Flexible and transparent supercapacitor based on In_2O_3 nanowire/carbon nanotube heterogeneous films

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In this paper, a supercapacitor with the features of optical transparency and mechanical flexibility has been fabricated using metal oxide nanowire/carbon nanotube heterogeneous film, and studies found that the power density can reach 7.48 kW/kg after galvanostatic measurements. In addition, to study the stability of flexible and transparent supercapacitor, the device was examined for a large number of cycles and showed a good retention of capacity (~88%). This approach could work as the platform for future transparent and flexible nanoelectronics. © *2009 American Institute of Physics*. [DOI: 10.1063/1.3069277]

There has been great interest recently in both flexible and transparent electronics such as transparent and flexible active matrix organic light-emitting diode display which may find applications in heads-up display, automobile wind-shield display, and conformable products.[1] However, to realize fully transparent and/or flexible devices, one may also consider making transparent and/or flexible energy conversion and storage units with high energy storage and power density. Electrochemical capacitor (supercapacitor) with properties of high energy storage, small size, and lightweight has become one of the best candidates of energy storage devices.[2–5] Although some supercapacitors built on carbon nanotubes (CNTs) have been reported,[6–9] the performance of these supercapacitors is usually not as good as redox supercapacitors made of metal oxide materials (e.g., RuO_2, MnO_2, and IrO_2).[10,11] On the other hand, these supercapacitors are usually neither transparent nor flexible, which greatly limit their real applications in flexible or transparent electronics. It is still of great interest to develop transparent and flexible supercapacitors.

In this paper, we report a prototype of high performance flexible and transparent electrochemical supercapacitors based on metal oxide nanowire/CNT heterogeneous films. The typical supercapacitor structure is made of a polymer electrolyte layer sandwiched between two transparent and flexible nanowire/nanotube film electrodes. The device structure includes the following features. First of all, we chose metal oxide nanowires dispersed on CNT films as active materials. Owing to their unique properties of high aspect ratio and short diffusion path length to ions, metal oxide nanowires can provide high surface area, fast charge/discharge, and facial redox reactions, and thus can be one of good candidates for electrochemical capacitors. Here, In_2O_3 nanowires are used as an example, and the general concept can be applied to many other nanowires. Second, we used transparent flexible polymer membrane with nonaqueous electrolyte to work as a separator and electrolyte. The third feature is that we optimized the nanowire/nanotube film thickness for mechanical flexibility and optical transparency, which allowed us to achieve flexible and transparent supercapacitors based on In_2O_3 nanowire/CNT heterogeneous films.

Hybrid In_2O_3 nanowires/CNT films were prepared as follows. First, CNT films were fabricated by vacuum filtration method following the previous report.[12–14] In brief, to make an uniform CNT film, a CNT suspension was filtered through a porous alumina filtration membrane. As the solvent went through the membrane, the CNTs were trapped on the membrane surface thus forming a homogenous entangled network. An adhesive and flat poly(dimethysiloxane) stamp was adapted to peel the CNT film off the filtration membrane and then released it onto a polyethylene terephtalate (PET) substrate on hotplate at 100 °C. The scanning electron microscopy (SEM) image of a transferred CNT film on PET substrate is shown in Fig. 1(a). The thickness of the film is roughly 60 nm and the conductivity is ~570 S/cm.

