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Research Article

Aligned Carbon Nanotubes Array by DC Glow Plasma Etching for Supercapacitor

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To open the end of carbon nanotubes and make these ends connect with functional carboxyl group, aligned carbon nanotubes (CNTs) arrays was etched by DC glow oxygen-argon plasma. With these open-ended carbon nanotubes array as electrode materials to build supercapacitor, we found that the capacity (32.2 F/g) increased significantly than that of pure carbon nanotubes (6.7 F/g).

1. Introduction

Carbon nanotubes (CNTs) have been extensively studied recently due to their unique structures and excellent mechanical [1–7], electrical [8–16], and chemical properties [14–22]. Recent studies have been focused on the improvement of the structural modification of CNTs to enable the mass fabrication. The open-ended CNTs were studied during the oxidation process to be connected with functional group [23, 24]. The plasma treatment improved the structural rigorousness and the stability of the emitted beam [25–28]. In the plasma treatment, especially, the formation of the amorphous carbon and the shaping of the self-organization of the carbon nanostructures could be achieved under the ion bombardment so that the plasma-assisted CNTs tip formation is a promising method for mass production with an excellent controllability as well as a good expandability during the tip fabrication process [29, 30]. Kim et al. utilized a direct current (DC) plasma source with xenon and neon gases in order to modify the structure of the open-ended CNT [27]. In the study, the uniformity of the height of CNT during the fabrication process was controlled by varying the voltage between the cathode and the anode electrodes and the treatment time. Huang and Dai produced the open-ended CNTs by using steam plasma [28]. Electrical energy storage is required in many applications demanding local storage or local generation of electric energy. Supercapacitors fill in the gap between batteries and conventional capacitors, covering several orders of magnitude both in energy and in power densities. In 1997, Niu et al. first suggested that CNTs could be used in supercapacitors [31]. The MWCNTs were functionalized in nitric acid with functional groups introduced on the surface. These functionalized MWCNTs had a specific area of 430 m^2/g. The redox response observed on the cyclic voltammetric (CV) plot of the SWCNT-based electrodes also indicated that the pseudocapacitance really occurred to the CNT-based capacitor due to the functional groups and impurities [32]. In this paper, we used the open-ended carbon nanotubes array as electrode materials to build supercapacitor and found that this supercapacitor capacity (32.2 F/g) increased significantly than pure carbon nanotubes as electrode material of capacity (6.7 F/g).

2. Experimental

2.1. Preparation of Aligned Carbon Nanotube Array. The aligned CNTs were synthesized through using a conventional CVD technique in an atmospheric pressure quartz tube furnace having the inner diameter of 2 inches. Ar (99.999%) with 6% H_2 (99.999%) was used as a carrier gas, and pure

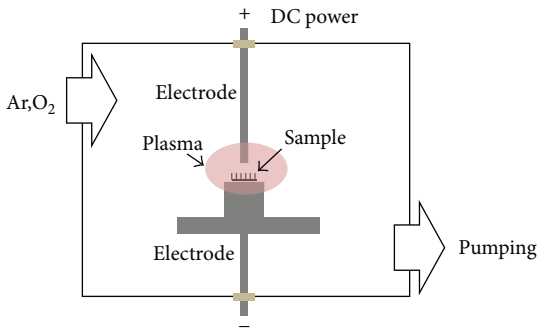

Figure 1: Schematic of plasma treatment to the aligned carbon nanotubes array.

ethylene served as the carbon source. Typical CVD growth was carried out at 750°C. Si wafers (5 mm × 5 mm) with 1 μm thickness SiO_2 layer were used as the substrate for the growth of long CNTs. The Al_2O_3 layer of thicknesses (10 nm) was used as a buffer layer between the Si/SiO_2 substrate and the catalyst. The Al_2O_3 layer was deposited on the substrate and on which thicknesses (1.0 nm) of Fe catalyst layer were deposited to grow CNTs. Both the catalyst and buffer layers were deposited by an e-beam evaporation technique.

2.2. Plasma Etching for Opening the Ends of Carbon Nanotube. Plasma etching treatment for the aligned CNT arrays was performed in a home-made cube vacuum chamber with a side length of 12 cm (Figure 1). Electrode distance from cathode to anode was 2 cm. A DC power supply was used to generate plasma. Ar and O_2 (high purity, 1 : 1) were employed as feed gas. Background vacuum of the equipment was 1×10^{-3} Pa and pressure levels (10 Pa) during plasma treatment were employed. Three plasma power levels (2, 10, and 50 W) were utilized for treatment. For all samples, the plasma treatment was performed for 1 min.

