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Graphene oxide nanoribbons and their applications in supercapacitors

Mohammad Fathi, Morteza Saghafi , Farzad Mahboubi *

Department of Mining and Metallurgical Engineering, Amirkabir University of Technology, Tehran, Iran

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** Corresponding author: mahboubi@aut.ac.ir ; Tel: +98 21 64542967*

Abstract
We report the enhanced capacitance of the Multi-Walled Carbon NanoTubes (MWCNTs) after a chemical unzipping process in concentrated sulfuric acid (H_2SO_4) and potassium permanganate ($KMnO_4$). The effects of the test duration and temperature were investigated on the unzipping process of the MWCNTs to synthesize the graphene oxide nanoribbons. The SEM and TEM studies were carried out on untreated and unzipped MWCNTs samples to investigate the cutting and unzipping of the MWCNTs. The results confirmed that the efficient tube unzipping with improved effective surface area was obtained from the 1h treatment at 60°C, at which most of the tubes were opened without any tube annihilation. The graphite plate deposited with the untreated and unzipped MWCNTs samples was investigated by electrochemical studies. Cyclic voltammetry studies showed that the MWCNTs after 1h unzipping at 60°C had better electrochemical behavior than the other samples. Galvanostatic charging/discharging measurements were carried out on the untreated and unzipped MWCNTs samples. A remarkable specific capacitance of 33 Fg^{-1} was obtained for the unzipped MWCNTs at a current density of 1 Ag^{-1} in 0.5 M KCl solution compared with 8 Fg^{-1} for pristine MWCNTs, again confirming the enhanced effective surface area and increased defect density in the tube surfaces after the unzipping process. These results make the unzipped MWCNTs a promising electrode material for all energy storage applications.

Keywords: *Supercapacitor, Unzipped MWCNTs, Specific capacitance, Enhanced effective surface area.*

1. Introduction

Supercapacitors have attracted worldwide research interest in many fields because of their intrinsic features such as potential energy storage systems [1, 2]. Supercapacitors can store substantially more energy than the conventional capacitors and show higher power density in contrast to batteries, which means these devices store and deliver a vast quantity of charge in a short cycle of time [3, 4]. Electrical double layer capacitors (EDLCs) and pseudocapacitors are two main types of supercapacitors with different charge storage mechanisms [5]. The EDLCs mechanism of energy storage is based on the electrostatic movement of ions between the solid state electrode surfaces and the surrounding

electrolyte, so the active interfacial surface area is a critical value to determine the specific capacitance [5, 6]. To improve their performance, especially the specific energy while retaining their inherent high power density, many efforts have been focused on improving the properties of the supercapacitor's electrode materials [6]. The major classes of materials applied for EDLCs are the various forms of carbon, such as activated carbon, MWCNTs and graphene [7]. Due to the inappropriate pore size distribution in activated carbon, all of the surface area cannot participate in charge storage and the high costs of graphene limits its application as electrode material. The MWCNTs are interesting as electrode materials in the EDLCs because of their nanostructured morphology, large surface area, high electrical conductivity and good corrosion resistance [4, 7]. Many efforts have been taken to improve the capacitance behavior of the MWCNTs. Wang *et al*., increased the specific capacitance of the MWCNTs by increasing the active surface area and defect density through exfoliation [8]. The enhanced surface defect density through the exfoliation treatment results in the possibility for the electrolyte ions to diffuse into the inner tube surfaces. In this work, we investigate several parameters and find the best condition to enhance the capacitance of the MWCNTs by increasing the active surface area and defect density through the unzipping process.

2. Experimental Procedure

2.1. Materials

Pristine MWCNTs (95%) were purchased from Iranian Nanomaterials Pioneers Co. Ltd., which were produced by the Chemical Vapor Deposition (CVD) method. The H_2SO_4 (98%), HNO_3 (65%), $KMnO_4$ (99%), H_2O_2 (30%) and other analytical grade chemicals were used.

2.2. Preparation and Characterization of Unzipped MWCNTs

First, 100 mg MWCNTs were dispersed into 100 ml H_2SO_4 by 30 min ultrasonication and left at room temperature for 12h. The solution was stirred for 1h and afterwards treated with 500 mg $KMnO_4$ and allowed to stir for 1h at room temperature. At the next step, the solution was stirred for different durations and temperatures as shown in Table 1. When the reaction of each sample was performed, the reaction mixture was quenched over 270 ml ice containing 3 ml of 30% H_2O_2. The solutions were filtered and washed with deionized water. The untreated and unzipped MWCNTs were examined with a Field Emission Scanning Electron Microscope (FESEM) Hitachi S4160 and CM30 Philips transmission electron microscope (TEM) operating at 150 kV.

