

## Fabrication and Capacitance of $\text{Co}_3\text{O}_4$ -Graphene Nanocomposites Electrode Prepared by Pulse Microwave-assisted Reduction Methods

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In recent years, with an impending exhaustion of fossil fuels and the rising global demand for an energy consumption, the effort to maximize the utilization of present energy sources and a search for alternative energy storage devices has intensified dramatically.<sup>1,2</sup> Supercapacitor attracted much attention because of their pulse power supply, long cycle ( $> 100,000$  cycles), simple principle, and high dynamics of charge propagation.

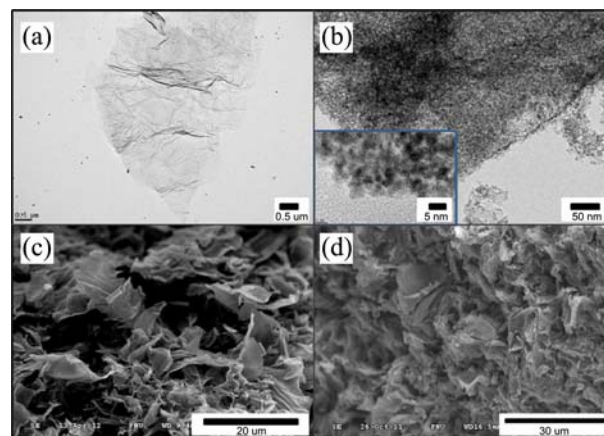
On the other hand, graphene nanosheets (GNS), new kind of carbon material, have attracted tremendous attention since its discovery by Geim and co-workers in 2004.<sup>3</sup> Graphene is a single layer of carbon atoms with a hexagonal arrangement in a two-dimensional lattice. Its unique structural and excellent physical, chemical and mechanical properties make it promising for potential applications in many technological fields, such as nanoelectronics, sensors, nanocomposite, batteries, supercapacitors, and hydrogen storage.<sup>4-6</sup> More recently, graphene-based materials as electrodes for supercapacitors have been reported with the specific capacitance ranging from  $117 \text{ Fg}^{-1}$  to  $205 \text{ Fg}^{-1}$  in aqueous solution.<sup>7-9</sup> It is well known that metal oxide such as  $\text{RuO}_2$ ,  $\text{IrO}_2$ ,  $\text{MnO}_2$ , and  $\text{NiOx}$  can improve the electrochemical performance of carbon-based supercapacitors, as they can contribute pseudocapacitance to the total capacitance apart from the double-layer capacitance from the carbon materials. Cobalt oxide ( $\text{Co}_3\text{O}_4$ ) is reported to be high performance electrode materials for supercapacitors because of its relatively low cost, high redox activity, high theoretical specific capacitance ( $\sim 3560 \text{ Fg}^{-1}$ ) and its great reversibility.<sup>10</sup> These advantages enable the promising commercialization and an extensive research of  $\text{Co}_3\text{O}_4/\text{GNS}$  as supercapacitor electrode materials.

In this work, we synthesized  $\text{Co}_3\text{O}_4/\text{GNS}$  composites by using a microwave-assisted polyol reduction process and studied their electrochemical performance for supercapacitors. The synthesis method is fast and effective to disperse particles on graphene sheets. It is expected that  $\text{Co}_3\text{O}_4/\text{GNS}$  composite could exhibit high specific capacitance and excellent cycleability. We present a simple preparation method for supercapacitor electrodes having advantageous electrochemical properties.