2.3. Fabrication of Supercapacitor. The supercapacitor (see Figure 2) was fabricated with the two-electrode configuration. The electrodes were made of aligned CNTs film, and the aligned CNTs film was made from aligned CNTs arrays pressed onto a glass slide. The two electrodes were separated by a thin gel polyvinyl alcohol-phosphoric acid (PVA-H_3PO_4) electrolyte. Here the gel PVA-H_3PO_4 electrolyte was prepared by dissolving PVA powder (0.5 g) into deionized water (5 mL) and H_3PO_4 (1 mL). The two-electrode configuration was finally sealed by use of a surlyn frame (thickness of 60 μm) as the spacer at a pressure of 0.2 MPa at 125°C.

3. Results and Discussion

In the etching process, oxygen pressure was set at 5 Pa and argon pressure was 5 Pa. Etching voltage at 500 V. Etching time was 1 minute. Etching power was set at different powers of 2, 10, and 50 W. Figure 3 shows that the SEM images of the top morphologies of CNTs array after plasma etching. Figures 3(a) and 3(b) show etching results of CNTs are not

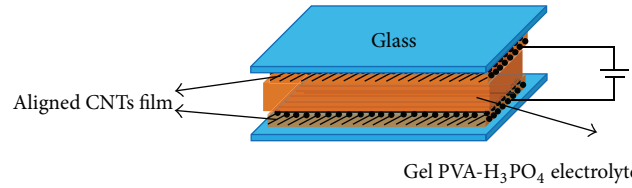

Figure 2: Structure diagram of electrical double-layer capacitor consisting of the carbon nanotube films.

obvious, so 2 W etching power was too low. Figures 3(c) and 3(d) show the results for applying 10 W etching power. They show that the top of carbon nanotube array was tidily cut. This kind of structure has a lot of applications, such as biological load medicine, graft functional polymer. Figures 3(e) and 3(f) show the results after 50 W power etching, because etching power was too high and the plasma was uneven distribution. The top of CNTs array was cut and we found that the end of carbon nanotube deposits a small amount of amorphous carbon, so the etching power is too high, and the plasma ion energy is higher. The CNTs cause greater impact damage, and the plasma is not stable. The distribution is uneven.

Some areas of the top CNTs array were etched excessively and some areas were not etched enough. Low power will lead to insufficient etching and cannot open the end of CNTs. So the etching power needs a right value. In the plasma etching process, the key parameters are etching power and etching time.

In order to clearly observe morphology of CNTs after plasma treatment, we used transmission electron microscope (TEM) as shown in Figure 4. Figure 4(a) shows TEM images after oxygen plasma etching; the end of carbon nanotube was opened; and the wall of carbon nanotube is clean. This is a further proof that oxygen ion etching in high-speed impact CNTs can open the end; at the same time it not only can oxidate off redundant amorphous carbon, but also can oxidate off CNTs. Figure 4(b) shows TEM images of CNTs after being etched by DC glow argon plasma. The end of CNTs has also been opened, but the wall of CNTs is not very clean: some black materials adhere to the wall. These black materials are amorphous carbon which, left after argon ion bombardment. That destroyed the structure of CNTs, and the amorphous carbon impurity increased and limited its application.

Figure 4(c) shows TEM image for CNTs treated by DC glow oxygen-argon hybrid plasma etching; we found a lot of opened ends of CNTs; the whole CNTs are clean and free of impurities. Figure 4(d) shows high magnification TEM image of the opened carbon nanotube, it was neatly cut open, and the wall was very clean. So this method made full use of the advantage of pure oxygen and argon ion plasma etching and effectively avoided shortcomings of the two etching methods. So we successfully used low-cost DC glow plasma to perfectly open the end of the CNTs.

Supercapacitors are generally classified into two types: pseudocapacitor and double-electric-layer capacitor. For the double-electric-layer capacitor, positive and negative ions are moving in the electric field under the bipolar; the positive

