



# In situ immobilized, magnetite nanoplatelets over holey graphene nanoribbons for high performance solid state supercapacitor



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## ARTICLE INFO

### Article history:

Received 22 November 2016  
Received in revised form 9 December 2016  
Accepted 9 December 2016  
Available online 10 December 2016

### Keywords:

magnetite  
hexagonal platelets  
graphene nanoribbons  
solid-state supercapacitors

## ABSTRACT

Among major phases of iron oxide, magnetite ( $\text{Fe}_3\text{O}_4$ ) is potential candidate for pseudocapacitors. Yet, the clustering of magnetite nanoparticles confines them from being exploited as charge storage material. Herein, magnetite hexagonal nanoplatelets are synthesized on holey graphene nanoribbons (GNRs) by hydrothermal route and tested for charge storage performance in solid-state supercapacitor incorporating gel electrolyte (PVA- $\text{H}_2\text{SO}_4$ ). GNR besides providing large surface for adsorption of magnetite platelets also improved the charge collection ability of nanocomposite through interconnected nanoribbon network. Mass loading over GNR is optimized to a maximum of 30 wt. (%) by ensuring mono dispersion of magnetite nanoplatelets and high conductivity ( $14.0 \text{ S m}^{-1}$ ) of nanocomposite. Above 50 wt. (%) magnetite loading, structural identity of nanoribbon is tempered and as a consequence increased network resistivity depletion in charge storage capacity is observed. Mass loading of magnetite over nanoribbon showed an inverse relationship with ion diffusion and electronic conduction. Balanced ionic and electronic conduction in 30 wt. (%) magnetite loaded nanoribbon results in a supercapacitor cell delivering  $1241.5 \text{ W kg}^{-1}$  while maintaining  $26.9 \text{ Wh kg}^{-1}$  energy density. About 95% capacitance retention over 3000 charge discharge cycles at  $2.3 \text{ A g}^{-1}$  demonstrate magnetite as a high performance supercapacitor electrode.

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## 1. INTRODUCTION

Supercapacitors (SCs) belong to an important class of energy storage devices those are capable of delivering high power while maintaining high energy density [1–3]. The charge discharge characteristics and cycling efficiency place them at a very important position between batteries and conventional capacitors [4–7]. Performance of SCs rely much on the electrode material and therefore these devices are classified on the basis of charge storage mechanism as pseudocapacitors and electrical double layer capacitors. Pseudocapacitive materials, basically transitional metal oxides like NiO [8,9],  $\text{SnO}_2$  [10],  $\text{Co}_3\text{O}_4$  [11],  $\text{RuO}_2$  [12] and  $\text{MnO}_2$  [13,14] and conducting polymers such as polypyrrole [14,15] and polyaniline [16] have been extensively investigated as high specific capacitance materials. On the other hand, magnetite ( $\text{Fe}_3\text{O}_4$ ), holding different valence states (+2, +3) is an excellent pseudocapacitive material owing to its easy redox transitions [17,18],

natural abundance, low cost and environmental compatibility [19–22]. Nevertheless, its ability to store and deliver charge restricted by the clustering of particles, significantly improves upon application of carbon support [23,24].

Among various carbon materials, graphene nanoribbons (GNRs) are quasi one dimensional structures with confined electronic movement [25–27]. Recently, GNRs have attracted a remarkable interest in energy storage devices. GNRs have been synthesized by our research group through chemical unzipping of the multi walled carbon nanotubes (MWCNTs). Prolonged treatment of MWCNTs with oxidizing agents infused holes in nanoribbon and subsequently defect/edge density is increased [28]. Apart from the electronic conduction, high density of edge planes in GNR enhances ion adsorption and increases charge storage capacity through pseudocapacitive functionalities [29] and edge induced double layer effects [30]. Holey structure of GNR besides increasing the edge plane density also enhances the effective material utilization through hole generated porous channel [31].

