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The Role of Antisolvents with Different Functional Groups in the Formation of Cs₄PbBr₆ and CsPbBr₃ Particles

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ABSTRACT: Compared to the high-temperature hot injection (HI) technique, the room-temperature supersaturated recrystallization (SR) approach is more hopeful to realize the industrialized production of CsPbX₃ (X = Cl, Br, and I) nanomaterials. However, accurate compositional control of the product is still difficult, and the role and underlying mechanism of antisolvents in the reprecipitation process remain unclear. Herein, CsPbBr₃ particles and CsPbBr₃/Cs₄PbBr₆ composites with certain proportions are synthesized using different antisolvents with the SR method. By adjustment of the polarity or functional group of antisolvents, it is found that the functional groups of antisolvents have a major impact on the composition of the products. Furthermore, the influential mechanism of different antisolvents on the compositions of products is investigated by combining electrostatic potential calculations and ultraviolet–visible absorption spectroscopy. It suggests that the interaction between functional groups of antisolvents have a major impact of the intermediate Pb-complex and further affects the separating rate of the Pb(II)-intermediate, leading to the formation of products with different compositions. A physicochemical mechanism is proposed to explain the formation of Cs₄PbBr₆ and CsPbBr₃. This work deepens the understanding of the formation mechanism of all-inorganic metal halide perovskite-related materials based on the SR method and provides new routes to achieve their controllable preparation.

1. INTRODUCTION

All-inorganic CsPbX₃ (X = Cl, Br, and I) perovskite materials have exhibited great application potential for optoelectronic devices, such as solar cells,¹⁻³ lasers,^{4,5} light-emitting diodes (LEDs,)⁶⁻⁸ and photodetectors.^{9,10} To achieve commercial applications of CsPbX₃ perovskite materials, several factors, i.e., high photoluminescence quantum yield (PLQY), accurate size controlling and composition adjusting, high stability, and mass production, are essential, which are related to appropriate synthetic methods. Two methods, high temperature hot injection (HI) and room temperature supersaturated recrystallization (SR), are usually adopted to synthesize CsPbX₃.^{11,12} As a common technique, the HI method can produce CsPbX₃ with high PLQY,^{13,14} and their sizes, morphologies, and phase structures can be adjusted by varying the reaction temperature, time, or the surfactants. $^{15-21}$ However, a high reaction temperature and inert atmosphere are required for the HI method, which seriously obstructs the industrialization process

of CsPbX₃. Compared with the HI method, the SR approach is more hopeful to realize the industrialized production of CsPbX₃ because of simple operation, low cost, and large-scale production. Thus, the SR technique has received much research attention.

Using the SR method, people have made great progress in controllable preparation of CsPbX₃ nanomaterials. Their composition, structure, morphology, and size of synthesized product can be adjusted by several main strategies, i.e., feeding rate of PbBr₂ and CsBr, the surfactant, and antisolvents with different polarities.^{22–25} One strategy for controlling the

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composition of the synthesized product is to adjust the feeding rate of PbBr₂ and CsBr. To achieve rational structural and compositional control, by adjusting the feeding rate of PbBr₂ and CsBr to 2:1, 1:2 or 1:1 and 5:1, CsPbBr₃, CsPbBr₃/ Cs₄PbBr₆, and CsPbBr₃/CsPb₂Br₅ can be obtained, respectively.²² In addition, to improve the stability of CsPbX₃, CsPbX₃/Cs₄PbX₆ heterostructures are prepared through optimizing the molar ratio of PbBr₂/CsBr and centrifugation time as well as the solution concentration, which exhibits better stability and higher PLQY than traditional CsPbX₃ nanocrystals.²³ The other strategy for engineering the morphology of the products is to adjust the surfactant. Organic ligands, as a surfactant, play imperative roles throughout the lifetime of the nanocrystals, such as aiding in solubilization and formation of monomers, influencing the availability of the monomers during the nucleation process, impacting the nucleation, passivating the formed nuclei, preventing further growth of the nanocrystals beyond the nanoscale, and offering colloidal stabilities.^{26,27} To adjust the morphology of products for further improving the optical performance of CsPbX₃, by varying the quantity of the ligands (oleylamine and oleic acid) and reaction time, CsPbBr₃ nanocrystals with six different morphologies (quantum dots, nanoplates, nanobars, nanocubes, nanorods, and nanowires) are fabricated.²⁴ Choosing appropriate antisolvents with different polarities is also an appropriate strategy because antisolvent is the trigger of the SR process and has significant effects on final products. For instance, to achieve large-scale preparation of perovskite-related Cs4PbBr6/CsPbBr3 microcrystals, Hu et al. synthesized CsPbBr₃/Cs₄PbBr₆ composites with different yields of CsPbBr3 to Cs4PbBr6 by selecting four antisolvents (toluene, dichloromethane, ethyl acetate, and ethanol) with different polarities and indicated that the size of the final product increases with the polarity difference between the polar solvent and the antisolvent.²⁵ However, the role and underlying mechanism of different types of antisolvents on the phase and structure of the synthesized products lack systematic study. In addition, up to now, no feasible characterization technique has been proposed to explore the complex reaction process due to the fast crystal growth rate of CsPbX₃ crystals. Hence, it is desirable to choose a practical characterization method and study the role of different antisolvents in the formation of synthesized products.

In this work, $CsPbBr_3$ crystals and $CsPbBr_3/Cs_4PbBr_6$ composites are prepared using a slightly adapted SR approach with different antisolvents. Extensive X-ray diffraction (XRD) analysis and electron microscopy examinations show that the type of antisolvent has significant influence on the constituents of synthesized products. The simple and practical ultraviolet–visible (UV–vis) absorption spectroscopy is combined with density functional theory (DFT) calculations to investigate the internal interactions between antisolvents and ligands. It is evidently demonstrated that the functional groups of antisolvents affect the coordination status of the Pb(II)-intermediate and further influence the reactants' precipitation rates. A reasonable mechanism is given to depict the influence of different antisolvents on formation of Cs_4PbBr_6 and $CsPbBr_3$ in the reprecipitation process.

