Electronic Supplementary Information

## A 3D Hybrid Nanowire/Microcuboid Optoelectronic Electrode for Maximised Light Harvesting in Perovskite Solar Cells<sup>†</sup>

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**Fig. S1** (a) XPS survey spectra of the as-prepared TNW. Fitted XPS result of (b) Ti2p and (c) O1s in TNW.



**Fig. S2** Digital photos of the bare FTO and FTO/TNW electrodes (TNW-PTO-0.100g). The TNW-PTO-0.100g electrode displayed an enhanced optical transparency.



**Fig. S3** Diffused reflectance spectra of the bare FTO glass and different FTO/TNW electrodes prepared using different amount of PTO precursor (as indicated).



**Fig. S4** Top-view SEM images of CMC capping layer deposited on top of (a) TNW-PTO-0.075g and (b) TNW-PTO-0.125g.



**Fig. S5** Cross-sectional SEM images of the FTO/TNW/CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub> electrodes constructed using (a) TNW-PTO-0.050g, (b) TNW-PTO-0.075g, (c) TNW-PTO-0.100g and (d) TNW-PTO-0.125g thin films. Thickness of the CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub>-infiltrated TNW layers is indicated using white dashed lines.

**Table S1** Morphological parameters of the FTO/TNW/  $CH_3NH_3PbI_3$  electrodes in this study.  $L_1$  is the thickness of the perovskite-infiltrated TNW layer.  $L_2$  is the thickness of the  $CH_3NH_3PbI_3$  capping layer and D is the grain size of the  $CH_3NH_3PbI_3$  cuboids in the capping layer.

| TiO <sub>2</sub> Film | $L_1$ (nm) | $L_2$ (nm)   | <i>D</i> (nm) |
|-----------------------|------------|--------------|---------------|
| TNW-PTO-0.050g        | 120±5      | 400±10       | 160-420       |
| TNW-PTO-0.075g        | 220±5      | 530±10       | 360-630       |
| TNW-PTO-0.100g        | 620±5      | $600 \pm 10$ | 520-1050      |
| TNW-PTO-0.125g        | $800\pm5$  | $780 \pm 10$ | 630-1800      |
|                       |            |              |               |



**Fig. S6** Cross-sectional SEM image of a complete PSC based on TNW-PTO-0.100g sample showing the good infiltration of perovskite into the pores of nanowires.



Fig. S7 UV-Vis absorbance spectra of the different TNW/CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub> films.



Fig. S8 J-V curves of the PCSs based on different TNW electrodes measured under dark.



**Fig. S9** Top-view SEM images of the perovskite capping layers prepared with second-step MAI dipping in (a) IPA; (b) IPA:CBZ = 2:1 and (c) IPA:CBZ = 1:1, respectively;



**Fig. S10** Photos showing comparison of the perovskite film formation dynamics in MAI/IPA and MAI/IPA/CBZ (IPA:CBZ=2:1) dipping/conversion step.



**Fig. S11** XRD patterns of the  $CH_3NH_3PbI_3$  films fabricated via a second MAI intercalation step using IPA, IPA:CBZ = 2:1 and IPA:CBZ = 1:1 solution as solvent, respectively.

**Table S2.** Photovoltaic parameters of the PSCs based on FTO/TNW-PTO-0.100g/CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub> electrodes fabricated via a second MAI intercalation step using IPA, IPA:CBZ = 2:1 and IPA:CBZ = 1:1 solution as solvent, respectively. These data were recorded under one sun illumination (AM 1.5G, 100 mW cm<sup>-2</sup>).

| Solvent composition | $J_{\rm sc}$ (mA cm <sup>-2</sup> ) | V <sub>oc</sub><br>(V) | η<br>(%) | FF   |
|---------------------|-------------------------------------|------------------------|----------|------|
| IPA                 | 21.8                                | 1.00                   | 15.3     | 0.70 |
| IPA:CBZ=2:1         | 23.0                                | 1.04                   | 17.7     | 0.74 |
| IPA:CBZ=1:1         | 22.5                                | 1.02                   | 16.5     | 0.72 |



**Fig. S12** Schematic illustration of step-by-step fabrication procedure for the perovskite film consisting of large grains with improved surface coverage.



**Fig. S13** *J-V* curves of the champion PSC device measured by forward scan (SC-FB, purple line) and reverse scan (FB-SC, blue line) with a scan rate of 0.1 V s<sup>-1</sup> under AM 1.5 G simulated sun light illumination. This solar cell was constructed using TNW-PTO-0.100g ETL and optimized  $CH_3NH_3PbI_3$  cuboids layers fabricated with three-step sequential deposition method.



Fig. S14 Light intensity dependent of *J*-*V* curves for the champion device.



Fig. S15 PL and TRPL measurement of TNW/CMC and TNP/CMC films.



**Fig. S16** PCE stability as a function of storage time in ambient conditions for nonencapsulated PSC based on the TNW/CMC hybrid electrode.