Research article

Facile synthesis of graphene nanosheets from humic acid for supercapacitors

Baolin Xing [a,c], Ruifu Yuan [b,*], Chuanxiang Zhang [a], Guangxu Huang [a], Hui Guo [a], Zhengfei Chen [c], Lunjian Chen [a], Guiyun Yi [a,c], Yude Zhang [a], Jianglong Yu [c,d,**]

[a] College of Chemistry and Chemical Engineering, Henan Polytechnic University, Jiaozuo 454003, China
[b] School of Energy Science and Engineering, Henan Polytechnic University, Jiaozuo 454003, China
[c] Chemical Engineering, University of Newcastle, Callaghan, NSW 2308, Australia
[d] School of Chemical Engineering, University of Science and Technology Liaoning, Anshan 114051, China

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ABSTRACT

A simple, cost-effective, and environmentally friendly route was developed to synthesize graphene nanosheets from humic acid via preliminary carbonization coupled with oxidation-exfoliation-thermal reduction. Such graphene nanosheets have a high specific surface area ($495~m^2 \cdot g^{-1}$) with large pore volume ($2.987~cm^3 \cdot g^{-1}$), unique interconnected mesoporous structure and uniform oxygen-containing functional groups in layered graphene framework, which offer a favorable and efficient pathway for the electrolyte propagation and transportation. The electrodes of supercapacitors made from these graphene nanosheets exhibit a maximum specific capacitance of $272~F \cdot g^{-1}$ at the current density of $50~mA \cdot g^{-1}$ in aqueous electrolyte, and possess excellent rate capability, low resistance, superior cycling performance with over 96.5% initial capacitance retention after 8000 cycles. The corresponding supercapacitors deliver a desirable energy density of $6.47~Wh \cdot kg^{-1}$ at a powder density of $2250~W \cdot kg^{-1}$. This study demonstrates a promising synthesis route for large-scale production of graphene nanosheets from renewable and green humic acid for high performance supercapacitors.

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1. Introduction

The limited availability of fossil fuels has led to an urgent need for sustainable and renewable sources and new technologies for energy conversion and storage. Supercapacitors, as a promising type of energy storage device, have attracted tremendous attention in recent years due to their high power density, fast charge/discharge processes, excellent cycle life and environmental friendliness [1–5]. It is well known that the electrochemical performance of supercapacitors strongly depends on the properties of electrode materials [6]. Among various carbon materials, graphene exhibits high theoretical surface area, extraordinary electrical conductivity and good electrochemical stability, making it an extremely promising electrode candidate for supercapacitors [7,8]. However, large-scale yet reasonable cost to produce graphene sheets is still one of the major challenges for industrial applications.

Several versatile approaches have been recently established for the synthesis of graphene, including mechanical exfoliation, chemical vapor deposition, epitaxial growth on silicon, and reduction from exfoliated graphite oxide [9]. Among them, reduction from exfoliated graphene oxide is the most commonly and widely accepted method for the production of graphene sheets due to the low cost, scalable process and potential for large-scale production [10,11]. However, high purity graphite is usually used as the main starting material in the reduction method to product graphene sheets, making graphite mineral become an important strategic resource worldwide [12]. It is noteworthy that natural graphite is a limited resource mainly distributed only in a few countries such as China, Czech, Mexico, Brazil and India, hindering its worldwide supply in the medium to long-term. According to the recent report from United States Geological Survey (USGS), world production of natural graphite in 2013 was only 1.11×10^6 t, and most of them were mainly consumed for refractories, steelmaking, brake linings, foundry facings and lubricants [13]. Additionally, graphite is a non-renewable resource that will be exhausted within a short time after large-scale exploitation and widespread utilization. Therefore, it is highly desirable to search for other inexpensive and renewable resources to replace traditional graphite and develop facile as well as cost efficient route for the preparation of graphene sheets.

Most recently, a wide variety of low-cost, abundant and eco-friendly natural resources have been selected as precursor for the synthesis of graphene sheets. For instance, various kinds of foods such as sucrose, gelatin protein, milk, butter, honey, cookies and chocolate [14–16],

biomass and biomass waste materials such as wood, grass, wheat straw and camphor leaves, bagasse and fruit wastes [16–19], animal wastes such as bone, cow dung and dog feces, and insect-derived (roaches) [16,17], have been chosen as the starting materials for the preparation of graphene sheets. However, it is difficult for commercial production of graphene sheets from these types of precursors due to their limited output, relatively low carbon content (organic matter) and inhomogeneous chemical compositions.

Humic acid is a natural aromatic polymer and is considered as green, renewable and inexpensive biomass materials, which consists of a skeleton of aliphatic or aromatic units cross-linked by various types of oxygen-containing functional groups [20–22]. It derives from microbial decomposition of organic substance and is abundantly available in soil, lake sediments, plants, coral skeletons, peat, brown coal and weathered coal, etc. Considering its characteristics of earth abundance and low-cost, carbon-enriched chemical composition, renewable and environmental friendly, humic acid has attracted great attention as a green raw material in preparation of high value-added nanostructure carbon products. Qiao and Yin et al. [20,21] reported that hierarchical porous carbons were successfully prepared from humic acid for high performance supercapacitors via KOH activation. Our previous work also synthesized highly porous carbons for supercapacitors through KOH and ZnCl₂ activation by using humic acid as raw materials [23,24]. To the best of our knowledge, there has been little information available in the open literature regarding the synthesis of graphene sheets from humic acid. Recently, Beall's research group firstly found that the morphology, carbon/oxygen ratios and framework structure of humic acid was very similar to that of graphene oxide, and synthesized single crystalline graphene by thermal annealing of humic acid over copper foils [25,26]. However, these studies do not provide sufficient information for the final graphene sheets derived from humic acid on either the microstructure characteristic and chemistry property or the associated performance in application. Additionally, it is well known that the structure and property of graphene sheets are not only dependent on the starting precursor but also on the preparation process.

