



## 2D Derivative Phase Induced Growth of 3D All Inorganic Perovskite Micro Nanowire Array Based Photodetectors

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3 **2D derivative phase induced growth of 3D all inorganic perovskite micro-**  
4 **nanowire array based photodetectors**

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13  
14 **Abstract:** A large number of derivative phases in inorganic perovskites have been  
15 reported with special structures and shown extraordinary performances in  
16 photoelectronic device applications. The reverse phase transition between derivative  
17 phases and perovskites usually induces recrystallization or forms mixed components.  
18 In this work, we report derivative phase induced growth of the CsPbBr<sub>3</sub> micro-nanowire  
19 (MW) array by utilizing phase transition of the two-dimensional CsPb<sub>2</sub>Br<sub>5</sub> phase.  
20 Owing to its layered structure and phase transition, annealing of CsPb<sub>2</sub>Br<sub>5</sub> at a  
21 temperature of 550 °C combined with solvent quenching led to a templating effect to  
22 form a high-quality CsBr MW array. Subsequent PbBr<sub>2</sub> deposition and the second  
23 annealing were employed to form the aligned CsPbBr<sub>3</sub> MW arrays. Based on this  
24 method, a CsPbBr<sub>3</sub> MW array based photodetector was fabricated. The large grain size,  
25 less grain boundaries (GBs) and lower surface potential of the CsPbBr<sub>3</sub> MW array led  
26 to high device performance with a responsivity of 7.66 A W<sup>-1</sup>, a detectivity of ~10<sup>12</sup>  
27 Jones and long-term operational stability over 1900 min.

## 28 29 **Introduction**

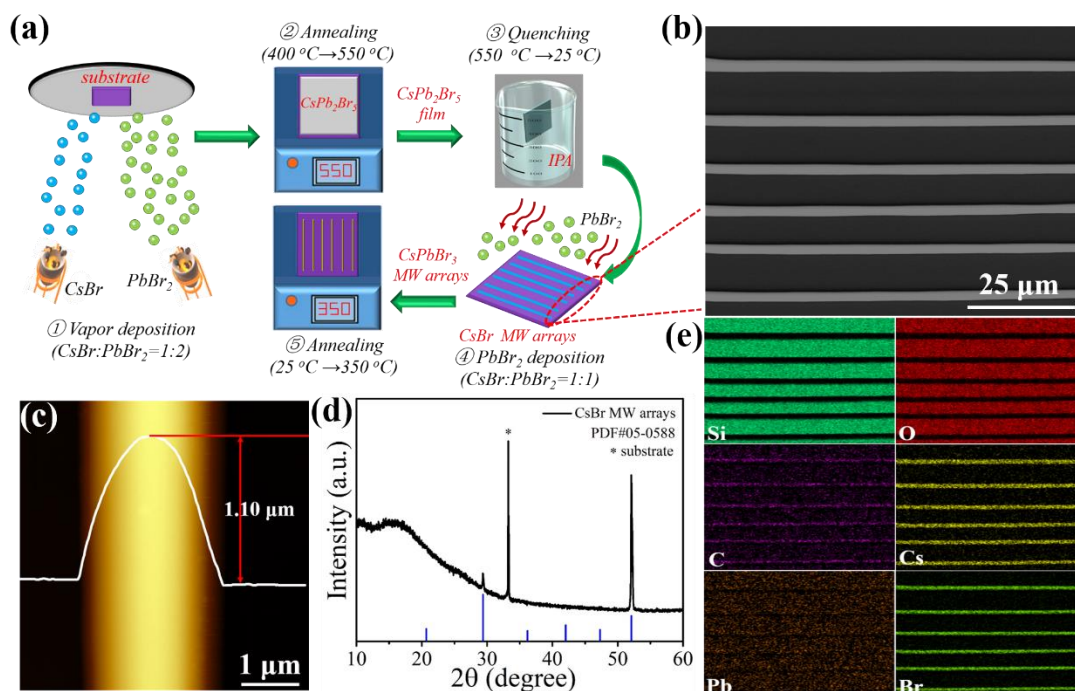
30 Inorganic halide perovskite materials CsPbX<sub>3</sub> (X=Cl, Br and I) have attracted great  
31 attention because of their applications in solar cells, light emitting diodes (LEDs), lasers  
32 and photodetectors (PDs).<sup>[1-4]</sup> Their unique properties such as tunable bandgap, high  
33 carrier mobility, long carrier diffusion length and high absorption coefficient make them  
34 strong candidates for optoelectrical device applications.<sup>[5-8]</sup> To date, the development  
35 of perovskites has evolved from initially three/two-dimensional (3D/2D) bulk films<sup>[9,</sup>

1 <sup>10]</sup> to low dimensional nano-structures, for example, one-dimensional (1D)  
2 nanowires/microwires (NWs/MWs)<sup>[11, 12]</sup> and zero-dimensional (0D) quantum dots<sup>[13,</sup>  
3 <sup>14]</sup>.

