Colloidal synthesis of lead-free all-inorganic $\text{Cs}_3\text{Sb}_2\text{Br}_x\text{I}_{9-x}$ nanocrystals

Weijiang Gan, Sunqi Lou and Jing Wang

Ministry of Education Key Laboratory of Bioinorganic and Synthetic Chemistry, State Key Laboratory of Optoelectronic Materials and Technologies, School of Chemistry, School of Materials Science and Engineering, Sun Yat-Sen University, Guangzhou, People’s Republic of China

ABSTRACT

Environment-friendly lead-free perovskite nanocrystals (NCs) are highly desirable in terms of optoelectronic applications. Reported herein is the synthesis of perovskite-related $\text{Cs}_3\text{Sb}_2\text{Br}_9$ NCs through a simple hot-injection approach. The morphologies and optical properties of NCs were controlled and optimized by varying the reaction temperature, time, and volume of surface ligands. Meanwhile, the $\text{Cs}_3\text{Sb}_2\text{Br}_9$ NCs showed bandgap emission in the blue region centered at 470 nm, and 63 nm full width at half maximum (FWHM). In addition, the $\text{Cs}_3\text{Sb}_2\text{Br}_9$ NCs displayed high stability when immersed in a polar solvent like ethanol. It was also found that the bandgaps of the $\text{Cs}_3\text{Sb}_2\text{Br}_x\text{I}_{9-x}$ NCs could be adjusted by regulating the composition of halogen.

1. Introduction

The lead halide perovskite $\text{ABX}_3$ ($\text{A} = \text{Cs}^+$, $\text{B} = \text{Pb}^{2+}$, and $\text{X} = \text{Cl}^−, \text{Br}^−$, and $\text{I}^−$) has attracted much attention and has been the subject of in-depth research because it has a high photoluminescence quantum yield (PLQY, $\sim 100$%), narrower full width at half maximum (FWHM, 12-35 nm), high intrinsic carrier mobility, and high defect tolerance, making it a good potential material for use in efficient optoelectronic devices [1–7]. The toxicity of lead, however, is a great hindrance to their practical application. To solve this problem, significant efforts have been made of late to develop lead-free perovskite nanocrystals (NCs) [8,9].

There are two typical strategies for obtaining lead-free metal halide perovskites. One is by replacing $\text{Pb}^{2+}$ with lead-free cations, which are isoelectronic with $\text{Pb}^{2+}$, such as $\text{Sn}(\text{II}), \text{Ge}(\text{II}), \text{Bi}(\text{III})$, and $\text{Sb}(\text{III})$ [10,11]. The other is based on the replacement of two divalent $\text{Pb}^{2+}$ ions with one monovalent $\text{M}^+$ and one trivalent $\text{M}^{3+}$ cation, generating quaternary $\text{A}_2\text{M}^+\text{M}^{3+}\text{X}_6$ double-perovskite compounds, which maintain a three-dimensional (3D) perovskite structure and charge neutrality [12,13]. Among the aforementioned lead-free metal halide perovskites, Sb-based perovskites show a nearly direct bandgap, a low trap state density, and long carrier diffusion as well as an electronic configuration and a phase structure similar to those of lead halide perovskites [14,15]. Therefore, Sb-based perovskites are highly expected to be promising alternatives to lead-free perovskite materials in the future. To date, however, only the solution phase synthesis of $\text{Cs}_3\text{Sb}_2\text{X}_9$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) quantum dots (QDs) and the colloidal synthesis of $\text{A}_3\text{Sb}_2\text{X}_9$ ($\text{X} = \text{Cl}, \text{I}, \text{A} = \text{Cs}, \text{Rb}$) have been reported [16–18]. The $\text{Cs}_3\text{Sb}_2\text{Br}_9$ colloidal QDs prepared through the solution phase method have a 46% PLQY and 41 nm FWHM. Unfortunately, this method cannot effectively control the morphology of NCs. For this, the colloidal route was used to synthesize uniform $\text{Cs}_3\text{Sb}_2\text{Cl}_9$ nanowires (NWs) up to several microns and change the aspect ratio of nanorods by turning precursors and ligands. Meanwhile, nanoplatelets and nanorods of $\text{Cs}_3\text{Sb}_2\text{I}_9$ and spherical $\text{Rb}_3\text{Sb}_2\text{I}_9$ NCs were prepared through the colloidal route, and the photoelectric properties were also characterized. There have been few reports, however, on the colloidal synthesis of $\text{Cs}_3\text{Sb}_2\text{Br}_9$ NCs and their optical properties.

