Exploiting the Lability of Metal Halide Perovskites for Doping Semiconductor Nanocomposites

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ABSTRACT: Cesium lead halides have intrinsically unstable crystal lattices and easily transform between perovskite and nonperovskite structures. In this work, we explore the conversion of the perovskite CsPbBr₃ into Cs₄PbBr₆ in the presence of PbS at 450 °C to produce doped nanocrystal-based composites with embedded Cs₄PbBr₆ nanoparticles. We show that PbBr₂ is extracted from CsPbBr₃ and diffuses into the PbS lattice with a consequent increase in the concentration of free charge carriers. This new doping strategy enables the adjustment of the density of charge carriers between 10¹⁹ and 10²⁰ cm⁻³, and it may serve as a general strategy for doping other nanocrystal-based semiconductors.

Research on metal halide perovskites is advancing rapidly, owing to the compelling electronic, optical, and structural properties of these ionic semiconductors, such as long diffusion lengths and carrier lifetimes, low exciton binding energies, low number of trap states despite the high concentration of vacancies, composition-tunable bandgap, and ease of processability. Because of the relatively labile crystal structure of metal halide perovskites, the understanding and control of the chemical and structural transformations that these compounds readily undergo are some of the most pressing questions.

Cesium lead halides can adopt perovskite and nonperovskite structures with different dimensionalities. Perovskites are composed of Cs⁺ cations stabilizing [PbX₆]⁴⁻ octahedra in a cubic or, upon slight distortion, tetragonal or orthorhombic phases, where all the corners of the [PbX₆]⁴⁻ octahedra are shared. All these compounds adopt regular CsPbX₃ stoichiometry (3D). Nonperovskite structures include polymorphs with various stoichiometries, but all of them lose the corner-sharing motif in the lattice. The first example of these structures is a polymorph that despite having the same CsPbX₃ stoichiometry crystallizes in an orthorhombic phase (δ-phase) with chains of edge-sharing octahedra (1D). Another example is the lead-depleted Cs₅PbX₆ structure where the [PbX₆]⁴⁻ octahedra are isolated (0D). A third closely related nonperovskite structure that has lower Cs⁺ content and does not contain [PbX₆]⁴⁻ octahedra, CsPb₁₋ₓXₓ⁺, can be described as layers (2D) of [Pb₂X₃]⁺ clusters separated by Cs⁺ ions. Because of the large difference in the involved atoms’ electronegativities, all these cesium lead halides exhibit mixed bonding nature. The lead halide framework is dominated by covalent bonds and balanced by ionically bound Cs⁺ cations. The lack of covalency between Cs⁺ and the anionic units enables crystal lability. As a direct consequence, the ions move easily and allow transformation between the different structures—provided that the stoichiometry is compensated.

Very common are the transformations between CsPbBr₃ and Cs₄PbBr₆ structures especially in nanocrystals (NCs). The transformation of Cs₄PbBr₆ into CsPbBr₃ is achieved by adding PbBr₂ to the structure, extracting CsBr by chemical complexation or intercalation, or diffusion and dissolution of CsBr in water. The chemical transformation from CsPbBr₃ to Cs₄PbBr₆ can be induced by removing PbBr₂ from the crystal lattice by its complexation with thiols or amines. In all
these reactions purification of the NCs is required to separate the undesired byproducts: either CsBr or PbBr₂.

PbS NC-based solids find application in various fields including transistors, solar cells, photodetectors, and thermoelectrics. In most of these applications adjusting the number of free charge carriers to control charge transport is crucial. The conventional n-type dopants for bulk lead chalcogenides are halides. Incorporation of halide ions (X= Cl⁻, Br⁻, I⁻) in the chalcogenide (Y= S²⁻, Se²⁻, Te²⁻) sublattice results in the addition of one electron in the conduction band per halide to compensate for the different valency of halides and chalcogenides. Strategies to dope bulk semiconductors require control over the composition at the impurity level; the straightforward translation into doping bottom-up assembled NC solids is to use doped NCs. However, impurity doping of NCs is energetically and kinetically unfavorable, because the diffusion path of impurity atoms to the surface is short. Although tuning NCs composition has been attempted, the introduction of a controlled amount of impurities in small structures is problematic for the preparation of heavily doped semiconductors. Alternative approaches to dope NC-based solids have focused on changing the NC surface chemistry, inducing partial cation exchange, and blending with other NCs.

