



Short communication

# A facile solution-free etching preparation of porous graphene nanosheets with high performances for lithium storage

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## HIGHLIGHTS

- A novel solution-free method is developed to prepare porous graphene nanosheets.
- Ferrocene is selected as precursor to form  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> nanoparticles as etchant.
- The phase transitions and pore forming process have been systematically studied.
- Porous graphene nanosheets have good rate capability and high reversible capacity.

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## ABSTRACT

Porous graphene nanosheets (PGNs) have attracted tremendous attention and research interest due to their unique porous structure in combination with inherent properties of graphene such as large specific surface area and excellent conductivity. Although several methods have been developed to prepare PGNs, solution-free synthesis of PGNs which could avoid the stacking of graphene nanosheets (GNs) in the solvent system has not been referred. Herein, we report a facile solution-free synthesis of PGNs through the etching of GNs by hematite nanoparticles (NPs) that derived from ferrocene. Microstructure and composition analyses reveal that ferrocene primarily transfers to  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> NPs depositing on GNs at 180 °C and then to  $\gamma$ -phase at 900 °C under Ar atmosphere. During high-temperature treatment, the nano-channels form accompanying the reduction of  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> NPs by consuming the lattice carbon atoms of GNs. The PGNs electrode retains a high reversible specific capacity of 963.4 mA h g<sup>-1</sup> at 100 mA g<sup>-1</sup> after rate tests and 200 activated cycles, and also exhibits good cycling stability and excellent rate performance. PGNs prepared by this solution-free etching method should be a promising high-performance support and conductive agent for LIBs.

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## 1. Introduction

Owing to its ultra-large specific surface area and excellent electronic transport properties, graphene nanosheets (GNs) has been considered to be a promising support and conductive agent for electrochemical devices such as Li-ion batteries (LIBs), supercapacitors, etc. [1–5]. However, there are two problems remained to be overcome. First, GNs aggregate severely due to the  $\pi$ - $\pi$  stacking interaction [6], which affects lithium ion insertion/extraction and limits the permeation of electrolyte. Second, the large open flat layers impart that the cross-plane diffusion of electron and lithium ion is extremely low. The above disadvantages severely influence

the reversible capacity and the rate capability under high discharge/charge current density [7,8].

Porous graphene nanosheets (PGNs) have attracted tremendous attention and research interest due to their unique porous structure in combination with inherent properties of pure graphene [9]. The nano pores on graphene layers could be served as direct channels for lithium ion, which can enhance the rate capability in theory [10,11]. Additionally, these pores may provide more lithium ion binding sites, thus the energy density of the electrode could be increased obviously [12]. Thus, the as-prepared PGNs tested as anode materials exhibited high specific capacity, excellent rate performances, as well as good cycling stability, indicating great application potential in LIBs [12–15]. To date, various means have been exploited to synthesize PGNs, which can be split into two categories: physical and chemical methods. Various physical approaches have been developed, such as surface-assisted coupling

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of designed molecular building blocks [16], steam-etching [17], the focused electron beam of a transmission electron microscope [18], and so on. However, the yield of physical methods mentioned above is relatively low, and high-cost instruments are usually employed. Apart from physical method, a variety of chemical ways are also developed, such as long term ultrasonication of graphene oxide (GO) under harsh acidic condition [19], oxidization of GO by  $\text{H}_2\text{O}_2$  with gold or AgO nanoparticle as catalyst [20,21], and photo-degradation of GO sheets on the top of ZnO nanorods arrays [22]. Apparently, GO is the precursor and a solution system is needed in the current chemical methods. However, the aggregation or restacking of PGNs is inevitably happened in solvent system in these processes, which leads to consequently significant degradation of the unique properties of individual sheets, such as high specific surface area and fast ion transport behaviors of PGNs. Therefore, it is still a great challenge on the development of low-cost, high yield and facile way to prepare high quality PGNs.

Recently, several research groups reported that metal nanoparticles, such as nickel, iron and cobalt, could be used as a 'knife' to cut the graphene sheet with nanoscale precision via catalytic hydrogenation process [23,24]. Besides, Ramasse et al. observed that metal atoms could etch the suspended, single-layer graphene to form nanoscale holes [25]. Although most of the preparations of metal oxide nanoparticles need the solution system, a gaseous route is also possible. For example, it is well known that ferrocene sublimates at a low temperature of 100 °C and pyrolyzes at about 400 °C, indicating its potential as a good gas precursor for iron oxide [26]. By means of the thermal behavior of ferrocene, Balducci's group sublimated it at 200–300 °C and prepared  $\text{Fe}_2\text{O}_3$  nanoparticles by pyrolyzing at 1050 °C [27]. In view of these, herein we propose a solution-free approach for the preparation of PGNs to avoid the puzzles of solvent system. A simple metal oxide etching method using graphite oxide and ferrocene as the starting materials was developed. Specifically,  $\text{Fe}_2\text{O}_3$  nanoparticles derived from ferrocene deposit on the surface of graphene nanosheets and etch carbon atoms to form nanoscale holes in the solution-free system. The whole phase transition and pore-forming process, and electrochemical performance as anode material for LIBs are systematically investigated. It shows a high reversible specific capacity, excellent cyclability and rate capability. In consideration of the high specific surface area (SSA), porous structure and excellent conductivity of PGNs, it could be a promising support of active materials and conductive agent for LIBs.