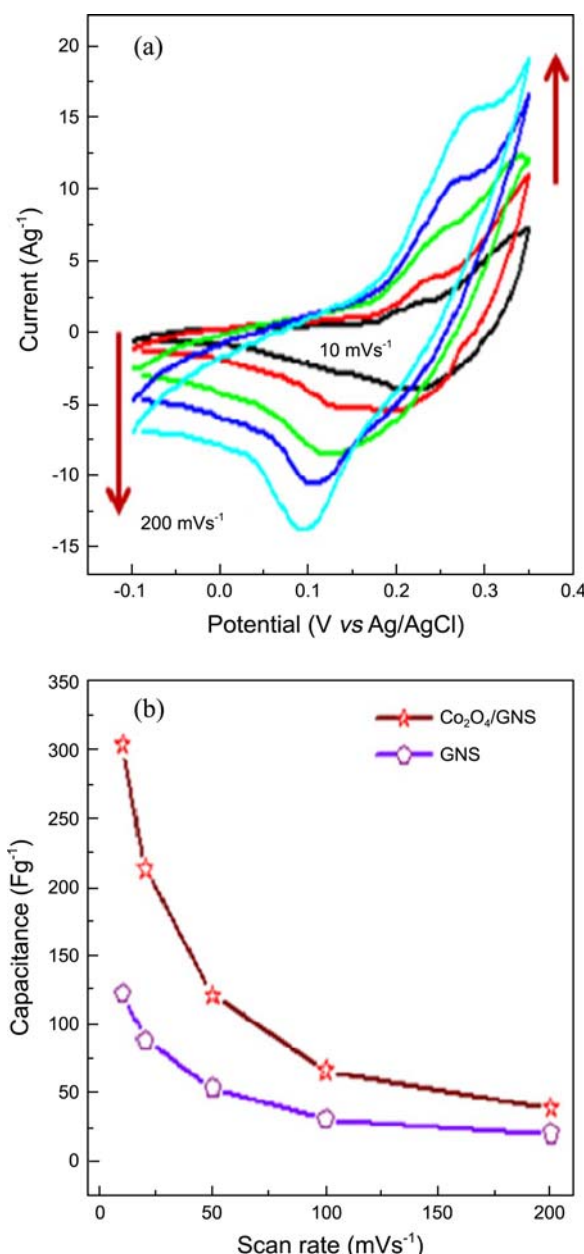
## Results and Discussion

**Morphologies of Graphene and  $\text{Co}_3\text{O}_4/\text{GNS}$ .**  $\text{Co}_3\text{O}_4/\text{GNS}$  nanocomposites are prepared in the presence of GO (Graphite oxide) suspension by microwave irradiation method. This method is simple, energy efficient and less time-consumption.<sup>11</sup> A possible linkage between surface groups (carboxyl and hydroxyl) of Co precursors and GO may promote the formation of composites. After calcinations,  $\text{Co}_3\text{O}_4/\text{GNS}$  composites were obtained. These microwave-assisted reduction methods could be applied to other composites containing various kinds of metal oxides and carbonaceous materials.

Figure 1 shows TEM and SEM images of GNS and  $\text{Co}_3\text{O}_4/\text{GNS}$  composites. GNS were overlapped together with inter-graphene (Fig. 1(a)). The pristine GNS have smooth surfaces and multilayer. Compared to pristine GNS,  $\text{Co}_3\text{O}_4/\text{GNS}$  composites exhibit rough surface and particle-deposited morphology that is due to  $\text{Co}_3\text{O}_4$  particle nucleation (Fig. 1(b)).  $\text{Co}_3\text{O}_4$  particles were nucleated on the edges of graphene sheets. In addition,  $\text{Co}_3\text{O}_4$  particles with the average size of 6 nm were dispersed homogeneously on the surface of GNS. These structures provide an enhanced surface area and electrolyte ion intercalation spots during electrochemical reaction. In this work, the deposition of  $\text{Co}_3\text{O}_4$  on GNS may be



**Figure 1.** TEM images of prepared (a) GNS and (b)  $\text{Co}_3\text{O}_4/\text{GNS}$  and SEM images of prepared (c) GNS, (d)  $\text{Co}_3\text{O}_4/\text{GNS}$ .



**Figure 2.** (a) Specific capacitance of GNS and  $\text{Co}_3\text{O}_4/\text{GNS}$  with various scan rates ( $10 \text{ mVs}^{-1}$  to  $200 \text{ mVs}^{-1}$ ). (b) CV curves of the  $\text{Co}_3\text{O}_4/\text{GNS}$  with various scan rates ( $10 \text{ mVs}^{-1}$  to  $200 \text{ mVs}^{-1}$ ).

expected to promote electrochemical performance as electrodes for supercapacitor. The SEM images of GNS and  $\text{Co}_3\text{O}_4/\text{GNS}$  showed no prominent difference because the deposited  $\text{Co}_3\text{O}_4$  particle is nano-meter scale.

**Electrochemical Performances of  $\text{Co}_3\text{O}_4/\text{GNS}$ .** The electrochemical performance of graphene and  $\text{Co}_3\text{O}_4/\text{GNS}$  was analyzed using CV curve in 6.0 M KOH solution. CV curves

of  $\text{Co}_3\text{O}_4/\text{GNS}$  composites are shown in Figure 2(a). It indicates redox peaks ( $\sim 0.3 \text{ V}$  oxidation peak and  $\sim 0.1 \text{ V}$  reduction peak) and that provide pseudocapacitance reactions. The specific capacitance of the electrode can be calculated according to the following equation.

$$C = \frac{\int IdV}{vmV} \quad (1)$$

$C$  is the specific capacitance based on the mass of electroactive materials ( $\text{Fg}^{-1}$ ),  $I$  is the response current density ( $\text{Acm}^{-2}$ ),  $V$  is the potential scan rate ( $\text{mVs}^{-1}$ ), and  $m$  is the mass of the electroactive materials in the electrode (g).<sup>12</sup>

