

Electronic Supplementary Information (ESI) for

Efficient fiber-shaped perovskite photovoltaics using silver nanowires as top electrode

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Experimental

Synthesis of CH₃NH₃I (MAI)

CH₃NH₃I (MAI) was synthesized according to previous report. 10 mL of hydroiodic acid (57 wt% in water, Aldrich) was added to 24 mL of methylamine (40% in methanol, TCI) in a 250 mL round bottomed flask at 0 °C, which reaction was kept with stirring for 2 h. The solvent was removed at 50 in rotary evaporator and the white precipitate was collected. The product of MAI was dissolved in ethanol, recrystallized by diethyl ether, and this procedure was repeated twice. The final product was obtained by further drying at 60 °C in a vacuum oven for 24 h.

Polishing

Ti wires (Sigma-Aldrich, 127 μm in diameter and purity of 99.99%) were ultrasonic treated in acetone, ethanol and isopropanol and then dried in air. Subsequently, the cleaned Ti wire was anodized in a mixed electrolyte of Ethanol (70ml), isopropanol (30ml), ZnCl₂ 25g and AlCl₃ (4g) to polish the surface. The electropolishing was carried out at 60V and 25°C for 20s by using a Pt gauze as counter electrode.

Anodization

The dimple compact layer structure onto Ti-wire was prepared by electrochemically anodizing Ti wire in a two-electrode electrochemical configuration with a Ti wire as working electrode and a Pt gauze as counter electrode. Firstly, Ti wires were cleaned by ultrasonication in acetone, ethanol and propanol in order and then dried in air before use. The cleaned Ti wire was anodized in a 80 mL ethylene glycol (EG) solution containing 0.3 wt% NH₄F and 4wt% deionized H₂O at 40V, 60V for particular time and bath temperature of 0, 5 and 15°C. The obtained TNT film was removed by ultrasonication for 10 minutes, leaving

behind ordered dimple structure. In order to completely exfoliate TNT, hydrogen peroxide (H_2O_2 , 37% in water) was added into deionized water up to 30% in volume ratio.

Solar cell fabrication

The modified Ti wire was sequentially washed with ethanol and distilled water. Ti wire was immersed in diluted TiO_2 nanoparticle solution for making mesoporous TiO_2 film, which was moved to muffle furnace and annealed at 450 °C for 30 min. After cooled to room temperature, resulting Ti wire was immersed in 40mM TiCl_4 aqueous solution for 30 min at 70 °C in oven. Followed by washing with distilled water and heating at 450 °C for 30min on hot plate. 1M $\text{CH}_3\text{NH}_3\text{PbI}_3$ solution (DMF : NMP (1:1, v/v)) was prepared from PbI_2 (Aldrich) and synthesized MAI powders. $\text{CH}_3\text{NH}_3\text{PbI}_3$ film was deposited by simple dip coating to above solution for 10 s. For making uniform perovskite films, after dipping $\text{CH}_3\text{NH}_3\text{PbI}_3$ solution for 10 s and directly moved to prepared toluene bottle and immersed in solution. Each of the prepared films was kept on hot plate at 100 °C for 30 min. Following the $\text{CH}_3\text{NH}_3\text{PbI}_3$ film deposition, the hole transporting material (HTM) was coated by dipping into prepared HTM solution (72.3 mg spiro-MeOTAD, 17.5 μL lithium bis(trifluoromethylsulphonyl)imide/acetonitrile (500 mg mL^{-1}), and 28.8 μL 4-tert-butylpyridine in 1 mL chlorobenzene.). The AgNWs, 10 μm long and 60nm in diameter were provided by Sigma-Aldrich. Purchased solution was diluted with IPA to 0.4 mg mL^{-1} for spray deposition. Air gas at a rate of 3 mL min^{-1} was delivered to the nozzle. AgNWs were then deposited by spray coating method on the spiro-MeOTAD/ TiO_2 /Ti fiber. The Ti fiber was placed in a vertical lab made spin coater with a spin coating speed of 2 rpm. Followed by Ti fiber was moved to on hot plate and annealed at 70 °C for 10 min.

