SnO$_2$-microtube-assembled cloth for fully flexible self-powered photodetector nanosystems†

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Integrating an energy conversion or storage device with photodetectors into a self-powered system provides a promising route to future devices aimed at reduced size, low weight and high flexibility. We reported here the fabrication of a fully flexible self-powered photodetector nanosystem by integrating a flexible SnO$_2$-cloth-based ultraviolet photodetector with a flexible SnO$_2$-cloth-based lithium-ion battery. The flexible SnO$_2$-cloth-based ultraviolet photodetectors showed fast response to ultraviolet light with excellent flexibility and stability. Using SnO$_2$-on-carbon-cloth as the binder-free anode and commercial LiCoO$_2$/Al foil as the cathode, a flexible full lithium-ion battery was assembled, exhibiting a reversible capacity of 550 mA h g$^{-1}$ even after 60 cycles at a current density of 200 mA g$^{-1}$ in a potential window of 2–3.8 V. When integrated with and driven by the flexible full battery, the fully flexible self-powered photodetector nanosystem exhibits comparable performance with an analogous externally powered device. Such an integrated nanosystem could serve as a wireless detecting system in large areas, as required in applications such as environmental sensing and biosensing.

Introduction

Recently, flexible electronics have drawn great interest owing to their potential applications in roll up displays, wearable devices, and portable devices.$^{1,4}$ Many kinds of flexible functional devices have been developed, such as photodetectors$^{1,2}$ thin-film transistors,$^6$ and energy conversion and storage devices including dye sensitized solar cells,$^9,11$ supercapacitors,$^3,5$ nanogenerators$^{12}$ and lithium-ion batteries.$^{13}$ Among these fabricated flexible devices, flexible photodetectors have drawn considerable attention because of their extensive applications in environmental and biological research, optical communication, sensors and missile-launch detection.$^{14}$ However, traditional photodetectors are usually powered by external instruments, which not only greatly increase the system size but also greatly limit their mobility and independence for applications in areas such as large-area wireless environmental sensing and biosensing. Therefore, it is highly desirable to fabricate flexible energy conversion or storage devices and incorporate them into fully flexible self-powered systems, for application as self-powered detectors.$^{15,16}$

Self-powered systems are a promising concept in the design of future devices aimed at reduced size, weight, and thickness. Several types of self-powered systems have already been successfully developed, including an integrated power pack consisting of an energy conversion device with a storage device,$^{17–19}$ a self-powered electrochromic device driven by a nanogenerator$^{20}$ or a supercapacitor,$^{21}$ and a photodetector supplied by a fuel cell$^{22}$ or a supercapacitor.$^{23}$ Although self-powered photodetector systems have been fabricated, most of them are too bulky for use in flexible detecting applications. In this work, we designed a fully flexible self-powered photodetector nanosystem by integrating a flexible SnO$_2$-cloth-based ultraviolet photodetector with a flexible SnO$_2$-cloth-based lithium-ion battery. Compared with other kinds of energy storage devices, lithium-ion batteries exhibit both high energy density and a long cycle life.$^{13,24,25}$ The as-fabricated fully flexible nanosystem demonstrated comparable performance to that of a photodetector driven by an external power source, possessing good photo-response, excellent stability and high reproducibility.

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†Electronic supplementary information (ESI) available: Schematic illustration for the synthesis of a microtube-woven SnO$_2$ cloth, optical image of a large-sized SnO$_2$ cloth from the hydrothermal process, SEM image of the pure carbon cloth, SEM images of the as-grown SnO$_2$/C cloth from the hydrothermal process without the following heat treatment, the first five current–voltage curves of the SnO$_2$/C electrode in the potential range of 0.01–3 V at a scan rate of 0.5 mV s$^{-1}$, the first three current–voltage curves of the pure carbon cloth measured at a scan rate of 0.5 mV s$^{-1}$, the charge–discharge curves of the pure carbon cloth, the corresponding cycling performance at a current density of 200 mA g$^{-1}$ and the coulombic efficiency of the pure carbon cloth, the voltage vs. time curve of the flexible full battery under different bending states, the voltage vs. time profile of the flexible battery supply for the integrated device before and after photodetecting measurements. See DOI: 10.1039/c3nr02300a

