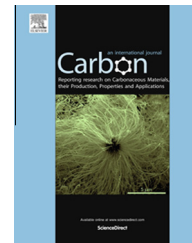


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Metal etching method for preparing porous graphene as high performance anode material for lithium-ion batteries

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ABSTRACT

Porous graphene (PG) has attracted tremendous attention and research interest due to its unique porous structure in combination with inherent properties of graphene. Herein, we report an efficient strategy for bulk preparation of PG by metal etching. The size of the pores and pore density in the basal plane of graphene sheets could be readily controlled by the reaction time and the ratio of the reactants. The PG electrode tested as anode materials exhibited high electrochemical performance with a first charge specific capacity of 933 mAh g⁻¹ at 50 mA g⁻¹, good cycling stability and demonstrated excellent rate performance than those of reduced graphene oxide.

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1. Introduction

Graphene, a single layer of sp² hybridized carbon atoms packing into a honeycomb network, has attracted growing interest for its wide spectrum of potential applications owing to the following features: large theoretical specific surface area, excellent carrier mobility, outstanding electrical and thermal conductivity, superior fracture strength, as well as high chemical stability, etc [1–5]. Although a variety of graphene-based materials have demonstrated application potentials in various fields, their performances need to be improved further for wider and more challenging applications [6–10]. Recently, porous graphene (PG) has attracted tremendous attention and research interest due to its unique porous structure in combination with inherent properties of graphene [11]. To date, researchers have exploited various methods to synthesize PG. Bieri et al. fabricated the regular 2D polyphenylene networks with single-atom wide pores and

sub-nanometer periodicity by surface-assisted coupling of designed molecular building blocks for the first time [12]. Han et al. prepared an electrically conductive, nanoporous reduced graphene oxide network via steam-etching of graphene oxide (GO) [13]. Additionally, Fischbein and his co-worker demonstrated that the suspended graphene sheets could be controllably sculpted under the focused electron beam of a transmission electron microscope [14]. At the same time, other ways were also reported, including photo-etching, chemical vapor deposition and chemical activation, etc [15–18]. As the methods mentioned above, the yield is relatively low, and high-cost electron based instruments are usually employed. Therefore, it is still a great challenge on the development of low-cost, high yield and facile way to prepare high quality PG.

Recently, several papers reported that metal nanoparticle, such as nickel, iron or cobalt, could be used as a ‘knife’ to cut the graphene sheet with nanoscale precision via catalytic

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hydrogenation process [19–21]. Besides, Ramasse et al. observed that metal atoms could etch the suspended, single-layer graphene to form nanoscale holes [22]. They also emphasized the requirement and importance of oxygen atoms in this process. Taking these, here we report an efficient approach to prepare PG in a large scale via a simple metal etching method using GO as the starting material. The choice of GO is critical to successful preparation of PG. The size of the pores and pore density in the basal plane of graphene sheets could be readily controlled by the reaction time and the ratio of the reactants. Moreover, the as-prepared PG tested as the anode material for lithium-ion batteries (LIBs) exhibited a high specific capacity and excellent rate performance, as well as good cycling stability, indicating great application potential in LIBs.

2. Experimental

2.1. Preparation of GO and PG

GO was synthesized from natural graphite flakes using a modified Hummers method as reported in our previous work [23], and the detailed synthetic procedure is as following. 1.0 g of graphite and 1.2 g of KNO_3 was added into 46 ml of concentrated H_2SO_4 (98%) under stirring. Then 6.0 g of KMnO_4 was added slowly. The mixture was then heated to 40 °C and stirred for 6 h. Subsequently, 80 ml of water was added dropwise under vigorous stirring. The slurry was further stirred at ~80 °C for another 30 min. Afterwards, 200 ml of water and 12 ml of H_2O_2 solution (30 wt.%) were added in sequence to dissolve insoluble manganese species. The resulting graphite oxide suspension was washed repeatedly by a large amount of water until the solution pH reached a constant value of ~5.0. The complete delamination of graphite oxide into GO was achieved by ultrasonic treatment. The final suspension of GO was concentrated to a content of 1 wt.%.

