Optical Properties and First-Principles Study of CH₃NH₃PbBr₃ Perovskite Structures

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ABSTRACT: Solution-processed organic–inorganic hybrid perovskites have attracted attention as light-harvesting materials for solar cells and photonic applications. The present study focuses on cubic single crystals and microstructures of CH₃NH₃PbBr₃ perovskite fabricated by a one-step solution-based self-assembly method. It is seen that, in addition to the nucleation from the precursor solution, crystallization occurs when the solution is supersaturated, followed by the formation of a small nucleus of CH₃NH₃PbBr₃ that self-assembles into bigger hollow cubes. A three-dimensional (3D) fluorescence microscopy investigation of hollow cubes confirmed the formation of hollow plates on the bottom; then, the growth starts from the perimeter and propagates to the center of the cube. Furthermore, the growth in the (001) direction follows a layer-by-layer growth model to form a complete cube, confirmed by scanning electronic microscopy (SEM) observations. Two-dimensional (2D)–3D fluorescence microscopy and photoluminescence (PL) measurements confirm a peak emission at 535 nm. To get more insights into the structural and optical properties, density functional theory (DFT) simulations were conducted. The electronic and optical properties calculated by DFT are in agreement with the obtained experimental values. The density-of-state (DOS) calculations revealed that the valence band maximum (VBM) consists of states contributed by Br and Pb, which agrees with the X-ray photoelectron spectroscopy valence band (XPS VB) measurements.

INTRODUCTION

Organic–inorganic perovskites in the form of thin films, microcrystals, nanoparticles, and bulk single crystals exhibit outstanding optoelectronic properties. They are attractive candidates in many cutting-edge applications such as solar cells, light-emitting diodes (LEDs), lasers, and photodetectors and are a competitive material to many standard semiconductors. The properties of perovskites highly depend on their composition, crystallinity, and morphology. They belong to a large crystallographic family that has the same crystal structure as calcium titanate (CaTiO₃) and has the general ABX₃, three-dimensional (3D) structural framework, where A and B are cations of different sizes and X is an anion. Different perovskite nanostructures, such as thin films for solar cells, two-dimensional (2D) nanoplates, one-dimensional (1D) nanowires, and quantum dots, have been studied at the microscale and nanoscale levels. Also, the trap-state density and carrier diffusion length have been investigated in bulk perovskite single crystals. However, low-dimensional halide perovskites show optical and electrical properties that are different from those of bulk halide perovskites. Hence, controlling the scale and shape of the synthesized perovskites is necessary for fundamental and applications research. The changes in the optical and electrical properties are attributed to...
the quantum size effects, large surface-to-volume ratio, and anisotropic geometry. Several synthesis methods were used to prepare single-crystal CH₃NH₃PbX₃, such as top-seed solution growth, inverse temperature crystallization, and antisolvent vapor-assisted crystallization. Recently, researchers have been interested in the nucleation and growth mechanisms of perovskite structures prepared by the inverse temperature crystallization method, using grazing incidence X-ray diffraction (XRD) or in situ Fourier transform infrared spectroscopy. These techniques can accurately explain the crystallinity of the material and its chemical composition. For example, Chen et al. have used filter paper inserted between substrate and precursor solution droplet to separate CH₃NH₃PbBr₃ from the DMF solution, followed by crystallization mechanisms. However, not many studies were conducted on the detailed growth mechanism of cubic CH₃NH₃PbBr₃, evolution of its morphology, and optical properties followed by an in-depth analysis using first-principles methods.

In this work, CH₃NH₃PbBr₃ microstructures were synthesized using a one-step solution self-assembly method. The morphology and the structure were analyzed using scanning electron microscopy (SEM) and X-ray diffraction. Scanning electron microscopy (SEM) and 3D fluorescence microscopy were used to explain the growth mechanism. Further, the optical properties were studied by photoluminescence (PL) and correlated to 2D fluorescence microscopy measurements. We also carried out first-principles-based density functional theory (DFT) simulations to explain the electronic and optical properties of cubic CH₃NH₃PbBr₃ microstructures.

