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Highly Luminescent $CsPbX_3$ (X = Cl, Br, I) Nanocrystals Achieved by a Novel Rapid Anion Exchange at Room Temperature

Shaofan Fang[a], Guangshe Li[b], Yantong Lu[b] and Liping Li*[a]

Abstract: Cesium lead halide perovskite ($CsPbX_3$) nanocrystals (NCs) exhibit excellent photoelectric performance, which is directly governed by composition fine-tuning and preparation of materials with special phase structure and morphology. However, it is still facing challenges to achieve highly stable and luminescent $CsPbX_3$ NCs at room temperature. Herein, we report on a novel exchange reaction, in which metal halides MX_2 (M = Zn, Mg, Cu, Ca; X = Cl, Br, I) solids act as anion source to directly prepare $CsPbX_3$ NCs at room temperature without any pretreatment. Introducing small amount of oleic acid and oleylamine speed up the exchange reaction through different promotion mechanisms. Oleic acid coordinates on the NCs surface that increases the reaction activity, and oleylamine greatly enhances the dissolution of $ZnCl_2$. XRD and TEM tests demonstrate that cubic phase structure and morphology of the parent $CsPbX_3$ were well preserved. Moreover, the bandgap energies and photoluminescence (PL) spectra were readily tunable over the entire visible spectral region of 406−685 nm. Our findings would open up the possibilities of using metal halide solids as new anion sources to prepare high-quality $CsPbX_3$ NCs at room temperature.

Introduction

Lead halide perovskite colloidal NCs (typically 2-20 nm) are being studied intensively for their excellent optical properties such as high photoluminescence quantum yields and sharp emission line widths that can span the visible spectrum.[1] When using hybrid organic-inorganic lead halides $MAPbX_3$ (MA = CH_3NH_3, X = Cl, Br, I) as semiconducting absorber layers,[2] the certified power conversion efficiencies could approach 22% for highly efficient photovoltaic devices. Even so, the development of hybrid organic−inorganic[3] or fully inorganic[4] perovskite NCs is still hampered, since there are many un-resolved problems associated with perovskite nanocrystal syntheses. For example, Kovalenko and his colleagues[5] firstly reported on a high degree of compositional bandgap engineering for cesium lead halide perovskite NCs $CsPbX_3$ (X = Cl, Br, I) through an arrested precipitation of Cs-oleate and Pb(II)-halide precursors in octadecene and uncovered the formation mechanism by means of a droplet-based microfluidic platform.[6] Re-precipitation methods were widely used to synthesize $CsPbX_3$ NCs with different morphologies.[7] Ion exchange reaction is established recently to provide a route for compositional fine-tuning or otherwise inaccessible materials and morphologies, especially for cesium lead halide perovskites ($CsPbX_3$, X = Cl, Br, I).[8]

Among all ionic exchange reactions, halide exchange could be an advantageous post-synthetic route that may modify $CsPbX_3$ compositions. For maintaining the cubic structure and luminescent emission of the final products, as reported by most of the literature, anion exchange reactions for $CsPbX_3$ have to be performed using oleylamine-X, PbX_2 (X = Cl, Br and I), and so on, as anion sources. Nevertheless, this kind of routes has two obvious shortages: (i) complicated pretreatment is required, and (ii) anion exchange reaction is conducted using a Schlenk line.[8b] For example, oleylamine-X could be synthesized with oleylamine and HX overnight under a flow of nitrogen gas, and the products have to be evaporated in vacuum. The anion source PbX_2 has to be dissolved in 1-octadecene through a heat treatment. These complicated treatment processes prevent anion exchange from shining in the wide syntheses of $CsPbX_3$ NCs, but also easily introduce non-luminescent impurity. Thus, there is an urgent need to find a new room temperature route to prepare $CsPbX_3$ NCs more simply and practically. This could greatly advance the widespread applications of halide perovskite NCs.