4 In comparison with bulk films and quantum dots with many small grains and long-  
5 chain ligands, the 1D NWs/MWs exhibit well-aligned structures, lower lateral  
6 dimension, less GBs and confined carrier transport in 1D channels/structures, which  
7 leads to high crystallinity, less recombination and superior electronic transport  
8 behaviors.<sup>[15]</sup> Additionally, multiple synthesis methods making use of forward growth  
9 have been developed such as the solution method<sup>[11, 16]</sup> (hot-injection,<sup>[17]</sup> anion  
10 exchange<sup>[18]</sup> etc.) and chemical vapor deposition (CVD).<sup>[19, 20]</sup> The solution process is  
11 a facile, low-cost technique, and has been employed in fabrication of MAPbI<sub>3</sub>  
12 perovskite nanowires, because of the low synthesis temperature and a precise ratio of  
13 precursor materials.<sup>[2, 21]</sup> However, the existence of residue organic solvents such as  
14 DMF, DMSO will affect the quality of perovskites and accelerate the  
15 decomposition/degradation of perovskite materials.<sup>[22-24]</sup> In contrast, the vapor  
16 deposition enables high purity of the materials and easy controllability without the  
17 adverse effects of residue solvents to ensures long-term stability.<sup>[2, 25, 26]</sup> In addition,  
18 low solubility of all-inorganic perovskites is difficult due to the lower solubility of  
19 inorganic perovskites and more complex Cs-Pb-X phase diagram.<sup>[21, 23]</sup> In parallel, the  
20 vapor deposition technique (e.g., all vacuum deposition, CVD) provides a non-solvent  
21 environment and high temperature/vacuum system, which allows preparation of highly  
22 crystalline NWs without the impurity phase.<sup>[21, 27]</sup> These strategies have shown ~~showing~~  
23 great advantages in light sources and photodetectors. For example, Wang, Pan and  
24 coworkers developed wavelength-tunable in-plane aligned CsPbX<sub>3</sub> perovskite NWs  
25 lasers with a low pumping threshold of 4 μJ cm<sup>-2</sup>.<sup>[28]</sup> Moreover, Meng and coworkers  
26 reported a vapor-liquid-solid growth technique to grow high quality CsPbX<sub>3</sub> NWs and  
27 realized PDs in the visible light regime with an impressive responsivity of 4489 A W<sup>-1</sup>  
28 and detectivity over 7.9 × 10<sup>12</sup> Jones.<sup>[29]</sup> Although perovskite NWs have shown  
29 promising performance in optoelectronic devices, random dispersion and short length  
30 make it difficult to integrate them into optoelectronic devices. Recently, NW arrays

1 were proposed to solve this issue because of their controlled alignment and high  
2 uniformity in large area. Feng and coworkers reported a 1D CsPbBr<sub>3</sub> perovskite NW  
3 array based photodetector with a high responsivity exceeding 1000 A W<sup>-1</sup> by using a  
4 micropillar-structured template with asymmetric wettability via the solution method.<sup>[11]</sup>  
5 In addition, Waleed and coworkers reported a vertical CsPbI<sub>3</sub> NW array based  
6 photodetector with a responsivity of 6.7 mA W<sup>-1</sup> by combining chemical vapor  
7 deposition (CVD) with anodic alumina membrane (AAM) templates.<sup>[30]</sup> It is worth  
8 noting that the formation of NW arrays usually depends on the templates such as  
9 AAO/AAM templates<sup>[30, 31]</sup>, CD/DVD disks<sup>[32, 33]</sup> and photoetching<sup>[34]</sup> or special  
10 substrates like M-template substrates<sup>[21, 28]</sup> and asymmetric wettability substrates<sup>[11, 35]</sup>.  
11 Use of these templates not only leads to increased cost but also makes it difficult to  
12 upscale. A facile and template-free method is desirable for upscaling of NW arrays.

13       Herein, we propose a two-step method of facile phase induced growth of CsPbBr<sub>3</sub>  
14 MW arrays by using CsBr as the intermediate product and controlling the  
15 decomposition of the CsPb<sub>2</sub>Br<sub>5</sub> perovskite derivative phase. In the first step, a height of  
16 1.1 μm CsBr MW arrays is obtained by controlling the decomposition from CsPb<sub>2</sub>Br<sub>5</sub>  
17 film (CsPb<sub>2</sub>Br<sub>5</sub> → CsBr + 2PbBr<sub>2</sub>↑). Then, the CsBr MW arrays are post-treated with  
18 extra PbBr<sub>2</sub>, leading to CsPbBr<sub>3</sub> MW arrays with large grain sizes (over 5 μm) and a  
19 larger height of 1.72 μm (CsBr + PbBr<sub>2</sub> → CsPbBr<sub>3</sub>). By investigating the growth  
20 mechanism of CsBr MW and CsPbBr<sub>3</sub> MW arrays, we find that the layered structure of  
21 CsPb<sub>2</sub>Br<sub>5</sub><sup>[36]</sup> serves as a nominal template, which makes the intermediate product of  
22 CsBr MWs possible to grow along the CsPb<sub>2</sub>Br<sub>5</sub> template to form arrays. Finally, a  
23 high-performance photodetector is achieved with an impressive responsivity of 7.66 A  
24 W<sup>-1</sup>, high detectivity of ~10<sup>12</sup> Jones and long-term operational stability over 1900 min