Table 1. Production parameters for the unzipping processes

Sample	Temperature (°C)	Time (h)
S1	50	1
S2	60	1
S3	75	1
S4	90	1
S5	60	0.5
S6	60	2

2.3. Preparation and Characterization of Electrodes

For preparation of the electrodes, 20 mg of each powder sample with 10 wt% graphite powder and 10 wt% polyvinylidene fluoride (PVDF) emulsions were mixed to form well-proportioned slurry. The slurry was deposited on a 1×1 cm graphitic plate and dried in an oven at 50°C. The graphite plate does not show oxidation/reduction peaks in the cyclic voltammetry studies and was expected to have low contact resistance with our materials. The electrochemical properties were investigated in a standard three-electrode cell using cyclic voltammetry and galvanostatic charge/discharge techniques with an Autolab PGSTAT30 electrochemical instrument. The voltammetric measurements were performed at room temperature, with stainless steel and Ag/AgClas the counter and the reference electrodes, respectively. A 0.5 M KCl aqueous solution was used as the electrolyte.

3. Results and Discussion

SEM studies were employed to investigate the cutting and unzipping of the MWCNTs. Figure 1 shows the SEM images of untreated and unzipped MWCNTs samples. Figure 1a shows that the untreated MWCNTs have a

tubular structure with smooth surfaces. Figure 1b shows that the tubular structure of the MWCNTs became partially unzipped after the oxidation process at 50˚C in the S1 sample. The best results were achieved from the S2 sample (Fig. 1c), in which the unzipping process was done efficiently and most of the MWCNTs were completely unzipped without any tube annihilation. Figure 1d shows the SEM image of the S3 sample. It can be seen that the severe oxidation temperature in S3 sample caused the tube annihilation.

To investigate the unzipping process of the nanotubes in more detail, the TEM observation has been exploited. Figures 2a and b show the TEM images of the raw MWCNTs and the S2 sample. Figure 2a shows that the raw MWCNTs have a smooth and clean surface with a hollow tube structure. The tubular structure of the MWCNTs cannot be observed in Figure 2b and the pristine MWCNTs are completely opened to the thin layer structure of the GNR oxides in the S2 sample. From Figure 2 it can be easily seen that the S2 sample has a much broader width than the raw MWCNTs.

