Grinding Synthesis of APbX₃ (A = MA, FA, Cs; X = Cl, Br, I) Perovskite Nanocrystals

Daqin Chen,*‡§∥ Junni Li,‡ Xiao Chen,‡ Jiangkun Chen,‡§∥ and Jiasong Zhong‡

†Fujian Provincial Key Laboratory of Quantum Manipulation and New Energy Materials, College of Physics and Energy, Fujian Normal University, Fuzhou 350117, China
‡College of Materials & Environmental Engineering, Hangzhou Dianzi University, Hangzhou, Zhejiang 310018, P. R. China
§Fujian Provincial Engineering Technology Research Center of Solar Energy Conversion and Energy Storage, Fuzhou 350117, China
∥Fujian Provincial Collaborative Innovation Center for Optoelectronic Semiconductors and Efficient Devices, Xiamen 361005, China

ABSTRACT: Currently, metal halide perovskite nanocrystals have been extensively explored due to their unique optoelectronic properties and wide application prospects. In the present work, a facile grinding method is developed to prepare whole-family APbX₃ (A = MA, FA, and Cs; X = Cl, Br, and I) perovskite nanocrystals. This strategy alleviates the harsh synthesis conditions of precursor dissolution, atmosphere protection, and high temperature. Impressively, the as-prepared perovskite nanocrystals are evidenced to have halogen-rich surfaces and yield visible full-spectral emissions with maximal photoluminescence quantum yield up to 92% and excellent stability. Additionally, the grinding method can be extended to synthesize widely concerned Mn²⁺-doped CsPbCl₃ nanocrystals with dual-modal emissions of both excitons and dopants. As a proof-of-concept experiment, the present perovskite nanocrystals are demonstrated to be applicable as blue/green/red color converters in UV-excitable white-light-emitting diodes.

KEYWORDS: perovskite, CsPbBr₃, optical materials, luminescence, LED

INTRODUCTION

Recently, metal halide semiconductor nanocrystals (NCs) or quantum dots (QDs) with perovskite crystal structures, showing superior optical performance of narrow full width at half maximum (FWHM, down to 12 nm), high photoluminescence quantum yield (PLQY, up to 90%), and wide color gamut, have attracted intensive attention for promising applications in displays, lasers, and photodetectors.¹–¹⁸ Currently, APbX₃ perovskite NCs (PNCs), where A is CH₃NH₃⁺ (MA), CH(NH₂)₂ (FA⁺), or Cs and X is Cl⁻, Br⁻, or I⁻, are widely explored, and several synthesizing strategies have been developed. In 2014, Pérez-Prieto et al. reported the preparation of 6 nm sized hybrid organic-inorganic MAPbBr₃ PNCs for the first time by using ammonium bromide with a medium-sized chain that enables PNCs to disperse in a wide range of organic solvents.¹⁹ Subsequently, Zhong et al. and Zeng et al. developed a ligand assisted supersaturated recrystallization method to fabricate MAPbX₃ and CsPbX₃ PNCs, respectively¹⁷,¹⁸ and later Levchuk et al. synthesized FAPbX₃ PNCs through a similar approach.¹⁹ Importantly, a widely used synthetic route called hot injection was concurrently developed by Protesescu et al.¹ One then, emulsion synthesis, solvothermal synthesis, microfluidic synthesis, and so on²⁰–³⁴ have also been reported to prepare APbX₃ PNCs.