2. EXPERIMENTAL SECTION

2.1. Materials. Cesium bromide (CsBr, 99.5%, Aladdin), lead bromide (PbBr₂, 90.0%, Aladdin), *N*,*N*-dimethylformamide (DMF, 99.5%, SCRC), oleic acid (OlAc, 90.0%, SCRC), oleylamine (OlAm,

90.0%, Aladdin), toluene (99.5%, SCRC), ethanol (99.7%, SCRC), acetone (99.5%, SCRC), n-propanol (99.5%, SCRC), n-butanol (99.5%, SCRC), isobutanol (99.5%, SCRC), ethyl acetate (99.5%, SCRC), benzene (99.5%, SCRC), *p*-xylene (99.5%, SCRC), and hexane (99.0%, SCRC). All chemical reagents were used directly without further purification.

2.2. Synthesis of the CsPbBr₃ Particles and CsPbBr₃/ Cs₄PbBr₆ Composites. 0.15 mmol of CsBr and 0.15 mmol of PbBr₂ were dissolved in 3.5 mL of DMF and stirred for 1 h in air at 30 °C. Then, 50 μ L of OlAm and 200 μ L of OlAc were added into the precursor solution to stabilize it. Subsequently, 10 mL of the antisolvent was quickly added into the precursor solution under vigorous stirring. Within 30 s, a yellow suspension was obtained. In the preparation procedure for CsPbBr₃ particles and CsPbBr₃/ Cs₄PbBr₆ composites, only the antisolvent was changed. Herein, four types of antisolvents were utilized, including aromatic hydrocarbons (toluene, benzene, and *p*-xylene), alcohols (ethanol, n-propanol, nbutanol, and isobutanol), acetone, and ethyl acetate.

To isolate all products from the crude solution, the solution was centrifuged at 10000 rpm for 15 min, and the resulting precipitate was washed twice and subsequently redispersed in corresponding antisolvents. To obtain particles with a uniform morphology and size, a two-step centrifugation process was implemented. Initially, the crude solution was centrifuged at 1500 rpm for 5 min. Subsequently, the precipitate (primary centrifugation products) was discarded, and the supernatant was centrifuged at 10000 rpm for 10 min. The resultant supernatant was then discarded, and the precipitate (secondary centrifugation products) was washed twice and redispersed in the corresponding antisolvents. The detailed yields of all products and primary and secondary centrifugation products are summarized in Table S1.

2.3. Characterization. X-ray diffraction (XRD) patterns were conducted on a Rigaku SmartLab SE apparatus using a Cu–K α_1 radiation source ($\lambda = 1.5406$ Å) between 10° and 70°. Inductively coupled plasma-optical emission spectroscopy (ICP-OES) measurements were made on a PerkinElmer Avio 500 Max Series ICP-OES. Scanning electron microscopy (SEM) images were obtained on a Regulus 8100 scanning electron microscope operating at 10 kV. The bright-field (BF) imaging and selected-area electron diffraction (SAED) were performed using a JEOL JEM 2100F transmission electron microscope (TEM) operating at 200 kV. To conduct the UV–vis absorption spectra measurements, a Macy UV-1900 spectrometer was used. The photoluminescence (PL) spectra were recorded using a Cary Eclipse fluorescence spectrophotometer. The ¹H NMR patterns were conducted on a Bruker Avance III HD 400 MHz.

XRD and ICP-OES measurements were performed for all the synthesized products obtained by high-speed centrifugation of the crude solution. SEM, TEM, UV-vis absorption, and PL spectroscopy measurements were performed for secondary centrifugation products.

To study the interaction mechanism between different antisolvents and OlAc, we carried out UV-vis spectra measurements according to the following procedure: (i) 4.5 μ L of OlAc diluted in 40 μ L of nonpolar hexane was used to obtain the UV-vis absorption spectrum of OlAc. (ii) 4.5 μ L of OlAc diluted in the mixture of 40 μ L of hexane and 20 μ L of OlAm was used to obtain the UV-vis absorption spectrum of carboxylate anions (OlAc⁻). (iii) 4.5 μ L of OlAc diluted in the mixture of 40 μ L of hexane, 20 μ L of OlAm, and 20 μ L of antisolvent (toluene, benzene, *p*-xylene, ethanol, n-propanol, nbutanol, isobutanol, acetone, or ethyl acetate) was used to obtain the UV-vis absorption spectrum of OlAc⁻ in different antisolvents.

2.4. Computation Methods. The geometry optimization and electrostatic energy calculation of antisolvent molecules were performed using the DMol³ program package in Materials Studio. The exchange-correlation potential was approximated by generalized gradient approximation (GGA) using Becke-Lee–Yang–Parr (BLYP) parametrization. Considering the solvent effects in experiments, dimethyl sulfoxide (DMSO), whose polarity is similar to that of DMF, is adopted to replace DMF in all the calculations based on a solvation model (COSMO).



Figure 1. (a) XRD patterns of as-synthesized products with toluene, ethanol, and acetone as antisolvents, respectively. (b-g) Corresponding SEM images and statistical size distributions of synthesized products. (All of the scale bars represent 3 μ m.) Insets are the corresponding enlarged SEM images. (All of the scale bars represent 300 nm.)

