MJoSHT
Malaysian Journal of Science, Health & Technology
[mjosht.usim.edu.my]

Article

Preparations, Characterizations and Comparative Study on Electrochemical Performance of ZnO/SWNT and TiO_2 /SWNT Nanocomposites

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***Abstract*— This work has successfully prepared and characterized the nanocomposite based metal oxides, Zinc Oxide and Titanium Dioxide (ZnO and TiO_2) with Single-Walled Nanotubes (SWNTs). Metal oxides are well-known alternatives to graphite as anode materials for lithium-ion batteries, due to their ability of highly capacities. In this study, green synthesis ZnO and TiO_2 were synthesized from Kaffir Lime and Ilmenite mineral respectively, and their composite is prepared in the presence of SWNTs. The as prepared ZnO/SWNT and TIO_2/SWNTs composite have been characterized by field emission scanning electron microscope (FESEM), Raman, and electron dispersive X-ray (EDX). The result of FESEM and EDX shows the metal oxide nanoparticles with average size 11.3 ± 3.0 nm was successfully deposited onto the SWNT. Electrochemical characterization of the prepared nanocomposites was carried out using cyclic voltammetry, and galvanostatic charge/discharge tests. The main difference found between these two nanocomposite is the internal resistance, thus giving specific capacitance 3.56 F/g and 0.78 F/g for SWNT/TiO2 and SWNT/ZnO respectively. The investigation highlights the importance of anchoring of green synthesis metal oxides nanoparticles on SWNTs for maximum utilization of electrochemically active ZnO, TiO_2 and carbon nanotubes (CNTs) for energy storage application.**

***Keywords*— Supercapacitor; Carbon nanotubes; ZnO; TiO_2 ; Green synthesis.**

I. INTRODUCTION

Electrochemical supercapacitor is considered as an ideal device to benefit both the electrical and electronic industries due to the long cycle life and high power density. The performance of the supercapacitor are electrode and electrolyte dependent [1]-[2]. Due to chemical stability, conductivity, and large surface area, (CNTs) are gaining attention as electrode [3]. Several metal oxide such as ruthenium oxide (RuO_2) and iridium oxide (IrO_2) were tested to work well with CNT electrode. However, the new challenge rise as the cost of those metal oxide are expensive and gave poor performance [4]. Research made by [5] has proven that ZnO possesses high potential as optoelectronic devices due to its promising electrical and optical properties. The CNT/ZnO composite film electrode and polyvinyl alcohol (PVA) – poly(methacrylate) (PMA) electrolyte resulted in specific capacitance of 126.3 F/g. TiO_2 is a promising material due to its low cost and less toxicity [6]. The addition of titanium dioxide (TiO_2) into the hybrid supercapacitor are supposed to help in the improvement of the performance. In a recent study, the addition of anatase TiO_2 into reduced graphene as anode and AC as cathode resulted in positive results that could be a competitor to energy storage available at the market [7]. This paper will demonstrate the synthesis of functionalized SWNT with Kaffir Lime based ZnO and Ilmenite based TiO_2. The electrochemical performance of this material also was studied using three electrode systems.

II. MATERIALS

For this experiment, pristine SWNT was used alongside mineral Ilmenite based TiO_2 from [8] and Kaffir Lime based ZnO was the gift from other researchers in the group. Nitric acid (HNO_3) and sulfuric acid (H_2SO_4) were used for functionalization process. Dimethyl sulfoxide (DMSO) was used as surfactant agent for dissolution of ZnO and ethanol was used during synthesis of nanocomposite.

III. EXPERIMENTAL

A. *Functionalization of SWNT*

Basically, the functionalization step was taken from [9]. Taken into account the research made by [10], this functionalization method gives the best outcome and most active site on the side wall of the nanotubes. The SWNT was dispersed in the mixture of nitric acid (HNO_3) and sulphuric acid (H_2SO_4) in the ratio of 1:3 respectively. The solution was homogenized using water bath sonicator for 2 hours and refluxed at 70℃. The solution then was centrifuged at 6000 rpm and the sediment was taken and washed using deionized water for several times.