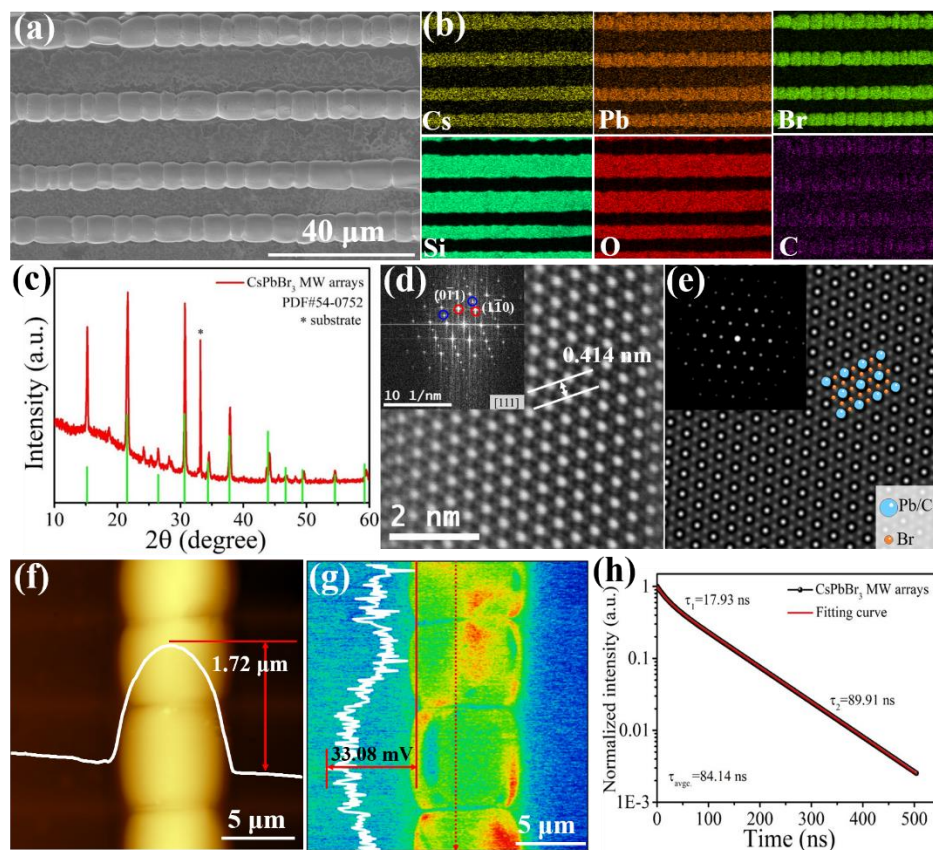
**Figure 1.** a) Schematic illustration of formation of CsBr MW arrays and CsPbBr<sub>3</sub> MW arrays. b) Scanning electron microscope (SEM) image, c) Atomic force microscopy (AFM) morphology image, d) X-ray diffraction pattern (XRD) and e) energy-dispersive X-ray spectroscopy (EDS) mapping of CsBr MW arrays.

## Result and discussion

**Figure 1a** illustrates the growth process of CsBr MW arrays and CsPbBr<sub>3</sub> MW arrays. The CsPb<sub>2</sub>Br<sub>5</sub> precursor layer with a thickness of 1 μm is first deposited on the Si/SiO<sub>2</sub> substrate by a sequential vapor deposition method (more details can be found in Experiment Section). Then the CsPb<sub>2</sub>Br<sub>5</sub> films are moved to a hotplate (400 °C) rapidly and annealed at a high temperature of 550 °C for 20 min. Solvent quenching is carried out by immersing the samples into an isopropanol (IPA) solution to cool down the samples to room temperature quickly in order to maintain the structure of long MWs. The well-aligned CsBr MW arrays with an average length of ~175 μm can be obtained (**Figure 1b, S1**) as follows: CsPb<sub>2</sub>Br<sub>5</sub> → CsBr + 2PbBr<sub>2</sub>↑. Notably, energy-dispersive X-ray spectroscopy (EDS) mapping in **Figure 1e, S2** shows that Cs and Br are uniformly distributed in the MW arrays. The absence of Pb indicates that PbBr<sub>2</sub> has evaporated completely. The Cs:Br composition ratio of 1:1 as seen in the corresponding EDS line scan in **Figure S3, S4** agree well with the stoichiometric ratio of CsBr. The high

1 crystallinity of the CsBr MW arrays is further confirmed by surface investigation.  
 2 Atomic force microscopy (AFM) topography images of the CsBr MW arrays and  
 3 individual MW are shown in **Figure 1c, S5, S6**. The smooth surface with an average  
 4 height of 1.1  $\mu\text{m}$  and uniform width of 1~2  $\mu\text{m}$  suggest high crystallinity of the CsBr  
 5 MWs and MW growth of the CsBr MW array according to Ostwald ripening  
 6 mechanism during the formation, which will be discussed later. The X-ray diffraction  
 7 (XRD) pattern in **Figure 1d, S7, S8** indicates that fabricated CsBr MW arrays exhibit  
 8 preferred orientation along (211).

9



10

11 **Figure 2.** a) SEM image, b) EDS mapping, c) XRD pattern of the CsPbBr<sub>3</sub> MW arrays. d)  
 12 Scanning transmission electron microscopy (STEM) image and e) simulated lattice pattern of  
 13 the single CsPbBr<sub>3</sub> MW. The inset shows the corresponding Fourier transform pattern. f) AFM  
 14 topography image and g) surface potential distribution of the single CsPbBr<sub>3</sub> MW. h) Time  
 15 resolved photoluminescence (TRPL) decay curve of the CsPbBr<sub>3</sub> MW arrays.

