

Electronic Supplementary Material (ESI) for Nanoscale

**Nano-grid structure made of perovskite SrTiO₃ nanowires for
efficient electron transport layers in inverted polymer solar cells**

Jeong Won Kim¹, Yo-han Suh¹, Chang-Lyoul Lee², Yong Seok Kim³, and Won Bae Kim^{1,4}*

¹School of Materials Science and Engineering, Gwangju Institute of Science
and Technology (GIST), 261 Cheomdan-gwagi-ro, Buk-gu, Gwangju 500-712, Korea

[*] Prof. Won Bae Kim

E-mail: wbkim@gist.ac.kr; Tel: 82-62-715-2317; Fax: 82-62-715-2304

²Advanced Photonics Research Institute (APRI), Gwangju Institute of Science and
Technology (GIST), 261 Cheomdan-gwagi-ro, Buk-gu, Gwangju 500-712, Korea

³School of Chemical and Biomolecular Engineering, Cornell University, 120 Olin Hall,
Ithaca, New York 14853-5201, USA

⁴Research Institute for Solar and Sustainable Energies (RISE), Gwangju Institute of Science
and Technology (GIST), Republic of Korea

Experiment Details

Synthesis of TiO₂ thin film by sol-gel solution

To prepare TiO₂ TF, sol-gel chemistry was used. The 0.625 ml of titanium butoxide was mixed in 2.5 ml of 2-methoxyethanol under vigorous stirring in N₂ atmosphere. Then, 0.25 ml of ethanolamine was added into the mixed solution. After 1 h stirring at room temperature, the mixed solution was heated at 80 °C for 1 h, followed by heating to 120 °C for 1 h. During all steps, the mixed solution should be stirred continuously under N₂ atmosphere. After cooling down to room temperature, the mixed solution was blended with 1.25 ml of methanol for stabilizing the sol-gel solution. For spin-coating TiO₂ TF on the ITO substrate, the blended sol-gel solution was diluted by 1:50 in isopropanol. The diluted solution was transparent. All chemicals were purchased from Aldrich Co. and used without further purification. This sol-gel solution was spin-cast onto the pre-cleaned ITO substrate at 3000 rpm for 30 sec. Finally, the obtained TF was calcined at 500 °C for 3 h in air.

Synthesis of SrTiO₃ thin film by sol-gel solution

Sol-gel solution for SrTiO₃ TF was prepared by blending 0.227 g of strontium isopropoxide, 0.188 ml of titanium butoxide, 2.5 ml of 2-methoxyethanol, and 0.25 ml of ethanolamine. During all steps, the mixed solution should be stirred continuously under N₂ atmosphere. After stirring for 1 h at room temperature, the mixed solution was heated at 80 °C for 1 h, followed by heating to 120 °C for 1 h. Then, the mixed solution was cooled down to room temperature and 1.25 ml of methanol was added into the solution for stabilizing sol-gel solution. For spin-coating SrTiO₃ TF on the ITO substrate, the sol-gel solution was diluted by 1:50 in isopropanol. The diluted solution was transparent with a little yellowish color. All chemicals were purchased from Aldrich Co. and used without further purification. This sol-gel solution was spin-cast onto the pre-cleaned ITO substrate at 3000 rpm for 30 sec.

Finally, the obtained TF was calcined at 500 °C for 3 h in air.

Preparation of nano-grid structure *via* electrospinning methods

Electrospinning solution for TiO₂ NWs was prepared by chemical synthetic processes. Firstly, 0.375 ml of titanium butoxide was mixed with solution of acetic acid (0.75 ml) and ethanol (0.75 ml) under vigorous stirring in N₂ atmosphere. The mixed solution was then blended with 0.112 g of polyvinyl pyrrolidone (PVP, Mw = 1,300,000 g/mol) dissolved in 1.875 ml of ethanol. The amounts of Ti were controlled in the range of 2 wt.% and that of PVP was fixed to be 3 wt.% in the total weight of electrospinning solution. The electrospinning precursor solution for SrTiO₃ NWs was also prepared similarly. Firstly, 0.113 g of strontium acetate and 0.188 ml of titanium butoxide were mixed in the solution consisting of 1.5 ml of acetic acid and 1 ml of ethanol under constant stirring at 60 °C in N₂-filled glove box. Herein, the nominal molar ratio of Sr:Ti was controlled to 1:1. After enough stirring at 60 °C, the precursor solutions were blended with the PVP solution which was homogeneously prepared by dissolving 0.108 g of PVP in 1 ml of ethanol. Then, the blended solution was changed to transparent and slightly yellowish solution. All chemicals were purchased from Aldrich Co. and used as received without further purification.

