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Letter

Wire-shaped perovskite solar cell based on TiO₂ nanotubes

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Abstract

In this work, a wire-shaped perovskite solar cell based on TiO₂ nanotube (TNT) arrays is demonstrated for the first time by integrating a perovskite absorber on TNT-coated Ti wire. Anodization was adopted for the conformal growth of TNTs on Ti wire, together with the simultaneous formation of a compact TiO₂ layer. A sequential step dipping process is employed to produce a uniform and compact perovskite layer on top of TNTs with conformal coverage as the efficient light absorber. Transparent carbon nanotube film is wrapped around Ti wire as the hole collector and counter electrode. The integrated perovskite solar cell wire by facile fabrication approaches shows a promising future in portable and wearable textile electronics.

Keywords: wire-shaped, perovskite solar cell, TiO₂ nanotubes, carbon nanotubes

To date, photovoltaic devices have been extensively investigated and applied in rooftops and outdoor plants to convert sunlight into electricity. However, the common rigid substrates from commercial silicon solar cells and thin film solar cells limit their application in flexible and portable electronic devices. The new generation of solar cells, including dye-sensitized solar cells (DSSCs) [1], organic photovoltaics (OPV) [2] and perovskite solar cells [3], have potential for flexible planar devices based on polymer substrate or metal substrate due to their solution-based, non-vacuum processes [4–9]. Beside the flexible planar devices, wire-shaped photovoltaic devices with high flexibility and light-weight are also highly desired in modern electronics since they can be woven into electronic textile for portable and wearable electronic devices, for example, embedded into clothing, large-area flexible displays, and roll-up portable displays, sensing electronic skins [10].

Currently, wire-shaped solar cells have two main types of configuration structure, that is, in the form of dye-sensitized solar cells and organic solar cells. Wire-shaped DSSCs usually adopted stainless steel wire or Ti wire coated by a thin layer of dye-sensitized TiO₂ nanoparticles or nanotubes as the working electrode and carbon nanotube (CNT) fibers or graphene fibers as the counter electrode with infiltrating liquid electrolyte between two electrodes [11–15]. Nevertheless, the unstable liquid electrolyte is not favorable for wearable devices. The all-solid-state, wire-shaped organic solar cell was materialized in 2009 by coating of an electron transport...
layer (TiO2), photoactive layer (P3HT:PCBM) and hole transport layer (PEDOT:PSS) on a metal wire [16]. A relatively low conversion efficiency of 2.3%–3.27% has been achieved for OPV devices so far [16–18]. Apart from DSSCs and OPV, the perovskite solar cell is a very promising and intriguing candidate for wire-shaped photovoltaic devices due to its high conversion efficiency (highest efficiency is up to 20.1%) [19] and all-solid-state structure [20, 21]. So far, a fiber-shaped perovskite solar cell has only been reported by Peng’s group in 2014 [22]. A stainless steel fiber was used as the wire-shaped substrate by dip-coating with a compact block layer and mesoporous TiO2 nanoparticle scaffold, and followed by dip coating of a perovskite absorber layer and hole transport materials. A CNT sheet was wound on perovskite wire as the counter electrode and an efficiency of 3.3% was yielded [22]. Up to now, there has been no report about a wire-shaped perovskite based on TiO2 nanotubes. Furthermore, the simultaneous conformal formation of TiO2 nanotubes and compact TiO2 blocking layer on Ti wire by anodization will simplify the fabrication process of wire-shaped perovskite solar cells.

In our work, a wire-shaped perovskite solar cell based on TiO2 nanotube/Ti wire was demonstrated for the first time. A schematic illustration of its structure and fabrication process is shown in figure 1(a). Conformal formation of a TNT layer on Ti wire (125 μm in diameter) is achieved by a facile and controllable anodization. Subsequently, a perovskite layer was deposited on the TNT/Ti wire by a dipping process, including single-step dipping and sequential-step dipping. A compact perovskite absorber layer with good coverage was attained by sequential dipping processes in PbI2 and CH3NH3I solutions and CNT film was wrapped as the transparent counter electrode. The corresponding band alignment is presented in figure 1(b). A large open circuit voltage of 0.920 V and power conversion efficiency of 1.16% has been achieved. Further optimization is under investigation to improve the power conversion efficiency.

For wire-shaped perovskite solar cell, deposition of each layer on wires with good coverage and uniformity is critical for high photovoltaic performance. Dipping process is the main approach to deposit thin film on wire-based substrate. In this work, the method of electrochemical anodization is employed for conformal growth of TNT layer on Ti wire, as illustrated in figure 1(a). After anodization of Ti wire at 20 V for 10 min in fluoride containing electrolyte, a uniform layer of TNT arrays is formed on the outer surface of the Ti wire. The experimental details are given in the supporting information. Top-view FESEM images of TNTs on Ti wire are shown in figures 2(a) and (b). TiO2 nanotubes show a porous morphology, which will act as the deposition scaffold for perovskite formation. As evident from cross-sectional view in figures 2(c) and (d), highly-ordered TNT arrays were vertically grown on Ti wire. There is a compact TiO2 layer formed between TiO2 nanotubes and Ti substrate during anodization (as indicated in figure 2(d)), which acts as the blocking layer in perovskite solar cells. Therefore, anodization is a facile method to grow the porous TiO2 nanotubes and compact TiO2 layer simultaneously on Ti wire for perovskite solar cells.