Notably, the abovementioned approaches belong to the so-called bottom-up strategy, and the monodisperse APbX₃ colloidal PNCs are produced via nucleation/growth of precursor ions in solution. Considering the soft feature of metal halide perovskites and their facile crystallization, a top-down strategy might also be applied to fabricate APbX₃ PNCs. For the top-down synthesis, external forces or energies were generally exerted on bulk materials to reduce the particle sizes into the nanoscale. Recently, solvent-free ball-milling synthesis was demonstrated to be applicable for preparing APbX₃ bulk powders.³⁵,³⁶ Interestingly, Protesescu et al. reported a facile mechanochemical synthesis of CsPbBr₃ and FAPbBr₃ PNCs using a commercial ball mill,¹⁷ which involved simple mechanical grinding of bulk perovskite materials and their facile crystallization, a top-down strategy might also be applied to fabricate APbX₃ PNCs. For the top-down synthesis, external forces or energies were generally exerted on bulk materials to reduce the particle sizes into the nanoscale. Recently, solvent-free ball-milling synthesis was demonstrated to be applicable for preparing APbX₃ bulk powders.³⁵,³⁶ Interestingly, Protesescu et al. reported a facile mechanochemical synthesis of CsPbBr₃ and FAPbBr₃ PNCs using a commercial ball mill,¹⁷ which involved simple mechanical grinding of bulk perovskite materials in the presence of mesitylene and oleylamine halide. Unfortunately, the usage of specific solvent and complex ligand limited the universal synthesis. For instance, compositional modifica-
tion of PNC band gaps by milling bulk CsPbBr3 and oleylammunium iodide was not successful so far.

Herein, we develop a universal manual grinding method to prepare whole-family MAPbX3, FAPbX3, and CsPbX3 PNCs for the first time. Impressively, this strategy does not require dissolving AX and PbX2 precursors in the solvent and can be operated in an open atmosphere and at room temperature. The procedure is quite simple, that is, putting raw materials into a mortar with cyclohexane, oleic acid (OA), and oleylamine (OM) and manually grinding for a certain duration with a pestle to obtain the products. The versatility of this synthesis approach is demonstrated by fabricating different kinds of perovskite nanoparticles. The brightly emitting APbX3 PNCs exhibit a high PLQY up to 92%, and the visible luminescence originating from exciton recombination can be regulated from 400 to 780 nm via modifying halogen components in PNCs. Moreover, it is interestingly found that this strategy can be extended to realize the substitution of Pb2+ ions by specific dopants, such as Mn2+ ions.

■ EXPERIMENTAL SECTION

Materials and Chemicals. Lead halides (PbX2, 99.99%; Aladdin), cesium halides (CsX, 99%; Macklin), methylammonium halide (MAX, 99.5%; Xi’an Polymer Light Technology), formamidine halide (FAX, 99.5%; Xi’an Polymer Light Technology), cesium acetate (CsOAc, 99%; Macklin), formamidine acetate (FAOAc, 99%; Macklin), OA (90%; Aldrich), OM (80−90%; Aldrich), cyclohexane (99.7%, Macklin), dimethyl sulfoxide (DMSO, 99.8%, Macklin), and poly(methyl methacrylate) (PMMA, Macklin) were used as received.

Grinding Synthesis of APbX3 PNCs. Taking MAPbX3 as a typical example, PbX2 (0.2 mmol) and MAX (0.16 mmol) powders were put into an agate mortar, and 2 mL of cyclohexane was added. After grinding for 20 min to mix these powders well, OA (150 μL) and OM (30 μL) were introduced and then continued to grind for 100 min. Because cyclohexane is volatile, it was continuously added during grinding. After completion of grinding, the product was dispersed in 4 mL of cyclohexane and further purified by appropriate centrifugation. In the purification process, the original sample needs to be centrifuged three times. First, the product was centrifuged at a speed of 2000 rpm for 5 min, and the sediment was discarded. Second, the supernatant was centrifuged again at 5000 rpm for 5 min, and the sediment was discarded. Finally, the supernatant was centrifuged at 12000 rpm for 5 min, and the precipitation was the target product. The obtained MAPbX3 PNCs were redispersed in...
cyclohexane for further usage. The synthesis of FAPbX_3 PNCs and CsPbX_3 PNCs is similar to that of MAPbX_3. The only difference is that MAX was replaced by FAX or CsX as the precursor.

