Self-Powered Energy Fiber: Energy Conversion in the Sheath and Storage in the Core

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The integration of multiple functionalities into one device is of great interest in the energy field.\(^1\)\(^-\)\(^4\) If energy conversion and storage can be simultaneously realized in a single device, then costly and inefficient electrical connections to external conversion and/or storage devices can be eliminated. In particular, integrated devices such as these are highly desired for portable and wearable electronic devices, for which light weight and small size are essential for future applications. To this end, considerable attention has been paid to integrating conventional dye-sensitized solar cells and supercapacitors by stacking them together, whereby photoelectric conversion and electrochemical storage are simultaneously achieved.\(^5\)\(^-\)\(^9\) However, the planar structure of these devices has limited their application in wearable products. Furthermore, it is difficult to scale up the fabrication process of these planar integrated devices. Presently, these devices lack elasticity, which is a necessity for wearable electronics. Otherwise, such thin integrated devices can be too easily broken by body movement during use. Recently, several attempts have been made to develop fiber-shaped solar cells\(^10\) and storage devices\(^11\) as well as integrated devices\(^12\) created by connecting photovoltaic and storage devices in series. However, connecting solar cells and supercapacitors is challenging in practical applications, and the resultant integrated devices are also inelastic.

In this Communication, a coaxial energy fiber is developed that converts solar energy into electric energy in its sheath and stores the electric energy in its core using aligned carbon nanotube (CNT) sheets as electrodes. The coaxial structure and the aligned nanostructure at the interface of the electrode enable a high overall energy conversion and storage performance that is robust to bending and stretching, a characteristic that paves the way toward practical application in wearable electronics.

Spinnable CNT arrays with a thickness of 230 µm are first synthesized via chemical vapor deposition (Figure S1).\(^13\)\(^-\)\(^15\) The CNTs have a diameter of approximately 10 nm and wall numbers of 4–6 (Figure S2). Continuous, aligned CNT sheets are dry-drawn from the array and serve as electrodes in the energy fiber. The fabrication process of the energy fiber is schematically illustrated in Figure S3. An aligned CNT sheet is wrapped around an elastic rubber fiber to serve as the internal electrode, which is then coated with a thin layer of poly(vinyl alcohol) (PVA)-H\(^3\)PO\(_4\) gel to serve as the electrolyte. The coated fiber is then wrapped with another CNT sheet electrode with the same thickness to form the energy-storage component. A vacuum post-treatment is typically applied to improve the infiltration of the electrolyte into the CNT sheets. The storage component is then inserted into an elastic plastic tube that separates it from the outer, photoelectric-conversion component. A third aligned CNT sheet is wrapped around the plastic insulator to form a cathode, and this assembly is inserted into a helical Ti fiber with perpendicularly grown TiO\(_2\) nanotubes that acts as the photoanode for the photoelectric-conversion component. The resulting device is inserted into an elastic and transparent polyethylene tube, which is then filled with the redox electrolyte.

The principle of operation is summarized in Figure 1c. To achieve photocharging, the photoanode (electrode #2) and the cathode (electrode #3) of the outer, photoelectrical-conversion component are first connected to electrodes #1 and #4 of the inner, energy-storage component, respectively. During illumination, the external electrons of the dye N719 molecules (Figure S3) are raised from the ground state into excited states, and the electrons are subsequently injected into the conduction band of the TiO\(_2\). The electrons are transported along the external circuit and reach the CNT electrode of the energy-storage component. The dye molecules return to the ground state by receiving electrons from I\(^-\) ions in the redox electrolyte, where the I\(^-\) ions are oxidized into I\(^3\)\(^-\) ions. The inherent potential derives from the energy band gap between the conduction band of TiO\(_2\) and the redox potential of the I\(^3\)/I\(^-\) electrolyte and provides the driving force to charge the energy-storage component. In this manner, the energy fiber converts solar energy into electric energy under illumination and then stores the electric energy. The stored energy can be used to power electronic devices by connecting electrodes #1 and #4 to electrodes #5 and #6, respectively. In the resulting discharging process, the I\(^3\)\(^-\) ions are reduced to I\(^-\) ions by receiving electrons, thereby completing the cycle.

**Figures** 1a and 1b show a photograph of the energy fiber and an illustration of its structure, respectively, and a cross-sectional illustration is provided in Figure S4 to further elucidate the coaxial structure.

**Figures** 2a and 2b present scanning electron microscopy (SEM) images of an energy fiber from the side and top views, respectively. The photoanode has a helical structure with a pitch of 700 µm and is prepared using an anodization method in which aligned TiO\(_2\) nanotubes are grown on the surface of a Ti fiber (Figures S6a and S6b). Figures 2c and 2d present magnified SEM images of the photoanode, which has a diameter of 150 µm, the TiO\(_2\) nanotubes range from 100 to 120 nm in diameter.
The inner, energy-storage component, with the electrolyte sandwiched between two aligned CNT sheets, is pictured in Figure 2e. Importantly, the CNTs remain highly aligned after being wound around the fiber substrate (Figures 2f and S6a), and this alignment enables high photoelectric conversion and storage performance under bending and stretching. Figures S7a and S7b further explain the stable performance of the energy fiber; i.e., a stable, wrinkled nanostructure is formed, and the CNTs remain tightly attached to the elastic fiber during bending and stretching.

