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High power density supercapacitors using locally aligned carbon nanotube electrodes

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Abstract

A new form of thin films formed by multi-walled carbon nanotubes exhibiting high packing density and local alignment were fabricated using a highly concentrated colloidal suspension of carbon nanotubes. Electrical double layer capacitors built from these film electrodes exhibited a close to rectangular cyclic voltammogram even at a high scan rate of 1000 mV s^{-1}, and produced very high specific power density of about 30 kW kg^{-1}, ideal for surge-power delivery applications. The preparation procedure is very simple, and does not require any binders. It has potential for highly efficient manufacturing of high power density supercapacitors and other similar electronic devices.

1. Introduction

Carbon nanotubes are attractive materials for electrodes of electrochemical energy storage devices due to their high conductivity, chemical stability, low mass density and large surface area. Consequently a wide range of potential applications for electrochemical energy storage systems has been proposed in recent years. For example, carbon nanotubes have been formed into electrodes for Li-ion secondary batteries [1–5], for hydrogen storage in fuel cells [6], and for supercapacitors [7–18].

As unique energy storage devices, supercapacitors are able to provide a huge amount of energy in a short period of time, i.e., high power density, making them indispensable for surge-power delivery [19]. The high power density of a supercapacitor is its most remarkable property as it is about ten times larger than that of secondary batteries. The maximum power density of a supercapacitor is given by $P_{\mathrm{max}} = V_{\mathrm{i}}^2/4R$ (where V_{i} is the initial voltage and R is the equivalent series resistance (ESR)) [20]. Accordingly, reducing both the internal resistance of the electrode materials and the contact resistance between the electrode and current collector is the key to attaining high power density. There have been several successful attempts to fabricate high power density supercapacitors. For example, Niu *et al* [10] reported that a power density >8 kW kg^{-1} was obtained by using free-standing mats of entangled nanotubes as electrodes. An [7, 15] obtained high power density with polished nickel foil for lower contact resistance and by conducting a heat-treatment at higher temperature to reduce the internal resistance of the carbon nanotube electrode. More recently, Yoon [14] lowered the contact resistance by directly growing carbon nanotubes on metal current collectors.

We report here a simple approach to lower the equivalent series resistance by fabricating thin film electrodes using a highly concentrated colloidal suspension of carbon nanotubes. The carbon nanotubes in the thin films are with very high packing density and possess some local alignment. The supercapacitors built from these electrodes have exhibited rectangular cyclic voltammograms even at a high scan rate of 1000 mV s^{-1}, an indication of a significantly small ESR, and a very high specific power density of about 30 kW kg^{-1} was thus obtained. Most importantly, this suspension preparation technique does not require the addition of any binder, and is easy and fast. All of these make it a potentially attractive route for fabricating electrodes for high power density supercapacitors and other similar devices.

2. Experimental section

The multi-walled carbon nanotubes (MWNTs) used for this study were made via chemical vapour deposition (CVD) in our laboratory. Synthesis of MWNTs was conducted

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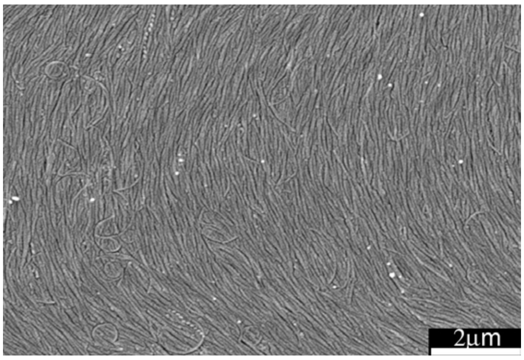

Figure 1. SEM image of a nanotube thin film fabricated by depositing a highly concentrated colloidal suspension, showing the local alignment of carbon nanotubes.

in a horizontal quartz tube in a furnace. Catalyst powder (Fe/Al_2O_3) was placed in a ceramic boat which was then loaded into a tube furnace. Hydrogen was then introduced into the furnace before it was heated up to 700 °C, where it was held for 30 min during which ethylene was introduced. The ethylene supply was then shut off and the system was cooled to room temperature.

The so-obtained powder of Fe/Al_2O_3 /MWNTs was then treated with an HF aqueous solution and hydrochloric acid at room temperature successively to extract the nanotubes by dissolution of Al_2O_3 and iron particles. The nanotubes were then collected by filtration, washed with distilled water and finally dried.

The purified nanotubes were refluxed with concentrated boiling nitric acid for several hours, and then washed with distilled water followed by rinsing with ethanol and drying at 60 °C. To prepare the colloidal suspension of the carbon nanotubes, predetermined and refluxed carbon nanotubes were placed in a scintillation vial containing 10 ml of dimethylformamide (DMF), and the vial was then capped and sonicated for 30 min. The colloidal suspensions remain stable for many months with no aggregated materials precipitating over time at all.

