

A Thermally Reduced Graphite Oxide and Carbon Nanotube Composite for Supercapacitor Applications

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A thermally reduced graphite oxide and carbon nanotube (TRGO-CNT) composite is synthesized for supercapacitor applications by using a simple chemical method. The TRGO-CNT composite shows higher capacitance than the precursors (TRGO and CNT), and its impedance is lower than that of CNT, meaning that TRGO of high surface area connected with a CNT could provide highly efficient surface area and good connection for supercapacitor electrodes. Different weight ratios of TRGO to CNT are investigated, and the results show that the composite with more TRGO has better performance in the electrochemical measurements. Based on these findings, the proper TRGO amount is necessary for a high-performance supercapacitor. Neither CNT nor TRGO by itself can give the highest electrochemical performance for the supercapacitor; thus, the synergistic effect of TRGO and CNT is important.

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I. INTRODUCTION

Supercapacitor is known as a complementary device of other power sources such as batteries and fuel cells, and it can have long life cycles and rapid charging time by high power density due to its highly reversible charge storage process [1]. Researches on the supercapacitor are, therefore, very important for alternative energy storage devices, and various materials as an electrode have been studied [2].

Carbon nanotube (CNT) has been investigated as an electrode of the supercapacitors since it has unusual properties, such as high electric and thermal conductivities and extraordinary mechanical properties [3–6]. However, CNT itself has still provided limited capacitance because of typical agglomeration and non-uniform dispersion problems [7].

Graphene has also been studied as the electrode of the supercapacitors [8, 9]. It is a two dimensional allotrope of carbon with the honeycomb structure, and it

has the precious properties such as high thermal conductivity ($\sim 5000 \text{ Wm}^{-1}\text{K}^{-1}$) and skyscraping electron mobility ($200,000 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$). Moreover, graphene can be made from graphite which is cheap and has a large reserve in nature so that it has become the “rising star” for high technology research work. Among many routes to produce graphene, graphite oxide (GO) is considered as an easy and economical way. GO, however, is an insulator unfortunately so it is needed to reduce oxygen functional groups for recovering the aromatic structure and high electric conductivity.

It is necessary to remove oxygen functional group of GO in order to recover its conjugated structure. Thermally reduced GO (TRGO) could be obtained after thermal treatment at high temperature at $800 \text{ }^\circ\text{C}$ for 1 h in the argon atmosphere, resulting in significant reduction of the functional groups of GO [9–11]. TRGO, however, is still needed to improve electric conductivity for better performance of supercapacitors. Therefore, it needs to mix with CNT for the best performance of supercapacitors.

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In this paper, TRGO is mixed with CNT to make TRGO-CNT composites, and the electrochemical properties of the composites are investigated in an aqueous electrolyte (H_2SO_4) for the supercapacitor applications. CNT has very high conductivity with relatively low surface area ($\sim 100 \text{ m}^2\text{g}^{-1}$). In the other hand, TRGO has low conductivity, but it has higher surface area (as high as $2,630 \text{ m}^2\text{g}^{-1}$) than that of CNT. It is, therefore, expected that the TRGO-CNT composites result in higher capacitance due to lower impedance and larger surface area, demonstrating a synergic effect of the composite.

II. EXPERIMENTAL

GO is synthesized by a simple modified Brodie method [3]. 1 g of natural graphite ($>75\%$, 100 mesh, Sigma Aldrich) was ground with 6.5 g of sodium chlorate (99%, Sigma Aldrich) and stirred in 20 ml of the nitric acid for 24 h. GO powder was obtained after vacuum filtration with deionized water (DI) several times followed by drying in a vacuum oven at 60°C for overnight. The next pathway is to reduce GO by thermal treatment only at high temperature. GO of 50 g was placed in a round calcination boat and annealed at 800°C for 1 h in the argon atmosphere. The thermally reduced GO was obtained and named as TRGO. Multi-walled CNT (MWCNT, CM-150, 87 - 93% purity, Hanwha Chemical Ltd.) was also purified as follows: 1 g of CNT was mixed with 50 ml of the nitric acid in a round vial and then stirred in flux condition at 50°C for 5 h followed by washing several times with DI water based on typical purification techniques. The obtained CNT was dried overnight in a vacuum oven.

