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Impeding anion exchange to improve composition stability of $CsPbX_3$ (X = Cl, Br) nanocrystals through facilely fabricated Cs_4PbX_6 shell*

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Inorganic lead halide perovskite nanocrystals (NCs) with superior photoelectric properties are expected to have excellent performance in many fields. However, the anion exchange changes their features and is unfavorable for their applications in many fields. Hence, impeding anion exchange is important for improving the composition stability of inorganic lead halide perovskite NCs. Herein, $CsPbX_3$ (X = Cl, Br) NCs are coated with Cs_4PbX_6 shell to impede anion exchange and reduce anion mobility. The Cs_4PbX_6 shell is facily fabricated on $CsPbX_3$ NCs through high temperature injection method. Anion exchange experiments demonstrate that the Cs_4PbX_6 shell completely encapsulates $CsPbX_3$ NCs and greatly improves the composition stability of $CsPbX_3$ NCs. Moreover, our work also sheds light on the potential design approaches of various heterostructures to expand the application of $CsPbM_3$ (M = Cl, Br, I) NCs.

Keywords: $CsPbX_3$ @Cs_4PbX_6 , anion exchange, composition stability, core–shell constructure

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1. Introduction

Inorganic lead halide perovskite nanocrystals (NCs) have emerged as an attractive semiconductor material and been widely used in various fields, such as solar cells,[1] light-emitting diodes (LED_S),[2] lasers,[3] and photodetectors.[4] The studies of Yang *et al.* showed that inorganic lead halide perovskite NCs are very soft,[5,6] and can easily exchange ions with other salts or other halogen perovskites.[7,8] Therefore, the energy levels and related photoelectronic features of perovskite NCs can be easily tuned in this way. Although this property is valuable for adjusting photoelectronic features of NCs, it also induces the composition stability problems. For example, anion exchange with other halide salts and halide elements in the environment during storage or application can change the material features and limit the application of NCs. The loss of an anion is caused by the high ions mobility of halide anions. Though improving the composition stability has become increasingly important and urgent, there are few reports about how to imped the anion exchange to improve the composition stability and reduce the loss of anion.

Previous efforts mainly focus on improving water and oxygen stability and crystalline phase stability of perovskite NCs. Alkyl phosphinic acid, a kind of traditional surface ligand, was used to replace oleic acid and effectively prevented α-$CsPbI_3$ from transforming into δ-$CsPbI_3$.[9] However, surface ligands have no effect on anion protection. Using poly (methylmethacrylate) (PMMA) to encapsulate $CsPbBr_3$ can obviously protect $CsPbBr_3$, because PMMA has a low ion diffusion rate and water-resistance ability.[10] However, those coated NCs are less likely to be applied in the field of optoelectronics due to PMMA's insulation characteristics. Hydrolyzing (3-aminopropyl) triethoxysilane (APTES) can form a fully covered shell to improve NCs' stability significantly, but the silicon shell usually encapsulates a large number of NCs together.[11] $CsPb_2Br_5$ decorated on the surface of $CsPbBr_3$ NCs can extend the life of coated NCs in water.[12] $CsPbBr_3$/ZnS and $CsPbBr_3$/Ta_2O_5 NCs heterostructures have been synthesized and the stability of $CsPbBr_3$ NCs was improved,[13,14] but $CsPbBr_3$ NCs were not completely covered. More importantly, these approaches are complex and difficult to be used in mass production.

Cs_4PbM_6 (M = Cl, Br, I) NCs, indirect bandgap semiconductor materials, have become hotspots in recent years.[15] Differing from $CsPbM_3$ NCs, 0-dimensional PbM_6^{4-} is separated in Cs_4PbM_6 and the bond energy of Cs_4PbM_6 NCs is stronger than that of $CsPbM_3$ NCs.[15,16] Recent studies have

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demonstrated that Cs_4PbBr_6 coated $CsPbBr_3$ can form the first type of quantum well, but the size uniformity of coated NCs is poor and the prepared products have large particle size.[17] Li's group treated $CsPbBr_3$ NCs as seeds to form Cs_4PbBr_6 shells by adding Cs_2CO_3 and $ZnBr_2$.[18] But $ZnBr_2$ is likely to undergo cation exchange and introduces impurities into products.[7]