The specific capacitance of GNS and  $\text{Co}_3\text{O}_4/\text{GNS}$  composites was shown in Figure 2(b) and the calculated values were shown in Table 1.  $\text{Co}_3\text{O}_4/\text{GNS}$  showed enhanced capacitance of  $305 \text{ Fg}^{-1}$  at  $10 \text{ mVs}^{-1}$  and  $40 \text{ Fg}^{-1}$  at high scan rates ( $200 \text{ mVs}^{-1}$ ). This enhanced capacitance for composite electrodes was related to the synergy effect by  $\text{Co}_3\text{O}_4$  and GNS. GNS could be functioned as an electric double layer capacitance (EDLC) for a fast charge-discharge. GNS could also be functioned as stable layer-structured blocks for preventing the volume change of  $\text{Co}_3\text{O}_4$ . Besides,  $\text{Co}_3\text{O}_4$  particles on GNS provided electrochemical reaction sites and ion intercalation spots that were accessible to electrolytes ion effectively.

The cycle stability of supercapacitors is a crucial factor for their applications. Many reported results show an excellent cycling stability of EDLCs consisting of porous carbon due to the nonexistence effect.<sup>13</sup> Incorporation of pseudo-capacitive materials into carbon materials is effective to improve their cycle performance.<sup>14</sup> The cycle performance of  $\text{Co}_3\text{O}_4/\text{GNS}$  composites was evaluated between  $-0.1 \text{ V}$  and  $0.35 \text{ V}$  at a scan rate of  $100 \text{ mVs}^{-1}$  for 1000 cycles. The capacitance retention ratios of composites are presented in Figure 3(b). The  $\text{Co}_3\text{O}_4/\text{GNS}$  composites showed capacitance retention ratios of 72%. The improved retention properties may be originated from the fact that GNS in composites can not only efficiently buffer the volume change of cobalt oxide during charge and discharge processes but also provide the high electrical conductivity of GNS.

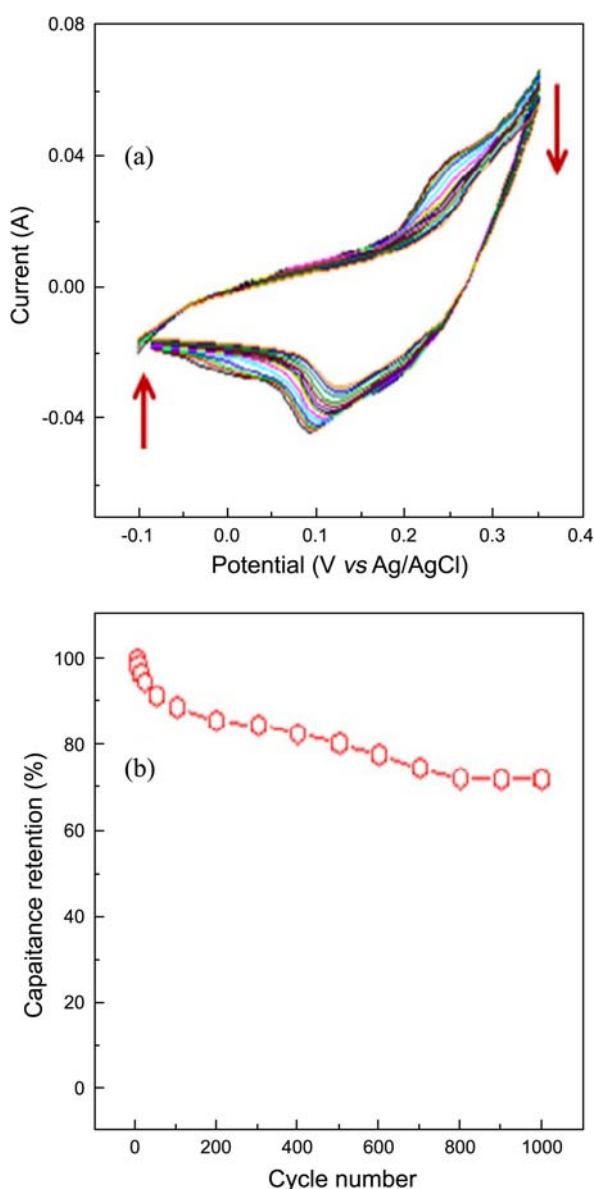
## Conclusions

In this study,  $\text{Co}_3\text{O}_4/\text{GNS}$  composites were prepared using microwave-assisted reduction methods. The specific capacitance of  $\text{Co}_3\text{O}_4/\text{GNS}$  composites was  $305 \text{ Fg}^{-1}$  at  $10 \text{ mVs}^{-1}$  compared to  $123 \text{ Fg}^{-1}$  of GNS. The capacitance retention ratios of  $\text{Co}_3\text{O}_4/\text{GNS}$  were 72% after 1000 cycles.