Herein, we report a preliminary carbonization coupled with oxidation-exfoliation-thermal reduction strategy to synthesize graphene sheets from humic acid. The renewable and green humic acid was firstly heated at a high temperature of 1800 °C in an inert atmosphere, where the aromatic units in the precursor experienced a carbonization step to form layered structure of graphite-like carbon. The resultant carbonized materials were converted into graphene oxide via modified Hummers method followed by thermal reduction at 900 °C for 5 min to obtain the final graphene nanosheets. The morphology characteristic, microstructure and surface chemistry property of obtained graphene nanosheets were investigated in detail. The electrochemical behaviors of graphene nanosheets applied as electrode materials for supercapacitors were also systematically evaluated in the electrolytes of basic, acid and neutral aqueous solutions.

2. Experimental

2.1. Carbonization of humic acid

A commercial humic acid sample sourced from Yunnan Province (China) was used as the precursor without further purification. The results of proximate and ultimate analyses for the humic acid are given in Table 1. The humic acid powder was placed in a graphite crucible, and heated in a graphitization furnace at 1000 °C for 1 h with a heating rate of 5 °C·min⁻¹, followed by further heating to 1800 °C at a heating rate of 10 °C·min⁻¹ in a high purity argon flow (99.99%) and held for 2 h. The sample was then cooled naturally to room temperature, and was ground by a mortar into powdered sample with a particle size less than 74 μm.

2.2. Synthesis of graphene nanosheets

The carbonized powder from humic acid was used as starting materials to synthesize graphene oxide by using a modified Hummers method. Briefly, 5 g carbonized powder, 30 g KMnO₄ and 5 g NaNO₃ were slowly added into 220 ml concentrated H₂SO₄ in sequence and vigorously stirred in an ice bath for 10 h. The mixture was then heated to 35 °C and maintained for 3 h with continuous stirring. The mixture was then diluted by 440 ml distilled water, and the temperature of mixture was controlled to be under 85 °C during the dilution process. After that, H₂O₂ (30 wt%) was added into the mixture drop by drop until the color of solution became bright yellow. The mixture was finally centrifuged (8000 rpm, 6 min) and the supernatant was discarded. The remaining solid was then successively washed with 1 M HCl solution and deionized water several times by centrifugation until the pH of the solution was neutral. The obtained solid was ultrasonicated in deionized water for 8 h, and the resultant suspension was then dried by freeze drying to obtain graphene oxide. For the thermal exfoliation-reduction of graphene oxide process, 1 g of obtained graphene oxide was placed in a quartz crucible (with a lid) and heated at 900 °C for 5 min in a muffle furnace under nitrogen atmosphere. The graphene nanosheets were collected after a natural cooling. The synthesis procedure for graphene nanosheets is illustrated in Fig. 1.

2.3. Characterization of graphene nanosheets

The morphological characteristic of graphene nanosheets was examined using a Quanta FEG 250 scanning electron microscope (SEM) and a JEM-2100 transmission electron microscope (TEM). Specimens for TEM observation were prepared by ultrasonic dispersion of graphene nanosheets powder in alcohol and then deposited on standard carbon copper grids using the drop casting method. X-ray diffraction (XRD) of samples was measured through a Bruker D8 Advance diffractometer with Cu Kα radiation (λ = 0.154187 nm) at 40 kV, 100 mA, and the 2θ range from 5 to 80°. The Brunauer-Emmett-Teller (BET) specific surface area and total pore volume of graphene nanosheets were evaluated by nitrogen adsorption at −196 °C on a Quantachrome Autosorb-iQ-MP automatic adsorption instrument and pore size distribution was evaluated by the density functional theory (DFT) from the adsorption branch. Sample was degassed at 200 °C for 10 h prior to nitrogen adsorption measurement. Raman spectroscopy was performed using Raman spectrometer (Renishaw) with an argon ion laser (λ = 514 nm) at room temperature. Fourier transform-infrared spectroscopy (FT-IR) spectra of the samples were carried out on a Bruker Vector-22 spectrometer with a KBr beam splitter. The chemical composition and surface functionality of samples were analyzed by a Thermo Scientific Escalab 250Xi X-ray photoelectron spectroscopy (XPS).

2.4. Electrochemical measurements

The electrochemical measurements were carried out using a symmetrical two-electrode cell without a reference electrode. The carbon electrode was fabricated by mixing of a mixture of 85 wt% graphene nanosheets powder, 10 wt% carbon black (BP2000), and 5 wt% polytetrafluoroethylene (PTFE), and then pressed to form a disk-like carbon sheet with a diameter of 13 mm. Supercapacitors were assembled with two similar carbon electrodes separated by a polypropylene film separator. 3 M KOH (basic), 1 M H₂SO₄ (acid) and 1 M Na₂SO₄

Table 1
Proximate and ultimate analyses of humic acid.

Proximate analysis (wt%)			Ultimate analysis (wt%, daf)			
M_{ad}	A_d	V_{daf}	C	H	O[a]	N
8.91	4.35	41.42	63.76	3.58	31.41	1.25

ad, air dry basis; d, dry basis; daf, dry and ash-free basis.
[a] By difference.