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# Tuning the Optical Properties of CsPbBr<sub>3</sub> Nanocrystals by Anion Exchange Reactions with CsX Aqueous Solution

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## **Abstract**

Topotactic anion exchange has been developed to tune the composition and band gap energies of cesium lead halide (CsPbX<sub>3</sub>) perovskite nanocrystals (NCs). However, current anion exchange methods either require harsh conditions or take a long time to realize substantial substitution. Here, we present a method to modulate the composition of colloidal CsPbBr<sub>3</sub> NCs through ultrasonication-assisted anion exchange with CsX (X = Cl, I) solution. Efficient anion exchange of CsPbBr<sub>3</sub> NCs with Cl<sup>-</sup> or I<sup>-</sup> is realized with substitution ratio up to 93% and preservation of the pristine shape and structure of CsPbBr<sub>3</sub> NCs. This anion exchange results in tunable emission, covering the whole visible spectral range, with relatively high photoluminescence quantum yield, narrow emission bandwidths, and good stability. This work provides a facile and efficient way to engineer the properties of halide perovskite NCs and has great potential for large-scale production of compositionally diverse perovskite NCs.

Keywords: CsPbBr<sub>3</sub> nanocrystals, Anion exchange, CsX aqueous solution, Ultrasonication, Photoluminescence

## **Background**

All-inorganic CsPbX<sub>3</sub> (X=Cl, Br, and I) perovskite nanocrystals (NCs) have gained significant attention owing to their high photoluminescence (PL) quantum yield (QY) [1], narrow emission line width [2], defect tolerance [3, 4], and wide range of band gaps tunable by control of both composition [5, 6] and morphology [7–9]. The promise of CsPbX<sub>3</sub> NCs has been examined in the context of their applications in optoelectronic devices, such as light-emitting diodes [10–14], Photodetectors [15, 16], lasing [17], and photovoltaics [18, 19].

Especially, the capability of anion exchange of CsPbX<sub>3</sub> NCs has opened the door to many interesting applications of these materials. A broad range of tunable PL from CsPbX<sub>3</sub> NCs could be obtained via a simple post-synthetic procedure, where mixing the solution of NCs with the reactive anion precursors results in the

formation of the anion-exchanged NCs with tunable bandgap [5, 6, 20-22]. The labile nature of the halide anions in the perovskite system is generally responsible for their facile exchange in perovskite NCs and other processes involving ion transport, such as long-range anion diffusion under weak perturbation [23, 24] and phase segregation in the methylammonium lead-mixed halide system [25]. Due to the simple and wide tunability of the photophysical properties of perovskite NCs, anion exchange has been extensively explored using various sources of anions for different applications [26, 27]. Most of the reported anion exchange methods generally require presynthesized halide precursors, and the reactivity of the halide containing precursors determines the extent and efficiency of the anion exchange. It has been reported that anion exchange of CsPbBr3 NCs with low-active precursors, such as PbX<sub>2</sub>, takes a long time (~1 day or longer) to proceed, and complete exchange of Br anion with X has been shown to be difficult [5]. Halide-containing precursors such as oleylamine halides (OLAM-X) and tetrabutylammonium halides (TBA-X) are highly reactive [5-7], which makes the anion exchange process very efficient, and complete anion exchange can be achieved. However,

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these highly reactive precursors are toxic and the anion exchange processes need to be carried out under inert and anhydrous conditions. Therefore, a new method for efficient and green anion exchange of CsPbX<sub>3</sub> NCs is still worth pursuing.

