## Supporting Information

Saturated Vapor-assisted Growth of Single-Crystalline Organic-Inorganic Hybrid Perovskite Nanowires for High-performance Photodetectors with Robust Stability

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Institute of Functional Nano & Soft Materials (FUNSOM), Collaborative Innovation Center of Suzhou Nano Science and Technology (NANO-CIC), Jiangsu Key Laboratory for Carbon-Based Functional Materials & Devices, Soochow University, Suzhou Jiangsu 215123, P. R. China. **Table S1:** Comparison of the preparation methods, crystal qualities, growth atmospheres, and morphologies of the perovskite NWs in this work with these in literatures.

Materials	Methods	Growth atmospheres	Grain boundaries/ surface defects	Morphologies	Ref
CH3NH3PbI3 NW	One-step	Organic solvent vapor	Few	5 <u>00 nm</u>	Our work
CH3NH3PbI3 NW	Template-as sisted one-step method	Organic solvent vapor	Few	0.2 µm	1
CH3NH3PbI3 NW	Two-step	CH <sub>3</sub> NH <sub>3</sub> I vapor	Many	300 nm	2
CH3NH3PbI3 NW	One-step	Air	Many		3
CH3NH3PbI3 NW	One-step	Air	Many	b	4
CH3NH3PbI3 NW	Two-step	Solution	Few	500 nm	5
CH <sub>3</sub> NH <sub>3</sub> PbBr <sub>3</sub> porous NW	Two-step	Organic solvent	Many	200 nm	6

Concentration (mol/L)	0.0025	0.005	0.0075	0.01
Average size (nm)	500	580	910	1100

Table S2. As-grown CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub> NWs with different concentrations.



Figure S1. In situ observation of the CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub> NWs growth process.



**Figure S2**. (a) Cross-polarized optical micrograph of the CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub> NWs grown in ambient air. (b) SEM image of the CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub> NWs grown in ambient air. (c) Magnified SEM image of the CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub> NW grown in ambient air. (d) AFM image of the CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub> NW grown in ambient air.



Figure S3. (a, b) SEM images of the  $CH_3NH_3PbI_3$  NWs grown in dry box (humidity ~15%).



Figure S4. (a, b) SEM images of the  $CH_3NH_3PbI_3$  NWs grown in  $N_2$  glove box.



Figure S5. (a, b) SEM images of the CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub> NWs grown in ethanol vapor atmosphere.



**Figure S6**. Optical and SEM images of as-grown CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub> NWs with different concentrations: (a, b) 0.0025 mol/L, (c, d) 0.005 mol/L, (e, f) 0.0075 mol/L, and (g, h) 0.01 mol/L.



Figure S7. Dark/photo current of the photodetector based on  $CH_3NH_3PbI_3$  NW synthesized under saturated vapor and in ambient air, respectively. The light intensity was fixed at 60  $\mu$ W/cm<sup>2</sup>.



**Figure S8.** *I-V* curves of the photodetector measured in the dark and under illumination with a different wavelength. The light intensity was fixed at  $60 \,\mu\text{W/cm}^2$ .



**Figure S9.** Time-resolved photoresponse of the CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub> NW-based photodetector. The 600 nm-light source was turned on/off by a signal generator to generate pulsed light.



**Figure S10.** (a-d) Histograms of *R*,  $D^*$ ,  $t_r$  and  $t_d$  measured from 50 devices under the same conditions (460 nm, 60  $\mu$ W/cm<sup>2</sup>).



Figure S11. Band alignment between grains and GB.

Photoresponsivity of the photodetector is calculated by the following equation:

$$R_{\lambda} = \frac{J_{ph} - J_d}{L_{light}} = \frac{I_{light} - I_{dark}}{A \times L_{light}}$$

where  $I_{\text{light}}$  is the photo-generated current under light illumination,  $I_{dark}$  is the current in dark, A is the active area ( $A = W \times L$ , where W is the width of the NW, L is the channel length of the device) of the photodetector, and  $L_{\text{light}}$  is the light intensity. In this case,  $I_{\text{light}}$  and  $I_{dark}$  for the single CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub> NW at light wavelength of 460 nm were measured to be  $3.37 \times 10^{-9}$  and  $1.57 \times 10^{-11}$  A, respectively. Active area for the CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub> NW-based device was  $\sim 1.215 \times 10^{-7}$  cm<sup>2</sup> (W is 0.45 µm and L is 27 µm). The light intensity for the incident light was fixed at 60 µW/cm<sup>2</sup>, which was calibrated with a silicon photodiode (Newport, 918D-UV-OD3R). Thus the highest Rvalue was estimated to be 460 A/W at an incident light wavelength of 460 nm.

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