■ RESULTS AND DISCUSSION

The scanning electronic microscopy (SEM) observations of CH₃NH₃PbBr₃ structures show a wide range of shapes, cubes, plates, wires, and hollow cubes (Figure 1a), formed on a silicon substrate. The length range of the wires is from a few microns to more than 100 μm, and the width range is from a few hundred nanometers to 40 μm. Most of the wires were found to have rectangular cross sections, as shown in Figure 1a,b. Cubes and plates with sharp edges existed with different sizes. Also, hollow cubes appeared with a sharp edge (see Figure 1c). These hollow cubes are in the early crystallization stages due to the formation of agglomerate crystals, and it seems that growth starts from the perimeter and propagates to the center of the cube.

To identify the phases of the crystalline CH₃NH₃PbBr₃ perovskite, the powder X-ray diffraction (XRD) spectrum is presented in Figure 2. The XRD patterns of these microstructures exhibit a cubic phase structure of CH₃NH₃PbBr₃ with the Pm3m space group symmetry. The diffraction peaks correspond to the planes (001), (002), (210), (211), (022), and (003). The cubic phase of CH₃NH₃PbBr₃ appears in the absence of other impurities and the lattice parameter a is equal to 5.9403 Å, which is consistent with the literature. We note that all of the shapes present the same X-ray diffraction because the temperature was kept constant during the growth; in contrast, Peng et al. showed that rising temperature can affect the structure, shape, and size of perovskite nanostructures. Based on the diffraction peaks in the XRD spectrum, the (001) series of crystal planes contribute to the growth in the thickness direction.

To explain the growth mechanism through surface evolution, several plates, cubes, and hollow cubes were observed using 2D and 3D fluorescence microscopy coupled with SEM observations. The schematic representation in Figure 3a presents the growth and crystallization mechanisms of CH₃NH₃PbBr₃ structures.

The growth starts when crystallization occurs in the supersaturated CH₃NH₃Br·PbBr₂·DMF precursor solution, and the CH₃NH₃PbBr₃ molecules condense into small seeds. These CH₃NH₃PbBr₃ seeds coalesce into bigger particles in a short time. Then, CH₃NH₃PbBr₃ particles gradually self-assemble into a hollow structure like a hollow cage and the growth starts from the perimeter and propagates to the center (see Figure 1b), giving forms of hollow cubes when the growth is not finished due to the lack of crystal. These crystals are twisted, and their faces are peculiarly inclined toward each other. 3D fluorescence microscopy and SEM observations, as shown in Figure 3b,c, confirm the presence of hollow cubes.
with the formation of a hollow plate at the bottom, and then CH₃NH₃PbBr₃ crystals accumulate in a layered stacked structure and continue to grow in the (001) direction until the final cubic single crystal is formed. Indeed, the CH₃NH₃PbBr₃ crystals in the (001) direction were grown by a layer-by-layer model, also known as the Frank–van der Merwe growth model, until the formation of the complete cube. To explain the growth mechanism of these structures in the (100) direction, a schematic scenario is presented in Figure 3e. Small plates of the CH₃NH₃PbBr₃ crystal appeared on the bottom of the substrate on the (100) facet to play a role of independent seed crystal to form the frame of the cube by self-assembly, as described in Figure 3e. During this step, new layers arise on the top to form cubic plates. Indeed, this growth model of the CH₃NH₃PbBr₃ (100) facet is proceeded by a layer-by-layer assembly. In general, growing a macroscopic film needs a balance of surface energies of the substrate γₐ and the deposit γₐ and the energy of the interface γₖ formed between the two (Figure 3e), which are controlled by the change in Gibbs free energy needed for the creation of the surface or interface. The layer-by-layer growth will be characterized by the balance of energies that will support the increase of the area of the deposit (and the interface) over leaving an exposed substrate surface (γₐ + γₖ < γₐ). This growth will result in the completion of one layer before the nucleation of subsequent layers. This proposed model was confirmed by 3D fluorescence microscopy and SEM observations, which clearly indicate the formation of layers, as shown in Figure 3c, as well as support the approach of Chen et al.25 Also, it seems that these cubic plates will connect with the nearest ones to form bigger cubes and cover a larger surface. Furthermore, 2D and 3D fluorescence microscopy shows uniform green emission with the same geometrical form as shown in the SEM images. To confirm this green emission, the CH₃NH₃PbBr₃ structures were characterized using photoluminescence (PL). The PL and the optical absorption of CH₃NH₃PbBr₃ were studied and are presented in Figure 4. The optical absorption shows a peak at 523 nm. The PL emission has a sharp emission peak at 535 nm with full width at half-maximum (FWHM) equal to 21 nm.

