



# Synthesis of a novel magnetite/nitrogen-doped reduced graphene oxide nanocomposite as high performance supercapacitor



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## ARTICLE INFO

### Article history:

Received 16 April 2016

Received in revised form 22 July 2016

Accepted 24 August 2016

Available online 25 August 2016

### Keywords:

Supercapacitor

Fe<sub>3</sub>O<sub>4</sub> nanostructures

N-doped graphene

Nanocomposite materials

Electrochemical properties

## ABSTRACT

In this research, magnetite/nitrogen-doped reduced graphene oxide (Fe<sub>3</sub>O<sub>4</sub>/NRGO) nanocomposites were synthesized through sonochemical route. The morphology and structure of the synthesized samples were characterized by X-ray diffraction (XRD), X-ray photoemission spectroscopy (XPS), Brunauer–Emmett–Teller (BET) method, field emission scanning electron microscopy (FE-SEM), and Raman spectroscopy. The synthesized nanocomposites display amorphous morphologies, with micro-mesoporous Fe<sub>3</sub>O<sub>4</sub> particles that are uniformly distributed on the NRGO sheets. The electrochemical performance of nanocomposite-based electrodes were evaluated by cyclic voltammetry (CV), galvanostatic charge/discharge, electrochemical impedance spectroscopy (EIS) and continues cyclic voltammetry (CCV). The prepared nanocomposite-based electrodes showed superior supercapacitive performance including good rate capability, high specific capacitance, and excellent cyclic performance. The Fe<sub>3</sub>O<sub>4</sub>/NRGO nanocomposite electrodes exhibited specific capacitance of 355 F g<sup>-1</sup> at scan rate of 2 mV s<sup>-1</sup> in 0.5 M Na<sub>2</sub>SO<sub>4</sub> electrolyte, indicating considerable improvement in supercapacitive performance compared with pristine Fe<sub>3</sub>O<sub>4</sub> and magnetite/reduced graphene oxide (Fe<sub>3</sub>O<sub>4</sub>/RGO) electrodes. Moreover, in CCV measurements, excellent capacitance retention (97.1%) was also observed for Fe<sub>3</sub>O<sub>4</sub>/NRGO nanocomposite during 4000 continuous potential cycling. Therefore, the prepared nanocomposite has great potential as an electrode materials for supercapacitors.

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## 1. Introduction

Supercapacitors (SCs) are considered as one of the most important energy storage devices for numerous applications such as portable electronic devices, electric vehicles, and sustainable energy generation devices. SCs fill the gap between batteries and conventional capacitors in terms of their specific energy and specific power [1]. Based on their energy storage mechanism, SCs are classified into two major categories of pseudocapacitors and electrical double-layer capacitors (EDLCs). In pseudocapacitors the electrodes are made of electroactive materials like transition metal oxides, as well as conducting polymers. However, in construction of EDLCs, carbon based materials such as activated carbon, carbon nanotube, and graphene are mainly used [2].

Recently, transition metal oxide nanoparticles, have gotten attention to be used in SCs. Among them Co<sub>3</sub>O<sub>4</sub>, MnO<sub>2</sub>, and Fe<sub>3</sub>O<sub>4</sub> have been

thoroughly investigated in construction of SCs, due to their abundance, low cost, non-toxic nature, and high theoretical specific capacitance [3–4]. Nevertheless, their high relative electrical resistance and poor electrochemical reversibility have hindered their wide application in commercial SCs [5–6]. In order to improve the conductivity of transition metal oxides, considerable research efforts have been placed on synthesizing their composite with conductive fillers such as graphite, carbon black, carbon nanotube, and graphene. [7–8]. Among carbon materials, graphene is promising candidate owing to its extraordinary electrical conductivity, large theoretically surface area (2630 m<sup>2</sup> g<sup>-1</sup>), great chemical stability, light weight, and high mechanical flexibility [9–10]. Another interesting development in this area is application of RGO decorated with different proportion of nanomaterials for production of novel hybrid materials with different and various properties, which can be altered through changing the extent of loading, as well as the nature of the loaded material [11–12]. The combination of RGOs with metal oxide nanoparticles in this area has been found to prevent the loss of surface area of RGOs due to the restacking of the RGO sheets. This combination making the RGO surface more accessible, through acting as spacers among the RGO sheets [13–14]. Furthermore, in this case the pores between graphene layers significantly reduces the internal

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resistance and facilitates the diffusion of electrolyte into the electrode [15].

