Polymer photovoltaic wires based on aligned carbon nanotube fibers†

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Compared with the conventional planar structure, a wire-shaped polymer solar cell which is weavable exhibits unique and promising applications. However, it is rare to realize such a useful structure in polymer solar cells due to the difficulty in finding appropriate electrodes. Herein, we have fabricated polymer photovoltaic wires by using aligned carbon nanotube fibers as electrodes. The high flexibility, high electrical conductivity, and elaborate nanostructure of the nanotube fiber electrode enables an effective charge separation and transport. The resulting wire cell showed an open-circuit voltage, short-circuit current density and fill factor of 0.42 V, 0.98 mA cm⁻² and 0.36, respectively, which produce an energy conversion efficiency of 0.15%.

Introduction

Organic photovoltaic wire has recently attracted increasing interest due to the unique advantage of being weavable compared with a conventional planar structure. In the case of a wire structure, dye-sensitized solar cells have been widely explored, while polymer solar cells are rare although they can be more conveniently fabricated through a solution process without the use of a liquid electrolyte in the device, which enables a higher stability during the use. This fact may be explained by the different requirements in electrodes. A wire is typically made by twining two wire electrodes, such as metal wires or polymer fibers coated with conductive layers on the outside. Both of them are relatively rigid with smooth surfaces, which are fine for dye-sensitized solar cells due to the use of a liquid electrolyte in the device, which enables a higher stability during the use. However, it remains challenging for polymer photovoltaic wires as the resulting ineffective interface between the two rigid wire electrodes can not provide an effective charge separation and transport. Therefore, new electrodes with a high flexibility and elaborate surface are urgently required to produce polymer photovoltaic wires.

Recently, aligned carbon nanotube (CNT) fibers have been widely investigated due to their combined excellent properties, such as light weight, good flexibility, high electrical conductivities, high mechanical strengths and high electrocatalytic activities. In addition, the elaborate nanostructure on the surface of CNT fibers can also improve the charge separation and transport. They could be used as either working or counter electrodes, or even as the conductive substrates for both working and counter electrodes in dye-sensitized solar cells.

On the other hand, an interpenetrating network between polymeric donor and fullerene acceptor was generally designed to enhance the charge separation and transport due to a high interfacial area in polymer photovoltaics. Although this structure can decrease the diffusion distance of excitons toward the heterojunction interface to reduce the free charge recombination, a large efficiency loss resulted from inefficient charge transport in the active polymer layer with a disordered bulk heterojunction structure. Therefore, a lot of efforts have been made to increase the charge transport ability by optimizing the morphology of donor–acceptor interfaces, e.g., aligned semiconductive nanotubes, nanorods and nanowires including titanium dioxide and zinc oxide were introduced to the hybrid organic–inorganic photoactive layer.

Herein, aligned CNT fibers have been developed as electrodes to fabricate polymer photovoltaic wires. Fig. 1a and b schematically show the structure of a typical wire cell in which a CNT fiber is twined with a TiO₂ nanotube-modified Ti wire where poly(3-hexyl-2,5-thiophene) (P3HT) and (6,6)-phenyl-C₇₁ butyric acid methyl ester (PC₇₀BM) are used as photoactive...
the electrons are transported through PC70BM or TiO2 and dipping it into a TiO2 colloid (TPP3, purchased from Dalian titanium dioxide nanoparticles was coated onto a Ti wire by

stress–strain curves were obtained from a Shimadzu S-4800 operated at 1 kV) and TEM (JEOL JEM-2100F operated at 200 kV). The height of the TiO2 nanotubes was designed to increase the charge transport capability, and they were grown on a Ti wire by electrochemical anodic oxidation.16–19 The Roya...
nanotube arrays could be controlled from 350 nm to 7 \mu m by tuning the time of anodic oxidation from 1 to 30 min. The array height plays a critical role in the performance of the polymer photovoltaic wires and will be discussed later. The anodizing oxidation time of 5 min is first investigated. Fig. 2b and d show that the TiO2 nanotubes are stably attached on the Ti wire. The diameters of TiO2 nanotubes range from 40 to 80 nm (Fig. 2e), and the height of the TiO2 nanotube array is calculated as ~1.7 \mu m from SEM images. Fig. 2f further shows that the TiO2 nanotubes are perpendicularly aligned on the Ti wire.

The polymer photovoltaic wire was then assembled by twisting a CNT fiber and a modified Ti wire coated with a photoactive P3HT/PC70BM layer. Fig. 3a shows a representative SEM image in the middle part of a wire cell with a uniform structure. Due to the high tensile strength and high flexibility of the CNT fiber, the two fiber electrodes could be tightly twined with a good surface contact (Fig. 3b and c), which was critically important for the effective separation and transport of charges. Fig. 3e further shows that the CNT fiber maintained its structural integrity when it was bent during the twining process. The photovoltaic components were also found to be efficiently infiltrated into the array and uniformly dispersed among the TiO2 nanotubes (Fig. 3d and S3†). The polymer photovoltaic wires exhibited a high flexibility and weavability, and could be easily made into a knot (Fig. 3e) or integrated into the other textiles.