Reported herein is the one-pot synthesis of colloidal $\text{Cs}_3\text{Sb}_2\text{Br}_9$ NCs with good control over the morphologies of the final product by turning the reaction conditions, including the temperature, time, and volume of surface ligands, so that pure-phase $\text{Cs}_3\text{Sb}_2\text{Br}_9$ NCs, which have
NC and NW morphologies, can be synthesized. The NCs exhibited blue emission at 470 nm, with a 0.6% PLQY and 63 nm FWHM, on account of the radiative recombination caused by excitons. In the same approach, Cs₃Sb₂Br₉ samples were prepared by regulating different proportions of SbBr₃ and SbI₃ in a precursor solution to adjust the optical properties. The synthesized Cs₃Sb₂Br₉ NCs showed excellent ambient and ethanol stability. These results can contribute to the future application of lead-free perovskites in optoelectronic devices [14,18].

2. Experiment section

2.1. Chemicals

Oleic acid (OA, 90%, Aldrich), antimony (III) tribromide (SbBr₃, 99%, Sigma), antimony (III) iodide (SbI₃, 98%, Aldrich), 1-octadecene (ODE, tech, 90%, Aldrich), oleylamine (OAm, tech, 80-90%, Aldrich), octanoic acid (OnA, tech, 98%, Aladdin), and cesium carbonate (Cs₂CO₃, 99.99%, Aladdin) were used without further purification.

2.2. Preparation of Cs-Oleate

Cesium oleate was prepared by dissolving Cs₂CO₃ (2.0 mmol) with 1-octadecene (20.0 mL, ODE) and oleic acid (2.5 mL) in a three-neck flask. The mixture was first degassed under vacuum at 120°C for 1 h, and then heated up to 150°C under N₂ flux with vigorous stirring for 3 h, until the solution became clear. The resulting product was cooled to room temperature and was stored in a vial under air.

2.3. Synthesis of Cs₃Sb₂Br₉ and Cs₃Sb₂Br₉I₉₋ₓ NCs

In a typical synthesis, a mixture of 10.0 mL ODE, 0.4 mL OAm, 1.0 mL OnA, and 0.1 mmol SbBr₃ was loaded into a three-neck flask and was degassed under vacuum at 80°C for 1 h. After further being heated up to 180°C under a nitrogen atmosphere, 0.3 mL of the as-prepared Cs-oleate solution was swiftly injected under vigorous stirring. The transparent solution instantaneously turned yellow green, indicating the formation of the target NCs. After a specific reaction time (e.g. 10, 30, 60, and 300 s), the reaction mixture was cooled with an ice water bath. The final solution was centrifuged at 7800 rpm for 5 min to separate the precipitates and the supernatant. After adding 5.0 mL hexane, the precipitates and the supernatant solution were centrifuged at 12,500 rpm for 5 min to obtain Cs₃Sb₂Br₉ NCs and Cs₃Sb₂Br₉ NWs, respectively. The as-obtained Cs₃Sb₂Br₉ NCs and Cs₃Sb₂Br₉ NWs were finally dispersed into hexane for further characterization.

The Cs₃Sb₂Br₉I₉₋ₓ (x = 0, 3, 6, 8, 9) NCs were synthesized through a similar process.

2.4. Characterization

The X-ray diffraction (XRD) patterns were identified through the laboratory powder X-ray diffraction system (Rigaku D/MAX 2200 VPC) at a scanning rate of 10°/minute in the 2θ range from 10 to 60°, with Cu Kα radiation (λ = 1.5405 Å) at 40 kV and 26 mA. The morphologies and structures of the as-prepared products were inspected using transmission electron microscopy (TEM, FEI Tecnai G2 Spirit). The collection time during the energy-dispersive X-ray (EDX) was 30 s. The infrared (IR) spectra were obtained through Fourier transform infrared spectrometry (FTIR) coupled with infrared microscopy (EQUINOX 55). The time-resolved photoluminescence (PL) decay and emission spectra were recorded by a steady-state fluorescence spectrometer (Edinburgh Instruments FLS1000) equipped with a 450 W xenon lamp as the excitation source and an RP928 photodetector.