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Experimental section

Synthesis of SnO₂ cloth

Using carbon cloths as the templates, SnO₂-microtube-assembled cloths were fabricated via a common hydrothermal method. Typically, commercially available carbon cloths were cut into the desired sizes and treated with acetone, deionized water, and ethanol in sequence. A piece of the prepared carbon cloth was placed in a Teflon-lined stainless steel autoclave containing a mixture of 0.2 g of SnCl₂·2H₂O and 34 ml of diluted hydrochloric acid (0.65 M). After sealing, the autoclave was heated in an oven at 180 °C for 20 h. Once the reaction finished, the cloth was washed with deionized water and ethanol before being dried in air. The dried samples were then either annealed at 500 °C for an hour or calcinated at 800 °C for 3 h, depending upon the intended application.

Characterization

The phase of the product was identified by using an X-ray diffractometer (X’Pert PRO, PANalytical B.V., The Netherlands) with radiation from a Cu target (Kα, λ = 0.15406 nm). The morphology was characterized by scanning electron microscopy (SEM, FEI Sirion 200 (10 kV)). A 500 W Hg lamp was used as the UV source, supplying a light intensity of 145 mW cm⁻². I–V and I–T characteristics were measured using an Autolab station (model AUT84315).

Cell assembly and electrochemical measurements

The electrochemical performance of the SnO₂/C cloth was measured by assembling CR2032 coin-type half cells, which consist of a lithium foil counter electrode and reference electrode, Celgard 2300 as the separator membrane, a piece of SnO₂/C cloth as the working electrode without any conductive agent or polymeric binder, and 1 M LiPF₆ in a mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC) (v/v = 1:1) as the electrolyte. A flexible full battery was fabricated by using LiCoO₂/Al foil as the counter electrode and SnO₂/C cloth as the working electrode. The loading density of the SnO₂ active material was calculated to be about 2 mg cm⁻². Cyclic voltammetry (CV) measurements were performed on an electrochemical station (CHI 760D, CH Instruments Inc., Shanghai) at a scanning rate of 0.5 mV s⁻¹. The galvanostatic discharge–charge measurements were carried out on a Land Battery Measurement System (Land, China) at different current densities with a voltage window of 0.01–3.00 V for the coin-type half cells and 2–3.8 V for the flexible full batteries.

Results and discussion

The schematic illustration for the synthesis of microtube-woven SnO₂ cloth is presented in Fig. S1†. Typically, commercially available flexible carbon cloths were used as the sacrificial template. The pre-treatment of the carbon cloths using SnCl₄, also called the seeding process, is a key step for the following SnO₂ growth. After hydrothermal growth, the carbon cloths were found to be uniformly coated with SnO₂ nanoparticles. To prepare the product for use as the anode in a flexible lithium battery, it was annealed at 500 °C for an hour to increase the contact between the SnO₂ nanoparticles and the carbon cloth, where the carbon cloth served as the current collector. If the product was to be used as the active material in the flexible photodetector, the product was calcinated at 800 °C in air for 3 h to remove the inner carbon cloth.

Fig. 1a shows an optical image of the final SnO₂ cloth, exhibiting excellent flexibility and a well woven structure. Using the current method, we were able to produce flexible SnO₂ cloth on a large scale. Fig. S2† presents a large SnO₂ cloth with a size of about 4 × 4 cm². The crystal phases of the as-prepared products, namely, the hydrothermally grown product (sample I), the 500 °C annealed product (sample II), and the 800 °C calcinated product (sample III), were studied by X-ray diffraction (XRD) and the corresponding results are presented in Fig. 1b. In the patterns for samples I and II, all of the peaks except the two peaks marked with stars, which proved to come from the carbon template, agree well with the rutile SnO₂ phase (JCPDS Card, no. 77-447). The two patterns did not show any obvious difference, indicating that low temperature sintering did not change the composition and phase of the product. After high temperature calcination at 800 °C (sample III), there are no