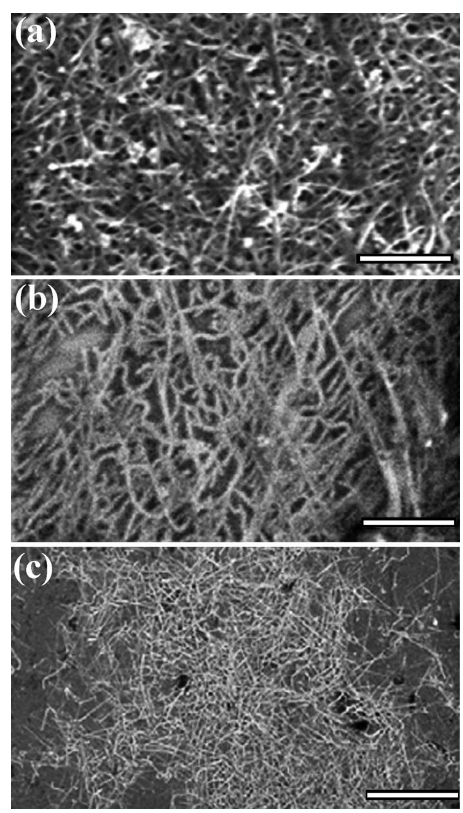

FIG. 1. (a) SEM images of CNT films, scale bar: 200 nm. (b) PEDOT:CNT films, scale bar: 200 nm. (c) In_2O_3 nanowire/CNT heterogeneous film, scale bar: 2 μm.

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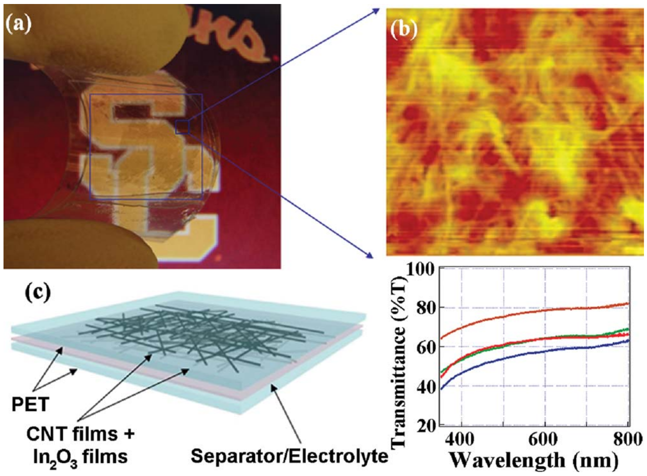

FIG. 2. (Color online) (a) Photograph of a flexible and transparent supercapacitor fabricated using CNT films. (b) AFM image of entangled CNT networks sitting on a transparent PET substrate. (c) Schematic of a flexible and transparent supercapacitor. The gray color represents a Nafion film as separator between two In_2O_3 nanowires/CNT heterogeneous film electrodes. (d) Transmittance spectra of three different electrochemical capacitors and a single CNT film.

In_2O_3 nanowires with a diameter of ~20 nm and a length of ~5 μm were synthesized by a pulsed laser deposition method.[15] The as-grown nanowires were sonicated into Isopropanol solutions and then dispersed on transferred CNT films to form In_2O_3 nanowire /CNT heterogeneous film [Fig. 1(c)] for transparent and flexible supercapacitor study. For comparison, we also fabricated supercapacitors using transferred CNT films and poly(3,4-ethylenedioxythiophene) (PEDOT)/CNT hybrid films. The PEDOT:CNT films were made by spin coating of a PEDOT film with a thickness of ~10 nm. The SEM image shown in Fig. 1(b) exhibited a uniform PEDOT:CNT film with a the scale bar of 200 nm.

Figure 2(a) shows a photograph of a supercapacitor made of transferred CNT films, which gives mechanical flexibility and optical transparency. A typical atomic force microscopy (AFM) image of a transferred CNT film on a PET substrate is shown in Fig. 2(b). It can be seen that dense and homogenous networks of entangled CNTs are formed. The schematic diagram of the supercapacitor in this work is depicted in Fig. 2(c). The device was composed of two transparent electrodes (In_2O_3 nanowire/CNT heterogeneous films on PET substrates) sandwiched with a Nafion 117 membrane. Here, the Nafion 117 membrane served as a transparent spacer and nonaqueous 1 M $LiClO_4$ [$LiClO_4$ in a mixture of ethylene carbonate (EC), diethyl carbonate (DEC), and dimethylene carbonate (DMC) in a volume ratio of EC/DEC/DMC=1:1:1] was adapted as electrolyte in this study. The transparency of the supercapacitors built on In_2O_3 nanowires/CNT heterogeneous films, transferred CNT films, and PEDOT:CNT films was measured and the results are shown in Fig. 2(d). As is well known, In_2O_3 is a wide band gap material (3.57 eV), which has been widely applied in the transparent electronics. With an existence of 30 wt % In_2O_3 nanowires above CNT films, the transmittance of a In_2O_3 nanowires/CNT heterogeneous film supercapacitor exhibits merely 3%–5% degradation in whole spectral region in comparison to a transferred CNT film supercapacitor and a PEDOT:CNT film supercapacitor. The transparency of the PEDOT:CNT film supercapacitor (green line) is almost the same as a transferred CNT film supercapacitor (brown line) over a spectral range from 300 to 800 nm.

