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Twisted Aligned Carbon Nanotube/Silicon Composite Fiber Anode for Flexible Wire-Shaped Lithium-Ion Battery

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Increasing interest has recently been devoted to developing small, rapid, and portable electronic devices. To this end, it is critically important to provide matachable energy-storage systems, such as lithium-ion batteries, to power them.^[1-9] However, the conventional, heavy planar structure cannot effectively meet this requirement, and some new and general platforms should be developed to achieve the goal. Learning from the history of the material science, that chemical fibers have changed our life through the textile technology in the last century, it is proposed that if the batteries can be made into wire or fiber structures, they may be scaled up for practical applications by the well-developed textile technology, and well satisfy modern electronics. However, it remains unavailable to achieve such high-performance batteries in a weaveable fiber format due to the difficulty in finding appropriate electrode materials.

Silicon has been widely studied as a promising anode material due to the high gravimetric capacity, though the large volume change up to 400% during the Li⁺ intercalation and de-intercalation process remains severely challenging on the battery stability.^[10-13] In contrast, carbon nanotubes (CNTs) are used for electrode materials in battery due to their high cyclic stability, but they are limited by a low capacity.^[14-17] Therefore, a lot of effort has been devoted to synthesizing CNT/Si composite materials, which are expected to combine their individual advantages to offer both high specific capacity and cyclic stability. However, the improved degrees are much lower than expected, as CNTs are typically produced with network structures and the many boundaries that are formed decrease the charge separation and transport.^[14-17] In addition, although CNT/Si composite materials have been explored for their conventional planar structures, they have not studied for wireshaped electrodes or batteries to date.

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Miniature energy-storage systems such as microbatteries have attracted increasing attention due to their promising applications in a wide variety of fields, such as low-power electronics, miniature robots, and implantable medical devices.^[5,6] A solid microbattery is typically composed of thin layers of cathode, electrolyte, and anode. Various film electrode materials have been extensively explored for such microbatteries.

In this Communication, we report the development of novel twisted, aligned multiwalled carbon nanotube (MWCNT)/Si composite fiber anodes for flexible, wire-shaped lithium-ion batteries. A thin layer of silicon is coated on the outer surface of the aligned MWCNT to form a core-sheath structure that can effectively and simultaneously exploit the high specific capacity of the silicon and high electrical conductivity of the MWCNT, while the designed space with sizes of tens to hundreds of nanometers among the aligned composite nanotubes can effectively counterbalance the volume change of the silicon component. As a result, the aligned MWCNT/Si fiber electrode shows a combined high specific capacity and cyclic stability. In addition, this fiber electrode could be further made into a flexible wire-shaped battery, which offers unique advantages, such as being lightweight and weaveable compared with the conventional planar structure. Here, a half-cell had been studied as a demonstration.

Spinnable MWCNT arrays were first synthesized by chemical vapor deposition.^[18–22] The array with a height of appropriately 250 µm was mainly studied in this work, and the diameter of the MWCNTs was ca. 10 nm. Aligned MWCNT sheets could be drawn out of the array with widths of millimeters to centimeters and thicknesses of ca. 20 nm. Silicon was then deposited onto the MWCNT sheet through an atomic layer deposition method followed by a twisting treatment to form a flexible composite fiber electrode (Figure 1). As the MWCNT sheet was ultrathin, silicon can be uniformly coated on the surfaces of individual MWCNTs, and the thickness could be controlled by varying the sputtering time.

Figure 2a-d and Figure S1a in the Supporting Information compare MWCNT fibers based on the same MWCNT sheet, before and after deposition of Si. The fiber was increased from 30 to 60 μ m in diameter, but remained uniform after the formation of composite fiber. In addition, the MWCNTs were maintained as highly aligned, and no obvious aggregates were observed in the composite fiber (Figure 2d), which indicates a uniform Si deposition on the MWCNT surface. Figure 2e shows a typical X-ray diffraction pattern of the MWCNT/Si composite with two characteristic peaks of the carbon and a characteristic peak of the silicon.^[23] The low intensity of the Si (111) reflection observed for the composite is due to the low content and amorphous structure of Si.