Recently, Yin et al. reported one efficient method to transform the nonluminescent Cs<sub>4</sub>PbX<sub>6</sub> NCs into CsPbX<sub>3</sub> NCs [28, 29]. These presynthesized Cs<sub>4</sub>PbX<sub>6</sub> NCs were dispersed in nonpolar hexane, and the excess CsX was stripped and dissolved into the water through the interfacial reaction, and further etching of resultant CsPbBr3 NCs was prohibited by the interface between water and nonpolar solvent. Based on this report, we propose one facile anion exchange method to tune the composition and optical properties of the CsPbBr<sub>3</sub> NCs. The presynthesized CsPbBr3 NCs are dispersed in hexane, and the anion exchange is realized through the interfacial reaction with CsX (X=Cl, I) aqueous solution assisted by ultrasonication. The extent and rate of the anion exchange reaction are controlled by ultrasonic time and CsX concentration. Compared to most of the reported anion exchange methods [5–7, 20–22], this anion exchange scheme is very facile and environment-friendly. The halide precursors for anion exchange can be dissolved into water instead of organic solution, and after anion exchange, halides dissolved in water can be easily separated by desiccation. Most importantly, the reaction can be carried out under normal condition, instead of the inert and anhydrous conditions. The proposed mechanism of the anion exchange of CsPbX<sub>3</sub> NCs in CsX aqueous solutions is illustrated in Fig. 1 Br ions in the CsPbBr<sub>3</sub> NCs exchanges with the Cl<sup>-</sup> or I<sup>-</sup> ions, resulting in the formation of CsPbX<sub>3</sub> NCs. By adjusting the reaction time or the CsX aqueous solution, complete tunable composition of CsPbX<sub>3</sub> NCs and emission covering the full visible spectral range with narrow band widths can be achieved.

## Methods

## Synthesis and Purification of CsPbBr<sub>3</sub> NCs

CsPbBr<sub>3</sub> NCs are synthesized following the method reported by Protesescu et al. [1]. In a typical experiment, 0.8 g of Cs<sub>2</sub>CO<sub>3</sub>(99.9%, Aldrich), 2.5 ml of oleic acid (OA; 90%, Aldrich) and 30 ml of octadecene (ODE; 90%, Aldrich) are added into a 100-ml 3-neck flask, degassed at room temperature for 30 min, and then dried for 1 h at 120 °C under Ar until all Cs2CO3 reacted with OA. 0.136 g of PbBr<sub>2</sub> (99.9%, Aldrich), 2 mL of oleylamine (OALM; Aldrich, 80-90%), 1.5 mL of OA, and 8 mL ODE are added to a 25-mL 3-neck round bottom flask. The solution is evacuated and refilled with Ar followed by heating to 120 °C for 30 min. The solution is heated to 180 °C and kept for another 10 min. Then the Cs-oleate (1 mL) is injected and after 10 s the solution is cooled with an ice bath. The NCs are precipitated with acetone (AR, Sinopharm) and then centrifuged followed by dissolving in hexanes (AR, Sinopharm).

## **Anion Exchange Reactions**

5-ml of CsX (1 mol/L, 0.2 mol/L, X=Cl, I) aqueous solution is loaded in a 25-mL glass bottle and 3 ml of CsPbBr<sub>3</sub> NCs/hexane solution (4.5 mmol/L in Br<sup>-</sup>) is dropped inside, and then by bath-sonication (KQ-50B, ultrasonic cleaner) at a power of 50 W (total power) for some time. After ultrasonication, the system is then kept undisturbed for 5 min, and then the organic phase layer is collected (CsX aqueous solution can be reused by purification). Afterwards, the product is centrifuged at 2500 rpm for 5 min to discard the precipitates.



Fig. 1 Illustration of the mechanism for anion exchange of perovskite nanocrystals in aqueous solutions

## Characterization

The phases of the products are examined by X-ray powder diffractometer (D8 Advance, Bruker) and high-resolution transmission electron microscope (HR-TEM, JEM 2100F, JEOL, Japan) operating at 200 kV. Absorption spectra of the colloidal CsPbX $_3$  NCs are recorded using an UV/Vis/NIR spectrophotometer (UV3600, Shimadzu, Japan).

## **Photoluminescence Measurements**

Photoluminescence (PL) spectra of the colloidal CsPbX<sub>3</sub> NCs are collected by a Photo Technology International (PTI) OM/TM/NIR spectrophotometer with a 914 photomultiplier detection system and using a 75-W xenon lamp as the excitation source. All the optical measurements are carried out at room temperature. 400 nm of light is used as the excitation source for all the CsPbX<sub>3</sub> NCs, except 360 nm for CsPb(Br/Cl)<sub>3</sub> NCs. Following the method proposed by Prato et al. [5], four measurements are performed for PLQY: (i) the sample emission (SEM) that collects the photons emitted by the sample, (ii) the blank emission(BEM), which is a measurement performed with the cuvette containing only the solvent (blank) in the same spectral range used for the SEM measurement, (iii) the sample excitation (SEX), which records the photons at the pumping wavelength that are not absorbed by the sample, and (iv) the blank excitation (BEX), which records the photons at the pumping wavelength going through the blank. The photoluminescence quantum yield PLQY is then calculated as