The TiO₂ and SrTiO₃ precursor solutions for electrospinning, blended with PVP, were loaded into a plastic syringe equipped with a cutted 23 gauge (inner diameter of ca. 0.42 μm) needle made of stainless steel, respectively. The needle was connected to a high-voltage supply (DC high voltage generator, CPS-40K03VIT). The feeding rate for the electrospinning solution was controlled using a syringe pump. The ITO glass substrate coated with metal oxides TF (~10 nm) *via* sol-gel process was loaded on a metallic collector using an adhesive tape. The viscous mixed solution was ejected at a rate of 0.3 ml/h toward a substrate on the metallic collector that was 12 cm away from the syringe needle. When applying a high

voltage of 10 kV between the syringe needle and the substrate, the electrospun nanowires were collected on the substrate. Then, the collected nanowires on the substrates were calcined at 500 °C for 3 h in air to remove the organic materials and to produce the metal oxide nanowires as well as to enhance crystallinity of the nanowires.

The structural properties of TiO₂ NWs and SrTiO₃ NWs were characterized by field emission scanning electron microscopy (FE-SEM, JEOL-JSN7500F), transmission electron microscopy (TEM, JEOL-2100) and energy-dispersive X-ray spectroscopy (EDX). X-ray diffraction (XRD, Rigaku Rotaflex RU-200B) was performed with a Cu K α source ($\lambda = 1.5405 \text{ \AA}$) to obtain the crystalline patterns of the NWs. The UV absorbance of NWs was carried out using UV-Vis absorption spectroscopy (Lambda 750 UV/VIS Spectrometer).

Fabrication of inverted polymer solar cells

To investigate photovoltaic performance with the different ETLs (e.g., TiO₂ TF, TiO₂ TF/NWs and SrTiO₃ TF/NWs), inverted PSCs consisting of ITO/*n*-type metal oxides/poly[3-hexylthiophene](P3HT):*phenyl-C₆₁-butyric acid methyl ester* (PCBM)/MoO₃/Ag were fabricated. The P3HT:PCBM layer was spin-coated on the different ETLs and used as the photo-active layer in the inverted PSCs. The blend solution of P3HT (25 mg/ml) and PCBM (25 mg/ml) in 1,2-dichlorobenzene was filtered through a 0.2- μm PTFE filter and then spin-coated on the electron transport layers with 600 rpm for 60 s (150 nm). The post-annealing process was performed at 150 °C for 10 min under N₂ atmosphere. As a hole transfer layer, MoO₃ (100 nm thickness) was evaporated by thermal evaporation under high vacuum ($< 10^{-6}$ Torr). Further, patterned Ag electrode (100 nm thickness) was thermally evaporated as an anode on the hole transfer layer. The active area was $4.75 \times 10^{-6} \text{ cm}^2$. Solar cell performance was measured using a Keithley 2611 source measurement unit under air mass (AM) 1.5 G

illumination with light-source operation at 100 mW/cm^2 in a N_2 -filled glovebox. The light intensity was calibrated using reference silicon solar cells (Oriel, P/N: 91150V). The incident photon-to-current efficiency (IPCE) measurements were carried out using a QEX 10 Solar Cell Spectral Response/QE/IPCE measuring system (PV measurements). For measuring carrier lifetime from Bode plots, the EIS characteristics were recorded with a Gamry Reference 600 measurement unit under 100 mW/cm^2 . The frequency range was explored from 0.1 Hz to 1 MHz with an AC oscillation potential amplitude of 10 mV between anode and cathode at room temperature. The applied bias voltage were set at -0.6 V (open-circuit voltage).