B. *Synthesis of SWNT/ZnO and SWNT/TiO$_2$*

The nanocomposite was synthesized using chemical mixing method. In details, 30 mg of SWNT was dispersed into ethanol solution and sonicated for 20 minutes and was marked as solution A. An amount of 9 mg of Kaffir lime based ZnO was added into the mixture of DMSO and ethanol solution and was sonicated for 30 minutes and marked as solution B. Solution A and B were and sonicated for 30 minutes at ambient temperature. Similar process for the synthesis of SWNT/TiO_2 except the DMSO addition was excluded.

C. *Electrode Preparation and Electrochemical Measurement*

Following the developed method by [11], first the glassy carbon electrode (GCE) was polished using alumina powder using circular motion onto the soft cloth, then rinsed using ethanol solution and deionized water using sonicator for 5 minutes. After a few minutes, the prepared nanocomposites in Nafion solution was coated at the tip of GCE. Finally, the GCE was left to dry at room temperature.

In order to study the electrochemical properties of materials, the experiment using Metrohm Autolab 1.11 software was conducted. Three electrodes system were used which are glassy carbon electrode (GCE), platinum wire, and Ag/AgCl as working electrode, counter electrode, and reference electrode. 6M potassium hydroxide (KOH) was used as electrolyte. The experiment was carried out at potential range from 0 V to -0.8 V.

IV. CHARACTERIZATION

Raman spectroscopy Witec Alpha 300R wavelength 488 nm was used to check the degree of defects of the sp^2 carbon in SWNT. The morphology of the prepared composite was determined using field emission scanning electron microscope (FESEM) using model JEOL JSM-7600F and energy dispersive X-ray was used to check the element composition in the composite.

V. RESULTS AND DISCUSSION

A. *Functionalization of SWNT*

The electrochemical behavior of the electrode was studied using cyclic voltammetry (CV) for the potential range of 0 V to -0.8 V. Fig. 1 shows that both SWNT/TiO_2 (a) and SWNT/ZnO (b) exhibited capacitive behavior based on asymmetry rectangular shape [11]-[12]. Besides, the shape indicated that the redox reaction occurred due to the synergistic effect between the SWNT and metal oxides. The faradaic peak for both metal oxides indicated good reversibility and a fast charge flow process at the surface where the redox reaction took place. Comparing these two graphs, the higher current area detected for SWNT/TiO_2 because of greater pseudo capacitance properties of the metal oxide [13]. The increase of scanning rates gives a higher area of the curve, showing a good rate properties and capacitance properties [11].

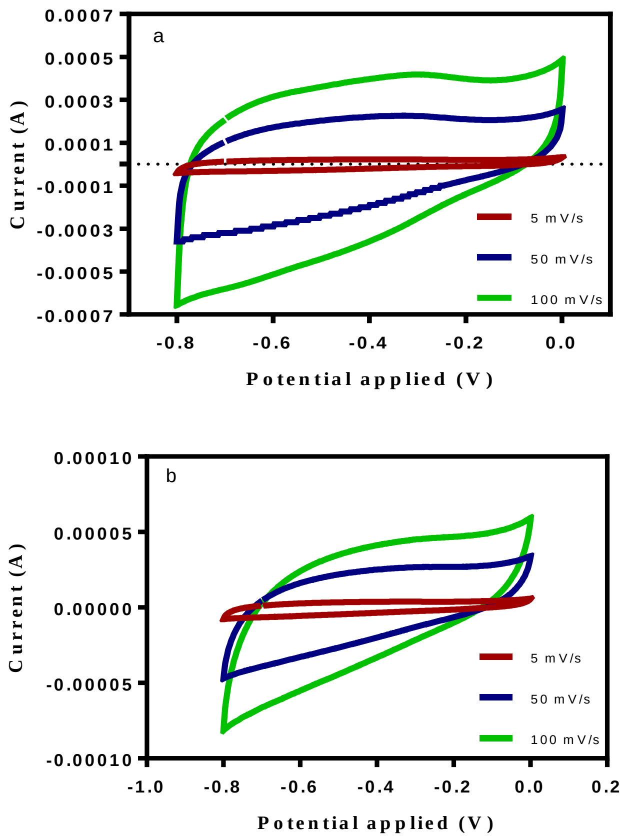

Fig. 1 Cyclic voltammetry of (a) SWNT/TiO_2 and (b) SWNT/ZnO at different scan rates