$$PLQY(\%) = \frac{SEM\text{-BEM}}{BEX\text{-SEX}} \times 100$$

Any reabsorption correction factor is neglected in our calculation of the PLQY, since the solutions investigated are diluted to the point that reabsorption of the PL could be neglected.

## **Stability Test**

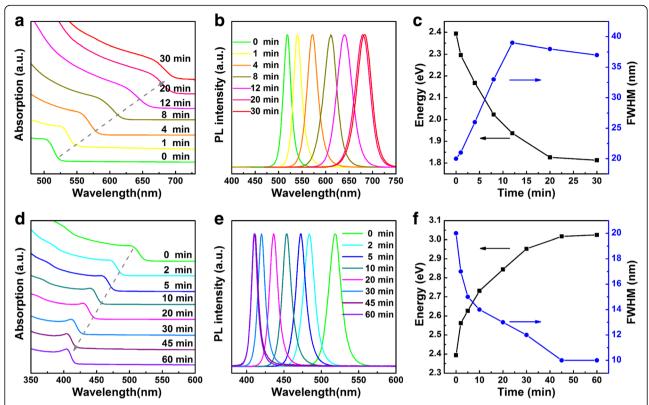
The perovskite NCs are dispersed in hexane and sealed into glass bottles, which are kept under ambient condition for several weeks. Changes in the absorption and PL of these anion-exchanged perovskite NCs are recorded at an interval of 7 days.

## **Results and Discussion**

Figure 2 summarizes the continuous changes in the absorption and emission spectra of mixed anion  $CsPbX_3$  NCs obtained through ion-exchange with CsI aqueous solution (Fig. 2a, b) and CsCl aqueous solution (Fig. 2d,e). The time-trace and full width at half maximum (FWHM) of the emission peaks are also shown

for both reactions (Fig. 2c,f). Absorption and emission peaks of CsPbX<sub>3</sub> NCs showed obvious red shift with anion exchange with CsI solution, indicating the exchange of bromide with iodide and formation of CsPb(Br/I)<sub>3</sub> NCs. Upon 30-min ultrasonication, absorption and emission peaks stabilize at 675 nm (Fig. 2a) and 685 nm (Fig. 2b), respectively. With CsCl solution, both absorption and emission peaks of CsPb(Br/Cl)<sub>3</sub> NCs show gradual blue shift upon continuous ultrasonication. With ultrasonication, the absorption peak shifts to 405 nm (Fig. 2d) and the emission peak shifts to 411 nm (Fig. 2e) within 45 min and stabilizes. This process allows the formation of CsPbX<sub>3</sub>NCs with tunable band gap energies (Fig. 2c, f) and emission spanning over the whole visible spectral range. It has to be pointed out that the FWHM of CsPb(Br/I)<sub>3</sub> NCs gradually increases from 20 nm to a maximal value of 39 nm (Fig. 2c), while the FWHM of CsPb(Br/Cl)<sub>3</sub> NCs monotonically decreased from 20 to 10 nm (Fig. 2f). These changes in the FWHM values show that the size dispersion of the pristine CsPbBr3 NCs is largely maintained.

