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Self-Patterned CsPbBr₃ Nanocrystals for High-Performance Optoelectronics

Bin Xin[†], Yusin Pak[†], Somak Mitra[†], Dhaifallah Almalawi[†], Norah Alwadai^{†‡}, Yuhai Zhang^{§*}, Iman S. Roqan^{†*}

[†] Physical Sciences and Engineering Division, King Abdullah University of Science and Technology (KAUST), Thuwal 23955-6900, Saudi Arabia

[§] Institute for Advanced Interdisciplinary Research (IAIR), University of Jinan, Jinan, 250022, Shandong Province, China

[‡] Department of Physics, College of Sciences, Princess Nourah bint Abdulrahman University (PNU), Riyadh 11671, Saudi Arabia

*E-mail: ifc_zhangyh@ujn.edu.cn and iman.roqan@kaust.edu.sa

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All-inorganic lead halide perovskites are promising materials for many optoelectronic applications. However, two issues that arise during device fabrication hinder their practical use, namely inadequate continuity of coated inorganic perovskite films across large areas and inability to integrate these films with traditional photolithography due to poor adhesion to wafers. Herein, for the first time, to address these issues, we show a room-temperature synthesis process employed to produce of CsPbBr₃ perovskite nanocrystals with two-dimensional (2D) nanosheet features. Due to the unique properties of these 2D nanocrystals, including the “self-assembly” characteristic, and “double solvent evaporation inducing self-patterning” strategy are used to generate high-quality patterned thin films in selected areas automatically after-drop-casting, enabling fabrication of high-performance devices without using complex and expensive fabrication processing techniques. The films are free from

micro-cracks. In a proof-of-concept experiment, photodetector arrays are used to demonstrate the superior properties of such films. We provide evidence of both high responsivity (9.04 A/W) and high stability across large areas. The photodetectors fabricated on flexible substrate exhibit outstanding photo-response stability. Advanced optical and structural studies reveal the possible mechanism. Our simple and cost-effective method paves the way for the next-generation nanotechnology based on high-performance, cost-effective optoelectronic devices.

1. Introduction

During the past several years, perovskite materials have attracted the interest of many researchers due to their unique characteristics that make them suitable candidates for a wide range of electronic, optoelectronic and photovoltaic applications. For example, the power conversion efficiency of solar cells based on organic–inorganic halide MAPbX_3 ($\text{MA} = \text{CH}_3\text{NH}_3$) hybrid perovskites was reported to exceed 22.7%¹⁻⁴. However, such hybrid perovskites suffer from many problems associated with instability, hindering their use in practical applications. For example, their extreme sensitivity to both oxygen and moisture induces constraints that require critical environmental conditions during storage, fabrication, and device operation. In addition, photo and thermal instabilities of such materials have also been observed due to the influence of organic groups⁵⁻⁷.

All-inorganic cesium lead halide (CsPbX_3) perovskite without any organic moiety has emerged as an alternative candidate for next-generation optoelectronic applications due to its superior stability compared to hybrid perovskites⁸⁻⁹. Its key advantages include high quantum yield (up to 90%), tunable photoluminescence (PL) emission spectra over the entire visible range with narrow line width, suppressed PL blinking, high carrier mobility, and large diffusion length¹⁰⁻¹¹. However, some issues related to inorganic CsPbX_3 perovskite must be overcome before its use in practical devices. As compact and smooth carrier channels are required for high device performance, it is essential that the perovskite active layer is of high crystal quality. Yet, due to several unresolved issues, it is currently challenging to meet these requirements for CsPbX_3 perovskite-based devices¹². First, during CsPbX_3 film fabrication, fast solvent