Figures and Tables

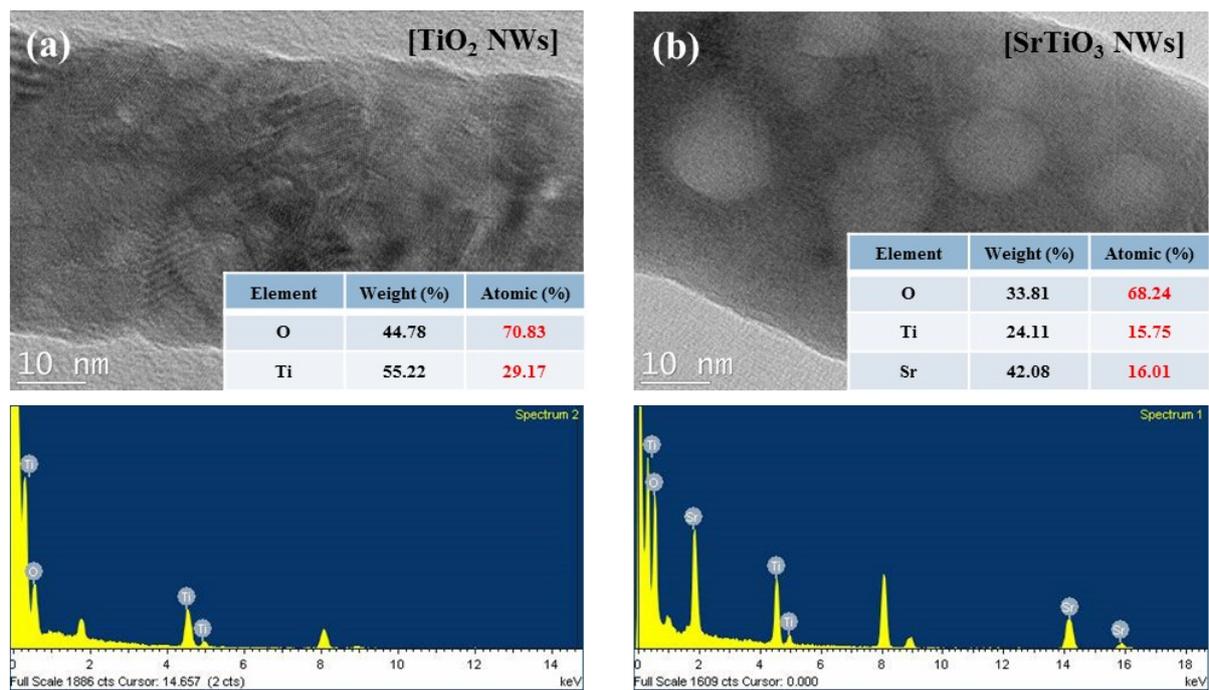


Figure S1. HR-TEM images of individual (a) TiO₂ NW and (b) SrTiO₃ NW with EDX atomic ratio analysis

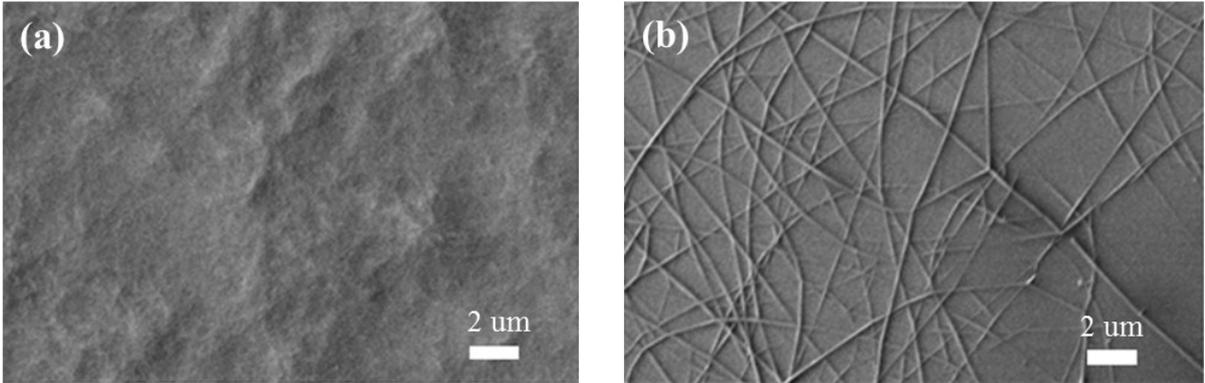


Figure S2. SEM images for the surface of the conjugated polymer (P3HT:PCBM) spin-coated over (a) TF and (b) NWs