Figure 1. Schematic illustration to the preparation of the aligned MWCNT/Si composite fiber.

Energy-dispersive X-ray spectroscopy and X-ray photoelectron spectroscopy also showed the formation of composite fiber (Figure 2f and Figure S2 in the Supporting Information).^[23,24]

To better understand the structure, the composite fiber was further analyzed by high-resolution transmission electron microscopy (HR-TEM). The image in the insert of Figure 2f and Makrials Views www.MaterialsViews.com

Figure S1b in the Supporting Information show a typical nanotube after deposition of Si with a weight percentage of 38.1%. The coresheath structure can be clearly observed. The thickness of the outer Si layer was approximately 20 nm, and it mainly appeared in an amorphous structure, which was verified by a broad peak at 470 cm⁻¹ in the Raman spectrum (Supporting Information, Figure S3).^[25]

The twisted aligned MWCNT/Si composite fiber was flexible and could be made into various structures such as a knot (Supporting

Information, Figure S4), and the twisted structure had been well maintained during deformation.^[26] Due to the aligned structure of the MWCNT, the MWCNT/Si composite fiber also exhibited excellent mechanical and electrical properties, such as high tensile strength and electrical conductivity, which are important for electronic devices. The flexible composite



Figure 2. a,b) SEM images of a bare aligned MWCNT fiber at low and high magnifications, respectively. c,d) SEM images of an aligned MWCNT/Si composite fiber with Si weight percentage of 38.1% at low and high magnifications, respectively. e) X-ray diffraction pattern of the MWCNT/Si composite. f) EDX analysis of the aligned MWCNT/Si composite fiber (insert: HR-TEM image of an aligned MWCNT/Si composite fiber with a Si weight percentage of 38.1%).

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Figure 3. Schematic illustration of a half lithium-ion battery based on the aligned MWCNT/Si composite fiber as a working electrode with a lithium wire as both counter and reference electrode.

fiber could be stably wound with the other fiber, and here the MWCNT/Si composite fiber was used as an effective electrode, to produce a half lithium-ion battery with a Li wire as the reference electrode (Figure 3).

To demonstrate the high performance of the composite fibers, a half-cell based on the aligned MWCNT/Si composite and bare MWCNTs fibers as lithium-ion battery anodes were galvanostatically charged and discharged within a voltage window of 0.02–1.20 V (vs. Li/Li⁺). **Figure 4**a shows the typical charge and discharge curves of the half-cells based on the aligned MWCNT/Si composite (Si weight percentage of 38.1%) and bare MWCNT fibers at a current density of 1.0 A/g, respectively. The current density was calculated on the basis of the active MWCNT and Si in the electrode. A significant increase in the specific capacity occurred in the composite fiber. Figure 4b further compares the specific capacity of composite fibers with increasing Si weight percentages at a current density of 1.0 A/g. The specific capacities are increased from 82, 554, 1090 to 1670 mAh/g with increasing Si weight percentages from 0, 18.7, 26.7 to 38.1%, respectively.

The cyclic performances of the MWCNT/Si composite fiber with Si weight percentage of 38.1% were also compared under different current densities in 30 cycles (Figure 4c). The first 10 cycles were performed at a current density of 2.0 A/g, then 10 cycles at 3.0 A/g, and finally 10 cycles at 2.0 A/g again. The specific capacity was maintained at 1042 mAh/g at 3.0 A/g. When the current density was reverted to 2.0 A/g, the composite electrode showed a retention capacity of 1168 mAh/g. Note that here the MWCNT component exhibited only about 100 mAh/g (Supporting Information, Figure S5) and contributed to less than 10% of total capacity of the composite electrodes. In addition, a low operating voltage of ca. 0.4 V, which corresponded to the lithium alloying/dealloying potential of Si, was observed, indicating that the aligned MWCNT/Si composite fiber served as an anode (Supporting Information, Figure S6).^[23,25,27-37] Figure 4d showed that the specific capacity was increased in the second cycle mainly due to the activation of Si, which had been verified by the cyclic voltammogram (CV) curves (Supporting Information, Figure S7). Moreover, the MWCNT/Si composite showed a good retention (Supporting Information, Figure S8). For instance, the MWCNT/Si composite electrode with Si weight percentage of 18.7% exhibited capacity retention



Figure 4. a) Typical charge and discharge curves of a half lithium-ion battery based on the bare aligned MWCNT and aligned MWCNT/Si composite fibers with a Si weight percentage of 38.1% at 1 A/g. b) Specific capacities of the wire-shaped bare and composite fibers with different Si weight percentages at 1 A/g. c) Dependence of the specific capacity on current density. d) Dependence of the specific capacity on cycle number.

