



Facile synthesis of few-layer graphene from biomass waste and its application in lithium ion batteries



Feng Chen, Juan Yang, Tao Bai, Bo Long, Xiangyang Zhou *

School of Metallurgy and Environment, Central South University, Changsha 410083, China

ARTICLE INFO

Article history:

Received 21 October 2015

Received in revised form 27 January 2016

Accepted 22 February 2016

Available online 23 February 2016

Keywords:

Biomass waste

Wheat straw

Few-layer graphene

Hydrothermal treatment

Lithium ion batteries

ABSTRACT

Graphene is an appealing two-dimensional material with superior mechanical, electrical, and thermal properties. Mass production of high-quality graphene is attracting more and more researchers' attention in recent years. Most of the current methods for synthesizing graphene use purified chemical reagents that could be expensive for large-scale production. In this study, we have developed a less expensive method to synthesise high-quality graphene sheets from wheat straw via a combined hydrothermal and graphitization approach. The resulting graphene sheets show favorable features such as ultrathin nanosheet frameworks (2–10 atomic layers), high graphitization (up to 90.7%), graphite-like interlayer spacing (0.3362 nm), and the mesoporous structure. When used as an anode material for lithium ion batteries, the few-layer graphene delivers high reversible capacity (502 mAh g⁻¹ at 0.1 C), superior rate capability (463.5, 431.4, and 306.8 mAh g⁻¹ at 1, 2, and 5 C, respectively), and good cycling performance (392.8 mAh g⁻¹ at 1 C after 300 cycles). The wheat straw-derived graphene sheets also display the relatively flat voltage profiles with a negligible charge/discharge voltage hysteresis. Moreover, this low-cost, highly efficient, and catalyst-free technique is a significant milestone towards environmentally-sustainable, commercially feasible fabrication of carbon nanomaterials from renewable natural resources.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

Graphene, in its monolayer form, is an appealing two-dimensional (2D) material with an atomically thick hexagonal packed structure [1]. Due to its high theoretical surface area (over 2600 m² g⁻¹), excellent electrical conductivity, extraordinary mechanical flexibility, and good thermal conductivity, graphene has very promising applications in nanoelectronic components and nanocomposites including high-powered ultracapacitors, transistors, solar cells, molecular sensors, lithium ion batteries, and highly conducting and sturdy materials [2,3].

Up to now, versatile methods for fabrication and synthesis of graphene have appeared in the literatures. In flake graphite, the contiguous graphene layers are linked by weak van der Waals forces [4]. Hence, the mechanical exfoliation of pyrolytic graphite using Scotch tapes can obtain original graphene sheets directly [5]. Chemical vapor deposition (CVD) synthesis has been allowed the preparation of mono- and few-layer graphene flakes on the metal surfaces, such as Ni and Mo. Large crystalline graphene sheets about several micrometers in size can be subsequently transferred to other substrates [6,7]. However, these methods are unrealistic for large-scale solution-based procedures. The epitaxial growth also provides large-sized graphene on

wafers, but the cost of this graphene is quite high on account of the price of the substrate silicon carbide (SiC) [8]. Reducing exfoliated graphite oxide has been able to prepare graphene sheets in scalable ways. Unfortunately, the use of highly hazardous chemicals (acids and wastes) as well as complicated chemical synthesis procedure has restrained the scaling up of these processes. Moreover, the quality of the resulting graphene sheets scatters considerably [9]. Recently, green synthesis of graphene sheets using eco-friendly biomass precursors (e.g., gelatin, butter, honey, and other foodstuffs) has been demonstrated [10–12]. However, multi-step process, precursor purification, relatively harsh operating conditions, scalability, and cost pose serious problems. Hence, it is highly desirable to develop a facile and scalable technology to generate graphene sheets through a cost efficient route from low-cost and renewable natural resources.

Here, we demonstrate that it is possible to prepare large amounts of few-layer graphene by an environment-friendly method that uses biomass waste as the precursor. Wheat straw was chosen as the starting material in our research due to its enormous worldwide output (about 350 million tons per year all over the world) [13]. This ample supply has led wheat straw to attract enough attention as a raw material in generating nano-materials with high additive value such as nano-silica [14] and activated carbon [15]. In this work, we confirmed that the useless wheat straw could successfully convert to value-added graphene sheets by a combined hydrothermal and graphitization process. Using this method, high-quality, few-layer pristine graphene

* Corresponding author.

