Nitrogen-doped 3D macroporous graphene frameworks as anode for high performance lithium-ion batteries

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HIGHLIGHTS

- N-3D GFs (graphene frameworks) were prepared by heating PS@GO composite in ammonia.
- The formation of pyridinic N and pyrrolic N in N-3D GFs leads to improved electronic conductivity.
- The N-3D GFs delivers an excellent reversible capacity and high rate performance.

ARTICLE INFO

ABSTRACT

Nitrogen-doped 3D graphene frameworks (N-3D GFs) were synthesized by a facile two-step method: Polystyrene (PS) encapsulated in graphene oxide (GO) composites (denoted as PS@GO) are first synthesized, followed by a post–thermal annealing in ammonia step to get N-doped 3D GFs. The resulting N-3D GFs inherit the advantages of graphene, which possesses high electrical conductivity and high specific surface area. Furthermore, the well-defined 3D interconnected structure can facilitate the access of the electrolyte to the electrode surface, thus shortening the diffusion length of both Li^+/e^-, keeping the overall electrode highly conductive and active in lithium storage. Simultaneously, the in-situ formation of pyridinic N and pyrrolic N in 3D GFs provide high electronic conductivity and structure stability for lithium storage. The designed N-3D GFs electrode delivers a high specific capacity of 1094 mAhg^{-1} after 100 cycles at 200 mAg^{-1} and superior rate capability (691 mAhg^{-1} after 500 cycles at 1000 mAg^{-1}) when used as anode for LIBs. We believe that such an inherently inexpensive, scalable, facile method can significantly increase the feasibility of building high performance energy storage system.

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1. Introduction

Lithium-ion batteries (LIBs) have been widely used as the power source for portable electronics and show significant promise for applications in Electric vehicles (EVs) and Hybrid Electric Vehicles (HEVs) [1–6] In principle, the performance of LIBs depends largely on the electrochemical properties of electrode materials, especially the anode material [7]. Development of alternative anodes with high reversible capacity, long cycle life, and high rate capability for current commercial graphite materials is highly desired [8]. To improve the rate performance of a bulk material, it is very important to improve both the electrons and Li-ions transport in its bulk or shorten the diffusion length of both electrons and Li-ions [9]. It is ideal to obtain the materials with high electrical conductivity for fast electron transport and a 3D interconnected porous structures with short diffusion distances for fast lithium ion diffusion [10]. Many efforts have been made to develop new electrode materials with both high energy and high power densities of LIBs. Among them, new carbon-based materials such as carbon nanotubes, carbon nanofibers and graphene have attracted numerous attentions [11–14].

Graphene, a honeycomb network of sp^2 carbon atoms, has attracted numerous attentions all over the world for its high electron conductivity, superior electron mobility, flexibility and high

surface area [15–17]. These properties have made graphene be a good candidate material for energy storage and conversion. When used as anode for LIBs, it could deliver a theoretical capacity of about 764 mAhg^{-1}, which is twice of traditional graphite materials [18]. Besides, the excellent electron conductivity of graphene nanosheets and the high chemical diffusivity of Li ($\sim 10^7$–10^6 cm^2 s^{-1}) on a graphene plane also benefit for the rate capability of LIBs [19]. Recently, it has been demonstrated that preparation of graphene with well-developed porous structures could facilitate high Li$^+$ transfer and alleviate the volume expansion during lithiation/delithiation [9,20–26]. In addition, heteroatoms (especially N)-doped carbon materials have recently received significant attention as electrode materials for LIBs, because of their better electrode/electrolyte wettability, thermal stability, and improved electrical conductivity [20,27–32]. For instance, Wu et al. reported that the N-doping graphene sheets shows improved reversible capacity (>1040 mAhg^{-1} at 50 mAg^{-1}) and enhanced rate capability (~199 mAhg^{-1} at 25 Ag^{-1}) [9]. For the N-doped graphene sheets, the improved lithium storage performance is ascribed to the obtained defect and edge sites that are active for the Li$^+$ ion adsorption [29]. To construct a LIB with both high energy and power density, it is ideal to fabricate N-doped 3D macroporous graphene frameworks electrode, in which fast charge and discharge rates could be achieved. Recently, Jiang et al. have synthesized nitrogen-doped graphene hollow microspheres by using silicon microspheres as sacrificing template, which shows excellent electrochemical performance [20]. However, the synthetic route is complicate and the using of HF may results in environmental pollution. Herein, we designed a simple two-step route to prepare nitrogen-doped 3D interconnected graphene frameworks (denoted as N-3D GFs) using polystyrene (PS) colloidal particles as a sacrificial template, following heating in NH$_3$. The result graphene frameworks exhibits superior lithium ion storage performance and improved rate capability.

