## Supplementary information

## Solvent engineering for high conversion yields of layered raw materials into large-scale freestanding hybrid perovskite nanowires

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**Figure S1. Crystal phase characterizations of PbI<sub>2</sub>, INT-1, INT-2 and PV-1 nanowires.** The XRD patterns of the PbI<sub>2</sub>, INT-1, INT-2 and PV-1 for showing the details of low-angle diffraction peaks.

The low-angle diffraction peaks of INT-1 indicate that the white precipitate was the intermediate phase with longer interplanar distances than that of PbI<sub>2</sub> phase. After rinsing treatment of IPA, the peaks of the PbI<sub>2</sub> crystal phase come under observation. After heating, the low-angle diffraction peaks disappear and new peaks of perovskite phase are observed, indicating that the perovskite CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub> appeared. Unfortunately, the pure phase of the perovskite materials cannot be obtained.



Figure S2. Morphological characterizations of the products prepared with one-step progress. (a) SEM image of the INT-1 nanowires. Scale bar is 4  $\mu$ m. (b) SEM image of the INT-2 nanowires. Scale bar is 4  $\mu$ m. (c) SEM image of the PV-1 nanowires. Scale bar is 2.5  $\mu$ m.

These products are all 1D nanowire-shaped structures. The surface morphology changes from smooth to rough, finally, the sample surface became porous.



**Figure S3. Crystal phase characterizations of the intermediate phase prepared using the poor solvents with different polarity.** XRD patterns of the intermediate phase prepared using H<sub>2</sub>O, IPA and Toluene as poor solvents.

The XRD patterns of the intermediate phases have the similar low-angle diffraction peaks (in red dashed circles) regardless of poor solvents, which suggest that the introduction of poor solvent could not have effects on the crystal phases of the final intermediate phase PbI<sub>2</sub>-DMF.



**Figure S4.** SEM images of the intermediate phase nanowires using H<sub>2</sub>O, IPA, toluene as poor solvent under the presence of good solvent DMSO.

The obtained products were all nanowires with high density, smooth outer surfaces and sharp edges, regardless of H<sub>2</sub>O, IPA or toluene.



Figure S5. The photograph of the suction filtration device. The suction filtration device was consisted of the suction flask, vacuum pump, sintered discs, clamp and aspirator. The microfiltration membrane (Shanghai Xingya purifying equipment factory,  $0.22 \mu m$ ) was used for separation of the as-prepared products.



**Figure S6. Surface morphological characterizations of INT-3 and INT-4 nanowires.** SEM images of a single INT-3 nanowires and a single INT-4 nanowires. Scale bars are 3 μm.

The INT-3 nanowires have smooth outer surfaces and sharp edges. When INT-3 nanowires were rinsed with IPA, INT-4 nanowires with the rough surface were obtained, which preserved the 1D morphology of INT-3 nanowires.



**Figure S7. Crystal phase evolution from INT-3 nanowires to INT-4 nanowires by rinsing.** XRD patterns of PbI<sub>2</sub> powders, INT-3 nanowires and INT-4 nanowires.

The XRD patterns show that the INT-4 nanowires obtained from INT-3 with rinsing are in good agreement with the pattern of  $PbI_2$  powders, indicating the formation of the pure  $PbI_2$  nanowires with rinsing.



**Figure S8. Crystal phase characterizations of MAPbI**<sub>3</sub> **nanowires.** XRD patterns of PV-2 and PV-3 nanowires.

The XRD peaks of PV-2 and PV-3 nanowires can be perfectly indexed to the tetragonal phase of MAPbI<sub>3</sub> (a=b=8.896 Å, c=12.707 Å, space group of *I4/mcm*). No extra diffraction peaks emerged, implying that pure MAPbI<sub>3</sub> nanowires were successfully obtained with this synthetic strategy.



Figure S9. The EDS spectrum of the PV-2 nanowires.



**Figure S10.** UV-vis absorption (dark line) and photoluminescence spectrum (red line) of the PV-2 nanowires.

The PV-2 nanowires shows typical UV-vis absorption along with a PL peak at 797 nm, which is in agreement with characteristic features of the CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub> materials.



**Figure S11. Surface morphological characterizations of PV-2 nanowires.** SEM images of a single PV-3 nanowire. Scale bar is 3 µm.

After placing the INT-3 nanowires into a MAI/IPA solution, PV-2 with preserving the 1D morphology of INT-3 nanowires were obtained, where surface morphology did not undergo notable changes during the conversion process.



**Figure S12. Morphological evolution of PV-3 nanowires synthesized using INT-4 nanowires with different reaction times.** (a-f) SEM images of the as-grown PV-3 morphological evolution with a reaction time of 5 min, 30 min, 1h, 2h, 4h and 6h.

The as-grown morphology evolution clearly indicated that the small nanomaterials formed and continued to grow on the surface of the nanowire with increase of reaction time. At a growth time of 5 min, the morphology of as-converted MAPbI<sub>3</sub> exhibited many crystalline particles-like grains with flat facets. At 1 h, we can clearly see nanorods, nanoplates and nanocubes have grown from the surface. The size of these MAPbI<sub>3</sub> nanomaterials continues to increase as the reaction time increases.



**Figure S13. Crystal phase characterizations of PV-3 nanowires with different reaction times.** XRD patterns of PV-3 nanowires with a reaction time of 1 min, 5 min, 10 min, 30 min, 1h, 2h, 4h and 6h.

The gradual disappearance of the diffraction peaks associated with  $PbI_2$  over at least 1 h indicates the  $PbI_2$  nanowire was slowly converted to MAPbI\_3 nanowires via the solventgrowth process. In addition, the sharpening and splitting of the diffraction peaks (14.08°, 28.48°) as the increase of reaction time indicate a significant enhancement of the crystallinity of the MAPbI\_3 phase.



**Figure S14. Crystal phase characterizations of other perovskite-based materials.** XRD patterns of PV-4, PV-5, PV-6 and PV-7 nanowires.

The XRD peaks of PV-4 and PV-5 nanowires can be perfectly indexed to the cubic phase of MAPbBr<sub>3</sub> (a=5.948 Å, space group of *Pm-3m*). The XRD peaks of PV-5 and PV-6 nanowires can be perfectly indexed to the orthorhombic phase of CsPbBr<sub>3</sub> (a=8.2440 Å, b=11.7351 Å, c=8.1982 Å, space group of *Pnma*). No extra diffraction peaks emerged, implying that pure perovskite nanowires were successfully obtained with this synthetic strategy.