



# Anchoring High-dispersed MnO<sub>2</sub> Nanowires on Nitrogen Doped Graphene as Electrode Materials for Supercapacitors



Jun Mei, Long Zhang\*

Jilin Provincial Engineering Laboratory for the Complex Utilization of Petro-Resources and Biomass, Changchun University of Technology, Changchun, 130012, PR China

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## ABSTRACT

Nanostructured MnO<sub>2</sub>/nitrogen doped graphene (MnO<sub>2</sub>/N-RGO) hybrids were synthesized by a facile and economic method at low temperature with ammonia pretreatment. Characterizations show nitrogen atoms were embedded into graphene lattice during pretreatment followed by MnO<sub>2</sub> nanowires anchored onto graphene flakes. Compared with MnO<sub>2</sub>/graphene (MnO<sub>2</sub>/RGO) hybrids, the novel hybrids exhibited higher capacitance value and enhanced cyclic stability. At a current density of 2 mA cm<sup>-2</sup>, the capacitance of as-obtained hybrids was up to 275.2 F g<sup>-1</sup> and retained 98.3% of initial capacitances after 1000 cycles. These results illustrate that ammonia pretreatment is effective for nitrogen atom doping and the hybrids are potential as electrode materials for supercapacitors.

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## 1. Introduction

Supercapacitors, with rapid charge/discharge rates and high power density, rank the most popular power storage devices due to their longer cycle life than batteries and fuel cells [1–4]. The electrochemical performances largely depend on electrode materials. Among various electrode materials, the low-cost MnO<sub>2</sub> nanoparticles, together with other desirable advantageous features, such as nature abundance and environmental compatibility, offer particularly exciting opportunities in energy storage devices [5–7]. However, the common perception is that, MnO<sub>2</sub> nanoparticles, as well as other nanostructured manganese oxides, possess low conductivity and high volume change during cyclic life, which seems not ideal for electrode materials [8–9]. In many cases, a method to avoid parts of these drawbacks is to assemble nanostructured MnO<sub>2</sub> with conductive materials, such as carbon, carbon nanotubes (CNT) and graphene [10–13]. Recent exponentially increasing research advancements in the development of electrode materials have been pursued on MnO<sub>2</sub>/graphene hybrids [14–22]. Except for its high conductivity, one other fundamental property to be taken into account for the employment of graphene is its high specific surface area. These characteristics contribute to improve the conductivity and reduce the volume expansion of MnO<sub>2</sub> nanoparticles. Besides, for graphene flakes, which have a

strong tendency to irreversibly aggregate or restack, nanostructure MnO<sub>2</sub> dispersed on the surface of graphene sheets also can weaken the  $\pi$ - $\pi$  stacking interactions. The synergistic effects make electrochemical performances of the hybrids outstanding [23–26].

To further enhance the electrochemical performances, structural modifications of graphene, such as introducing surface functional groups, controlling specific surface area, adjusting pore size distribution, and embedding heterogeneous atoms, are applied for further functionalization, aiming to strengthen binding force between nanoparticles and graphene [27]. The reason is that the inherent structure of graphene, a two-dimensional (2D) atomic crystal with the sp<sup>2</sup>-hybridized carbon atoms arranged in a honeycomb lattice, has an enormous impact on binding force between nanoparticles and graphene, leading to a relatively low cyclic stability. Relying on these technologies, the surface charge distribution is changed and more anchoring sites are created for nanoparticles. Taking complexity and costs into consideration, embedding graphene with heteroatoms, is a promising approach. In terms of dopant atoms, nitrogen, a larger electronegativity than carbon, has been extensively studied to improve electrochemical performances [28,29].