The galvanostatic charge discharge was carried out to test the performance of the capacitor. In this test, the material was charged and discharged between -0.8 V to 0 V at different current density. From the figure, all three materials show a triangular shape indicating capacitive characteristic [14]. It can be seen SWNT/TiO_2 have a longer period of charging and discharging time. This outcome proven that the synergistic effect between Ilmenite based TiO_2 and SWNT is much better compared to Kaffir lime based ZnO. The poor performance of SWNT/ZnO may be due to the poor faradaic reaction as shown from the small area under the curve of current in Fig. 1 (b). The increase in internal resistance (iR) drop from SWNT/TiO_2, SWNT, and SWNT/ZnO owing to increasing of the resistance of electrode and electrolyte of the material [11][15]. It is one of the reasons why metal oxide cannot be used alone as supercapacitor due to its high resistance properties. Low internal resistances are crucial for capacitor as it can lead to less energy wasted and unnecessary heat during charging and discharging process [11]. The calculated specific capacitance is 3.56 F/g, 3.02 F/g, and 0.78 F/g for SWNT/TiO_2, SWNT, and SWNT/ZnO.

B. *Structural Analysis*

So far, there is not much paper reported for the chemical mixing method for the synthesis of carbon nanotubes and metal oxide. From the Fig. 1 and Fig. 2, sample SWNT/TiO_2 shows the most positive result in terms of electrochemical behavior as discussed in the previous part. Hence, the structural properties were analyzed using FESEM, EDX, and Raman. FESEM images of SWNT/TiO_2 (Fig. 3) showed a small nanoparticles with shown average size about 11.3 ± 3.0 nm, believed it is ilmenite based TiO_2 even though the size is smaller than the value stated by [8]. This findings may be due to the sonication step to form a homogeneous solution. Another possibility is the combination of sulphur and TiO_2 based on the insert image of EDX analysis shows the 8.57% amount of TiO_2, followed by sulphur at 7.69% (Fig. 4). The low performance of this material due to high amount of sulphur, which is not metal oxide that have pseudo capacitive properties. This experiment shows that the functionalization method can influence the outcome since a high amount of sulphuric acid was used and not properly washed. However, the functionalization of SWNT using this method have made it is possible to bonding of metal oxide to the wall of SWNT due to the highest amount of carboxyl group formed (Table I) [10].

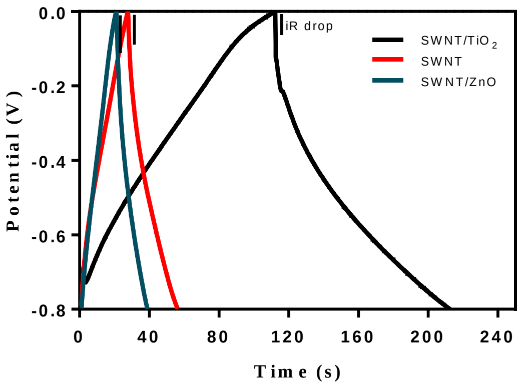

Fig. 2: Galvanostatic charge discharge (GCD) of SWNT, SWNT/TiO_2, and SWNT/ZnO at 0.02 A/g current density

