

**OIST**OKINAWA INSTITUTE OF SCIENCE AND TECHNOLOGY GRADUATE UNIVERSITY
沖縄科学技術大学院大学

Inverse Growth of Large-Grain-Size and Stable Inorganic Perovskite Micronanowire Photodetectors

Author	Guoqing Tong, Maowei Jiang, Dae-Yong Son, Longbin Qiu, Zonghao Liu, Luis K. Ono, Yabing Qi
journal or publication title	ACS Applied Materials & Interfaces
volume	12
number	12
page range	14185-14194
year	2020-03-05
Publisher	American Chemical Society
Rights	(C) 2020 American Chemical Society This document is the Accepted Manuscript version of a Published Work that appeared in final form in ACS Applied Materials & Interfaces, copyright (C) American Chemical Society after peer review and technical editing by the publisher. To access the final edited and published work see https://pubs.acs.org/doi/10.1021/acsami.0c01056 .
Author's flag	author
URL	http://id.nii.ac.jp/1394/00001393/

doi: info:doi/10.1021/acsami.0c01056

1 **Inverse Growth of Large Grain Size and Stable Inorganic Perovskite Micro-**
2 **Nanowire Photodetectors**

3 Guoqing Tong, Maowei Jiang, Dae-Yong Son, Longbin Qiu, Zonghao Liu, Luis K.
4 Ono, and Yabing Qi*

5 Energy Materials and Surface Sciences Unit (EMSSU)
6 Okinawa Institute of Science and Technology Graduate University (OIST)
7 1919-1 Tancha, Onna-son, Kunigami-gun, Okinawa 904-0495, Japan

8 *Corresponding author: Yabing Qi, E-mail: Yabing.Qi@OIST.jp
9

10 **ABSTRACT:** Control of the forward and inverse reactions between perovskites and
11 precursor materials is key to attaining high quality perovskite materials. Many
12 techniques focus on synthesizing nanostructured CsPbX₃ materials (e.g., nanowires)
13 via a forward reaction ($\text{CsX} + \text{PbX}_2 \rightarrow \text{CsPbX}_3$). However, lower solubility of
14 inorganic perovskites and complex phase transition make it difficult to realize the
15 precise control of composition and the length of nanowires using the conventional
16 forward approach. Herein, we report a self-assembly inverse growth of CsPbBr₃ micro-
17 nanowires (MWs) ($\text{CsPb}_2\text{Br}_5 \rightarrow \text{CsPbBr}_3 + \text{PbBr}_2 \uparrow$) by controlling phase transition
18 from CsPb₂Br₅ to CsPbBr₃. Two-dimensional (2D) structure of CsPb₂Br₅ serves as
19 nucleation sites to induce the initial CsPbBr₃ MW growth. Also, phase transition allows
20 crystal rearrangement and slows down the crystal growth, which facilitates the MW
21 growth of CsPbBr₃ crystals along the 2D planes of CsPb₂Br₅. A CsPbBr₃ MW
22 photodetector constructed based on the inverse growth shows a high responsivity of
23 6.44 A W⁻¹ and detectivity of ~10¹² Jones. Larger grain size, high crystallinity and
24 bigger thickness can effectively alleviate the decomposition/degradation of perovskites,
25 which leads to storage stability over 60 days in moisture (45% relative humidity) and
26 operational stability over 3000 min under illumination (400 nm, ~20.06 mW cm⁻²).

1 **KEYWORDS:** *inorganic perovskite, micro-nanowire, inverse growth, photodetector,*
2 *operational stability*

3 **1. INTRODUCTION**

4 Inorganic perovskite materials (CsPbX_3 , $X = \text{I, Br or Cl}$) have shown a great
5 potential for applications in solar cells, light-emitting diodes (LEDs), photodetectors
6 (PDs) and lasers because of their remarkable physical and chemical characteristics (e.g.,
7 tunable bandgap, strong optical absorption, high carrier mobility and long diffusion
8 length) and low-cost fabrication.¹⁻⁶ Besides inorganic perovskite based thin films and
9 quantum dots, nanowires (NWs) / micro-nanowires (MWs) exhibit outstanding
10 performance in optoelectronic devices. Because of the confined carrier transport in one-
11 dimensional channels/structures, it has been reported that fast charge transport could be
12 realized to improve the electric performance.⁷ In addition, compared with perovskite
13 thin films, these NWs tend to have large grain size and less grain boundaries, which
14 would reduce the trap /defects density and recombination rate resulting in a long carrier
15 lifetime of photogenerated carriers and low leak current.⁷⁻¹¹ For example, Eaton and
16 coworkers synthesized inorganic single crystalline perovskite CsPbBr_3 NWs with well-
17 defined facets, which is beneficial for the high quality laser cavities.¹² The Fabry-Pérot
18 lasing was detected in CsPbBr_3 NWs with a low threshold ($5 \mu\text{J cm}^{-2}$). In parallel, Yang
19 and coworkers developed single-crystalline CsPbI_3 nanorods with a uniform diameter
20 ($\sim 150 \text{ nm}$) and length ($\sim 2 \mu\text{m}$).¹³ These high quality single-crystalline nanorods show
21 a reduced trap density and enhanced carrier mobility leading to high performance PD
22 with a responsivity of 2920 A W^{-1} and a fast response time ($\tau_{\text{rise}}/\tau_{\text{fall}}$) (the photocurrent

1 increase from 10% to 90% (τ_{rise}) and decrease from 90% to 10% (τ_{fall}) of maximum) of
2 50/150 μs .

3 Several advanced techniques have been developed to synthesize perovskite NWs,
4 including solution-phase synthesis and chemical vapor deposition (CVD).¹⁴⁻¹⁷ The
5 solution method is the simplest strategy, yet showing great advantage in the fabrication
6 of NW arrays because a precise ratio of precursor materials can be controlled and it
7 only requires low-temperature synthesis processes ($< 80\text{ }^\circ\text{C}$).^{18, 19} For instance, Zhang
8 and coworkers used an anion-exchange method to realize the CsPbX_3 alloy NWs by
9 controlling the reaction between CsPbBr_3 NWs and halide precursors.²⁰ However, the
10 solution growth methods are usually affected by the solvent, surfactant and low-
11 solubility of inorganic perovskite precursor materials, which has a significant influence
12 on the formation/nucleation process and optical properties.^{7, 21} In contrast, CVD as an
13 alternative process provides advantage to be solvent-free and direct growth on the
14 substrates.^{22, 23} The vapor-based method employing vacuum systems allows researchers
15 to achieve a stoichiometric and highly crystalline NWs due to the absence of any
16 solvent or surfactant.^{22, 24} In addition, impurities in precursor materials can be removed
17 from the sublimed precursors at a high temperature during evaporation.²⁵ Furthermore,
18 the composition, diameter, length and growth direction of NWs can be controlled by
19 experimental conditions such as catalyst,²⁶ substrates,¹⁷ growth pressure/temperature.^{26,}
20 ²⁷ Specifically, highly oriented NWs can be realized via a vapor-phase epitaxial growth
21 on the crystalline substrates such as sapphire and mica substrates.²⁸ Chen and co-
22 workers prepared high-quality CsPbBr_3 NWs along the [001] directions on mica (001)

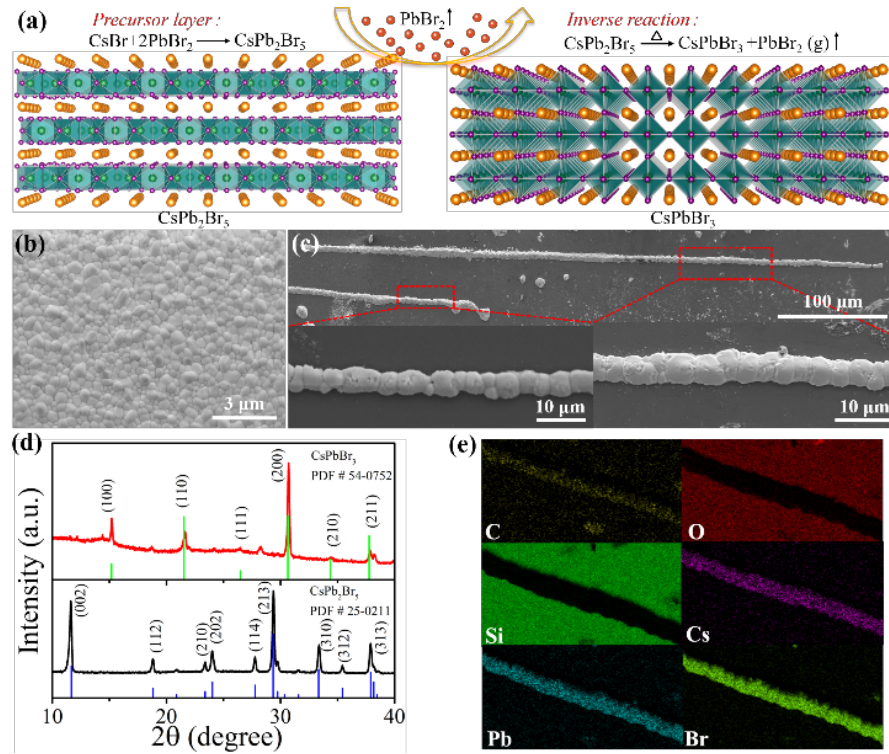
1 substrates through a vapor-phase epitaxy technique.²⁸ In addition, the horizontally
2 oriented CsSnX₃ (X = Br, I) NWs / MWs along [001] were realized on mica substrates
3 via a vapor phase growth by Jin, Chen and coworkers.²⁹ Despite the great results
4 achieved by vapor phase synthesis, the formation of NWs is favorable only at a high
5 temperature (~600 °C) or with the aid of catalyst in a high vacuum system, which
6 represents an obstacle for their commercial application (especially on flexible
7 substrates).^{26, 30-32}