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**Fig. 1** (a) Optical image of the as-prepared flexible pure SnO₂ cloth. (b) XRD patterns of the as-obtained samples I, II, and III. (c and d) Typical SEM images of the SnO₂ cloth woven by microtubes at different magnifications. (e and f) Amplified SEM images of a single SnO₂ microtube assembled by numerous nanoparticles.
SnO$_2$ has great potential applications in many practical devices. A cross-section SEM image of a single SnO$_2$ template. A higher magnification SEM image depicted in Fig. 1d displays several fibers with diameters of 6–8 μm, a little smaller than the pure carbon fibers with diameters of around 10 μm (Fig. S3†). These diminished diameters are caused by shrinking after the thermal treatment at high temperature. At high temperature, the small nanoparticles tended to connect with each other, which led to a relative decrease in the diameters in the cloth. Similar phenomena were also found in the growth of other nanomaterials using carbon cloth as templates. A cross-section SEM image of a single SnO$_2$ fiber is shown in Fig. 1e, clearly revealing its hollow nature and extremely thin wall. Fig. 1f shows the high-resolution SEM image taken from the SnO$_2$ fiber, where numerous nanoparticles with sizes of about 50–80 nm can be clearly seen. The above results revealed the formation of the pure SnO$_2$-microtube-assembled cloth after calcination at high temperature.

As an important n-type semiconductor with a wide band gap of 3.6 eV and a high quantum efficiency in the ultraviolet region, SnO$_2$ has great potential applications in many practical devices such as ultraviolet photodetectors, optical switches, photocatalysts and gas sensors. After synthesis and calcination at 800 °C, the flexible pure SnO$_2$ cloth was directly used as the active material in flexible photodetectors, to investigate its photoresponse to ultraviolet irradiation. The flexible photoresponse device was fabricated by cutting the as-obtained SnO$_2$ cloth into the desired size and then fixing two silver wires to the two ends of the SnO$_2$ cloth with silver paste as the glue. The inset in Fig. 2a shows a schematic diagram of the flexible device. Fig. 2a presents the current–voltage (I–V) characteristics of the SnO$_2$-cloth-based device both in the dark and under UV light irradiation supplied by a 500 W Hg lamp with a power density of 145 mW cm$^{-2}$. At a fixed bias of 3 V, the photo-excited current was increased to about 8 μA, which is about 4 times higher than the dark current ($I_{\text{dark}} = 2\ \mu\text{A}$), indicating a good photoresponse to UV light irradiation of the device. The corresponding time-dependant photoresponse curve of the device is shown in Fig. 2b by adopting a continuous UV light irradiation with an on–off interval of 80–120 s. From the curve, we can see that, upon illumination, the current of the device periodically increased to a relatively stable value of about 8 μA and then rapidly decreased to its initial level when the light was turned off. The results revealed the excellent stability and reproducible feature of the SnO$_2$-cloth-based device. It should be noted that the dark current should be higher than that of an individual SnO$_2$ nanostructure, which is thought to be caused by the fact that the as-obtained SnO$_2$ cloths are woven, poly-crystalline, film-like structures with a continuous network structure, in accordance with previous reports.

To get information about the relationship between the photocurrent and the intensity of UV light, we illuminated the device with UV light at light intensities ranging from 0 to 145 mW cm$^{-2}$, and the corresponding I–V curves are shown in Fig. 2c. The photocurrent was found to increase with increasing light intensity, which is in good agreement with previous reports. According to the value of the photocurrent at a bias of 1 V, we can obtain the fitting current–light intensity characteristic, as shown in Fig. 2d, which gives a power function law of $I \sim P^{0.288}$, where $I$ is the value of photocurrent and $P$ is the light intensity. The complex process of electron–hole generation, trapping and recombination within the semiconductor may be the reason for the non-unity exponent. By adjusting the intensity of the irradiated light, the photocurrent can be reversibly changed 3 times without damaging the SnO$_2$ cloth. The excellent photoresponse can be attributed to the hollow nature and dense arrangement of the SnO$_2$ cloth, which can achieve the high-speed transmission of electrons and proper generation and recombination of the electron–hole pairs.

