Carbon Nanostructured Fibers As Counter Electrodes in Wire-Shaped Dye-Sensitized Solar Cells

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ABSTRACT: Carbon nanotubes (CNT), core–sheath CNT/reduced graphene oxide nanoribbon (RGONR), CNT/RGO composite, and RGO fibers have been compared as counter electrodes to fabricate novel dye-sensitized solar cells. For the I−/I3− electrolyte, the core–sheath CNT/RGONR fiber shows the best catalytic activity, which in turn produces the highest energy conversion efficiency of 5.64%. In contrast, for the organic T2+/T2− electrolyte, the highest energy conversion efficiency has been produced from the CNT fiber counter electrode with the maximal value of 4.78%. The different electrocatalytic activities among these four carbon nanostructured fibers on the two typical electrolytes of I−/I3− and T2+/T2− have been carefully investigated in this work.

INTRODUCTION

With the rapid advancement in microelectronic technology, miniaturized electronic products have attracted increasing attention and may dominate our life in the near future. To this end, it is necessary to develop miniature power systems with low cost, high efficiency, light weight, and high flexibility as the conventional silicon-based technologies cannot effectively meet them. The silicon-based solar cells are generally produced under high vacuum and appear in heavy plates. In contrast, dye-sensitized solar cells (DSCs), the next-generation photovoltaic devices, were fabricated by an easy solution process and could also be made into flexible structures. The DSCs had currently achieved high energy conversion efficiencies up to 12.3%. Therefore, the development of high-performance DSCs represents a new and general strategy to solve the above problem.

A typical DSC is composed of a working electrode, counter electrode, and electrolyte. The working electrode has been generally prepared by coating a dye-sensitized nanoporous TiO2 film on a transparent conductive substrate, while the counter electrode is formed by depositing a thin layer of platinum film also on a conductive substrate. The two electrodes play critical roles on the photovoltaic performances of DSCs; for example, the catalytic activities of counter electrodes greatly affect the short-circuit currents. A redox couple of I−/I3− is mostly studied as the electrolyte due to the low cost and easy preparation. However, some obvious disadvantages including low stability (it is corrosive to the metal-based current collectors such as copper and silver, and iodine may be easily sublimated) and absorption to the visible light may have greatly limited the practical application. Therefore, many efforts had also been paid to find alternative redox couples such as Co3+/Co2+, TEMPO/TEMPO+, T2+/T2−, and Br+/Br−. Among them, the organic T2+/T2− electrolyte had recently attracted extensive attention because it is noncorrosive with negligible light absorption. This organic electrolyte is particularly promising to the flexible DSCs for various portable electronic devices.

It is also critical to match the counter electrode according to the electrolyte to further improve the photovoltaic performances of DSCs. In other words, the same counter electrode may demonstrate different catalytic activities on different electrolytes. For instance, platinum has been widely explored for a high catalytic activity in the I−/I3− electrolyte, although it showed a much lower activity on the T2+/T2− electrolyte. Besides the conventional platinum electrode, many efforts have been recently paid to develop other electrode materials including conductive polymers (e.g., poly (3,4-ethylenedioxythiophene), polyaniline, and polypyrrole), carbon materials (active carbon, mesoporous carbon, carbon
nanotube (CNT), and graphene), and inorganic compounds. In particular, carbon nanomaterials such as CNT and graphene were mostly investigated for promising candidates due to large surface areas and remarkable electronic and catalytic properties. Currently, the DSCs are generally made into planar structures that remain challenging to many portable electronic facilities such as wearable devices. To this end, wire-shaped DSCs have been recently proposed with unique and promising advantages of being lightweight and woven into textiles (similar to the chemical fibers) compared with the conventional planar structure. In a typical fabrication, two fibers as working and counter electrodes are twisted together to form the wire-shaped DSCs. The electrolyte is infiltrated into two fiber electrodes and among them. Similar to the film-structured DSCs, the selection of the matching fiber counter electrode and electrolyte is critically important to produce high energy conversion efficiencies in DSCs, although it remains unavailable for a systematical study.

Herein a family of carbon nanostructured fibers based on CNT and reduced graphene oxide (RGO) has been studied as counter electrodes to fabricate wire-shaped DSCs with the same Ti wire working electrode. The core–sheath CNT/RGO fiber was found to exhibit the highest energy conversion efficiency for the \( \Gamma^- /I_3^- \) electrolyte, while the bare CNT fiber produced the highest energy conversion efficiency for the \( T^-/T_2^- \) electrolyte. For both \( \Gamma^- /I_3^- \) and \( T^-/T_2^- \) electrolytes, the RGO fiber showed the lowest energy conversion efficiency mainly due to a low electrical conductivity.