The GNS in the composites has stable structures and perform a role as reaction sites for an electric double layer

**Table 1.** Specific capacitances of GNS and  $\text{Co}_3\text{O}_4/\text{GNS}$  as a function of scan rates

	$10 \text{ mVs}^{-1}$	$20 \text{ mVs}^{-1}$	$50 \text{ mVs}^{-1}$	$100 \text{ mVs}^{-1}$	$200 \text{ mVs}^{-1}$
Capacitance GNS ( $\text{Fg}^{-1}$ )	123	89	54	32	21
Capacitance $\text{Co}_3\text{O}_4/\text{GNS}$ ( $\text{Fg}^{-1}$ )	305	214	122	67	40



**Figure 3.** (a) CV curves of the  $\text{Co}_3\text{O}_4/\text{GNS}$  at  $100 \text{ mVs}^{-1}$  for 1000 cycles. (b) Capacitance retention of the  $\text{Co}_3\text{O}_4/\text{GNS}$  at  $100 \text{ mVs}^{-1}$  for 1000 cycles.

capacitance (EDLC).  $\text{Co}_3\text{O}_4$  particles ( $\sim 6 \text{ nm}$ ) were dispersed homogeneously. The enhanced capacitance for composite electrodes was related to the synergy effect by  $\text{Co}_3\text{O}_4$  and GNS.  $\text{Co}_3\text{O}_4$  particles on GNS provided electrochemical reaction sites and ion intercalation spots that were accessible to electrolytes ion effectively. These superior properties make it suitable and promising electrode material for supercapacitors.

### Experimental

**Synthesis of  $\text{Co}_3\text{O}_4/\text{GNS}$  Composite.** GO was synthesized from natural graphite (SP-1, Bay carbon) by a modified hummers method. First, the graphite powder (0.2 g) was added into a mixture of 46 mL sulfuric acid and 1 g sodium

nitrate and strongly stirred at  $0^\circ\text{C}$  for 15 min. Then 6 g potassium permanganate was added slowly to above solution and cooled for 15 min. After this, the solution was stirred for 2 h and 92 mL of water was added into solution slowly. Subsequently, the suspension was diluted by 280 mL of hot water and 8.7 mL of  $\text{H}_2\text{O}_2$  (34.5%) to reduce residual permanganate ions. The solution was filtered and washed with 150 mL of HCl (10%) and subjected to centrifugation (3600 rpm, 5 min) to remove residual graphite.

To prepare  $\text{Co}_3\text{O}_4/\text{GNS}$  composites, 0.1 g GO was added into the solution of 100 mL ethylene glycol, 0.2 g cobalt nitrate hexahydrate (Dae Jung chemical, Korea) The solution was sonicated for 90 min and pH value was adjusted to 11. The reaction mixture was placed in a house-hold microwave oven (700 W) and was heated by pulse mode (10 sec-on/10 sec-off) for total 6 min. The pulse microwave provides complete reduction of Co precursor and small particle size with ultrafine distribution. Subsequently, the black powder precipitation was filtered, washed with distilled water and absolute alcohol for several times, and dried at  $70^\circ\text{C}$  for 24 h in a vacuum oven. Finally, the samples were calcined in a muffle furnace at a temperature of  $200^\circ\text{C}$  for 2 h in air, and then cooled to room temperature. The resulting black powder was collected for the following characterization.

**Material Characterization.** The obtained samples were characterized by Scanning electron microscopy (SEM, HITACHI S3500N), and Transmission electron microscopy (TEM, JEOL JEM2010).

**Electrochemical Measurements.** The fabrication of working electrodes was carried out as follows. First, active materials, carbon black (Super-P, Alfa Aesar) and PVDF (Aldrich) were mixed in a mass ratio of 85:15:5 in NMP solution. Then the resulting mixture was coated on nickel foam substrate ( $1 \text{ cm} \times 1 \text{ cm}$ ) with spatula, which was followed by drying at  $100^\circ\text{C}$  for 16 h in a vacuum oven.

All electrochemical tests were done in a three electrode system. A nickel foam coated with  $\text{Co}_3\text{O}_4/\text{GNS}$  composites, a platinum foil and Ag/AgCl (3 M KCl,  $0.196 \text{ V vs SCE}$ , Metrohm) served as counter and reference electrode. The measurements were carried out in 6 M KOH electrolytes. Electrochemical measurements were performed in a Iviumstat (Ivium Technologies, Netherlands). Cyclic voltammetry (CV) tests were analyzed between  $-0.1 \text{ V}$  and  $0.35 \text{ V}$  at different scan rate at 10, 20, 50, 100,  $200 \text{ mVs}^{-1}$ .

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