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Figure 5. a,b) SEM images of a bent aligned MWCNT/Si composite fiber at low and high magnifications, respectively. c) Charge and discharge curves of a half-cell based on the aligned MWCNT/Si composite fiber with a Si weight percentage of 38.1% before and after bending for 100 cycles at 2 A/g. d) Dependence of specific capacity on cycle number for the composite fiber after bending for 100 cycles at 2 A/g. C₀ and C correspond to the specific capacities at the first and following cycle, respectively.

by 52% in 100 cycles at 1.0 A/g; when the weight percentage of Si in the composite fiber was increased to 38.1%, the fiber electrode showed a capacity retention over 32%. It exhibited 28% of capacity retention in 200 cycles at 2 A/g (Supporting Information, Figure S9). The relatively low capacity retention may be derived from the unstable solid-electrolyte interphase and the limited counterbalance of the Si volume change. It is critical to further improve the capacity retention by optimizing the composite structure. For instance, alternate bare MWCNT and composite nanotube structures have been found to greatly enhance the electrochemical stability of the wire-shaped battery as the Si volume change could be more effectively alleviated by the aligned MWCNTs. More research is underway along this direction.

As a comparison, the electrochemical performance of Si deposited on a copper foil with thickness of 100 nm was conducted at a rate of 0.6 C. The bare Si exhibited a high capacity of 3537 mAh/g in the first cycle while it faded seriously and remained at only 1648 mAh/g in 30 cycles with a low retention of 46.6% (Supporting Information, Figure S10). As a strong contrast, the aligned MWCNT/Si composite fiber (Si: 38.1 wt%) showed a capacity retention of 58% at ca. 0.6C (1 A/g) over 50 cycles. Besides the improvement in cyclic performance, the MWCNT/Si composite fiber showed a higher specific capacity than the bare MWCNT, although it exhibited a relatively low capacity compared with the pure Si material due to the incorporation of MWCNTs. However, when the specific capacity of the composite electrode was calculated based on the mass of Si, it achieved a higher value of ca. 1970 mAh/g at the 50th cycle,

compared with 1648 mAh/g at the 30th cycle in the pure Si material. Therefore, the MWCNT/Si composite fiber electrode had efficiently taken advantages from the two components (i.e., MWCNT and Si) to simultaneously achieve high capacity and stability.

Due to the twisted and aligned structure of the used MWCNTs, the composite fibers were flexible and could be bent for over a hundred cycles without an obvious decrease in the structure integrity (Figure 5a,b). Therefore, the half-cell based on the aligned MWCNT/Si composite fiber was also flexible and stable, which was further verified by comparing the galvanostatic charge-discharge curves before and after bending. For the half-cell fabricated from the aligned MWCNT/Si composite fiber with a Si weight percentage of 38.1%, the specific capacity was maintained at 1460 mAh/g after bending for 100 cycles, compared with 1548 mAh/g before bending (Figure 5c) (i.e., only a slight decrease of 6%). For the half-cell after bending for 100 cycles, the cyclic performance was further studied, and it was found that the capacity could be maintained at ca. 80% in 20 cycles at 2 A/g (Figure 5d). The twisted structure in the halfcell had been well maintained during and after bending.