The emission wavelength at 535 nm is in agreement with the green emission from a fluorescence microscope. Furthermore, the emission peak of the CH₃NH₃PbBr₃ structures is comparable to the emission peak measured on thin films and quantum dots by Zhang et al. and Gonzalez-Carrero et al.30,31 To further understand the dependence of the intensity of the PL peak on the excitation energy densities, we investigated the emission characteristics of CH₃NH₃PbBr₃ structures at room temperature using different laser densities, as shown in Figure 5. At room temperature, no notable shift in the position of the single PL peak at 535 nm was observed over a range of excitation densities. The PL intensity of the perovskite structures shows an over-linear dependence on the laser density with a slope of 0.6 in the power dependence line until the laser power of 2.01 mW (inset in Figure 5). This increase in the carrier density leads to the saturation of nonradiative recombination centers, which improves the effective internal quantum efficiency.32 Zhang et al. showed a PL dependence on...
laser energy with a slope of 0.7 for CsPbBr6 microdisks using a 405 nm excitation laser. Furthermore, by increasing the laser power, the linewidth remains constant around 20 nm (FWHM).

Since we have obtained the cubic phase for CH3NH3PbBr3 perovskites in our experiments, the unit cell of a simple cubic structure is considered for the calculations, and the optimized crystal structure is shown in Figure 6. The room-temperature crystal structure of CH3NH3PbBr3 is cubic with the Pm̅3̅m space group, and we have obtained a bulk lattice parameter of 5.92 Å after optimization, which agrees with the experimentally reported value of 5.94 Å.

The total density of states (DOS) and the projected density of states calculated for the individual atoms plotted using GGA + U are presented in Figure 7a at a temperature of 0 K. We can see that the main contribution close to the valence band maximum (VBM) comes from the halogen (Br) 4p states. The absorption coefficient is an important optical parameter that shows the extent to which light will penetrate the material before it is absorbed. The absorption coefficient depends on the material thickness and on the wavelength range of the incident light. We found that both the theoretical absorption and experimental absorption have the same band gap of ~2.3 eV of CH3NH3PbBr3 structures.

We also calculated optical constants such as dielectric constants and refractive index (n) of CH3NH3PbBr3 to understand the optical response in detail. The dielectric constant is calculated using the expression ε = ε1 + iε2, where ε1 is the real part that represents the capacitance and ε2 is the imaginary part that represents the loss of electromagnetic energy in the system. The dielectric constant represents the polarization of the system in the presence of a static electric field. The calculated values of dielectric function are plotted in Figure 9 (solid red line). For the real and imaginary parts, the peaks are found between 2−3 and 3−4 eV, respectively. The maximum value of static dielectric constant obtained is about 7 eV for both real and imaginary parts. For comparison, the real and imaginary parts of the modeled ε of CH3NH3PbI3 are included in Figure 9 (dashed black line) from ref 36. The overall ε spectral shapes of these two materials look similar. However, CH3NH3PbBr3 shows a larger band gap as expected37,38 than that for CH3NH3PbI3 with a band gap of
The calculated refractive index is shown in Figure 9 (blue line), which shows the largest peak similar to that of the real part of dielectric constant. The refractive index reduces for higher energy values; it is around 2.48 at 535 nm for CH$_3$NH$_3$PbBr$_3$ structures, while it is 2.29 for the CH$_3$NH$_3$PbBr$_3$ thin film. All single crystals exhibit 2–8% higher refractive index. A higher refractive index of around 25% is also observed for the CH$_3$NH$_3$PbBr$_3$ perovskite single crystals compared to the equivalent thin films.