The folding degree and stability are the two key parameters for flexible devices. Fig. 3a shows the typical I–V curves of the as-fabricated flexible device after bending the device for 0, 20, 40, 80, 100 cycles. No obvious performance decline was found, indicating the excellent stability of the device. Fig. 3b shows the current–time (I–T) curves of the devices after being subjected to varying degrees of bending, and the corresponding optical images of the device under different bending stages are shown in the figure inset. The current was found to be stable at around 10 nA during all of these bending stages, further confirming the flexibility and stability of the devices even under the effect of external bending stress.

To construct fully flexible self-powered photodetector nano-systems, a flexible energy storage device such as a flexible lithium ion battery is obviously required. Initially, insight into the electrochemical performance of the present SnO$_2$ cloth was gained by constructing a half-cell using the 500 °C calcinated SnO$_2$ cloth as the anode and the inner carbon fibers as the...
A galvanostatic cycling test of the assembled cell was also carried out, to investigate its electrochemical performance, which was performed in the potential range of 0.01–3 V at a current density of 200 mA g⁻¹. Fig. 4a shows the voltage-specific capacity curves of the electrodes for the 1st, 2nd, 20th, 50th and 100th charge–discharge cycles. It can be seen that the plateau was reached at around 0.8 V in the first discharge curve, corresponding to the formation of the solid electrolyte interface (SEI) layer and Li₂O.³⁹ Fig. 4b shows the cycling performance of the SnO₂/carbon cloth at a current density of 200 mA g⁻¹. The specific discharge and the charge capacity for the first cycle are around 1433 and 1114 mA h g⁻¹, respectively, with a coulombic efficiency of around 78%. The coulombic efficiency in the following cycles remains as high as around 100% and is relatively stable throughout the entire cycle tests, indicating the completeness of the SEI layer and the good reversibility of the electrochemical reactions. Besides, the reversible capacity of the SnO₂ electrodes is stable at 550 mA h g⁻¹ after 100 cycles, which is still higher than that of commercial graphite (Fig. 4b). To eliminate the influence of the carbon cloth, the capacity of the pure carbon cloth was also studied and the result is presented in Fig. S7.† The extremely low capacity of the pure carbon cloth indicated that the carbon cloth contributes little to the overall capacity of the SnO₂ electrodes. Therefore, the present SnO₂/carbon cloth is proved to be a good candidate for application in high performance lithium-ion batteries, possessing the advantage of requiring no ancillary materials such as polymeric binder and carbon black.

The electrochemical performance of the as-synthesized SnO₂ cloth was further studied at different current densities in the range of 100–1600 mA g⁻¹. From Fig. 4c, it can be seen that the capacity can reach 860 mA h g⁻¹ when first cycled at 400 mA g⁻¹, 540 mA h g⁻¹ at 800 mA g⁻¹, 420 mA h g⁻¹ at 1200 mA g⁻¹ and 245 mA h g⁻¹ at 1600 mA g⁻¹. When returning to a current density of 100 mA g⁻¹, the specific capacity tended to be stable at 550 mA h g⁻¹, in accordance with the original cycle.
performance shown in Fig. 4b. Although different current densities are gradually applied, the coulombic efficiency is still high at around 100%, as shown in Fig. 4d, demonstrating the excellent reversible performance of the SnO$_2$-based electrode. Based on the above results, we attribute the improved performance to the relatively small nanoparticle-assembled microtubes and the good contact between nanoparticles and carbon cloth, which offer a suitable distance for the lithium-ion's transportation and excellent electrical conductivity, similar to previous reports.$^{11}$

