Self-assembled ultrafine CsPbBr₃ perovskite nanowires for polarized light detection

Zixing Peng^{1†}, Dandan Yang^{1†}, Bozhao Yin¹, Xin Guo², Shuang Li¹, Qiuqiang Zhan², Xiudi Xiao^{3*}, Xiaofeng Liu⁴, Zhiguo Xia¹, Zhongmin Yang¹, Jianrong Qiu⁵ and Guoping Dong^{1*}

ABSTRACT One-dimensional (1D) metal halide perovskite nanowire (NW) arrays with high absorption efficiency, emission yield and dielectric constants, as well as anisotropic optoelectronic properties have found applications in energy harvesting, flexible electronics, and biomedical imaging devices. Here, a modified two-step solvothermal method is developed for the synthesis of self-assembled cubic CsPbBr₃ NW arrays. This method provides facile access to continuous and uniform ultrafine perovskite NWs and well-aligned pure perovskite NW arrayed architectures. Under excitation at 365 nm, the CsPbBr₃ NWs give a strong blue emission observable to the naked eyes. The CsPbBr₃ NWs also exhibit strong two-photon excited luminescence under the irradiation with an 800 nm pulse laser. By rotating the polarization angle of the 800 nm laser, strong polarization dependence with a polarization degree up to ~0.49 is demonstrated in the self-assembled CsPbBr₃ NW array, although the CsPbBr₃ NWs have an isotropic cubic structure. Based on density functional theory (DFT) calculations, this polarization-dependent emission is correlated with the anisotropic charge density distribution of the perovskite NWs. These findings suggest that the ultrafine CsPbBr₃ NWs with a well-defined self-assembled architecture could be applied as next-generation polarization-sensitive photoelectronic detection materials.

Keywords: ultrafine perovskite nanowires, self-assembly, perovskite nanowire array, anisotropy, polarization-sensitive detection

INTRODUCTION

Low-dimensional semiconductor nanosystems, such as nanowires (NWs), nanorods (NRs), and nanobelts (NBs), play an indispensable role in enabling nanodevices and relevant technologies over a broad range of applications including nanolasers, waveguides, light-emitting diodes, photoelectronic sensors, and photovoltaics [1–5]. Among them, one-dimensional (1D) semiconductor NWs, benefiting from their high anisotropic optoelectronic properties, demonstrate strong polarization-dependent light emission, absorption, and photoconductivity [4,6,7]. For instance, polarized emission has been observed in GaN NRs and InP NWs, which have been explained by different theories including intrinsic and extrinsic transition dipole moments as well as dielectric confinement of the optical electric field [8–10]. These theories can be applied to 1D semiconductor NWs irrespective of their fabrication processes, such as epitaxial growth and colloidal chemistry methods [11,12]. In addition, owing to the excellent photon and carrier confinement capabilities, semiconductor NWs can be used as building blocks for electronic circuits and photonic chips [1,12,13]. Hence, 1D semiconductor NWs represent novel building blocks for constructing polarization-sensitive nanoscale photodetectors, which are useful in integrated photonic circuits, optical switches and interconnects, near-field imaging, as

¹ State Key Laboratory of Luminescent Materials and Devices, Guangdong Provincial Key Laboratory of Fiber Laser Materials and Applied Techniques and Guangdong Engineering Technology Research and Development Center of Special Optical Fiber Materials and Devices, South China University of Technology, Guangzhou 510640, China

² Centre for Optical and Electromagnetic Research, South China Academy of Advanced Optoelectronics, South China Normal University, Guangzhou 510006, China

³ Key Laboratory of Renewable Energy, Guangdong Key Laboratory of New and Renewable Energy Research and Development, Guangzhou Institute of Energy Conversion, Chinese Academy of Sciences, Guangzhou 510640, China

⁴ School of Materials Science and Engineering, Zhejiang University, Hangzhou 310027, China

⁵ College of Optical Science and Engineering, State Key Laboratory of Modern Optical Instrumentation, Zhejiang University, Hangzhou 310027, China

[†] These authors contributed equally to this work.

* Corresponding authors (emails: xiaoxd@ms.giec.ac.cn (Xiao X); dgp@scut.edu.cn (Dong G))

well as high-resolution detectors [14–16].

In the past few years, all-inorganic metal halide perovskites (CsPbX_3 , $\text{X} = \text{Cl, Br, I}$) have triggered widespread interest in different fields due to their superior photoluminescence (PL) properties, such as narrow spectral width and high quantum yield [17–23]. Unlike conventional colloidal semiconductor nanocrystals (NCs), high defect tolerance endows CsPbX_3 with a near-unity quantum yield without an encapsulating shell, while the variation of halogen anion allows tunable absorption and emission bands of CsPbX_3 in a wide spectral range [24]. Accordingly, compared with semiconducting NWs like metal oxides and chalcogenides, CsPbX_3 NWs offer obvious advantages and more possibilities for optoelectronic applications. However, most investigations of the polarization characteristics of CsPbX_3 NWs focused on the CsPbX_3 quantum dots-doped organic matrix [25–27]. These doped organic matrixes are suitable for applications in display, imaging, and data communication, but not for polarization-sensitive photoelectronic chip because of the organic components which reduce the electrical properties. There are a few reports on polarized light emission from pure CsPbX_3 NWs, with most focusing on the single NW, rather than the more valuable arrayed self-assembled CsPbX_3 NWs [26,28]. Pure self-assembled CsPbX_3 NW arrays with controllable composition and orientation are therefore highly desired for polarization-sensitive applications.