## 2. Experimental

### 2.1. Synthesis of PGNs

Graphite oxide powder was obtained from Sinocarbon Materials Technology Co. Ltd. G250 was obtained according to method of the Ref. [28] and heated at 250 °C for 1 h. The preparation procedure of PGNs was as follows. In typical, firstly, 0.10 g of the obtained G250 and 0.1 g of ferrocene (AR grade) were placed into a 50 mL Teflon-lined stainless steel autoclave and sealed under Ar atmosphere. After heating autoclave in oven at 180 °C for 5 h, the primary product was further heat-treated at 900 °C for 1 h under Ar atmosphere. Finally, pickling of the product was carried out to removing the iron oxide nanoparticles and then dried in a vacuum oven at 70 °C for 12 h. For a comparison, two blank graphene samples were prepared. One is G900, which was prepared by directly heat-treating G250 at 900 °C for 1 h under Ar atmosphere. The other one is HCl-G900 which was prepared by further acid washing with 0.5 mol/L HCl and drying the sample of G900 at 80 °C for 12 h.

### 2.2. Characterization

The morphology, composition, and structure of the samples were characterized by field-emission scanning electron microscopy (SEM) (JSM-7001F, JEOL), high-resolution transmission electron microscopy (HRTEM; JEM 2010, JEOL, 200 kV), X-ray powder diffraction (XRD; Bruker, D8 Advance, using  $\text{Cu K}\alpha$  radiation),  $\text{N}_2$  adsorption-desorption isotherms (Micromeritics ASAP 2010 M), X-ray photoelectron spectrometer (XPS, Thermo ESCALAB 250XI, Thermo Fisher Scientific, US). Raman measurements were carried out on a Renishaw RM2000 Confocal Raman Spectrometer with an excitation line of 514 nm. Functional group of samples are measured by the Fourier transform infrared spectroscopy (FT-IR, Tensor 27, Bruker) with a wavelength range from 400 to 3000  $\text{cm}^{-1}$ .

### 2.3. Electrochemical measurement

Electrochemical measurements were performed by CR2016-type coin cells, which were assembled in an argon-filled glove box, in which  $\text{H}_2\text{O}$  and  $\text{O}_2$  concentration were kept <1 ppm. To prepare the anodes, the active materials (obtained samples), and polyvinylidene fluoride binder were mixed and dissolved in N-methyl-2-pyrrolidone at the weight ratio of 70:30 to form a well-mixed slurry, and the slurry was then coated on a copper-foil current collector followed by drying under vacuum at 120 °C for 12 h. The electrodes used were cut into wafers with a 12 mm diameter). Lithium foil was used as the counter/reference electrode, polypropylene film (Celgard 2400) as the separator, and the electrolyte solution was 1 M  $\text{LiPF}_6$  in ethylene carbonate and dimethyl carbonate (1:1 v/v). Finally, the cells were stored for 12 h before tests. Galvanostatic charge-discharge tests were performed on a battery testing system (LAND CT2001A) in the potential range of 0–3.0 V vs. Li/Li+.

## 3. Results and discussion

Fig. 1(a) shows the XRD patterns of precursor (G250), two kinds of intermediate products ( $\alpha\text{-Fe}_2\text{O}_3$  NPs/G250 and  $\gamma\text{-Fe}_2\text{O}_3$  NPs/G900), and target product of PGNs. For G250, the broad, weak diffraction peaks at 25.1° and 43.1° can be ascribed to graphite-like (002) and (100) reflections, which are the typical patterns of amorphous carbon structures. After the low thermal treatment at 180 °C in a pressurized vessel, apart from the characteristic diffraction peak of G250, some additional peaks which belong to  $\alpha\text{-Fe}_2\text{O}_3$  crystal structure (JCPDS No. 33-0664) appear. These diffraction peaks are totally different with that of ferrocene (Fig. S1(a)). These weak peaks intensity could be due to the small size of  $\alpha\text{-Fe}_2\text{O}_3$  NPs and the homogeneous dispersion. By contrast, the product after the subsequent high heat treatment exhibits very strong diffraction peaks, such as 35.63°, 30.24°, 43.28°, 53.73°, and 57.27°, which could be well indexed to the (311), (220), (400), (422), and (511) planes of  $\gamma\text{-Fe}_2\text{O}_3$  (JCPDS, No.39-1346). The characteristic (002) diffraction peaks of PGNs are sharper than that of G250. It indicates the graphitization of PGNs is improved to a higher degree, but still exhibits porous carbon structure.

In order to determine the surface functional groups, FTIR spectra patterns (Fig. 1(b)) of G250,  $\alpha\text{-Fe}_2\text{O}_3$  NPs/G250,  $\gamma\text{-Fe}_2\text{O}_3$  NPs/G900 and PGNs are carried out in the range from 400 to 3000  $\text{cm}^{-1}$ . According to the preparation process, XRD results (Fig. 1a) and FTIR spectra of ferrocene (Fig. S1(b)), it could be found that ferrocene is oxidized to  $\alpha\text{-Fe}_2\text{O}_3$  NPs after the primary treatment at 180 °C. Meanwhile, G250 is reduced at certain degree. FTIR spectra reflect this changes that the absorption band at 1576  $\text{cm}^{-1}$  attributed to the skeletal C=C stretching vibration of graphene sheets is enhanced [29]. Meanwhile, two new bands at 680 and

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