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4 evaporation usually destroys film continuity, which leads to grain boundaries and
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6 cracks¹³. Second, surfactants required for achieving considerable colloidal dispersivity
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8 destroy carrier channels between perovskite nanostructures¹². These shortcomings
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10 pertain to all types of solution-processed CsPbX₃ films because of the low solubility of
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12 CsPbX₃ precursors. Consequently, one-step processed films exhibit poor continuity and
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14 limited thickness controllability¹⁴. In the past, a general strategy for enhancing film
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16 continuity based on improving inherent CsPbX₃ properties has been employed¹⁵⁻¹⁶.
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18 Oriented CsPbX₃ nanostructures, such as one-dimensional (1D) nanowires,
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20 nanocrystals or two-dimensional (2D) nanosheets, have been synthesized for this
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22 purpose^{15-17,18}. Nevertheless, these methods have failed to eliminate the grain
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24 boundaries that can hinder carrier transport. Recently, to enhance film continuity,
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26 additional treatment methods were employed, such as recyclable dissolution-
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28 recrystallization¹², carbon nanotube mixing¹³, sintering¹⁹, centrifugal-casting²⁰ and
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30 freeze-drying casting²¹. However, while employing these treatment methods makes the
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32 film fabrication process more complex and smooth surface could not be achieved.
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34 Hence, there is a significant need to enhance the CsPbX₃ perovskite synthesis methods
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36 for practical use in high-performance devices.
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48 In this work, we demonstrate a facile room-temperature synthesis method that can
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50 be adopted to obtain CsPbBr₃ nanocrystals (NCs) of high optical quality that exhibit
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52 2D nanosheet features. The self-assembly property of ligand interactions between
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54 nanosheets readily generates high-quality continuous perovskite films across a large
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56 area. “Double solvent evaporation inducing self-patterning” (DSEISP) strategy is used
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to fabricate photodetector (PD) devices in selected areas as a proof-of-concept application, which has not been reported previously. Owing to the inherent outstanding properties of CsPbBr₃ NCs, the obtained PDs were long-term thermally durable, and highly responsive, which are extremely desirable properties in optoelectronic applications.

2. Experimental Section

2.1 Chemicals: Lead(II) bromide (PbBr₂, 99.999% trace metals basis), cesium acetate (CsAc, 99.99% trace metals basis), octylamine (OcAm, 99%), octanoic acid (OcAc, 98%), 1-propanol (PrOH), n-hexane (Hex, 99%) and toluene (TOL, 99.8%) were purchased from Sigma-Aldrich. All chemicals were used without any further purification.

2.2 Synthesis and purification of CsPbBr₃ NCs: CsPbBr₃ NCs were synthesized by a modified procedure reported previously²². Typically, Cs precursor and PbBr₂ precursor were prepared separately, and the reaction was initiated by injecting the latter into the former. First, Cs precursor solution was prepared by dissolving 32 mg of CsAc in 1 mL of 1-PrOH in a 20-mL vial under stirring in air at room temperature, followed by addition of 6 mL of Hex and 2 mL of 1-PrOH. Second, PbBr₂ precursor solution was prepared by dissolving 245 mg of PbBr₂ into a mixture solution of 0.45 mL of 1-PrOH, OcAc and OcAm each at 90 °C in air under vigorous stirring. Third, the hot PbBr₂ precursor was injected into the Cs precursor swiftly under vigorous stirring at room temperature. The system turned green immediately, and the reaction completed in two minutes. The CsPbBr₃ NCs were isolated by centrifugation at 7,000 rpm, and the pellet

was dispersed into 2 mL of toluene.

2.3 Characterization: X-Ray Diffraction (XRD) measurements were performed using a Bruker D8 Advance X-ray diffractometer equipped with Cu K α radiation source ($\lambda = 1.5418 \text{ \AA}$). The samples were prepared by drop-casting the nanosheet suspension on a clean glass slide, followed by drying at room temperature. High-resolution transmission electron microscopy (HRTEM) measurements were conducted on a Titan CT operating at 200 kV. Scanning electron microscopy (SEM) images were captured with a Zeiss Merlin. The Cary 6000i UV-Vis-NIR spectrophotometer was used to detect the NC absorption. Photoluminescence (PL) and PL excitation (PLE) measurements were carried out on Edinburgh FLS980 attached to a 900 W Xenon lamp (Newport 66923) at room temperature. PL quantum yield (PLQY) was performed using the same system by employing integrated sphere. Room-temperature. Time-resolved photoluminescence (TRPL) measurements were performed with a mode-locked Ti:sapphire laser (Coherent Mira 900) having a laser power output of 1.90 W at 800 nm. A second harmonic generator (APE-SHG /THG) was used to excite the sample by an output wavelength of 400 nm (pulse width 150 fs, pulse repetition rate of 76 MHz). A pulse select (APE) was used to reduce the frequency from 76 MHz to 2 MHz. The sample was placed on a closed temperature-dependent sample stage with transparent windows. Laser power incident on the sample was kept below 1 mW and the laser spot diameter was 60 μm . Emission produced by the sample was detected by the monochromator attached to a Hamamatsu C6860 streak camera with a temporal resolution of 2 ps. The integration time of 100 ms was adopted for all

500 integrations.