Emission photograph of the anion-exchanged perovskite NCs is shown in Fig. 3a. Upon exchange with CsCl or CsI aqueous solution, emission color of the NCs gradually changes to blue or red. Most importantly, size and morphology of the CsPbBr<sub>3</sub> NCs template are preserved during the anion-exchange process (Fig. 3b-d). As confirmed by the TEM images, after the anion exchange, average sizes of CsPb(Br/Cl)<sub>3</sub> NCs with sonication time of 60 min (Fig. 3b) and CsPb(Br/I)<sub>3</sub> NCs with sonication time of 30 min (Fig. 3d) are almost the same as the pristine CsPbBr<sub>3</sub> NCs (Fig. 3c), and the shape still remains as cubic. CsPbX3 NCs obtained with other sonication time (Additional file 1: Figure S1 for CsI aqueous solution and Additional file 1: Figure S3 for CsCl aqueous solution) show the same cubic shape, although after exchange of Br ions with I ions their size increased slightly from  $(9.6 \pm 1.3)$  to  $(11.1 \pm 1.5)$  nm (Additional file 1: Figure S2), whereas the exchange with Cl<sup>-</sup> ions led to a slight decrease in size, to  $(8.2 \pm 1.4)$  nm (Additional file 1: Figure S4). The selected area electron diffraction pattern (Additional file 1: Figure S5) confirms that these CsPbBr<sub>3</sub> NCs and exchanged CsPbX<sub>3</sub> NCs all had the same cubic structure with space group of  $Pm\overline{3}m$  (221). The HR-TEM images (Fig. 3e-f) evidenced the high quality of the pristine CsPbBr<sub>3</sub> NCs (Fig. 3f), the exchanged CsPb(Br/Cl)<sub>3</sub> NCs (Fig. 3e) and CsPb(Br/I)<sub>3</sub>NCs (Fig. 3g). These results shows that the anion exchange with CsX aqueous solution does not deteriorate or etch the perovskite NCs. Successful exchange of Br ions with Cl or I ions is further confirmed by the changes in the lattice distance shown in Fig. 3e-g. For the perovskite NCs obtained through exchange with CsCl aqueous solution for 60 min, the

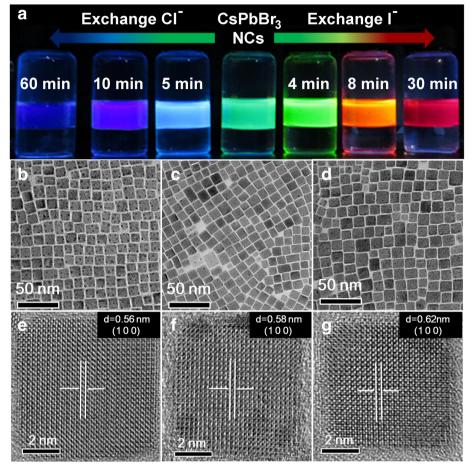


**Fig. 2** Ultrasonication time dependent absorption and emission of CsPbBr<sub>3</sub> NCs exchanged with CsX aqueous solutions (1 mol/L). **a** Absorption spectra, **b** emission spectra, and **c** emission peak energy (black square) and emission bandwidth (blue circle) of CsPbBr<sub>3</sub> NCs exchanged in Csl aqueous solution. **d** Absorption spectra, **e** emission spectra, and **f** emission peak energy (black square) and emission bandwidth (blue circle) of CsPbBr<sub>3</sub> NCs exchanged in CsCl aqueous solution

(100) lattice constant is found to be 0.56 nm, almost identical to that of CsPbCl<sub>3</sub> NCs (JCPDF No.: 75-0411). For those NCs exchanged with CsI aqueous solution for 30 min, the (100) lattice constant increases from 0.583 nm of CsPbBr<sub>3</sub> NCs (JCPDF No.: 54-0752) to 0.615 nm, close to that of CsPbI<sub>3</sub> NCs [5-7]. For CsPb(Br/I)<sub>3</sub> NCs, the (100) lattice plane distance increases from 0.583 nm of CsPbBr<sub>3</sub> NCs to 0.591, 0.6, and 0.615 nm as the sonication time increases from 0 to 4, 8, and 30 min, respectively (Additional file 1: Figure S1). For CsPb(Br/Cl)<sub>3</sub> NCs, the (100) lattice plane distance decreased from 0.583 nm of CsPbBr<sub>3</sub> NCs to 0.575, 0.57, and 0.561 nm, as the sonication time increases from 0 to 5, 10, and 60 min, respectively (Additional file 1: Figure S3). X-ray diffraction pattern also shows that all the diffraction peaks of the CsPbX<sub>3</sub> NCs can be assigned to cubic perovskite, and they gradually shift towards higher angles approaching that of CsPbCl<sub>3</sub> NCs, and lower angles approaching that of CsPbI<sub>3</sub> NCs when exchanged with CsCl and CsI aqueous solution, respectively (Additional file 1: Figure S6).