3. RESULTS AND DISCUSSION

XRD was used to investigate the crystal structure of the synthesized products when toluene, ethanol, and acetone are used as antisolvents, as shown in Figure 1a. It is found that the as-prepared products have evident variations when different antisolvents are utilized. When toluene was used, Cs₄PbBr₆/ CsPbBr₃ composites are produced with dominant Cs₄PbBr₆ (rhombohedral phase, PDF#01-073-2478) and few CsPbBr₃ (orthorhombic phase, PDF#01-072-7929), confirmed by the diffraction peaks marked by "*" and " ∇ ", respectively. When ethanol was used, the diffraction peaks are consistent with those of orthorhombic CsPbBr₃ (PDF#01-072-7929). For acetone, the products are CsPbBr₃/Cs₄PbBr₆ composites with a predominant CsPbBr₃. Generally, the mass ratio of different contents in compounds can be approximated by the quantification analysis of the XRD pattern,28 while the XRD patterns of CsPbBr3 and Cs4PbBr6 have some overlapped peaks, which makes it very difficult to quantify their actual mass ratios using XRD analysis. Therefore, the mole fractions of CsPbBr₃ and Cs₄PbBr₆ are estimated by measuring the cesium content through ICP-OES. The mass fractions of cesium in the products are measured to be 42.1%, 25.3%, and 32.9% when toluene, ethanol, and acetone are used as antisolvents, as shown in Table 1. Then the molar fractions of CsPbBr3 and Cs4PbBr6 in different products are calculated using the formulas in the Supporting Information (SI), which are summarized in Table 1. Compared with the XRD analysis results in Figure 1, the calculated molar fractions of CsPbBr₃ and Cs₄PbBr₆ in the products obtained in ethanol are very

Table 1. Mole Fraction of CsPbBr₃ and Cs₄PbBr₆ in the Products Obtained in Different Antisolvents

		Mole fraction		Revised mole fraction $(k = 1.1)$	
Antisolvent	Mass percent concn of Cs in product	CsPbBr ₃	Cs ₄ PbBr ₆	CsPbBr ₃	Cs ₄ PbBr ₆
Toluene	42.1%	7.3%	92.7%	8.2%	91.8%
Ethanol	25.3%	78.0%	22.0%	100.0%	0.0%
Acetone	32.9%	52.0%	48.0%	58.7%	41.3%

unreasonable. Considering the nonstoichiometric defects on the exposed surfaces of particles, we introduced a correction coefficient k as described in the SI and revised the values of mole fractions of CsPbBr3 and Cs4PbBr6 in the different products. Figure 1b-g presents the corresponding SEM images and statistical size distributions of secondary centrifugation products. Figure 1b and c shows that the products prepared using toluene as the antisolvent have a dominant hexagonal shape with an average edge length of around 316 nm, corresponding to rhombohedral Cs₄PbBr₆. In addition, some orthorhombic phase CsPbBr3 nanoparticles with an average edge length of around 66 nm are also observed (Figure S1a and c). When ethanol is used as an antisolvent, pure CsPbBr₃ particles with an average edge length of around 244 nm form (Figure 1d and e). The synthesized products obtained in acetone are mainly CsPbBr3 particles with an average edge length of around 206 nm (Figure 1f and g). In addition, some large agglomerations with a blurred hexagonal shape are



Figure 2. Typical BF TEM images and enlarged BF TEM images of synthesized products with toluene (a and b), ethanol (c and d), and acetone (e and f) as antisolvents. Insets are the corresponding SAED patterns.

observed, as shown in Figure S1b and d, which should be Cs_4PbBr_6 . Furthermore, TEM examinations were performed to characterize the morphology of the synthesized products using different antisolvents. Figure 2 shows the typical TEM images and SAED patterns of the particles obtained in toluene, ethanol, and acetone. In Figure 2a, many hexagonal particles are observed as the main product, which is coincident with the SEM result. The SAED pattern of a single particle in the inset of Figure 2b indicates that it is single crystalline. Similar nanoparticles were found in the products of ethanol and acetone, as displayed in Figure 2c and e, respectively. The corresponding SAED patterns can be indexed to orthorhombic CsPbBr₃, which is consistent with the XRD results.

From Figures 1 and 2, we can see that the compositions and sizes of the as-synthesized products obtained in three antisolvents are different. However, the three antisolvents (toluene, ethanol, and acetone) have different polarities and functional groups. Therefore, it is really difficult to verify which factor plays a dominant role on the composition and size of the final products, although a previous report suggests that the polarity of antisolvents greatly affects the size and composition of the product.²⁵ On this account, we conducted several comparative experiments to identify the dominating roles of the antisolvent on the composition and size of final products.

To identify the influence factor on the composition of products, four alcohols (ethanol, n-propanol, n-butanol, and isobutanol) with different polarities were chosen as antisolvents. Figure 3a shows the XRD patterns of the final products obtained in the four alcohols. It can be found that all four products are pure orthorhombic CsPbBr₃, preliminarily indicating that the polarity of the antisolvent is not the determining factor for the composition of synthesized products. Subsequently, two sets of antisolvents with the same polarity but different functional groups, i.e., ethanol and ethyl acetate, isobutanol, and benzene, were used. It can be seen from Figure 3b that the corresponding products are greatly different, although ethanol and ethyl acetate have the same polarity (4.3). For ethanol, pure CsPbBr3 was synthesized. However, for ethyl acetate, Cs₄PbBr₆/CsPbBr₃ composites with predominant Cs₄PbBr₆ were produced. Similarly, when isobutyl alcohol and benzene with the same polarity (3.0) were used as antisolvents, the products are pure CsPbBr₃ and Cs₄PbBr₆/CsPbBr₃ composites, respectively. Figure 3a and b demonstrates that the compositions of the as-synthesized products are dominated by the functional group of the antisolvent. In addition, the products obtained in aromatic hydrocarbons (benzene, toluene, and *p*-xylene) are all Cs₄PbBr₆/CsPbBr₃ composites with predominant Cs₄PbBr₆, as shown in Figure S2, which further evidence that the functional



Figure 3. (a) XRD patterns of as-synthesized products prepared in four alcohols (ethanol, n-propanol, n-butanol, and isobutanol) with different polarities (4.3, 4.0, 3.9, and 3.0), respectively. (b) XRD patterns of as-synthesized products prepared in two sets of antisolvents with the same polarity but different functional groups (ethanol and ethyl acetate, isobutanol and benzene), respectively. (c-l) Corresponding SEM images and statistical size distributions of synthesized products. (All of the scale bars represent 5 μ m.)

group of the antisolvent has the dominant influence on the composition of products.