In this study, we demonstrate a facile and green method for synthesis of  $\text{Fe}_3\text{O}_4/\text{NRGO}$  nanocomposite materials under mild sonochemical conditions. The synthesized nanocomposites were characterized by XRD, XPS, BET, FESEM and Raman spectroscopy. Also, supercapacitive properties of the RGO, NRGO,  $\text{Fe}_3\text{O}_4$ ,  $\text{Fe}_3\text{O}_4/\text{RGO}$ , and  $\text{Fe}_3\text{O}_4/\text{NRGO}$  nanocomposite were examined by cyclic voltammetry (CV), FFT Continuous cyclic voltammetry (CCV), galvanostatic charge/discharge, and electrochemical impedance spectroscopy (EIS). Electrochemical characterizations prove that nanocomposite-based electrodes show enhanced supercapacitive performance compared to that of pristine graphene and pure  $\text{Fe}_3\text{O}_4$ .

## 2. Experimental

### 2.1. Reagents and apparatus

Graphite flakes, acetylene black, polytetrafluoroethylene (PTFE),  $\text{H}_3\text{PO}_4$ ,  $\text{KMnO}_4$ ,  $\text{Na}_2\text{SO}_4$ ,  $\text{N}_2\text{H}_4$ , and  $\text{NH}_4\text{OH}$  were purchased from Sigma-Aldrich Co.  $\text{FeSO}_4$ ,  $\text{H}_2\text{SO}_4$ ,  $\text{HCl}$ , and  $\text{H}_2\text{O}_2$  were all purchased from Merck Chemical Co. All reagents were used without any further modification.

The crystallinity of nanocomposite samples were characterized by X-ray diffraction (XRD) technique on a Philips PW-1730 X-ray diffractometer using  $\text{CuK}\alpha$  radiation ( $\lambda = 1.5405 \text{ \AA}$ ). Also, Field-emission scanning electron microscopy (FE-SEM) on a Zeiss SIGMA VP with gold coating was used for characterizing size and morphology of products. Raman spectra was recorded at ambient temperature on a Raman spectrometer (SENTERRA 2009, BRUKER) using 785 nm laser excitation. X-ray photoelectron spectroscopy (XPS) measurement was performed on a Perkin Elmer PHI 6000C ECSA system with monochromatic Al KR (1486.6 eV) irradiation. The specific surface area was calculated from the Brunauer-Emmett-Teller (BET) plot of the nitrogen adsorption isotherm. X-ray photoelectron spectroscopy (XPS) measurement was performed on a Perkin Elmer PHI 6000C ECSA system with monochromatic Al KR (1486.6 eV) irradiation.

### 2.2. Graphene oxide preparation

Graphene oxide (GO) was prepared from graphite flake powder based on the Tour's method [16]. In summary, 18 g of  $\text{KMnO}_4$  was added gradually to the mixture containing 400 mL of concentrated  $\text{H}_2\text{SO}_4/\text{H}_3\text{PO}_4$  with a volume ratio of 9:1 and 3.0 g of graphite flake powder. This mixture was stirred for 12 h at 50 °C. The color of the mixture turned to bright yellow with pouring it onto the ice and  $\text{H}_2\text{O}_2$ . The

product was centrifuged and washed several times with 5% HCl solution and distilled water. The final neutralized product was dried in an oven at 50 °C. At the final step, a brown suspension of GO was prepared by sonicating the graphite oxide in distilled water by using an ultrasonic probe.

