

Preparation and Characterization of Carbon Nanotube/Graphite/Zinc Oxide Composite as Supercapacitor Electrode Material

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Abstract. A simple method has been developed to prepare carbon nanotube/graphite/zinc oxide (CNT/GT/ZnO) composite on SS foil substrate which was employed for supercapacitor electrode materials. The XRD study reveals the formation of CNT/GT/ZnO structure. Scanning electron microscopy characterizations reveal that the combination of CNT/GT and ZnO can increase the conductive property of material. The electrochemical performance of composite electrode was investigated using cyclic voltammetry measurements in 1 M KCl aqueous electrolyte. The CNT/GT/ZnO composite electrode shows the specific capacitance up to 6.99 Fg^{-1} in scan rate of 25 mVs^{-1} with an energy density of 152.9 Wh kg^{-1} in the potential range -0.5 V to 0.5 V .

Introduction

Supercapacitors are one of promise energy storage devices. Their electrochemical system can give high specific energy and power. Carbon-based supercapacitors have outstanding attributes of low cost, light-weight, fast charge and discharge kinetics, long lifetimes [1,2]. Based on the above advantages, supercapacitors fill the gap between capacitors and batteries [3]. Based on the charge storage mechanism, supercapacitors can be divided into two types: (i) electrochemical double layer capacitors (EDLC) which store energy by utilizing the double-layer capacitance arising from the charge separation at the electrode-electrolyte interface and (ii) pseudocapacitors (redox capacitors) which store energy based on the fast and reversible faradaic reactions at the surface of electro-active materials [4].

Carbon nanomaterials including graphite, graphene and carbon nanotubes (CNT) have extensively shown their potential in a wide range of applications [5,6,7,8]. CNT has shown to have superior properties in energy storage devices, because it has a nanotubular structure with high conductivity, highly accessible surface area, excellent stability and excellent mechanical properties. CNT are considered as composite electrode materials for supercapacitors because of potential excellent mechanical properties and good electrical conductivity [9]. The addition of a metal oxide on the carbonaceous can increase the electrochemical performance of electrode material. Metal oxide is a material that has properties suited to optimizing the performance of a supercapacitor. Metal oxide such as zinc oxide (ZnO), iron oxide (Fe_2O_3), cobalt oxide (CoO) and manganese dioxide (MnO_2) are all proven to have good supercapacitors [10,11,12,13].

Zinc oxide (ZnO) exhibits excellent electrical properties and hence they have been widely used as electrode material in a battery active material. If the ZnO material is employed into supercapacitor electrode with CNT, this electrode will show improvement in the supercapacitor performance. Recently various methods like green synthesis [14], microwave assisted synthesis [15], mechanical mixing [16], ultrasonic spray pyrolysis [8] were employed for the preparation of ZnO/carbon composite electrode for achieving high performance supercapacitor. There was problem for these methods in which residual impurities carried over might affect electrochemical properties. These electrodes showed to have limited improvement in the supercapacitor

performance. Hence it is important to develop facile and dry process to modify electrodes that will show better results in the electrode performance. Aravinda, et. al. reported a binder free method for the preparation of ZnO/carbon nanotube composite for super capacitor electrodes using magnetron sputtering of ZnO over FWNTs. The advantages of this method over other existing methods include (a) solvent free synthesis and hence more eco-friendly, (b) superior quality of the coated materials and (c) the deposited film thicknesses can be tailored by adjusting the deposition time and other parameters [17].

In the present work, we have used a simple method to prepare carbon nanotube/graphite/zinc oxide (CNT/GT/ZnO) composites with treatment on drying temperature of ZnO. The CNT/GT was dispersed in the binder and was deposited onto the SS foil substrate by using the doctor blade method and drying in the certain temperature. ZnO nanoparticle liquid was sprayed onto CNT/GT substrate and formed CNT/GGT/ZnO composites. Characterizations of CNT/GGT/ZnO composites were done by using X-ray diffraction, scanning electron microscope and cyclic voltammetry measurements.