Motivated by this, we envision a solid anion source to replace the existed liquid anion sources, and expect to simplify greatly the reaction process and speed up the reaction rate. This new method could also overcome the shortcomings of adopting anion source for current ion exchange reactions in preparing $CsPbX_3$ NCs. Certainly, the more common solid anion sources for exchange reactions of $CsPbX_3$ NCs can be inorganic salts, i.e., metal halides. Nevertheless, these salts are hardly soluble in toluene or octadecene, which is very detrimental to ion exchange reaction. It should be emphasized that, the exchange reaction can be accelerated if certain reagents were found to achieve further dissolution of the solid anion source, or to reduce the reaction potential barrier. By the promotion of these reagents, the anion exchange could take place at room temperature, and we could obtain a series of perfect cubic structure $CsPbX_3$ NCs with PL covering the full entire visible spectrum.

Herein, we report on a novel route using solid metal halides (MX_2, M = Zn, Mg, Cu, Ca, etc.) as solid halide sources to exchange anion with $CsPbX_3$ without need of any pretreatment like heating in vacuum and dissolving in octadecene. Although metal halides, $ZnCl_2$, $CaCl_2$, $MgCl_2$, and $CuCl_2$, can provoke anion exchange reaction with $CsPbBr_3$ NCs, as indicated in Figure S1, we took zinc halide (ZnX_2, X = Cl, Br and I) as a specific example to explain the anion exchange reactions with

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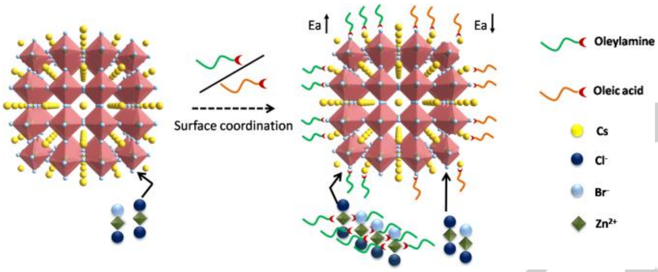
$CsPbX_3$ NCs. By adding oleic acid and oleylamine, we realized a fast anion-exchange at room temperature in tens of seconds. No impurity appeared in all compositions, and the phase structure and morphology inherited its parent NCs. The bandgap energies and PL spectra were readily tunable over the entire visible spectral region of 406−685 nm. Differing from the mostly reported anion sources, the metal halides we initiated are more efficient and convenient, since metal halides in solid form could be added directly in solutions. According to the kinetics analysis and the spectral results, oleic acid and oleylamine showed different promotion mechanisms, i.e. oleic acid reduces the reaction activation energy through surface coordination on $CsPbBr_3$ NCs, while oleylamine greatly promotes the dissolution of $ZnCl_2$. These observations prove that the methodology reported here is valid to achieve the desired $CsPbBr_3$ NCs, but also generates a model system for synthesizing other function materials by cation/anion exchanges.

Results and Discussion



Scheme 1. Diagram of anion exchange reaction for $CsPbBr_3$ using $ZnCl_2$ as solid anion source. This exchange reaction was accelerated by adding oleic acid and oleylamine despite of their different coordination roles to $CsPbBr_3$ NCs and $ZnCl_2$.

A schematic diagram in Scheme 1 illustrates the designed exchange process. We took $ZnCl_2$, a typical metal halide, as example to explain the exchange reaction. In this exchange system, if NCs and solid $ZnCl_2$ are simultaneously added in toluene solution without any additional reagents, the anion exchange reaction is very slow. While, when oleic acid and oleylamine were injected in the exchange system, the anion exchange reaction was accelerated significantly. This positive role might be closely related to two different effects of promoting dissolution and reducing activation energy. Oleic acid reduced the activation energy of exchange reaction, while increasing the exchange rate. Comparatively, adding oleylamine greatly enhanced the solubility of $ZnCl_2$ in toluene solution, which gives an exchange rate higher than that observed from adding oleic acid.

