



## Letter

## ARTICLE INFO

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## ABSTRACT

In this study, a novel high-performance electrode material based on MnO<sub>2</sub> nanoparticles coated onto recently discovered 2-D graphene nanoplatelets was fabricated by a hydrothermal method be used as composite for supercapacitor electrode. The maximum capacitance and energy density obtained for this nanocomposite were 542 F/g and 75.3 Wh/kg at a scan rate of 0.01 V/s in 2 M KCl. These impressive results were attributed to a synergistic effect between GNPs and MnO<sub>2</sub> which combine the remarkable electrical conductivity of GNPs with the high pseudocapacitance of the MnO<sub>2</sub> nanoparticles.

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## Graphene nanoplatelets supported MnO<sub>2</sub> nanoparticles for electrochemical supercapacitor

### 1. Introduction

Supercapacitors have attracted growing interest as an intermediate system between batteries and other power sources. From the first application as a low power, low energy, and long life back-up for VCRs to a more recent usage in emergency doors on the Airbus A380, supercapacitors have undergone substantial advances thanks to developments in material science [1,2]. On the basis of their energy storage mechanism, supercapacitor can be categorized as either electrochemical double-layer capacitors (EDLCs) or pseudo-capacitor.

EDLCs are presently the most common supercapacitors sharing a similar principle with a dielectric capacitor. The capacitance of EDLCs stems from the electrostatic charges accumulated from the electrode/electrolyte interface. Carbon and its allotropes are the most commonly used electrode materials for EDLCs due to their high surface area to weight ratio, long cycle life, excellent electrochemical stability and high electrical conductivity [3]. Activated carbon represents the foremost carbon material used in commercial devices due to its low cost and precursor availability; however research developments are heavily focused on designing new electrode materials through the employment of carbon nanotubes (CNTs), mesoporous or hierarchical templated carbons to achieve better performance than activated carbon. Graphene nanoplatelets (GNPs), an allotrope of carbon, were discovered only recently for possessing a unique morphology of single layer 2-dimensional (2D) carbon atoms with a high surface area. GNP distinguishes itself among other competitive carbon materials for exhibiting high electrical and thermal conductivity, mechanical strength and good chemical stability. This material has outperformed CNTs as an energy storage device with a high specific capacitance of (~100–200 F/g), energy density of 28.5 Wh/kg and power density of 10 kW kg<sup>-1</sup> in aqueous electrolyte [4–10]. With resilience comparable to CNTs, GNPs also provides a suitable substrate for the addition of pseudo-capacitive materials to enhance the energy charge capability.

Pseudocapacitor devices are manufactured from materials that undergo Faradaic oxidation/reduction reaction(s) at specific poten-

tials during charging and discharging due to thermodynamics reasons. The significance of pseudocapacitive materials is largely recognized by an enhanced capacitance relative to EDLC (10–100 times the capacitance), owing to the electron transfer reactions that occur during charging that contrast the electrostatic process defined by a process where no Faradaic reactions take place. As an excellent pseudo-capacitive material, MnO<sub>2</sub> has shown to be environmentally friendly, cost-effective and functional in neutral aqueous electrolytes. Unfortunately, the maximum achievable specific capacitance of MnO<sub>2</sub> is much smaller than the theoretical value (1100 F/g) resulting from limited charge transfer kinetics due to poor electronic conductivity and poor electrolyte ion penetration [11–14].

