



# Direct and environmentally benign synthesis of manganese oxide/graphene composites from graphite for electrochemical capacitors



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## HIGHLIGHTS

- The Mn<sub>3</sub>O<sub>4</sub>/graphene composites were directly synthesized from graphite.
- This method does not require the use of strong acids and toxic reducing agents.
- The Mn<sub>3</sub>O<sub>4</sub>/graphene composite had a specific capacitance of 367 F/g.
- The cycling and electrochemical stabilities of the Mn<sub>3</sub>O<sub>4</sub>/graphene were good.

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## ABSTRACT

We develop a direct and environmentally benign method to prepare manganese oxide (Mn<sub>3</sub>O<sub>4</sub>)/graphene composites via one-step hydrothermal synthesis from graphite without using strong acids and toxic reducing agents. Structural and morphological analyses reveals that the irregularly shaped Mn<sub>3</sub>O<sub>4</sub> nanoparticles are well-dispersed on the graphene flakes. Cyclic voltammetry and galvanostatic charge–discharge tests indicate that the charge-storing mechanism of the Mn<sub>3</sub>O<sub>4</sub>/graphene composites is pseudocapacitive. The Mn<sub>3</sub>O<sub>4</sub>/graphene composite exhibits a specific capacitance of 367 F/g at a current density of 5 A/g. After 3000 charge–discharge cycles, the Mn<sub>3</sub>O<sub>4</sub>/graphene electrode retains 91.8% of its initial specific capacitance. From electrochemical impedance spectra, it is evident that the changes in both the equivalent series resistance and charge-transfer resistance of the Mn<sub>3</sub>O<sub>4</sub>/graphene electrode before and after 3000 charge–discharge cycles are small, indicating good cycling and electrochemical stability of the Mn<sub>3</sub>O<sub>4</sub>/graphene electrode.

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## 1. Introduction

As energy storage systems, electrochemical capacitors (also known as supercapacitors) have attracted much attention because of their high power density, fast charge–discharge rates, and long and stable cycle life [1–5]. They find many applications including hybrid electric vehicles, peak power sources, lightweight electronic fuses, starting power devices for fuel cells, and so on [6–8]. Electrochemical capacitors are usually classified into two types

according to their charge-storage mechanism: electric double layer capacitors (EDLCs) and pseudocapacitors [2,6].

EDLCs store charges in a non-faradaic way such that the charges accumulate at the electrode-electrolyte interface. Carbon-based materials including activated carbon, carbon nanotubes, and graphene are predominantly used for EDLCs because of their relatively low cost and high specific surface area. In pseudocapacitors, charges are stored via reversible faradaic reactions of metal oxides and conducting polymers. Metal oxides (i.e., oxides of Ru, Mn, Co, Ni, Cr, etc.) are considered to exhibit better performance as electrochemical capacitors than conducting polymers because conducting polymers can swell and shrink during charge–discharge cycling.

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Among the metal oxides used in electrochemical capacitors, manganese oxides are popular because of their natural abundance, low cost, and relatively broad working potential in aqueous solution [9–11]. However, the electrochemical performance of pure manganese oxides is sometimes unsatisfactory because of their dense morphology and poor electrical conductivity [12]. To overcome these limitations to their use in electrochemical capacitor applications, combining manganese oxides with materials that have high specific surface areas and conductivities is thought to be an attractive option.

Graphene is an outstanding candidate as an electrode material for electrochemical capacitors owing to its high specific surface area (~2600 m<sup>2</sup>/g), high electronic mobility (>200,000 cm<sup>2</sup>/V s), excellent thermal conductivity (~5300 W/m K), and good chemical stability [13–16]. Recent studies on graphene-based metal oxide composites for electrochemical capacitors such as Co<sub>3</sub>O<sub>4</sub>/graphene, NiO/graphene, MnO<sub>2</sub>/graphene, and Fe<sub>3</sub>O<sub>4</sub>/graphene, have shown that they exhibited better electronic performance than pure metal oxides because of their excellent supercapacitive performance, which is supported by the two dimensional structure of sp<sup>2</sup>-hybridized carbon atoms in graphene sheets [17–20].

Graphene-based metal oxides are usually obtained by mixing graphene with metal oxides. In most cases, graphene is synthesized by reducing exfoliated graphene oxide (GO) using a reducing agent [21]. During the chemical reduction of GO, graphene layers can agglomerate through the loss of oxygen-containing groups. In addition, the synthesis of graphene via the reduction of GO requires a large amount of strong acid, such as sulfuric acid or hydrochloric acid, and toxic reducing agent, such as hydrazine. Thus, its environmentally harmful synthesis limited the commercial use of graphene in electrochemical capacitor applications.

Recently, we prepared Co(OH)<sub>2</sub> nanosheets on graphene from graphite without a graphene oxide step [22]. As an extension of the previous work, this study reports on a direct and environmentally benign method to prepare Mn<sub>3</sub>O<sub>4</sub>/graphene composites via a one-step hydrothermal method without the use of strong acids and toxic reducing agents. The structural and morphological characteristics of the Mn<sub>3</sub>O<sub>4</sub>/graphene composites were examined. The electrochemical properties of the Mn<sub>3</sub>O<sub>4</sub>/graphene composite were also investigated using cyclic voltammetry, charge–discharge tests, and electrochemical impedance spectroscopy.