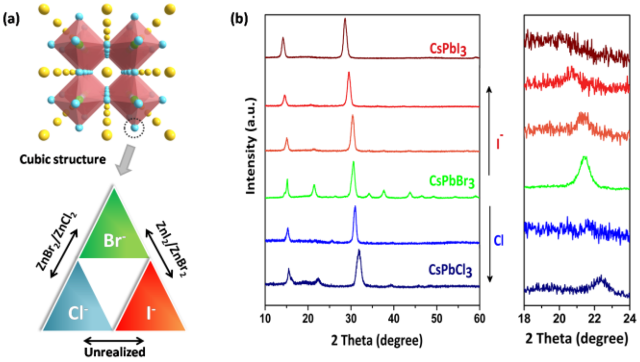


Figure 1. (a) Schematics that illustrate an anion exchange for cubic perovskite $CsPbX_3$ using a series of ZnX_2 (X = Cl, Br, I) for each reaction. A three-dimensional network is formed by corner-sharing PbX_6 octahedra with Cs^+ (yellow spheres) that occupies the interstitial voids. (b) Powder X-ray diffraction (XRD) patterns of the parent $CsPbBr_3$ NCs and anion-exchanged samples (using $ZnCl_2$ and ZnI_2 as halide sources), showing the retention of parent cubic perovskite structure. The right part is the magnified XRD plot in a narrow diffraction angle from 18 to 24°.

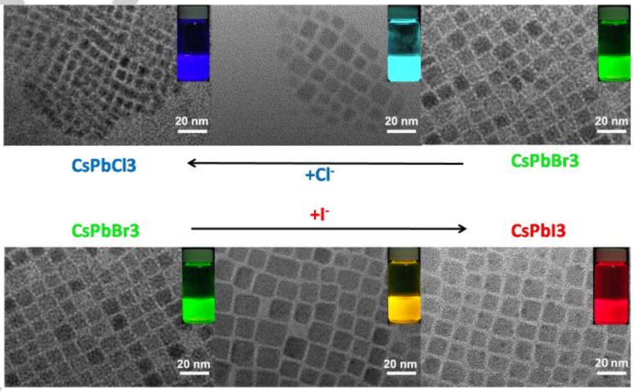


Figure 2. TEM images of 10 ~ 20 nm $CsPbX_3$ NCs, showing the morphology evolution with anion exchange process.

Through the exchange process illustrated in Scheme 1, the anion-exchange can be easily performed from Cl-to-Br, Br-to-Cl, Br-to-I, and I-to-Br to form homogeneous solid solutions. The feasibility that ZnX_2 reacted with $CsPbX_3$ is shown in Figure 1a. No mixed-halide solid solutions were obtained in $CsPbCl_3$ + ZnI_2 or $CsPbI_3$ + $ZnCl_2$ systems because of the large difference in ionic radii between Cl^- and I^- that could cause an instability of Cl/I solid solutions. From Figure 1b, one can see that the anion-exchanges for Br-to-Cl and Br-to-I just caused diffraction peak shift, and no impurity peaks from $ZnCl_2$ or ZnI_2 were detected. In order to observe the weak diffraction peaks, we magnified the XRD patterns from two theta of 18 to 24°, as shown in Figure 1b. The diffraction peak could be distinguished clearly, and shifts towards lower diffraction angle from I-to-Br and Br-to-Cl. The weakening of some diffraction peaks could be related to the film-like samples prepared for XRD test. In the process of characterization, XRD test samples were prepared by dropping colloid solution onto silicon chips that were dried at room temperature. Moreover, XRD patterns did not show any splitting for the diffractions at two theta ~15° and ~32°, which is characteristic of an orthorhombic phase.[9] These observations confirm that the anion-exchange manipulations of halide ions from Br-to-Cl and Br-to-I using ZnX_2 as exchanger do not affect the cationic sublattice, and that the cubic perovskite crystal structure (Figure 1a) was maintained well even though the exchange reactions were performed at a relatively low temperature. No splitting for XRD diffraction peaks and PL emission peaks (Figure 3) also prove that the anion-exchange reaction can be easily performed in the cases of Br-to-Cl and Br-to-I to form homogeneous solid solutions. Through regulating the reaction time, we could obtain a definite intermediate of $CsPbBr_xCl_{3-x}$ or $CsPbBr_xI_{3-x}$ with fixed composition. The variation of lattice parameter for solid solution should follow Vegard's law. Therefore, according to the lattice parameters for the parent $CsPbBr_3$ (a = 5.84 Å), exchanged intermediates (a = 5.76 Å in Br-to-Cl and a = 6.04 Å in Br-to-I) and final products of $CsPbCl_3$ (a = 5.62 Å) and $CsPbI_3$ (a = 6.22 Å), the intermediate compositions are determined to be $CsPbBr_{1.9}Cl_{1.1}$ in the Br-to-Cl reaction and $CsPbBr_{1.4}I_{1.6}$ in the Br-to-I reaction when reaction time was set at about 1 min. The size and shape of the parent NCs were also preserved in the course of the anion-exchange (Figure 2). Both parent NCs and the resulted NCs for $CsPbBr_3$ were 10-20 nm in diameters. Around NCs, no other shapes of particles were observed, further proving that ZnX_2 did not have any negative effect on the morphology and phase structure. The direct synthesis of single or mixed-halide $CsPbX_3$ at room temperature usually yields either large and polydisperse crystallites in orthorhombic phases (nonluminescent phase) or simply no crystalline products at all. For example, cubic $CsPbI_3$ would transform to the orthorhombic phase immediately when the temperature decreased to room temperature or low.[10] That is to say, orthorhombic $CsPbI_3$ is easy to form at low temperature. Lifting the curse, we successfully synthesized the cubic $CsPbI_3$ NCs at room temperature through anion exchange reactions.

