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# Indium-doped ZnO mesoporous nanofibers as efficient electron transporting materials for perovskite solar cells

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ABSTRACT

We introduce a viable electrospinning route for the development of highly porous indium-doped (In-doped) ZnO nanofibers as electron transporting materials (ETMs) in perovskite solar cells (PSCs) for the first time ever. The nanofibers ETMs with optimal thickness leads to highly efficient and hysteresis-free PSCs with an average power conversion efficiency ($PCE_{avg}$) of 16.03% and a best power conversion efficiency ($PCE_{best}$) of 17.18%, thanks to high porosity and high crystallinity of the nanofibers, better infiltration of the absorber and rapid charge transport characteristics due to indium (In) doping. Furthermore, the modification of In-doped ZnO nanofibers ETMs, by coating a thin layer of a polymer polyethyleneimine (PEI) further enhances the $PCE_{avg}$ to 16.86% ($PCE_{best}$ = 18.69%) by effectively reducing the energy barrier for electron extraction due to a reduced work function. This study reveals that In-doped ZnO nanofibers are the best ETMs for generating the inexpensive and high efficiency PSCs with long-term stability.

## 1. Introduction

Perovskite solar cells (PSCs) have drawn huge attention of photovoltaics community owing to their inexpensive and simple fabrication processes and high power conversion efficiency (PCE) and ease of band gap tuning [1–8]. In the certain cases of mesoscopic PSCs, the electron transporting materials (ETMs) such as ZnO are usually engineered to be highly porous in nature in order to facilitate better loading of perovskite absorber, larger surface area, and fast charge transport [9–12]. In recent times, especially the one-dimensional (1-D) ZnO nanostructured ETMs (nanorods, nanosheets, and nanotubes) were presented to promote the larger internal surface area, promising loading of perovskite absorber and diverse light-scattering characteristics compared to nanoparticles films [11,13–17]. However, the PCEs achieved for nanostructured ZnO ETM-based PSCs have not produced performance improvements to date [18–20]. Considerable further advances are required in the construction of mesoscopic ETMs in order to achieve remarkable PCEs using scalable manufacturing schemes. Keeping in view, we are motivated to develop the nanostructures with low defect sites, larger surface area and rapid electron extraction that can be the root of multifunctional ETMs for mesoscopic PSCs. Electrospinning preparations of 1-D metal-oxide (ZnO and $TiO_2$) nanofibers has recently developed as a rapid, facile, and inexpensive route to produce nanomaterials that demonstrate potential for practical applications [8,21,22]. Besides, in order to develop the effective ETMs using a scalable technique such as electrospinning, further improvements in terms of enhancing the electron transport properties are also needed. Recently, ZnO has been doped with different metallic elements such as aluminium (Al), indium (In) and gallium (Ga) in order to enhance the optical/electrical characteristics [23–25]. In is a most suitable dopant since it has less reactivity and better resistivity to oxidative environment than the Al and Ga. Moreover, In doping can also increase the carrier concentration of ZnO providing the basis for superior conductivity [25]. Besides the ETM modifications, effective engineering of various interfacial layers is also important in order to reduce surface recombination, work function and to overcome the interface barriers for charge accumulation, which will eventually influence the device performance. The usage of organic dipole layers such as poly(ethyleneimine) (PEI) [26], or poly-(ethyleneimine)-ethoxylated (PEIE) [27] does modify the work function that improves the device performance [10]. This technique effectively enhances the device performance by reducing the work function between the oxide and active layers.