Here, we propose the concept of using Cs_4PbX_6 shell to impede the anion exchange of $CsPbX_3$ NCs, and present a new method to build a Cs_4PbX_6 shell on the surface of $CsPbX_3$ NCs. $CsPbX_3$ NCs are synthesized by high temperature injection method and are cooled to room temperature after being bathed in water. Then CsX and oleylamine (OLM) are added into the solution of $CsPbX_3$ NCs to synthesize Cs_4PbX_6 shells. X-ray diffraction (XRD) peaks of both $CsPbX_3$ and Cs_4PbX_6 are obtained. Anion exchange experiments prove that Cs_4PbX_6 shells are fully covered on the surface of $CsPbX_3$ NCs and could significantly improve the composition stability of coated $CsPbX_3$ NCs and reduce the loss of an anion.

2. Material and methods

2.1. Chemicals

Cs_2CO_3 (99.995%), $PbBr_2$ (99.999%), CsBr (99.999%), ethyl acetate (anhydrous, 98%), octadecene (ODE, anhydrous, 90%), hexane (HEX, anhydrous 99%), oleylamine (OLAM, anhydrous, 70%), and oleic acid (OA, anhydrous 90%) were purchased from Sigma-Aldrich. All chemicals were used without any further purification.

2.2. Synthesis of $CsPbX_3$ NCs

To prepare Cs-oleate solution, 0.4-g Cs_2CO_3, 15-mL ODE, and 1.2-mL OA were mixed in a 100-mL three-necked flask with vigorous stir and dried under Ar flow at 120 °C for 30 min, and then the solution was subsequently heated at 150 °C under Ar flow for at least 30 minutes. 0.188-mmol PbX_2 and 5-mL ODE were degassed in another 100-mL three-necked flask and stirred at 120 °C for 30 minutes under Ar flow. After being added with 0.5-mL OA and 0.5-mL OLM at 120 °C, the PbX_2 solution was kept at 150 °C for 30 minutes under magnetic stir. 0.6-mL Cs-oleate solution was quickly injected into PbX_2 solution to synthesize $CsPbX_3$ NCs. The reaction mixture was cooled by an ice-water bath after 5 s.

2.3. Synthesis of Cs_4PbX_6 shells

When the solution temperature of $CsPbX_3$ NCs declined to room temperature, 0.229-mmol CsX and 3.75-mL OLM were added into NCs solution. Then, the 100-mL three-necked flask containing NCs solution and CsX was put to an oil bath pot that has been heated to 100 °C. The reaction process lasted for 20 min with vigorous stir and Ar flow. Then, the obtained NCs were cooled by water bath and centrifuged at 6500 rpm for 8 min with ethyl acetate. The core–shell structure NCs were redispersed in 3-mL hexane.

2.4. Characterization

The prepared NCs were characterized by XRD, transmission electron microscopy (TEM), and photoluminescence (PL) measurements as in the previous experiments.[19] The XRD patterns were collected with a D/max 2200 V x-ray powder diffractometer with Cu $K\alpha$ radiation ($\lambda = 1.540$ Å). The TEM images were obtained from a JEOL JEM-1400 microscope with a thermionic gun operating at a 100 kV acceleration voltage. High resolution transmission electron microscopy (HRTEM) measurements and energy dispersive spectrometer (EDS) element mapping were carried out by a JEM-2100F operating at 200 kV. Steady-state PL spectra were collected with a Hitachi F4500 fluorescence spectrophotometer with an Xe lamp that was equipped with a monochromator. The ultraviolet (UV)-absorption spectra were measured on a Shimadzu UV-3101 PC spectrophotometer. The PL decay process was carried out on a Horiba Fluorolog phosphorescence lifetime system equipped with a 373 nm, 45-ps pulse laser and a time corrected single-photon counting (TCSPC) system. The samples of PL emission spectra, UV-absorption spectra, and PL decay were prepared by adding 100-μl crude NCs solution in 2900-μl n-hexane. All of the spectral measurements were performed at room temperature.