To identify the influence factor on the size of the products, systematic SEM examinations were carried out. Figure 3c, e, g, i, and k displays typical SEM images of synthesized products obtained in n-propanol, n-butanol, isobutanol, ethyl acetate, and benzene, respectively. The corresponding statistical size distributions in Figure 3d, f, h, j, and l show an average edge length of around 256, 260, 289, 270, and 301 nm, respectively. From the statistical size distributions, it can be seen that the polarity of the antisolvents with the same functional group, i.e., alcohols, actually influences the size of the synthesized products. This is consistent with a previous report that the

size of the product increases with the increase of polarity difference between the polar solvent and the antisolvent.²⁵

To further identify the phase composition of the products, optical absorption spectroscopy was used. Figure S3a presents the absorption spectra of the synthesized products prepared in different antisolvents. The absorption peak located at about 320 nm is characteristic of Cs_4PbBr_6 , and the absorption at around 520 nm results from $CsPbBr_3$.²⁵ Therefore, the products of aromatic hydrocarbons, acetone, and ethyl acetate are $CsPbBr_3/Cs_4PbBr_6$ composites. In addition, the weak absorption peak at 317 nm of products obtained in acetone indicates a low content of Cs_4PbBr_6 . However, for alcohols, the absorption peak at about 520 nm is related to $CsPbBr_3$, and no



Figure 4. XRD patterns of as-synthesized products with 5, 10, 15, and 20 mL of toluene (a), ethanol (b), acetone (c), or ethyl acetate (d) as antisolvents, respectively.

other absorption peak is detected, which demonstrates the purity of CsPbBr₃. From the PL emission spectra in Figure S3b, these products exhibit green emissions with different wavelengths, which can be observed from the photographs of their dried powder under daylight and UV light, as shown in Figure S3c. The size distribution of particles generated in different antisolvents reflected by the full width at halfmaximum (fwhm) of PL emission spectra is consistent with statistical results. Furthermore, the photographs of synthesized products reveal that the fluorescence intensity of the CsPbBr₃/ Cs_4PbBr_6 composite surpasses that of pure $CsPbBr_3$, consistent with previous findings.^{23,25} These results imply that the different molar ratios of CsPbBr3/Cs4PbBr6 have a great impact on the optical performance of cesium-based inorganic halide perovskite materials, which needs to be further studied in the future. Moreover, the stability of products obtained in different antisolvents was preliminarily studied, as shown in Figure S4. It can be seen that compared with CsPbBr₃ nanocrystals, the CsPbBr₃/Cs₄PbBr₆ composite especially for

products with dominant Cs₄PbBr₆ demonstrates enhanced stability, which is consistent with previous reports.^{23,25}

To gain deeper insights into the influence of antisolvents on the composition of products, we carried out a series of experiments involving the manipulation of the antisolvent quantities. Figure 4 shows the XRD patterns of as-synthesized products obtained in different amount of antisolvents such as toluene, ethanol, acetone, and ethyl acetate. For toluene and ethanol, it can be found that the quantities have no obvious impact on their products, which are uniform Cs₄PbBr₆/ CsPbBr₃ composites with predominant Cs₄PbBr₆ and pure CsPbBr₃, respectively. However, when acetone and ethyl acetate were used as antisolvents, the composition of the products displayed some changes. For acetone, as displayed in Figure 4c, all products obtained in different amounts of acetone are CsPbBr₃/Cs₄PbBr₆ composites with predominant CsPbBr₃. Whereas, as the amount of acetone increased, the concentration of Cs₄PbBr₆ in products decreased first and then increased, as indicated by the relative intensity of the



Figure 5. ESP projected on the surface of 0.016 au electron density for the antisolvent molecules: toluene, benzene, *p*-xylene, ethanol, n-propanol, n-butanol, isobutanol, acetone, and ethyl acetate.

characteristic peaks of Cs_4PbBr_6 and $CsPbBr_3$ marked by the red and black arrows, respectively. When adding 15 mL of acetone, the concentration of Cs_4PbBr_6 in the as-prepared $CsPbBr_3/Cs_4PbBr_6$ composites fell to the lowest level. For ethyl acetate, all products are $Cs_4PbBr_6/CsPbBr_3$ composites with predominant Cs_4PbBr_6 . In addition, the concentration of $CsPbBr_3$ in the products exhibits an upward trend with an increasing amount of ethyl acetate. From above, we can see that by adjusting the amount of antisolvents, the composition of products remains unchanged for toluene and ethanol or changes in different ways for acetone and ethyl acetate. Thus, we suggest that the composition change of the products with antisolvent quantity is related to different functional groups of antisolvents.