## Experimental Section

### 1. Materials and Reagents

Phosphoric acid, sulfuric acid, potassium permanganate, hydrogen peroxide (30% in water), hydrogen iodide, ethylene glycol, iodine, and calcium chloride were all obtained from Sinopharm Chemical Reagent, China. Graphite powder (40 μm) was ordered from Qingdao Henglide Graphite, China. Ammonium fluoride and S-mercaptop-1-methyltetrazole were provided by Aladdin Reagent, China. Titanium wire (diameter of 127 μm), platinum wire (diameter of 25 μm), and ethylene carbonate were obtained from Alfa. Tetramethylammonium hydroxide (10% in methanol) was ordered from TCI. The dye of N719, that is, RuL2(NCS)2 (L = 4,4′-dicarboxylate-2, 2′-bipyridine), was provided by Heptachroma, China. The synthesis of the organic redox couple of \( T^-/T_2^- \) (Scheme 1) was described elsewhere.

![Scheme 1. Structure of Redox Couple (T- and T2-)](image)

### 2. Synthesis of Carbon Nanostructured Fibers

Spinnable CNT arrays were used to fabricate wire-shaped DSCs. For the convenience of measurements, the wire-shaped DSCs were prepared through a wet-spinning method by injecting a GO dispersion (2 wt %) into a coagulation bath with an injecting speed of 100 μL/min (diameter of syringe needle, 410 μm). The coagulation bath was prepared by mixing 5 wt % CaCl2 solution in ethanol/water (1:3 v/v). After immersion in the coagulation bath for 30 min, the GO fibers were transferred into ethanol and water baths to remove the residual coagulation solution and dried at room temperature. The GO fibers were then obtained by reducing the GO fibers in the HI aqueous solution (45 wt %) at 80 °C for 8 h, followed by washing with deionized water and drying for 12 h.

### 3. Fabrication of Wire-Shaped Dye-Sensitized Solar Cells

TiO2 nanotube arrays were synthesized by electrochemical anodization of Ti wires in a fluoride-containing electrolyte. Ti wires were sonicated successively in acetone and isopropyl alcohol and then rinsed with ethanol before drying. Typically, the anodization occurred at 0.3 wt % NH4F/ethylene glycol solution containing 8 wt % H2O and a voltage of 60 V in a two-electrode electrochemical cell with a Pt sheet as a counter electrode for 6 h. The anodized Ti wires were rinsed with deionized water and then annealed in air at 500 °C for 1 h. They were then immersed in a 0.1 M TiCl4 aqueous solution at 70 °C for 30 min and annealed again in air at 450 °C for 0.5 h. The treated wires were cooled to 120 °C before being immersed in a 0.3 mM N719 solution of dehydrated acetonitrile and tert-butanol (v/v 1/1) for 16 h. The carbon nanostructured fiber was twisted around the dye-absorbed working electrode with a screw pitch of ~1 mm to form wire-shaped DSCs. For the convenience of measurements, the resulting wire-shaped DSCs could be sealed in a glass capillary (diameter of 0.5 mm). The two electrodes were connected to the external circuit by indium, and the redox electrolyte was finally injected through the capillary force.

### 4. Characterization

The structures were characterized by TEM (JEOL JEM-2100F operated at 200 kV), AFM (SHIMADZ SPM-9500J3), field-emission scanning electron microscopy (Hitachi FE-SEM S-4800 operated at 1 kV), and
Raman spectroscopy (Renishaw inVia Reflex with excitation wavelength of 632.8 nm and laser power of 20 mW). J−V curves were recorded on a Keithley 2400 Source Meter under illumination (100 mW/cm²) of simulated AM1.5 solar light coming from a solar simulator (Oriel-Sol3A 94023A equipped with a 450 W Xe lamp and an AM1.5 filter). The light intensity was calibrated using a reference Si solar cell (Oriel-91150). Electrochemical impedance spectroscopy (EIS) was carried out by an electrochemical workstation (CHI660a, CH Instruments) in dark. The cyclic voltammetry was performed in an acetonitrile solution containing 0.5 mM I₂, 5 mM LiI, and 0.05 M LiClO₄ with a scan rate of 50 mV s⁻¹ through a three-electrode setup. For the T⁺/T₂ electrolyte, it was composed of 5 mM T⁺, 0.5 mM T₂, and 0.1 M LiClO₄ in an acetonitrile solution.

