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Core-Sheath Carbon Nanostructured Fibers for Efficient Wire-Shaped Dye-Sensitized Solar Cells

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On a list of cutting-edge materials for high-performance fibers, carbon nanomaterials are expected to rank near the top for its outstanding properties including high surface area, exceptional electrical conductivity, and superior mechanical strength.^[1-4] As an emerging branch of the carbon nano-family, graphene nanoribbons (GNRs) have inspired exploitations for various applications such as photovoltaic devices and supercapacitors.^[5,6] Many methods have been developed to prepare GNRs, e.g., plasma etching, lithium intercalation and exfoliation, organic synthesis, and chemical unzipping of carbon nanotubes (CNTs).^[7–10] However, it remains a challenge to assemble GNRs into continuous fibers.

In this study, a novel core-sheath carbon nanostructured fiber has been created through a simple solution process (Figure 1). A CNT fiber was first dry-spun from a CNT array and then treated by an oxidizing solution. A proportion of the CNTs was observed to be transformed into carbonaceous materials including graphene oxide (GO) nanoribbons at the outer surface to form a core-sheath structure.^[9,11,13] The following treatment by hydroiodic acid reduced GO nanoribbons into GNRs. The highly aligned CNTs in the core offer both high tensile strength and electrical conductivity, while the GNRs and other carbonaceous residues in the sheath have more edges exposed to enable a high electrocatalytic activity. The flattened graphene sheets also favor the attachment or impregnation of a second functional phase. As a demonstration, wire-shaped dyesensitized solar cells (DSCs) are studied with high energy conversion efficiencies up to 6.83%, much higher than the other carbon-nanostructured fibers.

CNT arrays with heights of ~200 μ m were synthesized by chemical vapor deposition,^[12] from which continuous CNT fibers were dry-spun with diameters of ~20 μ m (**Figure 2**a). Figure 2c further shows that the CNTs in fibers are highly aligned, which is believed conducive to extend the properties of individual CNT to macroscopic scale. A CNT fiber was immersed into an oxidizing solution containing concentrated sulfuric acid, phosphoric acid, and potassium permanganate

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DOI: 10.1002/adma.201305241



for treatment at 75 °C for 1 hr (Figure S1). Figure 2b displays a typical scanning electron microscopy (SEM) image of a treated CNT fiber that has a rippled surface and aligned nanostructure.

Figures 2d–h show the resulting surface morphologies of CNT fibers after chemical oxidation at increasing temperatures from 60 to 80 °C. Obviously, CNTs were well survived in the fiber at temperatures below 70 °C but smashed into pieces and dispersed in solution at temperatures above 80 °C. Between 70 and 80 °C, the fiber structure maintained, though some CNTs were cleaved into carbonaceous materials by oxidation reactions. As the aligned CNT materials had been widely considered to be hydrophobic,^[13,14] the oxidation mainly occurred for the outer CNTs.

Figure 3 exhibits a typical SEM image of the core-sheath nanostructured fiber with the carbonaceous sheath peeled off to unveil the CNT core. The sheath was estimated 20 nm in thickness. The resulting carbonaceous sheath had been further inspected by high resolution transmission electron microcopy (HRTEM) and atomic force microscopy (AFM), which validated the existence of GNRs in the carbonaceous sheath. **Figure 4**a shows a representative HRTEM image where a GNR (labeled by the arrow) with width of appropriately 50 nm was observed. This result agrees with the size of the precursor CNT with



Figure 1. Schematic illustration to the core-sheath nanostructured fiber.