2.4 Device Fabrication and Characterizations

Patterned Film Fabrication: Perovskite NCs were dispersed into a hexane/toluene mix solution before drop-casting the solution on a horizontal electrode-patterned wafer. Next, NCs self-assembled spontaneously on the patterned electrode areas, resulting in a self-patterned perovskite film. The hexane and toluene volume, as well as perovskite concentration in toluene, are the key parameters affecting the patterning quality.

Flexible Photodetector Fabrication: Perovskite NCs in toluene solvent were drop-casted on the patterned Au/Ti/polyimide film substrates. After the solvent dried, the Polyethylene terephthalate (PET) substrates were placed on a hotplate and were annealed for 10 minutes.

Photodetector measurements: A 300 nm Au/5 nm Ti electrode was deposited on SiO₂/Si substrates by thermal evaporation assisted by photolithography technology. The electrode channel length was 100 μ m. The PD responses were measured using PD with a 3 μ m channel length and 242 μ m channel width. The patterned PD electrode with a 1.6 mm channel length was used. In this experiment, we used a continuous instead of a patterned film. The CsPbBr₃ solution was drop-casted on the electrode. After the solution was allowed to dry, the sample was put on a hotplate and was thermally annealed in ambient conditions.

Electrical Characterizations: Keithley DC power supply was used as the voltage source for I–V measurements, whereby the photocurrent was recorded using LABVIEW program (current vs timeframe). A solar simulator was utilized to eliminate

white light and a filter was placed in the light path to adjust the light intensity.

3. Results and Discussion

The CsPbBr₃ NCs were synthesized through a room-temperature co-precipitation method described in detail in the Experimental Section. As indicated by the HRTEM image in Figure 1a, the as-synthesized NCs adopt the desired nanosheet shape with a widespread distribution of lateral lengths, ranging from 10 nm (resembling quantum dots) to 100 nm, which differs significantly from uniform-sized NCs reported by other authors^{9, 15, 17, 23-24}. However, the obtained thicknesses are confined to a much narrower range, with an average of ~3 nm, which corresponds to the exciton confinement range. The CsPbBr₃ NCs spontaneously stack into a face-to-face assembly, which is attributed to the organic matrix²⁵⁻²⁶, as observed in the HRTEM image shown in Figure 1b.

The as-synthesized NCs are easily dispersed in nonpolar solvents, such as toluene and hexane, forming a stable colloid with bright PL emissions centered at 506 nm when excited by a 365 nm UV source, as shown in Figure 1c. Compared to the CsPbBr₃ NCs reported previously^{8, 23, 25}, the colloid NCs show a relatively broad emission band with the full width at half maximum (FWHM) of 60 nm. Moreover, the minor peak at 465 nm can be attributed to quantum confinement due to the narrow range of NC thicknesses (~3 nm on average), including the quantum dots^{25, 27}, as such dimension is comparable to 7 nm Bohr diameter in cubic CsPbBr₃⁸. The absorption spectrum reveals presence of an absorption peak at 459 nm, which corresponds to the Stokes-shifted minor peak in the PL spectrum located at 465 nm.

The shallow slope of the absorption edge corresponds to the FWHM broadening of the PL peak at 506 nm, which can be attributed to different NC sizes^{22, 26}. The varying sizes are expected to have different strains and different surface states that would affect both their bandgap and their states-within their bandgaps. Findings yielded by PLE spectrum at 506 nm (Figure S1d in Supporting Information) also indicates that the peak emission are resulted from the NCs bandgaps with different sizes, thus producing broad emission peak.

The XRD pattern of the as-synthesized CsPbBr₃ drop-casted as a thin film on a substrate shown in Figure 1d demonstrates that these NCs possess a cubic structure. Remarkably, three additional peaks at 3.8°, 7.5° and 11.2° emerged (Figure S1a in Supporting Information). Such low-angle diffraction peaks are usually ascribed to the ordered stacking of NCs or superstructures¹⁷. Based on Bragg's law, the inter-plane spacing of 2.3 nm is calculated, which is about twice the molecular length of the ligands (i.e., octylamine and octanoic acid have similar chain length, and the ligand extension of octylamine is about 1.2 nm²⁸). The inset images presented in Figure 1d reveal that the CsPbBr₃ films retain highly bright PL emissions under UV. The PLQY of NCs in solution reached 99%, as shown in Figure S1b, whereas the PLQY of CsPbBr₃ remained high after drop-casting the NCs as a film (~65%, as shown in Figure S1c).