3. Results and discussion

Core $CsPbX_3$ NCs are synthesized based on the report of Protesecu *et al.*[20] and treated as seeds for the growth of Cs_4PbX_6. The growth process of Cs_4PbX_6 shell over $CsPbX_3$ NCs is shown in Fig. 1(a). As $CsPbX_3$ and Cs_4PbX_6 possess different element mole ratios, CsX needs to be added into the prepared $CsPbX_3$ NCs solution to construct a suitable atomic ratio.

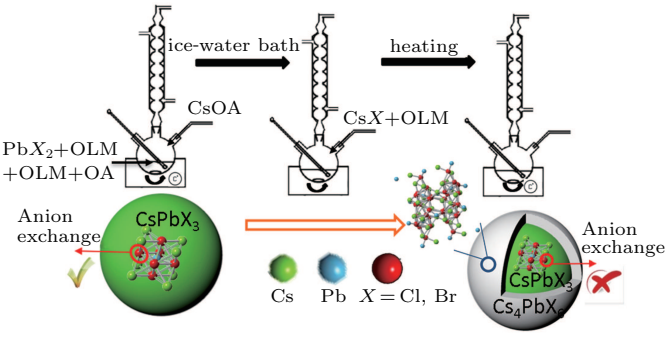


Fig. 1. Schematic diagram showing the growth process and effect of the core–shell structure.

As shown in Figs. 2(a) and 2(b), the prepared $CsPbBr_3$ NCs are monodisperse with a uniform size ranging from 9 nm–13 nm, and the size of $CsPbCl_3$ NCs is close to 10 nm. Because of a large amount of unreacted $PbBr_2$ when $CsPbX_3$ NCs are prepared by high temperature injection, no more

$PbBr_2$ needs to be added. OLM is utilized because Cs_4PbX_6 NCs are likely to be synthesized in a more OLM reaction environment.[16] Comparing Fig. 2(a) with Fig. 2(c), Fig. 2(b) with Fig. 2(d), it is easy to find that the size of coated NCs becomes bigger than before. The bigger size and shadowy outline in Figs. 2(c) and 2(d) are caused by the growth of Cs_4PbX_6 shells. The formation of Cs_4PbX_6 shells can also be inferred from XRD patterns in Fig. 2(e) which match well with $CsPbX_3$ and Cs_4PbX_6 standard cards, respectively. The UV-absorption peak near 300 nm in Fig. 3(a) also demonstrates that Cs_4PbX_6 is formed after adding OLM and CsX. The possibility that $CsPbX_3$ may convert to Cs_4PbX_6 when $CsPbX_3$ reacts with OLM and CsX is denied, because the transforming from $CsPbX_3$ to Cs_4PbX_6 requires a large amount of OLM. However, the amount of OLM in this experiment is far less than the required quantity.[21]