**Grinding Synthesis of Mn^{2+}-Doped CsPbCl_3 PNCs.** The synthesis of Mn^{2+}-doped CsPbCl_3 PNCs is similar to that of CsPbX_3 ones. The only difference is that extra MnCl_2 (0.08 mmol) was added in raw materials during grinding and the amount of PbCl_2 changed to 0.16 mmol to assure that Cs:Pb:Mn was 2:2:1.

**Supersaturated Recrystallization Synthesis of FAPbX_3 PNCs.** First, the precursor was prepared by dissolving PbX_2 (0.2 mmol) and FAX (0.2 mmol) in DMSO (5 mL). After complete dissolution, OA (100 μL) and OM (50 μL) were added to stabilize the precursor solution. Then, 0.1 mL of the precursor solution was quickly introduced into the toluene solution (5 mL) to induce supersaturated crystallization of PNCs with vigorous stirring. Bright green emission was immediately observed after the injection.

**Synthesis of PNCs Dispersed in PMMA Film.** 1g of PMMA was dissolved in 10 mL of toluene at 80 °C and cooled down to room temperature to form stock solution (100 mg/mL). Afterward, 1 mL of stock solution was mixed with 1 mL of PNC (prepared by grinding for 2 h) solution in toluene (10 mg/mL) and dropwise casted on the cleaned glass substrate followed by drying in vacuum. Notably, the blue, green, and red PNC films were prepared by dispersing MAPbCl_3, MAPbBr_3, and MAPbBr_3:FNCs in PMMA, respectively.

**Construction of PNC-Based White-Light-Emitting Diode (WLED).** As a proof-of-concept experiment, a WLED device was directly fabricated by coupling the UV chip with the as-prepared PNC gels in the order of red layer, green one, and blue one. Opaque silica gels were filled around the edges of the LED to avoid the leakage of UV light.

**Characterizations.** X-ray diffraction (XRD) patterns of the as-prepared APbX_3 PNCs were recorded using a powder diffractometer (MiniFlex600 RIGAKU) with Cu Kα radiation (λ = 0.154 nm). Transmission electron microscope (TEM) observation was performed on a JEOL JEM-2010 operated at 200 kV accelerating voltage. The surface states of MAPbBr_3 PNCs were examined by X-ray photoelectron spectroscopy (XPS) using a VG Scientific ESCALAB MkII spectrometer. Ar+ etching on MAPbBr_3 PNCs for 5 s each time was carried out to obtain the Br/Pb ratio at different depths. Absorption, PL spectra, and PLQY data for the APbX_3 PNCs were recorded on an Edinburgh Instruments (EI) FS5 spectrometer equipped with a continuous (150 W) xenon lamp and a 15 cm integrating sphere. Time-resolved PL spectra for exciton recombination of the obtained product were detected on a fluorescence lifetime spectrometer (EL, LifeSpec-II) based on a time correlated single photon counting technique under the excitation of 375 nm picosecond laser. The average decay lifetimes were evaluated via the equation of τ = ∫ I(t)dt/I₀, where I(t) is the time-related emission intensity and I₀ is the peak intensity. Electroluminescence (EL) spectra of the constructed devices were recorded in a HAAS-2000 spectroradiometer (Everline) under the forward bias of 20 mA. All the experiments were carried out at room temperature.