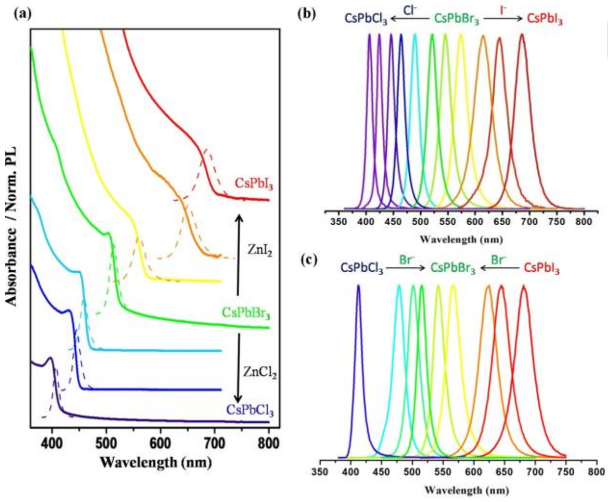


Figure 3. (a) Evolution of the optical absorption (solid lines) and PL (dashed lines) spectra of $CsPbBr_3$ NCs with the exchange reactions proceeding to form $CsPbCl_3$ and $CsPbI_3$, (b) PL of the exchanged NCs obtained from $CsPbBr_3$ using ZnX_2 (X = I, Cl) as exchangers, and (c) PL of $CsPbBr_3$ NCs obtained when starting from $CsPbCl_3$ and $CsPbI_3$ NCs using $ZnBr_2$ as exchanger.

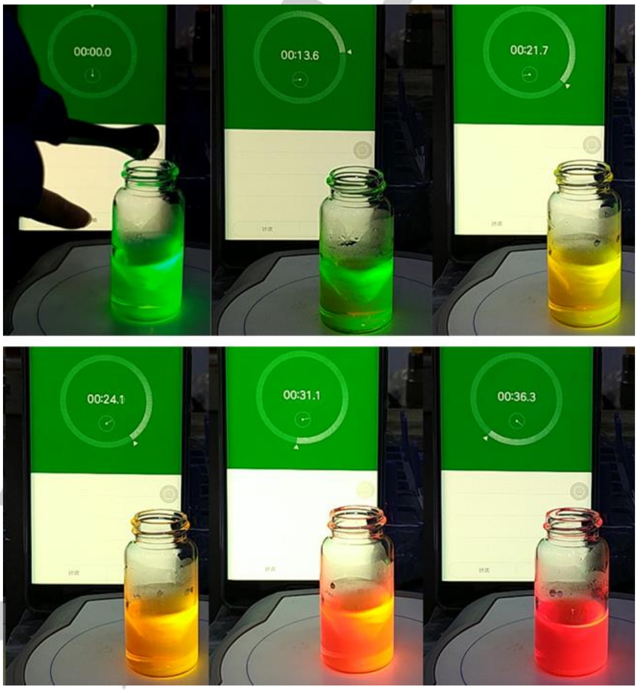


Figure 4. Image of time-dependent emission light under UV light irradiation (365 nm) during anion-exchange between ZnI_2 and $CsPbBr_3$, in which a drop of oleylamine was added.