Experimental Method

The materials used in this study were SS foil substrates (MTI, Malaysia), Zinc Acetat Tetrahydrate (Merck, Australia) as electrode material. Electrolyte consists of KCl (Merck, Germany) was used as the transport mechanism for the redox mediator of the electrode. The CNT powder which prepared using spray pyrolysis method as previous reported by Subagio, et al., 2009 [18] was used as electrode material. Ethanol (Merck, Germany), terpineol (Sigma Aldrich, USA), ethylcellulose (Sigma Aldrich, USA), monoethanolamine (Merck, Germany), and isopropanol (Merck, Germany) were used without purification.

The CNT/GT composites were synthesized using sol-gel method. Briefly, 0.2 g of ethylcellulose was dissolved in 4 mL ethanol in which was stirred for 10 minutes and followed by mixing 1.6 g of terpineol into the binder. The CNT/GT (composition of mass 1:1) was dispersed in the binder with stirrer for 10 minutes. The mixture was then deposited onto the SS foil substrate by using doctor blade method and drying in the temperature of 150 °C for 2 hours. The ZnO nanoparticles was synthesized by sol-gel method using 0.5 M $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ as sources of Zn. In addition, isopropanol (IPA: $(\text{CH}_3)_2\text{CHOH}$), monoethanolamine (MEA: $\text{HOCH}_2\text{CH}_2\text{NH}_2$) were stirred for 30 minutes. ZnO liquid was sprayed to cover CNT/GT film in different drying temperatures, such as in 300, 350 and 400°C. The surface structure of electrodes were characterized by X-ray diffraction spectroscopy (XRD, Philip Analytical X-Ray B.V) with Cu $K\alpha$ radiation ($\lambda=1.5418 \text{ \AA}$) at 40 kV and scanning electron microscope (JEOL-6510LA). The cyclic voltammetry measurements were used to study the electrode properties by using a standard double cell containing 1 M KCl aqueous solution.

Results and Discussion

Structure of CNT/GT/ZnO was evaluated by using XRD. The XRD patterns of CNT/GT and CNT/GT/ZnO-300 composites can be found in Figure 1. Figure 1(a) shows XRD pattern of CNT/GT composite. The characteristic graphite peak at $2\theta = 26.4^\circ$ referred to (002) reveals the crystallinity of the CNT. Moreover, the peaks at 44.0° , 51.2° and 75.3° can be observed and corresponding to carbon (PDF #43-1104). In figure 1(b) shows XRD pattern of CNT/GT/ZnO composite with temperature of ZnO covering of 300°C. The peak of (101) orientation at 38.4° can be seen in the profile of figure 1b and it is probably caused by the chemical residual impurity from ethyl cellulose and terpineol remaining in the CNT as well as resulted by Y. Zhang, et. al.[8]. The peaks at (102), (110) and (200) orientation reveal the crystallinity of the ZnO indicating the well-formed ZnO during coating process.

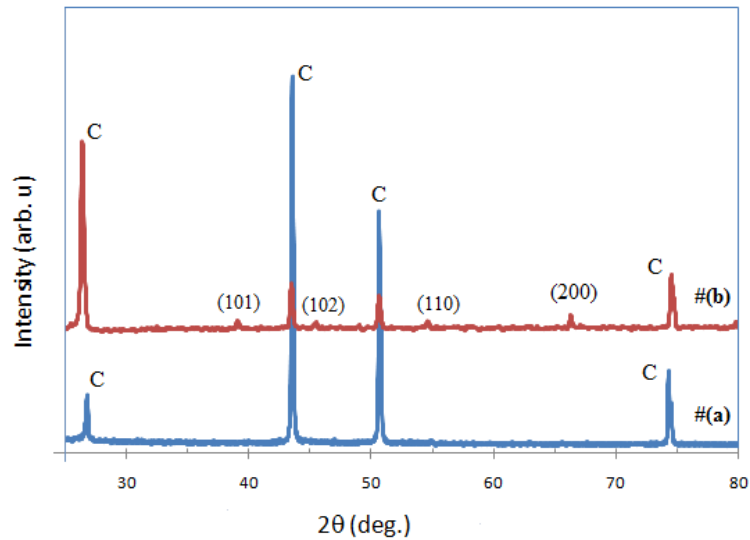


Figure 1. XRD patterns of (a) CNT/GT and (b) CNT/GT/ZnO-300 composites.

