound-assisted method (1.0). Using this method to prepare Mn-doped CsPbCl\textsubscript{x}Br\textsubscript{3-x} NCs is simple and time-saving, and is expected to be used in mass production.

Experimental section

Materials

PbBr\textsubscript{2} (lead (II) bromide 99%, Aladdin), MnCl\textsubscript{2}·4H\textsubscript{2}O (Mn (II) chloride 99%, Sinopharm Chemical Reagent Co., Ltd), CsOA (cesium acetate 99.9%, Aladdin), n-octylamine (≥99%, Aladdin), oleic acid (90%, Alfa Aesar), N,N-dimethylformamide (99.5%, Kelong), n-hexane (97%, Kelong), acetone (99.5%, Sinopharm Chemical Reagent Co., Ltd), toluene (C\textsubscript{7}H\textsubscript{8} AR, SCRC).

Synthesis of CsPbBr\textsubscript{3} NCs

The synthesis of CsPbBr\textsubscript{3} is following our previous work \cite{10}. 0.191 g of Cs(AC) was dissolved in 1 ml DMF forming the ‘aqueous phase’ Cs-precursor, and 0.367 g of PbBr\textsubscript{2} was dissolved in 1 ml DMF forming Pb-precursor, respectively. 6 ml oleic acid and 0.8 ml n-octylamine was mixed in 30 ml n-hexane under vigorous stirring forming the ‘oil phase’ solution. Then the Pb-precursor solution was added dropwise into the as-prepared ‘oil phase’ solution. Five minutes later, the ‘aqueous phase’ Cs-precursor solution was added into the above-mentioned solution. Along with the mixing, emulsion was formed and the color of solution turned from clear to slight white. The nanocrystals were precipitated with acetone and collected by centrifugation (6500 rpm, 15 min).

Ultrasonic irradiation-promoted post-synthetic ion exchange reaction

In a typical preparation, 1 M MnCl\textsubscript{2} DMF solution was dropped into the as-synthesized CsPbBr\textsubscript{3} toluene solution (10 ml) quickly with vigorous stirring and the mixed solution was subjected to a ultrasonic instrument at a power of 400 W for 15 min. After the reaction, the NCs were separated by centrifugation and dispersed in n-hexane.

Characterization

UV-vis absorption spectra (UV) were recorded with a Shimadzu 3600 UV-vis near-infrared spectrophotometer. Photoluminescence (PL) spectra were recorded with a Shimadzu RF-5301 PC spectrophotofluorometer. The excitation wavelength was set as 350 nm. The PL delay spectra probed 520 nm and 445 nm were recorded with a FluoroLog 3-TCSPEC spectrophotometer. The excitation wavelength was set as 350 nm. The PL quantum yield (QY) of NCs was calculated by comparison to that of rhodamine 6G, which possessed known QY of 95%. All optical measurements were performed at room temperature under ambient conditions. Transmission electron microscopy (TEM) was recorded by a JEM-2100 electron microscope with an acceleration voltage of 200 kV. Chemical composition of the Mn-doped CsPb(Cl/Br)\textsubscript{3} NCs were examined with a Quanta 200 FEI scanning electron microscope (SEM) equipped with an energy dispersive x-ray analysis (EDS) analyzer. X-ray powder diffraction (XRD) investigations were carried out using a thermos scientific escalab 250xi spectrometer with Al K\textalpha as the x-ray source. For XRD, all samples used are purifies powder.
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Conflict of interest

There is no conflict of interest.

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