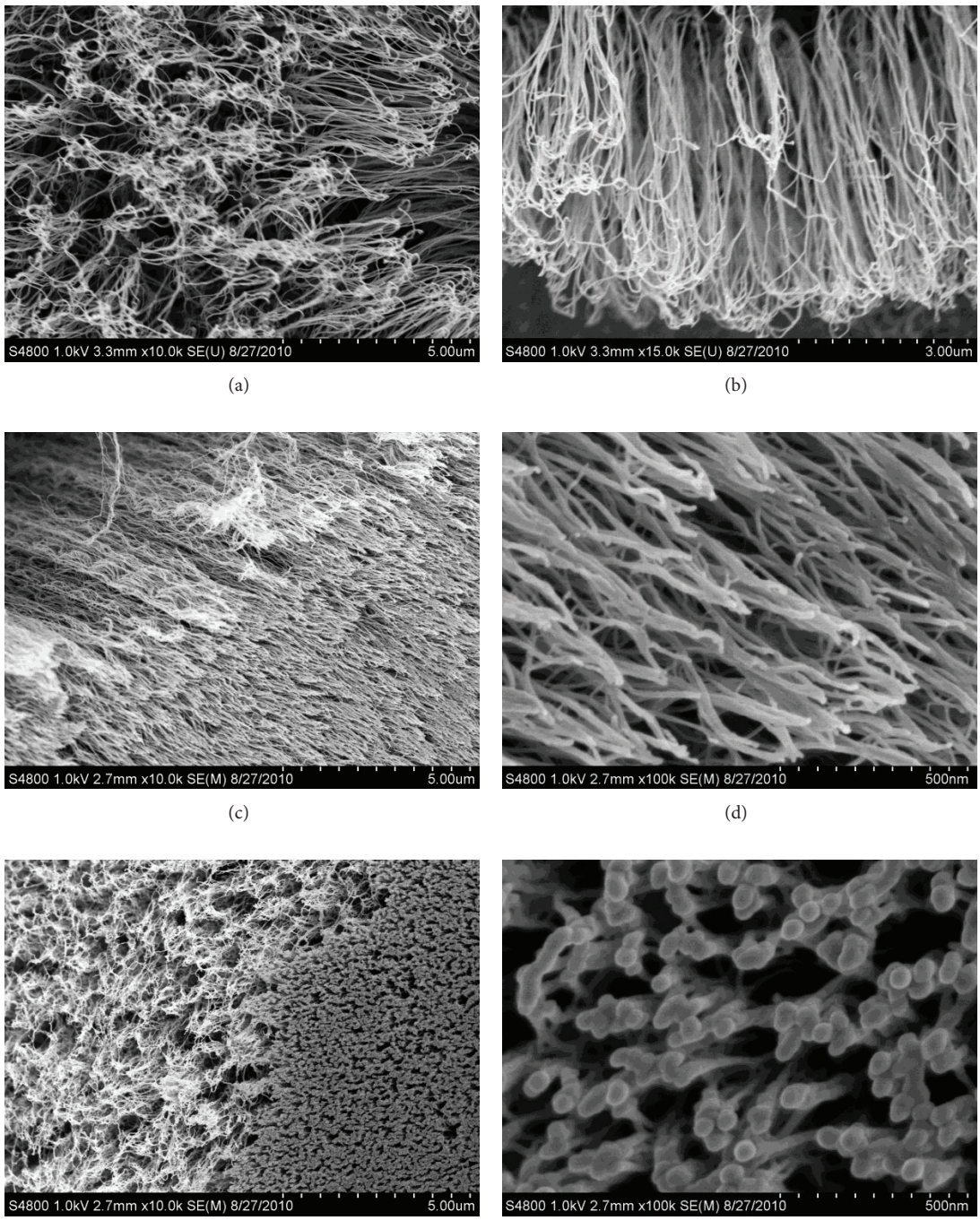

Figure 3: Transmission electron microscopy (TEM) images of etching effect with different powers: (a) and (b) corresponding to 2 watts, (c) and (d) corresponding to 10 watts, and (e) and (f) corresponding to 50 watts.

electrode attracts negative ions in the electrolyte; the negative electrode attracts positive ions; the two capacitive storage layers are separated from the positive ions in the vicinity of the negative electrode plate; the negative ions in the vicinity positive electrode plate are, respectively, formed close to electric double layer. For the pseudocapacitive, also called faraday quasicapacitance, the storage charge process includes not only the electric double layer of storage, but also through the electrode surface or body phase electric active substance to owe potential deposition, produce highly reversible chemical adsorption, stripping or oxidation, reduction reaction, produce and electrode charging potential the capacitance.

The CNTs have excellent electric conductivity and high specific surface area. After oxygen-argon plasma etching, CNTs active point increases and the CNTs film has catalytic activity as the electrical double layer supercapacitor.