3. Results and discussion

Cs₃Sb₂X₉ is known to have an ordered-vacancy perovskite structure consisting of bioctahedral Sb₂X₉⁻ dimer-like units surrounded by cesium cations (Figure 1a). The Cs₃Sb₂Br₉-perovskite-related NCs were synthesized via the hot-injection method (Figure 1b). OAm and OnA serve as ligands in this system, which can synergistically control the crystallization kinetics of Cs₃Sb₂Br₉ NCs. Specifically, OnA can form a chelate with Sb³⁺ metal ions whereas OAm can stabilize the resulting NC and NW formation. The morphology of Cs₃Sb₂Br₉ NCs in terms of NCs and NWs can be tuned by varying the proportion of ligands and the selective precipitation [19]. FTIR spectroscopy showed the presence of OAm, OnA, and OA on the surfaces of the Cs₃Sb₂Br₉ NCs (Figure 1c). The presence of C–H stretching frequencies (3037 and 2913 cm⁻¹) and C–O stretching frequency peaks (1403 cm⁻¹) in the Cs₃Sb₂Br₉ NCs indicates that OA and OnA were successfully bound onto the surfaces of the NCs. The presence of N–H bending vibration (1618 cm⁻¹) and N–H stretching vibration (3399 cm⁻¹) indicates that OAm interacted with the surfaces of the NCs [20]. Additionally, it is worth mentioning that unlike in the hot-injection synthesis of CsPbBr₃, an appropriate
Figure 1. (a) Illustrations showing the crystal structures of the ordered-vacancy perovskite structure of Cs$_3$Sb$_2$Br$_9$. (b) Schematic depiction of the synthesis of Cs$_3$Sb$_2$Br$_9$ NCs. (c) FTIR analysis results of Cs$_3$Sb$_2$Br$_9$ NCs. XRD patterns of the Cs$_3$Sb$_2$Br$_9$ NCs prepared under different conditions, (d) reaction temperatures, (e) reaction times, and (f) OAm amounts.

The XRD patterns of the NCs synthesized at different reaction times while keeping the same ratio of ligands and fixing the synthesis temperature at 180°C are shown in Figure 1e. The XRD pattern of the sample prepared at 180°C for 10 s was mainly consistent with the impurity phase of Sb$_2$O$_4$ (standard card PDF#17-0620) as well as a small target phase of Cs$_3$Sb$_2$Br$_9$ NCs (standard card PDF#77-1055). As the reaction time increased to above 30 s, the second and third strongest peaks of standard card PDF#17-0620 at 30.6 and 31.0° disappeared, suggesting that the impurity phase of Sb$_2$O$_4$ did not exist in the samples. Moreover, the XRD patterns of all the samples prepared at 180°C for 30, 60, and 300 s were consistent with that of the pure-phase Cs$_3$Sb$_2$Br$_9$. Similar to what is shown in Figure 1d, the first strongest peak changed from 32° (30 and 60 s) to 27.5° (300 s), which may have been due to the change in the crystal plane growth direction as the reaction time increased. To track the morphology evolution and growth process, the TEM micrographs were measured to monitor the reaction process (Figure 2d-f). The results revealed that the Cs$_3$Sb$_2$Br$_9$ NCs experienced fast nucleation and slow growth processes. At the same time, the size distribution of the NCs gradually broadened and reunited. At
10 s (Figure 2d), small NPs were already formed, indicating fast nucleation. At 30 and 60 s (Figure 2e and f), some small NPs gradually grew, forming regular NCs (∼25 nm in diameter). At 300 s, most of the particles were transformed into larger irregular NCs (∼100 nm in diameter), which was due to Ostwald ripening (Figure S3) [22].