16

17 Based on the as-synthesized CsBr MW arrays, the CsPbBr<sub>3</sub> MW arrays were

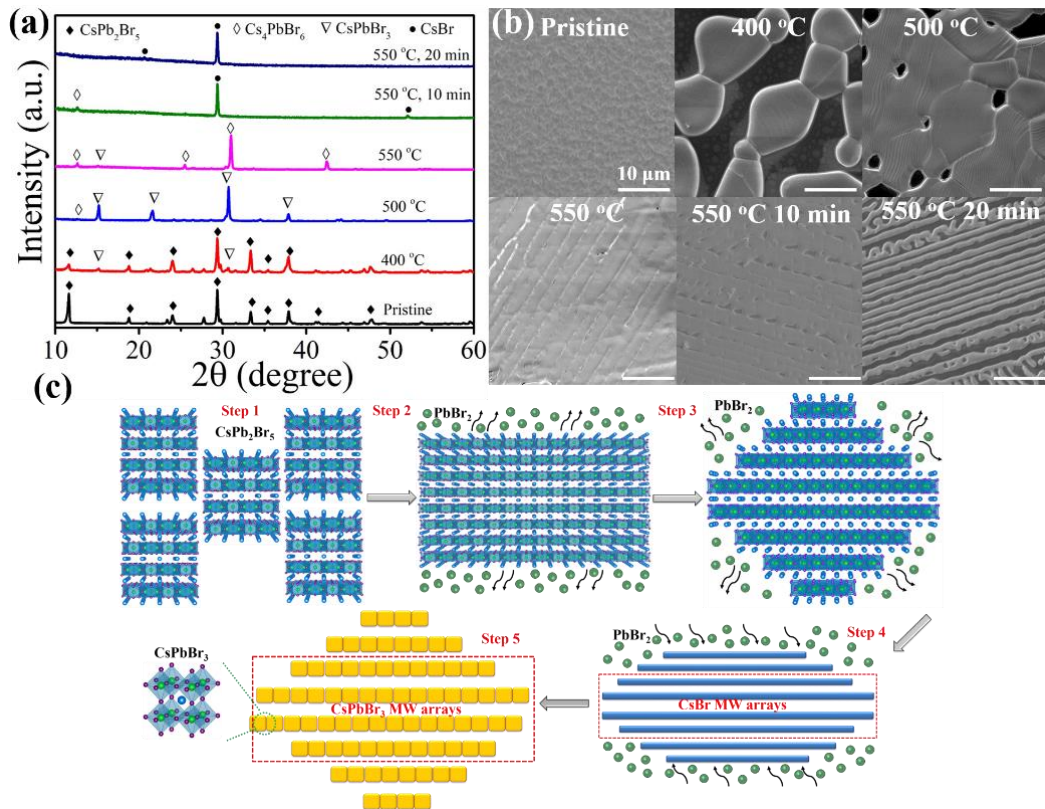
1 obtained (**Figure 2a**) after the post-treatment with an extra  $\text{PbBr}_2$  film (**Figure S9**)  
2 followed by annealing ( $\text{CsBr}+\text{PbBr}_2\rightarrow\text{CsPbBr}_3$ ), which show uniform distribution and  
3 silkworm-like grains. The average grain size is over  $5\ \mu\text{m}$  with the maximal size up to  
4  $11\ \mu\text{m}$  (**Figure S10**). The EDS element map (**Figure 2b, S11**) shows that the MW arrays  
5 are composed mainly of the Cs, Pb and Br elements. To extract the precise element ratio,  
6 the EDS line scan was performed (**Figure S12, S13**) and the corresponding element  
7 ratio of Cs, Pb and Br is close to 1:1:3, which agrees well with the stoichiometric ratio  
8 of the  $\text{CsPbBr}_3$  phase. In addition, the absence of Pb and Br in the gap between the  
9 MWs (**Figure S14**) indicates that the complete evaporation of extra  $\text{PbBr}_2$ . Furthermore,  
10 crystal structure characterization of MW arrays was conducted by XRD. The peaks at  
11  $15.19^\circ$ ,  $21.55^\circ$ ,  $26.48^\circ$ ,  $30.64^\circ$ ,  $34.37^\circ$ ,  $37.77^\circ$ ,  $43.89^\circ$ ,  $46.69^\circ$ ,  $49.38^\circ$  and  $54.51^\circ$  in  
12 **Figure 2c** can be assigned as (100), (110), (111), (200), (210), (211), (220), (300), (310)  
13 and (222) diffraction peaks, which indicate that the cubic  $\text{CsPbBr}_3$  perovskite (**Figure**  
14 **S8**) is formed after the post-treatment by extra  $\text{PbBr}_2$ . Note that  $\text{CsPbBr}_3$  MW arrays  
15 exhibit a polycrystalline structure without oriented growth. To gain more insight into  
16 the component and structure of the  $\text{CsPbBr}_3$  MWs, scanning transmission electron  
17 microscopy (STEM) measurements were conducted. The STEM characterization and  
18 corresponding simulation images in **Figure 2d, 2e** further demonstrate the crystalline  
19 character of  $\text{CsPbBr}_3$ , which is indexed to be the [111] crystal zone of the cubic  $\text{CsPbBr}_3$   
20 phase. AFM topography images in **Figure 2f, S15** illustrate that the  $\text{CsPbBr}_3$  MW has  
21 a height of  $1.72\ \mu\text{m}$  and width of MWs is close to  $6\ \mu\text{m}$ . Large grain size and high  
22 crystallinity of  $\text{CsPbBr}_3$  grains can effectively reduce recombination at the grain  
23 boundaries (GBs). To get a clear comparison with our  $\text{CsPbBr}_3$  MW arrays, a  $\text{CsPbBr}_3$   
24 film with a thickness of  $1.79\ \mu\text{m}$  was fabricated on the Si/SiO<sub>2</sub> substrates (**Figure S16**).  
25 Kelvin probe force microscopy (KPFM) measurements were carried out (**Figure 2g,**  
26 **S17**). In comparison with a conventional  $\text{CsPbBr}_3$  film that shows an uneven surface  
27 potential distribution in the film (**Figure S18**) under light illumination, the  $\text{CsPbBr}_3$   
28 MW shows a uniform surface potential distribution. This difference can be ascribed to  
29 the large and uniform perovskite grain in the MWs, which shows a reduced potential  
30 barrier at the GBs and thus is expected to promote carrier transport at GBs as seen in

1 **Figure S17b**. In contrast, the uneven grain size distribution indicates that overgrown  
2 grains exist in the perovskite film (**Figure S18c**), which can result in carrier  
3 accumulation at the GBs because of existence of the potential barrier. Carrier  
4 accumulation at GBs would significantly lower the valence and conduction band of the  
5 perovskite films as illustrated in **Figure S19**, which induces carrier recombination at  
6 the GBs.<sup>[37, 38]</sup> Furthermore, the steady-state photoluminescence (PL) measurements  
7 were carried out for CsPbBr<sub>3</sub> MW arrays and films. As seen in **Figure S20**, the  
8 enhanced PL intensity of CsPbBr<sub>3</sub> MW arrays can be attributed to high quality, less  
9 defects and reduced non-radiative recombination in the perovskite grains.<sup>[23]</sup> The  
10 lifetime of charge transport was investigated by time resolved photoluminescence  
11 (TRPL). By fitting with the following equation:<sup>[39, 40]</sup>

$$12 \quad \tau_{ave} = \frac{A_1\tau_1^2 + A_2\tau_2^2}{A_1\tau_1 + A_2\tau_2}$$

13 where  $A_1$  and  $A_2$  are the amplitudes,  $\tau_1$  and  $\tau_2$  represent non-radiative recombination  
14 and radiative recombination, respectively. The average lifetime is up to 84.14 ns  
15 (**Figure 2h**), which is much longer than the CsPbBr<sub>3</sub> film (36.38 ns, **Figure S18d**),  
16 indicating that the traps in MWs is effectively suppressed by reducing the GBs and  
17 obtaining a large grain size.