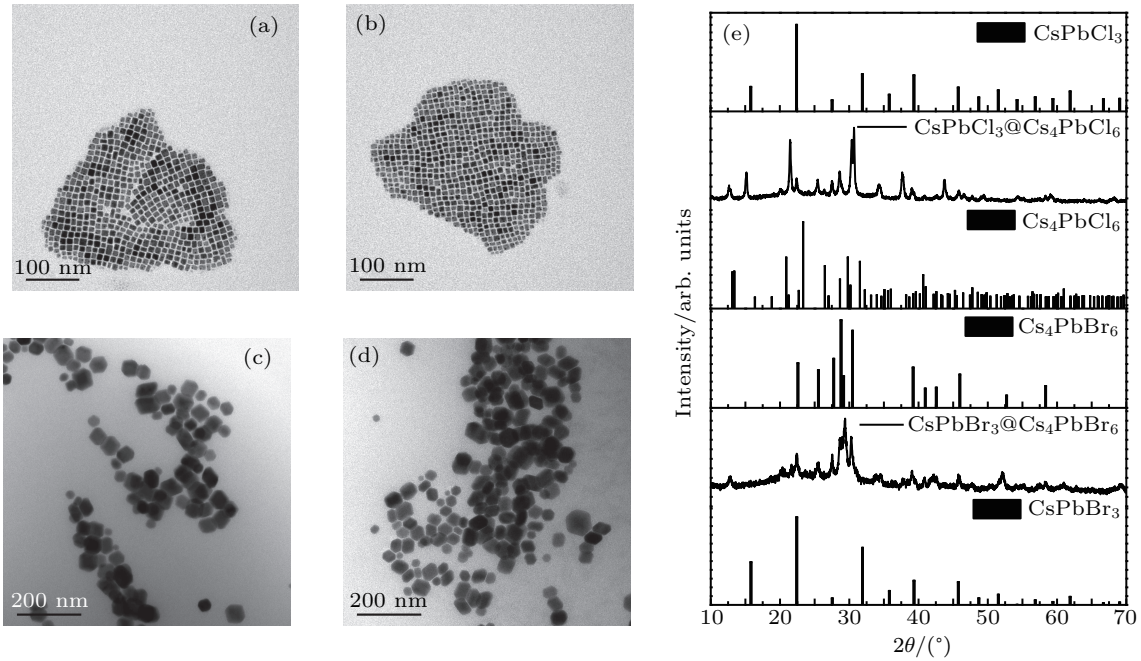


Fig. 2. The TEM images of (a) $CsPbCl_3$, (b) $CsPbBr_3$, (c) $CsPbCl_3@Cs_4PbCl_6$, and (d) $CsPbBr_3@Cs_4PbBr_6$ NCs. (e) XRD of $CsPbX_3@Cs_4PbX_6$ NCs.

It is expected to improve the composition stability of $CsPbX_3$ NCs by coating them with Cs_4PbX_6, because it is very difficult to break chemical bonds of Cs_4PbX_6 and cause ion exchange.[15] In order to confirm that the core–shell structure has been prepared and Cs_4PbX_6 shell can be used to reduce ions loss, anion exchange experiments before and after wrapping $CsPbX_3$ NCs are performed. The luminescence of $CsPbX_3$ NCs before and after anion exchange is detected and shown in Fig. 3(b). After mixing $CsPbCl_3$ and $CsPbBr_3$ NCs up, the luminous peak of alloy $CsPbCl_xBr_{3-x}$ NCs appears rapidly, while the PL emission locked at 408 nm and 512 nm vanishes. Comparing Fig. 3(c) with Fig. 3(d), slight peak position shifts from 408 nm of $CsPbCl_3$ to 410 nm of $CsPbCl_3@Cs_4PbCl_6$ and from 512 nm of $CsPbBr_3$ to 515 nm of $CsPbBr_3@Cs_4PbBr_6$ prove that the size of the core $CsPbX_3$ barely changes after being coated. The bigger size of NCs after encapsulated is due to the shell of Cs_4PbX_6 which has no contribution to peak positions. As shown in Fig. 3(c), the peak wavelength of alloy $CsPbCl_xBr_{3-x}$ NCs does not move after 30 s, indicating that anion exchange between $CsPbCl_3$ and $CsPbBr_3$ NCs already finishes within few seconds. However, anion exchange among coated NCs is impeded successfully, because there is blue emission of $CsPbCl_3@Cs_4PbCl_6$ and green emission of $CsPbBr_3@Cs_4PbBr_6$ in Fig. 3(e) after mixing both coated NCs for 11 min. The intensity of $CsPbX_3@Cs_4PbX_6$ NCs just changes slightly. More importantly, even after mixing $CsPbX_3@Cs_4PbX_6$ NCs for 3 hours, the blue and green emission in Fig. 3(d) still exist at the same time, and there are no significant changes compared with their initial peak positions. We do not conduct experiments about $CsPbI_3$ due to poor crystalline phase stability.

The above discussion leads to a conclusion that the Cs_4PbX_6 shell is completely covered on the surface of seeds NCs and can obviously prevent anion movement and reduce anion loss. This facile method is potentially used for building other kinds of shells and forming different heterojunctions. It is also possible to realize multilayer coatings. The NCs coated by Cs_4PbX_6 shell can be used to fabricate pure white optical devices by mixing $CsPbM_3@Cs_4PbM_6$ (M = Cl, Br, and I) NCs and improve the stability of inorganic lead halide perovskite NCs solar cells and LEDs. Cs_4PbX_6 coated $CsPbX_3$ NCs can form the first type of quantum well and are likely to improve the external quantum efficiency of quantum dot light emitting diodes LEDs.