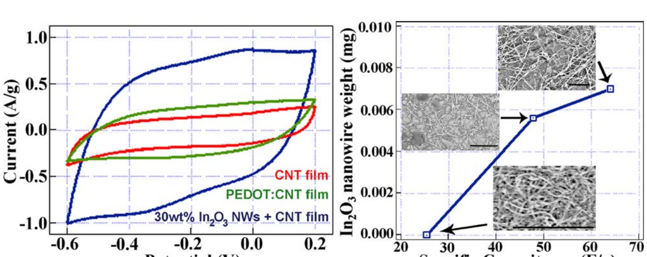

FIG. 3. (Color online) (a) Cyclic voltammograms of a CNT film supercapacitor, a PEDOT:CNT film supercapacitor, and a 30 wt % In_2O_3 nanowires on CNT film supercapacitors. (b) Specific capacitance vs different weights of In_2O_3 nanowires. The insets are SEM images with different weights of In_2O_3 nanowires. The scale bars in SEM pictures represent 2 μm.

The electrochemical properties and capacitance measurements of supercapacitors were studied in a two-electrode system by cyclic voltammetry (CV) and galvanostatic (GV) charge-discharge measurements using a Potentiostat/Galvanostat (Princeton Applied Research 273A). Figure 3(a) shows the results of typical CV measurements of three different electrochemical capacitors. The scan range is between 0.2 and −0.6 V with a scan rate of 20 mV/s. The capacitive behaviors of three different devices are clearly observed in this figure with near rectangular-shaped voltammograms and large CV currents. Specific capacitance of a supercapacitor can be obtained through the following equation:[6]

$$C(F/g) = \frac{i}{v}\left(\frac{1}{m}\right), \tag{1}$$

where ν is the scan rate, i is the corresponding current of the applied voltage, and m is the weight of the active electrodes. The calculated specific capacitance of transferred CNT film supercapacitor is about 25.4 F/g and PEDOT:CNT film supercapacitor is 33 F/g. These results are in a good agreement with the previously reported result from highly dense CNT network[6] and 85% CNT/15% PEDOT supercapacitors[16] in aqueous electrolyte. In addition, the specific capacitance of PEDOT:CNT film supercapacitor is much better than a supercapacitor made of PEDOT-poly(styrenesulfonate) CNT fibers (6.25 F/g) in nonaqueous electrolyte.[17] This can be attributed to larger surface to volume ratio of CNTs than CNT fibers (diameter: 5–500 nm), which improves the influence of different morphology. The effect of PEDOT coated over CNT films might result in a higher electric conductivity and provide more accessible area of CNT networks.[17,18] In addition, as one can see in Fig. 3(a), the In_2O_3 nanowire/CNT heterogeneous film supercapacitor exhibits an even higher specific capacitance (64 F/g) than both transferred CNT film and PEDOT:CNT film supercapacitors. We have further prepared and measured supercapacitors with various In_2O_3 nanowire quantity. With the increasing amount of In_2O_3 nanowires dispersed on CNT films, the specific capacitance of the heterogeneous supercapacitor can be dramatically improved up to 64 F/g (0.007 mg of In_2O_3 nanowire), which can be clearly observed in Fig. 3(b). This can be understood since the pseudocapacitance from the reversible redox transitions of adhesive In_2O_3 nanowires contributes to the overall capacitance.[19,20]

The result of GV measurements of In_2O_3 nanowire/CNT heterogeneous film supercapacitor is presented in Fig. 4(a). The charge/discharge experiment was carried out at a con-