Figure 2a shows SEM images of surface and cross section of CNT/GT composites that were screen printed directly on SS foil substrate. The network structures of CNT can increase surface area for double layer capacitance.

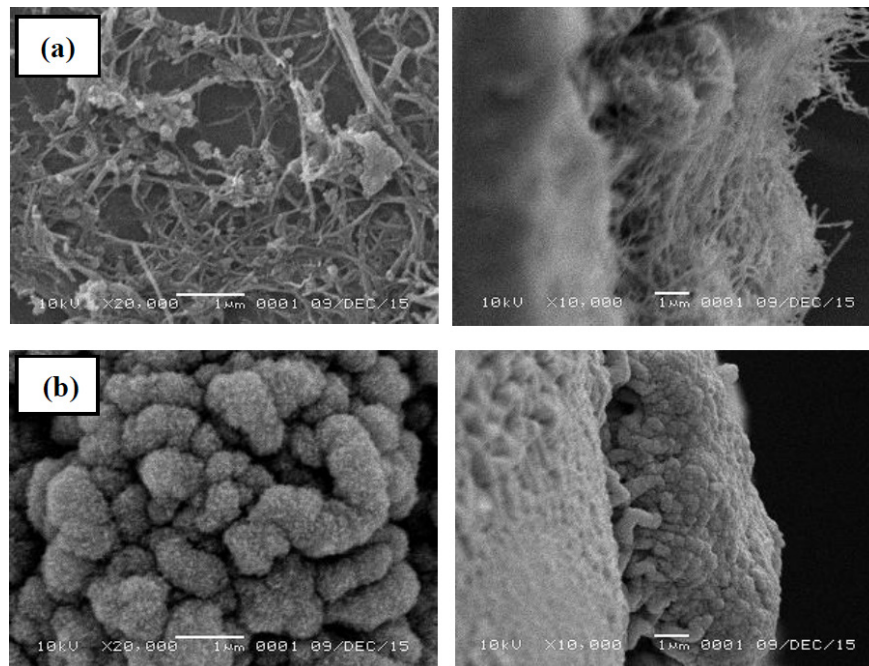


Figure 2. SEM images of surface morphology and cross section of (a) CNT/GT and (b) CNT/GT/ZnO-300 composites on the SS foil substrate.

The surface morphology of CNT/GT/ZnO-300 can be observed in Figure 2b. ZnO was distributed on surface of CNT/GT as islands. The CNT/GT sheets were covered by densely packed and regularly shaped ZnO grain. It can be ascribed to the overlapping between CNT/GT and ZnO layers with thickness of 4 μm . Change in the surface morphology can be observed from SEM images. Initially ZnO particles uniformly deposited on CNT/GT and it could provide better electrode/electrolyte interfacial contact. Thickness of the ZnO over CNT/GT increase leading to formation of clusters which block the pores in the electrode [17]. However, the CNT/GT are totally covered by ZnO which has a relatively high resistance and thus lower the conductivity of the electrodes significantly. Furthermore, the accumulation of ZnO destroys the net structure formed by CNTs and thus lowers the specific surface area, which disturbed the protons and electrons to be adsorbed on the surface of the electrode.

Test of cyclic voltammogram was carried out with -0.5 V to 0.5 V at different scan rates varying from 25 mV/s to 200 mV/s using 1 M KCl aqueous electrolyte. Table 1 shows the specific capacitance (C_s) can be calculated from the voltammogram by using equation (1):

$$C_s = 2 I / (s \times m) \quad (1)$$

where I , s and m are the charge current, scan rate and mass of the single electrode, respectively.