Furthermore, the effects of the different volume ratios of OAm and OnA (OAm = 0.2, 0.4, 0.6, 0.8 mL; OnA = 1 mL) were also examined. As shown in Figure 2f, when OAm was less than 0.2 mL, no pure Cs₃Sb₂Br₉ NCs were obtained, and the XRD patterns (Figure 2f) showed that CsBr and Cs₃Sb₂Br₉ were present. When OAm was more than 0.8 mL, only CsBr was present. The possible reason for this is that the increasing amount of OAm slows down the release of free Sb ions in the reaction, especially at a higher OAm concentration and a shorter reaction time (1 min), because OAm as a hard base can readily coordinate with Sb ions, which control the crystallization process of Cs₃Sb₂Br₉ NCs. These finally result in the presence only of CsBr in the samples when OAm was more than 0.8 mL. Sb ions may exist in solution in the form of soluble Sb-OAm complex cations [23–25]. The checking of the TEM of the final NCs (Figure 2g-i) revealed that when OAm was kept at 0.4-0.6 mL, NCs were found in the precipitation while NWs were found in the supernatant. These results suggest the amount of OAm that can contribute to the formation of ligands on the surfaces of the NCs and that will result in the self-assembly of the NCs to form a regular morphology. In addition, the reaction conditions showed effects on the absorption properties of the as-synthesized samples (Figure S4). There was an absorption tail on the longer-wavelength sides of all the NCs with different reaction conditions, which may have been due to the existence of some defect states [26–28].

The PL properties of Cs₃Sb₂Br₉ NCs are rarely investigated, but these are the subject of ongoing research. Excited wavelength- dependent PL spectra (Figure 3a) show Cs₃Sb₂Br₉ NCs exhibiting band edge emission with a peak at 470 nm, which gives a blue shift compared to the Cs₃Sb₂Br₉ single crystal (bandgap: 2.36 eV; crystal structure: P3m1 (no. 164)) [17,29–31]. Meanwhile, the tails in the PL spectra ranging from 550 to 700 nm suggest a defect-related contribution [16]. Unfortunately, the Cs₃Sb₂Br₉ NCs showed very weak emission, with only a ∼0.6% PLQY, similar to the other antimony halide perovskite NCs synthesized through hot injection [15–17].

**Figure 2.** (a-c) TEM images of Cs₃Sb₂Br₉ NCs with different reaction temperatures (°C). (d-e) TEM images of Cs₃Sb₂Br₉ NCs with different reaction times (s). (g-i) TEM images of Cs₃Sb₂Br₉ NCs with different OAm volumes (ml).
Figure 3. (a) PL spectra data of Cs$_3$Sb$_2$Br$_9$ NCs. (b) Time-resolved PL decay and fitting curve of a typical sample.

The PL decay curves (Figure 3b) were fitted with a bi-exponential decay model (equation 1), which gave a short lifetime $\tau_1$ and a long lifetime $\tau_2$, respectively. The $\tau_1$ was estimated to be 1.23 ns, with a 79% percentage, and the $\tau_2$ was 8.37 ns, with a 25% percentage. It is believed that the non-recombination decay associated with shorter lifetimes $\sim$ 1 ns comes from the deep or vacancy defects that lead to poor PL efficiency. Therefore, reducing the defect density is strongly expected to improve the luminescence performance in the future [32].

$$A(t) = A_1 \exp\left(\frac{-t}{\tau_1}\right) + A_2 \exp\left(\frac{-t}{\tau_2}\right)$$ (1)

Figure 4. Stability of the Cs$_3$Sb$_2$Br$_9$ NCs. (a) XRD patterns and (b) reflectance spectra of the Cs$_3$Sb$_2$Br$_9$ NCs after being immersed in ethanol for 12 h. (c) XRD patterns and (b) UV-vis absorption spectra of the NCs over a period of 30 days under ambient conditions.
Additionally, a series of Cs$_3$Sb$_2$Br$_x$I$_{9-x}$ ($x = 0, 3, 6, 8, 9$) NCs was prepared via the one-pot hot-injection method. Typical images of Cs$_3$Sb$_2$Br$_x$I$_{9-x}$ ($x = 0, 3, 6, 8, 9$) NCs under daylight are shown in Figure S5. The absorption of the NCs in this study is shown in Figure S6b. The absorption onset showed red shifts when the $x$ changed from 9 to 3, while it slightly shifted back (sky blue line) with the $x$ at 0. It is well known that the alloying of I in the original Br- terminated perovskites commonly leads to a red shift in absorption in the same phase structure [33]. Therefore, the obtained results imply that Cs$_3$Sb$_2$Br$_x$I$_{9-x}$ NCs are halide alloy NCs.

The NCs’ phase structure is shown in Figure S6a. The results showed that they had the same structure as space group P$ar{3}$m1. With the $x$ decreasing from 9 to 0, the (201) peak shifts gradually became smaller, which can be ascribed to the alloying of iodine ions with bromide with a larger ion radius. The Cs$_3$Sb$_2$Br$_x$I$_{9-x}$ NCs actually showed no visible emission. Nonetheless, they had the highest crystalline quality and an adjustable bandgap, implying their potential application in photovoltaics.