Figure 1. Structural characterizations of CsPbBr₃ NCs. (a, b) Representative HRTEM image of CsPbBr₃ NCs; (c) PL (black) and absorption (red) spectrum. The inset shows photographic images of the CsPbBr₃ NCs in solutions, which are yellow under room light (RL) and become bright-blue under UV light; (d) XRD pattern of CsPbBr₃ NCs and standard cubic CsPbBr₃ XRD patterns taken from an XRD database (ICSD 97852). The inset shows that the drop-casted NCs form a thin film when illuminated by RL and under UV light exposure; (e) The time-wavelength TRPL mapping; and (f) Normalized TRPL curve for different wavelength lines in the 450–510 nm range; (g) The PL lifetime of CsPbBr₃ NCs as a function of wavelength.

To understand the carrier dynamics of CsPbBr₃ NCs, 2D TRPL spectroscopy mapping was conducted in a Streak camera system, as shown in Figure 1e. We extracted

the delay traces at different wavelengths from the TRPL spectra, as shown in Figure 1f. The calculated results are presented in Table S1 and plotted in Figure 1g, indicating that the lifetime increases from 2.18 ns to 6.3 ns as the peak wavelength increases from 450 nm to 510 nm. As can be seen from the TRPL measurements, in the longer wavelength (500–510 nm) range (related peak with a dominant intensity is centered at 506 nm), the carrier PL lifetimes exhibit a slow mono-exponential decay. Based on the rate equation, this slower single exponential suggests high radiative recombination rate, which concurs with the high PL intensity and is in line with the results obtained in previous studies²⁹⁻³². On the other hand, in the shorter wavelength (450–490 nm) range, the carrier lifetimes exhibit faster bi-exponential decay, due to the presence of multiple centers resulting from different states. This double exponential decay is attributed to efficient energy transfer from the confined states related to narrow-sized NC thicknesses to the states associated with the other two dimensions, which are significantly greater than the thickness. It should be noted that a faster decay indicates a lower recombination rate.

Figure 2. (a) 45° view SEM image of perovskite film formed by drop-casting CsPbBr₃ NCs, whereby the red arrow points to the edge of the film; (b) Cross-sectional SEM image of perovskite film (of ~ 4.1 μm thickness) synthesized by NC self-assembly process; (c) Optical microscope image of a patterned perovskite film obtained by employing the DSEISP strategy; (d) Schematic diagram of the PD structure.

A uniform thin film of ~ 4 μm thickness was obtained within a few minutes after drop-casting the colloidal NCs and drying under ambient conditions. The colloidal NC concentration of 60 mg/mL is essential for tuning the film thickness during the solution-processed uniform thin film fabrication. The spontaneous self-assembly process employed here is driven by the Van der Waals attraction between the hydrophobic ligands and the perovskite NC cores as a result of slow evaporation of the concentrated colloidal NC solution when solvent is drop-casted on a solid substrate²⁶. As the CsPbBr₃ NC sizes are not uniform, NCs of greater sizes may be deposited first, forming the

“precursor” frame for the films. Conversely, the smaller-sized NCs (i.e., quantum dots) may fill any gaps between bigger NCs and thus enhance film continuity (Figure S2a in Supporting Information). During this process, the smaller-sized CsPbBr₃ NCs may float to the toluene solution surface to form a drifted layer, as can be shown in Figure S2b, assisting in eliminating any micro-cracks that have been reported in such films in extant literature.¹² Figure 2a and 2b show the cross-sectional and 45° view SEM image of the resulting perovskite films, respectively. No micro-cracks are observed in such films, as further confirmed by both the wide-field view SEM image of the film morphology (Figure S2c) and its high-resolution SEM image (the inset of Figure S2c). In addition, no grain boundaries reported previously^{17,19, 21} are observed in our films. None of these beneficial film characteristics have been attained via other methods, such as recyclable dissolution-recrystallization¹², thermal annealing recrystallization method¹⁹ or freeze-drying recrystallization method²¹, and have not been previously achieved in 2D perovskite nanosheet-formed films¹⁷. Although the film contained some distributed random small mesas 5–10 μm in length, these did not degrade film continuity and quality. Additionally, the large cross-sectional area of the film shown in the SEM image presented in Figure S2d indicates that film thickness is homogeneously continuous. It is worth mentioning that we applied some ingenuity to enhance film quality. First, drop-casting was used as a substitute for the rapidly evaporating solvents employed in spin-coating or sputter-coating methods, as the drop-casting method ensures that a greater quantity of solvent is retained. Second, in the method we adopted, short ligands (octylamine and octanoic acid surfactants) may replace longer ligands (oleic acid and