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Figure 2. SEM images of fibers. a,b) A CNT fiber before and after oxidation, respectively. c) High magnification of (a). d–h) Outer surfaces of oxidized CNT fibers at 60, 65, 70, 75, 80 °C, respectively.

an average diameter of ~11 nm (Figure S4). Figure 4b shows an AFM image of GNRs, and the height graph of a GNR was provided in Figure 4c. A typical platform with a height of 1.83 nm was displayed, which was evidently different from a curved graph of the tube-like CNT with a height of 8.46 nm (Figure S5). The structure evolution of the outer surface in the fiber was also traced by Raman spectroscopy (Figure S2). The intensity ratio of D to G band was increased from 0.81 to 1.49 after reduction.^[15]

Photovoltaic devices are traditionally manufactured as rigid, heavy plates based on the silicon technology or flexible films from organic materials.^[16–19] The planar structure cannot satisfy the ever-growing requirement of the light weight and weaveability in modern electronics. Recently, aspiring for the weavable, flexible, and stretchable electronic devices has boosted the upswing of interest in wire-shaped photovoltaic devices.^[20–22]



Figure 3. SEM image of a core-sheath nanostructured fiber with a sheath part peeled off to unveil the CNTs.

High performance fiber electrodes are badly needed to achieve high energy conversion efficiencies and stability.

To this end, the created core-sheath nanostructured fibers may represent a family of promising candidates. They showed electrical conductivities of 10^2-10^3 S/cm and tensile strengths of 10^2-10^3 MPa similar to the bare CNT fiber.^[20] The carbonaceous sheath also exhibited a high catalytic activity due to the exposure of atomic edges on the surface, which was verified by cyclic voltammetry. Figure S3 shows typical cyclic voltammograms of bare, oxidized and reduced CNT fibers in I_3^-/I^- redox system that is widely used in DSCs. Obviously, the peak-to-peak voltage separation of the CNT/GNR fiber records the lowest value, indicating the best capability in reducing the I_3^- ion.^[23] For this reason, the fiber was employed as a counter electrode in the wire-shaped DSC.

A Ti wire modified with vertically aligned TiO_2 nanotubes on the surface by electrochemical anodizing was employed as the working electrode (**Figure 5**a). Figures 5b and 5c show the side and top views of TiO_2 nanotubes that were densely packed and aligned along the radical direction. The TiO_2 nanotubes were ranged from 70 to 100 nm in diameter and were controlled as 30 µm in length by tuning the anodizing time. The N719 dye was absorbed onto the modified Ti wire by soaking. Finally, the core-sheath fiber was tightly intertwined around the modified Ti wire to fabricate a wire-shaped DSC (Figures 5d and 5e). Attributing to the high flexibility of the core-sheath fiber, the two electrodes can be closely and stably twisted, which is essential for high-performance DSCs.

The wire-shaped DSCs were measured under AM 1.5 illumination. As a comparison, bare CNT fiber, bare GNR fiber,^[11] and CNT/GO nanoribbon fiber, were also examined under the same condition (**Figure 6** and **Table 1**). Although the opencircuit voltage (V_{OC}) was close, the CNT/GNR fiber showed the highest short-circuit current (J_{SC}) and fill factor (FF). The highest energy conversion efficiency (η) of 5.16% was achieved among ten devices with an efficiency range from 4.85% to 5.16%. For the bare CNT fiber, V_{OC} , J_{SC} , and FF are all relatively lower. It is widely acknowledged that reactions prefer to take place at the defects and ends of the CNTs, where sharp atomic edges, serving as catalytic sites, are enriched.^[24,25] However,

Adv. Mater. 2014, 26, 1694-1698



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Figure 4. GNRs produced by unzipping CNTs. a) TEM image. b) AFM image of GNRs. c) Height graph of a GNR.

CNTs are densely twisted in the fiber with their defects and ends mostly embedded among their bundles. Therefore, the CNT fibers exhibit relatively lower electrocatalytic activities. In contrast, the produced GNRs and carbonaceous residues at the

a _____ 60 µm d ______ 150 µm

Figure 5. SEM images of wire-shaped DSCs. a) A TiO_2 nanotube-modified Ti wire. b,c) Side and top views of TiO_2 nanotubes, respectively. d,e) A wire-shaped DSC at low and high magnifications, respectively.

outer sheath with abundant edges directly contacted with the solution during reaction.