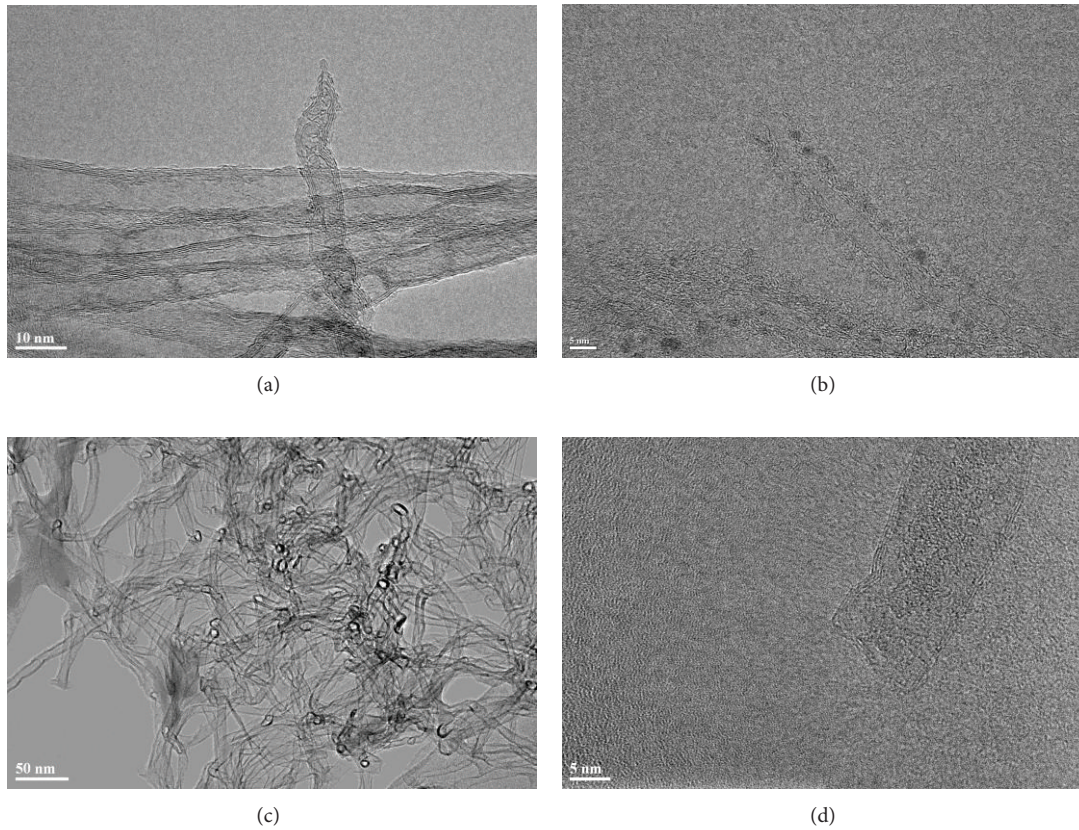

Figure 4: TEM images after etching by DC glow plasma, (a) by oxygen plasma, (b) by argon plasma, (c) low magnification by oxygen-argon plasma, and (d) high magnification by oxygen-argon plasma.

Electrode materials can reduce capacitor quality and improve the capacity of the capacitor. In the supercapacitor, we explore the comprehensive performance of etched CNTs array and pure CNTs array, because pure CNTs array shows favorable balance of trade hydrophobic properties, and etched CNTs array has a lot of carboxyl and shows favorable balance of hydrophilic, as shown in Figure 5. CNTs carboxyl and hydrophie can improve contact between the CNTs and polyvinyl alcohol-phosphate gel electrolyte. Test results show that etched carbon nanotube film significantly increased the capacity of the super capacitor.

The electrochemical characteristics of the capacitor and the specific capacity were tested by cyclic voltammetry and constant current charge and discharge. Figures 5(a) and 5(c) show circulation volt-ampere scanning volt-ampere curve from 0 to 0.8 V respectively, before and after plasma treatment with different sweep speeds (10 mV/s, 50 mV/s, and 100 mV/s). Pseudocapacitor can obtain higher energy density and capacity than the electric double-layer capacitor. The electric capacity of pseudocapacitive may be 10–100 times of the double electric layer capacitor's. The capacitors made from pure carbon nanotube arrays and etched the carbon nanotube array of IV curve have a rectangular shape without redox peak, the emergence of electric double-layer capacitor in the nature. Figures 5(b) and 5(d) were constant current charge and discharge curves. Supercapacitor performance of the capacity calculation formula is as follows:

$$C = \frac{2\,(I \times \Delta t)}{m \times \Delta V}, \tag{1}$$

C is the specific capacity. I is the discharge current. m is a single electrode mass. ΔV is the potential difference. Δt is the discharge time. According to Formula (1), the results show pure CNTs for control of the supercapacitor of the specific capacity 6.7 F/g and plasma etching CNTs for control of the capacitor-specific capacity 32.2 F/g. The capacitor improved performance.