PbY—perovskite nanocomposites have been used in photodetectors, LEDs, and photovoltaics. Remarkably, PbS NC inclusions can provide stability to the cubic phase of perovskites suppressing the cubic—ortorhombic phase transition, and perovskite passivation layers enhance charge carrier separation in PbS NCs by providing adequate energy alignment. Furthermore, PbY nanocomposites with secondary phases might be of great importance for thermoelectrics.

Herein we propose a strategy to produce doped PbS nanocomposites that makes use of the byproduct of the transformation of CsPbBr₃ into Cs₄PbBr₆ and PbBr₂ upon heating a mixture of CsPbBr₃ and PbS NCs (Scheme 1). Our approach simultaneously introduces dopant ions (Br⁻) and a secondary phase (Cs₄PbBr₆) in PbS nanocomposites (Figure 1).

We prepared nanocomposites by mixing PbS NCs with a controlled amount of CsPbBr₃ NCs in toluene. This NC blend was dried under vacuum and annealed with forming gas (5% H₂ in N₂, 1 bar) to yield a powder that was then pressed into pellets with relative densities of ~92% (Table S1) using spark plasma sintering (Figure 1).

Scheme 1. Chemical Transformation of CsPbBr₃ into Cs₄PbBr₆ Triggered by the Dissolution of PbBr₂ in PbS

To follow the chemical transformation of the perovskites, we performed in situ temperature-dependent X-ray diffraction (XRD) measurements of a mixture of PbS NCs and 30% wt. CsPbBr₃ NCs (Figures 2 and S1). This mixture was heated to 450 °C and kept at that temperature for 60 min, mimicking the annealing step. Upon heating to 150 °C, CsPbBr₃ NCs show strong sharpening of the reflections explained by accelerated ion migration between particles causing grain growth. After reaching 450 °C, CsPbBr₃ reflections progressively lose intensity, and peaks corresponding to Cs₄PbBr₆ become visible, shifted to lower angles because of thermal expansion of the lattice. This experiment demonstrates that CsPbBr₃ converts to Cs₄PbBr₆, necessarily releasing PbBr₂. This reaction could be enhanced by the binding affinity of PbBr₂ to PbS surface dangling bonds. Control experiments with CsPbBr₃ and Cs₄PbBr₆ pure phases showed that both phases are recovered after heating to 500 °C and cooling to room temperature and do not undergo any transformation on their own (Figures S9 and S10). Besides, annealing induces crystal grain growth in pure PbS NCs, evidenced by the narrowing of the XRD reflections and scanning electron microscopy (SEM) images (Figures S2 and S5). The addition of CsPbBr₃ enhances the growth of the PbS crystal domains leading to even narrower reflections (Figures S3 and S4 and Tables S3 and S4). This enhancement can be explained by the presence of PbBr₂, a phase with high solubility in PbS and a large difference in melting point, which lowers the activation energy for diffusion. Because no reflections associated with PbBr₂ are visible, we considered the possibility of other phases in the PbS—PbBr₂ phase diagram being formed. Still, Pb₄S₁₀Br₁₀, the only stable phase, was not observed in the diffraction patterns. Recently, the metastable phase Pb₂S₃Br₂ was reported in NCs; this phase is not present in the XRD

![Figure 1. TEM images of the used NCs and scheme of the bottom-up assembly process to produce doped PbS-Cs₄PbBr₆ nanocomposites. The nanocomposites are prepared by blending the NCs in solution, annealing the dried NCs at 450 °C to remove the organic ligands and induce the chemical transformation between CsPbBr₃ and Cs₄PbBr₆, and finally pressing the annealed powder at 45 MPa and 500 °C for 5 min to produce the pellets.](https://dx.doi.org/10.1021/acsenergylett.0c02448)
patterns, and we disregarded it because of the high temperature and long reaction time, which are not compatible with such a kinetically stabilized phase. Previous studies showed pure CsPbBr3 NCs undergo partial transformation to the lead-rich CsPb2Br5; this phase is not present in our experiments. These observations suggest that bromide substitutes sulfide in PbS, doping the matrix as expressed in the chemical reactions in Scheme 1.

To test the doping efficiency, we prepared pellets with the proper nominal CsPbBr3 concentrations to achieve charge carrier concentrations between $10^{19}$ and $10^{20}$ cm$^{-3}$, which is close to the optimal charge carrier concentration for thermoelectrics. The molar amount of Br introduced is referred to the amount of S, $X_\% = 0.25, 0.50, 1, 2, 3$ (see the Supporting Information, page S1).