8 Most of inorganic perovskite NWs/MWs in recent reports are synthesized by a
9 forward reaction mechanism.^{26, 33} In this technique, CsX and PbX₂ are dissolved in a
10 solvent (e.g., octadecene or DMF/DMSO)^{10, 20} or evaporated in a vacuum system^{17, 29}
11 at the optimized temperature in order to attain the final products of CsPbX₃ NWs as
12 follows (forward reaction): CsX + PbX₂ → CsPbX₃. The low solubility of inorganic
13 perovskite materials in solvents when considering solution-based processes or the high
14 evaporation temperature (~600 °C) as well as the capital cost of vacuum systems
15 employed for vacuum-based processes (e.g., CVD), and the complex Cs-Pb-X phase
16 diagram are not attractive for mass production of NWs using this forward route.^{20, 22, 29,}
17 ^{34, 35} How to realize NWs/MWs with an ultralong length over 100 μm with simple and
18 controllable processing is a challenge but a prerequisite for integrated semiconductor
19 devices.³⁶ It is worth noting that many derivative phases exist in the Cs-Pb-Br phase
20 diagram such as the two-dimensional (2D) structure of CsPb₂Br₅ and the zero-
21 dimensional phase of Cs₄PbBr₆.³⁷⁻³⁹ They easily convert to 3D CsPbBr₃ under certain
22 conditions as follows (inverse reaction): CsPb₂Br₅ → CsPbBr₃ + PbBr₂; Cs₄PbBr₆ →

1 CsPbBr₃ + 3CsBr,^{40, 41} and also can serve as nucleation sites to further promote the
2 continuous growth of CsPbBr₃ following the Ostwald ripening mechanism.^{42, 43}

3 In this work, we developed a catalyst/template-free and inverse growth of CsPbBr₃
4 MWs taking advantage of the synergy effect of a derivative phase transition and
5 Ostwald ripening. The CsPb₂Br₅ precursor layer was first deposited on the substrates
6 via vacuum vapor deposition and then annealed in air. CsPb₂Br₅ films were converted
7 to CsPbBr₃ (accompanied by volatilization of PbBr₂) during post-annealing because of
8 the inverse reaction between CsPbBr₃ and the CsPb₂Br₅ derivative phase (CsPb₂Br₅ →
9 CsPbBr₃ + PbBr₂ ↑) and thermodynamic stability of CsPbBr₃ (**Figure 1a**). During the
10 annealing process, the 2D CsPb₂Br₅ serves as nucleation sites, and the intermediate
11 phase of CsPb₂Br₅@CsPbBr₃ effectively slows down the crystal growth of CsPbBr₃
12 compared with forward growth. In parallel, the 2D layer structure of CsPb₂Br₅ can also
13 serve as a template during the phase transition/decomposition from the 2D CsPb₂Br₅ to
14 the 3D cubic CsPbBr₃ phase, which provides enough space and allows the crystal
15 rearrangement (2D → 3D) in the structure. The above characteristics facilitate
16 continuous growth of CsPbBr₃ crystals along the preferred orientation to form CsPbBr₃
17 MWs with an ultralong length of ~510 μm. Based on this inverse growth of CsPbBr₃
18 MWs, high performance photodetectors were realized with a high responsivity of 6.44
19 A W⁻¹ and a response time of 301/242 ms. The devices also exhibited outstanding
20 storage stability over 60 days in air (relative humidity RH ~ 45%) and operational
21 stability under monochromatic light (400 nm, ~20.06 mW cm⁻²) over 3000 min (Table
22 1) because of larger grain size, high crystallinity and bigger thickness. This inverse

- 1 growth of CsPbBr₃ MWs from the derivative phase offers a new way to fabricate
- 2 perovskite NWs / MWs and shows potential for applications in future integrated devices.



3
4 **Figure 1.** (a) The formation mechanism of CsPbBr₃ MW from CsPb₂Br₅ film after annealing at 450
5 °C for 1 h. SEM image of (b) the CsPb₂Br₅ film (250 °C) and (c) CsPbBr₃ MW. (d) XRD patterns
6 of the CsPb₂Br₅ film (250 °C) and CsPbBr₃ NW. (e) EDS mapping of a CsPbBr₃ MW.

7
8 **Table 1** Comparison of inorganic perovskite nanowires from previous works and this work.

Material	Formation direction	Method	Template	Length (μm)	Height (nm)	R (A W ⁻¹)	D* (Jones)	Operational Stability [min]	Storage Stability [h]	Ref
CsPbBr ₃ MW	Inverse	Vapor	No	~510	1360	6.44	2.88×10 ¹²	3000	1440	This work
CsPbI ₃ NR	Forward	Solution	No	~2	—	2920	5.7×10 ¹³	720	168	13
CsPbI ₃ NW	Forward	Solution	No	<20	—	—	—	140	—	44
CsPbI ₃ NW	Forward	Solution	No	>325	—	0.745	3.46×10 ¹⁰	—	—	33
CsPbBr ₃ NW	Forward	Vapor	Yes	~1500	—	4400	—	—	—	17

CsPbBr ₃ NW	Forward	Vapor	No	~40	—	3306	7.9×10 ¹²	—	—	26
CsPbBr ₃ NW	Forward	Vapor	No	~20	~420	0.001	—	—	—	28
CsPbBr ₃ NW	Forward	Solution	No	~12	—	—	—	—	—	45
Cs ₃ Sb ₂ Cl ₉ NW	Forward	Solution	No	~0.29	4	3616	1.25×10 ⁶	—	—	46
CsPbI ₃ NW	Forward	Solution	Yes	>150	250	1294	2.6×10 ¹⁴	—	720 h	10
CsPbI ₃ nanoarrays	Forward	Vapor	Yes	~10	~1000	0.0067	1.5×10 ¹²	—	—	23
CsPbBr ₃ nanoarrays	Forward	Vapor	No	<30	20~1000	—	—	—	—	11
CsPbBr ₃ nanoarrays	Forward	Solution	Yes	>28	200	1377	—	—	—	19
CsPbCl ₃ film	Forward	Vapor	—	—	—	0.1309	1.4 × 10 ¹³	—	720 h	4
CsPbBr ₃ film	Forward	Vapor	—	—	—	0.375	2.96 × 10 ¹¹	—	1560 h	39
CsPbBr ₃ film	Forward	Solution	—	—	—	0.64	—	—	12	47
Cs ₃ Cu ₂ I ₅ film	Forward	Solution	—	—	—	0.0649	6.9×10 ¹¹	—	—	48

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

3

4 2. RESULTS AND DISCUSSION

5 To grow CsPbBr₃ MWs, we first deposited the CsPb₂Br₅ thin film on the substrates,
6 which served as a precursor layer. As seen in Figure 1a, CsPb₂Br₅ showed a 2D layer
7 structure and was synthesized by excess PbBr₂ as follows:

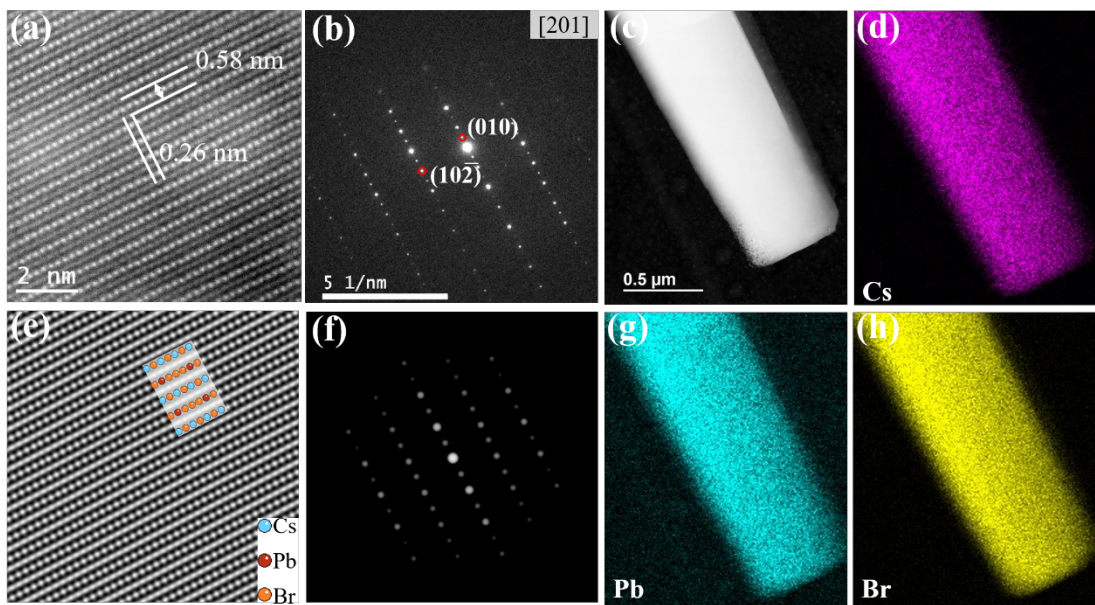


10 Therefore, we first deposited the CsPb₂Br₅ film with a thickness of 1 μm on the Si (100)

11 /SiO₂ (300 nm) substrates by sequential vapor deposition as discussed in our previous

