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Sub-100 °C solution processed amorphous titania nanowire thin films for high-performance perovskite solar cells

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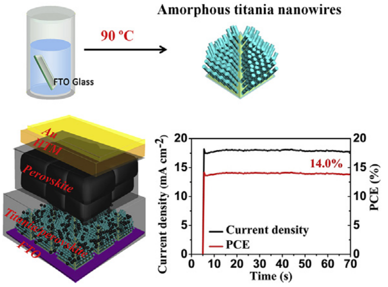
HIGHLIGHTS

- Amorphous titania nanowire thin films were prepared via a low temperature process.
- The titania evolved from nanoparticles to nanowires with increasing reaction time.
- Good titania coverage effectively blocked holes, suppressing charge recombination.
- PSCs based on ~150 nm titania nanowire thin films yielded an efficiency of 14.67%.

GRAPHICAL ABSTRACT



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ABSTRACT

The present work demonstrates a facile one-step process to fabricate thin films of amorphous titania nanowires on transparent conducting oxide substrates via hydrolysis of potassium titanium oxide oxalate in an aqueous solution at 90 °C. The resultant titania nanowire thin films (that have not undergone further annealing) are efficient electron transport layers in $CH_3NH_3PbI_3$ perovskite solar cells, yielding full sun solar-to-electricity conversion efficiencies of up to 14.67% and a stabilized efficiency of 14.00% under AM 1.5G one sun illumination, comparable to high temperature sintered TiO_2 counterparts. The high photovoltaic performance is attributed to the porous nanowire network that facilitates perovskite infiltration, its unique 1D geometry and excellent surface coverage for efficient electron transport, as well as suppressed charge recombination between FTO and perovskite.

1. Introduction

Recently, organic-inorganic hybrid perovskite solar cells (PSCs) have risen to the forefront in emerging photovoltaic research due to the advantages of $CH_3NH_3PbX_3$ (X = Cl, Br or I) based light harvesters, such as tunable optical properties, high absorption coefficients, very long charge carrier (electron-hole) diffusion lengths, as well as low-temperature solution processability [1–4]. The organo-lead iodide perovskite, $CH_3NH_3PbI_3$, acts not only as an efficient light harvester, but also an effective electron and hole conductor because of its ambipolar semiconducting nature [3,4]. In combination with a mesoporous oxide scaffold or compact layer, impressive efficiencies of up to ~16% have been obtained with

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either mesoscopic or planar device architectures [5,6].

The n-type TiO_2 electron-selective contact is a very effective scaffold to support the perovskite absorber material. The TiO_2 thin film is traditionally prepared by aerosol spray pyrolysis [7], spin-coating [8], thermal oxidation [9], atomic layer deposition [10], or electrochemical deposition [11]. Typically, the morphology, thickness, and crystallinity of the TiO_2 layer play a crucial role in the solar cell performance. However, it has been generally recognized that high-performance devices require high-temperature (>450 °C) sintering of the TiO_2 compact layer and/or TiO_2 porous layer to increase the crystallinity and achieve suitably high charge carrier mobility for good charge transport properties [12,13]. This processing condition leads to higher production cost and a slower fabrication rate, and will limit future applications of PSCs on non-temperature-resilient substrates, particularly in flexible formats. It is therefore critical to explore the possibility of making TiO_2 electron transport layers at low temperatures for efficient charge collection and thus high-performance PSCs.

A few approaches have been reported for the fabrication of low-temperature processed TiO_2 with comparable electronic properties to high-temperature processed TiO_2 in PSC technologies. For instance, Snaith and co-workers reported high-efficiency PSCs assembled with a low-temperature processed graphene/TiO_2 nanocomposite electron transport layer [14]. Grätzel and co-workers demonstrated a rutile nanocrystalline TiO_2 based PSC via a low-temperature chemical bath deposition method [15]. Although the above mentioned methods have achieved comparable performance to the conventional high temperature processed counterparts, challenges remain for low-temperature processed TiO_2 photoanode materials, such as unfavorable crystallinity of TiO_2, poor adhesion to the substrate or poor connectivity between particles [15]. Such drawbacks produce unexpected charge recombination at imperfect interfaces and structural defects in the TiO_2 films.

A one-step approach is employed here to fabricate the designed amorphous titania nanowire thin film on the fluorine doped tin oxide (FTO) substrates for application as the electron transport layer (ETL) in PSCs. The titania evolved from nanoparticles to nanowires with increasing reaction time at low temperature (90 °C). A champion power conversion efficiency (PCE) of 14.67% was obtained, which is comparable to the high-temperature annealed (500 °C) analogues (anatase TiO_2 nanowires, ~14.06%). This work shows the effectiveness and feasibility of using low-temperature processed amorphous titanium oxide layers for electron transport in thin film optoelectronic devices.