Along with the cubic crystal structure, the obtained $CsPbX_3$ NCs exhibited bright PL. FWHM widths of PL emission are in the range from 12.8 nm for $CsPbCl_3$ to 35.2 nm for $CsPbI_3$ (as shown in Figure 3a), comparable to that directly synthesized $CsPbX_3$ NCs reported elsewhere.[11] PL spectra of such exchanged NCs also exhibit Stokes-shift with respect to their absorption spectra. For example, $CsPbBr_3$ NCs gave an emission peak at 515 nm, and this peak showed a continue red shift as the exchange reaction went on to reach a final value of 685 nm for $CsPbI_3$. When the halide source ZnI_2 was replaced with $ZnCl_2$, PL peak of $CsPbBr_3$ NCs shifted towards shorter wavelengths and eventually reached the shortest wavelength at about 406 nm for $CsPbCl_3$. The exchange reactions are feasible, and the emission peaks displayed Stokes-shifts with the progress of anion exchange whether for anion exchanges of Br-to-Cl and Br-to-I or Cl-to-Br and I-to-Br with the halide source ZnX_2 (X = Cl, Br, I) (Figures 3b, 3c). Moreover, the obtained anion-exchanged NCs in the present work cover all compositions of halide ratio and exhibit whole PL spectrum emission in the visible region, the same as the directly synthesized mixed-halide NCs previously reported.[5] Figure 4 presents the image of time-dependent emission light under the UV light irradiation (365 nm) during anion exchange reaction

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between ZnI_2 and $CsPbr_3$ in which a drop of oleylamine was added. Most of the anion-exchange occurs within tens of seconds. The gradual shift of the PL color is consistent with the continuous formation of homogeneous $CsPbBr_xI_{3-x}$ solid solutions, which is more clear from the video presented in SI1. Importantly, the integrated intensities of the light for each exchanged sample remain comparable to that of the parent sample, indicating high PL quantum yields throughout the process. Thus, this anion exchange using metal halide solid as halide source is a novel desired method for obtaining high luminescent cubic $CsPbX_3$ NCs.

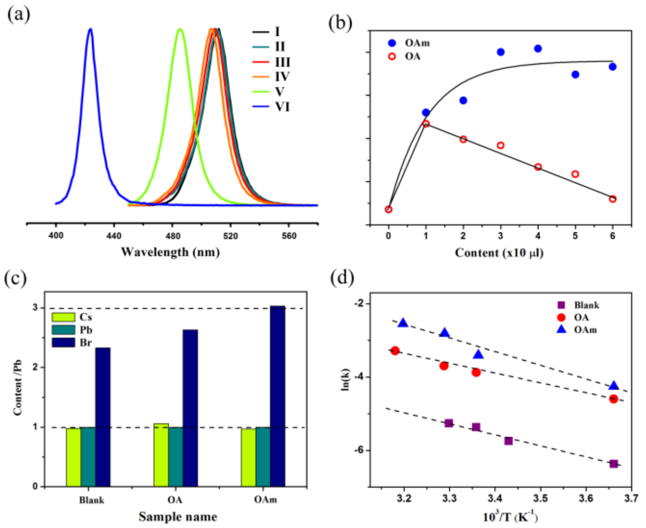

Figure 5. (a) PL spectra of $CsPbBr_3$ NCs, recorded after anion exchange reaction in different $ZnCl_2$ saturated toluene solutions or at different temperatures to compare the solubility of $ZnCl_2$ (I: $CsPbBr_3$ in toluene solution; II, III, IV: $CsPbBr_3$ in toluene solution adding $ZnCl_2$ saturated toluene solution at 273.15, 299.15 and 313.15 K, respectively; V, VI: $CsPbBr_3$ in toluene solution adding $ZnCl_2$ saturated toluene solution at 299.15 K mixed with oleic acid or oleylamine, respectively); (b) intensity variation of PL spectra for $CsPbBr_3$ when adding some contents of oleic acid or oleylamine in toluene solution, (c) normalized elemental ratio of Cs and Br based on XPS measurement by setting Pb content as 1; (d) Arrhenius plot fit for the temperature-dependent rate of exchange over the temperature range from 273.15 to 314.05 K for exchanges under different conditions (Blank: only in toluene solution; OA: adding 10 µl oleic acid in toluene solution before the reaction; OAm: adding 10 µl oleylamine in toluene solution before the reaction).