The aforementioned experimental results unveil the crucial impact of antisolvent functional groups on the composition of the products. To unravel the mechanistic insights into the influence of these functional groups on the product composition, we performed a comprehensive investigation of the potential reactions that might take place in the solution before and after the introduction of the antisolvent. In the precursor solution, CsBr and PbBr₂ are dissolved in DMF, and a couple of traditional ligands (OlAc and OlAm) are added to facilitate the dissolution of CsBr and PbBr₂. It has been reported that Cs⁺ ions are usually in a free state due to the high ionization, whereas Pb²⁺ and Br⁻ are coordinated to form sixcoordination $PbBr_n^{2-n}$ species in DMF.²⁹ When adding OlAc $(C_{17}H_{33}COOH)$ and OlAm $(C_{18}H_{35}NH_2)$, OlAc⁻ $(C_{17}H_{33}COO^{-})$ and $OlAm^{+}$ $(C_{18}H_{35}NH_{3}^{+})$ are generated through a neutralization reaction as follows.

$$C_{17}H_{33}COOH + C_{18}H_{35}NH_2 \rightarrow C_{17}H_{33}COO^- + C_{18}H_{35}NH_3^+$$
(1)

Then, OlAm⁺ ions combine with Br⁻ ions to form (OlAm⁺)-Br⁻, and OlAc⁻ ions combine with Pb²⁺ ions to form the coordination complexes $[PbBr_{6-x}(OlAc^{-})_x]^{4-}$. In our work, the molar ratio of the added PbBr₂ and OlAc is about 1:4, indicating that the coordination complexes should exist in the state of $[PbBr_2(OlAc^{-})_4]^{4-}$. These species achieved solubility equilibrium in DMF. However, upon the introduction of an antisolvent into the precursor solution, the existing solubility equilibrium was perturbed, resulting in a rapid recrystallization and the formation of CsPbBr₃ or Cs₄PbBr₆ particles.¹² The presence of six-coordinate [PbBr₆]⁴⁻ octahedral units as building blocks in both CsPbBr3 and Cs4PbBr6 suggests a correlation between their formation and the precipitation rate ratio of Cs⁺ ions and Pb(II)-intermediates. The coordination environment and bonding interactions of these compounds indicate that the kinetics of the Cs⁺ ion and Pb(II)intermediates play a crucial role in determining their crystal structure and composition. Therefore, it is reasonable to hypothesize that the relative precipitation rates of Pb(II)intermediates to Cs⁺ ions during the formation process affect the final product composition. Further investigation is necessary to determine the influence of the antisolvent, especially its functional group, on the precipitation rate ratio of Cs⁺ ion and Pb(II)-intermediates, providing insights into the underlying formation mechanisms of CsPbBr3 and Cs₄PbBr₆. In comparison to the unbound Cs⁺ ion, the Pb(II)-intermediate exhibits a higher propensity for interactions with the antisolvent. Consequently, our subsequent investigations are predominantly dedicated to elucidating the impact of antisolvent on the separating rates of Pb(II)intermediate.

Electrostatic potential (ESP) analysis is utilized to interpret the possible interactive behaviors of antisolvent molecules in the reprecipitation process.^{31–33} Figure 5 shows the ESP mapping on the surface of 0.016 au electron density for four types of antisolvent molecules, in which the positive and negative ESPs are represented by red and blue regions, respectively. From Figure 5, it can be clearly seen that ESP mappings for aromatic hydrocarbons present relatively small color difference, while ESP mappings for the rest of the antisolvents (alcohols, acetone, and ethyl acetate) demonstrate



Figure 6. UV-vis absorption spectra and the corresponding electronic transition of OlAc and $OlAc^-$ (a and b), as well as $OlAc^-$ in aromatic hydrocarbons (c and d), alcohols (e and f), acetone (g and h), or ethyl acetate (i and j).

relatively large color difference due to the existence of strong electronegative oxygen atoms. Moreover, it is evident that the antisolvent molecules with diverse functional groups display varying ESP values. For aromatic hydrocarbons such as toluene, benzene, and *p*-xylene, the light color around the molecules represents a small ESP value (-0.03-0.03 hartree), indicating the weak electron-donating and -accepting ability. That is to say, the reactivity of aromatic hydrocarbons is almost negligible, indicating that no bonding interaction exists between aromatic hydrocarbons and solute species. For alcohols such as ethanol, n-propanol, n-butanol and isobutanol, the most positive ESP (0.08 hartree) is localized at the

hydrogen atom in a hydroxyl group (-OH), and the oxygen atom provides a quite negative ESP (-0.07 hartree). For acetone, the oxygen atom within the carbonyl group (C=O)induces the lowest negative ESP (-0.08 hartree), and the hydrogen atoms located on the adjacent carbon atoms provide a slightly weaker positive ESP (0.05 hartree). As for ethyl acetate, the oxygen atom in the carbonyl group similarly displays the lowest negative ESP (-0.08 hartree). The hydrogen atoms attached to the neighboring carbon atoms, however, exhibit the weakest positive ESP (0.03 hartree). Based on the electrostatic interactions, we conclude that oxygen atoms with negative ESP are highly prone to interacting with Pb(II) in the intermediate complex $[PbBr_2(OlAc^-)_4]^{4-}$, whereas hydrogen atoms with positive ESP can potentially engage in hydrogen bonding with either Br⁻ or OlAc⁻. Through a comparative analysis of ESP values and optimized molecular structures, it is evident that alcohols and acetone exhibit enhanced propensity for hydrogen bond formation due to the presence of hydrogen atoms in the hydroxyl group with the higher positive ESP. Additionally, acetone/ethyl acetate molecules display a greater likelihood for bonding with cations, including Pb(II)-intermediates and OlAm⁺, owing to the spatial advantage provided by the

protruding oxygen atom within the carbonyl group.