**CONCLUSIONS**

In summary, perovskite CH$_3$NH$_3$PbBr$_3$ microstructures were synthesized using a one-step solution self-assembly method. The morphology of these microstructures consists of a mixture of plates and cubes. The growth process of the CH$_3$NH$_3$PbBr$_3$ single crystal was presented and was supported by 3D fluorescence microscopy coupled to SEM. We found that after crystallization of CH$_3$NH$_3$PbBr$_3$ hollow plates are formed on the substrate, and then a layer-by-layer growth model was used to grow CH$_3$NH$_3$PbBr$_3$ cubes in the (001) direction. Fluorescence microscopy shows a uniform green emission, which is confirmed by the PL emission at 535 nm. The electronic band structure, density of states, and optical properties calculated using the DFT method are in good agreement with the experimental results. The shapes and the optical properties of these perovskite microstructures are promising for next-generation light-emitting devices and nanolaser structures.

**EXPERIMENTAL SECTION**

**Synthesis of Hybrid Organic–Inorganic Perovskite CH$_3$NH$_3$PbBr$_3$.** The hybrid organic–inorganic perovskite under this study is CH$_3$NH$_3$PbBr$_3$. The CH$_3$NH$_3$PbBr$_3$ microstructures (hollow cubes, plates, cubes, and wires) were synthesized using a one-step solution self-assembly method, which has been reported in refs 42, 43. CH$_3$NH$_3$Br and PbBr$_2$ were independently dissolved in N,N-dimethylformamide (DMF) with the same concentration of 0.2 M. These two solutions were mixed at room temperature with a 1:1 volume ratio to form a CH$_3$NH$_3$Br–PbBr$_2$ solution with concentration equal to 0.1 M. The diluted solution was dip-cast onto a glass or silicon substrate, which was placed on a Teflon stage in a beaker. Dichloromethane (DCM, CH$_2$Cl$_2$) was placed in a beaker and sealed with a porous parafilm to control the evaporation speed. After 24 h, CH$_3$NH$_3$PbBr$_3$ perovskites microstructures were successfully synthesized on the silicon substrate.

**Physical Characterization.** The fabricated structures were then characterized using SEM and X-ray to study their morphology and crystallinity. A Jeol scanning electron microscope (SEM) operating at a 20 keV beam energy was used to analyze the structures. The X-ray powder diffraction measurements were performed on a Bruker system (D8 Avance) at room temperature and using a Cu Kα source with λ = 1.54056 Å. Room-temperature absorption measurements were carried out using a UV–vis Varian Cary 5000 spectrophotometer. PL measurements were performed at room temperatures using a Jobin Yvon LabRAM HR 800 UV system. A laser emitting at 407 nm was used as an excitation source for PL measurements. The incident laser power for the measurements was set to 5 mW. A fluorescence microscope, Olympus BX51, was used to study the structures in 2D and 3D with an excitation laser wavelength of 407 nm. X-ray photoelectron spectroscopy (XPS) studies were carried out in a Kratos AXIS Supra DLD spectrometer equipped with a monochromatic Al Kα X-ray source (hν = 1486.6 eV).
operating at 45 W, a multichannel plate, and a delay line detector under a vacuum pressure of \( \sim 10^{-9} \) mbar. All spectra were recorded using an aperture slot of 300 \( \mu \)m x 700 \( \mu \)m. Survey spectra were collected using a pass energy of 160 eV and a step size of 1 eV. A pass energy of 20 eV and a step size of 0.1 eV were used for the high-resolution spectra. For XPS analysis, samples were mounted in floating mode to avoid differential charging. Charge neutralization was required for all samples. Binding energies were referenced to the C 1s binding energy of adventitious carbon contamination, which was taken to be 284.8 eV.