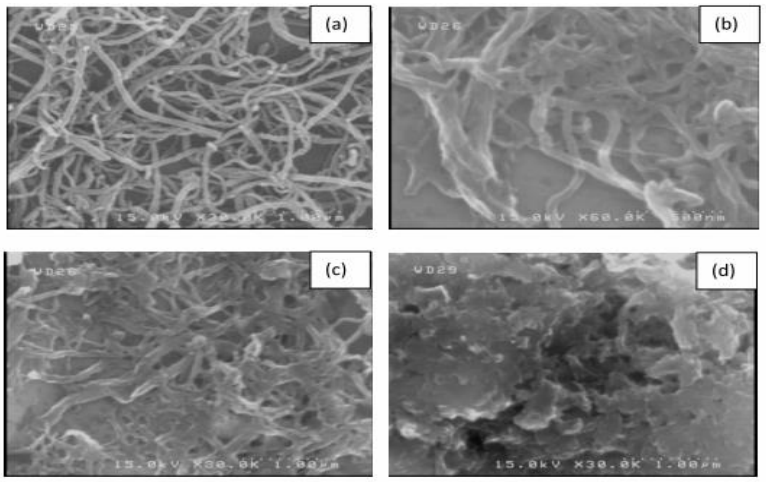

Fig. 1. SEM images of (a) untreated MWCNTs, (b) S1, (c) S2 and (d) S3

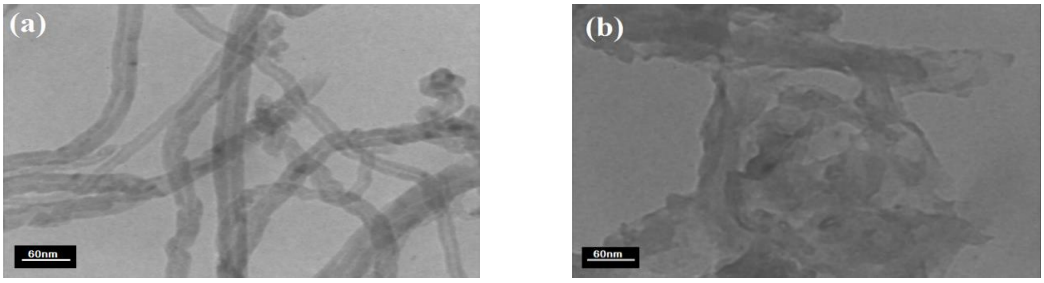

Fig. 2. Bright field TEM images of (a) raw MWCNT, (b) S2 sample

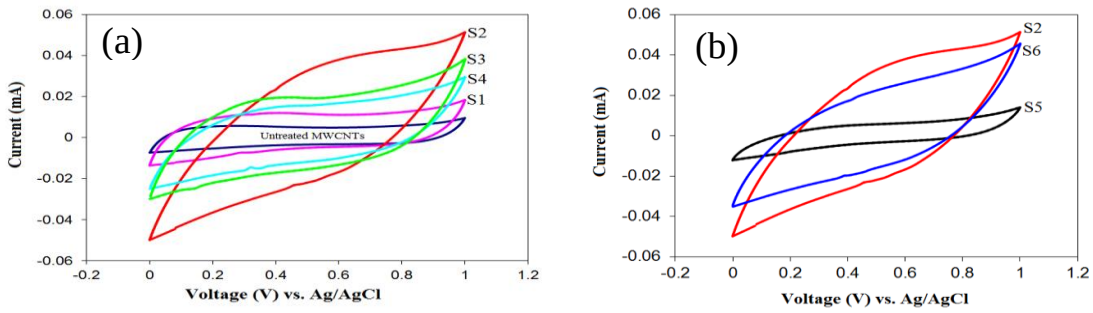

Fig. 3. a) CV curves of the untreated MWCNTs and S1 to S4 at a 50 mVs-1 scan rate, b) CV curves of S2, S5 and S6 at 50 mVs-1 scan rate

The electrochemical performance of the electrode materials were characterized by the cyclic voltammetry (CV) and galvanostatic charge/discharge techniques. Figure 3a compares the CV curves of the untreated and unzipped MWCNTs (S1 to S4) at 50 mVs^{-1} scan rate. The specific capacitance values could be calculated based on the CV curves according to Equation 1.

$$C_{Sp} = \frac{\int IdV}{\Delta V S m} \quad (1)$$

where C is the specific capacitance (Fg^{-1}), I is the response current (A), V is the potential (V), m is the mass of the electrode material (g) and S is the potential scan rate (Vs^{-1}). According to the equation, the specific capacitance harmonizes with the area of the CV curves, so it is clearly obvious that the best specific capacitance among the different oxidation temperatures is achieved from the S2 sample. The specific capacitances of the unzipped samples are higher than those of the untreated MWCNTs, which is due to the enhanced exposed surface area of the tubes through the unzipping processes. It also can be seen from Figure 3a that increasing the oxidation temperature from 50 to 60˚C causes the increase in specific capacitance, but when the temperature increases to 75 and 90˚C, the severe thermal condition annihilates some of the MWCNTs resulting in decreases in the specific capacitances. In the case of test duration, the CV curves of S2, S5 and S6 samples are presented in Figure 3b. It can be seen that the treatment at 60˚C for 1h in the S2 sample causes more specific capacitance than the other samples, which confirms the SEM results in Figure 1. In fact, long oxidation treatment (2h treatment) at 60˚C in the S6 sample caused many defects in the tube structure which resulted in less conductivity. There was not enough time (30 min) in the S5 sample to unzip the MWCNTs efficiently and the carbon nanotubes are very partially unzipped in this sample.

Figure 4 represents all the CV curves of the untreated MWCNTs and the S2 samples at different scan rates of 10 up to 200 mVs^{-1}. An ideal supercapacitor should be able to maintain a rectangular I–V curve over a wide range of the scan rate [9]. Figure 4a shows that the I–V curves maintain the rectangular shape while the scan rate is varied from 10-200 mVs^{-1} and fast charge/discharge behavior could be expected from the untreated MWCNTs. Figure 4b shows that the CV curves of the S2 sample are not similar to the ideal rectangular shapes, especially at the higher scan rates, due to the presence of the oxygen-containing groups in the tube surface, which reduces the conductivity of the material and decreases the power density.