The three different composites of TRGO and CNT were synthesized as follows: 15 g of TRGO and 15 g of CNT, 21 g of TRGO and 9 g of CNT, 9 g of TRGO and 21 g of CNT were mixed with 2 ml of DI water in a glass bottle with a cap and sonicated for 3 h. Total weight of the active material was 30 g fixed. The mixture solutions were then filtered by the anodic inorganic filter membrane (Whatman) and dried at 65°C in the vacuum oven overnight. A free-standing film of the composites were obtained and named as the TRGO(2)-CNT(2), TRGO(3)-CNT(1) and TRGO(1)-CNT(3), respectively.

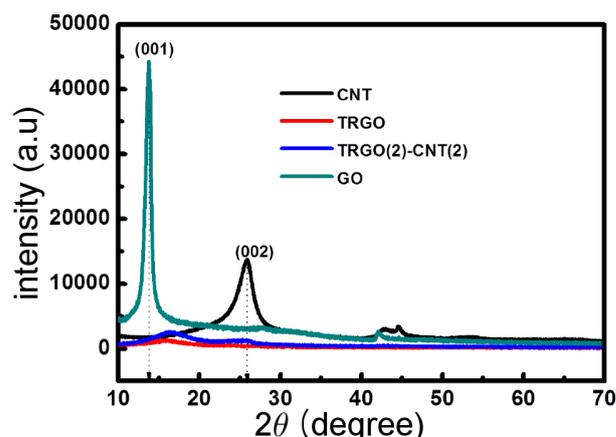


Fig. 1. (Color online) X-ray diffraction (XRD) of the samples.

Crystalline structure of the samples was investigated by using X-ray diffraction at 40 kV with $\text{Cu K}\alpha$ ($\lambda = 1.54 \text{ \AA}$). The electrochemical properties of the samples were studied in 1 M (H_2SO_4) electrolyte by using Potentiostat/Galvanostat with impedance spectroscopy (Bio-Logic SAS, SP-200). Cyclic voltammetry (CV), Galvanostatic cycling with potential limitation (GCPL) and Potentiostat electrochemical impedance spectroscopy (PEIS) measurement were performed. The samples were prepared as follows. 15 g of powder sample each was dispersed well in isopropyl alcohol solution of 2 ml by sonication for 3 h. The mixture of $5 \mu\text{l}$ was then drops casted onto the glassy carbon electrode (GCE) as a working electrode and dried completely. An Ag/AgCl electrode was used as the reference electrode, and platinum wire was employed as the counter electrode. CV was performed at the scanning rate 50 mVs^{-1} , and the frequency range of PEIS was from 100 mHz to 500 kHz.

III. RESULTS AND DISCUSSION

X-ray diffraction (XRD) results of the samples are shown in Fig. 1. Typical CNT peak is present at near 26° which is (002) diffraction peak [12] and GO shows the characteristic (001) peak near 14° , indicating the inter-layer distance 6.3 \AA . The (001) peak was changed to 16° after the thermal reduction, indicating removal of oxygen functional groups and regeneration of the graphite structure through the reduction process. After making the composites both of characteristic CNT and TRGO peaks are shown from the composite, meaning that the