**Computational Methodology.** We have carried out density functional theory calculations on bulk CH\(_3\)NH\(_3\)PbBr\(_3\) to get further insights into the experimentally observed properties employing the plane-wave pseudopotential code, Vienna Ab initio Simulation Package (VASP).\(^44,45\) The exchange and correlation are described in the generalized gradient approximation (GGA).\(^46\) The pseudopotentials are described using the projected augmented wave (PAW) method with Perdew–Burke–Ernzerhof (PBE) formalism.\(^47\) A kinetic energy cutoff of 650 eV is used to expand the plane waves included in the basis set. Since it is well known that GGA underestimates the band gap of halide perovskite structures,\(^48\) we have employed the Hubbard approximation with \( U \) parameter = 8 eV as implemented in the Dudaev approach in VASP.\(^49\) The Brillouin zone is sampled using a Monkhorst Pack grid of 8 \times 8 \times 8. The energy and force relaxations were performed within tolerances of 1 \times 10^{-6} eV and 1 \times 10^{-3} eV/Å, respectively.

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**Notes**

The authors declare no competing financial interest.

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**REFERENCES**

(1) Ding, J.; Xiaohua, C.; Lin, J.; Tianliang, Z.; Ying, Z.; Songjie, D. Polarization-Dependent Optoelectronic Performances in Hybrid Halide Perovskite MAPbX\(_3\) (\( X = \) Br, Cl) Single-Crystal Photo-detectors. *ACS Appl. Mater. Interfaces* 2018, **10**, 85–850.

(2) Dong, J.; Xu, X.; Shi, J. J.; Li, D. M.; Luo, Y. H.; Meng, Q. B.; Chen, Q. Suppressing Charge Recombination in ZnO-Nanorod-Based Perovskite Solar Cells with Atomic-Layer-Deposition TiO\(_2\). *Clin. Phys. Lett.* 2015, **32**, No. 078401.

(3) Wong, A. B.; Lai, M. L.; Eaton, S. W.; Yu, Y.; Lin, E.; Dou, L.; Fu, A.; Yang, P. D. Growth and Anion Exchange Conversion of CH\(_3\)NH\(_3\)PbX\(_3\), Nanorod Arrays for Light-Emitting Diodes. *Nano Lett.* 2015, **15**, 5519.

(4) Najar, A.; Shaфа, M.; Anjum, D. Synthesis, optical properties and residual strain effect of GaN nanowires generated via metal-assisted photochemical electronless etching. *RSC Adv.* 2017, **7**, 21697–21702.

(5) Najar, A.; Gerland, M.; Jouiaud, M. Porosity-induced relaxation of strains in GaN layers studied by means of micro-indentation and optical spectroscopy. *J. Appl. Phys.* 2012, **111**, No. 095315.

(6) Najar, A.; Omi, H.; Tawara, T. Scandium effect on the luminescence of Er-Sc silicates prepared from multi-nanolayer films. *Nanoscale Res. Lett.* 2014, **9**, No. 356.

(7) Najar, A.; Al-Jabr, A. A.; Slimane, A. B.; Alsunaidi, M. A.; Ng, T. K.; Ooi, B. S.; Sougrat, R.; Anjum, D. H. Effective Antireflection Properties of Porous Silicon Nanowires for Photovoltaic Applications. In *Saudi International Electronics, Communications and Photonics Conference*, IEEE, 2013; pp 1–4.

(8) Najar, A.; Omi, H.; Tawara, T. Effect of structure and composition on optical properties of Er-Sc silicates prepared from multi-nanolayer films. *Opt. Express* 2015, **23**, 7021–7030.

(9) Slimane, A. B.; Najar, A.; Elafandy, R.; San-Román-Alerigi, D. P.; Anjum, D.; Ng, T. K.; Ooi, B. S. On the phenomenon of large photoluminescence red shift in GaN nanoplates. *Nanoscale Res. Lett.* 2013, **8**, 342.

(10) Najar, A.; Jouiaud, M. Synthesis of InGaN nanowires via metal-assisted photochemical electronless etching for solar cell application. *Sol. Energy Mater. Sol. Cells* 2018, **180**, 243–246.

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

(12) Sarapov, B.; Mitzi, D. B. Organic–Inorganic Perovskites: Structural Versatility for Functional Materials Design. *Chem. Rev.* 2016, **116**, 4558–4596.

(13) Levy, M. R. Crystal Structure and Defect Property Predictions in Ceramic Material. Imperial College of Science, Technology and Medicine, 2005.

