RAPID COMMUNICATION

**TiO₂ nanotube arrays based flexible perovskite solar cells with transparent carbon nanotube electrode**

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**Abstract**
A solid-state, flexible solar cell based on titanium (Ti) foil/TiO₂ nanotubes (TNTs) with organic-inorganic halide perovskite absorber and transparent carbon nanotube electrode is demonstrated. TNT arrays together with an inherent blocking layer were simultaneously formed on Ti foil during one-step anodization. TNT arrays serve as deposition scaffold and electron conductor for perovskite absorber. Transparent conductive carbon nanotube network is laminated on top of perovskite and serves as hole collector as well as transparent electrode for light illumination. Under AM 1.5, 100 mW cm⁻² illumination, power conversion efficiency of 8.31% has been achieved, which is among the highest for TiO₂ nanotube based flexible solar cells. Interestingly, up to 100 mechanical bending cycles show little deterioration to the device performance, demonstrating good flexibility of the Ti foil based perovskite solar cells. The Ti foil based
solid-state, flexible perovskite solar cells have great potential for applications in building photovoltaics and wearable electronic devices. © 2014 Elsevier Ltd. All rights reserved.

Introduction

As a new member of the next generation photovoltaic materials, organometal halide perovskite (e.g., CH$_3$NH$_3$PbI$_3$, CH$_3$NH$_3$PbI$_3$$_x$Cl$_{3-x}$) was first demonstrated for efficient solar cells in 2009 [1], and soon become the most important candidate to replace silicon, with low material cost and high efficiency. Owing to the high light absorption coefficient ($1.5 \times 10^6$ cm$^{-1}$ at 550 nm) [2] and long electron-hole diffusion length ($\sim$100 nm for CH$_3$NH$_3$PbI$_3$ [3,4] and $\sim$1 $\mu$m for CH$_3$NH$_3$PbI$_3$$_x$Cl$_{3-x}$ [4]), perovskite solar cells have achieved a stunning success in a very short period in terms of efficiency, i.e., from 4% in 2009 [1] to 10% in 2012 [5,6], then 15% in 2013 [7] and 19.3% at present [8].

The rapid and significant progress in perovskite solar cell triggers vigorous research interest, as well as commercialization efforts. Flexibility is one of the development directions, which can be beneficial for both production (with roll-to-roll approaches) and applications (easy installation on buildings and integration on wearable devices). Flexible perovskite solar cells have been reported by a few groups since end of 2013 [9-14]. Polyethylene terephthalate (PET) coated by conductive indium tin oxide (ITO) was adopted as the flexible substrates [9-13]. PCBM and PEDOT:PSS were used as electron and hole transport layers, yielding efficiencies of 4.5% – 9.2% [9-12]. In addition, low-temperature processed ZnO layer has also been used as electron transport layer in flexible perovskite solar cells on PET substrate [13]. The efficiency limitation of the flexible perovskite solar cells on PET substrates may lie in the high series resistance of ITO on PET substrates. In contrast, conductive metal foils possess better conductivity and mechanical robustness compared to PET substrates. Furthermore, metal substrate can tolerate high temperature treatment for sintering TiO$_2$.

Among the electron transport materials used in perovskite solar cell, TiO$_2$ is still holding the efficiency record [8]. Mesoporous TiO$_2$ scaffold is also essential for solving the hysteresis problem of perovskite solar cells [15].

Titanium (Ti) foils with TiO$_2$ nanoparticles, nanotubes, or nanowires have been applied in flexible dye-sensitized solar cells (DSSCs) as photoanodes [16-23]. In particular, TiO$_2$ nanotube (TNT) arrays can be grown on Ti foil by a facile electrochemical anodization, which is a scaleable production technique. However, flexible DSSCs with TNT arrays have shown relatively poor performance with efficiencies lower than 4% [17,19] and all these devices required liquid electrolyte, which will cause sealing difficulty in large-scale production. To replace dye absorber in DSSCs, efficient perovskite absorbers will greatly increase the light absorption. More importantly, the monolithic all-solid-state device structure for perovskite absorber will render the flexible solar cells better performance stability during deformations. Recently Gao and co-authors reported perovskite sensitized liquid solar cells with TNTs on rigid FTO glass [24]. Fiber shaped, flexible perovskite solar cells have also been demonstrated with TiO$_2$ nanoparticle coated on stainless steel fibers, yielding efficiency of 3.3% [14]. However, solid-state flexible perovskite solar cells based on TiO$_2$ nanotubes have not been reported so far.