Panels a and b of Figure 3 show the electrical conductivity and Seebeck coefficient of the samples between room temperature and 900 K, respectively. At low temperatures, the absolute value of the Seebeck coefficient decreases and the electrical conductivity increases with the starting concentration of CsPbBr3, proving the doping effect of the transformation (Supporting Information, page S8). Besides, the negative sign of the Seebeck coefficient confirms the n-type character of the obtained nanocomposites. These results are consistent with the charge carrier concentrations measured by Hall effect (Table S2), which correspond exactly to one-half of the total Br concentration, as expected from the reaction in Scheme 1.

The observed tendencies in the electrical conductivity of nanostructured materials are a trade-off between many effects. On the one hand, the thermal excitation of carriers through energy barriers (grain boundaries) leads to an increase of the conductivity with temperature. This effect dominates at low temperatures in samples with smaller grains. On the other hand, an increase in temperature enhances charge carrier scattering. This is the typical behavior of heavily doped semiconductors and metals. Additionally, as the temperature increases, thermal excitation of minority carriers (bipolar effect) occurs. Consequently, the absolute value of the Seebeck coefficient starts decreasing. The higher the doping level, the higher the temperature at which this effect is perceptible.
The XRD patterns of the produced pellets show neither CsPbBr₃ nor Cs₂PbBr₆ reflections (Figure S6), which we associate with the low content of perovskite required for the doping level targeted. To demonstrate that the pelletized material contains Cs₂PbBr₆, we evaluated the microscopic structure of the bulk nanocomposites (Figure 4) by high-resolution transmission electron microscopy (HRTEM). A 0.5% pellet was thinned to electron transparency by Ar⁺ polishing to produce a self-suspended lamella. Figure 4d shows an HRTEM micrograph obtained from a large PbS grain (defined as the matrix) containing multiple precipitates. The power spectrum of the highlighted area shows diffraction spots of the matrix and the precipitates, along with satellite spots of the Moiré fringes, which are formed because of orientation differences between the matrix and precipitates. Inverse Fourier (frequency) filtering of the power spectrum allowed mapping the matrix and the nanodomains. The matrix phase (in red) is identified as FCC PbS (space group Fm3m) with a lattice parameter a = 0.5936 nm visualized along its [011] axis. The nanodomain (in green) corresponds to the same PbS phase visualized along the [001] zone axis. We performed the same analysis on the precipitate marked in Figure 4e. The diffraction spots observed in the power spectrum correspond to the matrix phase (in red) visualized along its [011] axis. The spots of the precipitate correspond to the hexagonal Cs₂PbBr₆ phase (space group R3c:H) with lattice parameters a = 1.373 nm and c = 1.732 nm, which is visualized along the [1102] zone axis. Because of the difficulty in analyzing all the precipitates crystallographically, to evaluate their nature we performed energy dispersion X-ray line scans across many precipitates. We found that they show no difference in composition with the matrix (Figure S7), proving that the vast majority of precipitates are PbS. The scans also show a small content of Br evenly distributed through the nanocomposites as expected in its role as a dopant. In short, HRTEM revealed that the doped samples are composed of a PbS matrix with a large amount of PbS nanodomains and randomly distributed Cs₂PbBr₆ nanoprecipitates (Figure 4), confirming the chemical transformation observed by XRD.

In summary, we showed that CsPbBr₃ and PbS react to give the lead depleted Cs₂PbBr₆ phase. The byproduct of the transformation, PbBr₂, dissolves in the PbS matrix, leading to doped nanocomposites and inducing grain growth while Cs₂PbBr₆ forms nanoprecipitates. We made use of this transformation to simultaneously dope and introduce a secondary phase in n-type PbS nanocomposites. These results validate this new doping strategy for nanocomposites based on NC blending that involves the reaction of one of the components. This approach is not limited to the preparation of bulk samples at high pressures but could also be applied to the preparation of films or other nanocomposites because the reaction that leads to doping is also demonstrated at ambient pressure. Finally, our results reassess the intrinsic instability of metal halide perovskites and are therefore of high relevance for applications where these materials are exposed to high energy densities.

**ASSOCIATED CONTENT**

**Supporting Information**

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsenergylett.0c02448.

Chlorides, syntheses and preparations of the pellets. Details on the structural characterization and transport measurements (PDF)

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Notes

The authors declare no competing financial interest.

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REFERENCES

(1) Shi, D.; Adinolfi, V.; Comin, R.; Yuan, M.; Alarousu, E.; Buin, A.; Chen, Y.; Hoogland, S.; Rothenberger, A.; Katsiev, K.; Losovyj, Y.; Zhang, X.; Dowben, P. A.; Mohiuddin, O. F.; Sargent, E. H.; Bake, O. M. Low Trap-State Density and Long Carrier Diffusion in Oganolead Trihalide Perovskite Single Crystals. Science 2015, 347 (6221), 519–522.