For this electrochemical application, two electrodes were prepared by directly depositing 0.1 ml of colloidal suspension (concentration: 26.7 mg of carbon nanotubes in 1 ml of DMF) on two 12 mm × 12 mm nickel foils (as the current collectors) respectively and followed by drying at room temperature. The microstructures of the electrodes were investigated by scanning electron microscopy (FEI XL30-SFEG). For the electrochemical measurement, a test cell of a capacitor was fabricated with 6N KOH used as electrolyte. A glass fibre filter paper immersed in the electrolyte was used as a separator, and was placed between the two electrodes. The cyclic voltammetry and galvanostatic charge/discharge tests were performed using a Potentiostat/Galvanostat (EG&G Princeton Applied Research, Model 263A).

3. Results and discussion

Figure 1 shows an SEM image of the nanotube thin film fabricated by depositing a highly concentrated colloidal suspension using DMF as the solvent. It can be seen that the packing density of the nanotubes in the film is relatively high, and that they are aligned locally. As has been demonstrated previously [21], the oxidation of carbon nanotubes induces a

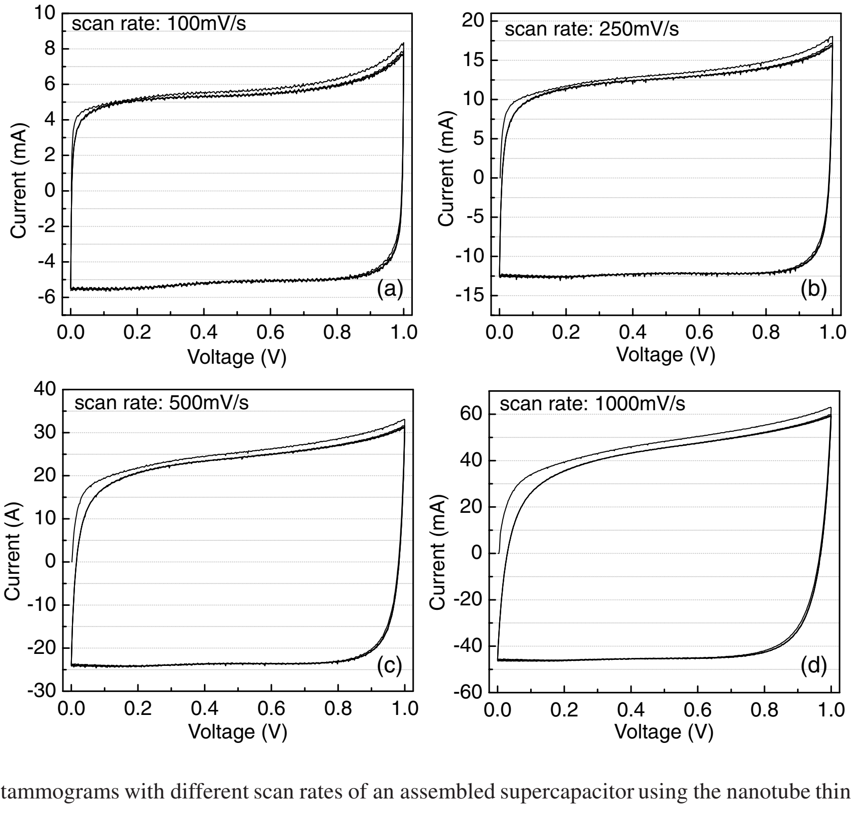

Figure 2. Cyclic voltammograms with different scan rates of an assembled supercapacitor using the nanotube thin films as electrodes.

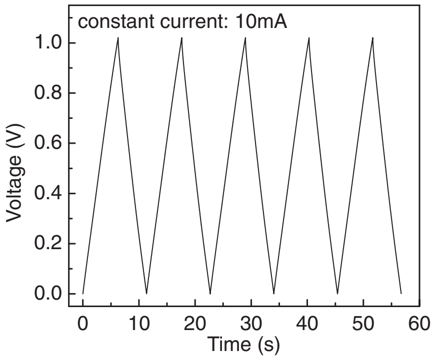

Figure 3. Constant current (10 mA) charge/discharge curve of the nanotube thin film electrodes.

negatively charged surface, particularly through the ionization of acidic surface groups. The resulting electrostatic repulsion leads to a dramatic increase in the stability of the colloidal suspension. The electrostatic repulsion between the nanotubes and the high packing fraction of nanotubes in the high concentration suspension are also the reasons for forming the ordered structure in the thin films.