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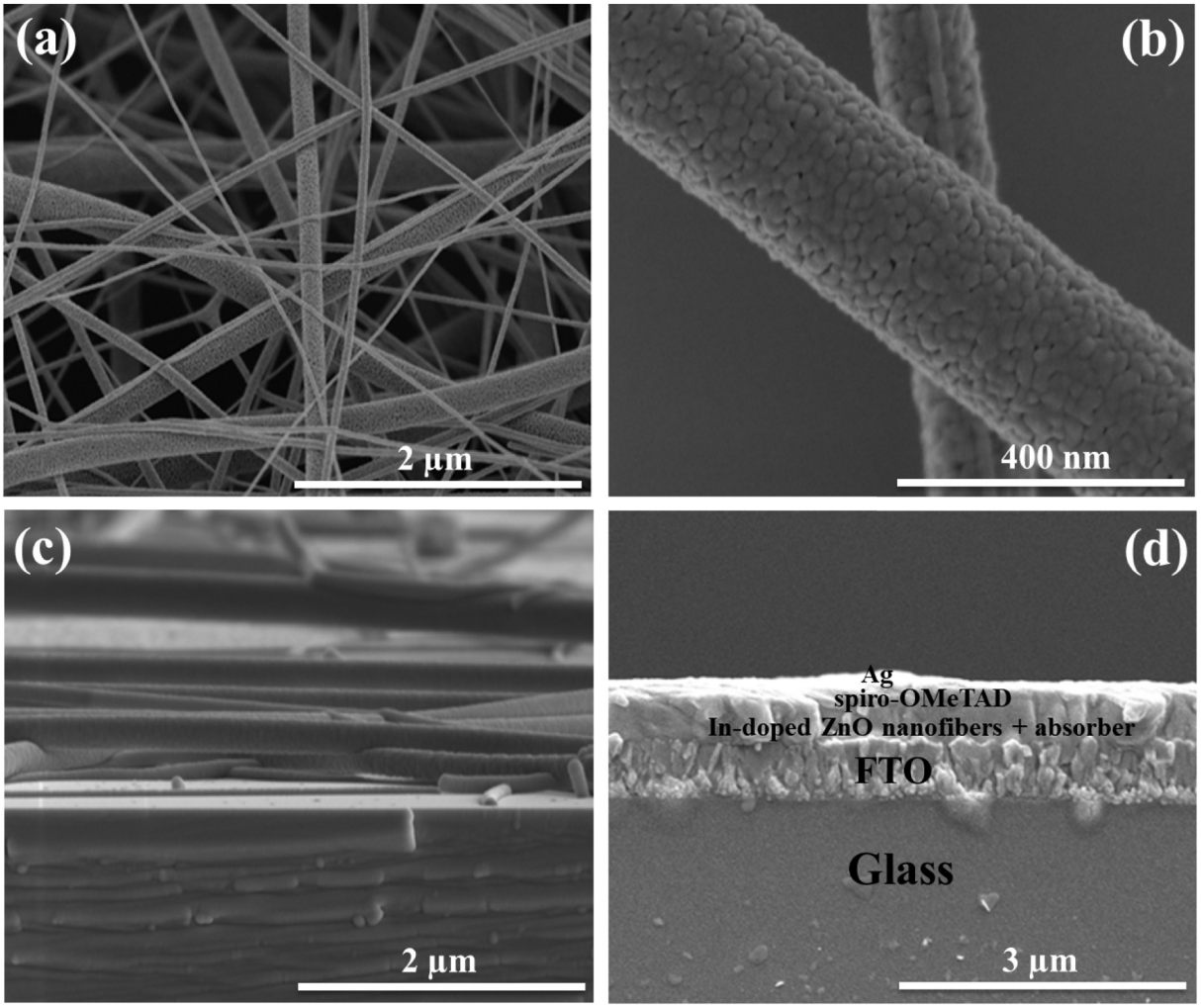


**Fig. 1.** SEM images showing (a) annealed indium-doped ZnO nanofibers ETM, (b) magnified view of nanofibers demonstrating their highly porous nature, cross-section view of (c) a 440 nm-thick film of nanofibers, and (d) complete device, respectively.

Besides the recombination, another severe issue is the instability of ZnO ETMs based PSCs [28–30]. The decrease of surface passivation and defects are usually practical for enhancing the stability of perovskite devices either. After surface passivation, the active surface of ZnO surface is coated with $TiO_2$ or PEI which have been shown not to react with perovskite layers [31]. By covering the ZnO surface with the stabilized materials the chemical instability prompted by chemical residues and ZnO can also is prevented [31]. Furthermore, extensive efforts have been made to improve the stability of ZnO nanostructured-based PSCs and found sound applications in perovskite optoelectronic devices [32–34].

This study aims the preparation of ZnO and In-doped ZnO nanofibers as the ETMs for PSCs using a scalable and easy to process electrospinning route for the first time ever. The In-doped ZnO nanofibers ETM, with high porosity and rapid electron transport lead to highly efficient mesoscopic PSCs with $PCE_{avg}$ of 16.03% and a $PCE_{best}$ of 17.18%. The increase of the ETM thickness significantly reduces the device performance due to the improper pore filling of nanofibers with perovskite absorber. The devices with optimal nanofibers ETM thickness (440 nm) showed the remarkable performance (with PCE of 16.10%) compared to the devices based on only mesoporous particulate ETM (PCE of 10.14%). Furthermore, the incorporation of PEI-coated In-doped ZnO nanofibers ETMs into devices based remarkably enhanced the device performance to a $PCE_{bes}$ of 18.69%, originated from stronger dipole-dipole or electrostatic interactions between the PEI and ZnO surface.

## 2. Experimental and characterization details

The electrospinning technique [10], was used to obtain the ZnO and indium-doped ZnO nanofibers under ambient conditions. A homogenous precursor solution of ZnO was prepared by dissolving 1:0.8 ratio of Zinc nitrate-hexahydrate ($Zn(NO_3)_2{\cdot}6H_2O$) and polyvinylpyrrolidone (PVP) into mixed solvent of ethanol and deionized water (DI) (8:3 v:v) under continuous magnetic stirring. After that, the spinable and transparent ZnO solution was shifted into the nozzle via syringe pump (KD100, KD Scientific Inc., U.S.A.). The applied potential and feeding rate were kept constant at 1.0 mL/min and 15.6 kV, respectively. Electrospinning time was adjusted accordingly to prepare the films of various thicknesses. Indium doping was realized by mixing the indium chloride ($InCl_3$) with doping concentration of 5 at.% into the above precursor solution. Fluorine doped tin oxide (FTO) glass substrates were cleaned ultrasonically using ethanol, DI water and acetone each for 15 min, respectively. Highly mesoporous ZnO nanofibers were then obtained after calcination of as-prepared nanofibers in air at 430 °C for 1 h. For comparison, a 440 nm thick In-doped ZnO mesoporous particulate film was prepared using electrospray without adding the PVP into the precursor solution as reported previously by us [12].

The perovskite devices were constructed via sequential deposition technique as reported previously [8]. Firstly, ZnO compact layer was