1 works.^{41, 49} Then, we annealed the as-prepared films at 250 °C (20 min) in order to
2 achieve high crystalline CsPb₂Br₅ grains. The scanning electron microscopy (SEM)
3 image of the CsPb₂Br₅ film in Figure 1b showed a uniform and compact layer with high
4 crystallinity after annealing. The atomic Cs/Pb/Br ratios determined by energy
5 dispersive X-ray spectroscopy (EDS) mapping in Figure S1 was 1:2.3:5.2 in good
6 agreement with the stoichiometry of the CsPb₂Br₅ phase. The structure of CsPb₂Br₅ was
7 determined by X-ray diffraction (XRD). As seen in Figure 1d, characteristic peaks at
8 11.67°, 18.83°, 23.39°, 24.03°, 27.77°, 29.36°, 33.34°, 35.44° and 37.90° were assigned
9 to (002), (112), (210), (202), (114), (213), (310), (312) and (313) diffraction planes of
10 the tetragonal CsPb₂Br₅ phase at 250 °C, respectively, (Figure S2). After annealing
11 CsPb₂Br₅ films at 450 °C for 1 h, ultralong CsPbBr₃ MWs (~510 μm) were obtained on
12 the Si (100)/SiO₂ substrates (Figure 1c, S3). As shown in Figure 1d, the CsPbBr₃ MW
13 showed a cubic phase (Figure S2). The peaks at 15.19°, 21.55°, 26.48°, 30.64°, 34.37°,
14 and 37.77° can be assigned to (100), (110), (111), (200), (210) and (211) lattice planes,
15 respectively. From the SEM images in Figure 1c, we found that the MWs were
16 composed of grains connected to one another. The average grain size was over 5 μm.
17 Additionally, the CsPbBr₃ MW also exhibited a height of 1.36 μm measured by atomic
18 force microscopy (AFM) as shown in Figure S4, which was about 36% thicker than the
19 precursor thickness of CsPb₂Br₅ layer, because of the growth of crystals and structure
20 reconstruction during annealing following the Ostwald ripening mechanism.^{42, 43} The
21 length to height ratio of MW was 375. To further evaluate the chemical composition of
22 MWs, we conducted EDS mapping on a single CsPbBr₃ MW (Figure 1e, S5). The single

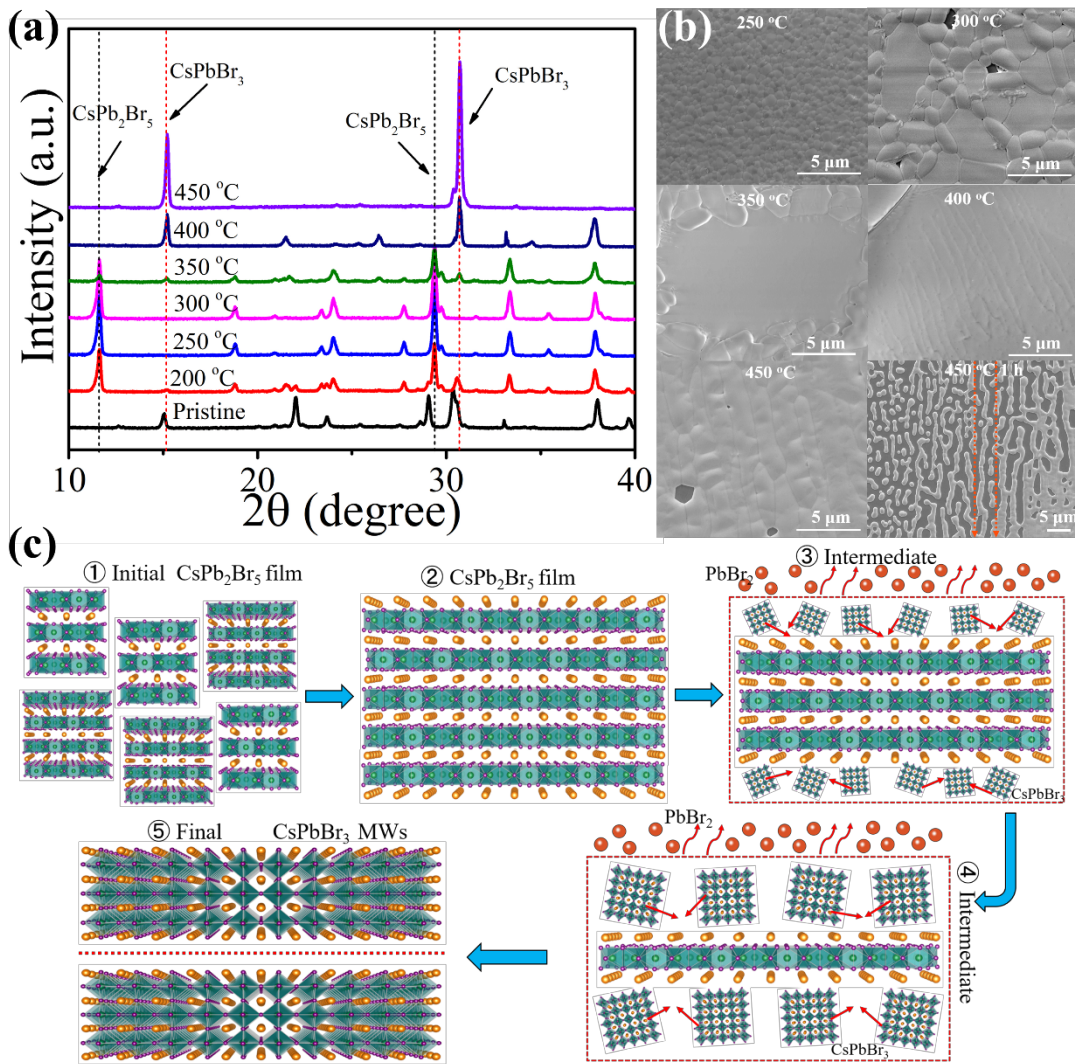
1 MW was mainly composed of Cs, Pb and Br elements showing a uniform distribution.
 2 In addition, the Si and O elements were also detected suggesting the presence of a SiO₂
 3 film around the MW. The EDS line scan was conducted to analyze the composition of
 4 the MW in Figure S6. A uniform elemental distribution of Cs, Pb and Br along the axial
 5 direction could be inferred with the estimated atomic Cs/Pb/Br ratios of 1:0.91:2.84,
 6 which was consistent with the stoichiometric ratio of the CsPbBr₃ phase.



7
 8 **Figure 2.** (a) STEM image resolving the lattice fringes and (b) SAED pattern of a CsPbBr₃ MW. (c)
 9 STEM image and corresponding EDS mapping of (d) Cs, (g) Pb and (h) Br. (e) Simulated lattice
 10 image and (f) SAED pattern of a CsPbBr₃ MW.

11 Based on Figure 1c, S4, our MWs exhibited a polycrystalline structure with oriented
 12 grains due to the self-assembly growth from the CsPb₂Br₅ film to CsPbBr₃ MWs during
 13 decomposition (inverse growth). However, each of the perovskite grains showed a
 14 single crystalline structure with a large grain size. To evaluate the crystallinity of the
 15 inversely grown CsPbBr₃ MWs, we conducted scanning transmission electron

1 microscopy (STEM) and selected-area electron diffraction (SAED) measurements
2 (Figure 2a, b). The lattice fringes with a spacing of 5.8 Å and 2.6 Å in Figure 2a,
3 respectively, correspond to the lattice spacing of (010) and (10 $\bar{2}$) planes, along [201]
4 zone axis of CsPbBr₃ (PDF#54-0752), which suggested the single crystalline nature of
5 the grains in the CsPbBr₃ MWs. In addition, a simulation was calculated to find out the
6 atom stacking along the [201] direction (Figure 2e). It was shown that the simulation
7 agreed well with the collected STEM image (Figure 2a). The simulated SAED pattern
8 (Figure 2f) also agreed well with the image in Figure 2b. Furthermore, a model of atom
9 stacking image was added in Figure 2e, indicating that the rows with the dark contrast
10 in Figure 2a might be derived from the secondary diffraction of the (010) plane.
11 Importantly, the EDS mapping in Figure 2c, d, g and h showed a uniform element
12 distribution of Cs, Pb and Br with the element ratios of 1:1:3 (Figure S7).



1
2 **Figure 3.** (a) XRD patterns of samples at different annealing temperatures. (b) SEM images of the
3 as-prepared CsPb_2Br_5 film grown at 250 °C, 300 °C, 350 °C, 400 °C, 450 °C, for 20 min at each
4 temperature, and 450 °C, for 1 h, respectively. (c) Schematic illustration showing the inverse growth
5 of the samples from the CsPb_2Br_5 film to CsPbBr_3 MWs.

6 To further understand the inverse growth of CsPbBr_3 MWs, we first investigated
7 the forward and inverse reactions between CsPbBr_3 and CsPb_2Br_5 and the
8 corresponding changes of structure and morphologies. The thermally evaporated
9 compact pristine layer was depicted in Figure S8, which showed small size grains and
10 low crystallinity at room temperature and 200 °C. The yellow color of sample (Figure