It is well known that the stability of perovskite materials is a crucial issue especially in their practical applications [34]. Therefore, the stability of Cs$_3$Sb$_2$Br$_9$ NCs was carefully studied in this work. As shown in Figure 4, after Cs$_3$Sb$_2$Br$_9$ NCs were soaked in ethanol for 12 h, their phase structure remained the same, and the fresh sample and bandgap absorption around 450 nm were unchanged, indicating that they have excellent stability in ethanol. To evaluate the water resistance properties of Cs$_3$Sb$_2$Br$_9$ NCs, they were kept suspended in air for 30 days. As can be seen in Figure 4c-d, the intensity of the peak at around 27.5° decreased and that of the peak at around 32° increased while both became narrower. These results indicate that the colloidal NCs may gradually grow along the (022) plane (32°) and turn into large particles while being kept under long-term air conditions with moisture. After exposure of the NCs to air for 30 days, the resulting extra absorption tail in the 500-700 nm wavelength might have been caused by some defects or by the scattering of the generated large particles [35–37]. Figure S7 shows the TGA data of the Cs$_3$Sb$_2$Br$_9$ NCs within the 25-800°C temperature range. Obviously, weight loss started after 350°C, and the NCs decomposed into CsBr and SbBr$_3$. It can thus be said that Cs$_3$Sb$_2$Br$_9$ NCs have outstanding thermal stability. In summary, the Cs$_3$Sb$_2$Br$_9$ NCs showed widely tunable absorbance and excellent ambient and thermal stability compared to lead-halide-based perovskites, suggesting that they are promising for use in Pb-free perovskite optoelectronic devices.

## 4. Conclusions

In conclusion, in this study, lead-free, air-stable, all-inorganic Cs$_3$Sb$_2$Br$_9$ nanocrystals (NCs) were synthesized using colloidal synthesis for the first time. The factors affecting the morphology and size of such NCs were systematically studied by controlling the temperature, time, and volume of the surface ligands, and their optical properties were characterized. The Cs$_3$Sb$_2$Br$_x$I$_{9-x}$ NCs formed NC and nanowire (NW) shapes when the temperature, time and ratio of the ligands were controlled. The growth mechanism was found to have similarities to Ostwald ripening. Cs$_3$Sb$_2$Br$_x$I$_{9-x}$ NCs were used to effectively adjust the bandgap by controlling the anion composition. It is firmly believed that the widely tunable absorbance and excellent ambient stability of Cs$_3$Sb$_2$Br$_9$ NCs make them highly promising materials for use in stable and efficient Pb-free perovskite optoelectronic devices.

## Associated content

Supporting information. The supporting information (EDX, TEM images, absorption spectra, optical images, TGA graph (PDF)) is available free of charge at the ACS Publications website of DOI.

## Disclosure statement

No potential conflict of interest was reported by the authors.

## Funding

This work was financially supported by the National Key R&D Program of China [grant numbers 2018YFB0406800 and 2018YFB0406801], NSFC [grant numbers 51772336, 51572302, and 51702373], the National Basic Research Program of China (the ‘973’ programs) [grant number 2014CB643801], Guangdong Provincial Science & Technology Project [grant numbers 2015B090926011, 2017A050501008, and 2019B010926001], and Guangzhou Science & Technology Project [grant numbers 201807010104 and 201802020033].

## Notes on contributors

Weijiang Gan is a Ph.D. candidate at the School of Chemistry of Sun Yat-Sen University. He received his B.S. Applied Chemistry degree from Beijing University of Chemical Technology, China in 2017. His current research is focused on the synthesis and understanding of the luminescent and structural properties of lead-free halide perovskites to stabilize them for optoelectronic applications.
**Sunqi Lou** is a Ph.D. candidate at the School of Chemistry of Sun Yat-Sen University. He received his B.S. Chemistry degree from Nanjing University of Information Science & Technology, China in 2015, and his M.S. Materials and Photoelectrons degree from East China Normal University, China in 2018. His current research interests are lead halide perovskite nanocrystals and their applications in light-emitting diodes and bio-imaging.