oleylamine) because such short ligands can be removed more easily by subsequent annealing, thus enhancing the film electric properties.

As a proof of concept, a DSEISP strategy was used to fabricate a PD based on our self-patterned perovskite that functioned solely as an active layer, to demonstrate the diverse range of optoelectronic applications for our NCs. To fabricate the PD, first, CsPbBr₃ NCs were dispersed into a toluene/hexane mix solution. Then, these colloidal NCs were drop-casted (with the drop volume of about 8 μ L) onto a horizontal 1.5 cm $\times$ 1.5 cm patterned interdigitated contact electrode (IDE)/280 nm thick SiO₂ substrate. The NCs spontaneously self-patterned (the inset image of Figure 2c) and crystallized only between the IDEs with well-defined edges (Figure 2c). This spontaneous self-patterning is completed within about 10 s after the drop-casting process (as shown in **the supporting video**) and does not affect the NC self-assembly process, thus allowing formation of a continuous and uniform film as well as patterned film. The possible mechanism behind the self-patterning phenomena characterizing these NCs was are discussed in Supporting Information, Section S4.

The patterning technologies aimed at metals, metal oxides, semiconductors, semiconductor oxides or conducting polymers are already widely used to adjust the charge separation or enhance light capture. However, as perovskite adhesion to the wafer is poor, it is highly unstable under certain conditions, such as UV light and chemical solution exposure³³⁻³⁵. Owing to these shortcomings, it is very difficult to integrate them using traditional photolithography and photoresist technologies, thus hindering the ongoing miniaturization and alignment efforts³⁶. The strategy adopted in

this work addresses this issue effectively. As our findings indicate that NCs can be deposited on selective areas automatically, application of our demonstrated strategy will not only enhance fabrication efficiency, but will also avoid contamination of adjacent areas, as shown in Figure S3a and S3b in Supporting Information, presenting images of patterned CsPbBr₃ films self-assembled on the electrode region only. The schematic diagram of a single PD is shown in Figure 2d.

Figure 3. The annealing temperature effect on the electric characteristics of PDs.

(a) Logarithmic I–V curve of a pristine PD; (b) The photocurrent (top panel) and dark current (bottom panel) as a function of annealing temperature when the annealing duration is kept constant at 10 minutes; (c-d) Logarithmic I–V curve of the PD after 100 °C and 110 °C annealing treatment, respectively; (e) Logarithmic I–t curve of the PD at different annealing temperatures at 1 V; (f) Thermal decay characteristics of the PD. The photocurrent and on/off ratio curve as a function of annealing duration at 110 °C. Here, the light source power is 100 mW/cm². Note that three different devices were used for Figures 3a/c/d, 3b/e and 3f, respectively.

All PDs fabricated using this method exhibited high performance. In our DSEISP

strategy, hexane and toluene volume, as well as perovskite concentration in toluene, are the key parameters affecting the patterning quality. The hydrophobic material could be any type of wafer, such as silicon, silicon oxide or glass substrate, as well as flexible substrates, whereas the metal electrode, ITO or selected UV-ozone treatment area on the wafer can serve as good hydrophilic material candidates³⁷. In comparison to transfer printing³⁸, inkjet printing^{33, 39-40}, or laser direct writing³⁴, our DSEISP strategy offers many advantages, as it is flexible, easy to fabricate, non-destructive, cost-effective and equipment-free, while greatly economizing on the raw materials.

