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# A hybridized electron-selective layer using Sb-doped SnO<sub>2</sub> nanowires for efficient inverted polymer solar cells

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## ABSTRACT

We developed a novel hybridized electron-selective layer comprised of Sb-doped SnO<sub>2</sub> nanowires for efficient inverted polymer solar cells. A device containing Sb-doped SnO<sub>2</sub> nanowires with 0.1 mg/ml concentration showed a significant increase in power conversion efficiency to 3.23% with an enhanced fill factor, compared to a reference device without the nanowires (2.89%). Such improvement is attributed to the high electrical conductivity of one-dimensional Sb-doped SnO<sub>2</sub> nanowires and to the good light transmittance through the wide band gap of tin oxide. Also the surface morphology of the hybridized electron-selective layer is made denser and improved by incorporating one-dimensional Sb-doped SnO<sub>2</sub> nanowires, resulting in the enhancement of the photovoltaic performance.

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## 1. Introduction

Inverted polymer solar cells (inverted-PSCs) have been considered as attractive photovoltaic devices because of the advantages they offer, such as high stability [1–3] and large-scale cell fabrication using ITO-free electrode and non-toxic solvent [4–10]. One of the critical factors in enhancing the photovoltaic performance of inverted-PSCs is the development of efficient electron-selective layers to facilitate electron transport and to have good light transmittance onto the cathode [11–13]. As a part of these efforts, ZnO nanoparticles have been developed into electron-selective layers and the beneficial effect of an annealed Cs<sub>2</sub>CO<sub>3</sub> layer has been reported for electron-injection materials [14,15]. The morphology of ZnO has also been modified from a thin film to nano-ridges by a controlled annealing process [16].

Since one-dimensional (1-D) nanostructures, such as nanowires or nanotubes, are widely known for their outstanding electrical conductivity and optical properties [17], the use of 1-D nanostructures in photovoltaic cells can enhance charge transport properties by providing direct pathways of charges along their anisotropic morphologies [18–24]. Vertically aligned ZnO nanowires have been used as photoanodes in dye-sensitized solar cells and CdSe nanorods have been employed as n-type electron acceptors for hybrid solar cells to improve their electron transport properties [22,23]. Electrospun TiO<sub>2</sub> nanowires with a conjugated polymer have also been demonstrated to be an

efficient electron-acceptor material with enhanced charge collection and transport properties in organic–inorganic hybrid solar cells [24]. Accordingly the implementation of 1-D nanostructure material would be of interest for use in electron-selective layers of inverted-PSCs because the electrons are likely to be transported to the cathode of inverted-PSCs through the 1-D nanostructures, thus reducing the recombination of charges and improving the photovoltaic performance of inverted-PSCs.

We synthesized Sb-doped SnO<sub>2</sub> nanowires (ATO NWs) by a simple one-pot electrospinning method. The ATO NWs, which had been applied to fuel cell electrodes with enhanced electron transport properties derived from high electrical conductivity [25], can be employed as electron-selective layers of inverted-PSCs because of their outstanding electrical conductivity and good light transmittance through transparent, electrically conducting, n-type oxide materials with a wide energy band gap (*ca.* 3.8 eV) [26–28]. In this work ATO NWs were employed, for the first time, in a sol–gel-processed ZnO thin film to enhance electron transport and to mitigate the recombination of charges over the electron-selective layers of inverted-PSCs. Our hybridized electron-selective layer containing the ATO NWs shows an improved photovoltaic performance, compared to ZnO thin film without the ATO NWs.

## 2. Material and methods

### 2.1. Synthesis of ATO NWs by electrospinning

To prepare Sb-doped SnO<sub>2</sub> nanowires using the one-pot electrospinning method, a precursor solution consisting of 0.1 g

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of  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$  (at least 99.995%) and 0.018 g of  $\text{SbCl}_3 \cdot 2\text{H}_2\text{O}$  (at least 99%) was mixed with 0.3 g of poly(vinyl pyrrolidone) (PVP,  $M_w=1,300,000$  g/mol) dissolved in 8 ml of methanol. The nominal molar ratio of Sn:Sb was controlled to 85:15. All chemicals were purchased from Aldrich Co. and used as received without further purification. After the solution was loaded into a syringe, the solution was ejected at the rate of 1.0 ml/h toward a vertically placed Si collector that was 10 cm away from the syringe needle. When a high potential of 9.5 kV was applied to the syringe needle, the precursor/PVP nanofibers were electrospun and collected on

the Si collector. The as-spun nanofibers were calcined at  $600^\circ\text{C}$  for 6 h in air to remove the organic material and produce the Sb-doped  $\text{SnO}_2$  nanowires.

## 2.2. Characterization of structural properties of ATO NWs

The microstructure of the ATO NWs was investigated by scanning electron microscopy (SEM, JEOL-JSN7500F) and transmission electron microscopy (TEM, JEOL-2100). X-ray diffraction (XRD, Rigaku Rotaflex RU-200B) was performed with a  $\text{Cu K}\alpha$  source ( $\lambda=1.5405 \text{ \AA}$ ) to obtain the crystalline patterns of the NWs. X-ray absorption near-edge spectroscopy (XANES) was conducted at the 3C1 beamlines of the Pohang Accelerator Laboratory (PAL; 2.5 GeV with stored currents of 130–180 mA) in Korea to evaluate the antimony phase in the ATO NWs. A Si (1 1 1) double crystal monochromator was employed to monochromatize the X-ray photon energy. The XANES spectra were taken in transmission mode for the K-edge of Sb (11,564 eV) under ambient conditions. Energy calibration was performed using a standard metal foil.