The good electrochemical performance can be explained by the designed core-sheath and aligned structures that have mostly effectively taken the advantages of the MWCNTs and Si. The core-sheath architecture can effectively counterbalance the volume change of Si,^[13] whereas the aligned MWCNTs enhance the charge transport between the MWCNT and the Si. Figure S11 in the Supporting Information shows electrochemical impedance spectra based on bare Si and MWCNT/



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Si composite electrodes. The half-cells were charged to 1.0 V and then relaxed for 1 h to measure the impedance. The as-prepared cells based on the bare Si and MWCNT/Si composite vs. Li with an open-circuit voltage of ca. 3.0 V showed a depressed semicircle due to the charge-transfer resistance in the highfrequency region.^[38-40] The charge-transfer resistances for the as-prepared cells and the ones after 30 cycles for the bare Si and MWCNT/Si composite were decreased from 390 and 185 to ca. 109 Ω and 68 Ω , respectively, whereas the corresponding double layer capacitances had been reduced from 158 and 58 to ca. 19 µF and 18 µF, respectively. The MWCNT/Si composite exhibited a smaller semicircle at the high frequency, even after 30 cycles, compared with the Si electrode, indicating a better charge transfer and electronic contact.^[23,41] The MWCNT served as a buffer to alleviate the Si volume change during the charge and discharge processes. In addition, the excellent mechanical properties of and aligned voids among MWCNTs can efficiently accommodate the volume change of Si.

In summary, novel aligned MWCNT/Si composite fiber electrodes, where Si was deposited on the outer surfaces of individual MWCNTs, have been designed for flexible, wire-shaped lithiumion batteries. The core-sheath architecture and aligned structure of the MWCNT/Si composite nanotubes display a remarkable electrochemical performance, including high specific capacity and cyclic stability. Further studies are underway to replace the lithium metal wire, to produce applicable wire-shaped batteries that can be scaled up by conventional textile technology.

Experimental Section

Aligned MWCNT arrays were synthesized by chemical vapor deposition, and have been reported elsewhere.^[18-22] Continuous MWCNT sheets with a density of 1.41 μ g/cm² were directly drawn from the array, followed by deposition of Si at a rate of 1 Å/s to produce aligned MWCNT/Si composite films through an electron beam evaporation technology. The composite films were further twisted into fibers with a rotating speed of 180 rounds per minute. No binder was used in the preparation of the fiber electrode. The MWCNT fiber could be made in tens of meters in length, and the weight percentage of Si was then calculated. The mass was obtained to be (3.44 \pm 0.01) $\mu g/cm$ for the composite fiber electrode with a diameter of ca. 60 µm, and the active material was calculated as ca. 0.12 g/cm³. Si was deposited on copper foil as a current collector with the thickness of 100 nm and was cycled at a rate of 0.6C as a comparison. The weights were determined by a balance with a resolution of 1 μ g. The half-cell was assembled by twisting the composite fiber as a working electrode and lithium wire as counter electrode in a glove box in argon atmosphere. The composite fiber and lithium wire were both further connected to copper wires as the current collector with silver for the electrochemical analysis. The electrochemical performance of the half-cell was characterized in a bottle sealed by parafilm. $LiPF_6$ in a mixture solution of ethylene carbonate, diethyl carbonate, and dimethyl carbonate (volume ratios of 1/1/1) with a concentration of 1 M served as the electrolyte. Galvanostatic charge/discharge measurements were made at current densities of 2.0 and 3.0 A/g at a potential range of 0.02-1.20 V using an Arbin electrochemical station. The current density was calculated from the mass of the whole electrode. The cyclic voltammetry measurements were made at a scan rate of 2 mV/s between 0 and 1.3 V using an electrochemical analyzer system (CHI 660D). Electrochemical impedance spectra were measured from 100 kHz to 0.01 Hz with an alternating current amplitude of 5 mV, using a CHI 660D instrument.

The structures and morphologies of aligned MWCNT/Si composite fibers were characterized by scanning electron microscopy (SEM)

(Hitachi FE-SEM S-4800 operated at 1 kV), transmission electron microscopy (TEM) (JEOL JEM-2100F operated at 200 kV), Raman spectroscopy (Renishaw in Via Reflex instrument with an excitation wavelength of 633 nm and laser power of 20 mW), and X-ray diffraction (Bruker AXS D8). X-ray photoelectron spectroscopy (XPS) measurements were carried out on a RBD upgraded PHI-5000C ESCA system (Perkin–Elmer) with Al K radiation (hv = 1486.6 eV).

Supporting Information

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

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