Here, we report a facile process to synthesis MnO<sub>2</sub> nanoparticles coated GNPs nanocomposite aiming to incorporate both the EDLC and pseudo-capacitance to attain a high capacitance as well as high electrochemical stability. Although a report of graphene oxide (GO) supported by needle-like MnO<sub>2</sub> nanocrystals for supercapacitor electrode was recently made, the capacitance attained was relatively low (~200 F/g) [15], which we believe is due to the low electrical conductivity of GO and inefficiency of the GO supported needle-like MnO<sub>2</sub> structure. We have also noticed that another report of graphene–MnO<sub>2</sub> composites had been published for supercapacitor electrode application after we submitted the first draft of the paper [16]. Although the concept and structure produced are similar, the synthesis method and procedure are totally different. The graphene synthesized by this *Carbon* paper used hydrazine as reducing agent, while we used sodium borohydride to maintain more functionality groups on the graphene to load MnO<sub>2</sub> nanoparticles. MnO<sub>2</sub> nanoparticles were produced by microwave irradiation in this paper and we used hydrothermal method. As a result, the MnO<sub>2</sub> nanoparticles we produced are smaller in size 4–5 nm with narrow distribution and uniformly distributed on the graphene surface. The cyclic voltammetry clearly shows the combination of EDLC behavior from graphene and pseudocapacitance from MnO<sub>2</sub> (redox-peak), while the cyclic voltammetry from the *Carbon* paper only showed rectangular box which is usually concerned as EDLC behavior with negligible pseudocapacitance from MnO<sub>2</sub>. Thus, the structure obtained here is a homogeneously distributed MnO<sub>2</sub> nanoparticle coating onto the surface of GNPs, offering a fast ion transportation pathway and a low resistance for

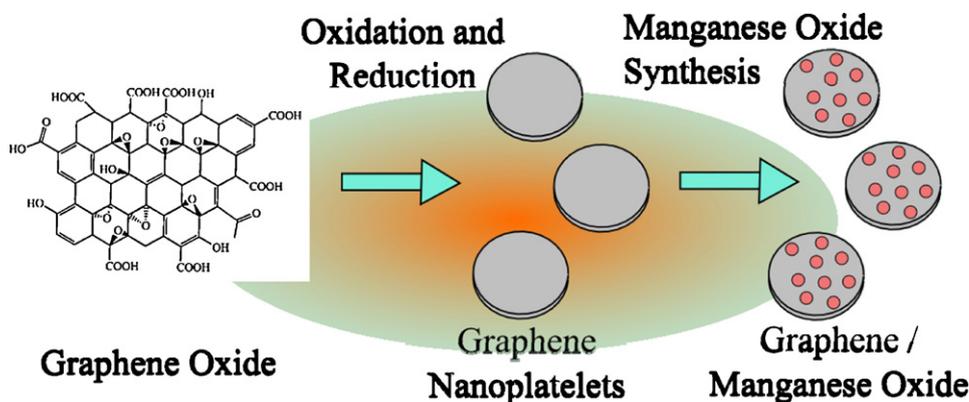


Fig. 1. Schematic illustration of the growth of the GNP supported  $\text{MnO}_2$  Nanoparticles.

charge and electrolyte diffusion, thus yielding a high capacitance of 542 F/g in 2 M KCl electrolyte at 0.01 V/s.

## 2. Experimental

### 2.1. Preparation of GNPs

GO was synthesized by Hummers' method [17]. The reduction of GO to obtain GNPs was followed by our previous publication [10]. The prepared GO was redispersed in water to yield a brownish suspension, which was centrifuged to completely remove residual salts and acids. To obtain graphene, 40 mg of GO was sonicated in 400 mL water until well dispersed and the pH was then adjusted to 9–10 using 3–5 mL of 5 wt%  $\text{Na}_2\text{CO}_3$ . 3 g of  $\text{NaBH}_4$  was dissolved in 50 mL water and added to the mixture, which was subsequently stirred at 80 °C for 36 h. The reduction process was repeated for another cycle to remove residual oxygen groups.

### 2.2. Preparation of GNP supported $\text{MnO}_2$ nanoparticles

For the synthesis of  $\text{MnO}_2$  coated GNPs, the procedure was demonstrated here: 29 mg of GNPs and 20 mL of  $\text{KMnO}_4$  (0.05 M) were added into 100 mL of DI water followed by a 15 min sonication. At room temperature, with vigorous stirring, 20 mL of 0.05 M citric acid was added drop-wise until the purple tint faded. Followed by refluxing for 7 h at 80 °C [18], the product designated as GMO, was filtered and dried in a vacuum oven at 80 °C for 12 h. The schematic illustration of the growth of the GMO is shown in Fig. 1, where we believe that the leftover  $-\text{COOH}$  and  $-\text{OH}$  groups on the GNP surfaces attract the  $\text{Mn}^{4+}$ , facilitate the nuclei growth and form  $\text{MnO}_2$  nanoparticles. The detailed growth mechanism is under investigation.