Table 1 shows that the specific capacitance of the CNT/GT/ZnO-300 sample was much higher than the others. The specific capacitances increase to 6.99 F/g for the sample with CNT/GT/ZnO-300 at the scan rate of 25 mV/s. However, there is a decreasing in capacitance of the CNT/GT/ZnO-300 sample in the scan rate from 20 to 200 mV/s. The reason may be that insufficient time available for ion diffusion and absorption inside the smallest pores within a large particle at high scan rates [19].

Table 1. Specific capacitance of samples determined via cyclic voltammetry method.

Samples	Specific capacitance (F/g)				
	Scan rate 25 mV/s	Scan rate 50 mV/s	Scan rate 100 mV/s	Scan rate 150 mV/s	Scan rate 200 mV/s
CNT/GT	0.17	0.11	0.07	0.06	0.06
CNT/GT/ZnO-300	6.99	4.49	2.89	2.31	2.20
CNT/GT/ZnO-350	5.52	3.96	2.92	2.63	2.45
CNT/GT/ZnO-400	5.22	2.89	1.79	1.36	1.35

CV curves of the electrodes measured at various scan rates are collected in figure 3. All the CV curves exhibit a rectangular-like shape, which reveals the ideal capacitive behavior and fast charge-discharge behavior. Rounding of corners in these patterns indicates some internal resistance that exists in the electrode material [20].