In a recent report, nitrogen doped graphene and ultrathin MnO<sub>2</sub> sheet composites were synthesized by one-step hydrothermal method at 120 °C [30]. However, this *in situ* reduction with concomitant nitrogen atoms doping is uncontrollable. There are few reports on the controllable synthesis of weakly crystallized MnO<sub>2</sub> nanoparticles and nitrogen doped graphene hybrids. Weakly crystallized MnO<sub>2</sub> nanoparticles possess a high specific surface

\* Corresponding author. Tel.: +86 431 8571 7216; Fax: +86 431 8571 6328.  
E-mail address: [zhanglongzhl@163.com](mailto:zhanglongzhl@163.com) (L. Zhang).

area, favorable for ionic diffusion. One of the problems lies in that different reaction conditions are needed for growth of such type of  $\text{MnO}_2$  nanoparticles on the graphene surface and insertion of nitrogen atoms into graphene skeletons. Generally speaking, a high temperature is favorable for nitrogen atoms doping and the crystallinity of  $\text{MnO}_2$  nanoparticles increasing [31–33]. Therefore, finding a facile routine and choosing a suitable temperature for controllable synthesis of  $\text{MnO}_2$  nanoparticles and nitrogen doped graphene hybrids is significance.

In this paper, a kind of nanostructured  $\text{MnO}_2$ /nitrogen doped graphene hybrids ( $\text{MnO}_2$ /N-RGO) was obtained by a facile and economic method with ammonia pretreatment. Compared with  $\text{MnO}_2$ /graphene hybrids ( $\text{MnO}_2$ /RGO) without ammonia pretreatment, the novel hybrids show enhanced electrochemical performances. This controllable method is convenient for scalable application and provides an example for synthesis of other metal oxides nanoparticles and nitrogen doped graphene hybrids.

## 2. Experimental

### 2.1. Materials and Reagents

Natural graphite (500 meshes, >99%) was purchased from Shanghai Yifan Graphite Ltd. China. Concentrated sulfuric acid ( $\text{H}_2\text{SO}_4$ , 98%), ammonia ( $\text{NH}_3 \cdot \text{H}_2\text{O}$ , 28 wt%), hydrochloric acid (HCl, 37.5%), potassium permanganate ( $\text{KMnO}_4$ ), peroxide ( $\text{H}_2\text{O}_2$ , 30 wt%), potassium nitrate ( $\text{KNO}_3$ ), urea ( $\text{CO}(\text{NH}_2)_2$ ) and ethanol were purchased from Sinopharm Chemical Reagent Co., Ltd. China. All chemicals are of analytical grade, which are used without any further purification. Water used was distilled and purified by a Milli-Q system.

### 2.2. Preparation of GO powder

For preparation of GO powder, a modified Hummers method with ultrasound assisted was used [34,35]. Briefly, graphite (1.00 g) and  $\text{KNO}_3$  (1.20 g) were added into  $\text{H}_2\text{SO}_4$  (46 mL) and stirred in ice bath for 10 minutes. Then,  $\text{KMnO}_4$  (6.00 g) was slowly added and the reaction was carried on for 6 hours at 35 °C. Followed by adding water (80 mL), the reaction was maintained at 80 °C for another 30 minutes. Then,  $\text{H}_2\text{O}_2$  (6 mL) was added and the solution was washed by diluted hydrochloric acid ( $1 \text{ mol L}^{-1}$ ) and water repeatedly. After dried at 60 °C overnight, the brown powder were dispersed in DI water by ultrasonic vibration (280 W) for 90 minutes to form a homogeneous brown suspension at a concentration of  $1.0 \text{ mg mL}^{-1}$ . The GO powder was obtained by freeze-dried for 5 hours.

### 2.3. Synthesis of nanostructured $\text{MnO}_2$ /N-RGO Hybrids

In a typical synthesis routine, the as-prepared GO powder (0.05 g) was re-dispersed into  $\text{NH}_3 \cdot \text{H}_2\text{O}$  (50 mL, 1 wt%) by an ultrasonic vibration for 10 minutes and stirred at 90 °C for 6 hours. After cooling to room temperature,  $\text{KMnO}_4$  (0.32 g) and  $\text{CO}(\text{NH}_2)_2$  (1.00 g) were added successively and stirred for another 10 minutes. Subsequently, the mixture was transferred into a Teflon-lined autoclave (80 mL) and then maintained at 90 °C for 24 hours. The cooling mixture was filtered, washed with water and ethanol for three times, respectively. Finally, the solid, labeled as  $\text{MnO}_2$ /N-RGO, was collected after vacuum-dried at 40 °C overnight.

