Short communication

Single-walled carbon nanotubes modified by electrochemical treatment for application in electrochemical capacitors

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Abstract

An electrochemical process for modifying the pore-size distribution (PSD) of single-walled carbon nanotubes (SWNTs) is developed. The effect of electrochemical treatment time on the PSD of SWNTs is investigated, and the results show that such treatment provides an effective and controllable method for changing the PSD of SWNTs. In particular, a remarkable volume of the small mesopores in the 3.0–5.0 nm diameter range is increased. The SWNTs treated for 24 h at 1.5 V have a higher specific surface-area ($109.4 \, m^2 \, g^{-1}$) and larger volume of small mesopores ($0.048 \, cm^3 \, g^{-1}$ in 3.0–5.0 nm diameter range), compared with the as-grown SWNTs ($46.8 \, m^2 \, g^{-1}$ and $0.026 \, cm^3 \, g^{-1}$, respectively). The as-grown SWNTs and the electrochemically-treated SWNTs are investigated as electrochemical capacitor electrodes, and it is found that the specific capacitance is increased three-fold after electrochemical treatment.
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1. Introduction

Surface and pore characteristics are very important for porous materials, and the pore-size distribution (PSD) is a key factor for applications such as electrochemical capacitors (ECs) [1,2]. This is because the accessibility of ion molecules in an electrolyte strongly depends on the pore size of the electrode [3]. Therefore, ECs using carbon electrodes with different porous structures have different double-layer capacitances and their specific power is strongly dependent on the porous structure of the carbon electrode materials [1]. In particular, small mesopores are important for this application. It has been estimated that only those mesopores with diameters above 2.0 nm in carbon materials can be utilized in electrochemical capacitors containing aqueous electrolytes [2]. Therefore, suitable methods to control the PSD of carbon electrode materials are of great importance.

Due to their characteristics of high stability, low mass density, low resistance, high accessible surface-area and narrow pore-size distribution, nanostructured carbons such as single-walled carbon nanotubes (SWNTs) and multiwalled carbon nanotubes (MWNTs) are considered as attractive materials for electrochemical capacitors [4–8]. Generally, activation with potassium hydroxide is applied to change the PSD and increase the specific surface-area of nanostructured carbons [9,10]. This can result in a great increase of micropores in the treated material. Nevertheless, the loss of carbon is high, so that it is not beneficial for treating SWNTs. Electrochemical-treatment strategies have been proposed to purify SWNTs [11] or open the caps of MWNTs [12,13]. On the other hand, little attention has been paid to the PSD of carbon nanotubes after the electrochemical process. In this study, electrochemical treatment is applied to SWNTs and its influence on PSD is investigated. In addition, the electrochemically treated SWNTs are used as electrodes for an electrochemical capacitor.

2. Experimental

The SWNT sample was synthesized by an hydrogen arc discharge method that used graphite as the carbon feedstock. The fabrication process has been described in detail elsewhere [14].

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Briefly, the electric arc was operated with a direct current of 150 A in a hydrogen atmosphere of 200 Torr as the buffer gas. A mixture of 10 wt.% Ni, 3 wt.% Fe, and 3 wt.% Co as a metal catalyst, 4 wt.% FeS as a promoter and the graphite powder was packed into a graphite cylinder that served as the anode. The cathode was a pure graphite rod. The purity of the SWNTs in the product was about 60 wt.% with the metal catalysts accounting for most of the impurity content.

Electrochemical treatment was conducted in a 6 M KOH aqueous solution at room temperature and atmospheric pressure using a two-electrode cell. The as-grown SWNT sample was placed in a cylindrical steel mold and a pellet of 8 mm diameter was formed by pressing the SWNTs under 2 MPa. A nylon cloth was sandwiched between two identical SWNT pellets. During the electrochemical treatment, a voltage of 1.5 V was applied for 12, 24, 36, 48 and 60 h, respectively.

Capacitors were assembled in two-electrode Swagelock-type cells in which stainless-steel rods were used as current collectors. A 6 M KOH aqueous solution was chosen as the electrolyte. In the capacitor, the two electrodes were separated by a nylon cloth. The specific capacitance was measured in galvanostatic experiments using an Arbin BT-2000 system. Voltammetry measurements were performed with a Solartron 1287 potentiostat/galvanostat.