4. Conclusion

In order to ensure the functional processing of carbon nanotube array body material morphology, we used DC glow plasma etching process to open the end of the CNTs array so that the opened carbon nanotube could connect with the carboxyl group of the functional group. We systematically studied oxygen, argon, and oxygen-argon mixed gas plasma etching. The results showed that oxygen-argon mixed gas plasma etching had the best effect. The end of CNTs was clearly opened in TEM images. Infrared characterization of

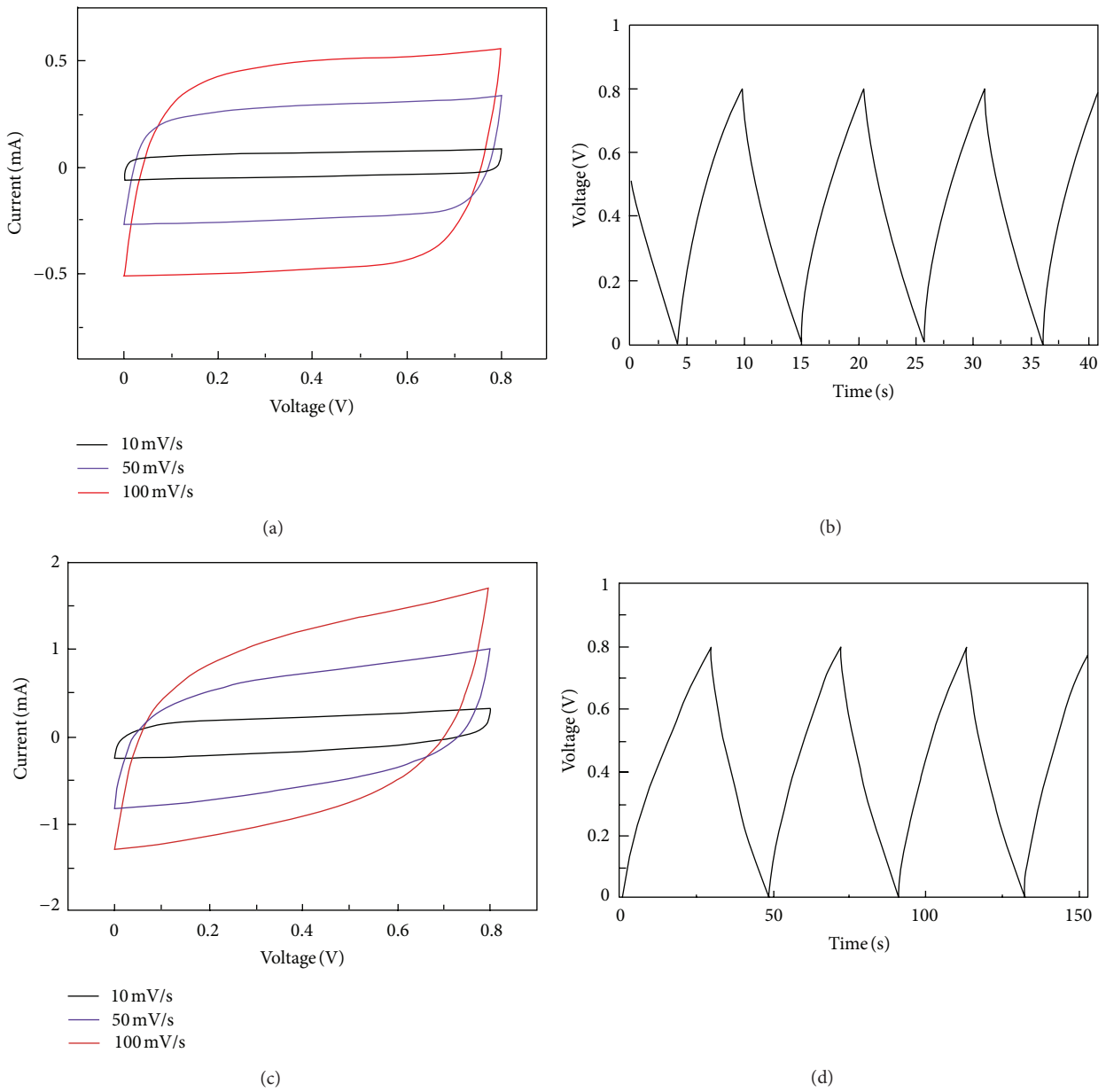

Figure 5: CNTs circulation current-voltage and constant current charge and discharge: (a) and (b) for the pure CNTs and (c) and (d) for the etched CNTs.

the etched carbon nanotube array was successfully carboxylated as an electrode material to construct a supercapacitor. It was found that this supercapacitor capacity (32.2 F/g) increased significantly than pure CNTs as electrode material of capacity (6.7 F/g).

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