Previous studies focused mainly on supercapacitors based on liquid electrolytes. However, their limited applications to portable electronic devices laid a setback [32]. While on the other hand

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small size, low weight, excellent reliability, mechanical integrity [33–35] ease of handling and simplified configuration of solid-state supercapacitors conquered the shortcomings [36,37]. Their functioning as smart portable electronics demands much more attention towards size/weight miniaturization, high energy and power delivery with long cycling life.

Present article describes a simplistic approach to in-situ immobilize magnetite hexagonal platelets evenly on holey graphene nanoribbons (GNR). Our results indicate optimum range of magnetite loading from 30–50 wt. (%) for high performance  $\text{Fe}_3\text{O}_4/\text{GNR}$  supercapacitor. As a function of magnetite loading, resistivity shows increasing trend while the diffusivity of electrolytic ions and resulting specific capacitance of  $\text{Fe}_3\text{O}_4/\text{GNR}$  composite show an inverse relationship. Balanced electronic and ionic conductivity in 30 wt. (%)  $\text{Fe}_3\text{O}_4/\text{GNR}$  nanocomposite results in excellent capacity retention (95%) over 3000 GCD cycles at high charging current density ( $2.3 \text{ A g}^{-1}$ ). This work for the first time reports the synthesis of magnetite nanoplatelets over holey graphene nanoribbons for solid state supercapacitor cell that outperforms with a high energy density of  $26.9 \text{ Wh kg}^{-1}$  and power density of  $1241.5 \text{ W kg}^{-1}$  at  $1.0 \text{ A g}^{-1}$ .

## 2. EXPERIMENTAL

### 2.1. Materials

Ferrous sulphate heptahydrate ( $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ ), ferric chloride ( $\text{FeCl}_3$ ), ammonium hydroxide ( $\text{NH}_4\text{OH}$ , 25%), hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) were purchased from Merck and MWCNT was purchased from Shenzhen Nanotech Port, Co. Ltd. All reagents were of analytical grade and used as received.

### 2.2. Synthesis of Magnetite Nanoplatelets

Magnetite nanoplatelets were synthesized by two-step process as reported in earlier articles [38]. Aqueous solutions of  $0.20 \text{ M FeSO}_4 \cdot 7\text{H}_2\text{O}$  and  $0.40 \text{ M FeCl}_3$  (20 mL each) were mixed together and to this mixture  $1.6 \text{ M NH}_4\text{OH}$  was added under stirring. After mixing, resulting solution (50 mL) was transferred into a Teflon-lined stainless steel autoclave for hydrothermal treatment at  $250^\circ\text{C}$  (8 h). So obtained product was filtered and dried at  $110^\circ\text{C}$  for 12 h.

### 2.3. Synthesis of $\text{Fe}_3\text{O}_4/\text{GNR}$ Nanocomposite

Graphene Oxide nanoribbon (GONR) was synthesized by chemical unzipping of MWCNT using a mixture of oxidizing agents ( $\text{KMnO}_4$ ,  $\text{H}_3\text{PO}_4$  and  $\text{H}_2\text{SO}_4$ ) as reported earlier by Sahu et al.

[28]. In order to prepare homogeneous suspensions, different weights of GONR were ultrasonically mixed in 30 mL water separately using a probe sonicator in the frequency range (20–25 kHz) for 5 min. To these suspensions magnetite precursors ( $0.2 \text{ M FeSO}_4 \cdot 7\text{H}_2\text{O}$  and  $0.4 \text{ M FeCl}_3$ ) were added separately under stirring followed by addition of  $1.6 \text{ M NH}_4\text{OH}$ . Pure GONR suspension was also treated with  $1.6 \text{ M NH}_4\text{OH}$  in absence of magnetite precursors. Above suspensions was transferred to different Teflon-lined stainless steel autoclaves (vol. 50 mL) for hydrothermal treatment (8 h at  $250^\circ\text{C}$ ) as illustrated in Fig. 1. After hydrothermal treatment, the products were filtered using  $0.45 \mu\text{m}$  cellulose nitrate membrane and washed with copious amount of DI water. It was observed that GONR in the  $\text{NH}_4\text{OH}$  media reduced to GNR and the details are discussed in subsequent sections.