### 2.3. Preparation of electrodes

The glassy carbon (5 mm in diameter) electrodes were polished subsequently with 1.0, 0.3 and 0.05  $\mu\text{m}$  alumina slurry, and then sonicated in water for several times. An ink was prepared by dispersing 4 mg of GMO (or GNPs) into 2 mL of ethanol followed by sonication. 20  $\mu\text{L}$  of the ink was deposited at increments of 5  $\mu\text{L}$  onto the glassy carbon electrode. This enabled a 40  $\mu\text{g}$  loading of the active material onto the electrode. Then they were dried in air before use.

### 2.4. Instruments and measurements

High-resolution TEM was performed with a FEI-Philips CM300 microscope. The SEM was measured using LEO1530 FE-SEM

equipped with EDAX Pegasus 1200 integrated EDX/OIM. X-ray diffraction (XRD) data was obtained by using Inel XRG 3000 with  $\text{CuK}\alpha$  radiation. The electrochemical properties and capacitance measurements were measured by cyclic voltammetry (CV), chronopotentiometry (also called charge/discharge (CD)) and electrochemical impedance spectroscopy (EIS). All measurements were conducted using a three-electrode system in 2 M KCl solution with a Chi Instruments CHI7600D. The CV was conducted at various scan rates with the potential ranging between 0 and 1 V. CD was carried out with a constant charge density of 1 A/g. The EIS was measured with a sinusoidal signal at rate of 0.01 V over the frequency of  $10^6 \text{ Hz} - 0.01 \text{ Hz}$ .

## 3. Results and discussion

Fig. 2 shows the XRD patterns of starting graphite, GNPs and the GMO composite. For graphite, a peak at  $2\theta \approx 26^\circ$  (002) is very sharp corresponding to its high crystallinity. Following the conversion of graphite to GNP, the (002) peak shows a much broader and weaker characteristic diffraction feature, owing to a loss of graphitic crystallinity. XRD data clearly confirms the transition from millions of graphitic layers of natural graphite to a few graphitic layers graphene. The GMO composite shows a very weak (002) feature of GNPs, and a mixture of birnessite-type (JCPDS 42-1317) and amorphous  $\text{MnO}_2$  [19]. The weakness of the graphite peak indicates that the surfaces of graphene are fully covered by nanoscale  $\text{MnO}_2$ . The two broad peaks around  $37^\circ$  and  $66^\circ$  can be indexed to the (110) and (020) of birnessite-type  $\text{MnO}_2$ , respectively. It

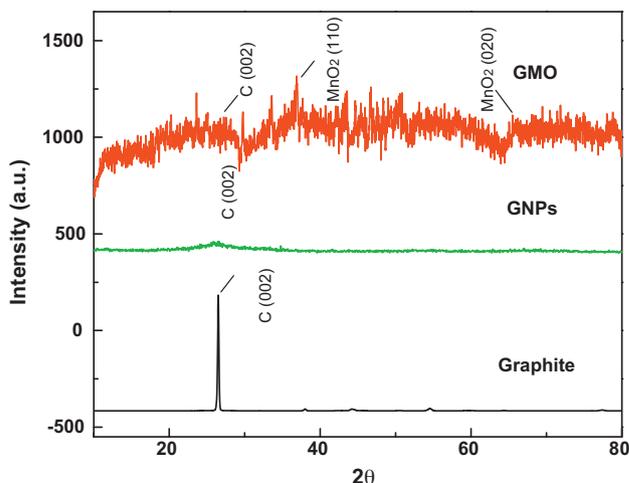


Fig. 2. XRD images of starting graphite, GNPs and GMO composite.

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