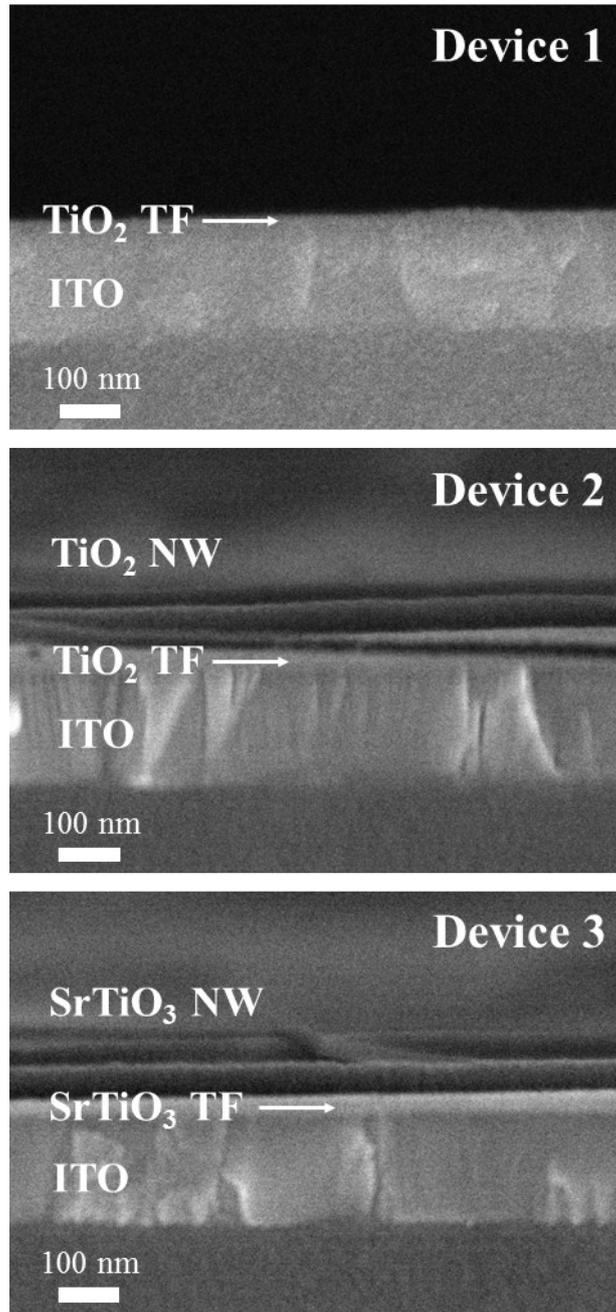


Figure S3. Cross section SEM images of TiO_2 TF, TiO_2 TF/NWs and SrTiO_3 TF/NWs as ETL in the inverted PSCs