Traditionally, 1D CsPbX_3 NWs are grown epitaxially by a chemical vapor deposition (CVD) method [29]. 1D CsPbX_3 NWs prepared by this method have advantages of high crystallinity and uniformity. However, this method is complicated and it is difficult to control the composition of the products. More importantly, the 1D CsPbX_3 NWs synthesized by this method have poor maneuverability and the large lattice mismatching between the NWs and the substrate strongly impedes the exploration of chemical and optical properties of the NWs [29,30]. Using the solution method to prepare CsPbX_3 NWs avoids the influence of substrate, but it is exceedingly difficult to obtain continuous ultrafine CsPbX_3 NWs with high crystallinity, uniformity, and chemical yield [18,31].

Herein, we report a simple two-step solvothermal method to obtain uniform and continuous pure CsPbX_3 NWs with unique polarization characteristics, which allows for facile composition control. Under optimized conditions, we obtain ultrafine blue-emitting CsPbBr_3 NWs with an average width of ~ 3.8 nm and photoluminescence quantum yield (PLQY) as high as 29%. Through a simple direct-dripping approach, the as-pre-

pared CsPbBr_3 NWs can directly self-assemble into an ordered and directional array over large areas. Under the excitation of an 800-nm femtosecond (fs) laser, remarkable excitation polarization-dependent emission is detected from the self-assembled CsPbBr_3 NW array via a two-photon process. Based on density functional theory (DFT) calculations, this polarization dependence is due to the NWs' anisotropic charge distribution. The developed synthetic process represents a novel and facile method to prepare self-assembled perovskite NWs. Our results are important for next-generation optoelectronic devices, especially the polarization-sensitive integrated chips, and also advance fundamental understanding of the anisotropic optical properties of perovskite NWs.

EXPERIMENTAL SECTION

Raw materials

The starting materials were cesium carbonate (Cs_2CO_3 , 99.995%), lead bromide (PbBr_2 , 99.99%), 1-octadecene (1-ODE, 90%), oleic acid (OA, 80%–90%), and oleylamine (OLA, 85%) from Alfa Aesar.

1-ODE, OLA and OA were first degassed in a 2-neck flask by heating to 110°C with stirring under vacuum for 2 h. After heating, the flasks were cooled down to room temperature and the resultant solvent was used in the following experiment. Other chemicals were used without any further purification.

Synthesis of CsPbBr_3 NWs

In this work, solvothermal synthesis was used to prepare uniform and well crystalline ultrafine CsPbBr_3 NWs. In a typical synthesis of ultrafine CsPbBr_3 NWs, 0.092 mmol of Cs_2CO_3 , 7 mL of 1-ODE, and 0.5 mL of OA were added into a 2-neck flask, while 0.376 mmol of PbBr_2 , 8 mL of 1-ODE, 0.5 mL of OA and 1 mL of OLA were also added into another 2-neck flask for the pre-dissolution process. Both flasks were heated to 110°C under stirring and maintained for 2 h. After heating, the two solutions were mixed and placed in a Teflon lined autoclave (50 mL) and heated at different temperatures (100 – 160°C) for 1–6 h. After the reaction finished and the whole system was cooled down to room temperature, 40 mL of anhydrous methyl acetate was added to the crude solution until the mixture turned turbid. Then the mixture was centrifuged at 10,000 rpm for 5 min, making sure that most of the NWs were separated. The supernatant was discarded, and the precipitate dispersed in *n*-hexane for further measurements.

Characterizations

The crystal structure of CsPbBr₃ NWs was investigated by an X'Pert Pro X-ray diffraction (XRD, PANalytical, Netherland) with Cu K α radiation operating at 40 kV and 40 mA ($\lambda = 0.15418$ nm, scanning step 0.02°, scanning speed 0.1 s per step). The transmission electron microscopy (TEM) images and high-resolution TEM (HRTEM) images of the products were obtained by an HRTEM 2100F (JEOL, Japan). The PL properties were investigated using a high-resolution ultraviolet-visible (UV-Vis) spectrofluorometer (Edinburgh Instruments FLS 920) equipped with a single-photon counting photomultiplier (Hamamatsu R928P) in a Peltier aircooled house. UV-Vis spectra were measured using a UV-Vis spectrophotometer (Hitachi U3010, Japan). Raman spectra were measured using a Raman spectrometer (Renishaw in Via, Gloucestershire, UK) equipped with a 532-nm laser as the excitation source. The PLQY of the as-prepared CsPbBr₃ NWs was measured using a Hamamatsu absolute quantum yield spectrometer (C11347 Quantaury QY). The ¹H nuclear magnetic resonance (¹H NMR) spectra of the as-prepared CsPbBr₃ NCs were recorded on a Bruker AVANCE digital 500 spectrometer.