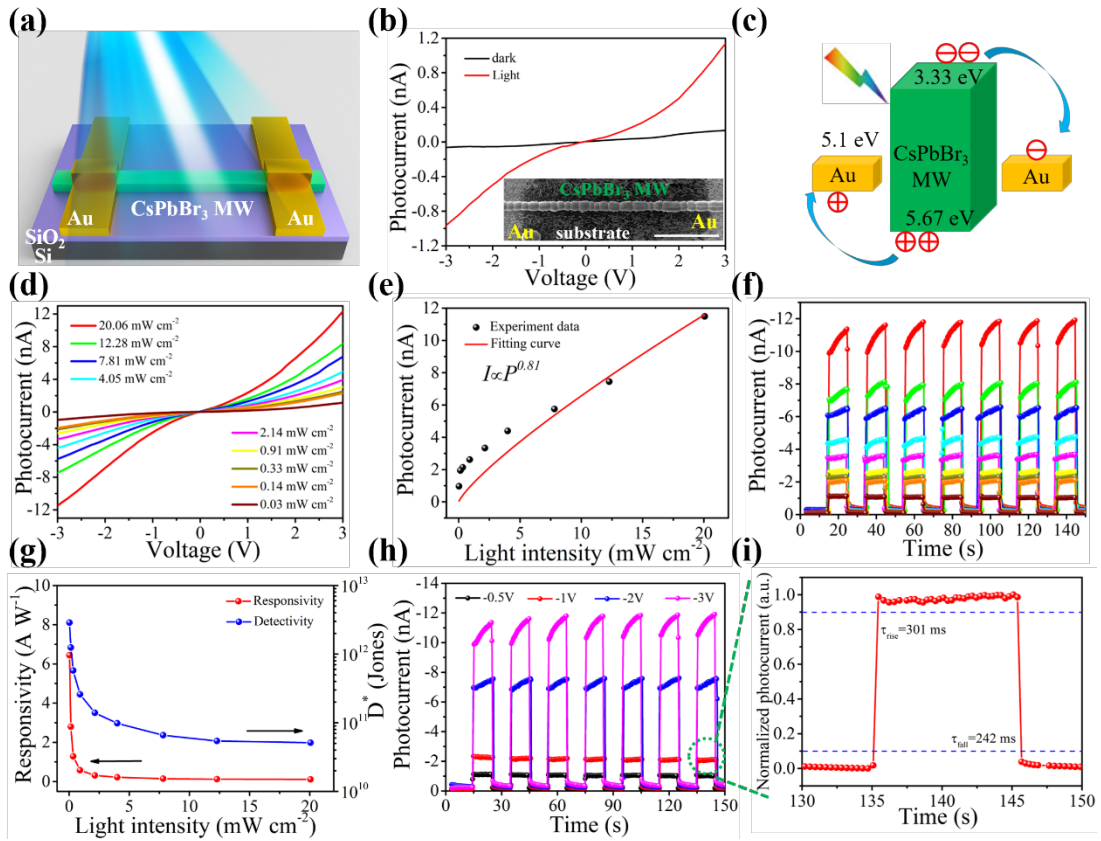
1 S9) suggested the co-existence of CsPbBr₃ and derivative phases in the pristine film
2 (Figure 3a, Figure S10a, b). As the annealing temperature increased, the color of as-
3 prepared film gradually turned white (250 °C) and the grains grew quickly from 100
4 nm to 1 μm (Figure 3b) because of diffusion and reaction between precursor materials
5 of CsBr and PbBr₂, which indicated the appearance of CsPb₂Br₅ in the as-prepared film.
6 Subsequent increase of temperature (300 °C) led to further grain size growth of
7 CsPb₂Br₅ with some grains reaching more than 5 μm (Figure 3b, c, Steps (1) and (2)).
8 CsPb₂Br₅ is a PL-inactive semiconductor material with a wide bandgap of ~2.9 eV,
9 indicating that it shows almost no photoluminescence under 365 nm irradiation as seen
10 in Figure S8.^{50, 51} However, the CsPb₂Br₅ phase is unstable at high temperature or
11 humidity conditions and induces the self-decomposition (inverse reaction, CsPb₂Br₅ →
12 CsPbBr₃ + PbBr₂ ↑) as discussed before.⁴⁰ Therefore, when the annealing temperature
13 increased further, starting from the grain boundaries, the large CsPb₂Br₅ grains
14 decomposed to several small CsPbBr₃ crystallites forming the CsPb₂Br₅@CsPbBr₃
15 intermediate phase.^{41, 51} The green color could be detected at the edge of the film under
16 365 nm irradiation in Figure S9 (~300 °C), which corroborates the formation of
17 CsPbBr₃. In this case (Figure 3c, step (3)), CsPb₂Br₅ served as extra heterogeneous
18 nucleation sites and also provided sufficient CsPbBr₃ that was originated from self-
19 decomposition. PbBr₂ has a lower melting temperature (357 °C) than CsBr (630 °C).⁴¹
20 Therefore, when the annealing temperature was close to this melting temperature (~350
21 °C), the excess PbBr₂ was melted/vaporized gradually, which would reduce the
22 concentration of PbBr₂ and promote decomposition of CsPb₂Br₅ in a controlled way. In

1 parallel, because of the volatility of PbBr_2 at a high temperature of $916\text{ }^\circ\text{C}$, PbBr_2 at
2 grain boundaries or edges began to evaporate slowly. Therefore, it would take a long
3 time to complete this process. According to the Ostwald ripening theory, the small
4 CsPbBr_3 particles generated during decomposition had a high surface energy and tend
5 to dissolve and grew together to become a large particle in a closed system to reduce
6 this energy (Figure 3c, step (3) and (4)).⁴² The largest size of CsPbBr_3 was $10\text{ }\mu\text{m}$
7 (Figure 3b). It was noted that the appearance of phase transition from CsPb_2Br_5 to
8 CsPbBr_3 with volatilization of PbBr_2 , instead of the direct forward reaction from CsBr
9 and PbBr_2 , could slow down the formation of CsPbBr_3 crystals at a high temperature.
10 As the treatment temperature rose to $400\text{ }^\circ\text{C}$, CsPbBr_3 with large grain sizes with high
11 crystallinity and some aligned grain boundaries could be detected in Figure 3b.
12 Correspondingly, the XRD data in Figure S10e revealed that the CsPbBr_3 crystal phase
13 is the major phase in the film after treatment at $400\text{ }^\circ\text{C}$, although there still existed a
14 few remnant peaks corresponding to the CsPb_2Br_5 phase or other intermediate states. In
15 addition, it was noticed that the relative intensity of CsPbBr_3 (100)/ (200) peaks was
16 much higher than that of CsPbBr_3 (110) peak in comparison with the CsPbBr_3 standard
17 PDF card (PDF # 54-0752), which indicated that the CsPbBr_3 crystals were grown
18 along the (100) direction. Enhanced photoluminescence with green color was observed
19 under 365 nm irradiation (Figure S9), which could be explained by the formation of
20 high quality of CsPbBr_3 crystals and consumption of the indirect bandgap material of
21 CsPb_2Br_5 , reducing the nonradiative recombination and improving the charge transport
22 process.⁵² As we continued to heat the sample to even higher temperatures, for example,

1 450 °C, the SEM image in Figure 3b presented a high crystallinity and aligned grains.
2 The corresponding XRD patterns in Figure S10f displayed two main peaks at 15.20°
3 and 30.66° indexed to the CsPbBr₃ (100) and (200) crystal planes, suggesting the high
4 crystallization of the CsPbBr₃ phase with an orientation along (100) and disappearance
5 of CsPb₂Br₅ (Figure 3c, step (5)). This preferred growth was possibly because the
6 consumption of 2D CsPb₂Br₅ provided enough space for the crystal rearrangement from
7 a 2D layer to a 3D cubic structure.⁴¹ Besides, CsPbBr₃ has a higher
8 decomposition/evaporation temperature (~580 °C) than PbBr₂.⁵³ The volatile PbBr₂ as
9 a byproduct further facilitated the proposed phase transformation process and no
10 external residues remained in the final products, which allowed us to achieve a high
11 quality CsPbBr₃ crystals. Upon subsequent extended annealing time (from 20 min to
12 1h at 450 °C, Figure 3b), the CsPbBr₃ grains continuously grew and PbBr₂ desorbed
13 preferentially from the edges of CsPbBr₃ grains leading to physical separation from the
14 adjacent grains. After one hour annealing at 450 °C, a long CsPbBr₃ MW were obtained.
15 Additionally, if the annealing time was prolonged to 1.5 h, some MWs break into
16 several disconnect MWs with short length as seen in Figure S11. To realize MWs with
17 long lengths, we also investigated the influence of the thickness of the precursor
18 CsPb₂Br₅ film on the length of CsPbBr₃ MWs, because the formation of MWs depended
19 on decomposition of CsPb₂Br₅. As we gradually increased the film thickness of
20 CsPb₂Br₅ from 200 nm to 1000 nm, both the length and the diameter of the CsPbBr₃
21 MWs increased (Figure S12-S13). This could be explained as the thicker layer was
22 beneficial for the growth of the compact perovskite film compared with the thin layer

1 growth, which resulted in the formation of perovskite grains with larger sizes during
 2 high temperature annealing.

3



4

5 **Figure 4.** (a) Schematic illustration showing a CsPbBr₃ MW photodetector. (b) I-V curves of the
 6 CsPbBr₃ MW photodetector under dark and light (400 nm, 30 μW cm⁻²) condition. SEM image of
 7 device is shown as the inset, and the scale bar is 40 μm. (c) Energy band diagram of device. (d) I-V
 8 curves and (f) I-t curves of the CsPbBr₃ MW photodetector under light with a wavelength of 400
 9 nm and different intensities. (e) Photocurrent and (g) responsivity/detectivity of the device as a
 10 function of irradiated intensities. (h) I-t curves of the CsPbBr₃ MW photodetector under different
 11 bias at 400 nm, 20.06 mW cm⁻². (i) Response time of the device during one-cycle.