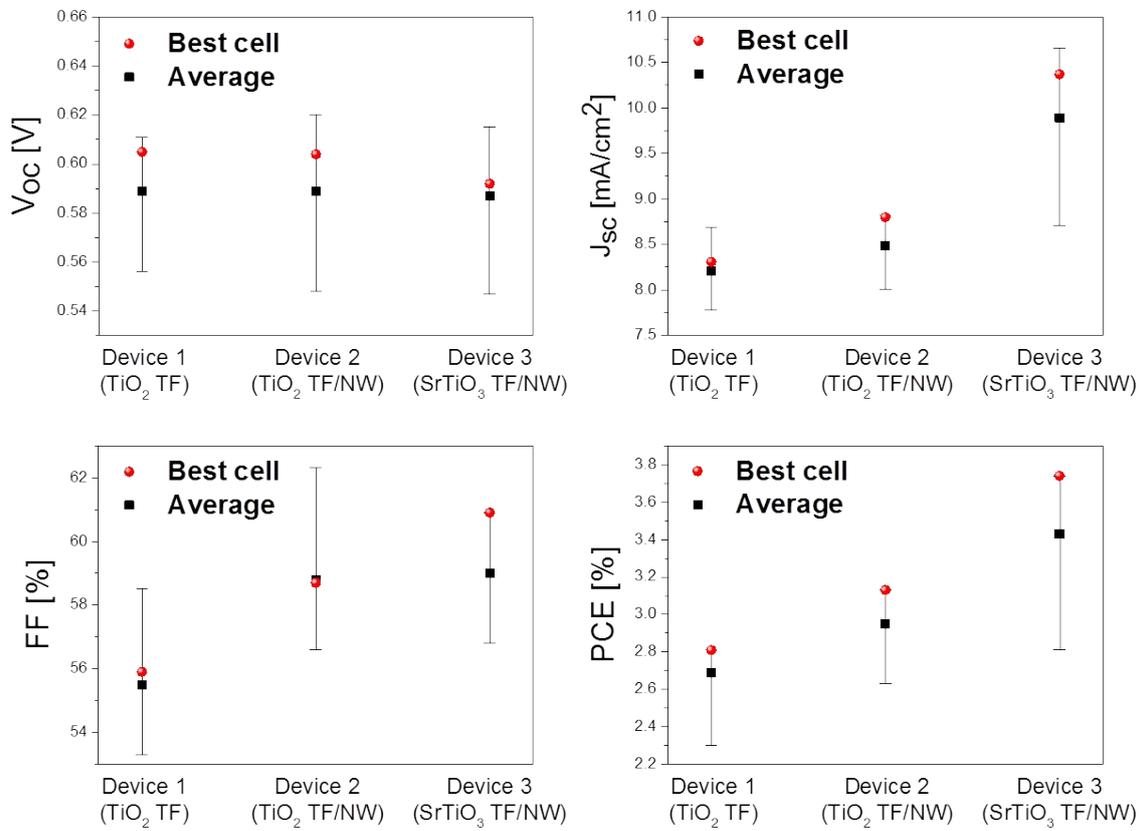


Figure S4. Statistical analysis of the photovoltaic parameters in the inverted PSCs employing the different ETLs. Each data represent the mean values of 20 or more individual devices.

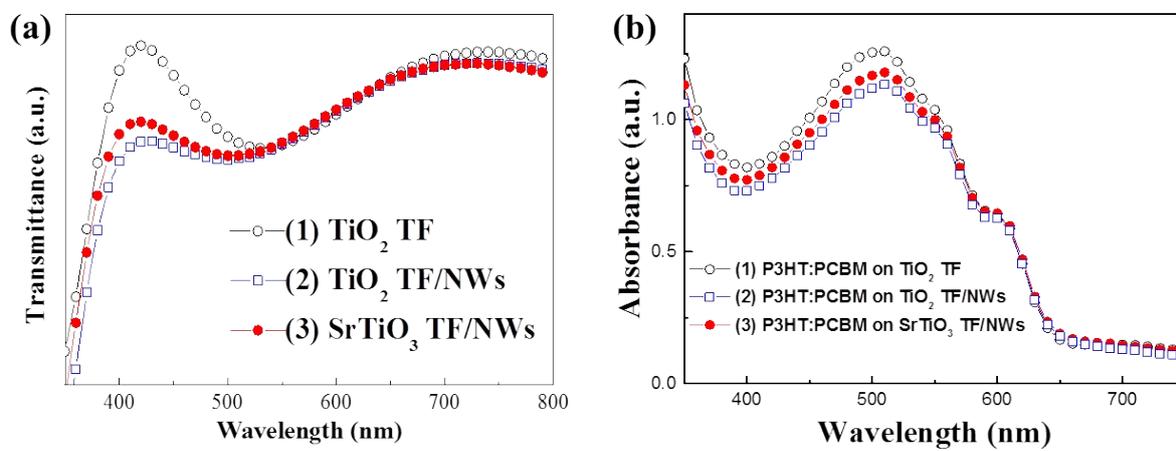


Figure S5. (a) Transmittance spectra of the different ETLs synthesized on transparent ITO substrate and (b) absorbance spectra of photo-active layers (P3HT:PCBM) spin-coated on the different ETLs.