Research Paper

Scalable Synthesis of High-Tapped-Density N-doped Graphene by Polyethyleneimine-Mediated Thermal Treatment of Graphene Oxide and Its Application for Supercapacitors

Fang Yue[a], Yiqun Zheng[b], Jinglei Liu[b], Xiaoxiao Song[c], Hua Wang[b], Fengting Li[a], Yangyang Tian[a], Junfeng Zhang[b], Shifeng Hou[b,c,*]

[a] School of Chemistry and Chemical Engineering, Shandong University, Jinan, Shandong 250100, PR China
[b] National Engineering Research Center for Colloidal Materials, Shandong University, Jinan, Shandong 250100, PR China
[c] Jining Research Center for Carbon Nanomaterials, Jining, Shandong Province 272100, PR China

ABSTRACT

Development of high-tapped-density graphene-based materials with satisfactory Brunauer–Emmett–Teller (BET) surface area can be beneficial to the optimization of the volumetric performance of supercapacitors for practical use. Herein, we report a simple and scalable route for the synthesis of high-tapped-density N-doped graphene (HNG). The success of this work relies on the use of polyethyleneimine (PEI) to react with graphene oxide under ambient conditions to realize fast cross-linking and thus rapid sedimentation, followed by thermal treatment of the precipitates. The resultant HNG exhibits a good balance between the tapped density and BET surface area, where the tapped density can be tuned in the range of 0.90–1.20 $g\,cm^{-3}$ and the BET surface area is maintained in the range of 457.0–119.6 $m^2\,g^{-1}$. The interaction between PEI and graphene oxide successfully prevents restacking of the graphene layers during thermal treatment while allowing maximal volume shrinkage. When applied as an electrode material in supercapacitors, the HNG exhibits a volumetric capacitance up to 547.8 $F\,cm^{-3}$ at a scan rate of 10 $mV\,s^{-1}$ and 317.3 $F\,cm^{-3}$ at a current density 0.2 $A\,g^{-1}$, and it shows no apparent decrease in the specific capacitance after 5000 cycles at 2 $A\,g^{-1}$. The results demonstrate the feasibility of the new strategy for designing high-tapped-density graphene-based materials for supercapacitors.

© 2017 Elsevier Ltd. All rights reserved.

1. Introduction

Graphene is a type of two-dimensional carbon nanomaterial that is composed of a single layer of carbon atoms packed in a hexagonal lattice [1]. The unique structure of graphene allows it to possess many excellent physicochemical properties such as high electron mobility [2,3], large specific surface area (theoretical value: 2630 $m^2\,g^{-1}$) [4], high thermal conductivity [5], remarkable elasticity and stiffness [6]. Owing to these properties, graphene and graphene-based materials have attracted wide attention in many fields such as supercapacitor [7], solar cell [8], adsorption for

organic pollutants and heavy-metal ions [9], transparent electrode materials [10], bioelectronics [11,12].

Despite these promising applications, the practical use of graphene is still plagued with several problems. For example, the restacking or irreversible agglomeration (or both restacking and irreversible agglomeration) of graphene layers, caused by the strong van der Waals forces and π–π attraction between the layers, can greatly affect the intrinsic performance of graphene [13]. To solve this problem, researchers have proposed the assembly of graphene nanosheets into 3D structures such as foam [14], hydrogel [15], aerogel [16], cuboidal graphene [17], aerographite [18]. However, the large interlayer spacing led to another problem of low tapped density and thus low space utilization [19,20]. Many of the reported graphene materials have low density of < 0.5 $g\,cm^{-3}$, with some reporting values as low as 2.1 ± 0.3 mg cm^{-3} [21], which severely limits the practical use of graphene-based energy-conversion and energy-storage devices like

* Corresponding author at: National Engineering Research Center for Colloidal Materials, Shandong University, Jinan, Shandong 250100, PR China.
 E-mail address: shifenghou@sdu.edu.cn (S. Hou).

supercapacitors. Many studies have been conducted to attain high gravimetric capacitance by employing graphene-based materials in supercapacitors [22–26], such as three-dimensional graphene frameworks [22], nitrogen-doped graphene [23], and reduced graphene oxide/MnO_2 paper [24]. Nevertheless, they still exhibit low volumetric performances owing to their low mass densities. The volumetric performance of supercapacitors is an increasingly important parameter because the space available for supercapacitors in a practical mobile device is limited [19]. Thus, the development of novel graphene materials with high volumetric capacitance is urgently required for actual supercapacitor devices.

To date, much research effort has been focused on increasing the tapped density of graphene while keeping the BET surface area within an acceptable range to attain high volumetric capacitance: (i) On the basis of graphene hydrogels, some densely packed graphene materials with high densities ($1.1–1.58\,g\,cm^{-3}$) have been fabricated through evaporation-induced drying at room temperature [27,28]. Nonetheless, this approach is accompanied by large volume shrinkage caused by capillary contraction, which can lead to the restacking and agglomeration of graphene layers, and seriously decrease the BET surface area of the material (typically in the range of $7.8–449\,m^2\,g^{-1}$). (ii) The use of a low-dimensional or non-volatile material as a spacer doped into graphene can effectively prevent restacking of the graphene layers, which can greatly increase the BET surface area. However, the pore size of the resulting composite is usually large because some spacer materials have dimensions of tens or hundreds of nanometers, which could severely reduce the tapped density of the material [29–31]. (iii) By adding a sacrificial pore former or activating agents, the obtained material shows a very high micropore volume and high surface area, as well as high tapped density [30,32]. However, the graphene structure can be seriously damaged by the chemical reactions occurring during the pore-forming or activation process, which will seriously affect the inherent performance of graphene. Moreover, the process of removing the pore former or activating agents is very tedious and can easily introduce impurities. Recently, graphene materials with tunable sub-nanometer pores have been obtained by controlling the gap between graphene layers with conductive molecular linkers, which can generate pores of the appropriate sizes with a high volume density [33]. However, the pore size was limited to the range of $0.51–0.89\,nm$, which would not improve the BET surface area. In a sense, the fabrication of high-tapped-density graphene with satisfactory BET surface area remains a technical challenge.