12

13 A single CsPbBr₃ MW photodetector (PD) was fabricated as depicted in Figure 4a.

1 80 nm Au layer was deposited on the top surface of MW with a 100 μm spacing by a
2 shadow mask to construct a device (Figure 4b, inset). The well distribution of grain size
3 ranges from 3 μm to 11.5 μm (Figure S14) ensure light capture and carrier transport. In
4 addition, as mentioned above, despite the MW shows us a polycrystalline structure,
5 each grain is single crystal structure, which indicates lower trap defects in the grains.
6 Figure S15 shows the photoresponsivity spectrum of a CsPbBr₃ MW under a fixed bias
7 voltage of -5 V. As we can see, the device exhibits a high photoresponsivity in the region
8 between 350 and 600 nm, which is consistent with the absorption spectrum. Figures 4b
9 and S16 show the photocurrent-voltage (I-V) curves of the CsPbBr₃ MW PD under 400
10 nm light irradiation and dark conditions. A linear relationship suggested that an Ohmic-
11 contact between MW and electrode was formed, which would accelerate the carrier
12 transport under built-in electric field (Figure 4c). The photocurrent of the device
13 increased by more than one order of magnitude under 400 nm ($\sim 30 \mu\text{W cm}^{-2}$) irradiation
14 compared to dark current. The corresponding responsivity (R) and detectivity (D^*) are
15 extracted from the equation as follows:⁵⁴⁻⁵⁶

$$16 \quad R = \frac{I_{light} - I_{dark}}{PA} \quad (1)$$

$$17 \quad D^* = \frac{R\sqrt{AB}}{i_n} = R \sqrt{\frac{A}{2qI_{dark}}} \quad (2)$$

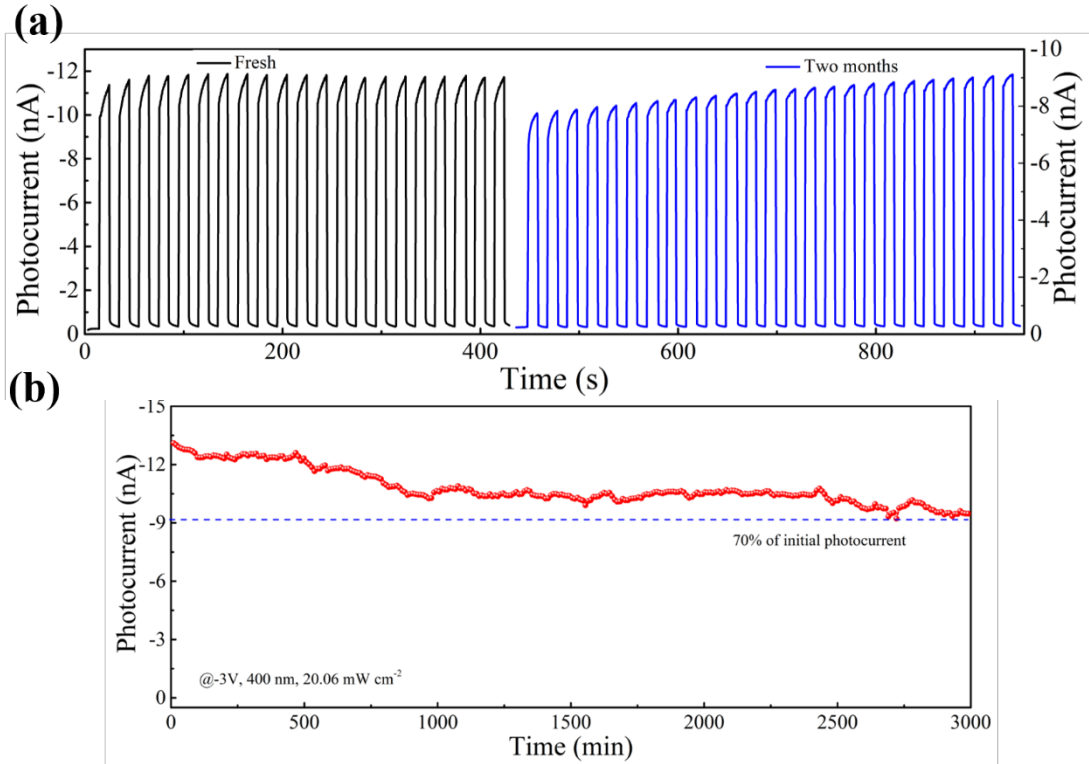
18 where I_{light} and I_{dark} are the photocurrent and dark current, respectively. P is the power
19 intensity; q is the elementary charge; A is the active area; B is the electrical bandwidth
20 of noise measurements; i_n is the noise current. Here, the MW is regarded as a
21 rectangular-shaped structure and the corresponding active area is estimated as
22

1 follows:²⁶ $A = a \times b$; a is the width of the nanowire (1 μm) and b is the length of the
2 channel (100 μm). The dark current and photocurrent were -6.35×10^{-11} A and
3 -9.66×10^{-10} A under a bias of -3 V, respectively. The lower dark current is ascribed to
4 i) High crystallinity of each grain shows low defects; ii) The existence of grain
5 boundaries (GBs) serving as energy barriers for carrier transport under a bias voltage
6 in dark condition, which could effectively suppress the dark current of CsPbBr₃ MW
7 PD.⁵⁷ On the other hand, under incident light irradiation, excessive photo-generated
8 holes could quickly migrate to GBs due to the p-type of perovskite materials, which
9 could effectively lower the energy barrier height and promote carrier transport under
10 the internal electric field.⁵⁷ It is assumed that the dark current is dominated by the shot
11 noise for estimating detectivity.⁵⁵ Therefore, the corresponding R and D^* are estimated
12 to be 6.44 A W^{-1} and 2.88×10^{12} Jones (Jones = $\text{cm Hz}^{1/2} \text{ W}^{-1}$), respectively. To further
13 evaluate the performance of the CsPbBr₃ MW PD, we conducted the photocurrent-
14 voltage tests under different light intensities from $30 \mu\text{W cm}^{-2}$ to 20.06 mW cm^{-2} under
15 400 nm illumination (Figure 4d). The photocurrent rose sharply as the light intensity
16 increased and the photocurrent of the device showed a strong dependence on the
17 irradiation intensity with a best fitting of $I = P^\theta$, where I and P are the photocurrent and
18 irradiation, respectively. θ is a proportionality constant related to recombination
19 processes of photo-generated carriers. By fitting the curve in Figure 4e, we extracted θ
20 = 0.81 for 400 nm irradiation that is close to the ideal value of 1, which suggested low
21 recombination in the device and exhibited a good linearity for light detection.⁵⁸ In
22 addition, the device also showed an excellent response characteristic measured by the

1 time-dependent photocurrent (I-t) at various intensities (from 0.03 mW cm⁻² to 20.06
2 mW cm⁻²) under a bias voltage of -3 V (Figure 4f). The photocurrent increased sharply
3 when the light was turned on and also dropped fast when the light was turned off.
4 Importantly, the CsPbBr₃ MW PD showed a stable and repeatable current under the
5 light ON/OFF process upon the increase in power intensity. It was worth noting that the
6 R and D* values, as seen in Figure 4g, decreased significantly with the enhancement of
7 irradiation power intensity. This reduction could be explained by the increased carrier
8 recombination by deep traps or surface defects when the device was under strong light
9 irradiation.⁵⁹ Besides the power intensity, the operational bias voltage also showed
10 influence on the device. We compared the I-t curves of the device under -0.5 V, -1 V,
11 -2 V and -3 V under 400 nm, ~20.06 mW cm⁻² irradiation. The corresponding
12 photocurrent improved monotonously from 1.02 nA to 11.8 nA and showed a stable
13 and repeatable states under light ON/OFF process (Figure 4h). Moreover, the response
14 speed is another key parameter for PDs, which reflects the sensitivity to the incident
15 light. As depicted in Figure 4i, the device showed a fast response time of 301/242 ms
16 under 400 nm irradiation.

17 The stability of inorganic perovskite devices is affected by several factors
18 including interface diffusion, phase transition to the non-perovskite structure, light
19 irradiation and thermal/humidity conditions. To investigate the storage stability, we
20 placed the device in air (RH ~ 45%) for over two months without any encapsulation.
21 As depicted in Figure 5a, the device exhibited excellent durability against humidity and
22 a long-term stable and repeatable performance under light ON/OFF cycles.

1 Furthermore, investigation of operational stability of devices under continuous light
2 illumination is also important considering practical applications. Song and coworkers
3 reported a CsPbBr₃ single crystal PD and found that the device are able to keep almost
4 the same photocurrent as the initial value (loss of only 2.1%) over 360 min.⁶⁰ Here, we
5 studied the operational stability of CsPbBr₃ MW PDs under 400 nm (20.06 mW cm⁻²)
6 illumination at bias voltage of -3 V. The photocurrent of the device remained ~70% of
7 the initial performance after 3000 min (Figure 5b), which shows enhanced stability than
8 the previous reports (Table 1). This performance improvement is originated from the
9 larger grain size, high crystallinity and bigger thickness. Decomposition of perovskite
10 materials usually starts at GBs after long term illumination, where water and oxygen
11 easily penetrate into the perovskites resulting in continuous decomposition/degradation
12 because of weaker chemical binding and ion migration at GBs in low crystallinity
13 perovskites.^{61, 62} Different from many GBs in the polycrystalline thin films, the less
14 GBs in the MWs can effectively alleviate the moisture attacks. Besides, the extra top
15 layer of the high-quality crystallites in the thicker grains (Height ~ 1.36 μm) of the
16 MWs naturally protect the inner crystallites from degradation in comparison of thin
17 height of single crystal NWs (Table 1).⁶¹



1

2 **Figure 5.** (a) I-t curve of the CsPbBr₃ MW photodetector taken shortly after fresh fabrication (black
3 curve) and after storage in air (RH ~ 45%) (blue curve) for over two months (400 nm, ~20.06 mW
4 cm⁻²). (b) Operational stability of the CsPbBr₃ MW photodetector under a bias of -3 V and light
5 illumination (400 nm, ~20.06 mW cm⁻²).

6

7 **3. CONCLUSION**

8

9 In summary, we demonstrated an inverse growth method to achieve ultralong
10 CsPbBr₃ MW (~510 μm) by controlling the decomposition of 2D CsPb₂Br₅ layer. This
11 inverse growth mechanism allowed us to control the length of nanowire by regulating
12 the thickness of CsPb₂Br₅ precursor layer. The high temperature procedure also ensured
13 us to obtain a high crystalline CsPbBr₃ MW with large grain size. An outstanding
14 performance of CsPbBr₃ MW photodetector was realized with an impressive
15 responsivity of 6.44 A W⁻¹ and detectivity of ~10¹² Jones. Importantly, the device
exhibited an excellent storage stability (RH~45%) for more than two months and

1 operational stability for over 3000 min. Overall, this inverse growth of CsPbBr₃ MW
2 displayed to be a simple, yet controllable and versatile technique to make highly
3 crystalline lead halide perovskite MWs and high performance photoelectronic devices.