Optical setup for polarized emission study of the as-prepared CsPbBr₃ NCs

A lab-made optical system was built to perform the polarization characteristics of different CsPbBr₃ NCs, as displayed in Fig. S1. The 800-nm fs laser (76 MHz) beam was obtained by a single-mode diode laser (B&A Technology Co. Ltd., Shanghai). A halfwave plate (P) was placed in the optical path to control the polarization of the 800-nm fs laser. After passing through the half-wave plate, the 800-nm fs laser beam was reflected by a 775-nm short-pass dichroic mirror (DM1, ZT775Sp-2p-UF3, Chroma), and focused on the sample using an oil-immersed objective (OL1, PLAPO $\times$ 60/1.35, Olympus). The visible emissions (400–750 nm) were collected through the same objective and filtered by a 775-nm short-pass filter (F, FF01-775/sp-25, Semrock), and then captured by a spectrometer (QE65000, Ocean Optics).

Calculation method

The first-principles calculations were performed based on the DFT method, as implemented in the Vienna *ab initio* simulation package (VASP), employing the generalized gradient approximations (GGA) [32] of Perdew-Burke-Ernzerhof for the exchange correlation functional. The electron density and distribution of Cs⁺, Pb²⁺ and Br[−] ions in both NW and nanocube structures were described by

using the augmented-plane-wave method [33]. An energy cutoff of 320 eV was adopted, and *k* points *via* a 3 $\times$ 3 $\times$ 3 Monkhorst Pack scheme were sampled.

RESULTS AND DISCUSSION

As a proof-of-concept experiment, a modified solvothermal method was employed to prepare self-assembled CsPbX₃ NWs with ultrasensitive excitation polarization-dependent PL (see details in the experimental section). Using the conventional solvothermal method (Fig. S2a), which is widely used to prepare various uniform CsPbX₃ NCs with high crystallinity, we found that after extracting the products from the reaction solution, there were still large amounts of unreacted materials left at the bottom of the Teflon reactor, implying a low product yield. We therefore introduced a pre-dissolution process to enhance the product yield. OA and OLA were used to dissolve the Cs₂CO₃ and PbBr₂, respectively, and then these two mixtures were heated under stirring. After heating, these two suspensions become clear, and then they were mixed for further crystallization (Fig. S2b). Interestingly, the TEM image in Fig. 1a shows the obtained CsPbBr₃ NCs are well-dispersed ultrafine continuous NWs with a width of $\sim$ 3.8 nm. Fig. 1b shows the as-prepared ultrafine NWs are pure cubic phase (JCPDS #54-0752). In the corresponding HRTEM image (the bottom inset in Fig. 1a), a series of crystal facets with a spacing value of $\sim$ 0.30 nm are observed, which is in good agreement with the (200) planes of cubic-phase CsPbBr₃. It is worth noting that the diffraction peak intensity of the (200) crystal planes in Fig. 1b is much higher than that of other crystal planes for CsPbBr₃ NWs. This is different from the intensity ratios in the standard XRD pattern, suggesting the ultrafine NWs are aligned with a preferred orientation.

For comparison, we also used the conventional solvothermal method for the synthesis of pure CsPbBr₃ NCs. The TEM image (Fig. 1c) shows the CsPbBr₃ NCs prepared by the conventional solvothermal method are well-dispersed homogeneous nanocubes with a diameter of $\sim$ 7.3 nm. The lattice fringe of 0.30 nm in the corresponding HRTEM image (the bottom inset in Fig. 1c) matches well with the (200) planes of cubic-phase CsPbBr₃, confirming the CsPbBr₃ nanocubes are also cubic phase. Identical Raman spectra of the NWs and nanocubes (Fig. S3) indicate they belong to the same crystalline phase. Under the excitation of 365 nm, bright green emission at 515 nm from the CsPbBr₃ nanocubes is detected (Fig. 1d), which can be observed by the naked eye (the top inset in Fig. 1c). Compared with the CsPbBr₃ nanocubes, under the excitation of 365 nm, the emission

Figure 1 Structural characterization and PL spectra of CsPbBr₃ NWs and nanocubes. (a, c) TEM images of CsPbBr₃ NWs and nanocubes, respectively. Insets: photographs of the colloidal hexane solution of CsPbBr₃ NWs and nanocubes under the excitation of 365-nm UV light, and corresponding HRTEM images showing the crystal lattice information (scale bar is 5 nm). (b) XRD patterns of CsPbBr₃ NWs. (d) UV-Vis absorption and PL spectra of CsPbBr₃ NWs (160°C, 1 h) and nanocubes (160°C, 2 h).

peak of CsPbBr₃ NWs moves towards shorter wavelength, and a bright blue emission at 455 nm is observed, as shown in Fig. 1d and the inset in Fig. 1a. The sharp absorption peak indicates that the ultrafine NWs are uniform in diameter, in consistent well with the ultra-narrow edge width of ~3.8 nm for the NWs in the TEM image (Fig. 1a). In agreement with the absorption spectra, PL spectra (Fig. 1d) of the NWs exhibit a relatively narrow peak at 455 nm (2.72 eV) with a full width at half maximum (FWHM) of 17 nm, and a typical Stokes shift of 6 nm. More importantly, the CsPbBr₃ NWs show a PLQY of 28.8% (Fig. S4), almost the highest in the reported CsPbBr₃ NWs [10,34].