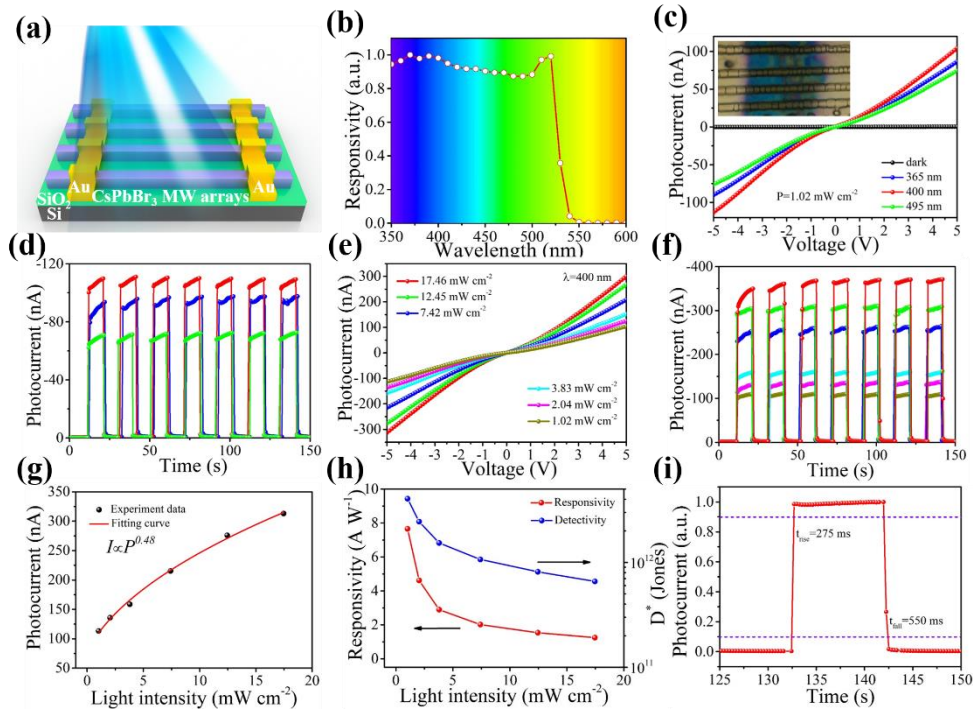
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2 **Figure 3.** a) XRD patterns and b) corresponding SEM images showing the conversion of the  
 3 CsPb<sub>2</sub>Br<sub>5</sub> precursor layer to the CsBr MW array at different temperatures. c) Schematic  
 4 illustration of formation of the CsBr MW arrays and CsPbBr<sub>3</sub> MW arrays.

5

6 How to understand the formation of CsBr and CsPbBr<sub>3</sub> MW arrays? We first  
 7 investigated the inverse and forward reactions in CsPb<sub>2</sub>Br<sub>5</sub>. As mentioned above, CsBr  
 8 reacted with PbBr<sub>2</sub> in a molar ratio of 1:2 to form CsPb<sub>2</sub>Br<sub>5</sub>. In contrast, CsPb<sub>2</sub>Br<sub>5</sub>  
 9 would easily decompose to CsPbBr<sub>3</sub> or CsBr because of the thermal instability at the  
 10 temperature above 300 °C.<sup>[41]</sup> As seen in **Figure 3a, 3b**, the pristine CsPb<sub>2</sub>Br<sub>5</sub> film  
 11 shows high crystallinity and full coverage (Figure 3b, Pristine). Perovskite grains would  
 12 quickly melt on the hotplate at 400 °C and grow into large ones in order to reduce the  
 13 surface energy (Figure 3b). Meanwhile, part of the CsPb<sub>2</sub>Br<sub>5</sub> phase decomposed to  
 14 CsPbBr<sub>3</sub> with evaporation of PbBr<sub>2</sub> because of the low melting point of PbBr<sub>2</sub> (357 °C)  
 15 (Figure 3a, 400 °C).<sup>[37]</sup> This procedure can be explained by the following equation:  
 16  $\text{CsPb}_2\text{Br}_5 \rightarrow \text{CsPbBr}_3 + \text{PbBr}_2 \uparrow$ . As the annealing temperature was increased to 500 °C,  
 17 the grains would grow larger according to the Ostwald ripening mechanism,<sup>[42]</sup> and