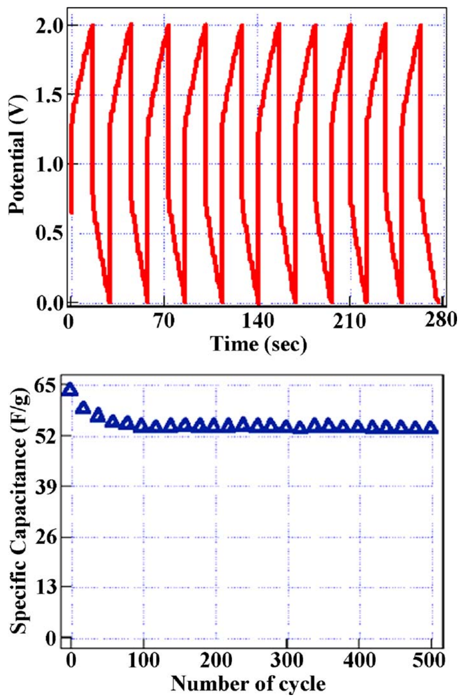

FIG. 4. (Color online) (a) Charge-discharge behavior of a In_2O_3 nanowire/CNT heterogeneous film electrochemical capacitor in 1*M* $LiClO_4$ electrolyte. (b) Cycle-life data of In_2O_3 nanowires/CNT heterogeneous film electrochemical capacitor. Specific capacitance was calculated from GV measurements at constant current of 0.5 A/g.

stant current of 0.5 A/g and a high operation voltage of 2.0 V. The slope of the discharge curve can be used to determine the specific capacitance by using the equation below,[2]

$$C_{\mathrm{sp}} = \frac{I}{dV/dt}\left(\frac{1}{m_1} + \frac{1}{m_2}\right), \tag{2}$$

where I represents the discharge current, dV/dt is the slope of the discharge curve, and m is the weight per electrode of the active material. The specific capacitance for this device shown is about 64 F/g, confirming qualitatively the results from the *CV* measurements. In addition, the specific energy density ($W=CV^2/2$, where V is the potential) is 1.29 W h/kg and power density ($P=W/\Delta t$, where Δt is the discharge time) is 7.48 kW/kg. These values reveal that the performance of In_2O_3 nanowire/CNT film supercapacitor is competitive to early reported work[3] in terms of high power density and energy density. Besides similar observation with other early literatures, internal resistance (IR) drop was observed in each branch of the entire curves in Fig. 3(a) because of the equivalent series resistance of the In_2O_3 nanowire/CNT film electrodes, the nonaqueous electrolyte, and the contact resistance between the electrodes. Through using different nanostructured materials (example: Au/CNT core-shell structures[21]) or right combination of active materials/electrodes and electrolyte, one can minimize the IR and thus improve the device performance in terms of higher specific capacitance and power density.

In order to study the stability of In_2O_3 nanowire/CNT heterogeneous film supercapacitor, the device was examined by GV measurements for 500 cycles with the same conditions. Figure 4(b) reveals the variation in specific capacitance as a function of cycle number. After first 100 cycles, there is a little specific capacitance decrease from 64 to 53 F/g. Then, the specific capacitance retains the same values and minimal fades up to 500 cycles. The specific capacitance fading of In_2O_3 nanowire/CNT heterogeneous film supercapacitors probably can be attributed to the dissociation of In_2O_3 nanowire during the redox process in GV measurements, which is also reported in the literatures for other metal oxide nanostructured materials.[20,22] More works need to be done in clarifying the mechanism. In comparison to supercapacitors made by other transition metal oxide nanostructured materials,[22,23] this observation indicates a good stability of In_2O_3 nanowire/CNT heterogeneous films for long-term capacitor applications.

In summary, we made a prototype of flexible and transparent supercapacitors built on In_2O_3 nanowires/CNT heterogeneous films. Studies found that the performance of CNT heterogeneous film supercapacitors can be significantly improved by dispersion of In_2O_3 nanowires on CNT films due to the redox transitions of In_2O_3 nanowires without degradation in transparency. Enhanced specific capacitance, power density, energy density, and long operation cycles have been realized with the incorporation of In_2O_3 nanowires. Extensive studies are underway to further improve the device performance and fill the gap of practical applications.

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