To analyze the pore structure of SWNTs, nitrogen cryo-adsorption measurements at 77.35 K were carried out using a volumetric adsorption apparatus (ASAP 2010). The resulting adsorption isotherms were analyzed by means of the Barrett–Joyner–Halenda (BJH) equation [15] to elucidate the PSD of the SWNTs in a mesopore range.

3. Results and discussion

3.1. Pore structure analysis

As shown in Fig. 1(a), all the nitrogen cryo-adsorption isotherms of the as-grown SWNTs and the SWNTs electrochemically treated for different times can be divided into four ranges. The isotherms in each adsorption pressure range have different characteristics and this indicates that nitrogen adsorption on SWNTs is a multi-stage process and that the SWNTs have different types of pores. In range I, the isotherms are of a type I characteristic, as indicated by the fact that the amount adsorbed increases rapidly at ultra-low pressures ($P/P_o = 10^{-6}$ to 0.01). It is commonly recognized that such a process occurs in pores with a molecular size that are possibly contributed by the open inner cavities of the SWNTs. This is indicative of the existence of micropores. Nitrogen molecules, whose diameter is 0.364 nm, can fill these pores under an ultra-low adsorption pressure. In range I, adsorption by the modified SWNTs is higher than that by the as-grown SWNTs. This indicates an increase of the micropore volume and is due to the opening of the nanotube tips and damage of the nanotube sidewalls through the electrochemical treatment. New range II of the isotherms, which occurs in the medium pressure zone ($P/P_o = 0.01–0.45$), shows a surface adsorption process in which the amount of nitrogen adsorption slowly increases. This is indicative of the existence
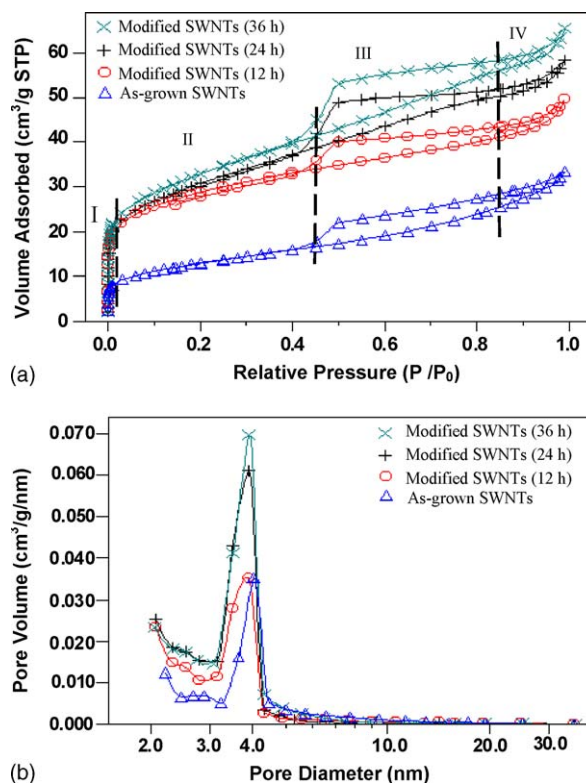

Fig. 1. (a) Nitrogen cryo-adsorption isotherms and (b) mesopore-size distribution of as-grown SWNTs and SWNTs electrochemically modified for 12, 24 and 36 h.

of a nonporous surface, attributed by amorphous carbon and external surface of the SWNTs. Furthermore, the evident differences between the as-grown and modified SWNT samples can be observed in range III, which corresponds to capillary condensation occurring in the medium relative pressure range ($P/P_o = 0.45–0.85$), and results from capillarity in the mesopores [16]. The modified SWNTs have a larger hysteresis loop than their as-grown counterpart. This accounts for the existence of small mesopores with a size of 3.0–5.0 nm [17], and indicates a much higher volume of small mesopores in the modified SWNTs. The hysteresis loop in range IV ($P/P_o = 0.85–0.99$) of the isotherms corresponds to the larger pores of 20.0–40.0 nm [18].