Actual compositions of the exchanged perovskite NCs analyzed using energy dispersive X-ray spectroscopy (EDX) are listed in Table 1, along with the measured

PLQY and emission peak energy. With continuous anion exchange with CsX aqueous solution, the Br - to Cl - substitution ratio can reach 93% in CsPb(Br/Cl)<sub>3</sub> NCs, and the Br to I substitution ratio can reach 90%. These substitution ratios are comparable to those achieved with highly reactive precursors such as OLAM-X and TBA-X [5–8], demonstrating that anion exchange through CsX aqueous solution was also a powerful route to tune the chemical composition of CsPbX<sub>3</sub> NCs. With anion exchange, the PLQY of CsPb(Br/Cl)<sub>3</sub> NCs firstly increases from 76% of the pristine CsPbBr<sub>3</sub> NCs to 85% of the CsPbBr<sub>2,3</sub>Cl<sub>0,7</sub> NCs, and then rapidly drops to 32% (CsPbBr<sub>2.0</sub>Cl<sub>1.0</sub> NCs) and 5% (CsPbBr<sub>0.2</sub>Cl<sub>2.8</sub> NCs). The PLQY of the CsPb(Br/I)<sub>3</sub> NCs monotonically declines from 76% of the pristine CsPbBr<sub>3</sub> NCs to 31% of CsPbBr<sub>0.3</sub>I<sub>2.7</sub> NCs. This trend is in line with that reported by Pellet et al. [30]. It has to be pointed out that PLQY of the CsPbX<sub>3</sub> NCs obtained through the longest sonication is comparable to those of directly synthesized CsPbI<sub>3</sub> and CsPbCl<sub>3</sub> NCs [30–32], further confirming that anion exchanged through CsX aqueous solution does not lead to the deterioration of the optical properties of the CsPbX<sub>3</sub> NCs. Even though these CsPbX<sub>3</sub> NCs are exchanged with aqueous solution, they still maintain



**Fig. 3 a** Emission photograph of perovskite NCs exchanged with 1 mol/L CsX aqueous solution under 365-nm light illumination. TEM and HR-TEM images of CsPb(Br/Cl)<sub>3</sub> NCs obtained from 60 min exchange (**b**, **e**), pristine CsPbBr<sub>3</sub> NCs (**c**, **f**), and CsPb(Br/l)<sub>3</sub> NCs obtained from 30 min exchange (**d**, **g**)

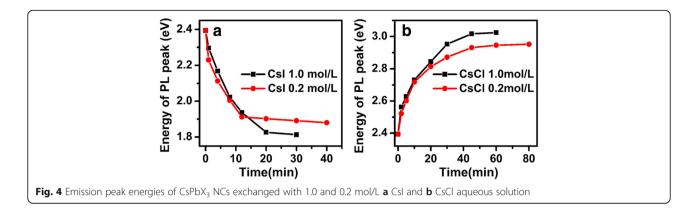
relative good room temperature stability when stored in hexane, mainly due to the low solubility of water in hexane (9.5 mg/L) [28]. For CsPb(Br/Cl) $_3$  NCs obtained through 45 min sonication, the PL intensity decreased to  $\sim 30\%$  of the original intensities within 4 weeks (Additional file 1: Figure S7a). While for CsPb(Br/I) $_3$  NCs obtained through 20 min sonication, only 5% of the

**Table 1** Composition, emission energy, and PLQY of CsPbBr<sub>3</sub>NCs exchanged under different conditions

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Aqueous solution	Sonication time (min)	EDX composition	PL energy (eV)	PL QYs (%)
1 mol/L CsCl	60	CsPbBr <sub>0.2</sub> Cl <sub>2.8</sub>	3.04	5
	10	$CsPbBr_{2.0}Cl_{1.0}$	2.74	32
	5	$CsPbBr_{2.3}Cl_{0.7}$	2.62	85
Pristine	0	CsPbBr <sub>3</sub>	2.39	76
1 mol/L CsI	4	$CsPbBr_{2.5}l_{0.5}$	2.25	52
	8	$CsPbBr_{2.2}I_{0.8}$	2.03	46
	30	CsPbBr <sub>0.3</sub> l <sub>2.7</sub>	1.83	31
	<u> </u>		<u> </u>	

original PL intensities was retained within 4 weeks (Additional file 1: Figure S7b).