The ESP analysis suggests a possible interaction between the antisolvent and the solute species in the precursor solution. In particular, the interaction between antisolvent molecules and intermediate complex $[PbBr_2(OlAc^-)_4]^{4-}$ is more critical. Therefore, we focus on the separation rates of Pb(II)intermediate in different antisolvents. However, it is difficult to characterize the Pb(II)-intermediate directly due to the complex reaction system and the rapid reaction process. Therefore, we replace the Pb(II)-intermediate with OlAc⁻ and perform UV-vis absorption spectroscopy to investigate the change of electronic states for OlAc⁻ in different antisolvents, further exploring their interaction mechanism. Initially, the typical UV spectra of OlAc and OlAc⁻ are performed, as shown in Figure 6a. Two clear characteristic peaks of OlAc are located at 208.4 and 231.4 nm, which reflect the typical electronic transitions from $\pi \to \pi^*$ and $n \to \pi^*$, respectively.³ When OlAc is transformed into OlAc⁻ through the neutralization reaction with OlAm, the two absorption peaks are both red-shifted. This can be explained by the fact that the deprotonation of carboxy (-COOH) increases the nonbonding electrons of the oxygen atom, which induces the decrease of the energetic gap between n and π^* orbitals. Meanwhile, due to the n- π conjugation effect, the electronic transition energy from π to π^* is also decreased. The change of electronic transition energy is illustrated schematically in Figure 6b. After the deprotonation of carboxy, the original nonbonding (n) and π -bonding (π) orbitals move to higher energy levels (n' and π'), indicating that n' π^* and $\pi'\pi^*$ transitions are easier than $n\pi^*$ and $\pi\pi^*$ transitions, respectively. Then, we investigated the influences of four types of antisolvents on the absorption of OlAc⁻ in sequence. For OlAc⁻ in aromatic hydrocarbons, only one broad absorption band is found at ~232 nm (Figure 6c), corresponding to the n' $\rightarrow \pi^*$ transition of OlAc⁻. This phenomenon is attributed to the incorporation of benzene rings, leading to the formation of a $\pi - \pi$ conjugated system. Consequently, the $\pi' \rightarrow \pi^*$ transition experiences a redshift, and the peak of $\pi' \to \pi^*$ transition coincides with the n' $\to \pi^*$ transition peak, resulting in their overlapping. The new higher energy level of the π -bonding orbital is marked as π_1 in Figure 6d. For OlAc⁻ in alcohols, it can be found that the absorption peak at 213 nm for the $\pi' \rightarrow \pi^*$ transition is blue-shifted to \sim 211 nm (Figure 6e), which is attributed to the hydrogen bonding (H-bonding) interaction between the hydroxyl group in alcohol molecules and oxygen atom of the -COO⁻ in OlAc^{-.34-36} The H-bonding introduces a constraint on the extent of electron delocalization, thereby causing a notable enhancement in the energy gap between the π and π^* orbitals. While the absorption band at ~232 nm has no evident change, indicating the energy of n' orbital remains unchanged. The corresponding change in electronic transitions is illustrated in

Figure 6f. For OlAc⁻ in acetone, the absorption peak at 211.4 nm (Figure 6g) indicates the formation of H-bonding between acetone molecules and OlAc⁻, which is similar to alcohols. Whereas, the red-shifted n' $\rightarrow \pi^*$ transition at 233.2 nm implies that the oxygen atom of the C=O group in acetone provides more nonbonding electrons, resulting in movement of the n' orbital to a new higher energy level marked by n₁ (Figure 6h). For OlAc⁻ in ethyl acetate, the unchanged absorption peak at 213 nm in Figure 6i indicates that no H-bonding forms between the ethyl acetate molecule and OlAc⁻. This may be due to the weakly positive ESP of ethyl acetate. Meanwhile, the red-shifted n' $\rightarrow \pi^*$ transition also reflects the contribution of the C=O group in ethyl acetate, which is similar to acetone.

The above ESP and UV-vis analysis results indicate that there are different interactions between the precursor solution and different antisolvents, leading to the formation of products with different compositions. Leveraging these findings, we present a compilation of potential reactions that could potentially take place during the formation of various products upon the introduction of four antisolvents such as aromatic hydrocarbons, alcohols, acetone, and ethyl acetate into the precursor solution.

For aromatic hydrocarbons, taking toluene as an example, the weak positive and negative ESPs imply that there is a nonbonding interaction between toluene and OlAc⁻. However, the UV–vis spectrum analysis demonstrates that the conjugation effect exists between toluene and OlAc⁻, indicating that toluene has a high solubility of OlAc⁻. That is to say, the intermediate complex $[PbBr_2(OlAc^-)_4]^{4-}$ is highly soluble in toluene, which slows down the separating rate of the Pb(II)-intermediate, leading to the preferential formation of Cs₄PbBr₆ rather than CsPbBr₃. The precipitation reaction can be described as follows.

$$4Cs^{+} + [PbBr_{2}(OlAc^{-})_{4}]^{4-} + 4(OlAm^{+})Br^{-}$$

$$\rightarrow Cs_{4}PbBr_{6} \downarrow + 4OlAc^{-} + 4OlAm^{+}$$
(2)

As the precipitation of Cs_4PbBr_6 keeps going on, the relative concentration of Cs^+ decreases, which triggers the formation of $CsPbBr_3$ according to the following equation.

$$Cs^{+} + [PbBr_2(OlAc^{-})_4]^{4-} + (OlAm^{+})Br^{-}$$

→ CsPbBr₃ ↓ +4OlAc^{-} + OlAm^{+} (3)

Therefore, $Cs_4PbBr_6/CsPbBr_3$ composites with predominant Cs_4PbBr_6 are produced when toluene is used as the antisolvent.