The photovoltaic performance of the wire cell was characterized under AM 1.5 illumination (light intensity of 100 mW cm\(^{-2}\)). The power conversion efficiency (\(\eta\)) is calculated by the equation of \(\eta = FF \times V_{oc} \times J_{sc} \times P_{in}\), where FF, \(V_{oc}\), \(J_{sc}\) and \(P_{in}\) represent fill factor, open-circuit voltage, short-circuit current density and incident light power density, respectively. The effective area was obtained by multiplying the length and diameter of the photovoltaic wire. The values of \(V_{oc}\), \(J_{sc}\) and FF were obtained as 0.42 V, 0.98 mA cm\(^{-2}\) and 0.36, respectively, which produced an \(\eta\) of 0.15% (Fig. 4a). As a comparison, if a metal wire such as an aluminum wire (diameter of 28 \mu m) was used in replacement of the CNT fiber, obvious gaps were observed between two electrodes (Fig. S4†), and no photocurrents were produced in the resulting wire cell. To better understand the photovoltaic wire, more control experiments were made. If a thin layer of TiO2 nanoparticles was used to replace the nanotubes on the Ti wire (Fig S5†), a decreasing photocurrent of 0.03 mA cm\(^{-2}\) was obtained (Fig. S6†). If a Ti wire coated with a thin layer of TiO2 film or a bare Ti wire was twined with the CNT fiber (Fig. S7†), almost no photocurrent was generated. These results show that the nanostructured surface on the electrode is critically important for the effective charge separation and transport, while the aligned TiO2 nanotubes further increase the cell performance. On the other hand, when no PC70BM was used in the photovoltaic layer, \(V_{oc}\), \(J_{sc}\), FF and \(\eta\) were 0.36 V, 0.17 mA cm\(^{-2}\), 0.31 and 0.02%, respectively. The introduction of PC70BM as the acceptor can efficiently enhance the separation of electron–hole pairs and the transport of electrons, although the TiO2 nanotubes may also transport the electrons.

To investigate the dependence of the photovoltaic performance on the thickness of the photoactive layer, Ti wires with different anodizing times were used to fabricate the polymer photovoltaic wires. The heights of the TiO2 nanotube arrays were increased from 350 nm to 1.7 \mu m, 3 \mu m, and 7 \mu m (Fig. 5) when the anodizing time was increased from 1 to 5, 10 and 30 min, respectively. Accordingly, \(J_{sc}\) was first increased from 0.5 to 0.98 and then decreased to 0.34 and 0.24 mA cm\(^{-2}\), and \(\eta\) was also increased from 0.06% to 0.15% and then decreased to 0.04% and 0.03% (Fig. 4b). This phenomenon can be explained by the different morphologies and lengths of TiO2 nanotubes. No uniform tubular structure had been formed during the growth for 1 min (Fig. 5a). Although the height of the TiO2 nanotubes was appropriate for a polymer cell, it was difficult for P3HT to be effectively infiltrated and uniformly dispersed, which produced low power conversion efficiencies. On the other hand, when the TiO2 nanotube array was equal to or thicker than 3 \mu m with an anodizing time of 10 min or longer, it became difficult for effective light harvesting, which increased the recombination.
between electrons and holes and also gave low power conversion efficiencies, although they owned an integrated tubular structure (Fig. 5c and d). The optimal anodizing time was found to be 5 min with a thickness of the TiO$_2$ nanotube array of ~1.7 μm. The stability of the polymer photovoltaic wires was also studied, and the value of $\eta$ remained almost unchanged in five days. More efforts are underway to further improve the power conversion efficiency and other performances.

Due to the unique structure, the parameters of the polymer photovoltaic wires remained almost unchanged under different incident angles with the same light intensity (Fig. 4c). Therefore, they can be efficiently used throughout the day. In addition, the output current and voltage can be further tuned to meet various applications by connection in series and in parallel (Fig. 4d), respectively. For instance, two photovoltaic wires with $V_{oc}$ of 0.46 and 0.49 V were connected in series to produce a $V_{oc}$ of 0.91 V, almost the sum of the two individual cells. Two wire cells with $I_{sc}$ of 8.5 and 9.7 μA were connected in parallel to produce an $I_{sc}$ of 17.2 μA, almost the sum of the two individual cells.

**Conclusion**

In summary, polymer photovoltaic wires have been realized on the basis of spun CNT fibers as the electrode, and a maximum energy conversion efficiency of 0.15% is obtained. Although the cell efficiency is currently low, this work provides an effective route to the development of wire-shaped polymer solar cells. More efforts will be paid to improve the photovoltaic performance by further increasing the electrical properties of the CNT fiber and tuning the morphology and structure of the titanium dioxide nanotube.

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**Notes and references**