(14) Yan, X.; Wang, W.; Yang, X.; Yi, W.; Wang, Y.; Li, H.; Gu, W.; Sheng, C. Origin of thermal instability of CH\(_3\)NH\(_3\)Pb\(_x\)I\(_{3-x}\) films for photovoltaic devices. *Mater. Lett.* 2016, **176**, 114–117.

(15) Tong, Y.; Ehrat, F.; Vanderlinden, W.; Cardenas-Daw, C.; Stolarczyk, J. K.; Polavarapu, L.; Urban, A. S. Dilution-Induced Formation of Hybrid Perovskite Nanoplatelets. *ACS Nano* 2016, **10**, 10936–10944.

(16) Zhang, D.; Eaton, S. W.; Yu, Y.; Dou, L.; Yang, P. Solution-Phase Synthesis of Cesium Lead Halide Perovskite Nanowires. *J. Am. Chem. Soc.* 2015, **137**, 9230–9233.

(17) Schmidt, L. C.; Pertegás, A.; González-Carrero, S.; Malinkiewicz, O.; Agouram, S.; Espallargas, G. M.; Bolink, H. J.; Galian, R. E.; Pérez-Prieto, J. Nontemplate Synthesis of CH\(_3\)NH\(_3\)PbI\(_3\) Perovskite Nanoparticles. *J. Am. Chem. Soc.* 2014, **136**, 850–853.

(18) Dong, Q.; Fang, Y.; Shao, Y.; Mulligan, P.; Qiu, J.; Cao, L.; Huang, J. Electron-hole diffusion lengths> 175 \( \mu \)m in solution-grown CH\(_3\)NH\(_3\)PbI\(_3\) single crystals. *Sci. Adv.* 2015, **1**, 347, 967–970.

(19) Erkülç, U.; Pablo, S. F.; Hyun, G. J.; Keinuku, S.; Yong, C. L.; Mina, M.; Kazu, S.; Susumu, O.; Kazunari, M.; Hiroki, A. Vapor Phase Selective Growth of Two-Dimensional Perovskite/WSe\(_2\) Heterostructures for Optoelectronic Applications. *ACS Appl. Mater. Interfaces* 2019, **11**, 40503–40511.

(20) Xing, J.; Liu, X. F.; Zhang, Q.; Ha, S. T.; Yuan, Y. W.; Shen, C.; Sum, T. C.; Xiong, Q. Vapor Phase Synthesis of Organometal Halide
Perovskite Nanowires for Tunable Room-Temperature Nanolasers. *Nano Lett.* 2015, 15, 4571–4577.

(21) Liu, Y.; Yang, Z.; Cui, D.; Ren, X.; Sun, J.; Liu, X.; Zhang, J.; Wei, Q.; Fan, H.; Yu, F.; Zhang, X.; Zhao, C.; Liu, S. F. Two-Inch-Sized Perovskite CH$_3$NH$_3$PbX$_3$ (X = Cl, Br, I) Crystals: Growth and Characterization. *Adv. Mater.* 2015, 27, 5176–5183.

(22) Rao, H. S.; Li, W. G.; Chen, B. X.; Kuang, D. B.; Su, C. Y. In Situ Growth of 120 cm$^2$ CH$_3$NH$_3$PbBr$_3$ Perovskite Crystal Film on FTO Glass for Narrowband-Photodetectors. *Adv. Mater.* 2017, 29, No. 1602639.

(23) 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.; Mohammed, O. F. Sargent, E. H.; Bakr, O. M. Low trap-state density and long carrier diffusion in organolead trihalide perovskite single crystals. *Science* 2015, 347, 519–522.

(24) Hu, Q.; Zhao, L.; Wu, J.; Gao, K.; Luo, D.; Jiang, Y.; Zhang, Z.; Zhu, C.; Schaible, E.; Hexemer, A.; Wang, C.; Liu, Y.; Zhang, W.; Gratzel, M.; Liu, F.; Russell, T. P.; Zhu, R.; Gong, Q. In situ dynamic observations of perovskite crystallisation and microstructure evolution intermediated from [PbI$_6$]$^4$- cage nanoparticles. *Nat. Commun.* 2017, 8, No. 15688.