Oleic acid and oleylamine play important roles in promoting the exchange reaction when metal halides, $ZnCl_2$, $CaCl_2$, $MgCl_2$, and $CuCl_2$ were used as anion sources. In the following, we will explain their promotion effect. To better understand the mechanism of anion exchange accelerated by oleic acid and oleylamine, the solubility of $ZnCl_2$ in OA and OAm should be first considered. $ZnCl_2$ is insoluble in toluene solution and toluene mixed solution with oleic acid, but slightly soluble in the mixed solution of toluen and oleylamine (Figure S2). Therefore, we assume that oleic acid and oleylamine could coordinate with $ZnCl_2$ molecules that slightly dissolved in toluene, and then the presence of anion exchange reaction could promote the further dissolution of $ZnCl_2$ solid. To confirm this assumption, PL spectra for $CsPbBr_3$ NCs were used to compare the solubility of $ZnCl_2$ in toluene under different conditions as shown in Figure 5a. Three kinds of $ZnCl_2$ saturated toluene solutions were prepared: one is the solution that contains sole toluene molecules, and other two are mixed toluene solutions with added oleylamine and oleic acid. All saturated solutions were stirred for 60 min, although $ZnCl_2$ has reached saturation for 40 min stirring as shown in Figure S4. The same amount of saturated solution containing oleic acid or olelamine was added in $CsPbBr_3$ toluene solution to give a reaction between $CsPbBr_3$ NCs and dissolved $ZnCl_2$. When the reaction completely proceeded, the position of emission peak showed a blue shift. The distance of blue shift represents the solubility of $ZnCl_2$. The solubility of $ZnCl_2$ is very small in toluene because toluene is a very weak polar solvent. Thus, $ZnCl_2$ saturated toluene solution caused only 3 nm shift from 512 nm for $CsPbBr_3$ solution to 509 nm. $ZnCl_2$ saturated solution with adding oleic acid made the emission peak shifted towards 480 nm, while the solution with adding oleylamine gave a blue shift towards 423 nm. These observations prove positively that more oleic acid/oleylamin does promote $ZnCl_2$ to dissolve, and oleylamine has a stronger coordination ability to $ZnCl_2$ than oleic acid. That is to say, a higher concentration of $ZnCl_2$ could achieve in OAm relative to that in OA/Blank, which may explain the increased exchange reaction rate in OAm rationally. Moreover, the temperature-independent solubility of $ZnCl_2$ is also confirmed in toluene. In Figure 5a, there are three PL spectra for $CsPbBr_3$ NCs that are mixed with $ZnCl_2$ saturated toluene solution at 273.15, 299.15 and 313.15 K. The emission peaks are found to give a nearly neglect shift. In our following discussion, we will treat the solubility of $ZnCl_2$ ($c(ZnCl_2)$) as a fixed value even under variable temperature conditions, which is important as a precondition for the kinetic model.

Next, we examine the effect of oleic acid and oleylamine on the activity of exchange reaction through their coordination with $CsPbBr_3$ NCs. As shown in Figure 5b and by the experimental process provided in Supporting Information, oleylamine greatly improved the luminescent emission of NCs. With increasing the amount of oleylamine, the emission intensity rose continuously and finally reached a stable high level. Comparatively, the variation of emission intensity with the concentration of oleic acid is a little complicated. Adding small amount of oleic acid increases the luminous intensity gradually. Continuously adding oleic acid made the emission intensity decease to the original one. That is, more oleic acid could destroy the stability of NCs surface seriously to form many defects and create a lot of non-radiative transitions. Therefore, both of oleic acid and oleylamine could be indeed adsorbed onto the surface of $CsPbBr_3$ NCs and improve luminescence. Because of a stronger coordination stability of oleylamine relative to oleic acid, oleylamine molecules could stabilize the coordinated surface of $CsPbBr_3$ NCs continuously. To further confirm the surface structure, XPS was used to determine the average value of surface elemental ratios for $CsPbBr_3$ NCs after dispersion in three different solutions. From Figure 5c, one can see that the molar ratios of Cs to Pb for three conditions were 0.98:1, 1.06:1, and 0.97:1 in Blank, OA, and OAm, respectively, which are closer to unity, an idea ratio. Comparatively, $CsPbBr_3$ NCs dispersed in three different solutions give different Br/Pb ratios. For example, Br/Pb ratio in OAm was 3.02:1, nearly the same as the stoichiometric ratio of 3:1. Comparatively, the ratios decreased to 2.64:1 and 2.37:1 in OA and Blank, respectively. In combination with the discussion given above for Figure 5b, the nearly stoichiometric ratio of ions on the surface of $CsPbBr_3$ NCs in OAm is associated with the coordination of oleylamine on the surface of NCs. Namely, the absorbed oleylamine molecules protect NCs well from the creation of surface defects. Differently, oleic acid could also coordinate with $CsPbBr_3$ NCs, and destroyed the surface structure of NCs that may produce some defects. This means that oleic acid could increase surface defects, which is consistent with the unsteady emission intensity when adding oleic acid in Figure 5b. The surface defects of $CsPbBr_3$ NCs caused by oleic acid could increase the activity of anion exchange reaction. Similar promotion role of defects in chemical reactions has be reported for several other semiconductor materials.[12]