To investigate electrical conductivity of nanowires, the TO NW and ATO NW were dispersed individually in isopropyl alcohol by sonication and then dropped on a silicon wafer with a  $\text{SiO}_2$  thickness of 100 nm. The silicon wafer is made from a highly doped p-type silicon, which can be used as a back gate electrode. Additionally, metal electrodes consisting of Ti (30 nm)/Au (50 nm) were deposited by an electron beam evaporator and

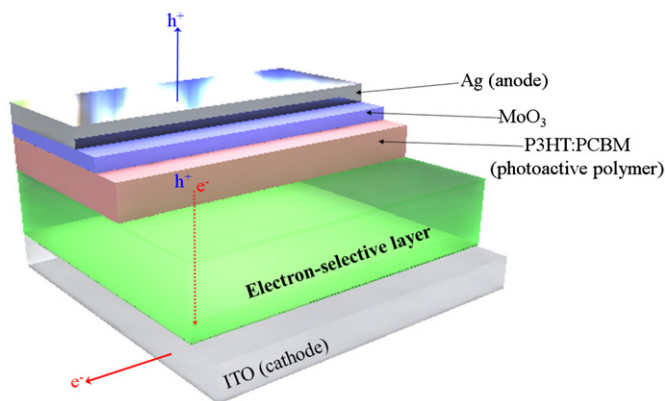


Fig. 1. Schematic illustration of inverted polymer solar cell as a reference device.

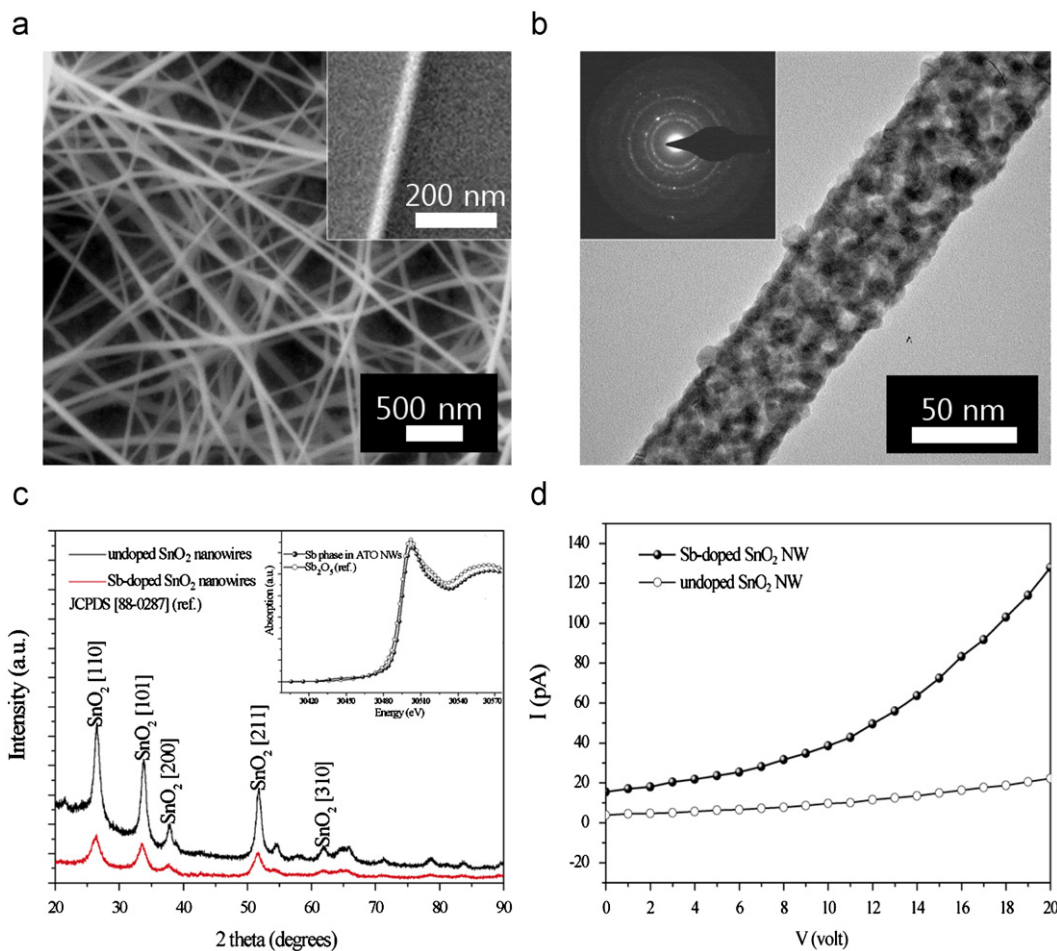


Fig. 2. (a) SEM and (b) HRTEM images (inset is selected area diffraction pattern) of ATO NWs. (c) XRD patterns of undoped  $\text{SnO}_2$  and Sb-doped  $\text{SnO}_2$  NWs; inset is XANES patterns of antimony in ATO NWs and  $\text{Sb}_2\text{O}_5$ . (d)  $I$ - $V$  curves of single undoped  $\text{SnO}_2$  nanowire and Sb-doped  $\text{SnO}_2$  nanowire.

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