To understand the influence of the pre-dissolution process on the CsPbBr₃ NC morphology, we conducted a comparative study of the growth mechanisms of these two CsPbBr₃ NCs. The TEM image of clusters in the pre-dissolved solution without heating shows the structures are short and fragmental NWs (Fig. S5a), while the clusters in the conventional original solution are dis-

persed nanodots (Fig. S5b). This reveals that the pre-dissolution process is the key step that leads to the morphology change of CsPbBr₃ NCs. In addition, according to the ¹H NMR results (Fig. 2a), there are lots of organic ligands on the surface of CsPbBr₃ NWs, including protonated OLA and OA. In contrast, the surface of CsPbBr₃ nanocubes are ligand-free (Fig. 2b). Based on these observations, a schematic diagram of the pre-dissolved crystal growth mechanism is shown in Fig. 2c and d. When the Cs₂CO₃ and PbBr₂ are pre-dissolved by OLA and OA, Cs⁺ ions can directly coordinate with OA, forming cesium oleate coordination complexes (CsOA) due to the higher activity of Cs⁺ ions and higher acidity of carbonic acid. While compared with Cs⁺ ions, the lower activity of Pb²⁺ ions makes the coordination with OA difficult. However, OLA can be protonated by OA, and protonated OLA can coordinate with Pb²⁺ and Br⁻. In the next growth process, OA and protonated OLA form an organic layer on the surface of CsPbBr₃ NCs, and the large steric hindrance of the OLA long chains slows down

Figure 2 (a, b) ^1H NMR spectra (CDCl_3 , 298 K, 500 MHz) of CsPbBr_3 NWs and nanocubes, respectively. (c, d) Proposed growth mechanisms of CsPbBr_3 NWs in pre-dissolved solution and CsPbBr_3 nanocubes in traditional mixed solution, respectively.

the reaction between the Cs^+ and octahedral $[\text{PbBr}_6]^{4-}$ in free dimensions. As a result, CsPbBr_3 only continues to grow in the axial direction and eventually forms NWs. When Cs_2CO_3 and PbBr_2 salts are simultaneously dissolved into OLA and OA, they can not fully coordinate with each ion, leading to a slow dissolution rate during the reaction. The low concentration of CsOA and Pb^{2+} allows the NCs to grow at the same rate in all directions, thus favoring the formation of CsPbBr_3 nanocubes.

The above results indicate that OA and OLA also play an important role in the formation of CsPbBr_3 NCs. Therefore, it can be speculated that the morphology adjustment can be realized by adjusting the amounts of OA and OLA. Adjusting the molar ratio of OA and OLA allows both methods to prepare CsPbBr_3 NWs and nanocubes, and blue and green emissions are obtained simultaneously (Fig. S6). Increasing the amount of OA, the products favor nanocubes. In comparison, using more OLA favors NWs. These results demonstrate that the OLA long chain is primarily responsible for the growth of CsPbBr_3 NCs in the axial direction. The optimal molar ratio of OA and OLA to prepare monomorphic CsPbBr_3

NCs is 1:1 for both methods. Besides, for the CsPbBr_3 nanocubes prepared by the conventional solvothermal method, the change in reaction temperature or reaction time does not shift the emission peak (Fig. S7). In comparison, after introducing the pre-dissolution process, with increasing temperature, the emission peak of products is red-shifted and the lifetime is increased (Fig. S8), indicating the morphology changed as temperature increased.

Short NWs (~ 2.8 nm in width) with poor crystallinity are observed in the pre-dissolved solution after being stirred for 2 h without heating (Fig. 3a and Fig. S5). After heating, the NWs start to grow into several micrometers in the axial direction, and NWs with larger width are obtained with increasing temperature (Fig. 3b–d). When the temperature reaches 120°C , NWs have the best continuity and uniformity in the axial direction. For synthesis temperatures above 140°C , NWs break into rods and an important crystal growth mechanism, “oriented attachment”, operates and makes the NWs gradually grow into nanocubes (Fig. 3e) [35]. This mechanism points out that under higher temperatures, the adjacent particles with the

Figure 3 (a) TEM image of products in the pre-dissolved solution without heating. (b–f) TEM images of CsPbBr₃ NCs prepared by pre-dissolution process under different temperatures: (b) 100°C; (c) 120°C; (d) 140°C; (e) 160°C; (f) 180°C.

same lattice orientation continue to grow through the ionic migration of the contact surfaces, which has been known as the mesocrystal route as observed in the non-classical crystallization of many oxide and non-oxide nanophases [36,37]. At reaction temperatures higher than 160°C, the NWs obtain enough energy to grow again, eventually leading to the formation of larger crystals (Fig. 3f). Therefore, a pre-dissolution process assists the formation of continuous and uniform ultrafine CsPbBr₃ NWs, providing a simple method for the formation of perovskite NWs with different widths and lengths.