Characterization and measurement

X-ray diffractometer (XRD) patterns were obtained with a Bruker D8 Advance, equipped with Cu $\text{K}\alpha$ radiation. The optical transmittance was identified with UV/Vis/NIR spectroscopy (Cary 5000, Agilent). Sheet resistance of Ag NWs film on spiro-MeOTAD/glass was measured by hole effect measurement system (HMS-5500, Ecopia). Surface morphology was inspected using field emission-scanning electron micro-scropy (FE-SEM, Nano230, FEI). The actual surface areas of modified Ti wires were measured using AFM (Multimode V, Veeco). The cross sectional microstructure and Energy-dispersive X-ray spectroscopy (EDX) on surface of Ti wire after annealing at 450 °C for 30 min were observed by High Resolution Transmission Electron Microscope (JEM-2100F, JEOL). Full device of cross sectional image was observed using focused ion beam (Helios 450HP, FEI) with Ga ions (30 kV). The Ga ion beam etched the structure until a cross-sectional view could be obtained at a tilted angle. The photocurrent density-voltage (J - V) characteristic of the fabricated perovskite solar cells was carried out using solar simulator (AM 1.5 G, 100 mW cm^{-2} , Sol3A, class AAA, Oriel) as a light source with the calibrated light intensity to 1 sun using a reference Si solar cell (PV Measurements, Inc.). The photovoltaic parameters were analyzed from photocurrent J - V curve. Bending test was measured in devices as a function of the number of bending cycles

in outward directions at a bending radius of ~15 mm. Active area was defined by multiplying the diameter of the Ti fiber and length of the fiber-shaped photovoltaic device.