**RESULTS AND DISCUSSION**

The grinding synthesis of APbX_3 PNCs is accomplished by simply grinding the mixture of the AX and PbX_2 powders with long-chain organic ligands (OA and OM) and cyclohexane for a certain duration. Purification of PNCs is realized via elaborately controlling separation procedures for the as-prepared products (Experimental Section). Notably, the as-prepared products will be unstable without the addition of OA and OM, indicating that appropriate amounts of ligands are necessary for the present grinding synthesis. A typical TEM image of the obtained MAPbBr_3 PNCs shows that they are cubic-shaped and monodispersed with sizes of 10–25 nm (Figure 1a). A high-resolution TEM (HRTEM) micrograph of an individual MAPbBr_3 particle (Figure 1b) verifies its single-crystalline nature with high crystallinity and well-resolved lattice fringes. A typical lattice spacing of 2.9 Å, corresponding to the (200) plane of the cubic perovskite phase, is clearly observed (Figure 1b). The microstructure of the cubic phase of MAPbBr_3 PNCs is based on a three-dimensional network of the corner-shared PbBr_6 octahedra linked by Br⁻ ions, where each Pb²⁺ ion coordinates with six Br⁻ ions and interstitial MA⁺ cations are located in the cages of PbBr_6 octahedra (Figure 1c). The PL spectrum of MAPbBr_3 PNCs shows a narrow emission band centered at 522 nm, and the corresponding absorption spectrum exhibits a typical exciton absorption peak at 526 nm, suggesting that the luminescence of the obtained product originates from direct exciton recombination. In fact, the emission spectra of MAPbX_3 can be tuned over the entire visible spectral region of 400–780 nm by adjusting halide compositions in raw materials. As demonstrated in Figure 1d, multicolor luminescence of MAPbX_3 PNCs without defects. XRD patterns of MAPbX_3 PNCs are well coincident with those of the cubic CsPbBr_3 phase (JPCDS No. 75-0412). Varying the halogen element and content in MAPbX_3 can induce a gradual shift of diffraction peaks but will not alter the cubic structure of MAPbX_3 PNCs (Figure 1f). Interestingly, halogen anion exchange can be also achieved by grinding the as-prepared MAPbX_3 PNCs with the extra introduction of PbX_2 (X = Cl, I), which is beneficial to regulate emissive color more precisely and conveniently (Figure S1).

FWHM values of different MAPbX_3 (X = Cl, Cl/Br, Br/Br, Br/I, I) PNCs were determined and are given in Figure 1e and Table S1. Apparently, the emission bandwidth of MAPbX_3 increases from 12 to 42 nm by changing X from Cl to I, which is probably attributed to size-induced inhomogeneous broadening. According to theoretical calculations by Proteescu et al., 3 Bohr exciton diameters for CsPbCl_3, CsPbBr_3, and CsPbI_3 are 5, 7, and 12 nm, respectively, and the variation trend of Bohr exciton diameters for MAPbX_3 is similar. Generally, the emission wavelength will not be altered when the sizes of PNCs are larger than the Bohr exciton diameter; however, a blue shift will occur when the sizes are smaller than the Bohr exciton diameter. Therefore, as X changes from Cl to I, the size-induced inhomogeneous broadening will become more significant for long-wavelength emission, leading to a gradual increase of FWHM. The X-dependent emission intensities for different MAPbX_3 PNCs are provided in Figure S2a. PL intensity significantly increases when X changes from Cl to Br and then slightly decreases with further alteration from Br to I. As a supplement, PLQYs for these MAPbX_3 PNCs were also determined and are tabulated in Table S1, showing a similar variation trend to emission intensity. Time-resolved PL spectra of MAPbX_3 (X = Cl, Br, I) PNCs exhibit a gradual increase in average decay lifetime (2–94 ns) as the composition changes from MAPbCl_3 to MAPbI_3 (Figure 2b, Table S1). The inverse correlation between halide-controlled band gap and decay lifetime has been well demonstrated in APbX_3 (A = MA, Cs, FA) PNCs previously prepared by other methods. The observed trend in decay lifetime is attributed to intrinsic optical properties of halide perovskites, where the overlap
between the electron and hole wave functions will be reduced and the nonadiabatic charge-phonon coupling will be weakened with the substitution of Cl by heavy Br or Br by heavier I.41