Based on the above characterizations, although the as-prepared CsPbBr₃ NWs and nanocubes have the same cubic crystal structure, the UV-Vis absorption peak and PL spectra of the ultrafine NWs have a strong blue-shift. Because NWs have much smaller edge dimensions than the Bohr radius (7 nm), the unique morphology of the NWs changes the position of the conduction band and the first absorption band [38]. To understand this unique phenomenon, a DFT calculation based on the ideal structure of the nanocubes and ultrafine NWs was carried out and the results are shown in Fig. 4a and c. The results show that due to the strong quantum confinement effect, the bandgap of ultrafine NWs is significantly larger than that of the nanocubes. Consequently, ultrafine NWs exhibit blue-shifted absorption and PL spectra. Moreover,

the blue-shifted emission peak demonstrates that an extraordinarily strong 2D quantum confinement effect occurred in the ultrafine NWs. Taking a step forward, we compared the fluorescence lifetime between the nanocubes and the ultrafine NWs (Fig. 4b and d). Ultrafine CsPbBr₃ NWs have a shorter lifetime than CsPbBr₃ nanocubes, which is probably due to a giant oscillator strength transition (GOST) effect from the ultrafine CsPbBr₃ NWs [39,40]. For low-dimensional (1D or 2D) nanostructures, when the size of a certain dimension is much larger than the Bohr radius, the oscillator strength of the exciton increases linearly with nanostructure volume, which is the so-called GOST effect [39]. The GOST effect enhances the absorption cross-section and significantly shortens the exciton radiative decay time [40]. The CsPbBr₃ nanocubes belong to the 3D nanostructures, and their sizes are close to the Bohr radius (Fig. 1c), and consequently, they have no GOST effect. According to Fig. 3, the length of ultrafine CsPbBr₃ NWs is much larger than the Bohr radius. More importantly, as shown in Fig. S9, the lifetime of NWs decreases with decreasing temperature, whereas their emission intensity increases. This fluorescence lifetime-temperature dependence is a unique signature of the GOST effect [40], suggesting there is probably a GOST effect for NWs. Therefore, the fluorescence lifetime of NWs is shorter than that of na-

Figure 4 (a, c) The density of states of CsPbBr₃ nanocubes and NWs based on DFT calculations, respectively. Insets: corresponding charge density of CsPbBr₃ nanocubes and NWs. (b, d) Fluorescence lifetime decay curves of CsPbBr₃ nanocubes and NWs, respectively.

nanocubes. The shorter lifetime of CsPbBr₃ NWs reveals its dual unique characteristics in the axial direction of continuity and the radial direction of the quantum confinement effect. These characteristics imply that the optical properties of the NWs are highly dependent on the direction, making them attractive for use as polarization-sensitive photodetection materials.

Precise assembly of the nanoscale building blocks is a crucial step to form solid state devices for practical applications. Dispersions of NWs with the surfaces properly functionalized with surfactants have been used to form self-assembled arrays by a mechanism known as evaporation-induced self-assembly (EISA) driven by the capillary force [41]. In the present work, the as-prepared CsPbBr₃ NWs have a large aspect ratio, and organic surfactants introduced by the pre-dissolution process (Fig. 2a) make the NWs maintain good monodispersity in cyclohexane solution. Therefore, we used a capillary tube to directly drip the cyclohexane solution of the as-prepared NWs on a substrate, glass slide or copper grid. As shown in Fig. 5a and Fig. 3, due to EISA, the ultrafine continuous CsPbBr₃ NWs form an ordered array over a large area *via* a self-assembled process. Using a confocal microscopy system (Fig. S1), we investigated the polar-

ized optical properties of the self-assembled CsPbBr₃ NW array. When a linearly polarized 800-nm fs laser propagates perpendicularly to the CsPbBr₃ NW array (Fig. 5c), with the polarization angle varying from 0° to 360°, the PL spectra of the CsPbBr₃ NW array in Fig. 5d clearly show periodic variation, as demonstrated by an obvious convergent polar plot (inset in Fig. 5d), indicating the self-assembled CsPbBr₃ NW array is highly polarization-sensitive. It should be mentioned that under the excitation of 800-nm fs laser, CsPbBr₃ nanocubes also show strong visible emission *via* a two-photon process. In comparison, when exciting the CsPbBr₃ nanocubes under the same conditions, their corresponding PL spectra remain almost unchanged, and as a result, a nearly circular curve is observed in the polar plot (Fig. 5e), demonstrating there is no polarization dependence for the as-prepared CsPbBr₃ nanocubes. Besides, there is also no distinct polarization behavior observed for unaligned NWs dripped using a thicker dropper (Fig. S10). The polarization degrees (ρ) (defined as $\rho = (I_{\max} - I_{\min}) / (I_{\max} + I_{\min})$), where $I_{\max}$ and $I_{\min}$ represent the maximum and minimum integrated luminescence intensities) are 0.49 for the self-assembled CsPbBr₃ NW array, 0.15 for CsPbBr₃ nanocubes, and 0.14 for CsPbBr₃ NWs dripped

Figure 5 (a) Schematic diagram of the direct-dripping method to form large-scale self-assembled CsPbBr₃ NW arrays on a glass slide. (b, c) Polarization measurement configuration of CsPbBr₃ nanocubes and CsPbBr₃ NW arrays, respectively. (d) Upconversion PL spectra of self-assembled CsPbBr₃ NW array, recorded at excitation polarization angles varying from 0° to 360°. Inset: polar plot of the luminescence intensity at 460 nm as a function of excitation polarization angle. (e) Upconversion PL spectra of CsPbBr₃ nanocubes, recorded at excitation polarization angles varying from 0° to 360°. Inset: polar plot of the luminescence intensity at 527 nm as a function of excitation polarization angle.

by a dropper, providing unambiguous evidence of the polarization in the PL of NW arrays.