The final products containing different  $\text{Fe}_3\text{O}_4/\text{GNR}$  ratios are abbreviated as FeGNR-7, FeGNR-5 and FeGNR-3 for 70 wt. (%) magnetite, 50 wt. (%) magnetite and 30 wt. (%) magnetite respectively.

### 2.4. Characterization

Structural analysis was performed on X-ray diffractometer (XRD) using D8 Discover with  $\text{Cu K}\alpha$  radiation ( $\lambda = 1.541 \text{ \AA}$ ). Morphological features of the composite samples were studied using transmission electron microscope (TEM) from Philips Technai T-300 microscope and scanning electron microscope (SEM) on Zeiss Ultra 55 microscope. Raman spectroscopic analysis was performed with the help of Renishaw Invia Reflex Micro-Raman spectrometer. Current voltage (I–V) characteristics were recorded using Keithley 6517 B electrometer.

Cyclic voltammetric (CV) and electrochemical impedance spectroscopic (EIS) responses were recorded using CHI 604 D workstation. Impedance tests were conducted in  $10 \text{ mHz}–100 \text{ kHz}$  range. Galvanostatic Charge Discharge (GCD) was performed at various current densities using PARSTAT 4000 electrochemical station (Princeton applied research Co., Ltd, USA).

### 2.5. Fabrication of Solid-State Supercapacitor Cell

5 mg of each material (FeGNRs, GNR and  $\text{Fe}_3\text{O}_4$ ) was separately dispersed in isopropyl alcohol with  $5 \mu\text{L}$  nafion binder using a probe sonicator. Obtained suspensions were spray deposited over  $1 \text{ cm}^2$  area of polished graphite plates and dried overnight in vacuum at  $100^\circ\text{C}$ . Loading of the active materials ( $\text{Fe}_3\text{O}_4$ , FeGNRs and GNR) on graphite sheet was  $0.3–0.5 \text{ mg cm}^{-2}$ . The graphite substrates coated with the above materials were used as electrodes to sandwich PVA- $\text{H}_2\text{SO}_4$  gel electrolyte membrane. Preparation of the PVA- $\text{H}_2\text{SO}_4$  membrane is described elsewhere [39]. To ensure

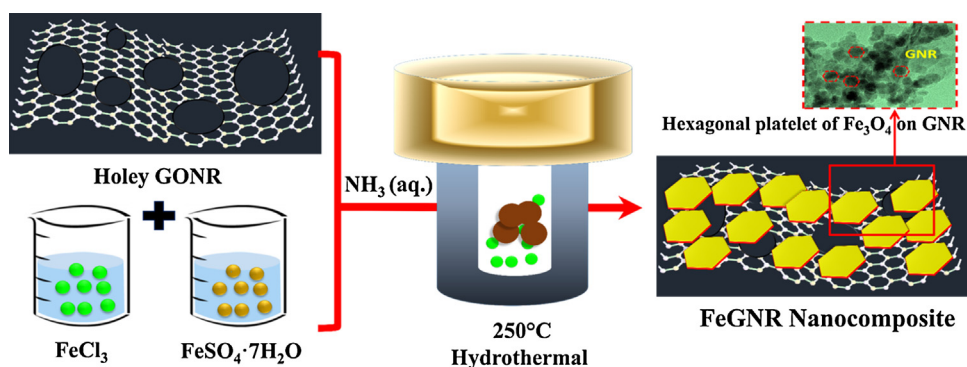


Fig. 1. Schematic for hydrothermal preparation of  $\text{Fe}_3\text{O}_4/\text{GNR}$  nanocomposites.

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