2. Experimental

2.1. Synthesis of titania thin films on FTO glass

The laser-patterned FTO glass substrates (TEC8, Dyesol) were cleaned by ultrasonication with soap (5% Hellmanex in water), Milli-Q water, ethanol and acetone. The cleaned substrate (2 cm × 1 cm), with the FTO side facing down at an angle of 45° (the angle is not important for the preparation), was then immersed into a Teflon-lined autoclave containing a 25 mL potassium titanium oxide oxalate dihydrate (PTO, 23 mM, Sigma-Aldrich) aqueous solution; the autoclave was sealed and heated at 90 °C for 1–6 h. After being cooled, the films were rinsed with Milli-Q water and ethanol several times and then dried at 70 °C for 1 h in air. It should be pointed out the glass side of the FTO substrate was covered with Kapton tape when preparing titania films on the FTO side. After the reaction, the Kapton tape was removed and the glass was washed using absolute ethanol. Thus the glass side was clean and not expected to be covered with titania.

2.2. Device fabrication

289 mg PbI_2 (Sigma-Aldrich) and 100 mg CH_3NH_3I (home-made) (1:1 molar ratio) were dissolved in 0.5 mL N,N-diethylformamide (DMF, Sigma-Aldrich) to obtain the $CH_3NH_3PbI_3$ precursor solution. Gas-assisted spin-coating of the $CH_3NH_3PbI_3$ precursor solution [16] was conducted at 6500 rpm for 30 s. The substrate was spun at 6500 rpm and after 2 s a dry argon gas stream (60 psi) was blown over the film to accelerate the film crystallization, and the films were spun for another 30 s. The films were then annealed on a hotplate at 100 °C for 10 min.

The hole-transporting material (HTM) solution was prepared by dissolving 41.6 mg spiro-MeOTAD (Taiwan, Lumtec), 7.5 μL of a stock solution of 500 mg mL^{-1} lithium bis(trifluoromethylsulphonyl)imide in acetonitrile and 14.4 μL 4-*tert*-butylpyridine (Sigma-Aldrich) in chlorobenzene (0.5 mL). The HTM layer was coated on top of the perovskite film by spin-coating at 3000 rpm for 30 s. Finally, an 80 nm Au layer was thermally evaporated on top of the device to form the back contact.

2.3. Characterization

The morphology of the as-prepared samples was observed by a field emission scanning electron microscope (FE-SEM, Quanta 200F FEI) and a transmission electron microscope (TEM, FEI Tecnai F20). Crystallinity and phase identification of the samples were conducted using X-ray diffraction (XRD) (Bruker D8 Advance Diffractometer) equipped with Cu Kα radiation ($\lambda = 1.5418$ Å). The transmittance and absorbance spectra were obtained with a UV–vis–NIR spectrophotometer (Lambda 1050, Perkin-Elmer) installed with a 150 mm integrating sphere. Photocurrent-photovoltage (*J-V*) characteristics were recorded using a Keithley 2400 source meter under AM 1.5G illumination (100 mW cm^{-2}) provided by an Oriel solar simulator. Before each measurement, the exact incident light intensity was determined using a calibrated Si reference photodiode (Peccell Technologies). The cells were masked with a black metal aperture of 0.16 cm^2. The IPCE spectra were recorded as a function of wavelength from 380 to 800 nm on a Keithley 2400 source meter under the irradiation of a 300 W xenon lamp fitted with an Oriel Cornerstone™ 260 1/4 m monochromator. The time-resolved photoluminescence (PL) measurements were performed using a time-resolved setup built in-house. Samples were photoexcited by 532 nm laser pulses (30 ps FWHM, 1 μJ cm^{-2} per pulse) at a frequency of 50 Hz, and the signal was recorded at 780 nm with 10 nm bandwidth. The intensity-modulated photocurrent/photovoltage spectroscopy (IMPS/IMVS) measurements were conducted on an electrochemical workstation (Zahner, Zennium) with a frequency response analyzer under modulated light emitting diodes driven by a source supply (Zahner, PP211).

3. Results and discussion

3.1. Preparation process, intrinsic morphological and optical characteristics of various titania thin films

The one-step process is an effective strategy to prepare various TiO_2 nanostructures as efficient photoanodes for photovoltaic application [17–23]. In this work, the potassium titanium oxide oxalate dihydrate (PTO) is hydrolysed in water at low temperature (90 °C) for several hours, resulting in the formation of nanowire structures in the absence of any surfactants or other shape-directing agents. The reaction time was varied to control the morphology and geometry of the thin films. Fig. 1a–d shows top-view scanning electron microscopy (SEM) images of the titania layer formed at 90 °C for 1, 2, 3 and 6 h. In the initial stage (1 h,