(2) Maculans, G.; Sheikht, A. D.; Abdelhady, A. L.; Saimadinov, M. I.; Haque, M. A.; Murali, B.; Alarousu, E.; Mohammed, O. F.; Wu, T.; Bakr, O. M. CH3NH3PbCl3 Single Crystals: Inverse Temperature Crystallization and Visible-Blind UV-Photodetector. J. Phys. Chem. Lett. 2015, 6 (19), 3781–3786.

(3) Saimadinov, M. I.; Abdelhady, A. L.; Murali, B.; Alarousu, E.; Burlakov, V. M.; Peng, W.; Dursun, I.; Wang, L.; He, Y.; MacLan, G.; Goriely, A.; Wu, T.; Mohammed, O. F.; Bakr, O. M. High-Quality Bulk Hybrid Perovskite Single Crystals within Minutes by Inverse Temperature Crystallization. Nat. Commun. 2015, 6 (1), 7586.

(4) Manser, J. S.; Christians, J. A.; Kamat, P. V. Intriguing Optoelectronic Properties of Metal Halide Perovskites. Chem. Rev. 2016, 116 (21), 12956–13008.

(5) Fang, H. H.; Adjokatse, S.; Wei, H.; Yang, J.; Blake, G. R.; Huang, J.; Even, J.; Loi, M. A. Ultrahigh Sensitivity of Methylammonium Lead Tribromide Perovskite Single Crystals to Environmental Gases. Sci. Adv. 2016, 2 (7), e1600534.

(6) Sutton, R. J.; Eperon, G. E.; Miranda, L.; Parrott, E. S.; Kamino, B. A.; Patel, J. B.; Höünter, M. T.; Johnston, M. B.; Haghighirad, A. A.; Moore, D. T.; Snait, H. J. Bandgap-Tunable Cesium Lead Halide Perovskites with High Thermal Stability for Efficient Solar Cells. Adv. Energy Mater. 2016, 6 (8), 1502458.

(7) McMeekin, D. P.; Sadoughi, G.; Rehman, W.; Eperon, G. E.; Saliba, M.; Höünter, M. T.; Haghighirad, A.; Sakai, N.; Korte, L.; Rech, B.; Johnston, M. B.; Herz, L. M.; Snait, H. J. A Mixed-Cation Lead Mixed-Halide Perovskite Absorber for tandem Solar Cells. Science 2016, 351 (6269), 151–155.

(8) Liu, X. K.; Xu, W.; Bai, S.; Jin, Y.; Wang, J.; Friend, R. H.; Gao, F. Metal Halide Perovskites for Light-Emitting Diodes. Nat. Mater. 2021, 20, 10–21.

(9) Noculak, A.; Noculak, A.; Morad, V.; Morad, V.; McCall, K. M.; Yakunin, S.; Shynkarenko, Y.; Yakunin, S.; Shynkarenko, Y.; Wöre, M.; Kovalenko, M. V. Bright Blue and Green Luminescence of Sb(III) in Double Perovskite Cs5MnCl10 (M = Na, K) Matrices. Chem. Mater. 2020, 32 (12), 5118–5124.

(10) Jena, A. K.; Kulkarni, A.; Miyasaka, T. Halide Perovskite Photovoltaics: Background, Status, and Future Prospects. Chem. Rev. 2019, 119 (5), 3036–3103.

(11) Brenner, P.; Bar-On, O.; Jakoby, M.; Allegro, I.; Richards, B. S.; Paetzold, U. W.; Howard, I. A.; Scheuer, J.; Lemmer, U. Continuous Wave Amplified Spontaneous Emission in Phase-Stable Lead Halide Perovskites. Nat. Commun. 2019, 10 (1), 1–7.

(12) Akkerman, Q. A.; Bainö, G.; Kovalenko, M. V.; Manna, L. Geniş, Challenges and Opportunities for Colloidal Lead Halide Perovskite Nanocrystals. Nat. Mater. 2018, 17 (5), 394–405.

(13) Bertolotti, F.; Protosescu, L.; Kovalenko, M. V.; Yakunin, S.; Cervellino, A.; Billinge, S. J. L.; Terban, M. W.; Pedersen, J. S.; Masciocchi, N.; Guagliardi, A. Coherent Nanotwins and Dynamic Disorder in Cesium Lead Halide Perovskite Nanocrystals. ACS Nano 2017, 11 (4), 3819–3831.