This facile ultrasonication-assisted anion exchange with CsX aqueous solution is mainly driven by the large concentration of CsX in the aqueous solution. Anion-exchange of CsPbBr<sub>3</sub> NCs with octadecylamine halides(ODA-X) and lead halides (PbX2) salts was found to be slow and incomplete [5], due to the low solubility of these compounds in the nonpolar toluene solvent. The relatively large solubility of OLAM-X and TBA-X in toluene makes the anion exchange of CsPbBr<sub>3</sub> NCs very fast and complete [5-8]. The fast anion exchange and wide tunable spectral range of absorption and emission reported in this work are mainly ascribed to the large solubility of CsX in water (1865 g/L for CsCl and 440 g/ L for CsI in water) [28], which provide the large driving force for the anion exchange. To further confirm the effect of CsX aqueous solution concentration on the anion exchange of CsPbX<sub>3</sub> NCs, CsPbBr<sub>3</sub> NCs are exchanged with CsX aqueous solution of 0.2 mol/L (Fig. 4). It is



found that the PL peak energy of CsPb(Br/I) $_3$  NCs gradually stabilized at 1.88 eV (Fig. 4a) with 40-min sonication, and the PL peak energy of CsPb(Br/Cl) $_3$  NCs gradually approaches at 2.95 eV (Fig. 4b) even with 80-min ultrasonication. The ultrasonication time dependence of the emission peak energy shows that concentration of the CsX aqueous solution does not affect the speed at the early stage, but determines the final composition of the CsPbX $_3$  NCs, providing a new route to precisely control the composition of the exchanged CsPbX $_3$  NCs.

### **Conclusions**

In conclusion, we report here a simple and environment-friendly ultrasonication assisted anion-exchange of CsPbBr<sub>3</sub> NCs with CsX aqueous solution. This anion-exchange happens at the interface of the CsX aqueous solution and hexane. By carefully selecting the anion-exchange condition, more than 90% of the Br<sup>-</sup> ions in CsPbBr<sub>3</sub> NCs can be substituted by X<sup>-</sup> ions, while maintaining the shape and structure of the pristine CsPbBr<sub>3</sub> NCs. Both absorption and emission of these exchanged CsPbX<sub>3</sub> NCs can span the full visible spectral range, with a relatively high PLQY and stability. This anion-exchange method provides another facile route to modulate the chemical compositions and optical properties of CsPbX<sub>3</sub> NCs.

## **Additional file**

**Additional file 1:** Additional XRD patterns, TEM images, and PL spectra (DOCX 4026 kb)

## **Abbreviations**

EDX: Energy-dispersive X-ray spectroscopy; NCs: Nanocrystals; OA: Oleic acid; OALM: Oleylamine; ODE: Octadecene; PL: Photoluminescence; TBA: Tetrabutylammonium; TEM: Transmission electron microscope; XRD: X-ray diffraction

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#### Availability of Data and Materials

The datasets generated during and/or analyzed during the current study are available from the corresponding authors on reasonable request.

#### **Authors' Contributions**

LC and ZX conceived and designed the experiments. YA and GY carried out the experiments. YA and LC co-wrote the manuscript. DZ and GY performed the TEM experiments. All authors contributed to data analysis and scientific discussion. All authors read and approved the final manuscript.

#### **Competing Interests**

The authors declare that they have no competing interests.