Figure 3 shows the performance of PDs fabricated by drop-casting CsPbBr₃ colloidal NCs on an as-prepared electrode substrate with 100 μm channel length. The I–V characteristics in dark and under 100 mW/cm^2 white illumination of the pristine (non-annealed) PD are shown in Figure 3a. The two curves almost coincide, indicating that PDs exhibit no photo-response because the NC boundaries filled with the remaining organic surfactants hinder the transport of photo-generated carriers. To activate the photo-response of the CsPbBr₃ film, the device was annealed to remove the surfactants and recrystallize the CsPbBr₃ NCs⁴¹ and hence induce the photo-response of the active layer of the as-fabricated PD. A significant enhancement in the photo-response is observed when the annealing temperature of $\geq 100\text{ }^\circ\text{C}$ is applied to the as-assembled PDs. Therefore, to systematically verify the dependence of the generated photocurrent on the annealing temperature, the photocurrent (under a white light with a 100 mW/cm^2 power density) and dark current dependence on the annealing temperature was examined at 1 V for PDs annealed at different temperatures, in 10 $^\circ\text{C}$

increments within the 100–300 °C range, as shown in Figure 3b. For all the PDs tested, we found that, on average, the photocurrent increases dramatically until 110 °C—the temperature at which the highest photocurrent (360 nA) is obtained. Above 110 °C, however, the photocurrent gradually decreases toward the minimum at ~160 °C. The dark current follows a similar pattern, as shown in Figure 3b. Specifically, from 170 °C to 290 °C, the dark current declines to a minimum value in the 2.6–28 pA range.

Figure 3c and 3d show the I–V characteristics of the PDs in dark and under white illumination that are annealed at 100 °C and at the optimized annealing temperature of 110 °C, respectively. Unlike the pristine PD shown in Figure 3a, in the annealed PDs, the dark current is markedly suppressed, which implies that recrystallized perovskite exhibits intrinsic semiconductor features with low defect density. As the annealing temperature increases, the photocurrent is initially suppressed (as shown in Figure 3c) compared to that measured for pristine PD (Figure 3a) and is subsequently reactivated (as shown in Figure 3d). The optimum photocurrent of 10^{-6} A is achieved after 110 °C annealing, whereas 4×10^{-8} A is obtained with 100 °C annealing at 4 V bias. Figure 3e shows on/off transient photocurrent cycles at different annealing temperatures (additional measurements pertaining to a different annealing temperature are presented in Figure S4 in Supporting Information). All PD devices examined in this study are stable and are capable of reversible and rapid switching between the dark and the illuminated state. The response-recovery times for all tested devices at 100, 110 and 150 °C annealing temperature do not exceed an average value of 80 ms.

A further study of the effect of thermal annealing process revealed that the device photo-responsivity is activated within the optimum temperature range. However, device performance degradation occurs when the thermal treatment duration increases even at the optimum temperature, as shown in Figure 3f. As CsPbBr₃ possesses greater thermal stability than MaPbBr₃⁵⁻⁶, the fabricated PD is capable of resisting thermal decay. The photocurrent and on/off ratio curve as a function of annealing duration at 110 °C under ambient conditions are shown in Figure 3f. As can be observed in the graph, in the first five minutes of annealing, the PDs are not fully activated. As the annealing time increases, PD activation occurs and optimum performance is achieved within the 10–30 minute range, followed by a performance degradation as the duration increases. After 30 minutes, the photocurrent declines by less than 20% of the maximum value and the PD maintains 50% of the peak efficiency after one hour. On the other hand, the on/off ratio of the PD is well above 500 (as an optimized on/off ratio value) after 40 minutes of annealing. These findings indicate that our PD has good thermal stability, as its functionality remained adequate for a period of 30 minutes even in the high-temperature environment of 110 °C.

To understand the influence of annealing treatment on the NC structural and optical quality, TEM, XRD, and TRPL measurements were conducted for both pristine and annealed CsPbBr₃ NCs. Annealing treatment was conducted on dry perovskite films for the XRD and TRPL experiments, whereas for the TEM experiments, perovskite kept in toluene solution was subjected to the annealing treatment before being drop-casted onto a TEM grid. As shown in Figure S5a in Supporting Information,

after annealing at 100 °C in toluene, the CsPbBr₃ NC size increased and their shape became rod-like as the NC thickness increased from ~3 nm to ~10 nm. The shape of a single NC can be clearly distinguished, indicating that crystal quality improved after annealing. The XRD spectra for pristine and annealed films are shown in Figure S5b, indicating that the pristine peaks at $2\theta = 7.5^\circ$ and 11.2° disappear after 110 °C annealing. Both TEM and XRD results reveal that the surfactants have been released after annealing and the NCs are “recrystallized” to a unit cell of higher quality, leading to a significant photo-response. In addition, Figure S5b illustrates the XRD scan of the film annealed at 150 °C, showing chemical phase transformation into tetragonal CsPb₂Br₅¹⁹, which leads to the photocurrent reduction shown in Figure 3b. When the $T > 110^\circ\text{C}$, it is expected that the thermal energy may be higher than the binding energy, resulting in the loss of capping ligands on the surface of NCs may occur due to the higher annealing temperature, which increases the number of defect states within the bandgap. As annealing temperature exceeds 110 °C, defect states can trap carriers, causing device performance degradation, as shown in figure 3e.