(14) Aebli, M.; Benin, B. M.; McCall, K. M.; Morad, V.; Thöny, D.; Grützmacher, H.; Kovalenko, M. V. White CsPbBr3: Characterizing the One-Dimensional Cesium Lead Bromide Polymorph. Helv. Chim. Acta 2020, 103 (7), e2000080.

(15) Piveoteau, L.; Abell, M.; Yazdani, N.; Millen, M.; Koreosce, L.; Krieg, F.; Benin, B. M.; Morad, V.; Piveoteau, C.; Shirooka, T.; Comas-Vives, A.; Copéret, C.; Lindenberg, A. M.; Wood, V.; Verel, R.; Kovalenko, M. V. Bulk and Nanocrystalline Cesium Lead-Halide Perovskites as Seen by Halide Magnetic Resonance. ACS Cent. Sci. 2020, 6 (7), 1138–1149.

(16) Yin, J.; Maity, P.; De Bastiani, M.; Dursun, I.; Bakr, O. M.; Bredas, J. L.; Mohammed, O. F. Molecular Behavior of Zero-Dimensional Perovskites. Sci. Adv. 2017, 3 (12), e1701793.

(17) Akkerman, Q. A.; Manna, L. What Defines a Halide Perovskite? ACS Energy Lett. 2020, 5 (2), 604–610.

(18) Kovalenko, M. V.; Protosescu, L.; Bodnaruch, M. I. Properties and Potential Optoelectronic Applications of Lead Halide Perovskite Nanocrystals. Science 2017, 358 (6364), 745–750.

(19) Li, Y.; Huang, H.; Xiong, Y.; Kershaw, S. V.; Rogach, A. L. Reversible Transformation between CsPbBr3 and CsPbBr3 Nanocrystals. CrystEngComm 2018, 20 (34), 4900–4904.
(20) Palazon, F.; Urso, C.; De Trizio, L.; Akkerman, Q.; Marras, S.; Locardi, F.; Nelli, I.; Ferretti, M.; Prato, M.; Manna, L. Postsynthesis Transformation of Insulating CsPbBr₃ Nanocrystals into Bright Perovskite CsPbBr₃ through Physical and Chemical Extraction of CsBr. ACS Energy Lett. 2017, 2 (10), 2445–2448.

(21) Wu, L.; Hu, H.; Xu, Y.; Jiang, S.; Chen, M.; Zhong, Q.; Yang, D.; Liu, Q.; Zhao, Y.; Sun, B.; Zhang, Q.; Yin, Y. From Nonluminescent CsPbX₃ (X = Cl, Br, I) Nanocrystals to Highly Luminescent CsPbX₃ Nanocrystals: Water-Triggered Transformation through a CsX-Stripping Mechanism. Nano Lett. 2017, 17 (9), 5799–5804.

(22) Palazon, F.; Almeida, G.; Akkerman, Q. A.; De Trizio, L.; Dang, Z.; Prato, M.; Manna, L. Changing the Dimensionality of Cesium Lead Bromide Nanocrystals by Reversible Postsynthesis Transformations with Amines. Chem. Mater. 2017, 29 (10), 4167–4171.

(23) Liu, Z.; Bekenstein, Y.; Ye, X.; Nguyen, S. C.; Swabec, J.; Zhang, D.; Lee, S. T.; Yang, P.; Ma, W.; Alivisatos, A. P. Ligand Mediated Transformation of Cesium Lead Bromide Perovskite Nanocrystals to Lead Depleted CsPbBr₃ Nanocrystals. J. Am. Chem. Soc. 2017, 139 (15), 5309–5312.

(24) Zhang, X.; Wu, X.; Liu, X.; Chen, G.; Wang, Y.; Bao, J.; Xu, X.; Liu, X.; Zhang, Q.; Yu, K.; Wei, W.; Liu, J.; Xu, J.; Jiang, H.; Wang, P.; Wang, X. Heterostructural CsPbX₂-PbS (X = Cl, Br, I) Quantum Dots with Tunable Vis-NIR Dual Emission. J. Am. Chem. Soc. 2020, 142 (9), 4464–4471.

(25) Miranto, R.; Shin, D.; Septianto, R. D.; Ibáñez, M.; Kovalenko, M. V.; Matsushita, N.; Iwasa, Y.; Biširi, S. Z. Exclusive Electron Transfer in Core@Shell PbTe@PbS Colloidal Semiconductor Nanocrystal Assemblies. ACS Nano 2020, 14 (3), 3242–3250.