**Jing Wang** is a professor at the School of Chemistry of Sun Yat-Sen University, China. He received his B.S. Chemistry degree from Northwest University, China in 1999, and his M.S. and Ph.D. Chemistry degrees from Changchun Institute of Applied Chemistry and Chinese Academy of Sciences, China in 2001 and 2004, respectively. From 2004 to 2005, he was a lecturer at the School of Chemistry of Sun Yat-Sen University, and from 2006 to 2013, he was an associate professor in the same school. In 2014, he was promoted to professor. His research concerns nanoscience and optical functional materials for display, lighting, bioimaging, and solar energy (luminescent materials, phosphors, glass-ceramic, nano-probe, persistent luminescence, rare earth, quantum dots, perovskite, etc.).

**References**

[1] K. Lin, J. Xing, L.N. Quan, F.P.G. de Arquer, X. Gong, J. Lu, L. Xie, W. Zhao, D. Zhang, C. Yan, W. Li, X. Liu, Y. Lu, J. Kirman, E.H. Sargent, Q. Xiong, and Z. Wei, Nature **562**, 245 (2018).

[2] Y. Cao, N. Wang, H. Tian, J. Guo, Y. Wei, H. Chen, Y. Miao, W. Zou, K. Pan, Y. He, H. Cao, Y. Ke, M. Xu, Y. Wang, M. Yang, K. Du, Z. Fu, D. Kong, D. Dai, Y. Jin, G. Li, H. Li, Q. Peng, J. Wang, and W. Huang, Nature **562**, 249 (2018).

[3] J. Xing, Y. Zhao, M. Askerka, L.N. Quan, X. Gong, W. Zhao, J. Zhao, H. Tan, G. Long, L. Gao, Z. Yang, O. Voznyy, J. Tang, Z.H. Lu, Q. Xiong, and E.H. Sargent, Nat Commun. **9**, 3541 (2018).

[4] S. Lou, T. Xuan, C. Yu, M. Cao, C. Xia, J. Wang, and H. Li, J. Mater. Chem. C, 5, 7431 (2017).

[5] C. Xie, P. You, Z. Liu, L. Li, and F. Yan, Light Sci Appl. **6**, e17023 (2017).

[6] L. Gu, and Z. Fan, Light Sci Appl. **6**, e17090 (2017).

[7] Y.C. Zhao, W.K. Zhou, X. Zhou, K.H. Liu, D.P. Yu, and Q. Zhao, Light Sci Appl. **6**, e16243 (2017).

[8] F. Igbari, Z.K. Wang, and L.S. Liao, Adv. Energy Mater. **9**, 1803150 (2019).

[9] W. Ning, and F. Gao, Adv. Mater. **31**, 1900326 (2019).

[10] M. Leng, Y. Yang, Z. Chen, W. Gao, J. Zhang, G. Niu, D. Li, H. Song, J. Zhang, and S. Jin, Nano Lett. **18**, 6076 (2018).

[11] A. Bernasconi, A. Rizzo, A. Listorti, A. Mahata, E. Mosconi, F. De Angelis, and L. Malavasi, Chem. Mat. **31**, 3527 (2019).

[12] M.K. Jana, S.M. Janke, D.J. Dirkes, S. Dovletgeldi, C. Liu, X. Qin, K. Gundogdu, W. You, V. Blum, and D.B. Mitzi, J. Am. Chem. Soc. **141**, 7955 (2019).

[13] J. Luo, X. Wang, S. Li, J. Liu, Y. Guo, G. Niu, L. Yao, Y. Fu, L. Gao, Q. Dong, C. Zhao, M. Leng, F. Ma, W. Liang, L. Wang, S. Jin, J. Han, L. Zhang, J. Etheridge, J. Wang, Y. Yan, E.H. Sargent, and J. Tang, Nature **563**, 541 (2018).

[14] B. Yang, Y.J. Li, Y.X. Tang, X. Mao, C. Luo, M.S. Wang, W.Q. Deng, and K.L. Han, J. Phys. Chem. Lett. **9**, 3087 (2018).

[15] K.M. McCall, C.C. Stoumpos, S.S. Kostina, M.G. Kanatzidis, and B.W. Wessels, Chem. Mat. **29**, 4129 (2017).

[16] J. Pal, S. Manna, A. Mondal, S. Das, K.V. Adarsh, and A. Nag, Angew. Chem.Int.Ed. **56**, 14187 (2017).