In Ti foil based perovskite devices, the opaque Ti foil hinders the light absorption from the photoanode, so the device will not work using a conventional metallic counter electrode and therefore a transparent counter electrode is required. Transparent graphene [25] and carbon nanotubes (CNT) [20-23,26,27] have been successfully employed as the counter electrode in DSSC devices. Recently, transparent CNT networks had been proved to be good hole conductor for perovskite solar cells [14,28]. These works inspired our proposed flexible perovskite solar cell architecture with Ti foil as a working electrode, TNT as mesoporous layer for perovskite loading and carbon nanotubes as hole conductor and transparent electrode for light illumination. To date, it is the first attempt of Ti metal foil substrate based flexible perovskite solar cell and a decent power conversion efficiency of 8.31% has been achieved.

Experimental

Fabrication of TiO$_2$ nanotube arrays

Two kinds of Ti foils with different thicknesses (125 $\mu$m, 99.7% purity, Sigma-Aldrich; 25 $\mu$m, 99.98% purity, Sigma-Aldrich) were employed. Prior to anodization, Ti foils were degreased ultrasonically in acetone, ethanol and deionized (DI) water for 20 min each and dried by air stream. Highly-ordered TiO$_2$ nanotube arrays were prepared by electrochemically anodization at 20 V for 10 min at room temperature (~20 °C). The anodizations were carried out with a two-electrode configuration with Ti foil as the working electrode and platinum gauze as the counter electrode. The electrolyte solution was ethylene glycol (extra pure, Merck) containing 0.3 wt% ammonium fluoride (98+%, Reagent, Sigma-Aldrich) and 2 vol% DI water. After anodization, the as-anodized TNT samples were rinsed in DI water to remove the electrolyte and then dried in air. For application in solar cells, the as-grown TNTs were subjected to thermal annealing at 450 °C for 3 h to convert amorphous titania into anatase phase. For better cell performance, the TNTs were also treated in 40 mM TiCl$_4$ aqueous solution at 70 °C for 10 h and then rinsed with ethanol and DI water.

Synthesis of carbon nanotubes

CNT network films were synthesized using the floating catalyst chemical vapor deposition (CVD) method using a tube furnace [29]. Ferrocene (0.36 M) as catalyst and sulfur (0.036 M) as growth promotion agent were dissolved in xylene to form a uniform precursor solution. The temperature for CVD was set to 1150 °C. Then 2500 sccm Ar and 600 sccm H$_2$ were introduced into the quartz tube as carrier
gas. When the temperature and gas flow stabilized, the precursor solution was injected into the quartz tube at a preheating zone of the furnace with a temperature of 180 °C. The precursor vaporized and was transported into the center zone of the furnace by the gas flow for CNT growth. CNTs grew from the floating Fe catalyst in the carrier gas flow. As shown in the Supporting materials (Fig. S1), the attained carbon nanotubes are mainly single and double-walled carbon nanotubes with diameters between 1 and 2 nm. After growth, the CNTs formed an aerosol carried by the gas flow to the end of the quartz tube with a temperature of 100-150 °C, where it was collected on a nickel foil. Individual nanotubes assembled into bundles with diameter of tens of nanometers and interweave to form a free standing CNT film.

Deposition of perovskite absorber

Perovskite absorber was deposited on TNT arrays by a sequential method. 1 M lead iodide (PbI2) were dissolved in N,N-dimethylformamide overnight under stirring condition at 70 °C. The PbI2 solution was spin coated on TNTs at 6000 rpm for 5 s, followed by drying on a hot plate at 70 °C for 30 min. In order to convert PbI2 into CH3NH3PbI3, the PbI2 loaded TNT samples were immersed in 8 mg mL−1 CH3NH3I solution in 2-propanol for 30 min. Subsequently, the samples were rinsed with 2-propanol and then dried at 70 °C for 30 min again.

Assembly of perovskite solar cell device

CNT films on nickel foil was lifted off by a taped substrate and transferred on the top of perovskite sensitized TNT/Ti foil [24]. Several drops of toluene were used to wet CNT film for improving the contact between CNTs and perovskite surface. After toluene vaporization, a hole transport materials, namely

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Fig. 1  Schematic of solid-state perovskite solar cells based on Ti foil/TiO2 nanotubes and carbon nanotubes.