To prepare PG, nickel (II) acetate powder of the desired ratio was dissolved in 30 mL of deionized water, then 20 mL of GO solution (4 mg mL^{-1}) was added under severe stirring. The mass ratio of GO/Ni was 10/1. After sonication, the final solution was quickly frozen by liquid nitrogen, transferred into freeze drying equipment and evaporated in vacuum at the temperatures below 0 °C for two days. The dry mixture powder was heated from room temperature to 800 °C at a rate of 10 °C min^{-1} in a tube furnace, and held at this temperature for 1 h under a flowing Ar gas. This intermediate product was denoted as Ni-G. Finally, the black Ni-G powder was treated by diluted hydrochloric acid, followed by washing with water. The resulting powder was dried under vacuum to obtain PG. The mass ratio of GO/Ni and holding time were adjusted in our experiments to tune the size of pore and pore density in the basal planes of graphene.

In order to investigate the reaction between other metals and graphene, iron (III) nitrate nonahydrate, copper (II) acetate monohydrate and cobalt (II) acetate tetrahydrate instead of nickel acetate were used to prepare PG with the same procedure, respectively. The corresponding intermediate products after annealing process were denoted as Fe-G, Cu-G and Co-G, respectively.

2.2. Sample characterization

Powder X-ray diffraction (XRD) patterns were recorded on an AXS D8 Advance diffractometer with $\text{Cu K}\alpha$ radiation. SEM and TEM images were acquired using a field emission scanning electron microscopy (S-4800, Hitachi) and an FEI Tecnai G2 F20 transmission-electron microscope, respectively. Raman spectra analysis was conducted by a Renishaw inVia Reflex Raman Spectrometer, with 532 nm-wavelength laser. The tail gas test was carried out on a Finetec Finesorb-3010 and a FGA-4100 five components gas analyzer. Nitrogen adsorption/desorption measurement was carried out at 77 K in Micromeritics ASAP 2020 M instrument.

2.3. Electrochemical measurement

The electrochemical properties of the PG electrodes were measured with CR2032 coin cells. Firstly, the paste was prepared by mixing active material and SP with PVDF in NMP solution. The weight ratio of active material:SP:PVDF was 80:10:10; then the paste was coated on an Cu foil and dried at 80 °C for 24 h in vacuum. After that, the resultant film was punched into discs of 13 mm in diameter to be used as the anode. Finally, the coin cells were assembled in an argon-filled glove box using PP film as the separator. 1 M LiPF_6 dissolved in a mixture of ethylene carbonate and dimethyl carbonate (1:1, by volume) was employed as the electrolyte. The galvanostatic charge/discharge tests were carried out within a voltage range of 0.01–3 V on a cell testing system (LAND CT2001A, China). The cyclic voltammogram (CV) was performed using the Solartron 1400 cell test system with a scan rate of 0.1 mV s^{-1} , and electrochemical impedance spectroscopy (EIS) in the frequency range from 100 kHz to 0.01 Hz with the amplitude of 10 mV at open circuit was also measured with the same instrument. All the tests were conducted at constant temperature (25 °C).

3. Results and discussion

Fig. 1 depicts a schematic diagram of the typical preparation process for the PG. The first step includes homogeneous mixing of GO and nickel acetate in solution, followed by freeze-drying to obtain solid mixture. The elemental mapping analysis (Fig. S1) shows that the whole basal plane of GO sheets contains a large amount of Ni with a uniform distribution density besides numerous C and O, evident of uniform scattering of nickel acetate on the GO surface. The solid powder was then subjected to thermal treatment under inert atmosphere. During this process nickel acetate firstly decomposed to form nickel nanoparticles, which then reacted with the carbon atoms of graphene to form nanopores, and GO was reduced simultaneously. Finally, the PG was obtained after acid treatment to remove the metal nanoparticles.

The scanning electron microscopy (SEM) image in Fig. 2a shows the morphology of a typical Ni-G sample heated at 800 °C for 1 h. A significant amount of pores appeared on the intact graphene surface. Many nickel nanoparticles with similar size as the pores distribute evenly on the surface of graphene, and some nanoparticles locate inside the pores. It

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