(25) Chen, F.; Xu, C.; Xu, Q.; Zhu, Y.; Zhu, Z.; Liu, W.; Dong, X.; Qin, F.; Shi, Z. Structure Evolution of CH$_3$NH$_3$PbI$_3$ Single Crystal Grown in N,N-dimethylformamide Solution. *Cryst. Growth Des.* 2018, 18, 3132–3137.

(26) Peng, L.; Dutta, A.; Xie, R.; Yang, W.; Pradhan, N. Dot–Wire–Platel–Cube: step growth and structural transformations in CsPbBr$_3$ perovskite nanocrystals. *ACS Energy Lett.* 2018, 3, 2014–2020.

(27) Zhang, W.; Peng, L.; Liu, J.; Tang, A.; Hu, J. S.; Yao, J.; Zhao, Y. S. Controlling the Cavity Structures of Two-Photon-Pumped Perovskite Microcubers. *Adv. Mater.* 2040, 2016, 27, No. 4046.

(28) Venables, J. A. Introduction to Surface and Thin Film. In *Chemistry of Thin Films*; Cambridge University Press: Cambridge, 2000.

(29) Burke, S. A.; Topple, J. M.; Gratzel, M. Origin

(30) Zhang, Z.; Wang, H. Y.; Zhang, Y. X.; Hao, Y. W.; Sun, C.; Yu, Z.; Rong, G. B.; Chen, Q. D.; Sun, H. B. The Role of Trap-assisted Recombination in Luminescent Properties of Organometal Halide CH$_3$NH$_3$PbBr$_3$ Perovskite Films and Quantum Dots. *Sci. Rep.* 2016, No. 27286.

(31) Gonzalez-Carrero, S.; Schmidt, L. C.; Rosa-Pardo, I.; Martinez-Sarti, L.; Sesso, M.; Galan, R. E.; Per’ez-Prieto, J. Colloids of Naked CH$_3$NH$_3$PbI$_3$ Perovskite Nanoparticles: Synthesis, Stability, and Thin Solid Film Deposition. *ACS Omega* 2018, 3, 1298–1303.

(32) Ibrahim, D. M.; Jacopin, G.; Meloni, S.; Mattoni, A.; Arora, N.; Boziki, A.; Zakeeruddin, S. H.; Rothlisberger, U.; Grätzel, M. Origin of unusual bandgap shift and dual emission in organic-inorganic lead halide perovskites. *Sci. Adv.* 2016, 2, No. e1601156.

(33) Zhang, H.; Liao, Q.; Wu, Y.; Chen, J.; Gao, Q.; Fu, H. Pure zero-dimensional Cs$_3$PbBr$_5$ single crystal rhombohedral microdisks with high luminescence and stability. *Phys. Chem. Chem. Phys.* 2017, 19, 29092–29098.

(34) Noh, J. H.; Im, S. H.; Heo, J. H.; Mandal, T. N.; Seok, S. I. Chemical management for colorful, efficient, and stable inorganic-organic hybrid nanostructured solar cells. *Nano Lett.* 2013, 13, 1764.

(35) Wei, L.; Kikue, S.; Li, X.; Kera, K.; Tang, U. Halide-Substituted Electronic Properties of Organometal Halide Perovskite Films: Direct and Inverse Photoemission Studies. *Appl. Mater. Interfaces* 2016, 8, 11526–11531.

(36) Lüpke, P.; Michael, S.; Bjorn, N.; Werner, J.; Filipić, M.; Soo, J. M.; Jun, H. Y.; Marko, T.; Stafan, D. W.; Christophe, B. Complex Refractive Index Spectra of CH$_3$NH$_3$PbI$_3$ Perovskite Thin Films Determined by Spectroscopic Ellipsometry and Spectrophotometry. *J. Phys. Chem. Lett.* 2015, 6, 66–71.

(37) Yin, W. J.; Yang, J. H.; Kang, J.; Yan, Y.; Wei, S. H. Halide Perovskite Materials for Solar Cells: A Theoretical Review. *J. Mater. Chem. A* 2015, 3, 8926–8942.