TRPL curves of the NCs before and after annealing are shown in Figure S5c and S5d. TRPL measurements reveal that the NC lifetime dramatically increases (by more than 16 times, i.e., from 5.16 ns to 86 ns), as shown in Table S2 in Supporting Information. According to the charge diffusion length equation $L_D = \sqrt{D\tau}$, where L_D is the carrier diffusion length, D is the diffusion constant, and τ is the charge carrier lifetime, the extended decay time may be due to the reduced defect density of the annealed CsPbBr₃ thin films and the increased carrier diffusion length¹².

Figure 4. (a) Normalized PD responsivity as a function of illumination wavelength; (b) Dependence responsivity vs irradiance (in log scale) under 5 V bias; (c) The stability characteristic of drop-casted CsPbBr₃ as a film on a flexible substrate. The bias voltage was 1 V and source light was supplied by a 100 mW/cm² white lamp light; (d) Cross-section sketches showing the difference between perovskite films without and with cracks upon bending.

Figure 4a depicts normalized responsivity of the annealed PD as a function of light source wavelength, indicating that maximum responsivity is achieved at ~500 nm. Above this wavelength, device responsivity declines, coinciding with the bandgap of CsPbBr₃ (refer to the absorption spectrum in Figure 1c). However, PD responsivity is

a critical parameter, as it is affected by many factors, such as electrode channel area, irradiance³⁷ and bias voltage¹⁷. To examine the effect of these factors on the device responsivity, PD responses were detected using 3 μm channel length and 242 μm channel width. Utilizing a 488 nm laser as the light source and employing power filters to control light intensity, the dependence relationship between responsivity and irradiance at a bias of 1 V and 5 V was obtained, as shown in Figure S6 in Supporting Information and Figure 4b, respectively. We found that higher bias with the lowest irradiance yields higher responsivity. The optimum responsivity of 9.04 AW^{-1} was obtained under $10.2 \mu\text{Wcm}^{-2}$ and 5 V. This value is much higher than the figures reported for commercial Si PDs (0.2 AW^{-1}) and is good performance compared to pure $\text{CsPbX}_3/\text{MaPbX}_3$ films¹⁷.

In sum, the evidence provided in the preceding sections indicates that the micro-crack-free uniform films based on CsPbBr_3 NCs obtained in this study can be employed in applications requiring great device flexibility and continuity across large areas. To demonstrate micro-crack-free structural relaxation as well as potential flexibility of as-obtained NCs films, CsPbBr_3 NCs in toluene solvent were drop-casted on patterned Au/Ti/polyimide flexible substrates. After the solvent dried, the polyimide substrate was annealed for 10 minutes at 110°C . Utilizing a bending-recovering process with the bending radius of 4 mm, a comparison of the on/off current before bending and after 10,000 bending cycles was obtained, as shown in Figure 4c. A very slight photocurrent decline (0.02 nA) with $\sim 2\%$ fluctuations is observed, indicating that the PD is extremely stable. Such superior device performance is attributed to the micro-crack-free films that

could bear the bending stress evenly, as described in the model shown in Figure 4d. Conversely, the stress will be released along the cracks when bending a cracked perovskite film and will result in unrecoverable damage.

