Stabilization of Lead-Reduced Metal Halide Perovskite Nanocrystals by High-Entropy Alloying

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ABSTRACT: Colloidal metal halide perovskite (MHP) nanocrystals (NCs) are an emerging class of fluorescent quantum dots (QDs) for next-generation optoelectronics. A great hurdle hindering practical applications, however, is their high lead content, where most attempts addressing the challenge in the literature compromised the material’s optical performance or colloidal stability. Here, we present a postsynthetic approach that stabilizes the lead-reduced MHP NCs through high-entropy alloying. Upon doping the NCs with multiple elements in considerably high concentrations, the resulting high-entropy perovskite (HEP) NCs remain to possess excellent colloidal stability and narrowband emission, with even higher photoluminescence (PL) quantum yields, $\eta_{\text{PL}}$, and shorter fluorescence lifetimes, $\tau_{\text{PL}}$. The formation of multiple phases containing mixed interstitial and doping phases is suggested by X-ray crystallography. Importantly, the crystalline phases with higher degrees of lattice expansion and lattice contraction can be stabilized upon high-entropy alloying. We show that the lead content can be approximately reduced by up to 55% upon high-entropy alloying. The findings reported here make one big step closer to the commercialization of perovskite NCs.

INTRODUCTION

Metal halide perovskites (MHPs), with the general formula of $\text{ABX}_3$, where $\text{A}$ is a monovalent organic/inorganic cation, $\text{B}$ is a divalent metal cation, and $\text{X}$ is a halide anion, have generated considerable research efforts aimed at demonstrating their outstanding optical properties. The most studied compounds of this family are based on lead, with the general formula $\text{APbX}_3$, because of their defect tolerance that originated from the shallowly populated defect states near the band edges. This unique property enables the $\text{APbX}_3$ nanocrystals to possess very high photoluminescence (PL) quantum yields, $\eta_{\text{PL}}$, and narrowband emission, which give rise to high-efficiency optoelectronic devices, including photovoltaics (PVs), photodetectors, and light-emitting diodes (LEDs).

The actual implementation of $\text{APbX}_3$ NCs in photonic devices toward commercialization, however, has faced a number of challenges. Inarguably, the greatest one is about the toxicity of lead. Following the development of lead-free MHP PVs, divalent cations with similar ionic radii, such as $\text{Sn}^{2+}$, $\text{Cd}^{2+}$, and $\text{Zn}^{2+}$, were examined. However, most lead-free perovskite NCs either compromised their optical properties or colloidal stability. Accordingly, lead-reduced MHPs, in which the B-site lead ions are partially replaced, have become increasingly attractive. Lead-reduced MHP NCs have been synthesized using the hot-injection (HI) method, where a complex reaction setup is required, as well as the postsynthetic approaches by doping with $\text{Mg}^{2+}$, $\text{Mn}^{2+}$, $\text{Sn}^{2+}$, $\text{Cd}^{2+}$, and $\text{Zn}^{2+}$.

It is noted that the latter approach had rather limited success as compared to the postsynthetic A- and X-site mixing owing to the structural rigidity of $\text{PbX}_6$ octahedron. For example, it has been shown that one can only add a relatively small amount of secondary elements in the $\text{CsPb}_{1-x}\text{M}_x\text{Br}_3$ perovskite NCs ($\text{M} = \text{Sn}^{2+}, \text{Cd}^{2+}, \text{or} \text{Zn}^{2+}; 0 < x \leq 0.1$). To our knowledge, it is not yet possible to significantly increase the content of secondary B-site ions without compromising the production yield and optical performance.

From a fundamental point of view, the partial replacement of lead ions in perovskite lattices is analogous to alloying, which has long been used to alter material properties. Traditional alloying usually refers to the addition of relatively small amounts of secondary elements to a primary element. Intriguingly, recent advance in high-entropy alloys (HEAs) suggests that the combination of multiple principal elements in high concentrations could increase the configurational entropy of mixing that overcomes the enthalpies of compound formation.

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formation, thereby stabilizing the HEAs. Very recently, A-site doping of lead halide perovskite (LHP) NCs has shown to improve the optical properties and chemical stability due to the entropy of mixing. Back to the 2010s, high-entropy perovskite materials, including high-entropy perovskite oxides (HEPOs) and high-entropy perovskite fluorides (HEPFs) had emerged. These high-entropy perovskite compounds have demonstrated outstanding catalytic properties, serving as efficient electrocatalysts in the oxygen evolution reaction. The preparation of HEPOs, however, demands a process temperature of greater than 1000 °C. Clearly, it is desirable to develop less energy-consuming approaches for the synthesis of high-entropy perovskite materials.