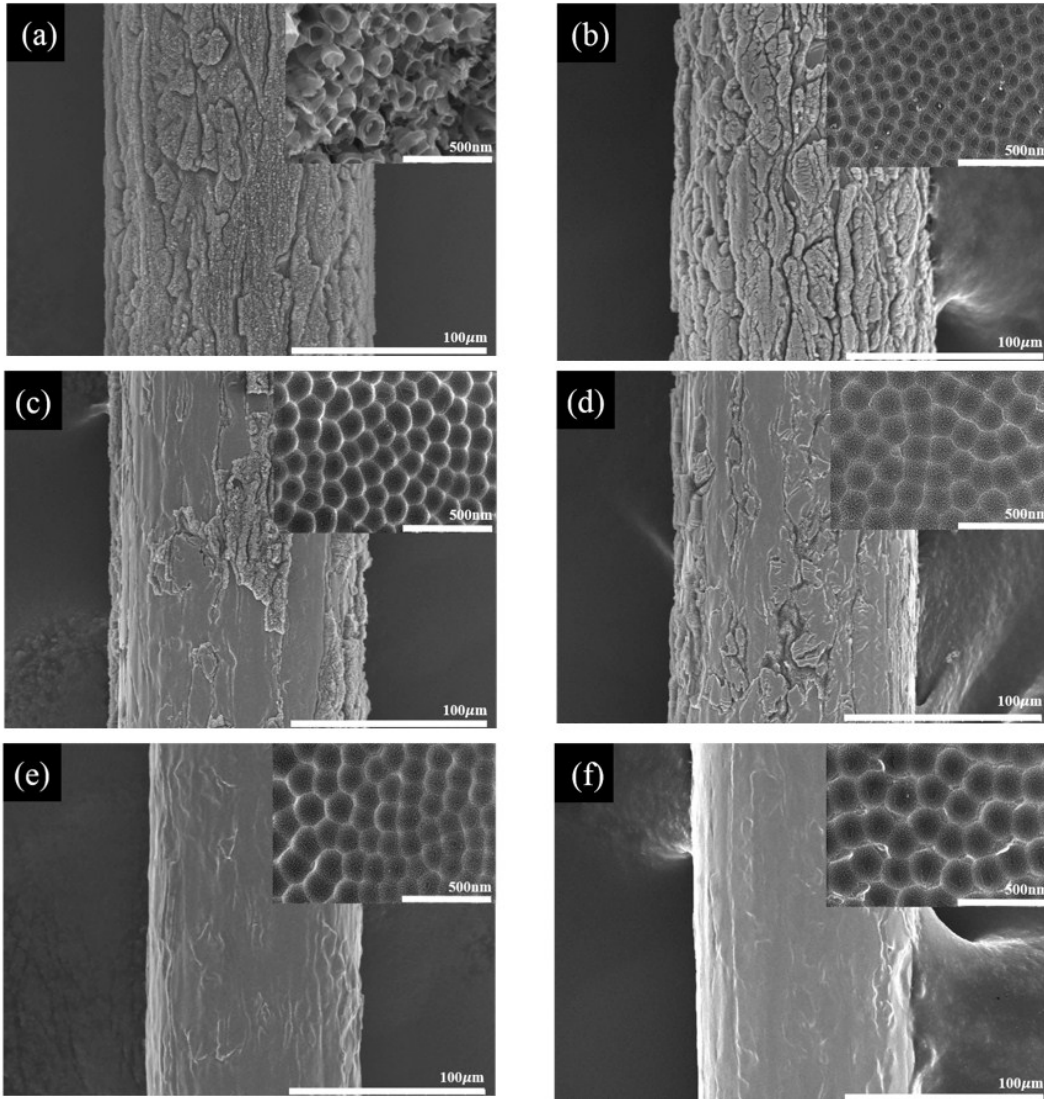


Fig. S1 SEM images of Titanium wire anodized for 4h at different voltage and temperature. The insets of (a)-(f) are dimple structure of each Titanium wire.

(a) 40V, 0 °C (b) 60V, 0 °C (c) 40V, 5 °C (d) 60V, 5 °C (e) 40V, 15 °C (f) 60V, 15 °C

As shown above, the diameter of dimples was varied by applying different voltages like that of TNTs. Note that TNTs grown on Ti-wire at a low bath temperature were hardly detached even with extended peeling off time. Interestingly, the depth of each dimple seems to be manipulated by bath temperature due probably to rapid ion mobility induced by temperature.

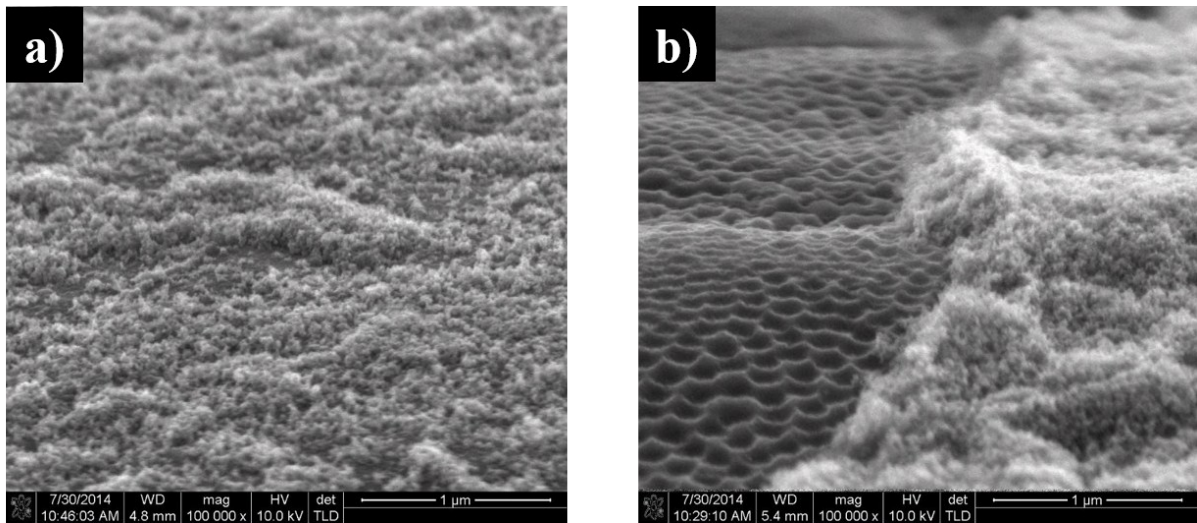


Fig. S2 SEM images of the surface morphology for different substrate after annealing m-TiO₂ on (a) polished Ti (b) dimple TiO₂/Ti substrate.