In order to identify the PSD variation of the SWNTs during electrochemical treatment, SWNT samples with different periods of treatment were investigated. The resulting isotherms were further analyzed to obtain information on the pore structure, as shown in Fig. 1(b). It is seen that the volume of the mesopores in the 3.0–5.0 nm size range increases with increase in treatment time. In detail, the volume of the mesopores in the 3.0–5.0 nm size range increases greatly for up to 24 h of treatment, but further increase in 36, 48 and 60 h brings little change in the mesopore volume of the SWNTs. A typical bundle of modified SWNTs is shown in Fig. 2 and it can be seen that part of the outer sidewall has been etched, as denoted by the arrow. Because the applied voltage of 1.5 V is sufficient for water electrolysis, oxygen evolution takes place. The nascent oxygen is highly activated and it can not only react with the amorphous carbon on
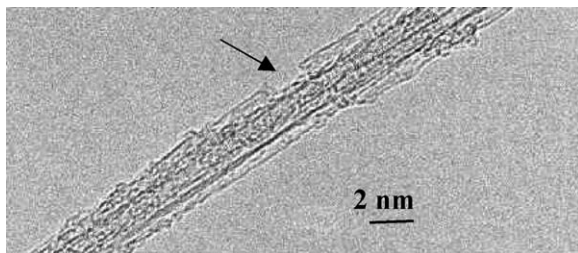
Fig. 2. HRTEM image of a bundle of modified SWNTs. The arrow denotes the etched wall of a SWNT.

the tubes to clean the surface of the SWNTs [11], but also open the nanotube caps and even etch the sidewall of SWNTs, which increases the number of micropores and mesopores. Therefore, through adjusting the electrochemical treatment time, the PSD of SWNTs can be modified in a controllable way.

Raman spectroscopy was also used to investigate the possible change in structure after the electrochemical treatment process as it is a powerful tool for characterizing the structure of SWNTs [19]. The Raman spectra of the as-grown SWNTs, 24 h modified SWNTs and SWNTs treated in Ar at 800 °C for 10 h, which were excited by a laser with a wavelength of 632.8 nm, are shown in Fig. 3. The resonant Raman spectra of the as-grown SWNTs have three main features: a radial breathing mode (RBM), a D band and a G band (Fig. 3(a)). By contrast, the Raman spectra of the modified samples show the disappearance of the RBM and a decrease in the intensity ratio of the G and D bands (Fig. 3(b)). This result suggests that the symmetry of the modified SWNTs is broken and that the structure of SWNTs is changed after electrochemical treatment to cause an increase in the micropores and mesopores. In order to prove the existence of the nanotubes, the electrochemically modified SWNT samples were heat treated at 800 °C in Ar for 10 h. Recovery of the RBM and an increase in the intensity ratio of the G and D bands of the heat-treated SWNTs is observed (Fig. 3(c)). This suggests that some of the defects in the electrochemically modified SWNTs are healed and the symmetry of the SWNTs is recovered.
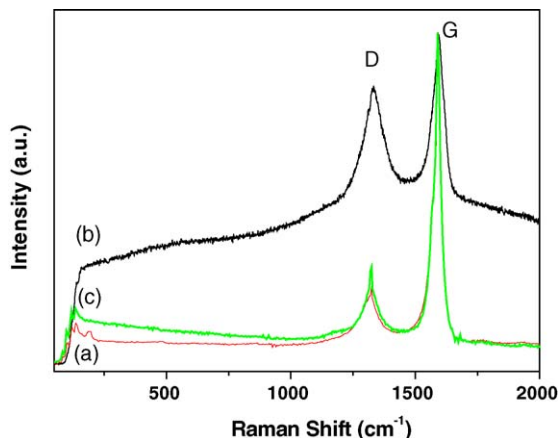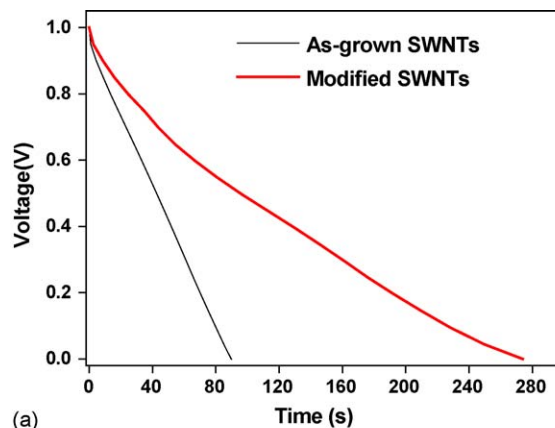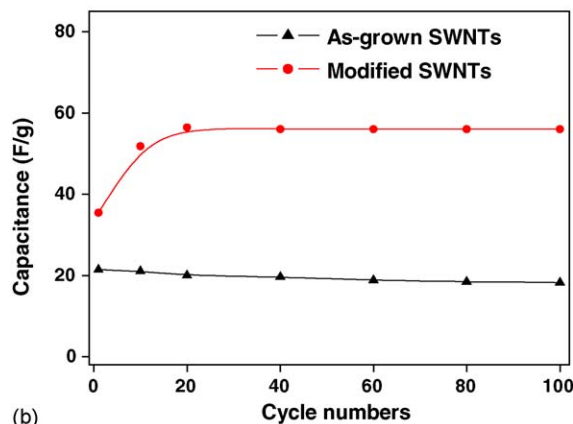

Fig. 3. Raman spectra of (a) as-grown; (b) modified; and (c) heat-treated SWNTs.