Inspired by the underlying principle of high-entropy alloying, we hypothesized that the entropy of mixing could favor the stabilization of lead-reduced perovskite NCs by mixing with multiple secondary B-site elements, termed the high-entropy perovskites (HEPs). In this report, we synthesized the HEP NCs for the first time and investigated their optical, crystallographic, and compositional characteristics.

## RESULTS AND DISCUSSION

The HEP NCs were synthesized using a modified protocol developed by our group to overcome the solubility difference between precursors, namely, the ligand-assisted solid-phase synthesis (LASPS). First, the parent colloidal MAPbBr₃ NCs were prepared and dispersed in toluene (MA⁺ = CH₃NH₃⁺). The NC solution was then stirred with an excess solid powder mixture of metal bromides, MBr₂ (M = Mg²⁺, Zn²⁺, and Cd²⁺), and a small amount of long-chain organic surfactants, such as oleic acid and oleylamine, forming dynamic binding on the NC surface. The surfactants assist gradual dissolution of MBr₂ solid powders by forming inverse micelles that increase the chemical potentials of secondary metal elements in solution, thereby slowly replacing lead in NCs. Metal bromide salts were chosen to prevent undesirable halide exchange. Each reaction was performed under magnetic stirring in nitrogen at room temperature for several hours to reach saturation of solid solubility, followed by removing excess surfactants and MBr₂ by a number of polar solvents, such as methyl acetate, acetonitrile, and ethanol.

The protocol presented here allows us easy access to the compositional space without taking into account the solubility limit of metal precursors in antisolvents, which is cumbersome in many HI and postsynthetic approaches, particularly suitable for studying the HEPs and their synthesis (Figure 1a). We noticed that the protocol developed here highly preserved the solution optical density, which is demonstrated by the photographs of the synthesized colloidal solutions under UV excitation, in which we label each sample with the B-site elements, for example, PbZnCd for MA(PbZnCd)Br₃ HEP NCs.

As compared to parent MAPbBr₃, the synthesized single-doped perovskite NCs and the HEP NCs exhibit different degrees of blueshift in their PL and absorption spectra (Figure 2a and Supplementary Figure S1), with the emission bandwidth remaining nearly unchanged. A possible explanation for the observed blueshift is the lattice contraction of the perovskite unit cell upon alloying. Surprisingly, upon alloying, the ηPL value increases from ~75% to up to ~95% (Figure 2b), together with a decrease in the average PL lifetime, τavg, from 27.3 ns to as low as 4.6 ns (Figure 2c). More notably, there seemed a stepwise trend that the fluorescence
lifetime becomes shorter when more secondary elements are involved, with the exception of MA(PbMgZnCd)Br3 HEP NCs. These results are of practical interest because fluorophores with high $\eta_{PL}$ and low $\tau_{avg}$ are desirable for most photonic applications. In general, our results suggest that high-entropy alloying does not compromise the NC optical performance, but rather enhances it. For the detailed values for the characterized optical properties, please see Supplementary Table S1.

Clearly, the mechanism responsible for the enhanced optical properties is beyond a simple picture of defect passivation, in which the enhancement of $\eta_{PL}$ comes with an elongated PL lifetime.49,50 For B-site doping (or Pb replacement), it has been reported that the incorporation of divalent metal cations could give a shorter lifetime.32 In the HEP NCs, the lifetime can be further shortened to 5 ns, which is significantly shorter than that of the single-doped systems, confirming that high-entropy B-site doping stabilizes the LHP structure with a higher degree of Pb replacement.