### 2.4. Synthesis of nanostructured $\text{MnO}_2$ and $\text{MnO}_2$ /RGO Hybrids

For comparison,  $\text{MnO}_2$  and  $\text{MnO}_2$ /RGO hybrids were synthesized under the same conditions without GO and ammonia pretreatment process, respectively.

### 2.5. Characterization

X-ray diffraction (XRD) patterns were recorded on a Rigaku D/max-2500 diffractometer using  $\text{Cu K}\alpha$  radiation ( $\lambda = 0.1542 \text{ nm}$ ) at 40 kV and a cathode current of 30 mA with a scanning speed of  $2^\circ \text{ min}^{-1}$  from 5 to 80°. Thermogravimetric analysis (TGA) was conducted on a SDT-Q600 analyzer under air atmosphere at a temperature range between 30 and 800 °C with a heating rate of  $10^\circ \text{ C min}^{-1}$ . X-ray photoelectron spectroscopy (XPS) was analyzed on Thermo Escalab 250 with a monochromatic  $\text{AlK}\alpha$  source. All the binding energies of samples were referenced to the C 1s peak at 284.8 eV. Morphologies of the sample were characterized by transmission electron microscopy (TEM, Tecnai G2 F20, FEI). The vario EL cube (Elementar, Germany) was used to measure the nitrogen content in the  $\text{MnO}_2$ /N-RGO Hybrids. Specific surface area measurements were performed by nitrogen adsorption at 77 K with a Micrometric ASAP 2020 physisorption analyzer according to the Brunauer-Emmett-Teller (BET) method.

### 2.6. Electrochemical investigation

Electrochemical measurements were performed in a three-electrode cell system (CHI 660E electrochemical workstation, Chenhua, China) at room temperature with 1 M  $\text{Na}_2\text{SO}_4$  aqueous as electrolyte. A platinum rod and a saturated calomel electrode (SCE) were used as counter and reference electrode, respectively. The working electrodes were fabricated in the following steps. The as-synthesized materials, acetylene black, and PTFE were mixed in a mass ratio of 85:10:5 in ethanol and then the slurry

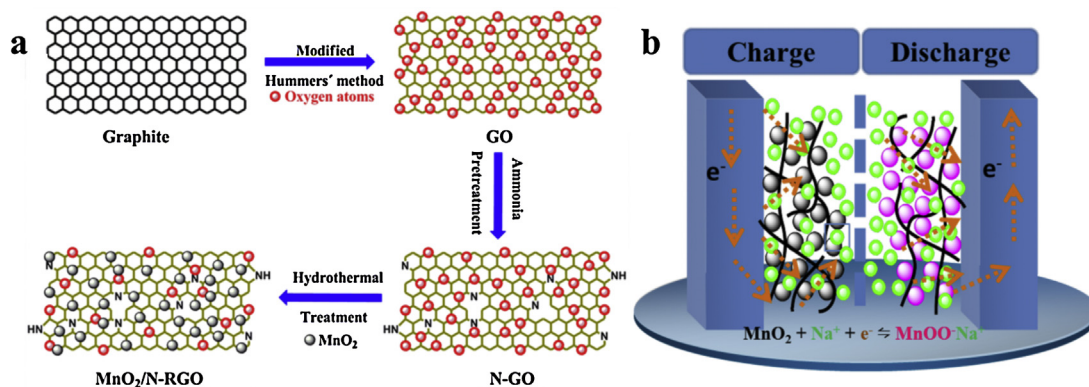


Fig. 1. Schematic illustrations of (a) the preparation process and (b) charge/discharge mechanism of nanostructured  $\text{MnO}_2$ /N-RGO hybrids.

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