■ RESULTS AND DISCUSSION

Figure 1 has compared the structures of CNT fiber, core−sheath CNT/RGONR fiber, CNT/RGO composite fiber, and RGO fiber by scanning electron microscopy (SEM). These nanostructured fibers shared a uniform diameter of ~33 μm. Figure 1a,b shows SEM images of a bare CNT fiber at different magnifications, and the CNT is highly aligned along the spinning direction. Figure 1c shows SEM image of a core−sheath CNT/RGONR fiber at low and high magnifications, respectively. (c,d) Core−sheath CNT/ RGONR fiber at low and high magnifications, respectively. (e,f) CNT/ RGO composite fiber at low and high magnifications, respectively. (g,h) RGO fiber at low and high magnifications, respectively.

RGO fiber by scanning electron microscopy (SEM). These nanostructured fibers shared a uniform diameter of ~33 μm. Figure 1a,b shows SEM images of a bare CNT fiber at different magnifications, and the CNT is highly aligned along the spinning direction. Figure 1c shows SEM image of a core−sheath CNT/RGONR fiber with smoother outer surface compared with the bare CNT fiber. Figure 1d further demonstrates that the CNT is highly aligned in the core and the RGONR sheets are covered on the aligned CNT core to form a thin and uniform sheath. Figure 2 in the Supporting Information shows a representative HRTEM image of a RGONR with width of ~40 nm. In contrast, the CNT/RGO composite fiber exhibits an obvious rippled structure on the surface (Figure 1f). At higher magnification, the CNT remains highly aligned with RGO sheets being connected among them (Figure 1f).

Figure 2. SEM images of the wire-shaped DSCs. (a,b) Electrochemically anodized TiO₂ nanotube arrays on a Ti wire at low and high magnifications, respectively. (c) Typical wire-shaped DSC by twisting a CNT fiber around the anodized Ti wire.

Figure 3. Cyclic voltammograms of CNT fiber, core−sheath CNT/ RGONR fiber, CNT/RGO composite fiber, and RGO fiber in the I⁺/ I₃⁻ electrolyte. The cyclic voltammetry was performed in an acetonitrile solution containing 0.1 M LiClO₄, 5 mM LiI, and 0.5 mM I₂ with a scan rate of 50 mV s⁻¹ through a three-electrode setup.

Figure 1. SEM images of CNT fiber, core−sheath CNT/RGONR fiber, CNT/RGO composite fiber, and RGO fiber. (a,b) CNT fiber at low and high magnifications, respectively. (c,d) Core−sheath CNT/ RGONR fiber at low and high magnifications, respectively. (e,f) CNT/ RGO composite fiber at low and high magnifications, respectively. (g,h) RGO fiber at low and high magnifications, respectively.
Although the modified TiO2 nanotubes-modified Ti wire was then wound with the carbon nanostructured fiber to produce a wire-shaped DSC. Figure 2c shows the twisted structure of a typical wire-shaped DSC with a pitch distance of ~1 mm that had been mainly studied in this work. Although the modified Ti wire working electrode was relatively rigid, the carbon nanostructured fibers were flexible and could be closely twisted with the Ti wire. The resulting good and stable contacts between the two electrodes are important for the rapid charge transportation with high-energy conversion efficiencies and high stability during use.

The CNT fiber, core−sheath CNT/RGONR fiber, CNT/RGO composite fiber, and RGO fiber had been further studied by Raman spectroscopy (Figure S4 in the Supporting Information). All fibers exhibited a D band at ~1325 cm$^{-1}$ and G band at ~1585 cm$^{-1}$. The intensity ratio of the D to G peaks ($I_D/I_G$) has been generally accepted to reflect the degrees of graphitizations and defects in carbonaceous materials. The $I_D/I_G$ value had been further increased to 1.25 for the core−sheath CNT/RGONR fiber as the Raman spectra were recorded mainly at their outer surfaces, where more RGO sheets had been produced than the CNT/RGO composite fiber. As expected, the bare RGO fiber showed the highest $I_D/I_G$ value of 1.45.