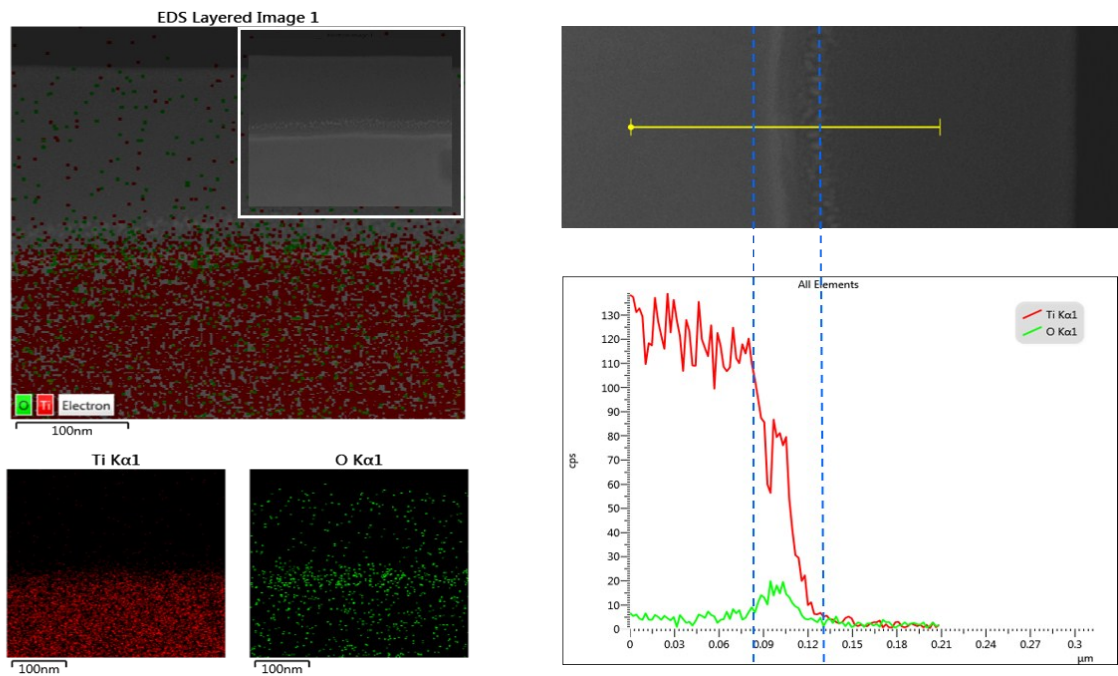


Fig. S3 EDX analysis for polished Ti substrate after annealing at 450 °C.

