Integrated Polymer Solar Cell and Electrochemical Supercapacitor in a Flexible and Stable Fiber Format

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The development of modern electronics requires the use of flexible devices for both energy conversion and storage. For instance, excitonic solar cells such as polymer and dye-sensitized solar cells that can be coated on flexible substrates are widely studied to offer the electrical properties of conventional, rigid silicon wafer-based technologies.[1–4] Electrochemical supercapacitors have been made into flexible films to expand the application scope, such as various portable electronic facilities.[5–9] Some attempts are also made to fabricate integrated devices to simultaneously realize the energy conversion and storage that meet a critical requirement of being self-powered in the future.[10–14] However, it remains difficult to make them at a large scale due to the complex fabrications, and these integrated devices are typically not flexible. In addition, they appeared in a conventional planar structure, which cannot meet the ongoing push of being lightweight, smaller, and weaveable in the electronics.

Increasing attentions are recently attracted to fabricate photovoltaic and electrochemical micro-devices in a wire format that satisfies the above development. Wire-shaped dye-sensitized solar cells have been mostly explored by twisting two fiber electrodes, and they can be further integrated with supercapacitors.[15] However, the wire-shaped dye-sensitized solar cell part had to be sealed separately,[16–18] and the resulting device still appeared in a planar structure. It cannot be really integrated for lightweight, portable devices as designed, and the requirement of sealing also made the fabrication very complex. In addition, when the dye-sensitized solar cell and supercapacitor were sealed together, the device failed to work even after bending for only five cycles (Figure S1, Supporting Information). The device also exhibited a very low mechanical stability as two fiber electrodes were peeled off from each other under bending. Therefore, it seemed deformable while cannot be used as a really flexible device. In summary, the use of dye-sensitized solar cells has severely limited the realization of flexible, fiber-like, and integrated devices.

Polymer solar cells have been widely studied without the use of liquid electrolytes.[19,20] In this Communication, we have, for the first time, introduced polymer solar cells to develop a novel, all-solid-state, flexible “energy fiber” that has efficiently integrated the functions of photovoltaic conversion (PC) and energy storage (ES). The design of a coaxial structure in the “energy fiber” enables promising advantages for both PC and ES. For the PC part, it is similar to the efficient planar polymer solar cell in the radial direction, so the generated charges can be rapidly separated and transported to produce high photocurrents. For the ES part, different from the explored twisted structure of two fiber electrodes with high electrical resistances,[21] the coaxial structure with much higher effective contact area also favors a rapid charge transport. In addition, the use of flexible, transparent, strong, and conductive multi-walled carbon nanotube (MWCNT) sheets can also greatly improve the photoelectric conversion and energy storage.

Figure 1 schematically shows the two main parts including the left PC and right ES in the “energy fiber”. This “energy fiber” has been realized on the basis of titania nanotube-modified Ti wire and aligned MWCNT sheet as two electrodes. The detailed fabrication is shown in Figure S2. For the PC part, perpendicularly aligned titania nanotubes are grown on a Ti wire by electrochemical anodization, followed by coating of poly(3-hexyl thiophene):-phenyl-C₆₁-butyric acid methyl ester (P3HT:PCBM) and poly(3,4-ethylenedioxythiophene): poly(styrene sulfonate) (PEDOT:PSS) layers. The MWCNT sheet is finally wrapped onto the modified Ti wire to produce the PC part. For the ES part, the poly(vinyl alcohol) (PVA)/H₃PO₄ gel electrolyte is coated on the titania nanotube-modified Ti wire, and MWCNT sheets are attached to form the ES part.

Figure 2a shows the photograph of an “energy fiber” with the PC and ES part. The fabrication process to this “energy fiber” had been traced by scanning electron microscopy (SEM). A bare Ti wire with diameter of 127 μm was used as the support
material to grow titania nanotubes (Figures S3a and 3b). Figures 2b and 2c show the resulting Ti wire after electrochemical anodization of 10 min by top and side views, respectively. The titania nanotubes were perpendicularly grown on the surface of the Ti wire with inner and outer diameters of 100 and 150 nm, respectively. The lengths of titania nanotubes could be controlled from 650 nm to 950 nm, 1.8 μm, 2.2 μm, 2.6 μm, and 4 μm by increasing the growth time from 1 to 5, 10, 15, 20, and 30 min, respectively. The aligned titania nanotubes were used as the electron transfer layer to improve both charge separation and transport in the PC part while increase the surface area to enhance the capacitance in the ES part.