Figure 2 shows the cyclic voltammograms (CVs) with different scan rates of the assembled supercapacitor. The CVs at scan rates of 100 and 250 mV s^{-1} show almost mirror images with respect to the zero-current line, except that there are strong oxidation peaks at 0.9–1.0 V that are attributed to redox reactions due to the functional groups on the nanotubes [11]. It should also be noted that both peaks gradually diminished after several tens of cycles, probably due to the removal of those functional groups. However, the CV curve still presents a quite rectangular shape that is a clear proof of well developed capacitance properties. The excellent CV shapes at scan rates of 100 and 250 mV s^{-1} reveal a very rapid current response on voltage reversal at each end potential. That is, perfectly rectangular and symmetric I–E responses of ideal capacitive behaviour were observed, and the straight rectangular sides indicate that there are negligible internal, interfacial and contact resistances [20]. In contrast, a large resistance will distort the response, resulting in a narrower loop with an oblique shape, especially at a high scan rate [7]. As shown in figures 2(c) and (d), for this new capacitor built from the film electrodes with a microstructure of local alignment of nanotubes, the CVs are still close to an ideally rectangular shape even at exceedingly high scan rates of 500 and 1000 mV s^{-1}, indicating an extremely low ESR of the electrodes.

A typical constant current charge/discharge (E–t) curve for the nanotube thin film electrodes is shown in figure 3. On both curves, the E–t responses of the charge process show almost the mirror image of their corresponding discharge counterparts, and no IR drop was observed, again owing to the negligible ESR of the electrodes.

A specific capacitance of about 20 F g^{-1} of the electrodes can be obtained from the constant current charge/discharge curves [20] shown in figure 3. Although this specific capacitance value is relatively low, the power density of the thin film electrodes is huge. The power density can be estimated from the inner integrated area (current × voltage) [7], and a power density of about 30 kW kg^{-1} is thus obtained from figure 2(d) based on electrode materials only, revealing that this nanotube colloidal suspension can be used to fabricate electrodes for supercapacitors for surge-power delivery.

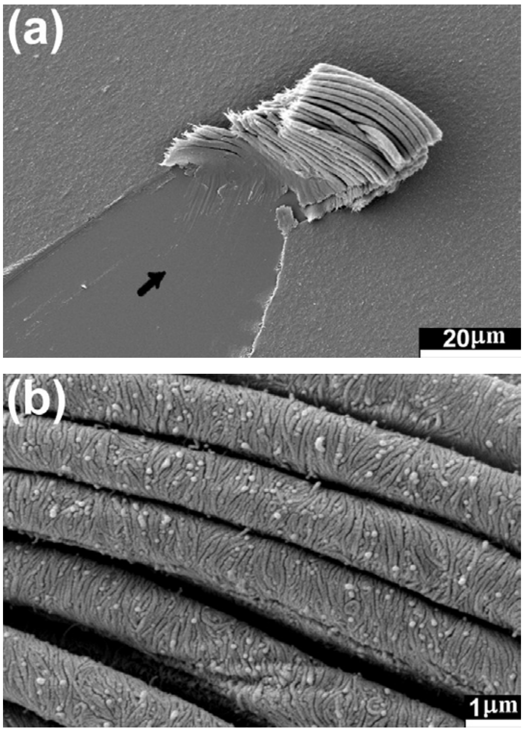

Figure 4. SEM images of the nanotube film fabricated from NT/DMF suspension, showing (a) the direction of the scratching and the pleats formed at the end of a scratch and (b) the structure of the pleats.

The high power density is attributed to the small internal resistance which results from the coherent structure of the thin films fabricated using a highly concentrated colloidal suspension of carbon nanotubes. To illustrate the coherent structure and the ductile nature of the film, we intentionally scratched a film fabricated from the NTs/DMF suspension; the arrow in figure 4(a) shows the scratching direction. It should be noticed that many pleats were formed due to the scratching, indicating that the nanotube thin film is likely to be very flexible. A higher resolution image of the pleats (figure 4(b)) clearly shows that the nanotubes at the bottom of the film (now on the surface of the pleats) are also well aligned. This coherent structure and the flexible nature of the films indicate that the nanotubes stick strongly together, forming a highly conductive nanotube network, leading to a greatly reduced NT-electrode resistance. In addition, we also noticed that the nanotube films could be readily manipulated during the experiments so that the adhesion between the film and the current collector is likely to be durable, and the contact between them is very good. Therefore the contact resistance was also reduced significantly because of the increase of the contact surface area.

4. Conclusion

In summary, we have demonstrated the ability to prepare thin films from highly concentrated suspensions of carbon nanotubes. The nanotube thin films fabricated from these suspensions show ordered structure and high packing density, and are very flexible. The supercapacitors built by using the thin film as electrodes exhibited nearly ideal cyclic voltammograms even at a high scan rate of 1000 mV s^{-1}, and a very high specific power density of about 30 kW kg^{-1} was obtained based only on electrode materials. This suspension preparation technique has the advantages that no binder is required, and it is simple and fast. All demonstrate that this is an attractive approach to fabricate electrodes for supercapacitors of high power density.

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