4 5 **METHODS**

6 **CsPbBr₃ nanowires and photodetectors.** All chemicals were purchased from TCI
7 (99%). The p-type silicon (100) substrates with a 300 nm thermal oxide layer (SiO₂)
8 were purchased from Nova Electronic Materials. The substrates were cleaned by
9 acetone, ethyl alcohol and deionized water, respectively. First, the 304 nm CsBr and
10 696 nm PbBr₂ films were sequentially deposited on the substrates by thermal
11 evaporation with a rate of ~1 Å/s to achieve 1 μm CsPb₂Br₅ layer in the vacuum
12 chamber with a vacuum degree of ~10⁻³ Pa. The density and Z factor of CsBr were set
13 as 4.44 g cm⁻³ and 1.414, respectively. The corresponding parameters of PbBr₂ were
14 6.69 g cm⁻³ and 1.000, respectively. The thickness of films is well monitored by the
15 quartz crystal microbalance. To synthesize the CsPbBr₃ nanowires, the as-prepared
16 samples were annealed at 450 °C for 1 hour. Thermally evaporated 80 nm gold
17 deposited on the MWs was used as electrodes. The devices were defined by a metal
18 shadow mask with a width of 100 μm. The STEM samples were prepared by the same
19 procedure on the silicon dioxide grids (TedPella, 40 nm membrane thickness) with a
20 thickness of 30 nm precursor layer. The thickness of CsBr and PbBr₂ precursor layers
21 were 9 nm and 21 nm, respectively.

22
23 **Characterization.** Surface morphologies were investigated by a field emission
24 scanning electron microscopy (SEM, Helios NanoLab G3 UC) and a scanning
25 transmission electron microscopy (STEM, JEM-ARM 200F). A silicon dioxide grid
26 (purchased from TED PELLA, INC.) was employed in STEM. The crystal structure
27 was determined by X-ray diffraction (XRD, Bruker AXS GmbH, Karlsruhe, Germany)
28 equipped with Cu wavelength $\lambda = 1.54 \text{ \AA}$ from 10 to 40° two theta degrees. AFM

1 measurements were performed in tapping mode with a frequency of ~ 71 KHz using an
2 Asylum AFM (Asylum Co. MFP-3D-SA-DV-OQ). The scanning area of sample was
3 $5 \times 5 \mu\text{m}^2$. All the electrical tests were conducted in the Lakeshore probe station (CRX-
4 6.5K), the corresponding data were collected by a semiconductor parameter analyzer
5 system (Keithley 4200-SCS). Monochromatic light was produced by a portable solar
6 simulator combined with a 400 nm filter slice (THORLABS, FGK01S). The light
7 intensities were calibrated by a power meter (THORLABS). All the procedures were
8 performed in air (~45% relative humidity and 25 °C) without any encapsulation.

9

10 **ASSOCIATED CONTENT**

11 **Supporting Information**

12 The Supporting Information is available free of charge on the ACS Publications website
13 at DOI: 10.1021/acsami. XXXX.

14 EDS mapping and line scan, SEM, XRD and AFM images of CsPbBr₃ MWs; Optical,
15 XRD and SEM images of as-prepared CsPb₂Br₅ samples at different annealing
16 temperatures; Grain size distribution of CsPbBr₃ MWs; Responsivity spectrum and I-
17 V curve of CsPbBr₃ MWs photodetector.

18

19 **AUTHOR INFORMATION**

20 Corresponding Author

21 *E-mail: Yabing.Qi@OIST.jp

22

23 **Notes**

24 The authors declare no competing financial interest.

25

1 **ACKNOWLEDGEMENTS**

2 This work was supported by funding from the Energy Materials and Surface Sciences
3 Unit of the Okinawa Institute of Science and Technology Graduate University, the OIST
4 R&D Cluster Research Program, and the OIST Proof of Concept (POC) Program.

5

6 **REFERENCES**

- 7 (1) Tai, Q.; Tang, K.-C.; Yan, F. Recent Progress of Inorganic Perovskite Solar Cells.
8 *Energy Environ. Sci.* **2019**, *12*, 2375-2405.
- 9 (2) Park, K.; Lee, J. W.; Han, J. D.; Jang, D. M.; Jeong, S.; Park, J.; Song, J. K. Light-
10 Matter Interactions in Cesium Lead Halide Perovskite Nanowire Lasers. *J. Phys.*
11 *Chem. Lett.* **2016**, *7*, 3703-3710.
- 12 (3) Du, P.; Li, J.; Wang, L.; Liu, J.; Li, S., Liu, N.; Li, Y.; Zhang, M.; Gao, L.; Ma, Y.;
13 Tang, J. Vacuum-Deposited Blue Inorganic Perovskite Light-Emitting Diodes. *ACS*
14 *Appl. Mater. Interfaces* **2019**, *11*, 47083- 47090.
- 15 (4) Yang, L.; Tsai, W.-L.; Li, C.-S; Hsu, B.-W; Chen, C.-Y; Wu, C.-I; Lin, H.-W. High-
16 Quality Conformal Homogeneous All-Vacuum Deposited CsPbCl₃ Thin Films and
17 Their UV Photodiode Applications. *ACS Appl. Mater. Interfaces* **2019**, *11*, 47054-
18 47062.
- 19 (5) Zhao, L.; Gao, Y.; Su, M.; Shang, Q.; Liu, Z.; Li, Q.; Wei, Q.; Li, M.; Fu, L.; Zhong,
20 Y.; Shi, J.; Chen, J.; Zhao, Y.; Qiu, X.; Liu, X.; Tang, N.; Xing, G.; Wang, X.; Shen,
21 B.; Zhang, Q. Vapor-Phase Incommensurate Heteroepitaxy of Oriented Single-
22 Crystal CsPbBr₃ on GaN: Toward Integrated Optoelectronic Applications. *ACS*
23 *Nano* **2019**, *13*, 10085-10094.

-
- 1 (6) Chen, T.; Tong, G.; Xu, E.; Li, H.; Li, P.; Zhu, Z.; Tang, J.; Qi, Y. B.; Jiang, Y.
2 Accelerating Hole Extraction by Inserting 2D Ti₃C₂-MXene Interlayer to All
3 Inorganic Perovskite Solar Cells with Long-Term Stability. *J. Mater. Chem. A* **2019**,
4 7, 20597-20603.
- 5 (7) Zhang, X.; Chen, S.; Wang, X.; Pan, A. Controlled Synthesis and Photonics
6 Applications of Metal Halide Perovskite Nanowires. *Small Methods* **2019**,
7 3, 1800294.
- 8 (8) Gao, Y.; Zhao, L.; Shang, Q.; Zhong, Y.; Liu, Z.; Chen, J.; Zhang, Z.; Shi, J.; Du,
9 W.; Zhang, Y.; Chen, S.; Gao, P.; Liu, X.; Wang, X.; Zhang, Q. Ultrathin CsPbX₃
10 Nanowire Arrays with Strong Emission Anisotropy. *Adv. Mater.* **2018**, 30, 801805.
- 11 (9) Liu, J.; Song, K.; Shin, Y.; Liu, X.; Chen, J.; Yao, K. X.; Pan, J.; Yang, C.; Yin, J.;
12 Xu, L.-J.; Yang, H.; El-Zohry, A. M.; Xin, B.; Mitra, S.; Hedhili, M. N.; Roqan, I.
13 S.; Mohammed, O. F.; Han, Y.; Barkr, O. M. Light-Induced Self-Assembly of
14 Cubic CsPbBr₃ Perovskite Nanocrystals into Nanowires. *Chem. Mater* **2019**, 31,
15 6642-6649.
- 16 (10) Chen, G.; Feng, J.; Gao, H.; Zhao, Y.; Pi, Y.; Jiang, X.; Wu, Y.; Jiang, L. Stable α -
17 CsPbI₃ Perovskite Nanowire Arrays with Preferential Crystallographic Orientation
18 for Highly Sensitive Photodetectors. *Adv. Funct. Mater.* **2019**, 29, 1808741.
- 19 (11) Oksenberg, E.; Sanders, E.; Popovitz-Biro, R.; Houben, L.; Joselevich E. Surface-
20 Guided CsPbBr₃ Perovskite Nanowires on Flat and Faceted Sapphire with Size-
21 Dependent Photoluminescence and Fast Photoconductive Response. *Nano Lett.*
22 **2018**, 18, 424-433.