(26) Balaz, D. M.; Bijlsma, K. I.; Fang, H.-H. H.; Dinin, D. N.; Döbeli, M.; Kovalenko, M. V.; Loi, M. A. Stoichiometric Control of the Density of States in PbS Colloidal Quantum Dot Solids. Sci. Adv. 2017, 3 (9), eaao1558.

(27) Gilmore, R. H.; Lee, E. M. Y.; Weidman, M. C.; Willard, A. P.; Tisdale, W. A. Charge Carrier Hopping Dynamics in Homogeneously Broadened PbS Quantum Dot Solids. Nano Lett. 2017, 17 (2), 893–901.

(28) Shulga, A. G.; Kahmann, S.; Dirin, D. N.; Graf, A.; Zaumseil, J.; Kovalenko, M. V.; Loi, M. A. Electroluminescence Generation in PbS Quantum Dot Light-Emitting Field-Effect Transistors with Solid-State Gate. ACS Nano 2018, 12 (12), 12805–12813.

(29) Speirs, M. J.; Balazs, D. M.; Dirin, D. N.; Kovalenko, M. V.; Loi, M. A. Increased Efficiency in 5n-Junction PbS QD Solar Cells via Improved Efficiency > 10%. Nano Lett. 2017, 18 (6), 4034–4039.

(30) Ibañez, M.; Hasler, R.; Liu, Y.; Dobrozhan, O.; Nazarenko, O.; Cadavid, D.; Kovalenko, M. V. Tuning P-Type Transport in Bottom-Up-Engineered Nanocrystalline Pb Chalcogenides Using Alkali Metal Chalcogenides as Capping Ligands. Chem. Mater. 2017, 29 (17), 7093–7097.

(31) Dalpian, G. M.; Chelikowsky, J. R. Self-Purification in Semiconductor Nanocrystals. Phys. Rev. Lett. 2006, 96 (22), 226802.

(32) Norris, D. J.; Efros, A. L.; Erwin, S. C. Doped Nanocrystals. Science 2008, 319 (5871), 1776–1779.

(33) Oh, S. J.; Berry, N. E.; Choi, J.-H. H.; Goulding, E. A.; Paik, T.; Hong, S.-H. H.; Murray, C. B.; Kagan, C. R. Stoichiometric Control of Nanocrystal Chalcogenide Nanocrystal Solids to Enhance Their Electronic and Optoelectronic Device Performance. ACS Nano 2013, 7 (3), 2413–2421.

(34) Buonsanti, R.; Milliron, D. J. Chemistry of Doped Colloidal Nanocrystals. Chem. Mater. 2013, 25 (8), 1305–1317.

(35) Du, M. H.; Erwin, S. C.; Efros, A. L. Trapped-Dopant Model of Doping in Semiconductor Nanocrystals. Nano Lett. 2008, 8 (9), 2878–2882.

(36) Yazdani, N.; Andermatt, S.; Yarema, M.; Farto, V.; Bani-Hashemian, M. H.; Volk, S.; Lin, W. M. M.; Yarema, O.; Luisier, M.; Wood, V. Charge Transport in Semiconductors Assembled from Nanocrystal Quantum Dot Nanomaterials. Nat. Commun. 2020, 11 (1), 2852.

(37) Ning, Z.; Voznyy, O.; Pan, J.; Hoogland, S.; Adinolfi, V.; Xu, J.; Li, M.; Kirmani, A. R.; Sun, J. P.; Minor, J.; Kemp, K. W.; Dong, H.; Rolny, L.; Labelle, A.; Carey, G.; Sutherland, B.; Hill, I.; Amassian, A.; Liu, H.; Tang, J.; Bakr, O. M.; Sargent, E. H. Air-Stable n-Type Colloidal Quantum Dot Solids. Nat. Mater. 2014, 13 (8), 822–828.

(38) Nagraha, M. I.; Kumagai, S.; Watanabe, S.; Syntyk, M.; Heiss, W.; Loi, M. A.; Takeya, J. Enabling Ambipolar to Heavy N-Type Transport in PbS Quantum Dot Solids through Doping with Organic Molecules. ACS Appl. Mater. Interfaces 2017, 9 (21), 18039–18045.

(39) Robin, A.; Livache, C.; Ithurria, S.; Lacaze, E.; Dubertret, B.; Luillier, E. Surface Control of Doping in Self-Doped Nanocrystals. ACS Appl. Mater. Interfaces 2016, 8 (40), 27122–27128.