It is widely known that polarized emission of low-dimensional semiconductor nanostructures can be induced by intrinsic anisotropy due to the anisotropic crystal structure or the anisotropic excitation field caused by dielectric confinement of optical electric field [9,10]. However, from the XRD pattern (Fig. 1b), the intrinsic dipole moment of the as-prepared CsPbBr₃ NWs is isotropic, and therefore, the first mechanism can be excluded. Meanwhile, the second mechanism can be ignored because the ultrafine NWs are formed onto a glass slide substrate with isotropic optical properties. These indicate there are other reasons for the polarization anisotropy of the ultrafine NWs.

For a deeper understanding of the mechanism of polarized emission from the self-assembled CsPbBr₃ NW array, a structure with 2D vacuum layers is constructed to simulate the practical ultrafine NWs with minimal size, and a block continuous model is used to represent the isotropic nanocubes. The corresponding DFT calculations are shown in Fig. 6. By calculating the charge density distribution, we observe that the ultrafine NWs have a large misalignment charge density on the model's surface, leading to the asymmetry of the perovskite NWs, both in structure and optical performances. A large dipole moment can be observed due to the strong quantum con-

finement effect. The uneven charge distribution is significantly increased when the atomic layer is reduced by radial dimension. The charge density in the Z axial direction is completely different from that in the radial direction. Accordingly, the 460-nm luminescence caused by the quantum confinement effect in the radial direction is also asymmetric, and CsPbBr₃ NWs present obvious polarization-dependent emission. In contrast, the block model shows highly symmetrical charge density in each dimension, leading to the low level of polarized emission measured in Fig. 5e. The polarization-dependent emission from the self-assembled perovskite NW array may enable the integration of the polarization sensitive devices with semiconductor technology at the nanometer level that may allow for the development of novel systems for photoelectronic-detection measurement and sensing.

CONCLUSIONS

In summary, we have demonstrated a modified solvothermal method with the assistance of a predissolution step to synthesize continuous and uniform ultrafine self-assembled CsPbBr₃ NWs. The CsPbBr₃ NWs show a strong blue emission that is associated with strong 2D quantum confinement effects. Although cubic-phase CsPbBr₃ NWs have isotropic crystal structure, obvious excitation polarization-dependent emission with polarization degree nearly up to 50% was detected. More im-

Figure 6 The difference in the charge density of each ion in CsPbBr₃ nanocubes and NWs. (a) (010) lattice plane and corresponding structural model of CsPbBr₃ nanocubes. (b, c) (010) and (001) lattice plane as well as corresponding structural model of CsPbBr₃ NWs.

portantly, well-aligned self-assembled CsPbBr₃ NW arrays are obtained using a facile direct-drip assembly strategy, providing facile access to the construction of polarization-sensitive devices. These results will not only provide a solution to fabricate pure perovskite NW array for photoelectronic applications, but also advance the fundamental understanding of emission polarization properties in all-inorganic perovskites by connecting them to the anisotropic distribution of charge densities.

Received 3 November 2020; accepted 18 January 2021;
published online 25 March 2021

- Liu Z, Xu J, Chen D, *et al.* Flexible electronics based on inorganic nanowires. *Chem Soc Rev*, 2015, 44: 161–192
- Zhai T, Ye M, Li L, *et al.* Single-crystalline Sb₂Se₃ nanowires for high-performance field emitters and photodetectors. *Adv Mater*, 2010, 22: 4530–4533
- Deng Z, Mansuripur M, Muscat AJ. Simple colloidal synthesis of single-crystal Sb–Se–S nanotubes with composition dependent band-gap energy in the near-infrared. *Nano Lett*, 2009, 9: 2015–2020
- Yang X, Lin X, Zhao Y, *et al.* Lanthanide metal-organic framework microrods: colored optical waveguides and chiral polarized emission. *Angew Chem Int Ed*, 2017, 56: 7853–7857
- Zhou H, Yuan S, Wang X, *et al.* Vapor growth and tunable lasing of band gap engineered cesium lead halide perovskite micro/nanorods with triangular cross section. *ACS Nano*, 2017, 11: 1189–1195
- Ghoshal D, Wang T, Tsai H, *et al.* Catalyst-free and morphology-controlled growth of 2D perovskite nanowires for polarized light detection. *Adv Opt Mater*, 2019, 7: 1900039
- Ma Z, Chai S, Feng Q, *et al.* Chemical vapor deposition growth of high crystallinity Sb₂Se₃ nanowire with strong anisotropy for near-infrared photodetectors. *Small*, 2019, 15: 1805307
- Fang Y, Dong Q, Shao Y, *et al.* Highly narrowband perovskite single-crystal photodetectors enabled by surface-charge recombination. *Nat Photon*, 2015, 9: 679–686
- Shi S, Sun LD, Xue YX, *et al.* Scalable direct writing of lanthanide-doped KMnF₃ perovskite nanowires into aligned arrays with polarized up-conversion emission. *Nano Lett*, 2018, 18: 2964–2969
- Yang D, Peng Z, Zhan Q, *et al.* Anisotropic excitation polarization response from a single white light-emitting β -NaYF₄:Yb³⁺,Pr³⁺ microcrystal. *Small*, 2019, 15: 1904298
- Tang B, Dong H, Sun L, *et al.* Single-mode lasers based on cesium lead halide perovskite submicron spheres. *ACS Nano*, 2017, 11: 10681–10688
- Cheng F, Li B, Li L, *et al.* Study of the polarization effect in InAs quantum dots/GaAs nanowires. *J Phys Chem C*, 2019, 123: 4228–4234
- Protasenko V, Bacinello D, Kuno M. Experimental determination of the absorption cross-section and molar extinction coefficient of CdSe and CdTe nanowires. *J Phys Chem B*, 2006, 110: 25322–25331
- Mukherjee S, Das K, Das S, *et al.* Highly responsive, polarization sensitive, self-biased single GeO₂-Ge nanowire device for broadband and low power photodetectors. *ACS Photonics*, 2018, 5: 4170–4178