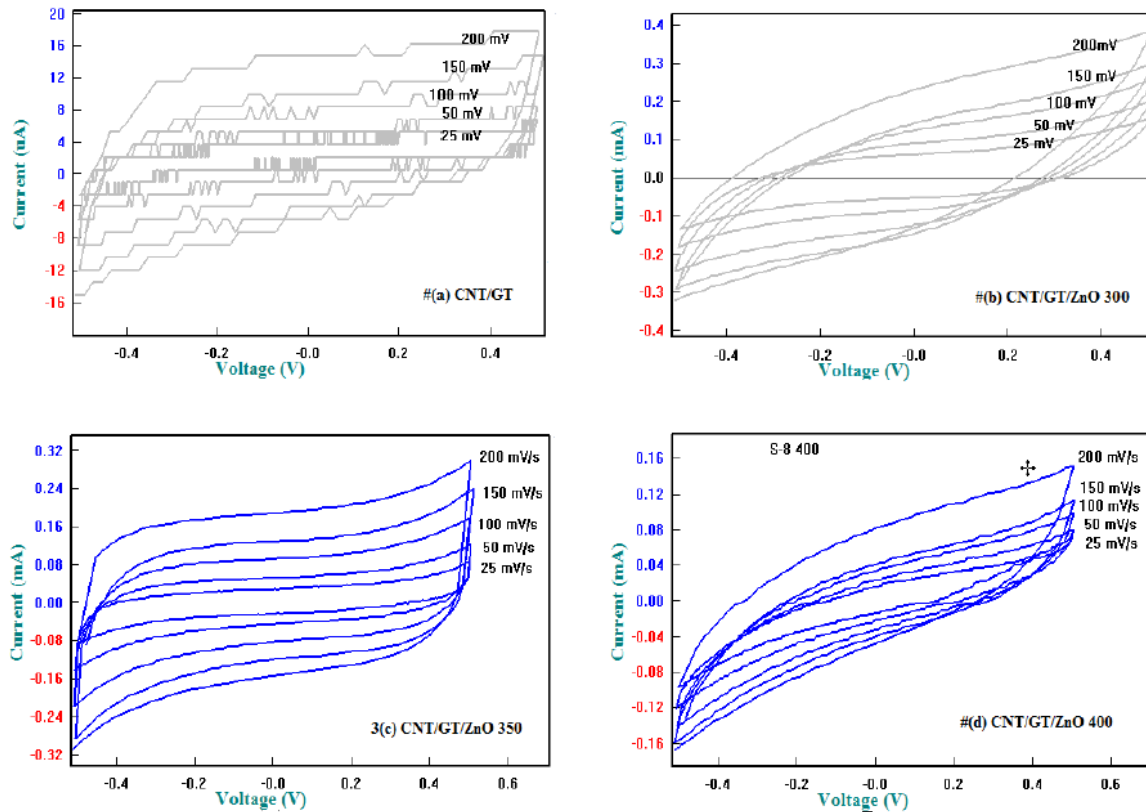


Figure 3. Cyclic voltammograms of (a) CNT/GT, (b) CNT/GT/ZnO-300, (c) CNT/GT/ZnO-350 and (d) CNT/GT/ZnO-400 electrode material at scan rates from 25 mV/s to 200 mV/s.

The value of specific capacitance decreased in increasing scan rate. At low scan rate, the ions have a long time to be able to diffuse into the porous carbon. Ions and electrons from the current collector will diffuse to the electrode surface through pores. Because of this mechanism, the width of the curve of charge and discharge current will be large which indicates a large capacitance value. In contrast to the high scan rate, the ions can diffuse rapidly but only up to the electrode surface. Ion only able to enter the macro pores. Porous of carbon electrodes that are not filled ion yield curves of charge and discharge currents are small which indicates a low capacitance value. Overall the addition of ZnO increase the capacitance value obtained the highest value achieved in CNT/GT/ZnO-300. The relatively higher capacitance in CNT/GT/ZnO-300 sample was caused by effect of the small crystallite size of ZnO. This effect will increases the surface area and electroactive sites, which effectively reduces the diffusion length of the K^+ ion in the electrode matrix [19,21].

Figure 4 shows curve of fast charge and discharger of the four electrodes using the current variation between 100 μ A - 0.1 mA. The purpose of this test is to determine the time required to perform the charging current to the electrodes. Figure 4(a) shows the CNT/GT electrode in the range of current best value 0.02 mA, the charged voltage value of 0.64 V and decrease drastically, but at discharge voltage of 0.44V decrease slowly during 2.5 seconds. Figure 4(b) shows CNT/GT/ZnO-300 electrode that has the best value on the current 0,1 mA with a voltage of 0.60 V. This electrode has the characteristics of filling of 12 seconds and storage current longer until 25 seconds. Figure 4(c) and 4(d) show a decrease in the current storage capacity of 100 μ A – 200 μ A, but still have the same characteristic of voltage value of 0.60 V.