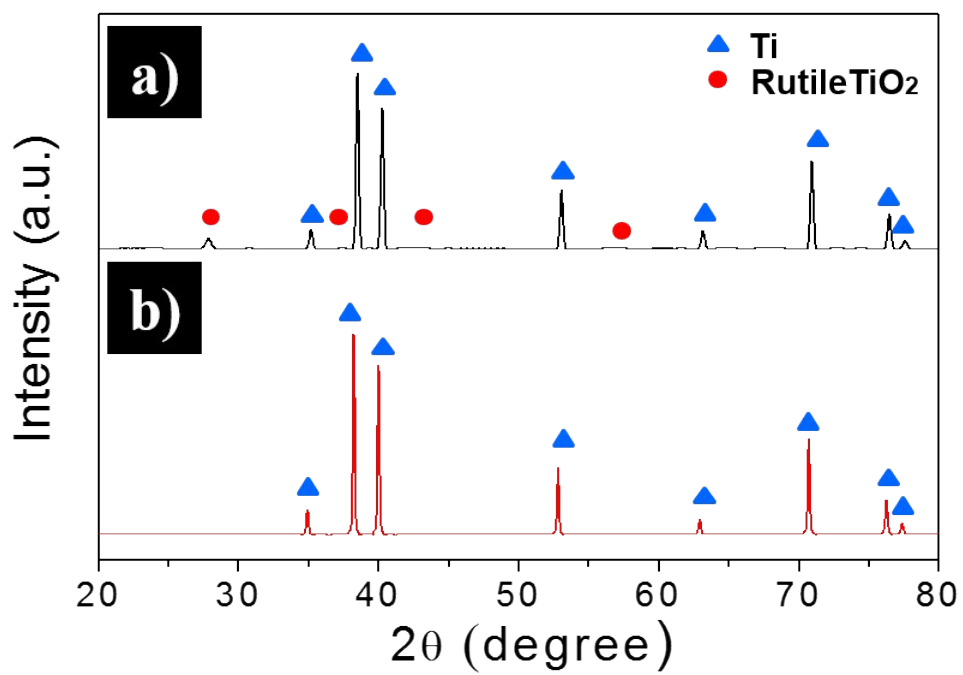


Fig. S4 XRD spectras after annealing at 450 °C (a) dimple TiO₂/Ti (b) polished Ti.

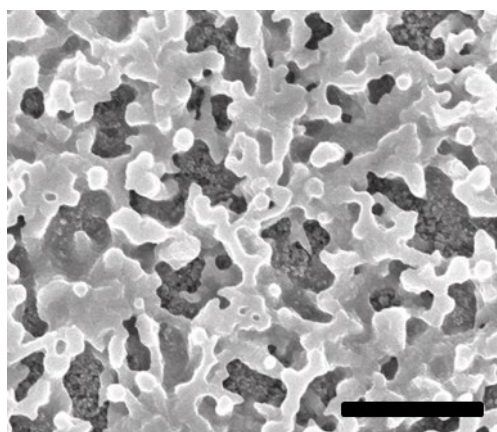


Fig. S5 Surface morphology of perovskite film with 1step method without toluene dipping. Scale bar represents 1 μm.

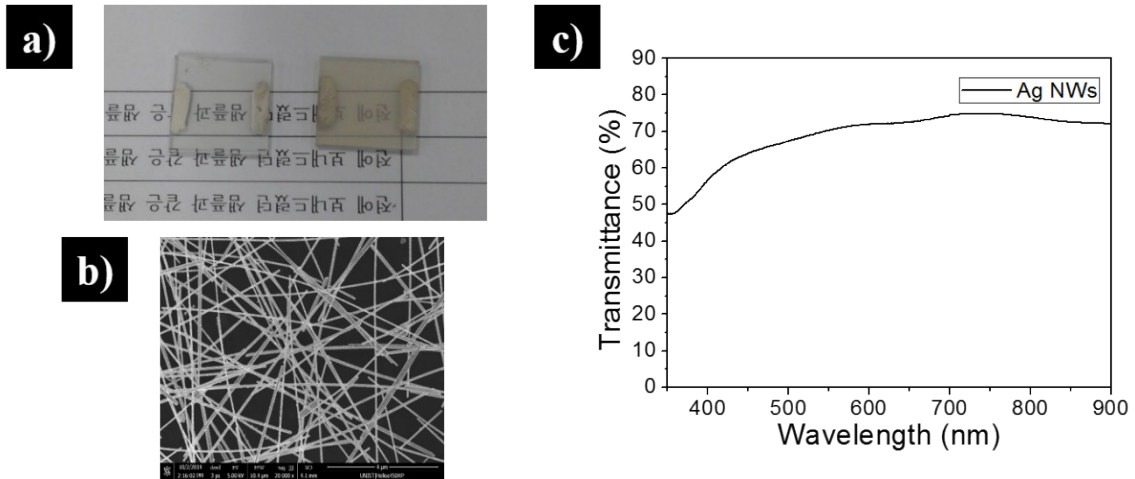


Fig. S6 Sprayed Ag NWs on spiro-MeOTAD/glass. (a) Optical images of the samples (left : bare glass, right Ag NWs on spiro-MeOTAD/glass) (b) SEM image of Ag NWs (c) transmittance spectra of Ag NWs deposited on spiro-MeOTAD/glass.