In order to deposit the uniform perovskite layer on top of TiO2 nanotube layers, spin coating is adopted following the recipes reported for planar perovskite solar cells [9]. However, for a wire-shaped perovskite solar cell, spin coating is not ideal due to difficulties in penetrating the wire-shape. Dip coating is thus adopted to deposit perovskite on stainless steel fiber [22]. In comparison to spin coating, the dip coating method is not restricted by substrate shape and size, which enables large-scale production. In this work, two kinds of dip coating technique are investigated, including single-step dip coating in CH3NH3PbI3 solution and sequential-step dipping in PbI2 solution followed by CH3NH3I solution. The effects of different dipping process on the perovskite morphology and film coverage on Ti wire are studied systematically.

For the single-step dipping, different CH3NH3PbI3 precursor concentrations (10 wt.%, 20 wt.%, 30 wt.% and 40 wt. %)
in dimethylformamide (DMF) are utilized to deposit the perovskite layer. For illustration, figures 3(a) and (b) show the characteristic morphology of the perovskite film by single dipping at 30 wt.% concentration. Ti wire is partially covered by perovskite film at valley locations, as presented in figure 3(a). The perovskite crystals exhibit a branch-like network appearance, which comprises small nanocrystals with sizes of a few tens to 100 nm (see figure 3(b)). Figures S1(a)–(d) of the supporting information give more details about perovskite morphology formed at different concentrations. At a lower precursor concentration of 10 wt.%, the coverage of perovskite is quite poor. By increasing the concentration from 10 wt.% to 40 wt.%, the perovskite coverage and uniformity is greatly improved, while none of the single dipping conditions result in complete coverage. The partial coverage of perovskite leads to severe shunting problems for this kind of solar cell device and thus only a small open-circuit voltage is attainable, as shown in figure S1(e) of the supporting information.

Sequential deposition on a planar substrate by spin coating has been demonstrated to be an efficient route to produce a high-performance perovskite layer [23]. To improve the quality of perovskite layer on the wire-shaped substrate, sequential step dipping coating of Ti wire in PbI2 and CH3NH3I solution is also studied for the first time in this work. The corresponding experimental procedure is detailed in the supporting information. Figures 3(c)–(f) present the top and cross-sectional morphology of the perovskite layer formed by sequential dipping. As evident from figure 3(c), the coverage of perovskite on Ti wire is greatly improved in comparison to that by single dipping. The compact perovskite nanocrystals have a cubic shape with sizes of ~150–500 nm (figure 3(d)). Cross-sectional views in figures 3(e) and (f) confirm the conformal formation of a perovskite layer on top of TNT arrays with good uniformity, and the layer thickness is ~200–300 nm. Therefore, sequential dipping is more suitable to produce perovskite layer on Ti wire.

Subsequently, perovskite-coated TiO2 nanotube/Ti wire by sequential dipping is assembled into the solar cell device. Semi-transparent, flexible CNT film is wrapped on the perovskite layer as the hole collector as well as transparent counter electrode, as displayed in the tilted FESEM image in figure 4(a). The CNT film is very loose and porous (see figure 4(b)), which allows light illumination from the CNT side, as reported previously [9, 24]. The photograph of a wire-shaped perovskite solar cell prototype is presented in figure S2 in the supporting information. The two electrodes from CNT film and Ti wire are soldered for better conductivity. Photocurrent density–voltage (J–V) curves are recorded in forward and reverse scan directions at various scan speeds (scan speed 0.2 V s−1) and showed negligible hysteresis effect [25]. The J–V curves recorded at forwards and reverse scans

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**Figure 2.** FESEM images of TiO2 nanotube arrays grown on Ti wire: (a) and (b) are top-view morphology and (c) and (d) are cross-sectional morphology under low magnification (a) and (c), and high magnification (b) and (d).
are shown in figure S3. Herein, the typical $J$–$V$ characteristics under AM 1.5G, one sun illumination and dark conditions are shown in figure 4(c). A power conversion efficiency of 1.16% with a $V_{oc}$ of 0.92 V, $J_{sc}$ of 2.62 mA cm$^{-2}$ and $FF$ of 0.48 was obtained. $V_{oc}$ of 0.92 V is much higher than that achieved from the single dipping technique for wire-shaped perovskite solar cells ($V_{oc}$ of 0.63 V is reported) [22]. The large $V_{oc}$ results from the low recombination rate, as determined from the dark $J$–$V$ curve in figure 4(c), which is in turn due to the good coverage and uniformity of the perovskite layer by the sequential dipping process (see figures 3(c) and (d)). The small $J_{sc}$ is affected by three factors. The first factor is low hole collection efficiency by the CNT film. The infiltration of the hole transport material spiro-OMeTAD in the CNT film can improve the hole collection efficiency and thus photocurrent [24]. The second factor is the light absorption due to back-illumination from the CNT side in the perovskite solar cell wires. The third factor is the incomplete coverage of the perovskite layer and its smaller thickness than the optimal thickness. Further optimization towards perovskite film deposition and the spiro-OMeTAD infiltration process will further enhance the photocurrent density and thus the power conversion efficiency. These are currently under investigation.
In summary, wire-shaped perovskite solar cells based on TiO$_2$ nanotube/Ti wire and CNT film are demonstrated. TNT arrays grown on Ti wire conformally by anodization serve as the working electrode and the deposition scaffold for perovskite formation. Sequential step dipping is determined as a suitable route to synthesize a cubic perovskite layer on TiO$_2$ nanotube/Ti wire with good coverage and uniformity. To our best knowledge, it is the first demonstration of a wire-shaped perovskite solar cell device based on TNT/Ti wire with a sequentially dipped perovskite layer. The integrated Ti/TiO$_2$ nanotube/perovskite/CNT solar cell wire exhibited a power conversion efficiency of 1.16%. The wire-shaped perovskite solar cell by facile fabrication processes has a promising future for application in wearable textile electronics.

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