In the case of bare GNR and CNT/GO nanoribbon fibers, the resulting DSCs showed lower $J_{\rm SC}$ and FF, which rendered

reduced efficiencies of 1.48% and 0.56% due to unsatisfactory electrical conductivities and inferior catalytic capabilities, respectively. In another control experiment, a HI-treated CNT fiber was used to fabricate the wireshaped DSC under the same condition, also giving a low efficiency of 3.95% (Figure S6).

Due to the featured wire shape, the efficiency of the DSC is independent on the incident angle (Figure S7). The wire-shaped DSCs were flexible and did not rupture under bending even at a bent angle of 180° (Figure S8). Even though the efficiency was decreased with the increasing bent angle, they could be fully recovered, which was proved by the overlapped J-V curves before and after bending (Figure S9). In addition, the three photovoltaic parameters of V_{OC}, J_{SC}, and FF remained unchanged after bending for 100 cycles (Figure S10).

The planar structure of GNRs is proved to possess good affinity with a second phase such as Pt nanoparticles to further enhance the DSC.^[26] **Figures** 7a and 7b show SEM images of electrodeposited Pt nanoparticles

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Figure 6. J-V curves of wire-shaped DSCs with different counter electrodes measured under AM 1.5 illumination.

on the outer surfaces of CNT and CNT/GNR fibers. Evidently, small Pt nanoparticles were uniformly distributed and closely attached on GNRs with sizes of ~50 nm, while much larger Pt agglomerates were loosely contacted with aligned CNTs with sizes of ~300 nm. Consequently, the CNT/GNR/Pt fiber was expected to offer a higher electrocatalytic activity to reduce the I₃⁻ ion. As a result, the wire-shaped DSC from the CNT/GNR/ Pt fiber yielded a much higher efficiency of 6.83%, compared with 5.31% of the CNT/Pt fiber (Figure 7c and Table 2). Electrochemical impedance spectroscopy was also used to explain the different performances between CNT/GNR/Pt and CNT/ Pt fibers (Figure S11). For the CNT/GNR/Pt fiber, a lower charge-transfer resistance at the counter electrode was observed assigning to the first semicircle in the Nyquist plot. Note that the synergetic effect between CNTs and GNR through π - π interactions also greatly contributed to the high efficiencies in the wire-shaped DSC by improving the charge transport.^[5]

To further expand the practical application, stretchable wireshaped DSCs were fabricated and discussed. To this end, an elastic rubber fiber was used as a substrate where aligned CNT sheets were wrapped on the surface. The CNTs could be also unzipped into GNRs as the sheath after chemical treatments by sulfuric acid and hydroiodic acid. Figures S13-16 exhibit SEM images of the stretchable fiber before and after chemical treatment. Subsequently, the stretchable fibers were employed as counter electrodes to fabricate stretchable wire-shaped DSCs (Figures S17 and S18). The experimental details are described in the Supporting Information. In the case of CNT sheets

Entry	V	1	FF	n	
	[V]	[mA cm ⁻²]	[%]	[%]	
CNT fiber	0.71	11.58	56.35	4.64	
CNT/GO fiber	0.67	3.43	24.35	0.56	
CNT/GNR fiber	0.70	12.07	60.95	5.16	
GNR fiber	0.62	4.24	56.34	1.48	

500 nm 16 CNT/GNR/Pt fiber Bare CNT/Pt fiber 14 12 10 8 6



Figure 7. a,b) SEM images of CNT and CNT/GNR fibers deposited with platinum nanoparticles, respectively. c) /-V curves of wire-shaped DSCs with bare CNT and CNT/GNR fibers both deposited with Pt nanoparticles as counter electrodes.

wrapped stretchable fiber, an energy conversion efficiency of 5.75% was achieved. A lower energy conversion efficiency of 3.70% was recorded for the GNR-sheathed fiber electrode (Figure S19). These results were different from the previous

Table 2. Photovoltaic parameters in Figure 7c.

Entry	V _{oc} [V]	∫ _{sc} [mA cm ⁻²]	FF [%]	η [%]
CNT fiber	0.69	11.83	64.98	5.31
CNT/GNR fiber	0.69	13.55	72.60	6.83

Table 1. Photovoltaic parameters in Figure 6.