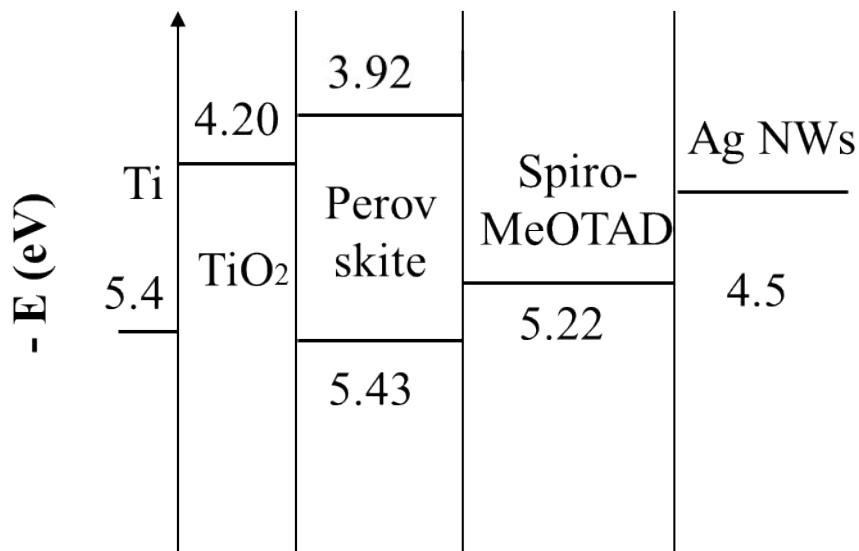


Fig. S7 Energy level diagram of CFPSCs.

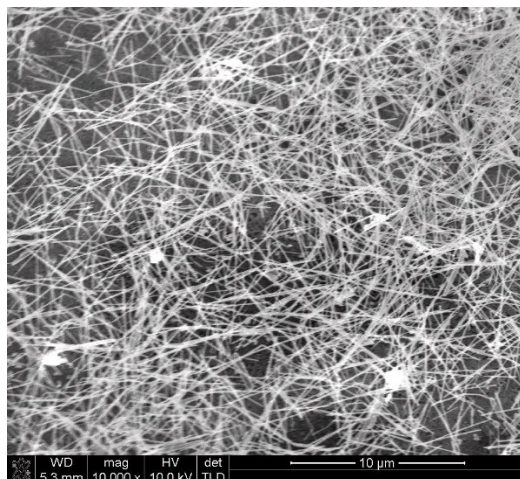


Fig. S8 SEM image of AgNWs electrode on the spiro-MeOTAD in devices.

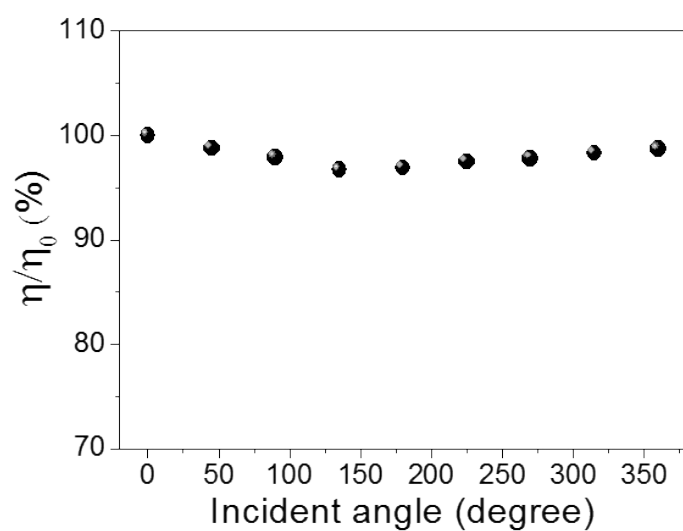


Fig. S9 Angle dependent efficiency for the devices. η_0 and η represents efficiencies measured at an incident angle of 0 and other angles, respectively.