We attribute the observed enhancement of emission characteristics upon alloying to the nature of intrinsic and surface defects and their interactions with metal cations.50−52 First, the divalent cations could rectify these intrinsic defects by occupying the vacancies within the crystal lattice, thereby increasing the short-range ordering in perovskite lattices.25,33 Second, the shallow surface trap states, which are responsible for the delayed fluorescence in perovskite NCs, were passivated by the metal and bromide ions, as reflected by the shortened lifetime and enhanced $\eta_{PL}$.35 The entropy of mixing (ED) patterns. For each sample, the two most intense diffraction rings, corresponding to (100) and (200) lattice planes, were preserved. In other words, the cubic crystalline structure of parent MAPbBr3 NCs is preserved. The size analysis reveals a small degree of size reduction for the metal-doped perovskite NCs. Specifically, metal-doped perovskite NCs have an average lateral size of $\pm$9 ± 2 nm, which is about 2 nm smaller as compared to parent MAPbBr3 NCs ($\pm$11 ± 3 nm). A similar degree of size reduction has also been observed for B-site-doped perovskite NCs synthesized via the hot-injection technique with mixed precursors.55 The difference in the size could result from the use of surfactants during the metal-doping process, whose polar nature is known to cause a degree of NC size reduction to quantum-confined

Figure 3. Structural characterization of HEP NCs. Cryo-STEM images, electron diffraction patterns, and corresponding size distribution graphs for (a) parent MAPbBr3, (b) MA(PbCd)Br3, (c) MA(PbMgZn)Br3, and (d) MA(PbMgZnCd)Br3 NCs, revealing that the NC shape, morphology, and crystallography are preserved upon alloying. Scale bars: 20 nm for STEM images and 2 nm for ED patterns.
matter.56 Although the metal-doped NCs possess similar sizes, they exhibit different PL emission wavelengths ($\lambda_{PL}$). In addition, there is a lack of extensive excitonic absorption features in the absorption spectra of the metal-doped perovskite NCs (Supplementary Figure S1), agreeing that the size of the NCs remains far larger than the excitonic Bohr radius, which is known to be $\sim$ 2 nm for MAPbBr$_3$.19 Overall, the small degree of size reduction of the single-doped NCs and the HEP NCs alone would not result in the considerable blueshift of the PL emission wavelength observed.

We carried out more crystallographic analysis for the drop-casted films using the powder X-ray diffraction (XRD) goniometer and the grazing-incidence wide-angle X-ray scattering (GIWAXS) at a synchrotron light source. Analogous to the ED patterns, the XRD patterns show two main peaks corresponding to the (100) and (200) lattice planes (Supplementary Figure S7). We determine the unit cell parameter $a = 5.9311(21)$ Å for the parent MAPbBr$_3$, cubic phase, consistent with the literature.60,61 The detailed crystallographic parameters are presented in Supplementary Table S2.

As for the HEP NCs, the XRD and GIWAXS patterns revealed a more complex picture. Because all the secondary elements considered here, Mg$^{2+}$, Zn$^{2+}$, and Cd$^{2+}$, have smaller ionic radius than Pb$^{2+}$, one would expect to see a degree of lattice contraction upon alloying.19 As expected for samples of nanosized crystallites, the reflections that originate from the perovskite NCs are very broad and also very weak for reflections at higher angles, which hampered the precise determination of the peak positions. No significant change in the average lattice parameter $a$ could be detected, revealing the complex nature of high-entropy alloying in colloidal perovskite NCs. The emergence of low-angle peaks in the XRD patterns could originate from the formation of layered structures (see Supplementary Figure S9). These findings are consistent with low-angle reflections in the GIWAXS patterns (Supplementary Figure S8). Furthermore, the formation of assembly structures during the high-entropy alloying process is suggested (scanning electron microscopy (SEM) image; see Supplementary Figure S9).

We further looked into the synchrotron GIWAXS patterns, which offer significantly higher resolution than benchtop XRD. Figure 4 magnifies the (100) plane peaks extracted from the GIWAXS patterns, revealing a clear trend that the diffraction peak becomes more asymmetric and multicomponent when more secondary elements are involved. We fitted each pattern with multicomponent Lorentzians according to the number of secondary elements involved in the system. Given the excellent agreement with the measured data, our observations are summarized as follows: (i) upon alloying, two sets of diffraction components emerge; one shift toward higher wavenumbers and the other toward lower wavenumbers, as compared to the parent MAPbBr$_3$ peak, (ii) when more secondary elements are involved, components with a higher degree of wavenumber shifts are attained; for example, for MA(PbMgZnCd)Br$_3$ HEP NCs, components centered at $q = 10.10$ and 11.07 nm$^{-1}$, corresponding to d-spacings of 6.22 and 5.67 Å were resolved, or remarkably $\sim$5.0% expansion and $\sim$4.5% contraction, and (iii) the summation of all components can therefore yield a peak maximum shifting to lower or higher wavenumbers.