Fig. 4. (a) Galvanostatic discharge curves and (b) cycling performance of electrochemical capacitors built from as-grown and 24-h modified SWNTs. Mass of each electrode = 10 mg.

3.2. Capacitance performance

Electrochemical capacitors based on the as-grown and 24-h modified SWNTs were tested under galvanostatic measurements by charging at a current density of 100 mA g^{-1} to 1 V, and then discharging to 0 V at the same current density after holding at 1 V for 5 min. The capacitance is estimated from the formula $C = (I \times \Delta t)/\Delta v$, where I is the constant discharging current, and Δt is the discharging time for the voltage change Δv, which was measured from 0.6 to 0.4 V (60 to 40% of the peak voltage). Capacitances of 20 and 56 F g^{-1} (on the basis of the electrode material) is obtained from the discharge curve of the as-grown and 24-h modified SWNTs, respectively, as shown in Fig. 4(a). The specific surface-areas of the as-grown SWNTs and 24-h modified SWNTs are 46.8 and 109.4 m^2 g^{-1}, respectively. The volume of small mesopores (3.0 to 5.0 nm) and the external surface-area are increased from 0.026 to 0.048 cm^3 g^{-1} and from 40.7 to 88.1 m^2 g^{-1}, respectively, after electrochemical treatment for 24 h. The micropore surface-area is also increased from 6.1 to 21.3 m^2 g^{-1}. The increased volume of small mesopores after electrochemical treatment allows more effective access of ions to the electrode|electrolyte interface to form sufficient electric double-layers and, consequently, the specific capacitance of the modified SWNTs is increased. From the cycling curves
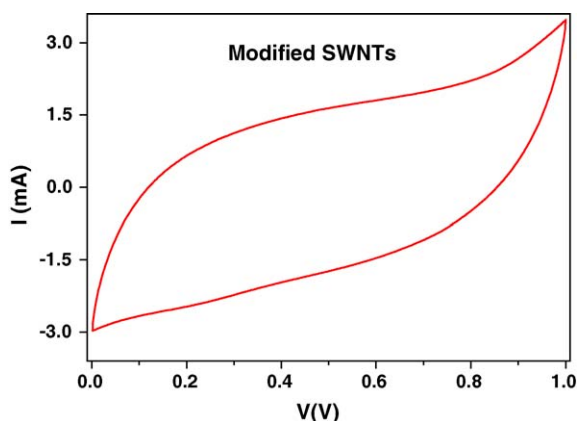
Fig. 5. Cyclic voltammetry of modified SWNTs. Mass of each electrode = 10 mg.

shown in Fig. 4(b), it is found that the capacitance of the modified SWNT capacitor increases initially, reaches a maximum value after about 20 cycles and then remains constant for 100 cycles. These phenomena are due to the abundant pore structure of the modified SWNTs, and the longer time that is required for electrolyte ions to penetrate into the electrode material and form sufficient double-layers.

A capacitor based on the modified SWNTs was evaluated by means of cyclic voltammetry. The voltammogram of the modified sample was recorded at a scan rate of $10 \, mV \, s^{-1}$, and is shown in Fig. 5. The current–voltage (*I–V*) curve is approximately rectangular, i.e., of similar shape to the curves reported for other nanotube-based capacitors [8,20]. This feature indicates that the capacitance arises is mainly from the double-layer capacitance of the SWNTs

4. Conclusions

The pore structure of SWNTs can be modified by electrochemical treatment. In particular, the amount of small mesopores in the diameter range 3.0–5.0 nm can be increased. The specific capacitance of SWNTs is increased three-fold after electrochemical treatment in 6 M KOH aqueous solution. The results show that electrochemical treatment may provide an effective technique for modifying the structure of SWNTs and, accordingly, can improve the performance of electrochemical capacitors based on SWNTs.

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