To trace the evolution of morphology and size of MAPbBr3 during grinding, SEM observation on the samples prepared by grinding for 10 min, 30 min, 1 h, 2 h, and 4 h (without centrifugation) was performed. It is evidenced that elongation of grinding duration can gradually reduce the size of cubic-shaped particles into the nanoscale and make them more uniform (Figure 2a–e). A SEM image of the MAPbBr3 sample (2 h) after elaborated centrifugation treatment in low magnification (Figure 2f) confirms that the product after purification is indeed nanoparticles with a uniform size distribution. TEM images of CsPbCl3 and CsPbI3 products (Figure S2c,d) clearly demonstrate that the particle sizes are in the range of 10–25 nm. It is seriously worthy to ponder about the mechanism to synthesize metal halide PNCs by such simple grinding. Herein, taking bromide as an example shown in Figure 3, we propose that the mixture of cubic MABr and orthorhombic PbBr2 (XRD data are presented in Figure S3a,b) will spontaneously and rapidly induce the formation of MAPbBr3 perovskite microcrystals and further grinding will break the bulk phase into smaller nanoparticles. As shown in Figure S3c, luminescence of perovskite quickly occurs after a simple mixing of MABr and PbBr2 for 5–10 s. After grinding for 10 min, the obtained product is pure cubic MAPbBr3 phase even without addition of any other solvents (Figure S3d), indicating easy occurrence of chemical reaction between MABr and PbBr2 to produce MAPbBr3.42,43 As we all know, halogen anion exchange in APbX3 is easily realized to obtain anion hybrid perovskites such as APb(Cl/Br)3 and APb(Br/I)3.44 In the present work, a single emission band was observed for the as-prepared MAPbX3 (X = Cl/Br, Br/I) hybrid perovskites (Figure 1e), confirming that two kinds of halogen ions are homogeneously distributed in perovskites prepared by grinding. This gives us a hint that the cations should experience the same process, that is, homogenization of MA and Pb ions followed by the conversion of the anorthic Pb polyhedron into the cubic one (Figure 3a), where the exorting manual grind is believed to be the driving force. Further grinding will break the perovskites into nanoparticles, and elongation of grinding time will get smaller and more homogeneous PNCs (Figure 3b). Since surfactants (OA and OM) were introduced in the grinding process, they were well attached on the new interface when the bulk phase was cut into smaller particles (Figure 3b), enabling them to well disperse in nonpolar solvents such as cyclohexane (Figure 1d). As demonstrated in Figure 3c, the product became yellow after grinding and can yield bright and uniform green luminescence under the irradiation of the UV lamp.

Furthermore, the influence of grinding time on optical properties of MAPbBr3 PNCs was investigated. As shown in
Figures S4 and S5, all the samples prepared with different grinding times are pure cubic phase. Importantly, it is found that grinding time has no obvious effect on the spectral profile and position (Figure S6), indicating that the target product can be produced in an extremely short time (10 min). As shown in Figure 4a and Figure S7a, high PLQYs up to 75−92% are obtained for the as-prepared MAPbBr3 PNCs via grinding for 10−120 min. However, the value tends to drop with the increase of grinding time. As a comparison, the variation of PLQYs for MAPbBr3 sediments (microcrystals) obtained after centrifugation is also given in Figure 4a, showing lower PLQYs than those for the corresponding PNCs. Herein, PLQYs were employed to characterize the stability of PNCs since the product will easily decompose after exposing in air. Figure S7b shows dependence of PLQY values on exposing time in air for the MAPbBr3 PNCs prepared by grinding for 30 min and the corresponding bulk materials (microcrystals). Apparently, PLQYs of MAPbBr3 PNCs are always higher than those of bulk materials (Figure S7b). After exposing in air for 30 days, about 60% of PLQY of MAPbBr3 PNCs can be remained while that of bulk materials is lowered down to 5% after 7 days, indicating that the stability of MAPbBr3 PNCs is better than that of bulk ones. Previously, Zhong et al. demonstrated that the coordination of solvents played an important role in

Figure 4. (a) Absolute PLQY values versus grinding time for MAPbBr3 PNCs (after purification) and microcrystals (obtained from sediment). High-resolution XPS spectra of (b) Pb 4f and (c) Br 3d for the MAPbBr3 PNCs. (d) Br/Pb ratio versus number of etching by Ar+ ions.