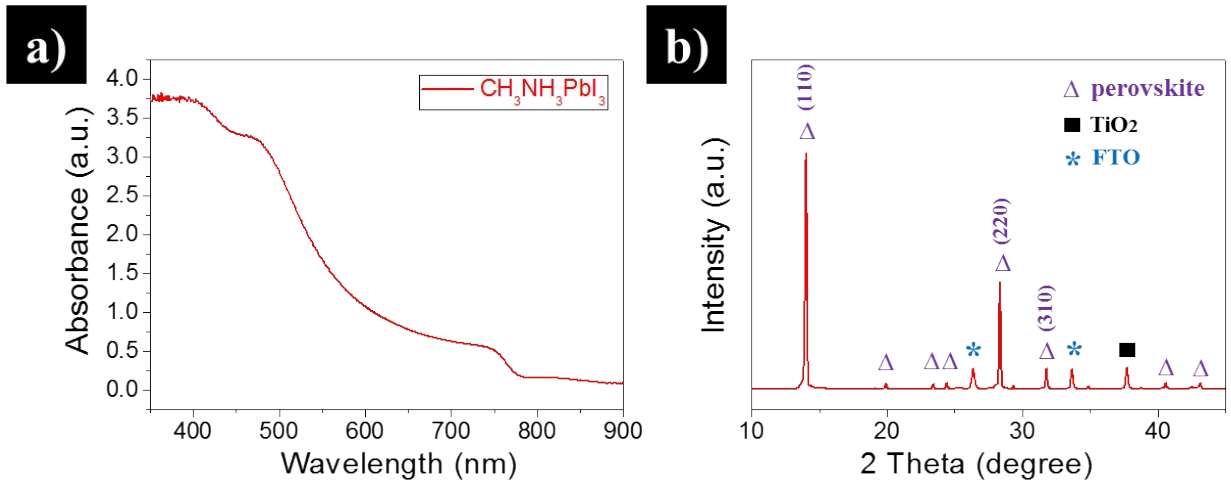


Fig. S10 (a) Absorbance (b) XRD spectra of perovskite layer.

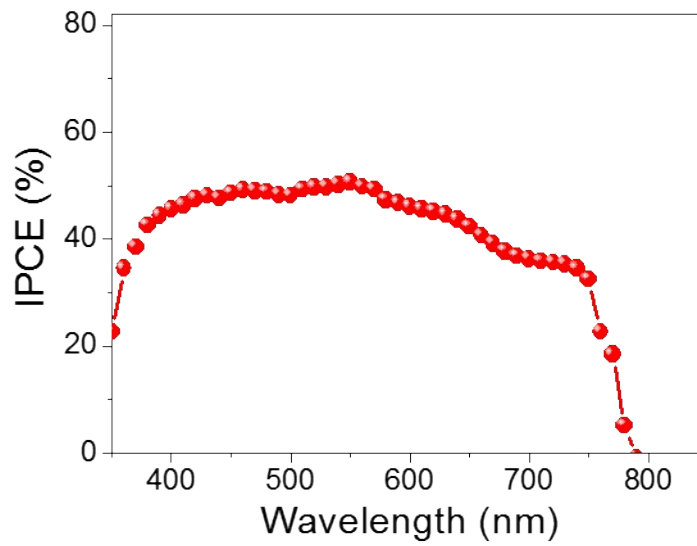


Fig. S11 IPCE data in fiber-shaped photovoltaic device.