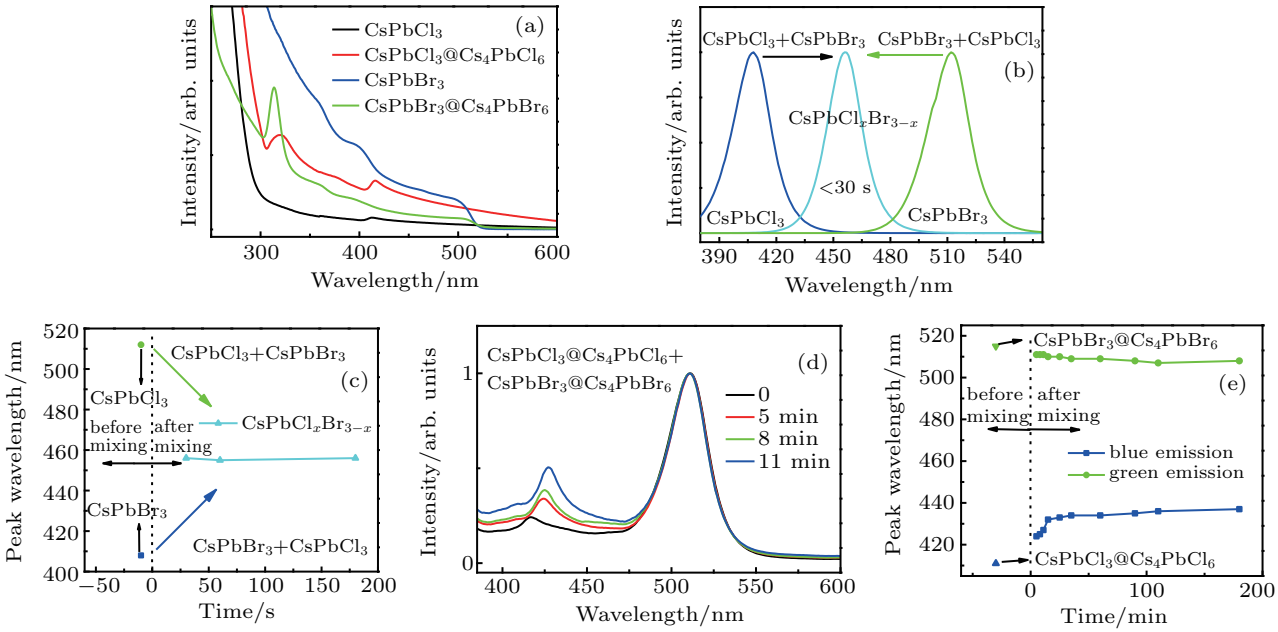


Fig. 3. (a) UV-absorption spectra of CsPbX_3 and CsPbX_3@Cs$_4$PbX_6 NCs. (b) PL of CsPbX_3 NCs before and after anion exchange. (c) Peak positions of CsPbX_3 NCs before and after anion exchange. (d) PL of mixed CsPbX_3@Cs$_4$PbX_6 NCs. (e) Peak positions of CsPbX_3@Cs$_4$PbX_6 NCs before and after mixing coated NCs up.

4. Conclusion

The core–shell structure CsPbX_3@Cs$_4$PbX_6 NCs has been successfully synthesized by adding CsX and OLM into prepared CsPbX_3 NCs. The absorption spectra and XRD have shown that core CsPbX_3 NCs are fully covered by Cs$_4$PbX_6. The anion exchange experiments have not only demonstrated the distribution of Cs$_4$PbX_6 but they have also proven that shells can effectively improve composition stability of CsPbX_3 (X = Cl, Br) NCs and block the influence of the external environment. This new coating method provides a way to form different core–shell structures or other forms of heterojunctions to improve the stability of inorganic perovskite NCs and expand its application fields. With additional research in the future, CsPbX_3@Cs$_4$PbX_6 NCs are likely to fabricate pure white optical devices and quantum dot light emitting diodes LEDs with high external quantum efficiency.