Fig. 2  (a) XRD patterns of the phase structures of TiO2 nanotubes/Ti, PbI2/TiO2 nanotubes/Ti and perovskite/TiO2 nanotubes/Ti. TiO2, PbI2 and perovskite peaks are marked by black box, circle and star respectively and the rest peaks from Ti substrate; (b) cross-sectional morphology of perovskite/TiO2 nanotubes/Ti electrode; (c) tilted scanning electron image of CNT film covering partially on perovskite surface; (d) magnified top morphology of CNT covered perovskite.
spiro-OMeTAD \((2,2',7,7'-\text{tetrakis-}(N,N\text{-di-p-methoxyphenylamined})\) 9,9'-spirobifluorene) in chlorobenzene \((120 \text{ mg mL}^{-1})\) were spin coated on CNTs covered substrate with a speed of 4000 rpm for better hole collection. Prior to cell testing, both Ti foil and CNT electrodes were soldered for better electrical contact.

**Film characterization and cell testing**

The phase structure of the TNT arrays, the deposited PbI2 and perovskite films were investigated by X-ray diffraction (XRD, Bruker-AXS D8 Advance). The cross-sectional morphology of perovskite sensitized TNTs and top views of CNT covered perovskite layers were examined by field-emission scanning electron microscope (FESEM, JSM-7600). The photocurrent density-voltage \((J-V)\) performance of the cell devices was characterized using solar simulator (San-El Electric, XEC-301S) under AM 1.5 with illumination from the CNT side. The illumination area was determined by the black mask with an area of 0.16 cm\(^2\) (small area testing) and 0.36 cm\(^2\) (larger area for bending testing). Incident photon to current conversion efficiency (IPCE) was determined using PVE300 (Bentham), with a dual xenon/quartz halogen light source, measured in DC mode and no bias light used.

**Results and discussion**

The cell configuration is shown in Fig. 1. From bottom to top in sequence are Ti foil, TNT arrays loaded with perovskite absorber and CNT networks composite with spiro-OMeTAD. Dense TNT arrays grown on Ti foil by electrochemical anodization serve both as a scaffold for perovskite deposition and as an electron collector. CNT network acts as hole collector and transparent electrode. For better hole collection, the hole transport material spiro-OMeTAD is infiltrated in carbon nanotubes network [28]. Light comes from CNT side, as indicated by arrow in Fig. 1. Since Ti foil and CNT network are flexible materials, the integrated solar cell device is expected to show good flexibility.

Highly ordered TiO\(_2\) nanotubes arrays are formed on Ti foil by electrochemical anodization [30,31]. The as-anodized TNTs are amorphous in nature. To facilitate electron transport, amorphous nanotubes are converted into anatase phase by thermal annealing at 450 °C for 3 h, as shown in the XRD patterns in Fig. 2(a). CH\(_3\)NH\(_3\)PbI\(_3\) perovskite are formed on TNT arrays by a sequential deposition method [7]. In the first step, PbI\(_2\) was deposited on nanotubes by spin coating, as revealed by the two peaks at 12.72 ° and 39.52 ° in the XRD patterns Fig. 2(a)). Thereafter, soaking of PbI\(_2\) loaded nanotube substrates in CH\(_3\)NH\(_3\)I solution and subsequent drying process at 70 °C leads to formation of CH\(_3\)NH\(_3\)PbI\(_3\). The characteristics XRD peaks of CH\(_3\)NH\(_3\)PbI\(_3\) are indicated by black stars in Fig. 2(a). It is in well agreement with previous report [32].

Cross-sectional morphology of perovskite loaded TiO\(_2\) nanotubes is presented in Fig. 2(b). The tube arrays formed on Ti foil are ~300 nm in length and ~60 nm in diameter. A dense layer of perovskite nanocrystals with a size of 100-400 nm completely covers the nanotubes. The flexible CNT network is transferred on top of the perovskite layer as the counter electrode, as shown in the tilted SEM image of Fig. 2(c). The CNT transfer
procedure is described in previous report [28]. The CNT film is highly transparent with transmittance between 60% and 80% all over the CH$_3$NH$_3$PbI$_3$ absorption wavelength range from 300 to 800 nm (see Fig. S2 in Supporting information). The CNT network is closely adhered to the perovskite by van der Waal force. From the magnified top morphology of CNT/perovskite in Fig. 2(d), it shows that the bundled CNT networks are sparse with pores for light transmittance. In order to enhance hole collection in perovskite solar cells, spiro-OMeTAD is infiltrated into CNT networks by spin coating [28].

Noticeably, there is a very thin TiO$_2$ compact layer formed between the TNT arrays and Ti foil during anodization (Fig. 2(b)) [33–35]. The simultaneous anodic formation of the TiO$_2$ blocking layer and nanotube scaffold has great advantages. The one-step anodization exempts the complex fabrication process of sequential depositing blocking layer and meso-porous TiO$_2$ layers. It is also highly controllable with the ability of forming uniform coating over large area, which is desirable for large scale production.