-
- 1 (12) Eaton, S. W.; Lai, M.; Gibson, N. A.; Wong, A. B.; Dou, L.; Ma, J.; Wang, L.-W.;
2 Leone, S. R.; Yang, P. Lasing in robust cesium lead halide perovskite nanowires.
3 *Proc. Natl. Acad. Sci. USA* **2016**, *113*, 1993-1998.
- 4 (13) Yang, T.; Zheng, Y.; Du, Z.; Liu, W.; Yang, Z.; Gao, F.; Wang, L.; Chou, K.-C.;
5 Hou, X.; Yang, W. Superior Photodetectors Based on All-Inorganic Perovskite
6 CsPbI₃ Nanorods with Ultrafast Response and High Stability. *ACS Nano* **2018**, *12*,
7 1611-1617.
- 8 (14) Cao, F.; Tian, W.; Wang, M.; Cao, H.; Li, L. Semitransparent, Flexible, and Self-
9 Powered Photodetectors Based on Ferroelectricity-Assisted Perovskite Nanowire
10 Arrays. *Adv. Funct. Mater.* **2019**, *29*, 1901280.
- 11 (15) Waleed, A.; Tavakoli, M. M.; Gu, L.; Wang, Z.; Zhang, D.; Manikandan, A.; Zhang,
12 Q.; Zhang, R.-J.; Chueh, Y.-L.; Fan, Z. Lead-Free Perovskite Nanowire Array
13 Photodetectors with Drastically Improved Stability in Nanoengineering Templates.
14 *Nano Lett.* **2017**, *17*, 523-530.
- 15 (16) Zhou, Q.; Park, J. G.; Nie, R.; Thokchom, A. K.; Ha, D.; Pan, J.; Pan, J.; Seok, S.
16 Il.; Kim, T. Nanochannel-Assisted Perovskite Nanowires: From Growth
17 Mechanisms to Photodetector Applications. *ACS Nano* **2018**, *12*, 8406-8414.
- 18 (17) Shoaib, M.; Zhang, X.; Wang, X.; Zhou, H.; Xu, T.; Wang, X.; Hu, X.; Liu, H.;
19 Fan, X.; Zheng, W.; Yang, T.; Yang, S.; Zhang, Q.; Zhu, X.; Sun, L.; Pan, A.
20 Directional Growth of Ultralong CsPbBr₃ Perovskite Nanowires for High-
21 Performance Photodetectors. *J. Am. Chem. Soc.* **2017**, *139*, 15592-15595.
- 22 (18) Deng, W.; Zhang, X.; Huang, L.; Xu, X.; Wang, L.; Wang, J.; Shang, Q.; Lee, S.-

-
- 1 T.; Jie, J. Aligned Single-Crystalline Perovskite Microwire Arrays for High-
2 Performance Flexible Image Sensors with Long-Term Stability. *Adv. Mater.* **2016**,
3 28, 2201-2208.
- 4 (19) Feng, J.; Yan, X.; Liu, Y.; Gao, H.; Wu, Y.; Su, B.; Jiang, L. Crystallographically
5 Aligned Perovskite Structures for High-Performance Polarization-Sensitive
6 Photodetectors. *Adv. Mater.* **2017**, 29, 1605993.
- 7 (20) Zhang, D.; Yang, Y.; Bekenstein, Y.; Yu, Y.; Gibson, N. A.; Wong, A. B.; Eaton, S.
8 W.; Kornienko, N.; Kong, Q.; Lai, M.; Alivisatos, A. P.; Leone, S. R.; Yang, P.
9 Synthesis of Composition Tunable and Highly Luminescent Cesium Lead Halide
10 Nanowires through Anion-Exchange Reactions. *J. Am. Chem. Soc.* **2016**, 138,
11 7236-7239.
- 12 (21) Tong, G.; Geng, X.; Yu, Y.; Yu, L.; Xu, J.; Jiang, Y.; Sheng, Y.; Chen, K. Rapid,
13 Stable and Self-Powered Perovskite Detectors via a Fast Chemical Vapor
14 Deposition Process. *RSC Adv.* **2017**, 7, 18224-18230.
- 15 (22) Zhou, H.; Yuan, S.; Wang, X.; Xu, T.; Wang, X.; Li, H.; Zheng, W.; Fan, P.; Li, Y.;
16 Sun, L.; Pan, A. Vapor Growth and Tunable Lasing of Band Gap Engineered
17 Cesium Lead Halide Perovskite Micro/Nanorods with Triangular Cross Section.
18 *ACS Nano* **2017**, 11, 1189-1195.
- 19 (23) Waleed, A.; Tavakoli, M. M.; Gu, L.; Hussain, S.; Zhang, D.; Poddar, S.; Wang, Z.;
20 Zhang, R.; Fan, Z. All Inorganic Cesium Lead Iodide Perovskite Nanowires with
21 Stabilized Cubic Phase at Room Temperature and Nanowire Array-Based
22 Photodetectors. *Nano Lett.* **2017**, 17, 4951-4957.

-
- 1 (24) Wang, Y.; Yasar, M.; Luo, Z.; Zhou, S.; Yu, Y.; Li, H.; Yang, R.; Wang, X.; Pan, A.;
2 Gan, L.; Zhai, T. Temperature Difference Triggering Controlled Growth of All-
3 Inorganic Perovskite Nanowire Arrays in Air. *Small* **2018**, *14*, 1803010.
- 4 (25) Creighton, J. R.; Ho, P. Introduction to Chemical Vapor Deposition (CVD). *ASM*
5 *International: Materials Park*, OH, **2001**, 1-22.
- 6 (26) Meng, Y.; Lan, C.; Li, F.; Yip, S.; Wei, R.; Kang, X.; Bu, X.; Dong, R.; Zhang, H.;
7 Ho, J. C. Direct Vapor-Liquid-Solid Synthesis of All-Inorganic Perovskite
8 Nanowires for High-Performance Electronics and Optoelectronics. *ACS Nano*
9 **2019**, *13*, 6060-6070.
- 10 (27) Pauzauskie, P. J.; Yang, P. Nanowire photonics. *Materials Today* **2006**, *9*, 36-45.
- 11 (28) Chen, J.; Fu, Y.; Samad, L.; Dang, L.; Zhao, Y.; Shen, S.; Guo, L.; Jin, S. Vapor-
12 Phase Epitaxial Growth of Aligned Nanowire Networks of Cesium Lead Halide
13 Perovskites (CsPbX_3 , X = Cl, Br, I). *Nano Lett.* **2017**, *17*, 460-466.
- 14 (29) Chen, J.; Luo, Z.; Fu, Y.; Wang, X.; Czech, K.; Shen, S.; Guo, L.; Wright, J. C.;
15 Pan, A.; Jin, S. Tin (IV)-Tolerant Vapor-Phase Growth and Photophysical
16 Properties of Aligned Cesium Tin Halide Perovskite (CsSnX_3 ; X=Br, I) Nanowires.
17 *ACS Energy Lett.* **2019**, *4*, 1045-1052.
- 18 (30) Meyers, J. K.; Kim, S.; Hill, D. J.; Cating, E. E. M.; Williams, L. J.; Kumbhar, A.;
19 McBride, J. R.; Papanikolas, J. M.; Cahoon, J. F. Self-Catalyzed Vapor-Liquid-
20 Solid Growth of Lead Halide Nanowires and Conversion to Hybrid Perovskites.
21 *Nano Lett.* **2017**, *17*, 7561-7568.
- 22 (31) Wang, Y.; Sun, X.; Shivanna, R.; Yang, Y.; Chen, Z.; Guo, Y.; Wang, G.-C.; Wertz,

-
- 1 E.; Deschler, F.; Cai, Z.; Zhou, H.; Lu, T.-M.; Shi, J. Photon Transport in One-
2 Dimensional Incommensurately Epitaxial CsPbX₃ Arrays. *Nano Lett.* **2016**, *16*,
3 7974-7981.
- 4 (32) Yang, Z.; Lu, J.; ZhuGe, M.; Cheng, Y.; Hu, J.; Li, F.; Qiao, S.; Zhang, Y.; Hu, G.;
5 Yang, Q.; Peng, D.; Liu, K.; Pan, C. Controllable Growth of Aligned
6 Monocrystalline CsPbBr₃ Microwire Arrays for Piezoelectric-Induced Dynamic
7 Modulation of Single-Mode Lasing. *Adv. Mater.* **2019**, *31*, 1900647.
- 8 (33) Zhou, Y.; Luo, J.; Zhao, Y.; Ge, C.; Wang, C.; Gao, L.; Zhang, C.; Hu, M.; Niu, G.;
9 Tang, J. Flexible Linearly Polarized Photodetectors Based on All-Inorganic
10 Perovskite CsPbI₃ Nanowires. *Adv. Optical Mater.* **2018**, *6*, 1800679.
- 11 (34) Tong, G.; Chen, T.; Li, H.; Song, W.; Chang, Y.; Liu, J.; Yu, L.; Xu, J.; Qi, Y.B.;
12 Jiang, Y. High Efficient Hole Extraction and Stable All-Bromide Inorganic
13 Perovskite Solar Cells via Derivative-Phase Gradient Bandgap Architecture. *Sol.*
14 *RRL* **2019**, *5*, 1900030.
- 15 (35) Chen, J.; Morrow, D. J.; Fu, Y.; Zheng, W.; Zhao, Y.; Dang, L.; Stolt, M. J.; Kohler,
16 D. D.; Wang, X.; Czech, K. J.; Hautzinger, M. P.; Shen, S.; Guo, L.; Pan, A.; Wright,
17 J. C.; Jin, S. Single-Crystal Thin Films of Cesium Lead Bromide Perovskite
18 Epitaxially Grown on Metal Oxide Perovskite (SrTiO₃). *J. Am. Chem. Soc.* **2017**,
19 *139*, 13525-13532.
- 20 (36) Kuo, T.-J.; Lin, C.-N.; Kuo, C.-L.; Huang, M. H. Growth of Ultralong ZnO
21 Nanowires on Silicon Substrates by Vapor Transport and Their Use as Recyclable
22 Photocatalysts. *Chem. Mater* **2007**, *19*, 5143-5147.