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#### References

- Protesescu L, Yakunin S, Bodnarchuk MI, Krieg F, Caputo R, Hendon CH, Yang RX, Walsh A, Kovalenko MV (2015) Nanocrystals of cesium lead halide perovskites (CsPbX<sub>3</sub>, X = CI, Br, and I): novel optoelectronic materials showing bright emission with wide color gamut. Nano Lett 15:3692–3696
- Swarnkar A, Chulliyil R, Ravi VK, Irfanullah M, Chowdhury A, Nag A (2016) Colloidal CsPbBr<sub>3</sub> perovskite nanocrystals: luminescence beyond traditional quantum dots. Angew Chem 127:15644–15648
- Brandt RE, Stevanović V, Ginley DS, Buonassisi T (2015) Identifying defecttolerant semiconductors with high minority-carrier lifetimes: beyond hybrid lead halide perovskites. MRS Commun 5:265–275
- Dirin DN, Protesescu L, Trummer D, Kochetygov IV, Yakunin S, Krumeich F, Stadie NP, Kovalenko MV (2016) Harnessing defect-tolerance at the nanoscale: highly luminescent lead halide perovskite nanocrystals in mesoporous silica matrices. Nano Lett 16:5866–5874
- Akkerman QA, D'Innocenzo V, Accornero S, Scarpellini A, Petrozza A, Prato M, Manna L (2015) Tuning the optical properties of cesium lead halide perovskite nanocrystals by anion exchange reactions. J Am Chem Soc 137: 11076–10281
- Nedelcu G, Protesescu L, Yakunin S, Bodnarchuk MI, Grotevent MJ, Kovalenko MV (2015) Fast anion-exchange in highly luminescent