We further fabricated a flexible full battery by using the SnO$_2$/C cloth directly as a binder-free anode. The structure of the flexible full battery, displayed in Fig. 5a, consists of the SnO$_2$/C cloth as the anode, a separator, the LiCoO$_2$/Al foil as the cathode, LiPF$_6$ containing electrolyte, and a flexible aluminum plastic film as the shell. Fig. 5b presents the optical image of the final packaged flexible full battery. It is well known that the capacity of a commercial LiCoO$_2$ cathode is 40 mAh, which is much larger than the biggest total capacity of the as-prepared SnO$_2$ cloth (about 15 mA h). Therefore the final flexible full batteries are anode-limited and the specific capacity is referenced to the mass of the SnO$_2$ electrodes. Fig. 5c displays the voltage-specific capacity curves of the device for the 1$^{st}$, 2$^{nd}$, 20$^{th}$, and 60$^{th}$ charge–discharge cycles at a current density of 200 mA g$^{-1}$ in the voltage window of 2–3.8 V, and the corresponding specific capacities were found to be 863 mA h g$^{-1}$, 818 mA h g$^{-1}$, 651 mA h g$^{-1}$ and 550 mA h g$^{-1}$, respectively. The detailed cycle performance of the battery is further plotted in Fig. 5d. The electrodes delivered about 550 mA h g$^{-1}$ of the reversible capacity over 60 charge–discharge cycles, revealing the relatively good cycling performance of the device. In addition, the corresponding coulombic efficiency (CE) was also plotted in Fig. 5d, which was found to remain as high as around 100%.

As we discussed above, the folding endurance is one of the important parameters for a flexible device. Thus we measured the voltage–time curve of the flexible full battery under different bending states and the corresponding results were shown in Fig. S8.$^\dagger$ The voltage of the flexible full battery remained constant at about 3.2 V under the different bending states, demonstrating that the battery is hardly affected by external bending stress.

Since both the SnO$_2$ cloth based photodetectors and the SnO$_2$ cloth based full battery have the features of high flexibility and stability, we have further demonstrated here the integration of these two devices into a self-powered, fully flexible, photodetector nanosystem and studied its unique performance. Fig. 6a shows the schematic illustration of the self-powered flexible device, constructed by integrating a flexible SnO$_2$ cloth based photodetector and a SnO$_2$ cloth based full battery. Fig. 6b presents the typical current–time curves for the device under periodic intermittent UV light irradiation with an intensity of 145 mW cm$^{-2}$. From these curves, we can see that, powered by the flexible battery, the photodetector showed a fast and stable response to UV light irradiation. The performance is similar to a common flexible photodetector driven by an external power supply, confirming that the SnO$_2$ cloth based flexible battery is a suitable power supply for a photodetector. The voltage profile of the flexible battery supply before and after photodetecting measurements is shown in Fig. S9.$^\dagger$ The constant voltage of the battery further confirms it is a suitable power supply for a photodetector to substitute the commonly used external power supply.

The flexibility and the stability of the integrated self-powered device were also studied by measuring the current change of the device under different bending states. Fig. 6c shows the current $i$ vs. time profile of the device in 4 bending states (optical images are shown in the insets). The curve in Fig. 6c was found to
remain flat, proving that the extent of bending had little influence on the performance of the integrated device. Therefore the integrated nanosystem has been proven to be an independent photodetecting device with the advantages of high flexibility and excellent photoresponse.

Conclusions

In summary, a fully flexible self-powered photodetector nanosystem was fabricated by integrating a flexible SnO$_2$-cloth-based ultraviolet photodetector with a flexible SnO$_2$-cloth-based lithium-ion battery. The active SnO$_2$ cloth material was synthesized via a conventional hydrothermal method using carbon cloth as the template. Both the SnO$_2$-cloth-based flexible photodetector and the flexible lithium ion battery showed excellent performance with the features of excellent flexibility and stability. The final integrated flexible self-powered nanosystem driven by the flexible battery showed comparable performance with a common photodetector driven by an external power supply. Such an integrated nanosystem could serve as a detecting system in large wireless areas for applications such as environmental sensing and biosensing. Our work here opens up a new strategy to realize fully flexible self-powered photodetection, and it may be extended to areas where there are needs for stretchable/ portable and small size electronics.

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Notes and references