For the PC part, the titania nanotube-modified Ti wires was successively coated with P3HT:PCBM and PEDOT:PSS layers. Figures S4 and 2d show SEM images after the coat of P3HT:PCBM and PEDOT:PSS layers, respectively. The outer surfaces appeared uniform without obvious aggregates or curved structure in both cases (Figures S3c and S3d). This is important to closely and stably wrap the MWCNT sheet to produce the PC part. Figure 2e further shows the formation of the uniform P3HT:PCBM and PEDOT:PSS layers by a side view on the surface. The thicknesses of the P3HT:PCBM and PEDOT:PSS layers were calculated to be appropriately 60 nm and 100 nm, respectively. Figures 2f and 2g show SEM images after the MWCNT sheet was wrapped around the Ti wire at low and high magnifications, respectively. The aligned MWCNT sheets could be tightly and uniformly attached on the surface, and the highly aligned structure of MWCNTs had been well maintained. Here aligned MWCNT sheets were prepared from MWCNT arrays which were synthesized by chemical vapor deposition through a dry drawing process.[22–24] The MWCNT sheets exhibited a width of approximately 1 cm and thickness of 20 nm. For the ES part, the same MWCNT sheet was continuously wrapped on the titania nanotube-modified Ti part (Figure S3e and S3f). Figure 2h shows that PVA electrolyte was finally injected between the Ti wire and MWCNT sheet. The Ti wire and MWCNT sheet were directly connected to external circuits for characterizations (Figure S5).

A bulk heterojunction layer of P3HT and PCBM was used to realize the photoelectric conversion, and the mechanism in the PC part is schematically shown in Figure S6. Upon the absorption of the sunlight, the heterojunction layer generates excitons that are separated into electrons and holes. The electrons are transported to the Ti wire through the aligned titania nanotubes, while the holes are collected by the aligned MWCNTs through the PEDOT:PSS hole transfer layer. The characterization of photoelectric conversion was made under standard AM 1.5 (100 mW cm⁻²) illumination conditions.[25,26] The effective area was calculated by multiplying the diameter and length of the fiber as generally recognized.[20] Figure 3 represents typical J–V curves for the PC part in the “energy fiber” with increasing lengths of 650 nm to 950 nm, 1.8 μm, 2.2 μm, 2.6 μm, 4 μm (Figure S7), and the efficiencies are 0.33, 0.37, 1.01, 0.88, 0.63, and 0.3%, respectively. The maximum efficiency occurs at 1.8 μm, which is mainly studied below. In addition, the photoelectric conversion efficiencies of the PC part were traced in argon and air for a period of ten days, and they had been maintained by more than 90% (Figure S8).

Figure 4a schematically shows the circuit connection state in the process of charging and discharging, respectively. Figure 4b exhibits the charge-discharge curves during the
light-energy density, and effective area in the PC part, respectively. Here the dependence of the $\eta$ on the MWCNT sheet thickness in the ES part has been compared in Figure 5. With the increasing MWCNT layer thickness from appropriately 0.5, 2, 5, and 10 to 20 $\mu$m, the values of entire photoelectric conversion and storage efficiencies are increased from 0.20, 0.35, 0.40, and 0.66 to 0.82%. With the further increase of the MWCNT layer thickness, the entire photoelectric conversion and storage efficiency remained almost unchanged.

The coaxial structure was found to be critically important for the stable performance as flexible devices. Figures S10a and S10b show SEM images of the coaxial MWCNT layer which is wrapped on a modified Ti wire under bending. The device structure can be well maintained during the deformation. In contrast, above self-powering process with the ES part connected with a potentiostat during the characterization. The thickness of the used MWCNT layer was 10 $\mu$m. For the discharging process, the PC and ES parts were disconnected, and the discharging process was performed at a current of 0.1 $\mu$A. Obviously, the charging process is very fast. The electrochemical properties of the “energy fiber” are measured by the galvanostatic charge-discharge and cyclic voltammetry (CV) (Figures 4c and 4d). The specific capacitance in length ($C_L$) was calculated by $C_L = \frac{I \times \Delta t}{(L \times \Delta V)}$, where $I$, $\Delta t$, $L$, and $\Delta V$ correspond to the current load (A), discharge time (s), length of the ES part (cm), and potential window (V), respectively. Figure 4c exhibits the galvanostatic charging-discharging curve of the self-powered “energy fiber” with the $C_i$ value of 0.077 mF cm$^{-1}$. Similarly, the specific capacitance in area ($C_S$) can be also calculated by $C_S = \frac{I \times \Delta t}{(S \times \Delta V)}$ with area of the ES part by multiplying the length and circumference of the fiber part (cm$^2$). According to the equation of $E = 0.5C_e \times V^2$, where $C_S$ and $V$ correspond to the specific capacitance and operating voltage, respectively, the energy density is 1.61*10$^{-7}$ Wh cm$^{-2}$. Figure 4d has compared CV curves with increasing scan rates from 100 to 5000 mV s$^{-1}$. The similar shapes of these CV curves indicate a high electrochemical stability. In addition, the energy storage efficiency in the ES part approaches to 65.6%.