Figure 5. (a) PL spectra of FAPbX3 PNCs prepared by grinding method and supersaturated recrystallization route. (b) Corresponding luminescence photographs of FAPbX3 PNCs under irradiation of UV (365 nm) lamp. (c) Variation of band gaps versus halogen component in the FAPbX3 (MAPbX3) PNCs prepared by the grinding method and FAPbX3 PNCs prepared by supersaturated recrystallization route.
determining the stability of iodide perovskites. In the present work, only cyclohexane was used as the solvent to assist manual grinding and no experiment concerning the role of different solvents on stability was carried out, which may be investigated in our further work.

XPS characterizations for the MAPbBr₃ PNCs (Figure S8, Figure 4b,c) were carried out to investigate their surface states. Typical Pb 4f and Br 3d signals are detected (Figure 4b,c). Specifically, the Br 3d signal can be fitted into two peaks at binding energies of 68 and 69 eV (Figure 4c), which are attributed to the inner and surface Br ions, respectively. To further confirm this, Pb 4f and Br 4d XPS spectra of MAPbBr₃ PNCs upon Ar⁺ etching 10 times were recorded. As evidenced in Figure 4d, the original MAPbBr₃ PNCs show the Br-rich surface with a Br/Pb ratio of 4.5 and after etching by Ar⁺ ions, the Br/Pb ratio is close to 3 (Figure 4d). Therefore, it is concluded that the high PLQY and superior stability for the present MAPbBr₃ PNCs are probably attributed to the self-passivating effect of the Br-rich surface, which has been previously demonstrated in all-inorganic CsPbBr₃ QDs prepared by the supersaturated recrystallization route.

Notably, an interesting phenomenon was observed when we intended to prepare FAPbX₃ PNCs (Figure S9), where the related spectroscopic data were not coincident with what we expected. Herein, all the FAPbX₃ (X = Cl/Br, Br/I) PNCs prepared by the grinding method were achieved by grinding the different Cl-to-Br or Br-to-I precursors for the same duration of 2 h. For instance, FAPbBr₁.₅Cl₁.₅ PNCs was previously reported to yield blue emission at ~465 nm. However, the product prepared by the grinding method exhibited green emission at 511 nm (Figure 5a), indicating that Br⁺ ions rather than Cl⁻ ones are dominant in FA-based halogen hybrid PNCs. Actually, the same issue occurred when we synthesized FAPbBr₁.₅I₁.₅ PNCs, which showed I⁻ dominant red emission (Figure 5a). For better comparison, using the same precursors and halogen ratios, a series of FAPbX₃ (X = Cl, Br, I, Cl/Br, Br/I) PNCs were also prepared by a supersaturated recrystallization route. As revealed in Figure 5a, both samples show typical multicolor emissions in the visible full-spectral region, but the emission peak positions gradually transformed into the orthorhombic CsPbX₃ and CsPbBr₃ PNCs crystallize in the cubic phase structure while the CsPb(Br/I)₃ and CsPbI₃ PNCs are orthorhombic (Figure S13). Notably, one-step synthesis of orthorhombic CsPbI₃ PNCs was rarely reported previously and most results showed that the cubic structured CsPbI₃ was generally produced first and then gradually transformed into the orthorhombic one. Finally, FAOAc and CsOAc instead of FABr and CsBr, respectively, were adopted to synthesize PNCs. XRD patterns (Figure 6a), and PL spectra (Figure S14) evidenced that different sources of A-site ions could be applied in the grinding synthesis. In fact, the (Cs/FA)PbBr₃ hybrid PNCs can be also prepared by this grinding method, as evidenced in Figure S15. Besides A-site ions and halogen ions, we also put sight in the B-site ions. As shown in Figure S16, Mn⁺⁺-doped...
CsPbCl\(_3\) PNCs can be successfully fabricated by the grinding method after introducing an extra Mn\(^{2+}\) source (such as MnCl\(_2\)) into the precursors. Besides sharp violet exciton recombination emission of CsPbCl\(_3\), broadband red luminescence assigned to the \(4T_1 \rightarrow 6A_1\) transition of Mn\(^{2+}\) was also detected (Figure 6b). Additionally, a Mn\(^{2+}\) decay curve was recorded (Figure S17). Evidently, the evaluated Mn\(^{2+}\) decay lifetime of 1.2 ms is close to the value previously reported\(^{49,50}\), verifying the feasibility of incorporating Mn\(^{2+}\) dopants into the CsPbCl\(_3\) crystalline lattice by the grinding method.