2. Experimental section

Synthesis of N-3D GFs: Graphene oxide (GO) was synthesized from natural graphite (QingdaoTianhe Reagent Co., Ltd.,325 mesh) by a modified Hummers method [33]. Polystyrene nanospheres (PS) were synthesized by emulsion polymerization [34]. N-3D GFs was synthesized by the electrostatic assembly of GO and PS, with further thermal treatment in NH$_3$/Ar. Briefly, 0.1 ml of 1 M HCl solution was added to 200 ml of polystyrene nanosphere dispersion (5 mg/ml) and GO suspension (1 mg/ml, 200 ml) under stirring for 10 min to adjust the pH value of both suspension to about 3–4. Then the two suspensions were mixed. PS nanospheres were assembled with GO sheets through electrostatic interaction and then coagulated. The result precipitation was isolated via filtration, followed by freeze drying. The as-collected PS@GO composite was heated in a tube furnace for 2 h at 550 °C under 5% NH$_3$/Ar flow with a heating rate of 5°Cmin^{-1} to get N-3D GFs.

Synthesis of 3D GFs: 3D GFs was synthesized using the same process as for N-3D GFs except that the further thermal treatment in Ar atomosphere.

Synthesis of N-RGO (nitrogen doped reduced graphene oxide): N-RGO was synthesized using the same process as for N-3D GFs except that no PS nanospheres were added.

Characterization: The crystal structure of the obtained materials were characterized by X-ray diffraction (XRD) (TTR-III, Rigaku, Japan) using Cu Kα radiation. Field-Emission Scanning electron microscopy (FESEM) measurements were conducted using a JSM-6700 field-emission scanning electron microscope (JEOL, Tokyo, Japan) operated at 5 kV. The morphology and microstructure of the as synthesized materials were investigated by A JEOL 4000EX

transmission electron microscope (HRTEM) (JEOL, Tokyo, Japan). The ASAP 2020 Accelerated Surface Area and Porosimetry instrument was used to measure the Nitrogen adsorption/desorption isotherms at 77 K. Thermogravimetric (TG) analysis was carried out on a TGA Q5000 instrument at a heating rate of 10 Kmin^{-1} in air. X-ray photoelectron spectroscopy (XPS) spectra were recorded with Axis Ultra Instrument (Kratos Analytical Ltd., UK) to investigate the surface components on the surface.

2.1. Preparation of electrode and electrochemical measurements

The electrodes were prepared by well dispersed the active materials (N-3D GFs or 3D GFs), acetylene carbon black (AC), and poly(Vinylidene fluoride) binder (PVDF) in a weight ratio of 80:10:10 in N-methyl-2-pyrrolidone (NMP) to form a slurry. The resultant slurry was pasted onto pure copper foil using a doctor blade and dried in vacuum oven at 100 °C for 6 h, followed by pressing. CR2032-type coin cells were assembled in an argon-filled glove box (MBRAUN LABMASTER 130, Germany) in which the content of H$_2$O and O$_2$ both below 1 ppm. Li metal was used as counter and reference electrodes, celgard 2400 fiber was used as the separator and the electrolyte solution was 1 M LiPF$_6$ dissolved in a mixture of ethylene carbonate (EC) and diethyl carbonate (DEC) with a volume ratio of 1:1. The loading amount of the working electrodes is about 0.7–1 mg/cm^2 (10 mm in diameter and the loading mass is 0.6–0.8 mg). The galvanostatic charge–discharge measurements were tested at different current densities with a NEWARE battery test system in the voltage range from 0.005 to 3 V vs. Li/Li$^+$ at ambient temperature. Cyclic voltammetry (CV) was conducted on a CHI 660D electrochemical workstation between 0.005 and 3 V vs. Li/Li$^+$ at room temperature at a scan rate of 0.1 mVs^{-1}. Electrochemical impendence spectra (EIS) was conducted at the frequency range of 100 kHz–10 mHz by applying a sine wave with amplitude of 10.0 mV on a CHI 660D electrochemical workstation.

3. Discussion

The synthetic process of nitrogen-doped 3D macroporous graphene frameworks (N-3D GFs) is summarized in Scheme 1. Firstly, PS nanospheres and GO sheets were assembly into a core–shell structure through electrostatic attraction at the pH of 3–4. Then, the obtained core–shell structure PS@GO composite converted into N-3D GFs when thermal treated in ammonia. During heating
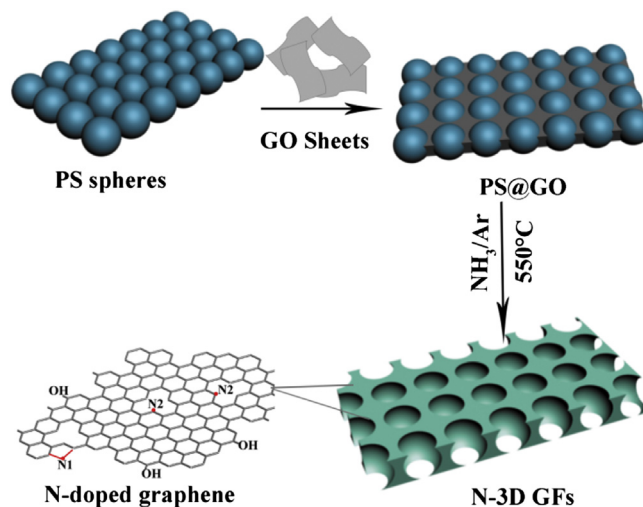
Scheme 1. Schematic illustration of the synthesis process for N-3D GFs.