Then, we employ kinetic equations to further verify the effect of above two factors.[13] The completed derivation process can refer to Supporting information. Figure S5 shows the time progression of bandgap change for $CsPbBr_3$ that reacts with $ZnCl_2$ under three different conditions. The anion exchange reactions in three different solutions follow first-order law ($c = c_0e^{-kt}$). The temperature-dependent time progression of bandgap change for $CsPbBr_3$ was performed when mixed with $ZnCl_2$ in all the three different solutions, i.e. no addition (Blank), oleic acid addition (OA) and oleylamin addition (OAm) (Figure S6), respectively. Figure 5d shows their Arrhenius plots in three different solutions. Based on Equation (1), the data were fitted linearly, and their intercept and slope were determined, as listed in Table 1.

$$\ln k' = -\frac{Ea}{R}\frac{1}{T} + \ln(Ac_{(ZnCl_2)}) \qquad (1)$$

Table 1. Values of intercept and slope data obtained by linear data fit of the Arrhenius data in Figure 1e.

Solutions	Intercept (ln(A·c($ZnCl_2$)))	Slope(-Ea/1000R)
Blank	5.05	-3.123
OA	5.07	-2.648
OAm	9.28	-3.709

The presence of OA does not increase the concentration of $ZnCl_2$ in the reacting solution obviously, but reduce the activation energy of exchange reaction by destroying the surface structure of NCs through the adsorption to give an accelerated reaction. But the effect of c($ZnCl_2$) on the anion exchange is far more important than activation energy, as c($ZnCl_2$) in OAm is nearly 67 times larger than that in OA or blank. The increase of $ZnCl_2$ solubility in OAm solution is coincided well with the experimental result of Figure 5a.

Therefore, adding oleic acid could create more surface defects, which could lead to a decrease in activation energy and are thus beneficial for the anion exchange reaction. Olelamine molecules are also clear to be coordinated with $ZnCl_2$ to promote its dissolution and accelerate the anion exchange reaction.

Conclusions

Perovskite $CsPbX_3$ NCs were prepared by an efficient anion exchange approach at room temperature using ZnX_2 etc. metal halide solids as novel halide source. The obtained $CsPbX_3$ NCs have cubic structure and showed luminescence emission covered in the whole visible region. It is also found that adding small amount of oleylamine or oleic acid accelerated this anion exchange reaction. Further, adding oleic acid reduces the activation energy of exchange reaction, and increases the exchange rate, while introducing oleylamine enhances the solubility of halide source in toluene solution greatly, which gives a higher exchange rate than that adding oleic acid.

Experimental Section

Materials and chemicals： Chemicals including cesium carbonate (Cs_2CO_3, Aladdin, 99.9%), oleic acid (Aladdin, AR), 1-octadecene (ODE, Aladdin, 90%), ethanol, oleylamine (Aladdin, 80%-90%), lead chloride ($PbCl_2$, Aladdin, 99.99%), lead bromide ($PbBr_2$, Adamas, 99%), lead iodide (PbI_2, Aladdin, 98%), zinc chloride ($ZnCl_2$, AR), zinc bromide ($ZnBr_2$, Aladdin, 98%), zinc iodide (ZnI_2, Aladdin, 98%), n-trioctylphosphine (TOP), and toluene were used as received without further purification.