- 15 Pan C, Dong L, Zhu G, *et al.* High-resolution electroluminescent imaging of pressure distribution using a piezoelectric nanowire LED array. *Nat Photon*, 2013, 7: 752–758
- 16 Jie J, Zhang W, Bello I, *et al.* One-dimensional II–VI nanostructures: Synthesis, properties and optoelectronic applications. *Nano Today*, 2010, 5: 313–336
- 17 Huang X, Guo Q, Yang D, *et al.* Reversible 3D laser printing of perovskite quantum dots inside a transparent medium. *Nat Photonics*, 2020, 14: 82–88
- 18 Chiba T, Hayashi Y, Ebe H, *et al.* Anion-exchange red perovskite quantum dots with ammonium iodine salts for highly efficient light-emitting devices. *Nat Photon*, 2018, 12: 681–687
- 19 Kovalenko MV, Protesescu L, Bodnarchuk MI. Properties and potential optoelectronic applications of lead halide perovskite nanocrystals. *Science*, 2017, 358: 745–750
- 20 Rainò G, Becker MA, Bodnarchuk MI, *et al.* Superfluorescence from lead halide perovskite quantum dot superlattices. *Nature*, 2018, 563: 671–675
- 21 Lin K, Xing J, Quan LN, *et al.* Perovskite light-emitting diodes with external quantum efficiency exceeding 20 percent. *Nature*, 2018, 562: 245–248
- 22 Xu YF, Yang MZ, Chen BX, *et al.* A CsPbBr₃ perovskite quantum dot/graphene oxide composite for photocatalytic CO₂ reduction. *J Am Chem Soc*, 2017, 139: 5660–5663
- 23 Ravi VK, Scheidt RA, DuBose J, *et al.* Hierarchical arrays of cesium lead halide perovskite nanocrystals through electrophoretic deposition. *J Am Chem Soc*, 2018, 140: 8887–8894
- 24 Protesescu L, Yakunin S, Bodnarchuk MI, *et al.* Nanocrystals of cesium lead halide perovskites (CsPbX₃, X = Cl, Br, and I): Novel optoelectronic materials showing bright emission with wide color gamut. *Nano Lett*, 2015, 15: 3692–3696
- 25 Zhou N, Bekenstein Y, Eisler CN, *et al.* Perovskite nanowire–block copolymer composites with digitally programmable polarization anisotropy. *Sci Adv*, 2019, 5: eaav8141
- 26 Lin C, Kang C, Wu T, *et al.* Giant optical anisotropy of perovskite nanowire array films. *Adv Funct Mater*, 2020, 30: 1909275
- 27 Raja SN, Bekenstein Y, Koc MA, *et al.* Encapsulation of perovskite nanocrystals into macroscale polymer matrices: enhanced stability and polarization. *ACS Appl Mater Interfaces*, 2016, 8: 35523–35533
- 28 Gao Y, Zhao L, Shang Q, *et al.* Ultrathin CsPbX₃ nanowire arrays with strong emission anisotropy. *Adv Mater*, 2018, 30: 1801805
- 29 Waleed A, Tavakoli MM, Gu L, *et al.* All inorganic cesium lead iodide perovskite nanowires with stabilized cubic phase at room temperature and nanowire array-based photodetectors. *Nano Lett*, 2017, 17: 4951–4957
- 30 Meng Y, Lan C, Li F, *et al.* Direct vapor-liquid-solid synthesis of all-inorganic perovskite nanowires for high-performance electronics and optoelectronics. *ACS Nano*, 2019, 13: 6060–6070
- 31 Xu J, Xu S, Qi Z, *et al.* Size-tunable CsPbBr₃ perovskite ring arrays for lasing. *Nanoscale*, 2018, 10: 10383–10388
- 32 Perdew JP, Burke K, Ernzerhof M. Perdew, Burke, and Ernzerhof reply. *Phys Rev Lett*, 1998, 80: 891
- 33 Blöchl PE. Projector augmented-wave method. *Phys Rev B*, 1994, 50: 17953–17979
- 34 Chen M, Zou Y, Wu L, *et al.* Solvothermal synthesis of high-quality all-inorganic cesium lead halide perovskite nanocrystals: from nanocube to ultrathin nanowire. *Adv Funct Mater*, 2017, 27: 1701121
- 35 Li D, Nielsen MH, Lee JRI, *et al.* Direction-specific interactions control crystal growth by oriented attachment. *Science*, 2012, 336: 1014–1018
- 36 De Yoreo JJ, Gilbert PUPA, Sommerdijk NAJM, *et al.* Crystalization by particle attachment in synthetic, biogenic, and geologic environments. *Science*, 2015, 349: aaa6760
- 37 Zhang J, Huang F, Lin Z. Progress of nanocrystalline growth kinetics based on oriented attachment. *Nanoscale*, 2010, 2: 18–34
- 38 Butkus J, Vashishtha P, Chen K, *et al.* The evolution of quantum confinement in CsPbBr₃ perovskite nanocrystals. *Chem Mater*, 2017, 29: 3644–3652
- 39 Wang Y, Herron N. Nanometer-sized semiconductor clusters: materials synthesis, quantum size effects, and photophysical properties. *J Phys Chem*, 1991, 95: 525–532
- 40 Ithurria S, Tessier MD, Mahler B, *et al.* Colloidal nanoplatelets with two-dimensional electronic structure. *Nat Mater*, 2011, 10: 936–941
- 41 Zhou X, Zhou Y, Ku JC, *et al.* Capillary force-driven, large-area alignment of multi-segmented nanowires. *ACS Nano*, 2014, 8: 1511–1516