A galvanostatic charge/discharge cycle of the untreated MWCNTs and the S2 carried out at 1 Ag^{-1}current density and specific capacitances of untreated MWCNTs and S2 were measured to be 8 and 33 Fg^{-1}, respectively. The large specific capacitance of the unzipped MWCNTs in contrast to the untreated MWCNTs again confirms the enhanced exposed surface area of the unzipped MWCNTs, which indicates the excellent ion accessibility between the unzipped MWCNTs and the electrolyte.

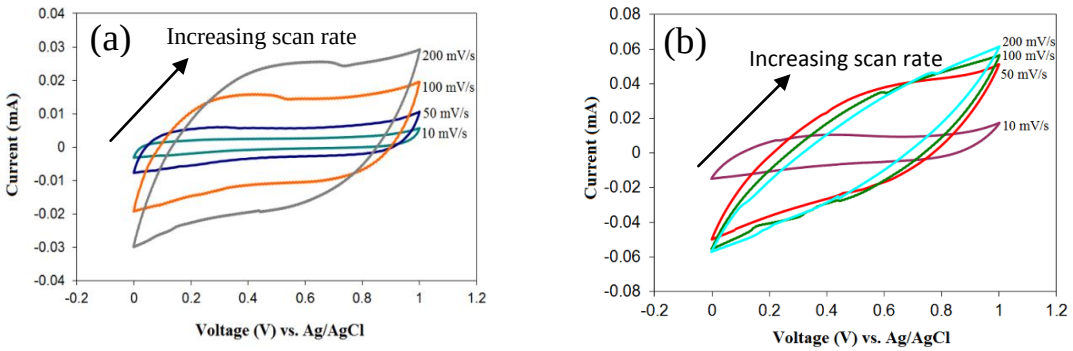

Fig. 4. All collected CV curves of (a) untreated MWCNTs and (b) S2 at different scan rates from 10 to 200 mVs^{-1}

A comparison of the specific capacitance among the CNT supercapacitors after different chemical modifications is given in Table 2. Frackowiak *et al*. showed that the specific capacitances of the MWCNTs were increased six-fold with chemical modifications in the KOH and microporosity of the MWNTs had been highly developed [10]. A few-fold increase of the specific capacitance of the CNTs was recorded in other modification methods in the literature. For example, Dai *et al*. showed that the modified MWCNT with HNO_3 has a specific capacitance increase from 8.9 to 22.6 Fg^{-1} [11]. Liu *et al*. showed that the modified CNTs prepared by the electrochemical treatment have a three-fold specific capacitance increase and also a remarkable volume of the small mesopores was increased through the modification [12]. The specific capacitance of the MWCNTs was increased 2.7-fold by partially oxidizing in air and subsequent chemical modification in the H_2SO_4/HNO_3 [13]. However, the S2 sample in this study has the specific capacitance of 33 Fg^{-1} which is 4.1 times that of the raw MWCNTs and is comparable with the literature.

Table 2. Comparison between the specific capacitance of CNT supercapacitors modified by several methods

Modification method	C_{sp} of CNT (Fg^{-1})	C_{sp} of modified CNT (Fg^{-1})	Electrolyte	C_{sp} of modified CNT/C_{sp} of CNT	Ref.
With KOH	15	90	0.1 M H_2SO_4	6	[10]
With HNO_3	8.9	22.6	0.1 M H_2SO_4	2.5	[11]
Ammoxidation	21	62	4 M H_2SO_4	3	[12]
With H_2SO_4/HNO_3	12.2	33.5	0.3 M H_2SO_4	2.7	[13]
Electrochemical	20	56	6 M KOH	2.8	[14]
Tour	8	33	0.5 M KCl	4.1	This work

4. Conclusions

We successfully synthesized the unzipped MWCNTs and investigated the effects of the duration and temperature of the experiments on the unzipping process. The SEM, TEM and CV experiment results showed that the treatment on the MWCNTs at 60°C for 1h is the best situation among all the investigated conditions to efficiently achieve the unzipped MWCNTs. Specific capacitance of the MWCNTs was measured to be 8 Fg^{-1} and increased to 33 Fg^{-1} with the unzipping process. The unzipped MWCNTs represented a better capacitive behavior than the untreated MWCNTs because of the enhanced exposed surface area and the defect density through the oxidation process. The unzipped MWCNT is a promising electrode material for supercapacitor applications, and can also be used in other electronic devices such as batteries.

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