## 2. Experimental

### 2.1. Synthesis of Mn<sub>3</sub>O<sub>4</sub>/graphene composites

Mn<sub>3</sub>O<sub>4</sub>/graphene composites were prepared by mixing graphene flakes with a manganese precursor. Two grams of graphite powders (Samchun Pure Chemical Co. Ltd., Korea) were ultrasonicated with 50 mL of water for 1 h. The prepared graphite powder solution was stirred in 10 mM of sodium dodecylsulfonate (SDS, Sigma–Aldrich) at room temperature for overnight to form graphene flakes. And then, 20 mL of the SDS-functionalized graphene flakes were mixed with 20 mL of 20 mM manganese chloride (MnCl<sub>2</sub>·4H<sub>2</sub>O, Hayashi Pure Chemical Co. Ltd., Japan) solution and 0.1 mL of 1.5 M sodium hydroxide (NaOH, Samchun Pure Chemical Co. Ltd., Korea). The mixture solution was further stirred at room temperature for 10 min. Then, it was transferred to a 50 mL Teflon-line autoclave and heated at 120 °C for 12 h. The resulting product, which was the Mn<sub>3</sub>O<sub>4</sub>/graphene powder, was collected, cleaned three or four times with double-distilled water and ethanol, and dried in an oven at 50 °C for 6 h.

### 2.2. Preparation of the Mn<sub>3</sub>O<sub>4</sub>/graphene electrode

A Mn<sub>3</sub>O<sub>4</sub>/graphene electrode was produced by loading Mn<sub>3</sub>O<sub>4</sub>/graphene powders onto a Ni foil (110 μm thick) current collector. Polytetrafluoroethylene (PTFE, 60 wt% dispersion in water, Sigma Aldrich) was used as a binder. The mixture of Mn<sub>3</sub>O<sub>4</sub>/graphene and PTFE had a weight ratio of 90:10. The mixture was homogenized in an agate mortar and then formed into electrodes by rolling the mixture into 50 μm thick sheets. The mixture-coated electrode was dried in an oven at 80 °C for 6 h.

### 2.3. Materials characterization

The morphological and structural analyses of the Mn<sub>3</sub>O<sub>4</sub>/graphene composites were carried out using a transmission electron microscope (TEM, FEI Morgagni™) and an X-ray diffractometer (XRD, Rigaku Ultima III), respectively. TEM images were taken at an acceleration voltage of 300 kV. XRD patterns were obtained using a Cu-Kα radiation source (λ = 0.15418 nm).

### 2.4. Electrochemical measurements of the electrode

Electrochemical properties of the Mn<sub>3</sub>O<sub>4</sub>/graphene electrode for electrochemical capacitors were evaluated using a computer-controlled potentiostat (Princeton Applied Research, VSP) equipped with a three-electrode cell system. A platinum-coated titanium mesh (2.5 cm<sup>2</sup> in size) and a saturated Ag/AgCl electrode were used as a counter electrode and a reference electrode, respectively. One M of Na<sub>2</sub>SO<sub>4</sub> was used as an electrolyte. Before the electrochemical analysis, the electrolyte was de-aerated by bubbling with nitrogen gas for 5 min. Cyclic voltammograms were recorded between –0.5 and 1.3 V vs. Ag/AgCl at various scan rates. Galvanostatic charge–discharge tests were carried out in the voltage range of –0.3 to +1.0 V vs. Ag/AgCl at different current densities. The electrode was discharged to –0.3 V (*i.e.*, at the fully discharged state) in the first cycle and charged to 1.0 V (*i.e.*, at the fully charged state) in the second cycle. Electrochemical impedance spectroscopy (EIS) measurements were performed under open-circuit potential vs. Ag/AgCl reference electrode over the frequency range of 100 kHz to 50 mHz.

The specific capacitance (C<sub>s</sub>) of an electrode can be calculated using the following equation:

$$C_s = \frac{I \times t}{m \times \Delta V} \quad (1)$$

where I is the constant discharge current, t is the discharge time, m is the mass of the electrode materials, and ΔV is the discharging potential range.

## 3. Results and discussion

### 3.1. Growth mechanism of Mn<sub>3</sub>O<sub>4</sub> nanoparticles on graphene flakes

Mn<sub>3</sub>O<sub>4</sub> nanoparticles were synthesized on graphene flakes via a hydrothermal method. Graphene flakes were directly prepared from graphite in the absence of strong acids and toxic reducing agents. The SDS-functionalized graphene flakes were obtained through ultrasonication and mixing of graphite with SDS. We ensured from the previous study that the prepared graphene flakes featured multiple crumples and scrolls [22].

The addition of manganese chloride to the solution containing the graphene flakes resulted in selective adsorption of manganese ions onto the graphene flakes because of the electrostatic interactions between the anionic surfactants and manganese ions.

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