Acknowledgements This work was financially supported by the Key R&D Program of Guangzhou (202007020003), the National Natural Science Foundation of China (62075063, 51772101 and 51872095), the Local Innovative and Research Teams Project of Guangdong Pearl River Talents Program (2017BT01X137), the Natural Science Foundation of Guangdong Province (2019B030301003), and the State Key Lab of Luminescent Materials and Devices, South China University of Technology. The authors thank Professor Gary Hestand for revising the paper.

Author contributions Peng Z and Yang D conceived the idea, proposed the strategy, and performed most of the experiments, with guidance from Xiao X and Dong G. Yin B and Li S assisted in the preparation of some materials. Guo X provided help with the polarization characterization under Zhan Q's guidance. Liu X, Xia Z, Yang Z and Qiu J modified the manuscript. Peng Z, Yang D, Xiao X and Dong G wrote the manuscript with feedbacks from other authors.

Conflict of interest The authors declare no conflict of interest.

Supplementary information Experimental details are available in the online version of the paper.

Zixing Peng received his BS and MS (2020) degrees at the school of Materials Science and Engineering, South China University of Technology (SCUT) under the supervision of Prof. Guoping Dong. His research interest focuses on the design, preparation, and optical performance investigation of perovskite nanocrystals.

Dandan Yang received her BS (2014), MS (2017) and PhD (2020) degrees at the School of Materials Science and Engineering, SCUT under the supervision of Prof. Guoping Dong and Prof. Jianrong Qiu. She is now a postdoctoral fellow in the State Key Laboratory of Luminescent Materials and Devices at SCUT. Her research interest focuses on the design, preparation, and optical performance investigation of micro/nano-particles.

Xiudi Xiao received her BS and MS degrees in materials sciences from Wuhan University of Technology and PhD degree from Shanghai Institute of Optics and Fine Mechanics, Chinese Academy of Sciences (CAS) in 2005, 2007, and 2010, respectively. In 2010, she joined Guangzhou Institute of Energy and Conversion, CAS, and became an associate professor in 2012. Currently, she leads a group of researchers working on stimuli-responsive photo-electronic functional systems and perovskite solar cells.

Guoping Dong received his MS (2007) and PhD (2010) degrees from Wuhan University of Technology and Shanghai Institute of Optics and Fine Mechanics, CAS, respectively. Then he worked at the School of Materials Science and Engineering, SCUT as a research assistant (2010) and an associate professor (2011). He became a full professor (2014) in the State Key Laboratory of Luminescent Materials and Devices at SCUT. His research focuses on the design, preparation, and optoelectronic properties of optical functional materials and devices.

用于偏振光探测的自组装超细CsPbBr₃钙钛矿纳米线

彭子兴^{1†}, 杨丹丹^{1†}, 尹博钊¹, 郭鑫², 李爽¹, 詹求强², 肖秀娣^{3*}, 刘小峰⁴, 夏志国¹, 杨中民¹, 邱建荣⁵, 董国平^{1*}

摘要 一维金属卤化物钙钛矿纳米线因具有较高的吸收和发射效率、较大的介电常数以及各向异性的光电特性等优势而在能源收集、柔性电子和生物成像设备等领域展现出潜在的应用价值。本论文提出了一种改进的两步溶剂热法用于制备自组装的立方相CsPbBr₃纳米线阵列, 为获得连续均匀的超细钙钛矿纳米线和有序排列的纯钙钛矿纳米线阵列提供了一个更为简便的方法。在365 nm紫外光的激发下, 肉眼可见地观测到来自CsPbBr₃纳米线的蓝光发射。同时, 在800 nm脉冲激光的激发下, CsPbBr₃纳米线也表现出较强的双光子发射。改变800 nm脉冲激光的偏振方向, 可以发现, CsPbBr₃纳米线虽然具有各向同性的立方结构, 但其自组装的纳米线阵列仍表现出较强的偏振依赖性, 偏振度达到~0.49。基于密度泛函理论计算, CsPbBr₃纳米线阵列的偏振依赖发射与其各向异性的电荷密度分布有关。上述结果表明具有良好自组装特性的超细CsPbBr₃钙钛矿纳米线有望用于下一代偏振敏感光电探测器件。