- nanocrystalsof cesium lead halide perovskites (CsPb $X_3$ , X = Cl, Br,I). Nano Lett 15:5635–5640
- Bekenstein Y, Koscher BA, Eaton SW, Yang P, Alivisatos AP (2015) Highly luminescent colloidal nanoplates of perovskite cesium lead halide and their oriented assemblies. J Am Chem Soc 137:16008–16011
- Zhang D, Yu Y, Bekenstein Y, Wong AB, Alivisatos AP, Yang P (2016)
  Ultrathin colloidal cesium lead halide perovskite nanowires. J Am Chem Soc 138:13155–13158
- Fang F, Chen W, Li Y, Liu H, Mei M, Zhang R, Hao J, Mikita M, Cao W, Pan R, Wang K, Sun X (2018) Employing polar solvent controlled ionization in precursors for synthesis of high-quality inorganic perovskite nanocrystals at room temperature. Adv Funct Mater 28:1706000
- Zhang X, Lin H, Huang H, Reckmeier C, Zhang Y, Choy WC, Rogach AL (2016) Enhancing the brightness of cesium lead halide perovskite nanocrystal based green light-emitting devices through the interface engineering with perfluorinated ionomer. Nano Lett 16:1415–1420
- Song J, Li J, Li X, Xu L, Dong Y, Zeng H (2015) Quantum dot light-emitting diodes based on inorganic perovskite cesium lead halides (CsPbX3). Adv Mater 27:7162–7167
- Li X, Wu Y, Zhang S, Cai B, Gu Y, Song J, Zeng H (2016) CsPbX<sub>3</sub> quantum dots for lighting and displays: room-temperature synthesis, photoluminescence superiorities, underlying origins and white lightemitting diodes. Adv Funct Mater 26:2435–2445
- Li J, Xu L, Wang T, Song J, Chen J, Xue J, Dong Y, Cai B, Shan Q, Han B, Zeng H (2017) 50-fold EQE improvement up to 6.27% of solution-processed all-inorganic perovskite CsPbBr<sub>3</sub> QLEDs via surface ligand density control. Adv Mater 29:1603885–1603893
- Yang D, Zou Y, Li P, Liu Q, Wu L, Hu H, Xu Y, Sun B, Zhang Q, Lee S-T (2018) Large-scale synthesis of ultrathin cesium lead bromide perovskite nanoplates with precisely tunable dimensions and their application in blue light-emitting diodes. Nano Energy 47:235–242
- Song J, Xu L, Li J, Xue J, Dong Y, Li X, Zeng H (2016) Monolayer and few-layer all-inorganic perovskites as a new family of two-dimensional semiconductors for printable optoelectronic devices. Adv Mater 28:4861–4869
- Dong Y, Gu Y, Zou Y, Song J, Xu L, Li J, Xue J, Li X, Zeng H (2016) Improving all-inorganic perovskite photodetectors by preferred orientation and plasmonic effect. Small 12:5622–5632
- Wang Y, Li X, Song J, Xiao L, Zeng H, Sun H (2015) All-inorganic colloidal perovskite quantum dots: a new class of lasing materials with favorable characteristics. Adv Mater 27:7101–7108
- 18. Swarnkar A, Marshall AR, Sanehira EM, Chernomordik BD, Moore DT, Christians JA, Chakrabarti T, Luther JM (2016) Quantum dot-induced phase stabilization of  $\alpha$ -CsPbl $_3$  perovskite for high-efficiency photovoltaics. Science 354:92–95
- Akkerman QA, Gandini M, Di Stasio F, Rastogi P, Palazon F, Bertoni G, Ball JM, Prato M, Petrozza A, Manna L (2016) Strongly emissive perovskite nanocrystal inks for high-voltage solar cells. Nat Energy 2:16194–16200
- Yoon SJ, Draguta S, Manser JS, Sharia O, Schneider WF, Kuno M, Kamat PV (2016) Tracking iodide and bromide ion segregation in mixed halide lead perovskites during photoirradiation. ACS Energy Lett 1:290
- Koscher BA, Bronstein ND, Olshansky JH, Bekenstein Y, Alivisatos AP (2016) Surface-vs diffusion- limited mechanisms of anion exchange in CsPbBr<sub>3</sub> nanocrystal cubes revealed through kinetic studies. J Am Chem Soc 138: 12065–12068
- 22. Parobek D, Dong Y, Qiao T, Son D (2017) Photoinduced anion exchange in cesium lead halide perovskite nanocrystals. J Am Chem Soc 139:4358–4361
- 23. Eames C, Frost JM, Barnes PR, O'regan BC, Walsh A, Islam MS (2015) Ionic transport in hybrid lead iodide perovskite solar cells. Nat Commun 6:7497
- Azpiroz JM, Mosconi E, Bisquert J, De Angelis F (2015) Defect migration in methylammonium lead iodide and its role in perovskite solar cell operation. Energy Environ Sci 8:2118–2127
- Hoke ET, Slotcavage DJ, Dohner ER, Bowring AR, Karunadasa HI, McGehee MD (2015) Reversible photo-induced trap formation in mixed-halide hybrid perovskites for photovoltaics. Chem Sci 6:613–617
- Palazon F, Akkerman QA, Prato M, Manna L (2016) X-ray lithography on perovskite nanocrystals films: from patterning with anion-exchange reactions to enhanced stability in air and water. ACS Nano 10:1224–1230
- Doane TL, Ryan KL, Pathade L, Cruz KJ, Zang H, Cotlet M, Maye MM (2016)
  Using perovskite nanoparticles as halide reservoirs in catalysis and as spectrochemical probes of ions in solution. ACS Nano 10:5864–5872
- 28. Wu L, Hu H, Xu Y, Jiang S, Chen M, Zhong Q, Yang D, Liu Q, Zhao Y, Sun B, Zhang Q, Yin Y (2017) From nonluminescent  $Cs_4PbX_6$  (X=Cl, Br, I) nanocrystals

- to highly luminescent CsPbX<sub>3</sub> nanocrystals: water-triggered transformation through a CsX-stripping mechanism. Nano Lett 17:5799–5804
- Hu H, Wu L, Tan Y, Zhong Q, Chen M, Qiu Y, Yang D, Sun B, Zhang Q, Yin Y (2018) Interfacial synthesis of highly stable CsPbX<sub>3</sub>/oxide Janus nanoparticles. J Am Chem Soc 140(1):406–412
- Pellet N, Teuscher J, Maier J, Gratzel M (2015) Transforming hybrid organic inorganic perovskites by rapid halide exchange. Chem Mate 27:2181–2188
- Xing G, Mathews N, Lim SS, Yantara N, Liu X, Sabba D, Grätzel M, Mhaisalkar S, Sum TC (2014) Low-temperature solution-processed wavelength-tunable perovskites for lasing. Nat Mater 13:476–480
- Stranks SD, Burlakov VM, Leijtens T, Ball JM, Goriely A, Snaith H (2014) Recombination kinetics in organic-inorganic perovskites: excitons, free charge, and subgap states. Phys Rev Appl 2:034007

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