Finally, we demonstrate the possible application of the present MAPbX\(_3\) PNCs prepared by the grinding method as color converters in solid-state-lighting. As illustrated in Figure 7a, the MAPbCl\(_{1.5}\)Br\(_{1.5}\), MAPbBr\(_3\), and MAPbI\(_3\) PNCs dispersed in PMMA yield three primary colors of blue, green, and red, respectively, under UV lamp irradiation. As a proof-of-concept experiment, LED devices were constructed by coupling blue MAPbCl\(_{1.5}\)Br\(_{1.5}\), green MAPbBr\(_3\), and red MAPbBr\(_3\)I emitting films as color converters with a UV chip. EL spectra show a blue emission band originating from MAPbCl\(_{1.5}\)Br\(_{1.5}\) PNCs, a green one assigned to MAPbBr\(_3\) PNCs, and an orange one attributed to MAPbBr\(_3\)I PNCs (Figure 7b–d). The proper adjustment of the thicknesses of blue, green, and red PNC films (2, 1, and 1.5 mm, respectively) can lead to bright white-light luminescence for the constructed LED device with a color rendering index (CRI) of 85, correlated color temperature (CCT) of 4460 K, luminous efficiency (LE) of 15 lm/W, and color coordinates of (0.360, 0.354) (Figure 7e,f). Compared to the previously reported values\(^{18,51−53}\), the optoelectronic performance for the fabricated WLED, especially LE, should be further optimized by improving PLQYs of blue- and red-emitting perovskite components. The related efforts are currently on the way.

**CONCLUSIONS**

In summary, we have developed a novel type of colloidal synthesis for the whole-family MAPbX\(_3\), FAPbX\(_3\), and CsPbX\(_3\) (X = Cl, Br, I and their mixtures) PNCs with multicolor tunable emissions via a simple grinding strategy, which can be operated at room temperature and in an open atmosphere. Grinding duration evoked experiments evidenced that the mixture of AX and PbX\(_2\) would spontaneously and rapidly induce the formation of APbBr\(_3\) perovskite microcrystals and further grinding was beneficial to break the bulk phase into nanoparticles with sizes of 10–25 nm. Taking MAPbBr\(_3\) as a typical sample, XPS data confirmed its Br-rich surfaces,
enabling to achieve high PLQY up to 92% and superior stability. Impressively, Mn2+ dopants were demonstrated to be able to incorporate into the CsPbCl3 crystalline lattice by this grinding method to produce both sharp violet exciton emission of PNCs and broadband orange emission of Mn2+ activators. As a result, a prototype LED device was constructed by employing the as-fabricated blue/green/red PNC films as color converters, producing bright white-light luminescence with excellent optoelectronic properties. It is believed that the present work will provide an effective route to easily synthesize perovskite nanoparticles with novel optical properties and even fabricate other low-Pb or Pb-free perovskite materials.

■ ASSOCIATED CONTENT

 Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.8b19002.

Extra absorption/PL spectra, time-resolved luminescence spectra, XRD patterns, SEM images XPS data, and luminescence photographs (PDF)

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: dqchen@fjnu.edu.cn.

ORCID

Daqin Chen: 0000-0003-0088-2480

Notes

The authors declare no competing financial interest.

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