Figure 3a shows a typical plot of current density vs voltage for the photoelectric-conversion component, which has an open-circuit voltage ($V_{OC}$) of 0.68 V, a short-circuit current density ($J_{SC}$) of 14.31 mA cm$^{-2}$ and a fill factor (FF) of 0.60. The photoelectric-conversion efficiency is thus calculated to be 6.47%. The high photovoltaic performance can be attributed to the aligned CNT sheets, which exhibit high electrocatalytic activity. The electrocatalytic activity was measured using cyclic voltammetry (CV). As shown in Figure 3b, two pairs of oxidation/reduction peaks appear in the electrocatalytic measurements, where the left redox peaks ($A_{OX}$ and $A_{RE}$) and the right redox peaks ($B_{OX}$ and $B_{RE}$) correspond to the redox reactions of $I_3^-/I^-$ in Equations (1) and (2), respectively.

$$I_i + 2e^- \leftrightarrow 3I^- \quad (1)$$
$$3I_i + 2e^- \leftrightarrow 3I^- \quad (2)$$

Generally, the left $A_{OX}/A_{RE}$ redox reaction reflects the catalytic activity of the electrode, where a lower peak-to-peak voltage difference ($V_{PP}$) indicates higher catalytic activity.[16] The CNT electrode exhibits a $V_{PP}$ of approximately 0.5 V, which is comparable to that of a traditional, high-efficiency platinum electrode.[16]

The electrochemical properties of the energy-storage component were investigated using CV and galvanostatic charge-discharge measurements. Figure 3c presents typical CV curves, where the rectangular shape represents the characteristic behavior of an electrochemical double-layer capacitor. The storage component can electrostatically store charge by reversibly adsorbing ions from the electrolyte onto the active material with a high specific surface area and separating charges at the electrode-electrolyte interface.[17] The rectangular shape is maintained as the scan rate increases from 20 to 100 mV s$^{-1}$, indicating a stable current during the charging and discharging processes and high electrochemical stability. However, as the voltage scan rate increases further, the rectangular shape in the CV plot becomes more rounded and oblique because a longer response time is required to form an electrochemical double-layer structure. Figure 3d shows the galvanostatic charge-discharge curve between 0 and 0.8 V at various current densities. The nearly symmetric triangular shape of the curve is maintained as the current density increases from 0.05 to 0.6 A g$^{-1}$, indicating a stable current during the charging and discharging processes and a high level of performance.
The photocharging and discharging performance of the self-powering energy fiber was then studied. Photocharging is enabled by connecting the outer, photoelectrical-conversion component to the inner, energy-storage component (Figure 4a) such that under illumination, solar energy is converted into electrical energy and stored. The voltage of the storage component increases to 0.65 V within less than 1 s and then remains stable during the photocharging process (Figure 4c). After the energy fiber is fully charged, it is able to supply electrical energy for 41 seconds at a current density of 0.1 A g\(^{-1}\) (Figures 4b and 4c). Figure S9 presents the self-discharge curve of the energy fiber in darkness after being fully photocharged. The voltages are 90% and 74% of the initial voltage after self-discharging for 100 and 2000 seconds, respectively, indicating high electrochemical stability. Next, the photocharging and discharging behaviors of the energy fiber were measured under bending and after stretching. As shown in Figure 4c, the photocharging and discharging processes remain largely unaffected by bending at radii of curvature ranging from 5 to 0.5 cm. Figure 4d presents the performance of the fiber before and after stretching under strains of 10%, 20%, 30% and 40%. The fiber maintains its high performance after being stretched by 10% and 20%, and the photovoltage slightly decreases when the fiber is stretched beyond 30%. However, the performance of the energy fiber is severely degraded after it is stretched beyond 40% because of damage to the helical structure of the photoanode. The performance of an energy fiber was tested after 50 cycles of stretching under a strain of 20% (i.e., the fiber was stretched to a length 20% greater than its original value). Figure S10 shows that the photocharge and discharge performance remained stable under these conditions, which is critically important for the application of fiber-like devices in portable and wearable electronics.

The total efficiency of energy conversion and storage (\(\eta_{\text{total}}\)) of the energy fiber can be calculated using the equation \(\eta_{\text{total}} = \frac{E_{\text{output}}}{E_{\text{input}}} = \frac{0.5C^2V^2}{(P_{\text{in}}S^*t)}\), where \(E_{\text{output}}\), \(C\) and \(V\) are the energy output and the capacitance and voltage of the energy-storage component, respectively, and \(E_{\text{input}}\), \(P_{\text{in}}, S\) and \(t\) are the total incident light energy, the incident light-energy density, the effective area of the energy-conversion component and the photocharging time, respectively. According to the photocharging and discharging curve presented in Figure 4c, the total efficiency of energy conversion and storage increases from 0 to 1.83% with increasing photocharging time up to 0.6 s and then decreases for longer photocharging times (Figure S11).