Accordingly, the crystallographic evidence presented here elucidates the effects of high-entropy alloying on perovskite NCs. First, similar to many high-entropy alloy metallic systems,35,36 the HEP NC systems are multiphase systems rather than single-phase, solid solutions. Second, alloying with more than one secondary element results in the emergence of lattice expansion phases. Here, we term these phases the “interstitial phases,” as the smaller secondary elements can occupy some of the spaces within the perovskite lattices, yielding lattice expansion.61 On the other hand, we refer the “doping phases” to the lattice contraction phases, in which the lead sites were replaced by the secondary elements (see the arrows in Figure 4).32,62 Third, most importantly, when more secondary elements were added, the phases with higher degrees of lattice expansion and lattice contraction were stabilized. The important findings promise the stabilization of “lead-reduced” phases upon high-entropy alloying.

We systematically carried out energy-dispersive X-ray spectroscopy (EDXS) in a scanning electron microscope for the semiquantitative analysis of the elemental composition of the parent MAPbBr$_3$ NCs, single-doped perovskite NCs, and HEP NCs (Supplementary Figures S10 and S11). Figure 5 presents the characterized atomic ratios of Br to Pb (left axis) and Br to the sum of Pb and M (right axis) for all samples considered here. The Br/Pb ratio for parent MAPbBr$_3$ NCs is $3.49 \pm 0.06$. Remarkably, there exists a trend that the Br/Pb ratio increases with the number of secondary elements, increasing up to $7.31 \pm 0.87$ for MA(PbZnCd)Br$_3$ NCs and $7.56 \pm 1.95$ for MA(PbMgZnCd)Br$_3$ NCs. In other words, the lead content is approximately reduced by 55% upon high-entropy alloying. On the other hand, the Br/(Pb + M) ratios for most HEP NCs are slightly below 3, the ideal perovskite stoichiometry, independent of the number of secondary elements. We attribute the reduced Br/(Pb + M) ratios in
HEP NCs to the formation of interstitial phases, echoing our findings in Figure 4. We notice that the composition heterogeneity for HEP NC systems with more than two secondary elements, such as MA(PbZnCd)Br₃ and MA-(PbMgZnCd)Br₃, HEP NCs, is relatively high, as reflected by the increased error bars. It may suggest a degree of phase segregation during the formation of the HEP NCs, for which advanced nanometer-scale characterization would be required. In addition, there is an outlier, MA(PbMg)Br₃, having an unusually high Br/Pb ratio because of the fact that the EDXS peak for Mg K transition is very close to that for Br L transition at an energy of ~1.254 keV. This issue becomes less considerable for other HEP NC systems because their Mg content is relatively low.

Finally, the protocol presented here also worked for Mn²⁺ doping, yielding a strong blueshift of the emission wavelength to 486 nm. Additionally, a broad and weak PL shoulder peaking around 600 nm is visible (Supplementary Figure S12), which corresponds to the nominally forbidden Mn²⁺ d→d transition. The low PL intensity of the Mn²⁺ d→d transition can be attributed to an ineffective excitation energy transfer between the bromide-based perovskite donor material and the Mn²⁺ acceptor. Because a different emission mechanism is involved, we did not include it in our HEP analysis.

**CONCLUSIONS**

In summary, we report an approach to synthesize an interesting class of lead-reduced perovskite NCs, the HEP NCs. With a reduction of lead of up to 55%, the HEP NCs remain to possess excellent optical properties and colloidal stability. According to our crystallographic analysis, the formation of interstitial and doping phases upon high-entropy alloying is responsible for the stabilization of lead-reduced perovskite lattices. Although we report the usage of Cd, we anticipate the concept of high-entropy alloying presented here will open an avenue toward less-toxic and more environmentally friendly materials, which are strongly desirable for future device applications.

**ASSOCIATED CONTENT**

*Supporting Information*

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/jacs.1c12294.

Experimental section, absorption and additional PL spectra, stability measurements, additional photographs of the colloidal solutions under UV excitation, additional STEM images with corresponding size distribution graphs, additional electron diffraction patterns, XRD patterns, GIWAXS patterns, SEM image, EDXS analysis, PL characteristics including carrier lifetimes, and crystallographic parameters (PDF)

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*Notes*

The authors declare no competing financial interest.

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