The entire photoelectric conversion and storage efficiency ($\eta$) was calculated by multiplying the photoelectric conversion efficiency ($\eta_{\text{conversion}}$) in the PC part and energy storage efficiency ($\eta_{\text{storage}}$) in the ES part (Figure S9), i.e., $\eta = \eta_{\text{storage}} \times \eta_{\text{conversion}} = \frac{E_{ES} \times S_{ES} \times (P_{in} \times S_{PC})}{P_{in} \times S_{PC}}$, where $S_{ES}$, $t$, $P_{in}$, and $S_{PC}$ correspond to the surface area of the ES part, photocharging time, illuminated light-energy density, and effective area in the PC part, respectively.$^{[15]}$ Here the dependence of the $\eta$ on the MWCNT sheet thickness in the ES part has been compared in Figure 5. With the increasing MWCNT layer thickness from appropriately 0.5, 2, 5, and 10 to 20 $\mu$m, the values of entire photoelectric conversion and storage efficiencies are increased from 0.20, 0.35, 0.40, and 0.66 to 0.82%. With the further increase of the MWCNT layer thickness, the entire photoelectric conversion and storage efficiency remained almost unchanged.

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solar energy to electric energy and stores it. The “energy fiber” is flexible and can be scaled up for the practical application by the well-developed textile technology, and may open a new avenue to future photoelectronics and electronics. 

Experimental Section

MWCNT sheets had been directly drawn from MWCNT arrays which were synthesized by chemical vapor deposition and described elsewhere. Perpendicularly aligned titania nanotubes were grown on the Ti wire by electrochemical anodization. The Ti wire typically with diameter of 127 μm was first washed by acetone, isopropanol and deionized water prior to the use. A mixture of NH4F (0.3 wt%) and H2O (8 wt%) in the ethylene glycol was used as the electrolyte. The growth was made in a two-electrode system with Ti wire and Pt plate as anode and cathode electrodes at 60 V for 1, 5, 10, 15, 20, and 30 min, respectively. The modified Ti wire with titania nanotubes was washed by deionized water and then annealed at 500 °C in air for 1 h. For the PC part, the polymer layers were dip-coated onto the modified Ti wire. Typically, the modified Ti wire was dipped into a chlorobenzene solution of P3HT (30 mg mL−1) and PCBM (24 mg mL−1) in a glovebox and taken out for annealing at 150 °C for 10 min. A mixture of PEDOT:PSS aqueous solution (PH1000) and 2-propanol (volume ratio of 4/1) was further coated on the outer surface and taken out for annealing at 150 °C for 10 min. MWCNT sheet was wrapped onto the polymer-coated Ti wire to produce the PC part. For the ES part, the electrolyte was coated on the titania nanotube-modified Ti wire, followed by the attachment of the MWCNT sheet. A mixture of PVA (10 g) and phosphoric acid (10 g) in water (90 mL) was used as the gel electrolyte. For the convenience of characterizations, the ends of Ti wire and MWCNT sheet were connected to indium by an ultrasonic soldering mate (USM-V, Kuroda Techno).

Supporting Information

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

Acknowledgements

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Figure 6. Flexibility and weaveability of “energy fibers”. a–d) “Energy fibers” being bent into various shapes. e) Change of the entire photoelectric conversion and storage efficiency of the “energy fiber” under bending for 1000 cycles. η0 and η correspond to the entire efficiency before and after bending. The arrow shows the “energy fiber”. f) “Energy fibers” being woven into a textile structure with each other. g) Photograph of two “energy fibers” being woven into a flexible aramid fibers textile. The arrow shows the “energy fiber”.

Figures S10c and S10d show SEM images of a MWCNT fiber which is twisted with the modified Ti wire, and the MWCNT fiber was separated from the modified Ti wire during the bending. Due to the high flexibility, the “energy fiber” could be bent into various forms depending on the application requirement (Figures 6a–6d). Figure 6e has further traced the change of entire photoelectric conversion and storage efficiency of an “energy fiber” during bending (Figure S11), which was slightly decreased by less than 10% after bending for 1000 cycles without sealing. Note that the twisted wire-shaped device didn’t work after bending for only five cycles even when the dye-sensitized solar cell and supercapacitor were sealed together (Figure S1). In the case of the flexible membrane device based on the gel electrolyte, it showed an entire photoelectric conversion and storage efficiency of 0.79% before bending, which was largely decreased to 0.05% after bending for 100 cycles. In addition, these “energy fibers” can be easily woven with each other or with other chemical fibers to form flexible textiles (Figures 6f and 6g). Figure S12 further shows the stability of the “energy fiber” in 7 days, and the entire photoelectric conversion and storage efficiency could be maintained by 75%.

In summary, we have developed an all solid-state, coaxial, and self-powered “energy fiber” which simultaneously converts