In summary, a novel self-powered, elastic energy fiber with a coaxial structure that collects energy in the sheath and stores that energy in the core has been developed. This energy fiber exhibits a total efficiency of energy conversion and storage of 1.83%, which is maintained under bending and after stretching. The energy fiber can be woven into wearable, self-powering energy textiles, which are highly desirable for next-generation electronics.

**Experimental Section**

**Preparation of the Photoanode:** A Ti fiber (127 \(\mu\)m in diameter) was first wound onto a rigid steel wire (1.9 mm in diameter) with a pitch of 700 \(\mu\)m to form a helical shape, or coil. An aligned TiO\(_2\) nanotube array was grown on the helical Ti fiber via electrochemical anodization at a voltage of 60 V for 6 h in a 0.3 wt% NH\(_4\)F/ethylene glycol solution (containing 8 wt% H\(_2\)O\(_2\)) in a two-electrode cell. The resulting Ti fiber was washed with deionized water to remove the electrolyte and then annealed at 500 °C for 30 min and then annealed again at 450 °C for 30 min. After the temperature had decreased to 120 °C, the fiber was immersed in a 0.3 mM N719 dye solution in a solvent mixture of dehydrated acetonitrile and tert-butanol (volume ratio of 1/1) for 16 h to form an elastic photoanode.\(^{[8]}\) The effective area of the photoanode (0.1214 cm\(^2\)) was calculated as the projected area.\(^{[9]}\)

**Fabrication of the Energy-Storage Component:** An elastic rubber fiber was stabilized by two motors, one attached to each end, and a
A spinnable CNT array was fixed on a precision motorized translation stage. The synthesis of the CNT array is summarized in the Supporting Information. A continuous, aligned CNT sheet was drawn out of the array and attached to the rubber fiber at an angle of 60°, with the two motors and the translation stage being operated simultaneously. The CNT electrode, which had a thickness of 0.66 µm, was prepared by repeating the process. The resulting fiber was then coated with a thin layer of PVA-H₃PO₄ gel, which served as the electrolyte, and then wound with another CNT sheet to form the outer electrode, which was equal in thickness to the inner electrode. A vacuum treatment was applied to improve the infiltration of the electrolyte into the aligned CNTs. The PVA-H₃PO₄ gel electrolyte was prepared by dissolving PVA powder (1 g) in deionized water (9 mL) and H₃PO₄ (1 mL).[20]

Fabrication of the Self-Powered Energy Fiber: The fiber-shaped energy-storage component was inserted into an elastic rubber tube with an inner diameter of 860 µm, which was then wound with a 0.95-µm-thick CNT sheet to form the cathode for the outer, photoelectric-conversion component. The resulting fiber was then inserted into the helical photoanode, and this assembly was inserted into an elastic and transparent polyethylene tube. Finally, a redox electrolyte composed of 0.1 M lithium iodide, 0.05 M iodine, 0.6 M 1, 2-dimethyl-3-propylimidazolium iodide and 0.5 M 4-tert-butylpyridine in dehydrated acetonitrile was injected and infiltrated into the device.

Calculation of the Masses of the CNT Sheet Electrodes: The mass of a CNT sheet electrode can be obtained by multiplying the area by the area density of the CNT sheet in the electrode. The thickness of a single layer of CNT sheet was approximately 18 nm, and the area density of the CNT sheet was 1.41 µg cm⁻².[3] The inner CNT electrode had a thickness of 660 nm and a length of 2 cm. The area was \(2\pi r \times 2 \times 660 \text{ nm} / 18 \text{ nm}\); therefore, the mass of the CNT electrode can be calculated to be 16.23 µg.[19]

Characterization. The structures were characterized via scanning electron microscopy (Hitachi FE-SEM S-4800 operated at 1 kV).
current density vs voltage (J–V) curves for the photoelectric conversion process were recorded using a Keithley 2400 Source Meter under illumination (100 mW cm\(^{-2}\)) with simulated AM1.5 solar light produced by a solar simulator (Oriel-Sol 3A 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). The CV measurements of the cathode of the photoelectric-conversion component were performed in an acetonitrile solution that contained 5 mM LiI, 0.5 mM I\(_2\) and 0.05 M LiClO\(_4\) using a scan rate of 50 mV s\(^{-1}\) and a three-electrode setup on a CHI 660D electrochemical workstation. The CV and galvanostatic charge-discharge measurements of the energy-storage component were performed by connecting electrode #1 to the working electrode and electrode #4 to both the counter and reference electrodes in a CHI 660D electrochemical workstation. The photocharging and discharging processes were evaluated using the photovoltaic measurement system in combination with the CHI 660D electrochemical workstation.

**Supporting Information**

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

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