Herein, we report the preparation of high-tapped-density N-doped graphene (HNG) via the rapid sedimentation caused by fast cross-linking between graphene oxide (GO) sheets and polyethyleneimine (PEI), followed by thermal treatment. The preparation was conducted under ambient conditions with stirring, but without any hydrothermal process, which makes it favorable for scalable production. The interaction between PEI and GO could not only prevent restacking of the graphene layers during volume shrinkage, but also decrease the amount of oxygen-containing groups to prevent inflation of the product during calcination. Characterizations via scanning electron microscopy (SEM), transmission electron microscopy (TEM), and N_2 adsorption–desorption measurements were carried out to confirm that the obtained material had a structure that was both compact and porous, which could improve the volume utilization and facilitate ion diffusion when used as an electrode material. By controlling the amount of PEI, the tapped density could be varied in the range of $0.90–1.20\,g\,cm^{-3}$ and the BET surface area could be maintained in the range of $457.0–119.6\,m^2\,g^{-1}$. The electrochemical tests demonstrated that the HNG material had a high volumetric capacity of $547.8\,F\,cm^{-3}$ at a scan rate of $10\,mV\,s^{-1}$ and $317.3\,F\,cm^{-3}$ at a current density of $0.2\,A\,g^{-1}$.

2. Experimental section

2.1. Materials

The aqueous GO dispersion ($5\,mg\,mL^{-1}$, purity: $\geq99\%$, oxygen content: 48–51%) was purchased from Leadernano Tech L.L.C., China. PEI (average Mw: ~2,000 by light scattering, 50 wt% in H_2O) and vitamin C (VC; purity: $\geq99.0\%$) were purchased from Sigma-Aldrich Co., USA. Polytetrafluoroethylene (PTFE) was purchased from Alfa Aesar (China) Chemical Co., Ltd. Ethanol (purity: $\geq99.7\%$), ethylenediamine (EDA; purity: $\geq99.0\%$), and potassium hydroxide (KOH) were obtained from Sinopharm Chemical Reagent Co., Ltd., China. Chitosan (CS; deacetylation degree: $\geq85\%$) was purchased from Jinan Haidebei Marine Bioengineering Co., Ltd., China. All chemicals were used without further purification. Ultrapure water (resistivity: $18.25\,M\Omega\cdot cm$) was supplied by a UPH-II-20 water-purification system (Ulupure, China) and used for all experimental processes. The quartz tube furnace (OTF-1200X) was purchased from Hefei Crystal Materials Technology Co., Ltd., China.

2.2. Preparation of high-tapped-density N-doped graphene (HNG)

The GO dispersion was diluted to $0.5\,mg\,mL^{-1}$ prior to use. In a typical procedure, 5 mL of the PEI solution (0.1 wt%) was added dropwise to 50 mL of the aqueous GO suspension with fast magnetic stirring, and GO–PEI assemblies immediately precipitated from the mixture. After the reaction, the mixture was aged and the precipitates were collected through filtration and thoroughly washed with ultrapure water to remove excess PEI; the washed precipitates were dried in air at room temperature. The HNG was prepared by annealing the washed and dried GO–PEI composite at $400\,°C$ for 1 h, with a heating speed of $5\,°C\,min^{-1}$ under a stable flow of Ar (200 sccm). The tapped density and porosity of HNG were tuned by controlling the concentration of the aqueous PEI solution. Hereafter, the samples are referred to as HNG-1, HNG-2, and HNG-3 to reflect the concentration of the PEI solution (0.02, 0.1, and 1 wt%, respectively). The control group was prepared via the standard procedure without the addition of PEI, and the obtained sample is referred to as reduced graphene oxide (rGO). Scalable synthesis of the HNG material was performed via the same procedure, except larger amounts of GO and PEI were used. Additional details of the preparation are shown in Fig. S1.

2.3. Characterization methods

The morphology and structure of the as-prepared materials were characterized with SEM (SU8010, Hitachi, Japan), TEM (JEM-1011, Japanese Electronics Co. Ltd, Japan), and high-resolution TEM (HRTEM; Tecnai G2 F20, FEI, USA) at $200\,kV$. X-ray powder diffraction (XRD) was performed using a diffractometer (D8 Advance, Bruker Ltd, Germany) with Cu K_α radiation. Raman spectra were measured using a high-resolution confocal Raman system (LabRam HR800, Horiba Jobin Yvon, Japan) with 514 nm lasers. The analysis of the presence of various elements and their proportions in the samples were carried out with an elemental analyzer (vario EL cube, Elementar, Germany). X-ray photoelectron spectroscopy (XPS) was performed using a photoelectron spectrometer (K-Alpha, ThermoFisher, USA) with a monochromatic Al K_α X-ray source, and the binding energies of the element peaks were calibrated against the peak of C 1 s at $284.8\,eV$. Thermogravimetric analysis (TGA) was conducted with a simultaneous thermal analyzer (STA 449 F3 Jupiter®, NETZSCH, Germany) from 30 to $900\,°C$ at a heating rate of $10\,°C\,min^{-1}$ under a N_2 atmosphere. Using a gas adsorption instrument (ASAP 2020, Micromeritics, USA), the surface area of the samples was obtained from N_2 adsorption and desorption isotherms by the Brunauer–Emmett–