Cyclic voltammetry was first carried out in two different electrolytes under the same condition to study the electrocatalytic activities of four carbon nanostructured fibers. Figure 3 has compared them in the redox couple of $I^-/I_3^-$, and the cyclic voltammogram of platinum wire is shown in Figure S5 in the Supporting Information. Two typical pairs of redox peaks are observed for these fiber electrodes. The left and right pairs correspond to eqs 1 and 2, respectively.

$$I_3^- + 2e^- \leftrightarrow 3I^-$$  \hspace{1cm} (1)

$$3I_2^+ + 2e^- \leftrightarrow 2I_3^-$$  \hspace{1cm} (2)

The left pairs had been generally used to study the electrocatalytic activities of counter electrodes in catalyzing the $I_3^+/I^- \rightarrow 1$. A lower peak-to-peak voltage separation ($V_{pp}$) indicated a higher catalytic activity.43 Obviously, the core−sheath CNT/RGONR fiber exhibited the lowest $V_{pp}$ value, while the RGO fiber showed the highest $V_{pp}$ value. The $V_{pp}$ values for the CNT fiber and CNT/RGO composite fiber were located between them. Therefore, the catalytic activities for the $I^-/I_3^-$ redox were continuously increased from RGO fiber, CNT/RGO composite fiber, CNT fiber, to core−sheath CNT/RGONR fiber. The highest catalytic activity of the core−sheath CNT/RGONR fiber had been produced by effectively combining the high electrical conductivity in the aligned CNT core and many active edge sites for catalysis in the RGONR sheath. The bare RGO fiber showed the lowest activity due to the low conductivity of ~150 S/cm compared with ~310 S/cm of the aligned CNT fiber, ~380 S/cm of core−sheath CNT/RGONR fiber, and ~320 S/cm of CNT/RGO composite fiber.

### Table 1. Photovoltaic Parameters in Figure 5

<table>
<thead>
<tr>
<th>counter electrode</th>
<th>$V_{oc}$/mV</th>
<th>$J_{sc}$/mA cm$^{-2}$</th>
<th>FF</th>
<th>$η$/%</th>
</tr>
</thead>
<tbody>
<tr>
<td>CNT fiber</td>
<td>707</td>
<td>11.56</td>
<td>0.55</td>
<td>4.47</td>
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<tr>
<td>core−sheath CNT/RGONR fiber</td>
<td>713</td>
<td>11.30</td>
<td>0.70</td>
<td>5.64</td>
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<tr>
<td>CNT/RGO composite fiber</td>
<td>714</td>
<td>10.48</td>
<td>0.40</td>
<td>3.02</td>
</tr>
<tr>
<td>RGO fiber</td>
<td>683</td>
<td>9.47</td>
<td>0.31</td>
<td>2.02</td>
</tr>
</tbody>
</table>
RGO composite fiber. Note that the resistances for the RGO fiber, CNT fiber, CNT/RGO composite fiber, and core–sheath CNT/RGONR fiber were 3900, 1900, 1800, and 1540 $\Omega$ at the same length of 5 cm and radius of 16.5 $\mu$m, respectively. The bare RGO fiber that was composed of much larger RGO sheets exhibited less active edges compared with the RGO nanoribbons in the core–sheath CNT/RGONR fiber.

Figure 4 has further compared the four carbon nanostructured fibers in the organic $\Gamma^−/T_2^+$ redox, and the corresponding cyclic voltammogram of platinum wire is displayed in Figure S6 in the Supporting Information. Typically, a pair of redox peaks had been observed for the redox reaction, that is, $2\Gamma^− \leftrightarrow T_2^+$.$^2e^−$. The obvious redox peaks had been detected for the CNT fiber, and they are not distinct for the core–sheath CNT/RGONR and CNT/RGO composite fibers. In the case of the RGO fiber, almost no redox peaks could be found from the cyclic voltammogram. Increasing catalytic activities were concluded from RGO fiber, core–sheath CNT/RGONR fiber, CNT/RGO composite fiber to CNT fiber for the $\Gamma^−/T_2^+$ redox. Similar to the $\Gamma^−/I_3^−$ redox, the RGO fiber exhibited the lowest activity mainly due to the low conductivity. However, different from the $\Gamma^−/I_3^−$ redox, here the CNT fiber showed the highest catalytic activity. It had been found that CNT exhibited higher catalytic activities for the $\Gamma^−/T_2^+$ redox compared with RGO sheets.$^{44,45}$ For the core–sheath CNT/RGONR and CNT/RGO composite fibers, the existence of RGO sheets may hinder the infiltration of the organic $\Gamma^−/T_2^+$ redox into fibers, so lower catalytic activities were observed.