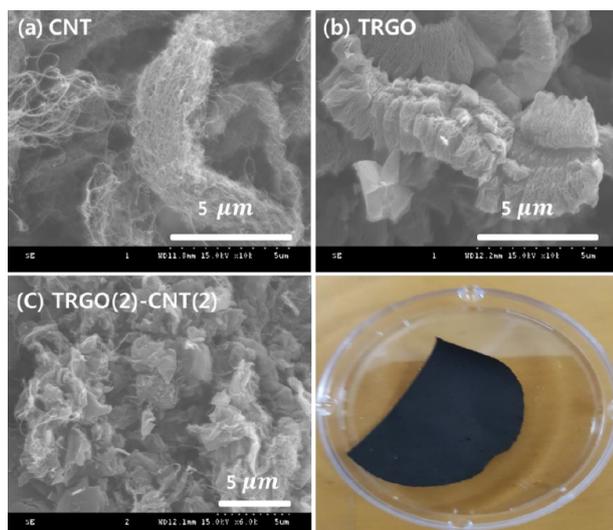


Fig. 2. (Color online) Scanning Electron Microscopy (SEM) results of (a) CNT, (b) TRGO, (c) TRGO(2)-CNT(2), and (d) a digital photo of the TRGO(2)-CNT(2) composite.

crystalline structure of each precursor was not changed even the composite film was formed [13].

Scanning electron microscopy (SEM) results of the samples are displayed in Fig. 2. CNT shows one-dimensional structure as tangled hairs with some light spots from a charge effect originated from oxygen functional groups while TRGO displays an exfoliated layered structure of crinkled sheets by the thermal explosion of the oxygen functional groups existed in GO. It seems that the thermal treatment expanded the grain size of samples like a pop-corn. Different morphology of CNT and TRGO is apparent. TRGO(2)-CNT(2) composite shows a three-dimensional structure with rough surface. CNT was distributed uniformly on or between layers of TRGO without agglomeration. It shows that sponge-like TRGO layers were connected with the tangled CNT. It could be expected from SEM result that TRGO(2)-CNT(2) has larger surface area compared with those of precursors (TRGO and CNT), affecting positive performance on the capacitance. The hydrophilic property of TRGO could also improve the dispersion degree of the TRGO-CNT solution compared to the CNT solution itself, resulting that the free-standing TRGO-CNT film could form with a synergic effect of each precursor (TRGO and CNT), as shown in Fig. 2(d).

Electrochemical properties of the samples are shown in Fig. 3. Corresponding specific capacitance was cal-

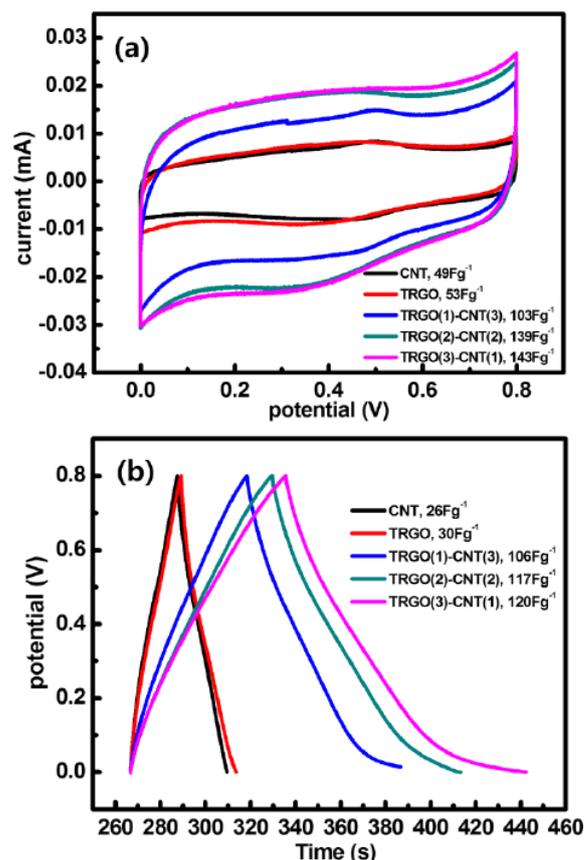


Fig. 3. (Color online) (a) Cyclic voltammetry (CV) and (b) Galvanostatic cycling with Potential Limitation (GCPL) results of the samples.

culated from the CV curves in Fig. 3(a) [2,3]. The obtained capacitance of CNT and TRGO were 49 and 53 Fg⁻¹, respectively, and all composite show higher capacitance compared to the precursor, demonstrating the synergic effect on the capacitance. TRGO(3)-CNT(1) has the highest capacitance (143 Fg⁻¹) among the other composites. However, addition of more TRGO or only TRGO electrode could not give higher capacitance than that of the TRGO(3)-CNT(1) composite due to synergic effect of CNT and TRGO.