The film continuity required for large-scale applications was further demonstrated by the conductive length between two electrodes. In particular, the channel length of our PD shown in Figure 3 (100 μm) is much longer than that obtained previously ($< 20 \mu\text{m}$)^{12-13, 17, 20, 42-44}. Furthermore, to confirm that the obtained film is super-continuous, the conductive length of our CsPbBr₃ film is in the order of centimeter, as measured by detecting current between two electrodes positioned 1 cm apart, which is considered a significant distance compared to that reported in other studies. In addition, a PD with 1.6 mm electrode intervals (with the two electrodes positioned as shown in Figure S3a, indicated by red line) was fabricated using continuous instead of patterned film to examine the high continuity of the CsPbBr₃ films in large-scale devices, which was proven challenging in previous studies. These findings therefore confirm that the PD possesses a rapid switching capability and produces photocurrent of about 7.5 nA under 100 mW illumination at a base voltage of 20 V, as shown in Figure S7 in Supporting Information. Thus, we demonstrate that, as our films are continuous across a large area, they can be employed in large-area device applications, such as perovskite solar cell panels⁴⁵.

4. Conclusion

In summary, ultrathin CsPbBr₃ NCs with 2D nanosheet features were synthesized to form uniform and self-patterned films that can be used for large-scale and flexible

cost-effective applications. Utilizing these features, large continuous-area, micro-crack-free, dense, high-quality CsPbBr₃ films were fabricated using the “self-assembly” approach. For the first time, self-patterned devices based on CsPbBr₃ NCs were fabricated by using a DSEISP strategy, whereby perovskite NCs can be deposited on areas of interest automatically, without the need for traditional photolithography processing. Our novel work demonstrated that this method not only enhances fabrication efficiency, but also avoids contamination of adjacent areas due to the self-patterning nature of the material, resulting in high-performance devices. Our outstanding method can be applied to fabricate perovskite-based lasers, as well as x-ray imaging, optoelectronic, photovoltaic and electronic devices.

ASSOCIATED CONTENT

Supporting Information

Supporting Information is available from ACS Publications website or from the author.

Details of TRPL parameters, XRD, PLQY, and PLE analyses, possible hypothesis of film formation, DSEISP strategy, On-off PD characteristics, optical and structural properties of annealed NCs, responsivity under 1 V bias, I-t curve of super-long channel PD.

The Video of DSEISP strategy.

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Conflict of Interest

The authors declare no conflict of interest.

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Figure 1. Structural characterizations of CsPbBr₃ NCs. (a, b) Representative HRTEM image of CsPbBr₃ NCs; (c) PL (black) and absorption (red) spectrum. The inset shows photographic images of the CsPbBr₃ NCs in solutions, which are yellow under room light (RL) and become bright-blue under UV light; (d) XRD pattern of CsPbBr₃ NCs and standard cubic CsPbBr₃ XRD patterns taken from an XRD database (ICSD 97852). The inset shows that the drop-casted NCs form a thin film when illuminated by RL and under UV light exposure; (e) The time-wavelength TRPL mapping; and (f) Normalized TRPL curve for different wavelength lines in the 450–510 nm range; (g) The PL lifetime of CsPbBr₃ NCs as a function of wavelength.

170x160mm (300 x 300 DPI)

Figure 2. (a) 45° view SEM image of perovskite film formed by drop-casting CsPbBr₃ NCs, whereby the red arrow points to the edge of the film; (b) Cross-sectional SEM image of perovskite film (of ~ 4.1 μm thickness) synthesized by NC self-assembly process; (c) Optical microscope image of a patterned perovskite film obtained by employing the DSEISP strategy; (d) Schematic diagram of the PD structure.

160x103mm (300 x 300 DPI)

Figure 3. The annealing temperature effect on the electric characteristics of PDs. (a) Logarithmic I–V curve of a pristine PD; (b) The photocurrent (top panel) and dark current (bottom panel) as a function of annealing temperature when the annealing duration is kept constant at 10 minutes; (c-d) Logarithmic I–V curve of the PD after 100 °C and 110 °C annealing treatment, respectively; (e) Logarithmic I–t curve of the PD at different annealing temperatures at 1 V; (f) Thermal decay characteristics of the PD. The photocurrent and on/off ratio curve as a function of annealing duration at 110 °C. Here, the light source power is 100 mW/cm². Note that three different devices were used for Figures 3a/c/d, 3b/e and 3f, respectively.

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Figure 4. (a) Normalized PD responsivity as a function of illumination wavelength; (b) Dependence of responsivity vs irradiance (in log scale) under 5 V bias; (c) The stability characteristic of drop-casted CsPbBr₃ as a film on a flexible substrate. The bias voltage was 1 V and source light was supplied by a 100 mW/cm² white lamp light; (d) Cross-section sketches showing the difference between perovskite films without and with cracks upon bending.

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83x35mm (300 x 300 DPI)