For alcohols, taking ethanol as an example, the initial intermediate complex $[PbBr_2(OlAc^-)_4]^{4-}$ is destroyed due to the hydrogen bonds formed between ethanol molecules and OlAc⁻. As a consequence, part of OlAc⁻ in the coordination sites is replaced by commensurable Br⁻, which converts $[PbBr_2(OlAc^-)_4]^{4-}$ into $[PbBr_{2+x}(OlAc^-)_{4-x}]^{4-}$. Hence, Cs⁺ and $[PbBr_{2+x}(OlAc^-)_{4-x}]^{4-}$ are precipitated proportionally, leading to the formation of CsPbBr₃ according to the following equations

$$[PbBr_{2}(OlAc^{-})_{4}]^{4-} + x(OlAm^{+})Br^{-} + xS$$

$$\rightarrow [PbBr_{2+x}(OlAc^{-})_{4-x}]^{4-} + xOlAc^{-}\cdot S + xOlAm^{+}$$
(4)



Figure 7. Schematic formation mechanism of Cs₄PbBr₆ and CsPbBr₃.

where x, $1 \le x < 4$, is the incremental number of Br in the lead polyhalide framework, and S is the antisolvent molecule, referring to alcohols in eq 5. Moreover, it can be found that both aromatic hydrocarbons and alcohols have a negligible effect on the precipitation of Cs_4PbBr_6 and $CsPbBr_3$, which can explain why the composition of the product obtained in toluene or ethanol is independent of the antisolvent quantity.

For acetone, a composite product of CsPbBr₃/Cs₄PbBr₆ is obtained, with CsPbBr₃ being a dominant phase. The quantity of acetone significantly affects the concentration of Cs₄PbBr₆ in the product, which is different from the case of aromatic hydrocarbons and alcohols. As the amount of acetone increases from 5 to 20 mL, the concentration of Cs₄PbBr₆ first decreases and then increases. Upon addition of 15 mL of acetone, the concentration of Cs₄PbBr₆ in the composite product drops to the lowest level. Compared with alcohols, a greater amount of acetone is required to obtain a relatively pure CsPbBr₃ product. This is attributed to the two reasons as follows. One reason is that the hydrogen bonding forms between acetone and OlAc-, leading to the formation of the new intermediate $[PbBr_{2+x}(OlAc^{-})_{4-x}]^{4-}$, and the subsequent formation of predominant CsPbBr₃, which is similar to alcohols. The other reason is that acetone interacts with $OlAm^+$ through the functional group -C=O, indicating that partial acetone molecules are consumed by OlAm⁺. The corresponding reactions are summarized as follows.

$$[PbBr_2(OlAc^-)_4]^{4-} + x(OlAm^+)Br^- + 2xS$$

$$\rightarrow [PbBr_{2+x}(OlAc^-)_{4-x}]^{4-} + xOlAc^- \cdot S + xOlAm^+ \cdot S$$
(6)

When a smaller amount (5 mL) of acetone is added into the precursor solution, the transformation of $[PbBr_2(OlAc^-)_4]^{4-}$ into $[PbBr_{2+x}(OlAc^-)_{4-x}]^{4-}$ in eq 6 is incomplete, resulting in

the precipitation process in eq 8 and then the formation of byproduct Cs_4PbBr_6 .

$$4Cs^{+} + [PbBr_{2}(OlAc^{-})_{4}]^{4-} + 4(OlAm^{+})Br^{-} + 8S$$

$$\rightarrow Cs_{4}PbBr_{6} \downarrow + 4OlAc^{-} \cdot S + 4OlAm^{+} \cdot S$$
(8)

Whereas, with a larger quantity (20 mL) of acetone added into the precursor solution, excessive acetone takes part in the coordination Pb-complexes as ligands, leading to the formation of the intermediate $[PbBr_{2+x}(OlAc^{-})_{4-x-y}S_y]^{4-}$. The process is described as follows

$$[PbBr_2(OlAc^-)_4]^{4-} + x(OlAm^+)Br^- + 2(x+y)S$$

$$\rightarrow [PbBr_{2+x}(OlAc^-)_{4-x-y}S_y]^{4-} + (x+y)OlAc^- \cdot S + xOlAm^+ \cdot S$$
(9)

where x and y, $1 \le x+y < 4$, are the incremental number of Br in the lead polyhalide framework and the number of S (acetone) coordinated with Pb ions, respectively. Meahwhile, this will reduce the concentration of reactive intermediate $[PbBr_{2+x}(OlAc^{-})_{4-x}]^{4-}$ and generate more Cs_4PbBr_6 , as shown in eq 10, which is consistent with the XRD results in Figure 4c.

$$4Cs^{+} + [PbBr_{2+x}(OlAc^{-})_{4-x}]^{4-} + (4-x)(OlAm^{+})Br^{-} + (8-2x) \cdot S$$

$$\rightarrow Cs_{4}PbBr_{6} \downarrow + (4-x)OlAc^{-} \cdot S + (4-x)OlAm^{+} \cdot S$$
(10)

For ethyl acetate, its chemical constitution is similar to that of acetone. But the products obtained in ethyl acetate and acetone are greatly different. This is because hydrogen-bond and coordination interactions are both forbidden for ethyl acetate due to the weakly positive ESP and steric hindrance, respectively. Therefore, the intermediate complexes $[PbBr_2(OlAc^-)_4]^{4-}$ dominate the precipitation of Cs_4PbBr_6 , as shown in eq 2. In addition, a small amount of accompanying $CsPbBr_3$ is formed through the reaction in eq 3, which is similar to the situation of aromatic hydrocarbons. Besides, the prominent oxygen atom in the ethyl acetate molecule can combine with $OlAm^+$, releasing Br^- ions, which accelerates the generation of $[PbBr_{2+x}(OlAc^-)_{4-x}]^{4-}$. The corresponding reactions are displayed as follows.

$$(OlAm^{+})Br^{-} + S \leftrightarrow OlAm^{+} \cdot S + Br^{-}$$
(11)

$$[PbBr_2(OlAc^-)_4]^{4-} + xBr^- \rightarrow [PbBr_{2+x}(OlAc^-)_{4-x}]^{4-} + xOlAc^-$$
(12)

Therefore, as the amount of ethyl acetate increases, more intermediate complexes $[PbBr_{2+x}(OlAc^{-})_{4-x}]^{4-}$ are generated, resulting in the formation of more CsPbBr₃, as reflected by the XRD pattern in Figure 4d.