Fig. 3(b) shows GCPL results of the samples, and the specific capacitance of the samples was also calculated from the discharge curves, as described in elsewhere [14]. Obtained capacitances were 26, 30, 106, 117 and 120 Fg⁻¹ for CNT, TRGO, TRGO(1)-CNT(3), TRGO(2)-CNT(2), and TRGO(3)-CNT(1), respectively. The capacitance of the composites is superior to the precursors, and TRGO(3)-CNT(1) shows again the best performance in GCPL measurement, which is consistent with the CV results.

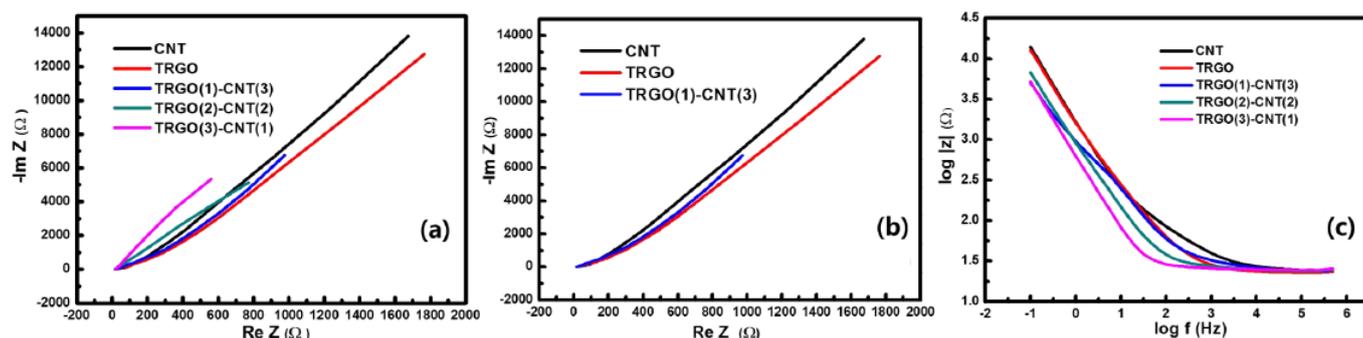


Fig. 4. (Color online) (a) Potentio electrochemical impedance spectroscopy (PEIS) results of the samples, (b) PEIS result of three samples, and (c) absolute impedance as a function of the frequency.

Impedance of TRGO(3)-CNT(1) is much lower than that of CNT, TRGO, TRGO(1)-CNT(3) and TRGO(2)-CNT(2), as shown in Fig. 4. Fig. 4(a) shows impedance of all samples, and Fig. 4(b) compares only three samples, demonstrating that TRGO(3)-CNT(1) has lowest impedance and TRGO(1)-TRGO(3) has even lower impedance compared to the precursors (CNT and TRGO). Fig. 4(c) displays absolute impedance of samples as a function of frequency, proving TRGO(3)-CNT(1) has the lowest impedance in the all frequency region. That is the reason why the current of TRGO(3)-CNT(1) in CV was dominant. Specially, the electrochemical impedance was affected significantly by the surface area. The higher ratio of TRGO to CNT shows the lower impedance, resulting in the higher capacitance of the composites, which is consistent with the CV and GCPL results.

IV. CONCLUSIONS

Thermal reduced graphite oxide and carbon nanotube (TRGO-CNT) composite was synthesized and investigated for supercapacitor applications. The TRGO-CNT composite displayed higher capacitance compared to those of precursors (TRGO and CNT), and its impedances were lower than that of CNT, meaning that TRGO layers connected with CNTs could provide high efficient surface area and good electrical conductivity. Different weight ratio of TRGO to CNT was also investigated, resulting that more ratio of TRGO in the composite shows better performance in electrochemical measurement. However, only CNT or TRGO itself did not give the highest electrochemical performance for the supercapacitor.

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