(40) Choi, M. J.; García de Arquer, F. P.; Propp, A. H.; Seifitokaldani, A.; Choi, J.; Kim, J.; Baek, S. W.; Liu, M.; Sun, B.; Biondi, M.; Scheffel, B.; Walters, G.; Nam, D. H.; Jo, J. W.; Ouellette, O.; Voznyy, O.; Hoogland, S.; Kelley, S. O.; Jung, Y. S.; Sargent, E. H. Cascade Surface Modification of Colloidal Quantum Dot Inks Enables Efficient Bulk Homojunction Photovoltaics. Nat. Commun. 2020, 11 (1), 103.

(41) Wang, H.; Butler, D. J.; Straus, D. B.; Oh, N.; Wu, F.; Guo, J.; Xue, K.; Lee, J. D.; Murray, C. B.; Kagan, C. R. Air-Stable CuInSe₂ Nanocrystal Transistors and Circuits via Post-Deposition Cation Exchange. ACS Nano 2019, 13 (2), 2324–2333.

(42) Chakraborty, P.; Jin, Y.; Barros, C. J.; Dunham, S. T.; Gamelin, D. R. Kinetics of Isovalent (Cd²⁺) and Aliovalent (In³⁺) Cation Exchange in Cd₁₋ₓInₓSe Nanocrystals. J. Am. Chem. Soc. 2014, 136 (38), 12885–12893.

(43) Liu, Y.; Cadavid, D.; Ibáñez, M.; Ortega, S.; Martí-Sánchez, S.; Brulobeam, O.; Kovalenko, M. V.; Arbiol, J.; Cadavid, D.; Kovalenko, M. V.; Cadavid, D.; Kovalenko, M. V.; Bawendi, M. G. Electron Doping in Bottom-Up Engineered Nanocrystalline Pb Chalcogenides Using Alkali Metal Chalcogenides as Capping Ligands. Nat. Chem. Mater. 2016, 2, 10766.

(44) Kovalenko, M. V.; Korkosz, R. J.; Luo, Z.; Riba, P.; Cadavid, D.; Ortega, S.; Cabot, A.; Kanatzidis, M. G. Electron Doping in Bottom-Up Engineered Thermoelectric Nanomaterials through HCI-Mediated Ligand Displacement. J. Am. Chem. Soc. 2015, 137 (12), 4046–4049.

(45) Xu, B.; Peng, T.; Li, Z.; Pantelides, S. T.; Wu, Y. Constructing Highly Porous Thermoelectric Monoliths with High-Performance and Improved Portability from Solution-Synthesized Shape-Controlled Nanocrystals. Nano Lett. 2018, 18 (6), 4034–4039.

(46) Ibañez, M.; Hasler, R.; Liu, Y.; Dobrozhan, O.; Nazarenko, O.; Cadavid, D.; Kovalenko, M. V. Tuning P-Type Transport in Bottom-Up-Engineered Nanocrystalline Pb Chalcogenides Using Alkali Metal Chalcogenides as Capping Ligands. Chem. Mater. 2017, 29 (17), 7093–7097.

(47) Cadavid, D.; Cabot, A. High-Performance Thermoelectric Nanocomposites from Nanocrystal Building Blocks. Nat. Commun. 2016, 7 (1), 10766.
(53) Zhao, D.; Huang, J.; Qin, R.; Yang, G.; Yu, J. Perovskite Photodetectors: Efficient Visible–Near-Infrared Hybrid Perovskite: PbS Quantum Dot Photodetectors Fabricated Using an Antisolvent Additive Solution Process. *Adv. Opt. Mater.* 2018, 6 (23), 1870090.

(54) Liu, C.; Peng, H.; Wang, K.; Wei, C.; Wang, Z.; Gong, X. PbS Quantum Dots-Induced Trap-Assisted Charge Injection in Perovskite Photodetectors. *Nano Energy* 2016, 30, 27–35.

(55) Piątkowski, P.; Masi, S.; Galar, P.; Gutiérrez, M.; Ngo, T. T.; Mora-Seró, I.; Doush, A. Deciphering the Role of Quantum Dot Size in the Ultrafast Charge Carrier Dynamics at the Perovskite-Quantum Dot Interface. *J. Mater. Chem. C* 2020, 8 (42), 14834–14844.

(56) Gong, X.; Yang, Z.; Walters, G.; Comin, R.; Ning, Z.; Beurregard, E.; Adinolfi, V.; Voznyy, O.; Sargent, E. H. Highly Efficient Quantum Dot Near-Infrared Light-Emitting Diodes. *Nat. Photonics* 2016, 10 (4), 253–257.