1 continuously decompose at such a high temperature. Due to the layered structure of  
2  $\text{CsPb}_2\text{Br}_5$ , the outmost layers would decompose faster than the inner layers (**Figure 3c**,  
3 step 3), which results in stepped structured grains (**Figure 3b**, **S21**, 500 °C). When the  
4 treated temperature was further increased to 550 °C, the  $\text{Cs}_4\text{PbBr}_6$  peaks could be  
5 detected in the XRD patterns, which suggests the continuous decomposition of  $\text{CsPbBr}_3$   
6 follows:  $4\text{CsPbBr}_3 \rightarrow \text{Cs}_4\text{PbBr}_6 + 3\text{PbBr}_2 \uparrow$ . In addition, the  $\text{Cs}_4\text{PbBr}_6$  MW arrays  
7 (**Figure S22**) could be formed based on the  $\text{CsPb}_2\text{Br}_5$  layer template. Prolonged  
8 annealing time (10 min and 20 min) induced the complete disappearance of  $\text{Cs}_4\text{PbBr}_6$   
9 phase by further extraction of  $\text{PbBr}_2$  ( $\text{Cs}_4\text{PbBr}_6 \rightarrow 4\text{CsBr} + \text{PbBr}_2 \uparrow$ ) and the  
10 intermediate products of CsBr MW arrays could be obtained because of the high  
11 melting point of CsBr over 660 °C and evaporation of  $\text{PbBr}_2$  (**Figure 3b** and **3c**, step  
12 4). This decomposition procedure makes the CsBr MW possible to keep the layered  
13 structure to construct arrays after fast evaporation of the low melting point component  
14 ( $\text{PbBr}_2$ ). Although the MWs appeared to grow along a certain direction within a local  
15 region of the substrate, on the scale of the whole substrate the MWs grew along different  
16 directions. As seen in Figure S1, in this specific sample location, some MWs showed  
17 the same orientation along the x direction. However, one of the MWs (Figure S1) was  
18 grown along the y direction. To realize the  $\text{CsPbBr}_3$  MW arrays, extra  $\text{PbBr}_2$  was  
19 deposited on the surface of the CsBr arrays (**Figure S9**). Then the as-prepared samples  
20 were annealed at a temperature of 350 °C for 30 min to ensure the further reaction  
21 between CsBr and  $\text{PbBr}_2$  to form highly crystalline  $\text{CsPbBr}_3$ . Finally, silkworm-like  
22  $\text{CsPbBr}_3$  MWs were obtained with an average grain size about 5  $\mu\text{m}$ .



**Figure 4.** a) Schematic illustration and b) responsivity spectrum of the CsPbBr<sub>3</sub> MW arrays photodetector. c) I-V and d) I-t curves of the CsPbBr<sub>3</sub> MW array based photodetector under dark and light illumination with different wavelengths. The inset is a photograph of the device. e) I-V and f) I-t curves of the CsPbBr<sub>3</sub> MW array based photodetector under light illumination with a wavelength of 400 nm with different power intensities. g) Photocurrent and h) responsivity/detectivity of the device as a function of incident power intensities. i) Response time of the photodetector during one cycle.

The CsPbBr<sub>3</sub> MW array based PDs (**Figure 4a**) were fabricated by coating 80 nm gold as the electrode using an aperture mask of 60 μm (**Figure 4c**, inset). The responsivity spectrum of the device (**Figure 4b**) shows a high photoresponsivity in the visible region, which is consistent with the absorption spectrum of CsPbBr<sub>3</sub> in our previous works.<sup>[7, 37]</sup> The current-voltage (I-V) curves in **Figure 4c** show a low dark current of  $-1.59 \times 10^{-10}$  A at a bias voltage of -5 V and photocurrent at a fixed power intensity of 1.2 mW cm<sup>-2</sup> under light illumination with different wavelengths. The high photocurrent of -113.20 nA was achieved at a bias voltage of -5 V under light illumination with a wavelength of 400 nm, which was much higher than the same thickness of CsPbBr<sub>3</sub> film photodetector (-50.76 nA, **Figure S23**). In parallel, the photocurrent under illumination light of 365 nm and 450 nm are -90.14 nA and -76.06 nA, respectively. The responsivity (R) and detectivity (D\*) of the PDs were extracted

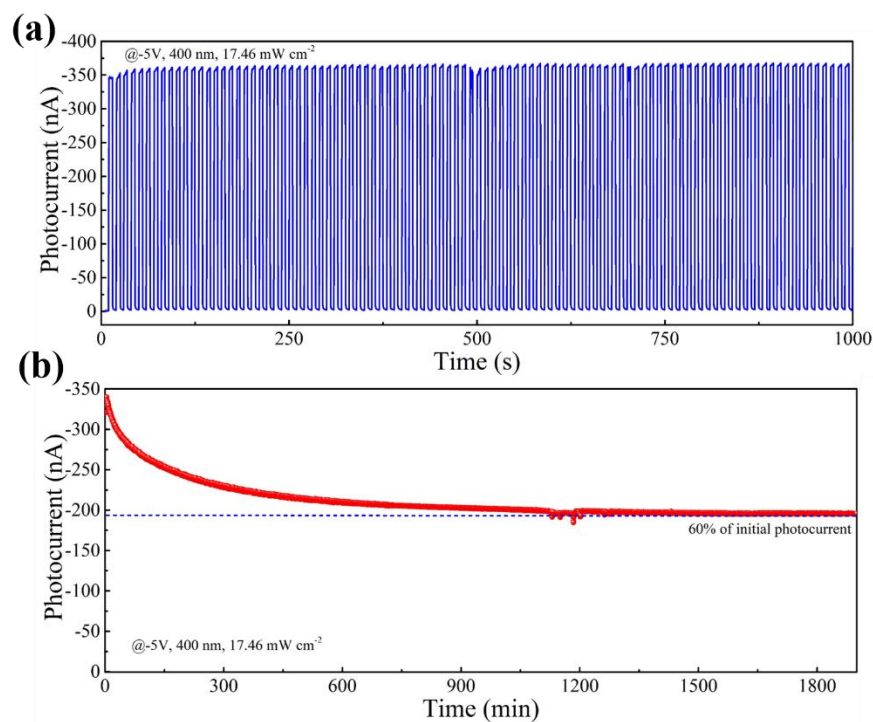
1 from the following equations:<sup>[43-45]</sup>

$$2 \quad R = \frac{\Delta I}{P_{\lambda} S} \quad (1)$$

$$3 \quad D^* = R \sqrt{\frac{S}{2qI_{dark}}} = \frac{R\sqrt{BS}}{i_n} \quad (2)$$