Synthesis of Cs-oleate: Cs_2CO_3 (0.814 g), oleic acid (2.5 ml), and ODE (40 ml) were added into a 100 ml 3-neck flask, dried at 120 °C for 1 h, and then heated in argon to 150 °C till all Cs_2CO_3 reacted with oleic acid. Cs-oleate precipitates steadily once out of ODE at room temperature, and thus has to be pre-heated to 100 °C before another injection.

Synthesis of $CsPbX_3$ NCs: In a typical synthesis, ODE (5 ml) and 0.188 mmol of PbX_2 (X = Cl, Br, I) were loaded into a 25 ml 3-neck flask and dried under vacuum at 120 °C for 1 h. Then, 0.5 ml oleic acid and 0.5 ml oleylamine were injected at 120 °C in Ar atmosphere. As PbX_2 salt was completely dissolved and formed a transparent solution, the temperature rose to 160 °C. At 160 °C, 0.4 ml of the previously synthesized Cs-oleate solution was swiftly injected. Then, the NCs solution was quickly cooled down to room temperature using an ice bath. For preparing $CsPbCl_3$, higher temperature of 150 °C and 1 ml trioctylphosphine (TOP) were required to solubilize $PbCl_2$. The crude NCs were first separated via a high speed centrifugation at 10,000 rpm for 5 min. After centrifugation, the supernatant was discarded, and the precipitates were re-dispersed in toluene. The toluene solution was centrifuged once more at 10,000 rpm for 10 min. The supernatant was discarded again, and the precipitates were re-dispersed in 5 ml toluene to form long-term colloidally stable solutions.

Anion-exchange reactions: Metal halide solids ($ZnCl_2$, $MgCl_2$, $CuCl_2$, $CaCl_2$, $ZnBr_2$, and ZnI_2) without any pretreatment were used as the anion sources. 1 ml $CsPbX_3$ toluene solution was diluted to 5 ml in a 20 ml reagent bottle. With continuous stirring, 10 mg metal halide solid were swiftly added into the solution. Under ultraviolet radiation, a fast color change was observed. We took 0.5 ml solution for PL measurement, which monitored the exchange reaction process essential for the discussion of exchange mechanism.

Characterization Methods

Absorbance: UV-VIS absorption spectra were collected using a SHIMADZU UV-2450 spectrometer.

Photoluminescence (PL) measurement: FLS920 Fluorescence Spectrometer was used to acquire PL spectra.

Powder X-ray diffraction (XRD) patterns were collected with a Rigaku miniflex600 with Cu Kα irradiation (λ = 1.5418 Å).

Transmission electron microscopy (TEM) images were recorded using a Tecnai G2 S-Twin F20 with 200 kV accelerating voltage.

X-ray Photoelectron Spectroscopy (XPS): The surface composition measurement was performed with X-ray photoelectron spectroscopy (ESCALAB250), and all the spectra were calibrated by C 1s peak at 284.6 eV.

Acknowledgements

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Keywords: ion exchange • luminescence • $CsPbX_3$ perovskite • metal halide • kinetic mechanism

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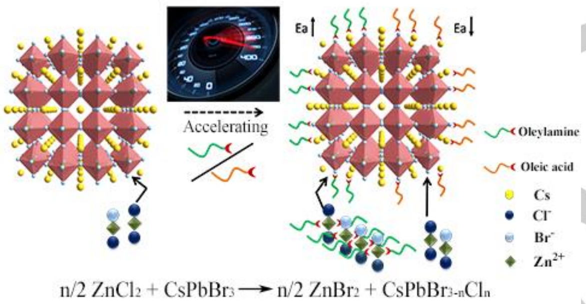
Entry for the Table of Contents

Layout 1:

FULL PAPER

We reported on a novel route using solid metal halides as solid halide sources that acheive an anion exchange with $CsPbX_3$ without any pretreatment. Introducing small amount of oleic acid and oleylamine speed up the exchange reaction rate, while showing different promotion mechanisms.



*Shaofan Fang, Guangshe Li, Yantong Lu and Liping Li**

Title: Highly Luminescent $CsPbX_3$ (X = Cl, Br, I) Nanocrystals Achieved by a Novel Rapid Anion Exchange at Room Temperature