References

[1] Abhishek Swarnkar E M S, Marshall A R, Chernomordik B D, Moore D T, Christians J A, Chakrabarti T and Luther J M 2016 *Science* **07** 92

[2] Liu Y, Li F, Wang H L, Zhan Q, Liu Q L and Xia Z G 2018 *Chem. Mater.* **30** 8546

[3] Pan J, Sarmah S P, Murali B, Dursun I, Parida M R, Liu J K, Sinatra L, Alyami N, Zhao C, Alarousu E, Ng T K, Ooi B S, Bakr O M and Mohammed O F 2015 *J. Phys. Chem. Lett.* **6** 5027

[4] Sun S B, Yuan D, Xu D, Wang A F and Deng Z T 2016 *ACS Nano* **10** 3648

[5] Pellet N, Teuscher J, Maier J and Grätzel M 2015 *Chem. Mater.* **27** 2181

[6] Akkerman Q A, D'Innocenzo V, Accornero S, Scarpellini A, Petrozza A, Prato M and Manna L 2015 *J. Am. Chem. Soc.* **137** 10276

[7] Stam W V D, Geuchies J J, Altantzis T, Van den Bos K H W, Meeldijk J D, Aert S V, Bals S, Vanmaekelbergh D and Donega C D M 2017 *J. Am. Chem. Soc.* **139** 4087

[8] Gao D, Qiao B, Xu Z, Song D D, Song P J, LiangZ Q, Shen Z H, Cao J Y, Zhang J J and Zhao S L 2017 *J. Phys. Chem. C* **121** 20387

[9] Wang C J, Chesman A S R and Jasieniak J J 2017 *Chem. Commun.* **53** 232

[10] Li X M, Wu Y, Zhang S L, Cai B, Gu Y, Song J Z and Zeng H B 2016 *Adv. Funct. Mater.* **26** 2435

[11] Sun C, Zhang Y, Ruan C, Yin C Y, Wang X Y, Wang Y D and Yu W W 2016 *Adv. Mater.* **28** 10088

[12] Qiao B, Song P J, Cao J Y, Zhao S L, Shen Z H, Gao D, Liang Z Q, Xu Z, Song D D and Xu X R 2017 *Nanotechnology* **28** 445602

[13] Chen W W, Hao J, Hu W, Zang Z, Tang X, Fang L, Niu T and Zhou M 2017 *Small* **13** 1604085

[14] Zarei M and Zarei M 2018 *Small* **14** 1800912

[15] Zhang Y H, Saidaminov M I, Dursun I, Yang H Z, Murali B, Alarousu E, Yengel E, Alshankiti B A, Bakr O M and Mohammed O F 2017 *J. Phys. Chem. Lett.* **8** 961

[16] Akkerman Q A, Park S, Radicchi E, Nunzi F, Mosconi E, De Angelis F, Brescia R, Rastogi P, Prato M and Manna L 2017 *Nano Lett.* **17** 1924

[17] Xu J W, Huang W X, Li P Y, Onken D K, Dun C C, Guo Y, Ucer K B, Lu C, Wang H Z, Geyer S M, Williams R T and Carroll D L 2017 *Adv. Mater.* **29** 1703703

[18] Jia C, Li H, Meng X M and Li H B 2018 *Chem. Commun.* (Camb) **54** 6300

[19] Liang Z Q, Zhao S L, Xu Z, Qiao B, Song P J, Gao D and Xu X R 2016 *ACS Appl. Mater. Interfaces* **8** 28824

[20] Protesescu L, Yakunin S, Bodnarchuk M I, Krieg F, Caputo R, Hendon C H, Yang R X, Walsh A and Kovalenko M V 2015 *Nano Lett.* **15** 3692

[21] Liu Z K, Bekenstein Y, Ye X C, Nguyen S C, Swabeck J S, Zhang D D, Lee S T, Yang P D, Ma W L and Alivisatos A P 2017 *J. Am. Chem. Soc.* **139** 5309