4 where  $\Delta I$  is photocurrent ( $\Delta I = I_{light} - I_{dark}$ ,  $I_{light}$  and  $I_{dark}$  are the current with light  
5 illumination and in dark, respectively).  $P_{\lambda}$  is the light illumination power intensity on  
6 the device and  $S$  is the active area of the device;  $q$ ,  $B$  and  $i_n$  are the elementary charge,  
7 electrical bandwidth of noise measurement and noise current, respectively. The  
8 CsPbBr<sub>3</sub> MW arrays can be regarded as a rectangular-shaped structure and the  
9 corresponding active area is estimated as follows:<sup>[29]</sup>  $S = n \times a \times b$ , where  $n$  is the number  
10 of MWs in the device ( $n=4$ ), and  $a$  and  $b$  are the width of the MWs (6  $\mu\text{m}$ ) and length  
11 of the channel (60  $\mu\text{m}$ ), respectively. The corresponding responsivity/detectivity of the  
12 devices under light illumination of 365 nm, 400 nm and 450 nm were 6.13 A W<sup>-1</sup>/  
13  $3.25 \times 10^{12}$  Jones, 7.66 A W<sup>-1</sup>/ $4.05 \times 10^{12}$  Jones and 5.18 A W<sup>-1</sup>/ $2.74 \times 10^{12}$  Jones,  
14 respectively. Time-dependent curves (I-t) in **Figure 4d** suggest that high repeatability  
15 of the devices under light illumination with different wavelengths. Moreover, the  
16 intensity dependent properties of the devices were also investigated by changing the  
17 irradiation power intensity from 1.02 to 17.46 mW cm<sup>-2</sup>. As the incident power intensity  
18 increased, the photocurrent of the device was greatly increased (**Figure 4d**) because  
19 more carriers were excited and separated. The corresponding I-t curves in **Figure 4e**  
20 also exhibited excellent reproducibility even at high power intensity. By fitting the  
21 curve in **Figure 4f** with the formula of  $I = P^{\theta}$ , where  $I$ ,  $P$  and  $\theta$  are the photocurrent,  
22 power intensity and proportionality constant, respectively, we found that  $\theta$  was 0.48 for  
23 400 nm incident light, which was not close to the ideal value of 1 because  $\theta$  was related  
24 to recombination processes of photo-generated carriers.<sup>[46, 47]</sup> This suggests that some  
25 traps and recombination centers exist in the device when the devices are operated under  
26 a high incident light intensity, but the devices still exhibit a good linearity for photo-  
27 detection.<sup>[46, 48]</sup> In addition, we also conducted the light power intensity investigation at  
28 365 nm and 450 nm in **Figure S24, S25**, which also exhibits an excellent dependence  
29 on the power intensity with a good fitting showing a linearity relationship for light

1 detection. **Figure S26** depicts the response characteristic under different operational  
2 biases from -1 V to -5 V, as the corresponding photocurrent increased from 14.4 nA to  
3 367.1 nA, which indicates that the devices could work well under even low bias  
4 voltages. Beside responsivity and detectivity, the response time is also an important  
5 parameter for photodetectors, representing the photo-sensitivity of the device and can  
6 be defined as the photocurrent increase from 10% to 90% ( $t_{\text{rise}}$ ) and decrease from 90%  
7 to 10% ( $t_{\text{fall}}$ ) of the maximum value.<sup>[49]</sup> We chose one cycle from Figure 4f. It is clear  
8 that the CsPbBr<sub>3</sub> MW array based PD shows a fast response time of 275/550 ms during  
9 ON/OFF operation under 400 nm (**Figure 4i**).  
10



11  
12 **Figure 5.** a) Time-dependent response of the CsPbBr<sub>3</sub> MW array based PD after 100 cycles of  
13 operation. b) Operational stability of CsPbBr<sub>3</sub> MW array based PDs under continuous  
14 illumination (@400 nm, -5 V, 17.46 mW cm<sup>-2</sup>).  
15

16 Furthermore, we also investigated the operational stability of our PD devices.  
17 Different from conventional storage stability under dark condition without bias, the  
18 operational stability was conducted under continuous light illumination and constant  
19 voltage, which reflected the more realistic performance of the PD devices during

operation. First, we switched ON/OFF by repeatedly turning light (400 nm, 17.46 mW cm<sup>-2</sup>) on and off under a bias voltage of -5 V (**Figure 5a**). The device exhibited excellent reproducibility and stability. After 100 cycles, the photocurrent of the device maintained the same value, which yielded a high ON/OFF ratio of ~10<sup>3</sup>. In parallel, continuously light illumination was also performed under 400 nm (~17.46 mW cm<sup>-2</sup>) at a fixed bias voltage of -5 V. The photocurrent of the device dropped rapidly at the first 600 min and then maintained at a stable value (**Figure 5b**). The devices remained 60% of the initial photocurrent even after 1900 min, which represents better operational stability than previous reports as seen in **Table 1**. The high stability performance can be explained by the improved grain crystallinity, larger grain size (about 5 μm), thicker layer (about 1.72 μm) and fewer grain boundaries. Decomposition/degradation of perovskite devices often starts from the grain boundaries, which serve as a pathway for moisture/oxygen penetration and gradually induce the phase transition/decomposition process toward the grain interiors because chemical binding at grain boundaries with low crystallinity is much weaker than that within the crystal domain interior.<sup>[50, 51]</sup> On the other hand, charge trapping at the GBs induced by light soaking in the moisture condition can trigger the irreversible degradation of perovskite.<sup>[52]</sup> In comparison with many GBs in the thin film, high crystallinity and fewer GBs in the CsPbBr<sub>3</sub> MW arrays alleviate moisture attacks and charge accumulation at the GBs under long-term illumination under the moisture condition. In parallel, the outmost layer of the thicker CsPbBr<sub>3</sub> crystallites in the MW arrays naturally protect the inner crystallites from decomposition/degradation.<sup>[50]</sup>

23

24 **Table 1** Comparison of inorganic perovskite nanowires from previous works and this work.