(57) Ning, Z.; Gong, X.; Comin, R.; Walters, G.; Fan, F.; Voznyy, O.; Yassitepe, E.; Buin, A.; Hoogland, S.; Sargent, E. H. Quantum-Dot-in-Perovskite Solids. *Nature* 2015, 523 (7560), 324–328.

(58) Yang, Z.; Jannamohedin, A.; Lan, X.; García De Arquer, F. P.; Voznyy, O.; Yassitepe, E.; Kim, G.-H.; Ning, Z.; Gong, X.; Comin, R.; Sargent, E. H. Colloidal Quantum Dot Photovoltaics Enhanced by Perovskite Shelling. *Nano Lett.* 2015, 15, 7539.

(59) Liu, M.; Chen, Y.; Tan, C. S.; Quintero-Bermudez, R.; Proppe, A. H.; Munir, R.; Tan, H.; Voznyy, O.; Schefl, B.; Walters, G.; Kam, A. P. T.; Sun, B.; Choi, M. J.; Hoogland, S.; Amassian, A.; Kelley, S. O.; García de Arquer, F. P.; Sargent, E. H. Lattice Anchoring Stabilizes Solution-Processed Semiconductors. *Nature* 2019, 570 (7759), 96–101.

(60) Sytnyk, M.; Yakunin, S.; Schöberger, W.; Lechner, R. T.; Burian, M.; Ludescher, J.; Killilea, N. A.; Yousufian, A.; Kriegner, D.; Stangl, J.; Groiss, H.; Heiss, W. Quasi-Epitaxial Metal-Halide Perovskite Ligand Shells on PbS Nanocrystals. *ACS Nano* 2017, 11 (2), 1246–1256.

(61) Wang, H.; Schechtel, E.; Pei, Y.; Snyder, G. J. High Thermoelectric Efficiency of N-Type PbS. *Adv. Energy Mater.* 2013, 3 (4), 488–495.

(62) Zhang, Q.; Wang, B.; Zheng, W.; Kong, L.; Wan, Q.; Zhang, C.; Li, Z.; Cao, X.; Liu, M.; Li, L. Ceramic-like Stable CsPbBr₃ Nanocrystals Encapsulated in Silica Derived from Molecular Sieve Templates. *Nat. Commun.* 2020, 11 (1), 31.

(63) Palazon, F.; Di Stasio, F.; Lauciello, S.; Krahne, R.; Prato, M.; Manna, L. Evolution of CsPbBr₃ Nanocrystals upon Post-Synthesis Annealing under an Inert Atmosphere. *J. Mater. Chem. C* 2016, 4 (39), 9179–9182.

(64) Palazon, F.; Dogan, S.; Marras, S.; Locardi, F.; Nelli, L.; Rastogi, P.; Ferretti, M.; Prato, M.; Krahne, R.; Manna, L. From CsPbBr₃ Nano-Inks to Sintered CsPbBr₃-CsPb₂Br₅ Films via Thermal Annealing: Implications on Optoelectronic Properties. *J. Phys. Chem. C* 2017, 121 (21), 11956–11961.

(65) Tang, J.; Kemp, K. W.; Hoogland, S.; Jeong, K. S.; Liu, H.; Levinia, I.; Furukawa, M.; Wang, X.; Debnath, R.; Cha, D.; Chou, K. W.; Fischer, A.; Amassian, A.; Asbury, J. B.; Sargent, E. H. Colloidal-Quantum-Dot Photovoltaics Using Atomic-Ligand Passivation. *Nat. Mater.* 2011, 10 (10), 765–771.

(66) Tang, J.; Brzozowski, L.; Barkhouse, D. A. R.; Wang, X.; Debnath, R.; Wolowiec, R.; Palmiano, E.; Levinia, I.; Pattanyus-Abraham, A. G.; Jamakosmanovic, D.; Sargent, E. H. Quantum Dot Photovoltaics in the Extreme Quantum Confinement Regime: The Surface-Chemical Origins of Exceptional Air- and Light-Stability. *ACS Nano* 2010, 4 (2), 869–878.

(67) Rabenau, A.; Rau, H. Über Sulfdialgenidene Des Bleis Und Das Pb₄Se₄B₆. *Z. Anorg. Allg. Chem.* 1969, 369 (3–6), 295–305.

(68) German, R. M.; Rabin, B. H. Enhanced Sintering through Second Phase Additions. *Powder Metall.* 1985, 28 (1), 7–12.

(69) Zovas, P. E.; German, R. M.; Hwang, K. S.; Li, C. J. Activated and Liquid-Phase Sintering—Progress and Problems. *J. Met.* 1983, 35 (1), 28–33.