[17] J. Zhang, Y. Yang, H. Deng, U. Farooq, X. Yang, J. Khan, J. Tang, and H. Song, ACS Nano, **11**, 9294 (2017).

[18] B. Pradhan, G.S. Kumar, S. Sain, A. Dalui, U.K. Ghosh, S.K. Pradhan, and S. Acharya, Chem. Mat. **30**, 2135 (2018).

[19] S.K. Mehetor, H. Ghosh, and N. Pradhan, J. Phys. Chem. Lett. **10**, 1300 (2019).

[20] R. Grisorio, M.E. Di Clemente, E. Fanizza, I. Allegretta, D. Altamura, M. Striccoli, R. Terzano, C. Giannini, M. Irimia-Vladu, and G.P. Suranna, Nanoscale **8**, 986 (2019).

[21] L. Zhou, Y.F. Xu, B.X. Chen, D.B. Kuang, and C.Y. Su, Small **14**, 1703762 (2018).

[22] M. Koolyk, D. Amgar, S. Aharon, and L. Etgar, Nanoscale **8**, 6403 (2016).

[23] H. Huang, J. Raith, S.V. Kershaw, S. Kalyuchk, O. Tomanec, L. Jing, A.S. Susha, R. Zboril, A.L. Rogach, Nat Commun. **8**, 996 (2017).

[24] F. Zhang, H. Zhong, C. Chen, X.G. Wu, X. Hu, H. Huang, and Y. Dong, ACS Nano **9** (4), 4533 (2015).

[25] M. Leng, Y. Yang, K. Zeng, Z. Chen, Z. Tan, S. Li, J. Li, B. Xu, D. Li, M.P. Hautzinger, Y. Fu, T. Zhai, L. Xu, G. Niu, S. Jin, and J. Tang, Adv. Funct. Mater. **28** (1), 1704446 (2018).

[26] B. Yang, F. Hong, J. Chen, Y. Tang, L. Yang, Y. Sang, X. Xia, J. Guo, H. He, S. Yang, W. Deng, and K. Han, Angew. Chem.Int.Ed. **58**, 2278 (2019).

[27] H. Wu, Y. Zhang, M. Lu, X. Zhang, C. Sun, T. Zhang, V.L. Colvin, and W.W. Yu, Nanoscale **10**, 4173 (2018).

[28] X. Shen, S. Wang, X. Zhang, H. Wang, X. Zhang, C. Wang, Y. Gao, Z. Shi, W.W. Yu, and Y. Zhang, Nanoscale **11**, 11464 (2018).

[29] G. Bastard, C. Delalande, M.H. Meynadier, P.M. Frijlink, and M. Voos, Phys. Rev. B, 29, 7042 (1984).

[30] R.A. Street, and N.F. Mott, Phys. Rev. Lett. **35**, 1293 (1975).

[31] M. Leng, Y. Yang, Z. Chen, W. Gao, J. Zhang, G. Niu, D. Li, H. Song, J. Zhang, S. Jin, and J. Tang, Nano Lett. **18** (9), 6076 (2018).

[32] B.J. Bohn, Y. Tong, M. Gramlich, M.L. Lai, M. Doblinger, K. Wang, R.L.Z. Hoyer, P. Muller-Buschbaum, S.D. Stranks, A.S. Urban, L. Polavarapu, and J. Feldmann, Nano Lett. **18**, 5231 (2018).

[33] T. Xuan, S. Lou, J. Huang, L. Cao, X. Yang, H. Li, and J. Wang, Nanoscale **10**, 9840 (2018).

[34] T. Xuan, J. Huang, H. Liu, S. Lou, L. Cao, W. Gan, R.-S. Liu, and J. Wang, Chem. Mat. **31**, 1042 (2019).

[35] Y. Cai, H. Wang, Y. Li, L. Wang, Y. Lv, X. Yang, and R.-J. Xie, Chem. Mat. **31**, 881 (2019).

[36] J. Chen, D. Liu, M.J. Al-Marriri, L. Nuuttila, H. Lehtivuori, and K. Zheng, Sci. China-Mater. **59**, 719 (2016).

[37] S. Huang, Z. Li, B. Wang, N. Zhu, C. Zhang, L. Kong, Q. Zhang, A. Shan, and L. Li, ACS Appl. Mater. Interfaces **9**, 7249 (2017).