The thickness of Ti foil affects the device flexibility. Herein, two kinds of Ti foils with different thicknesses (125 $\mu$m and 25 $\mu$m) were used in perovskite solar cell fabrication. For both thick and thin Ti foil based perovskite devices, TiCl$_4$ treatment was employed to improve the photovoltaic performance. TiCl$_4$ treatment has been widely used in dye-sensitized solar cells [36–38] and perovskite solar cells [5,7,28]. It fills the voids and cracks in TiO$_2$ blocking layer and therefore decreases recombination in solar cells. Fig. 3 shows the device performances of the TNT/CNT perovskite solar cells with different Ti foil thicknesses and with/without TiCl$_4$ treatment. The combined J–V curves are presented in Fig. 3(a) and the corresponding photovoltaic parameters are summarized in the table. Solar cells fabricated on 25 $\mu$m Ti foil exhibited higher photovoltage (0.83 vs. 0.70 V for non-TiCl$_4$-treated tubes; 0.99 vs. 0.78 V for TiCl$_4$-treated tubes) and improved fill factor (0.63 vs. 0.62 for non-TiCl$_4$-treated tubes; 0.68 vs. 0.62 for TiCl$_4$-treated tubes), in comparison to 125 $\mu$m Ti foil based solar cells. The Voc and fill factor improvement may be ascribed to the smaller surface roughness of the thinner Ti foil, as shown in Fig. S3 of the Supporting information. It is presumable that the smoother Ti surface improves the

![Image](image_url)

**Fig. 4** (a) Photograph of Ti foil/TNT and CNT based flexible perovskite solar cells; (b) combined J–V curves of flexible device with different bending cycles; (c) plot of photovoltaic parameters as a function of bending cycles.
flatness of perovskite layer and reduces the unfavorable current shunting, thus in return increases the Voc and fill factor.

As evident in Fig. 3(a), TiCl\textsubscript{4} treatment after anodization is beneficial to enhance all photovoltaic parameters, including photocurrent, Voc, fill factor and thus power conversion efficiency. Notably, Voc is greatly improved after TiCl\textsubscript{4} treatment (0.78 vs. 0.70 V for 125-μm-thick Ti; 0.99 vs. 0.83 V for 25-μm-thick Ti). It can be ascribed to the reduction of recombination sites by the newly formed nanoparticles from TiCl\textsubscript{4} treatment. The slight improvement of photocurrent can be also shown from the IPCE of perovskite solar cells with/without TiCl\textsubscript{4} treatment, as displayed in Fig. 3(b). From 400 nm to 700 nm, TiCl\textsubscript{4} treated TNTs exhibit higher IPCE, which indicates a higher charge separation efficiency thus results in photocurrent increase. Noticeably, the IPCE is relatively low at wavelength between 300 and 400 nm due to the strong light absorption of spiro-OMeTAD in this wavelength region (Fig. S2 in the Supporting information). Further improvement of photocurrent can be expected by adapting HTM materials with better transparency. For the 25-μm-thick Ti foils, the best perovskite solar cells with TiCl\textsubscript{4} treatment yield efficiency of 8.31%. The obtained efficiency is among the highest reported for flexible perovskite solar cells [10-13].

Besides photovoltaic performance, tolerance to mechanical bending is another important factor of consideration for flexible perovskite solar cells. A photograph of flexible TNT/CNT perovskite solar cell is shown in Fig. 4(a). The 25-μm-thick Ti foil based devices were used to investigate solar cell flexibility. The solar cell with length of 2.5 cm was bended to a bending radius of 0.75 cm by mechanical force up to 100 cycles. The dependence of the device performances on bending cycles is presented in Fig. 4(b and c). After 100 mechanical bending cycles, indicating their high flexibility.

Conclusions

In summary, flexible, solid-state perovskite solar cells based on Ti foil/TNTs and CNTs have been demonstrated. To our best knowledge, it is the first demonstration of flexible perovskite solar cells on Ti metal foil substrate. The Ti foil/TNTs act as scaffold for perovskite loading and electron transport layer, while the transparent CNT top electrode acts as hole collecting layer and light transmission. With 25 μm Ti foil and TiCl\textsubscript{4} treatment to TiO\textsubscript{2} nanotube arrays, power conversion efficiency up to 8.31% has been achieved. The solar cells on Ti foil maintain good performance after 100 mechanical bending cycles, indicating their excellent flexibility. Considering the high efficiency, good flexibility and simple fabrication technique, Ti foil/TNTs based flexible perovskite solar cells holds a promising future for roof-top photovoltaics and power sources for wearable devices.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.jnano.2014.11.042.

References

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