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core-sheath fiber, which can be explained that the CNT-wrapped rubber fiber showed much higher electrical conductivities than the GNR-sheathed rubber fiber as the supporting rubber was insulated. These stretchable wire-shaped DSCs could be stably performed under stretching for many cycles (Figure S20).

In conclusion, this novel core-sheath nanostructured fiber exhibits extraordinary electronic performances benefited from the synergetic interactions with the CNT core to realize high flexibility, tensile strength and electrical conductivity, and the GNR-contained carbonaceous sheath to enable a high catalytic activity. As application demonstrations, the core-sheath nanostructured fiber in conjunction with Pt nanoparticles was employed into wire-shaped DSCs with a maximal energy conversion efficiency of 6.83%.

Experimental Section

Preparation of the Core-Sheath CNT/GNR Fiber: CNT fibers were spun from CNT arrays synthesized by chemical vapor deposition.^[20] To prepare the core-sheath nanostructured fiber, 5 mL of H₃PO₄ (85%) was added to 45 mL of concentrated H₂SO₄, and the mixture was stirred for 15 min at room temperature. KMnO₄ (50 mg) was slowly added to the mixture solution under stirring (~15 min), and the resulting solution became emerald green. The CNT fiber was then immersed into the solution at 75 °C for 1 hr, followed by washing with 30% H₂O₂ (preventing precipitation of MnO₂) and deionized water.^[9,11,15] The reduction was carried out in a HI solution at 80 °C for 8 hr, followed by washing with deionized water and drying for 12 hr in air.

Deposition of Pt Nanoparticles: Pt nanoparticles were electrodeposited by a double potential step method with the first step at E₁ of -0.5 V for 5 s and the second step at E₂ of 0 V for 286 s. Pt wire and Ag/AgCl electrode were used as counter and reference electrodes, respectively. The electrolyte included an aqueous solution of 5 mM H₂PtCl₆ and 0.5 M H₂SO₄. The resulting fibers were washed with deionized water twice after electrodeposition. ^[27]

Fabrication of Wire-Shaped DSCs: The vertically aligned TiO₂ nanotube were grown on the surface of Ti wire by electrochemical anodization at 60 V for 6 hr in a 0.3 wt% NH₄F/ethylene glycol solution containing 8 wt% $H_2 O.^{\left[27\right]}$ The anodization was realized in a two-electrode system with Ti wire (diameter of 127 μ m and purity of 99.9%) and Pt plate as anode and cathode, respectively. Afterwards, the modified wires were cleaned with deionized water, followed by annealing in air at 500 °C for 1 hr. The wires were then immersed in a TiCl₄ aqueous solution (100 mM) and heated at 70 °C for 30 min. Subsequently, they were rinsed with deionized water, followed by annealing in air at 450 °C for 30 min. After that, the modified Ti wires were immersed into the N719 solution (0.3 mM) in a solvent mixture of dehydrated acetonitrile and tert-butanol (1/1, v/v) for 16 hr. To fabricate the wire-shaped DSC, the carbon nanostrutured fiber was twined around the N719-absorbed Ti wire. The DSC was encapsulated in a capillary tube or a flexible fluorinated ethylene propylene tube (Figure S12), followed by the injection of the electrolyte containing 0.1 M lithium iodide, 0.05 M iodine, 0.6 M 1, 2-dimethyl-3-propylimidazolium iodide and 0.5 M 4-tert butyl-pyridine in dehydrated acetonitrile.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements

This work was supported by NSFC (91027025, 21225417), MOST (2011CB932503, 2011DFA51330), STCSM (11520701400,



12nm0503200), Fok Ying Tong Education Foundation, the Program for Professor of Special Appointment at Shanghai Institutions of Higher Learning, and the Program for Outstanding Young Scholars from Organization Department of the CPC Central Committee.

> Received: October 22, 2013 Revised: November 14, 2013 Published online: December 17, 2013

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