### 2.3. Preparation of RGO and NRGO

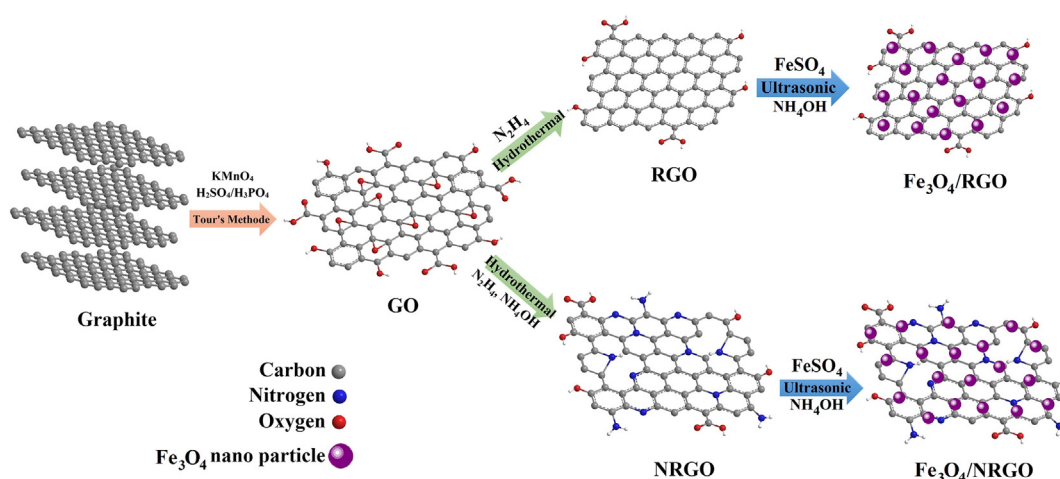
NRGO was prepared by the hydrothermal method [17]. 50 mg of GO was dispersed in 100 mL of distilled water and sonicated for 4 h, and then,  $\text{NH}_4\text{OH}$  was added to the suspension to achieve a pH of 11. After that, 100 mL of 50%  $\text{N}_2\text{H}_4$  was added into the GO suspension and immediately suspension solution was then transferred into a Teflon-lined stainless steel autoclave and heated at 120 °C for 24 h. After that, it was centrifuged at 5000 rpm, washed with distilled water and ethanol several times. Finally, the products were filtered and dried to obtain N-doped graphene.

For preparation of RGO, 100 mL of 50%  $\text{N}_2\text{H}_4$  was added into the GO suspension, and it was stirred and refluxed in a silicon oil bath at 100 °C for 12 h. Finally, the synthesized RGO was washed with distilled water and ethanol several times and dried [18].

### 2.4. Preparation of the $\text{Fe}_3\text{O}_4/\text{RGO}$ and $\text{Fe}_3\text{O}_4/\text{NRGO}$ nanocomposite

The  $\text{Fe}_3\text{O}_4/\text{RGO}$  and  $\text{Fe}_3\text{O}_4/\text{NRGO}$  nanocomposites were prepared through a facile sonochemical method. 100 mg RGO and 100 mg NRGO were added separately, to the aqueous solutions of 0.025 M Iron (II) sulfate heptahydrate with the total volume of 50 mL. The mixtures were irradiated with high-intensity ultrasound radiation with  $480 \text{ W cm}^{-2}$  input power and working frequency of 24 kHz. A titanium horn transducer system (UP 200H, Dr. Hielscher GmbH) with a 2 mm microtip was employed. The titanium horn was inserted to a depth of 2 cm into the solution. After 30 min sonication, ammonia was added slowly over 15 min to the resulting suspension to anchor nanoparticles on the surface of RGO and NRGO sheets. After washing the black precipitate, it was dried at 80 °C for 24 h designated as  $\text{Fe}_3\text{O}_4/\text{RGO}$  and  $\text{Fe}_3\text{O}_4/\text{NRGO}$ . We prepared the pure  $\text{Fe}_3\text{O}_4$  via a same procedure.

There are two reported methods for synthesis of graphene-based nanoparticles. In the first method, a precursor salts are adsorbed on the RGO or GO sheets and direct growth of nanoparticles on the sheet surface (in situ growth). Whereas, in the second method, prior synthesis of nanocomposite, and then anchoring them on the surface of RGO and GO (self-assembly approach) [19]. Hence, for better controlling the distribution and loading amount of the  $\text{Fe}_3\text{O}_4$  nanoparticles on the NRGO, the in situ growth was chosen. Scheme 1 presents the diagram of the synthesis process. The process employs no surface



Scheme 1. Schematic illustration for the synthesis of the  $\text{Fe}_3\text{O}_4/\text{RGO}$  and  $\text{Fe}_3\text{O}_4/\text{NRGO}$  nanocomposites.

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