Material	Formation direction	Method	Template	Length (μm)	R (A/W)	D* (Jones)	Operational Stability [min]	Ref
CsPbBr <sub>3</sub> MW arrays	Inverse	Vapor	No	>200	7.66	4.05×10 <sup>12</sup>	1900	This work
CsPbBr <sub>3</sub> NW arrays	Forward	Vapor	No	<30	—	—	—	[53]
CsPbBr <sub>3</sub> NW arrays	Forward	Solution	Yes	>28	1377	—	—	[11]

CsPbI <sub>3</sub> NW nanoarrays	Forward	Vapor	Yes	~10	0.0067	1.5×10 <sup>12</sup>	—	[30]
CsPbI <sub>3</sub> /CsPbBr <sub>3</sub> NW arrays	Forward	Solution	Yes	>750	0.125	—	—	[32]
MAPbI <sub>3</sub> MW arrays	Forward	Solution	Yes	>400	13.57	5.25×10 <sup>12</sup>	—	[15]
MAPbI <sub>3</sub> NW arrays	Forward	Solution	Yes	>130	0.012	7.3×10 <sup>12</sup>	10	[33]
MAPbI <sub>3</sub> NW arrays	Forward	Solution	No	>200	4.95	2×10 <sup>13</sup>	—	[54]
MAPbI <sub>3</sub> MW arrays	Forward	Solution	No	>650	0.16	1.3×10 <sup>12</sup>	—	[48]
MAPbI <sub>3</sub> NW arrays	Forward	Solution	Yes	>180	6660	6.85×10 <sup>12</sup>	—	[55]
MAPb(I <sub>1-x</sub> Br <sub>x</sub> ) <sub>3</sub> NW arrays	Forward	Solution	Yes	>230	12500	1.73×10 <sup>11</sup>	—	[34]
FAPbI <sub>3</sub> NW arrays	Forward	Solution	Yes	>75	5282	1.45×10 <sup>14</sup>	—	[35]
CsPbBr <sub>3</sub> film	Forward	Vapor	—	—	0.375	2.96×10 <sup>11</sup>	—	[45]
CsPbBr <sub>3</sub> film	Forward	Solution	—	—	0.010	4.56×10 <sup>8</sup>	—	[56]
CsPbBr <sub>3</sub> single crystal	Forward	Solution	—	—	2	—	360	[57]
CsPbBr <sub>3</sub> single crystal	Forward	Solution	—	—	0.028	—	—	[58]

1 ※Operational stability is defined as the stability when the device is under a bias voltage  
2 and continuous light illumination.

3

#### 4 **Conclusion**

5 In summary, we reported a 2D derivative phase CsPb<sub>2</sub>Br<sub>5</sub> induced growth of 3D all  
6 inorganic perovskite CsPbBr<sub>3</sub> MW arrays. Decomposition of layered structure of 2D  
7 CsPb<sub>2</sub>Br<sub>5</sub> induces the formation of single-crystalline CsBr MW arrays. The CsBr MW  
8 arrays are post-treated by extra PbBr<sub>2</sub> to convert to CsPbBr<sub>3</sub> phase. Impressively, the  
9 high performance of a high responsivity of 7.66 A W<sup>-1</sup> and long-term operational  
10 stability over 1900 min are simultaneously realized in the CsPbBr<sub>3</sub> MW array  
11 photodetectors because of the large grain size, fewer grain boundaries and lower surface  
12 potential barrier.

13

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#### 5 **Conflict of Interest**

6 The authors declare no conflict of interest.

7  
8 **Keywords:** inorganic perovskite, nanowire arrays, vapor deposition, photodetector,  
9 stability

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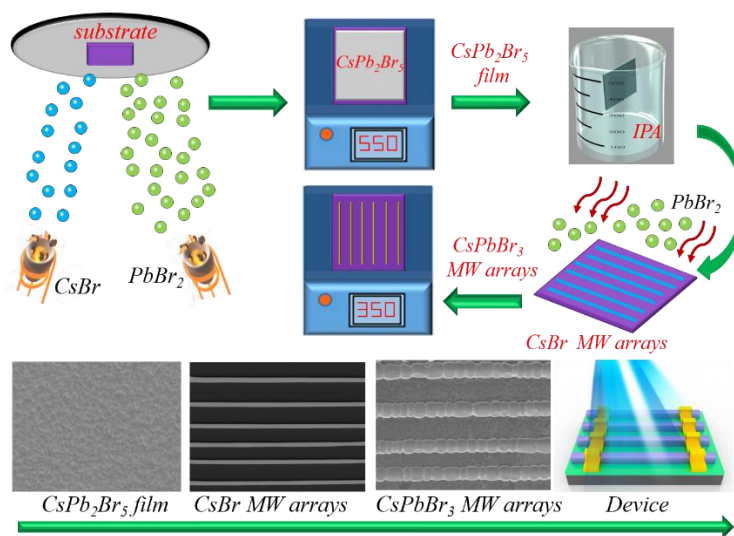
## TOC

**2D derivative phase induced growth of 3D all inorganic perovskite micro-nanowire array based photodetectors***Guoqing Tong, Maowei Jiang, Dae-Yong Son, Luis K. Ono and Yabing Qi*

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A well aligned CsPbBr<sub>3</sub> micro-nanowire (MW) array was synthesized by controlling growth of the intermediate CsBr MW array originated from the deposition of the 2D CsPb<sub>2</sub>Br<sub>5</sub> phase. Furthermore, a high-performance photodetector was demonstrated based on the CsPbBr<sub>3</sub> MW array.