Careful examination of the above chemical reaction equations reveals that $[PbBr_{2+x}(OlAc^{-})_{4-x}]^{4-}$ is the primary intermediate for the formation of CsPbBr₃, while $[PbBr_2(OlAc^{-})_4]^{4-}$ is the primary intermediate for the formation of Cs₄PbBr₆. The latter exhibits a higher concentration of OlAc⁻ than the former, suggesting that more ligands are adsorbed on Cs₄PbBr₆ particles than on CsPbBr₃ particles. Furthermore, due to direct participation of OlAc⁻ as an intermediate in the reaction, it is reasonable to infer that the quantity of adsorbed OlAc- in the products surpasses that of OlAm⁺. These findings are substantiated by the ¹H NMR measurements of dried products obtained in toluene, ethanol, acetone, and ethyl acetate, as depicted in Figure S5. In the ¹H NMR spectra, the peaks at approximately 7.90 ppm (marked by red arrows) and 2.75 ppm (labeled by black arrows) originate from the amino $(-NH_3^+)$ proton and the carboxyl $(-CH_2COO^-)$ proton, respectively, meaning that both OlAc⁻ and OlAm⁺ ligands are adsorbed on the products.¹⁹ For the products with predominant CsPbBr₃ derived from ethanol and acetone, the intensities of the amino and carboxyl proton peaks are relatively weak. Conversely, for the products with dominant Cs₄PbBr₆ obtained in toluene and ethyl acetate, both the amino and carboxyl proton peaks are clearly discernible. This indicates that a larger quantity of ligands is adsorbed on the surface of Cs₄PbBr₆ particles compared with CsPbBr₃ particles. In addition, for all the ¹H NMR spectra, the intensity of the carboxyl proton peak surpasses that of the amino proton peak, indicating that more OlAc⁻ ligands are adsorbed on the particles than OlAm⁺.

From the above, a potential mechanism for the formation of Cs₄PbBr₆ and CsPbBr₃ during the SR process is proposed, as depicted in Figure 7. Before the addition of antisolvent into the precursor solution, the coordination sites of the Pb(II)intermediate are occupied by two Br⁻ and four OlAc⁻, forming a complex denoted as $[PbBr_2(OlAc^-)_4]^{4-}$, as shown in the left diagram of Figure 7. Upon the addition of different antisolvents, the coordinated Pb-complex is influenced in different ways. Based on the different interactive behaviors, the antisolvents used in this work can be categorized into two types: antisolvent I (aromatic hydrocarbons and ethyl acetate) which exhibits weak interactions with OlAc⁻ and antisolvent II (alcohols and acetone) which can form hydrogen bonds with OlAc⁻. When antisolvent I is introduced into the precursor solution, the initial $[PbBr_2(OlAc^-)_4]^{4-}$ intermediate remains unaltered. More long ligands (OlAc⁻) in the coordination framework lead to a slow precipitation rate of the Pb(II)intermediate. Therefore, the main product is rhombohedral Cs₄PbBr₆. As for antisolvent II, the formation of the hydrogen bond between the antisolvent and OlAc⁻ turns $[PbBr_2(OlAc^-)_4]^{4-}$ into active $[PbBr_{2+x}(OlAc^-)_{4-x}]^{4-}$. This will accelerate the precipitation of the Pb(II)-intermediate and result in the formation of orthorhombic CsPbBr₃. In general, the formation of Cs₄PbBr₆ or CsPbBr₃ is influenced by the separation rate of the Pb(II)-intermediate, which depends on the coordination status of the intermediate Pb-complex.

4. CONCLUSIONS

In summary, CsPbBr₃ particles and CsPbBr₃/Cs₄PbBr₆ composites have been synthesized using a room temperature supersaturated recrystallization method by changing antisolvents. It shows that not polarity but the functional group of the antisolvent has the dominant influence on the composition of products. The inherent influential mechanism of antisolvents on the products is explored by combining DFT calculations and UV-vis absorption spectra measurements. It is concluded that the determining factor for the formation of Cs₄PbBr₆ or CsPbBr₃ is the coordination status of the intermediate Pb-complex, which can influence the separating rate of the Pb(II)-intermediate. The transformation of an intermediate relies greatly on antisolvents, especially their functional groups. Our work can deepen the understanding of the role of the antisolvent in the SR process and offer a theoretical guidance for the quality manufacture of allinorganic metal halide perovskite-related materials. Future work will focus on the size reduction to nanoscale to further improve the optical properties of synthesized products, as well as investigation on the relationship between the composition, stability, and optical properties of the product to realize industrialization and practical application of all-inorganic metal halide perovskite-related materials.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.inorgchem.3c03398.

Detailed calculation formulas of the mole fraction of CsPbBr₃ and Cs₄PbBr₆, the yields of all products, primary centrifugation products, and secondary centrifugation products obtained in different antisolvents, SEM images and corresponding statistical size distributions of products prepared in toluene and acetone, XRD patterns of synthesized products with benzene, toluene, and *p*-xylene as antisolvents, optical absorption and PL emission spectra of synthesized products obtained in different antisolvents, photographs of the dried products under daylight and UV light, normalized storage stability of products obtained in toluene, ethanol, acetone, and ethyl acetate, ¹H NMR spectra of dried products obtained in toluene, ethanol, acetone, and ethyl acetate, and some discussions of the results and their interpretations (PDF)

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Notes

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