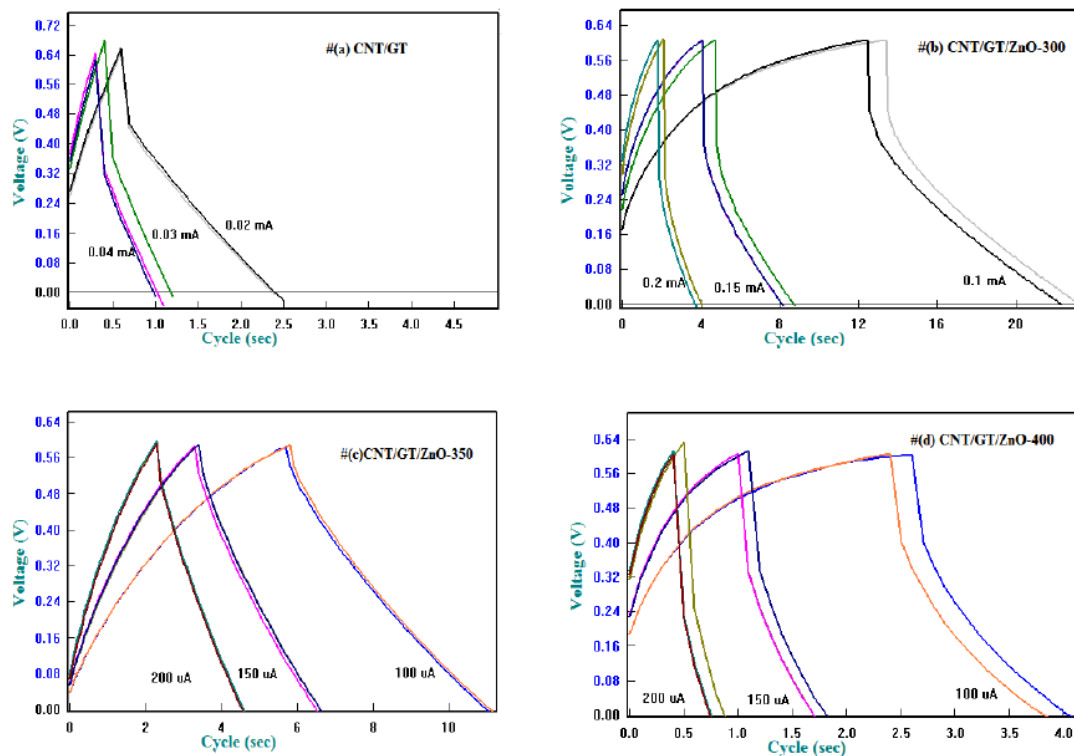


Figure 4. Galvanostatic charge discharge curve of (a) CNT/GT, (b) CNT/GT/ZnO-300, (c) CNT/GT/ZnO-350 and (d) CNT/GT/ZnO-400 electrode materials.

Figure 5 show a graph for comparing the electrode cycle stability each electrode to determine stability of the material with testing performed of 100 times. The capacitance efficiency appear on the addition of ZnO with drying temperature of ZnO of 300 $^{\circ}$ C, where it has value above 70%. The temperature of 300 $^{\circ}$ C is the best temperature for drying of ZnO material onto surface of CNT/GT. This is caused by limitation of evaporation of ZnO material and there is effectively incorporation of ZnO to CNT/GT material. The CNT/GT/ZnO-300 shows the best performance with a energy density of 152.9 Wh kg^{-1} in the potential range -0.5V to 0.5V.

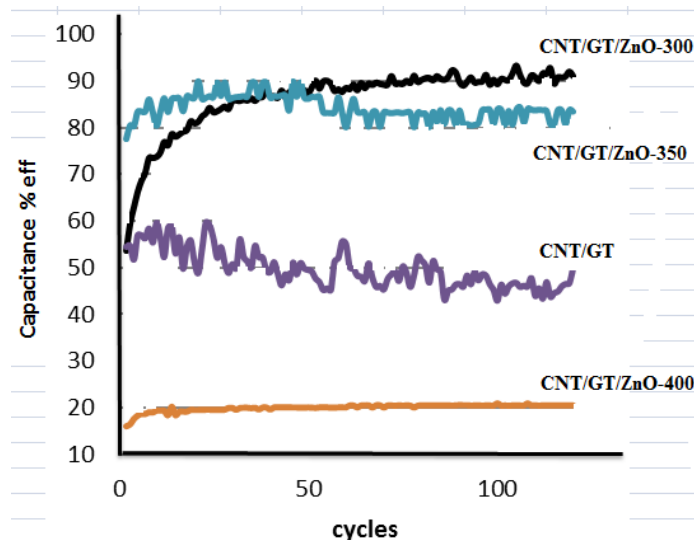


Figure 5. Graph of the electrode cycle stability of electrodes.

Summary

In summary, CNT/GT/ZnO has been prepared with simple method. The performance of CNT/GT/ZnO electrodes found to be dependent on the drying temperature of ZnO material. The CNT/GT/ZnO with the drying temperature of 300 °C reveals the C_s value up to 6.99 F/g in scan rate of 25 mVs^{-1} with a energy density of 152.9 Wh kg^{-1} in the potential range -0.5 V to 0.5 V.

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