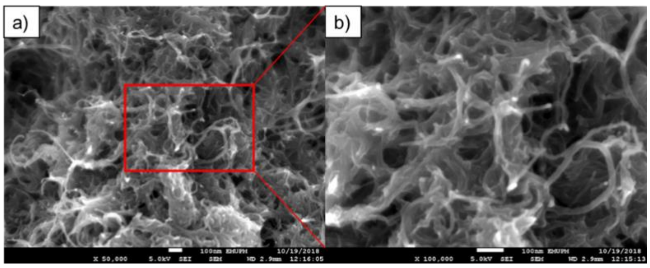

Fig. 3 FESEM images of SWNT/TiO_2 at magnification (a) x50,000 and (b) x100,000

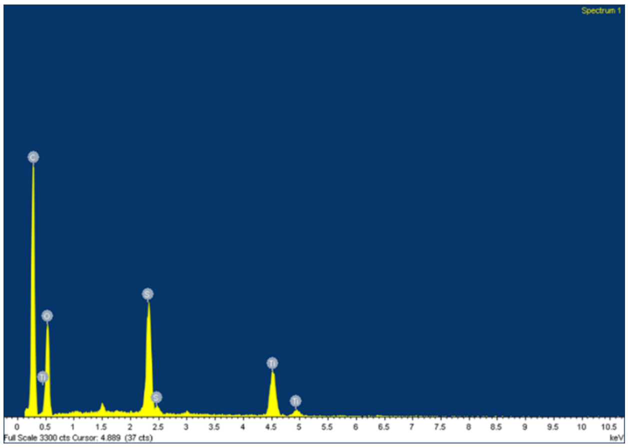

Fig. 4 EDX result of SWNT/TiO_2

TABLE I
ELEMENTAL COMPOSITION DATA OF SWNT/TIO2 FROM EDX

Element	C	O	S	Ti	Total
Weight percent (%)	56.18	27.57	7.69	8.57	100.00

Raman spectroscopy was employed in this experiment to determine the degree of defects of sp^2 carbon to sp^3 carbon (Fig. 5). D band and G band represent the defects and degree of graphitization. On the other hand, I_D/I_G ratio calculation is useful for the study of degree of defect in the sample. The lower the ratio means the higher of graphitization of SWNT [16]. The I_D/I_G ratio is 0.85 for all three samples meaning that the functionalization process does not cause damaged to sp^2 carbon. The G' band at 2704 cm^{-1} is a translation of another feature of sp^2 carbon. Usually in graphene, the G' band is the indicator to study the electronic and vibrational structure [17]. Another interesting fact about the G' band is the detection of n-type and p-type semiconductor material in this sample. Depending on the pattern of the G'band, one can differentiate between the undoped SWNT, p-type doped, and n-type doped semiconductor [18][19]. However, the pattern are not very clear in this experiment and the percentage amount is very low to see the differences.

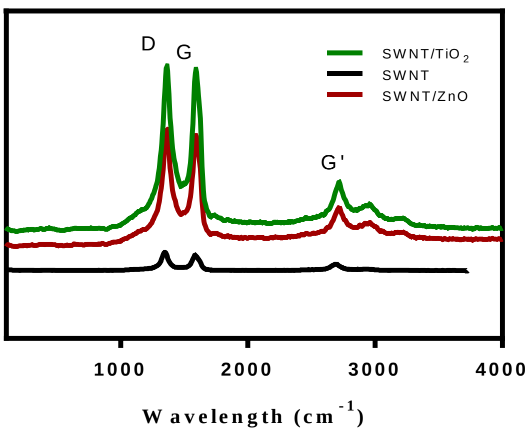

Fig.5 Raman spectroscopy of SWNT, SWNT/TiO_2, and SWNT/ZnO

VI. CONCLUSION

To conclude, the deposition of metal oxide nanoparticles onto the SWNT have been successfully carried out. The electrochemical studies of analysis of modified glassy carbon electrode from SWNT nanocomposite also have been carried out. The electrochemical behavior for both Kaffir Lime based ZnO and Ilmenite based TiO_2 also was compared and the specific capacitance was calculated. However, further improvement should be taken in the future work to avoid sulphur element left, hence may affect the electrode performance. The current study showed the comparable amount of TiO_2 and sulphur have limited the efficiency of the electrode. For future work, any possibilities of disturbance should be eliminated and the optimization of metal oxide percentage in SWNT should be taken into account.

ACKNOWLEDGEMENT

We would like to express our gratitude to the members of the NANOTEDD group in Biophysics Lab, Physics Department and every personnel in Electroanalysis Lab, Chemistry Department, UPM. We are also thankful to the Ministry of Education for Fundamental Research Grant Scheme (UPM/FRGS/5524949), Universiti Putra Malaysia through Dana Tautan (DT-9200802).

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