A series of wire-shaped DSCs had been fabricated by twisting a carbon nanostructured fiber around the modified Ti wire. Figure 5 has compared the $J−V$ curves based on the CNT fiber, core–sheath CNT/RGONR fiber, CNT/RGO composite fiber, and RGO fiber with the $\Gamma^−/I_3^−$ electrolyte. The photovoltaic parameters including open-circuit voltage ($V_{OC}$), fill factor (FF), short-circuit current density ($J_{SC}$), and photovoltaic conversion efficiency ($\eta$) are summarized in Table 1. The core–sheath CNT/RGONR fiber counter electrode showed the highest $\eta$ of 5.64%. The main difference lied in that the core–sheath CNT/RGONR fiber exhibited much higher FF of 0.70 compared with 0.55 for the bare CNT fiber, 0.40 for the CNT/RGO composite fiber, and 0.31 for the RGO fiber. The above difference can be explained by the highest catalytic activity of the core–sheath CNT/RGONR fiber in the $\Gamma^−/I_3^−$ redox, which agrees with the cyclic voltammetry. The corresponding $J−V$ curve based on the platinum wire in this redox couple is displayed in Figure S7 in the Supporting Information. Carbon fiber can be also used as the counter electrode with $V_{OC}$ of 0.725 $V$, $J_{SC}$ of 6.45 mA cm$^{-2}$, and FF of 0.57, which produced $\eta$ of 2.70%.$^{46}$

Figure 6 has also compared $J−V$ curves of the wire-shaped DSCs with the CNT fiber, core–sheath CNT/RGONR fiber, CNT/RGO composite fiber, and RGO fiber as counter electrodes and the organic $\Gamma^−/T_2^+$ redox couple as the electrolyte. The photovoltaic parameters are summarized at Table 2. The CNT fiber showed a $V_{OC}$ of 671 mV, $J_{SC}$ of 13.47 mA cm$^{-2}$, and FF of 0.53, which produced the highest $\eta$ of 4.78%. The CNT/RGO composite fiber shared the same $V_{OC}$ and FF but a little lower $J_{SC}$ of 12.13, which resulted in a lower $\eta$ of 4.42%. The core–sheath CNT/RGONR fiber demonstrated the same $V_{OC}$ while both lower FF and $J_{SC}$ and the $\eta$ value would be calculated as 3.70%. For the RGO fiber, the FF was only 0.19, and the resulting DSC exhibited a much lower $\eta$ of 1.46%. The energy conversion efficiencies were changed in the same rule as the cyclic voltammetry in the four carbon nanostructured fibers. The platinum wire exhibited an efficiency of 1.98% in the organic redox couple electrolyte (Figure S8 in the Supporting Information).

EIS had been used to investigate these wire-shaped DSCs in dark to further understand the different performances of the four fiber counter electrodes. In the case of the $\Gamma^−/I_3^−$ redox electrolyte (Figure 7, Figures S9 and S10 in the Supporting Information), the first semicircle in the Nyquist plot at the high-frequency range corresponded to the impedance at the counter electrode ($R_c$) for the reduction reaction of $I_3^−$ ions, while the second semicircle at the middle frequency range corresponded to the charge-transfer impedance ($R_{ct}$) at the interface among the electrolyte, dye, and TiO$_2$. Obviously, the
sizes of the first semicircles were continuously decreased from the RGO fiber, CNT/RGO composite fiber, and CNT fiber to core–sheath CNT/RGONR fiber. In other words, the core–sheath CNT/RGONR fiber showed the highest catalytic activity, and RGO fiber showed the lowest, which is also consistent with the cyclic voltammetry. Figure 8 has further shown the electrochemical impedance spectra of their wire-shaped DSCs in the organic T−/T2 redox electrolyte. The Bode plots were further shown in Figure S11 in the Supporting Information. The RGO fiber exhibited the largest size for the first semicircle with the lowest catalytic activity. Figure S12 in the Supporting Information showed the Nyquist spectra and bode plots of wire-shaped DSCs with the Pt wire as counter electrodes in the T−/T2 electrolyte.

■ CONCLUSIONS

In summary, we have fabricated a series of novel wire-shaped DSCs using nanostructured fibers based on CNT or RGO as counter electrodes. The photovoltaic performances of the CNT fiber, core–sheath CNT/RGONR fiber, CNT/RGO composite fiber, and RGO fiber had been carefully compared in two different electrolytes of I−/I3− and T−/T2. It was found that the core–sheath CNT/RGONR fiber showed the highest energy conversion efficiency of 5.64% in the I−/I3− electrolyte, while the bare CNT fiber produced the highest energy conversion efficiency of 4.78% in the T−/T2 electrolyte. The different catalytic activities had been mainly explored by cyclic voltammetry and Nyquist plot, which may provide useful clues for the development of high-performance wire-shaped energy devices including electrochemical supercapacitors besides DSCs explored in this work.

■ ASSOCIATED CONTENT

Supporting Information
TEM, AFM, and Raman spectra of fibers and Nyquist spectra and bode plots of wire-shaped DSCs. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes
The authors declare no competing financial interest.

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