-
- 1 (37) Tong, G.; Li, H.; Zhu, Z.; Zhang, Y.; Yu, L.; Xu, J.; Jiang, Y. Enhancing Hybrid
2 Perovskite Detectability in the Deep Ultraviolet Region with Down-Conversion
3 Dual-Phase (CsPbBr₃-Cs₄PbBr₆) Films. *J. Phys. Chem. Lett.* **2018**, *9*, 1592-1599.
- 4 (38) Tong, G.; Li, H.; Li, G.; Zhang, T.; Li, C.; Yu, L.; Xu, J.; Jiang, Y.; Shi, Y.; Chen,
5 K. Mixed Cation Perovskite Solar Cells by Stack-Sequence Chemical Vapor
6 Deposition with Self-Passivation and Gradient Absorption Layer. *Nano Energy*
7 **2018**, *48*, 536-542.
- 8 (39) Tong, G.; Li, H.; Li, D.; Zhu, Z.; Xu, E.; Li, G.; Yu, L.; Xu, J.; Jiang, Y. Dual-Phase
9 CsPbBr₃-CsPb₂Br₅ Perovskite Thin Films via Vapor Deposition for High-
10 Performance Rigid and Flexible Photodetectors. *Small* **2018**, *14*, 1702523.
- 11 (40) Palazon, F.; Dogan, S.; Marras, S.; Locardi, F.; Nelli, I.; Rastogi, P.; Ferretti, M.;
12 Prato, M.; Krahne, R.; Manna, L. From CsPbBr₃ Nano-Inks to Sintered CsPbBr₃-
13 CsPb₂Br₅ Films via Thermal Annealing: Implications on Optoelectronic Properties.
14 *J. Phys. Chem. C* **2017**, *121*, 11956-11961.
- 15 (41) Tong, G.; Chen, T.; Li, H.; Qiu, L.; Liu, Z.; Dang, Y.; Song, W.; Ono, L. K.; Jiang,
16 Y.; Qi, Y. B. Phase Transition Induced Recrystallization and Low Surface Potential
17 Barrier Leading to 10.91%-Efficient CsPbBr₃ Perovskite Solar Cells. *Nano Energy*
18 **2019**, *65*, 104015.
- 19 (42) Yang, M.; Zhang, T.; Schulz, P.; Li, Z.; Li, G.; Kim, D. H.; Guo, N.; Berry, J. J.;
20 Zhu, K.; Zhao, Y. Facile Fabrication of Large-Grain CH₃NH₃PbI_{3-x}Br_x Films for
21 High-Efficiency Solar Cells via CH₃NH₃Br-Selective Ostwald Ripening. *Nat.*
22 *Commun.* **2016**, *7*, 12305.

-
- 1 (43) Baldan, A. Review Progress in Ostwald Ripening Theories and Their Applications
2 to Nickel-Base Superalloys Part I: Ostwald Ripening Theories. *J. Mater. Sci.* **2002**,
3 37, 2171-2202.
- 4 (44) Lai, M.; Kong, Q.; Bischak, C. G.; Yu, Y.; Dou, L.; Eaton, S. W.; Ginsberg, N. S.;
5 Yang, P. Structural, Optical, and Electrical Properties of Phase-Controlled Cesium
6 Lead Iodide Nanowires. *Nano Research* **2017**, 10, 1107-1114.
- 7 (45) Tang, X.; Zu, Z.; Shao, H.; Hu, W.; Zhou, M.; Deng, M.; Chen, W.; Zang, Z.; Zhu,
8 T.; Xue, J. All-Inorganic Perovskite CsPb(Br/I)₃ Nanorods for Optoelectronic
9 Application. *Nanoscale* **2016**, 8, 15158-15161.
- 10 (46) Pradhan, B.; Kumar, G. S.; Sain, S.; Dalui, A.; Ghorai, U. K.; Pradhan, S. K.;
11 Acharya, S. Size Tunable Cesium Antimony Chloride Perovskite Nanowires and
12 Nanorods. *Chem. Mater* **2018**, 30, 2135-2142.
- 13 (47) Song, J.; Xu, L.; Li, J.; Xue, J.; Dong, Y.; Li, X.; Zeng, H. Monolayer and Few-
14 Layer All-Inorganic Perovskites as a New Family of Two-Dimensional
15 Semiconductors for Printable Optoelectronic Devices. *Adv. Mater.* **2016**, 28, 4861-
16 4869.
- 17 (48) Zhang, Z.; Li, C.; Lu, Y.; Tong, X.; Liang, F.; Zhao, X.; Wu, D.; Xie, C.; Luo, L.
18 Sensitive Deep Ultraviolet Photodetector and Image Sensor Composed of
19 Inorganic Lead-Free Cs₃Cu₂I₅ Perovskite with Wide Bandgap. *J. Phys. Chem. Lett.*
20 **2019**, 10, 5343-5350.
- 21 (49) Li, H.; Tong, G.; Chen, T.; Zhu, H.; Li, G.; Chang, Y.; Wang, L.; Jiang, Y. Interface
22 Engineering using a Perovskite Derivative Phase for Efficient and Stable CsPbBr₃

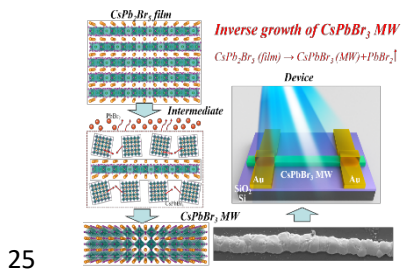
-
- 1 Solar Cells. *J. Mater. Chem. A* **2018**, *6*, 14255-14261.
- 2 (50) Li, G.; Wang, H.; Zhu, Z.; Chang, Y.; Zhang, T.; Song, Z.; Jiang, Y. Shape and
3 Phase Evolution from CsPbBr₃ Perovskite Nanocubes to Tetragonal CsPb₂Br₅
4 Nanosheets with an Indirect Bandgap. *Chem. Commun.* **2016**, *52*, 11296-11299.
- 5 (51) Wang, C.; Wang, Y.; Su, X.; Hadjiev, V. G.; Dai, S.; Qin, Z.; Benavides, H. A. C.;
6 Ni, Y.; Li, Q.; Jian, J.; Alam, Md. K.; Wang, H.; Hernandez, F. C. R.; Yao, Y.; Chen,
7 S.; Yu, Q.; Feng, G.; Wang, Z.; Bao, J. Extrinsic Green Photoluminescence from
8 the Edges of 2D Cesium Lead Halides. *Adv. Mater.* **2019**, *31*, 1902492.
- 9 (52) Wang, Y.; Li, W.; Zhang, T.; Li, D.; Kan, M.; Wang, X.; Liu, X.; Wang, T.; Zhao,
10 Y.; Highly Efficient (110) Orientated FA-MA Mixed Cation Perovskite Solar Cells
11 via Functionalized Carbon Nanotube and Methylammonium Chloride Additive.
12 *Small Methods* **2019**, 1900511.
- 13 (53) Kulbak, M.; Gupta, S.; Kedem, N.; Levine, I.; Bendikov, T.; Hodes, G.; Cahen, D.
14 Cesium Enhances Long-Term Stability of Lead Bromide Perovskite-Based Solar
15 Cells. *J. Phys. Chem. Lett.* **2016**, *7*, 167-172.
- 16 (54) Wu, D.; Guo, J.; Du, J.; Xia, C.; Zeng, L.; Tian, Y.; Shi, Z.; Tian, Y.; Li, X. J.;
17 Tsang, Y. H.; Jie, J. Highly Polarization-Sensitive, Broadband, Self-Powered
18 Photodetector Based on Graphene/PdSe₂/Germanium Heterojunction. *ACS Nano*
19 **2019**, *13*, 9907-9917.
- 20 (55) Wang, L.; Jie, J.; Shao, Z.; Zhang, Q.; Zhang, X.; Wang, Y.; Sun, Z.; Lee, S.-T.
21 MoS₂/Si Heterojunction with Vertically Standing Layered Structure for Ultrafast,
22 High-Detectivity, Self-Driven Visible-Near Infrared Photodetectors. *Adv. Funct.*

-
- 1 *Mater.* **2015**, *25*, 2910-2919.
- 2 (56) Miao, J.; Zhang, F. Recent Progress on Photomultiplication Type Organic
3 Photodetectors. *Laser Photonics Rev.* **2019**, *13*, 1800204.
- 4 (57) Liu, X.; Gu, L.; Zhang, Q.; Wu, J.; Long, Y.; Fan, Z. All-Printable Band-Edge
5 Modulated ZnO Nanowire Photodetectors with Ultra-High Detectivity. *Nat.*
6 *Commun.* **2014**, *5* 4007.
- 7 (58) Li, X.; Zhu, M.; Du, M.; Lv, Z.; Zhang, L.; Li, Y.; Yang, Y.; Yang, T.; Li, X.; Wang,
8 K.; Zhu, H.; Fang, Y. High Detectivity Graphene-Silicon Heterojunction
9 Photodetector. *Small* **2016**, *12*, 595-601.
- 10 (59) Zeng, L.-H.; Chen, Q.-M.; Zhang, Z.-X.; Wu, D.; Yuan, H.; Li, Y.-Y.; Qarony, W.;
11 Lau, S. P.; Luo, L.-B.; Tsang, Y. H. Multilayered PdSe₂/Perovskite Schottky
12 Junction for Fast, Self-Powered, Polarization-Sensitive, Broadband
13 Photodetectors, and Image Sensor Application. *Adv. Sci.* **2019**, 1901134.
- 14 (60) Song, J.; Cui, Q.; Li, J.; Xu, J.; Wang, Y.; Xu, L.; Xue, J.; Dong, Y.; Tian, T.; Sun,
15 H.; Zeng, H. Ultralarge All-Inorganic Perovskite Bulk Single Crystal for High-
16 Performance Visible-Infrared Dual-Modal Photodetectors. *Adv. Optical Mater.*
17 **2017**, *5*, 1700157.
- 18 (61) Liu, Z.; Qiu, L.; Juarez-Perez, M, J.; Hawash, Z.; Kim, T.; Jiang, Y.; Wu, Z.; Raga,
19 S. R.; Ono, L. K.; Liu, S. F.; Qi, Y. B. Gas-Solid Reaction Based over One-
20 Micrometer Thick Stable Perovskite Films for Efficient Solar Cells and Modules.
21 *Nat. Commun.* **2018**, *9*, 3880.
- 22 (62) Chen, Z.; Dong, Q.; Liu, Y.; Bao, C.; Fang, Y.; Lin, Y.; Tang, S.; Wang, Q.; Xiao,

1 X.; Bai, Y.; Deng, Y.; Huang, J. Thin Single Crystal Perovskite Solar Cells to
2 Harvest Below-Bandgap Light Absorption. *Nat. Commun.* **2017**, *8*, 1890.

3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24

TOC graph



25