E-mail address: hncsyjy308@163.com (X. Zhou).

sheets with high graphitization, graphite-like interlayer spacing, and moderate meso-porosity can be prepared. This biomass waste-derived graphene sheets exhibit excellent electrochemical properties when it is used as anode material in lithium ion batteries and show good application potential. Moreover, our process is simple, highly efficient, environmentally benign, cost-effective, and catalyst-free. We believe this novel approach will motivate the search for a new way for synthesis of graphene sheets from reproducible natural products.

2. Experimental

2.1. Graphene preparation

Wheat straw was used as the starting material to obtain few-layer graphene by carbonization and graphitization of its hydrothermal product. Detailed steps are as follows: the raw material was first cut into small pieces (approximately 3 cm in length) and washed with distilled water, and then dried at 60 °C for 12 h before use. Within the subsequent hydrothermal treatment, 4 g of the washed wheat straw was immersed in a 400 mL Teflon-lined stainless steel autoclave wherein 280 mL of homogeneous 3 M KOH solution was contained, and then the autoclave was heated at a temperature of 150 °C for 6 h. When cooled down to room temperature naturally, the resulting samples were fetched out, collected by vacuum filtration with quantitative filter paper, washed by ultrasonication in 120 mL deionized water for 30 min and dried in an oven at 80 °C. The following high temperature pyrolysis and chemically activation was carried out at 800 °C for 3 h under the protection of N₂ atmosphere at a heating rate of 5 °C min⁻¹ and a N₂ flow rate of 150 cm³ min⁻¹. After that, the carbonaceous product was thoroughly washed with 0.5 M HCl solution to remove the residual KOH and dried in a vacuum oven at 80 °C for 12 h. Finally, the as-prepared product was thermally treated at 2600 °C for 5 min using a graphite furnace in an argon atmosphere. The typical yield of few-layer graphene by using wheat straw as starting material was found to be ca. 11.3 wt.%.

2.2. Structural characterization

The morphologies and structures of the synthesized materials were characterized by scanning electron microscopy (SEM, Quanta FEG 250, Japan), transmission electron microscopy (TEM) and high-resolution TEM (HRTEM, JEM-2100F, Japan), selected area electron diffraction (SAED, Titan G2 60–300, Netherlands), atomic force microscopy (AFM, NanoScope (R) III, USA), X-ray diffraction (XRD, Rigaku-TTRIII, Japan), and Raman spectra (LabRAM Hr800, HORIBA Jobin Yvon). Specific surface area, pore size distribution and pore volume were recorded according to nitrogen adsorption–desorption isotherms performed by the Surface Area and Porosity Analyzer (ASAP 2020 HD88). The pore volume of the samples was calculated at a relative pressure of 0.999 (P/P₀). The specific surface area and pore size distribution were obtained according to the Brunauer–Emmett–Teller (BET) theory and the nonlocal density functional theory (NLDFT) model from the adsorption branch of the isotherm. X-ray photoelectron spectra (XPS) were recorded by using an X-ray photoelectron spectrometer (K-Alpha 1063) with a monochromatic Al K_α X-ray source. The elemental contents were measured by a EuroEA3000 Analyzer (Leeman, USA). Digital photographs were taken with a Nikon Camera (COOLPIX s4300). Following determination of d₀₀₂, the degree of graphitization was calculated according to

$$G = \frac{0.3440 - d_{002}}{0.3440 - 0.3354} \times 100\% \quad (1)$$

In the equation, 0.3440 refers to the interlamellar spacing of turbostratic graphite (in nm) and 0.3354 is the interlamellar spacing for single crystal graphite (in nm) [16].

2.3. Electrochemical measurement

Electrochemical tests were performed using 2025 coin-type cells with the resulting samples as the working electrode and lithium foil as the counter electrode. The working electrode comprised 80 wt.% active materials, 10 wt.% carbon black as the conductive agent, and 10 wt.% polyvinylidene fluoride (PVDF) binder dissolved in N-methyl-2-pyrrolidinone (NMP). The mixed slurry containing all the components was then coated on the copper foil using a scraper blade, followed by evaporating the NMP at 120 °C for 12 h in a vacuum drying oven, resulting in electrodes with the active material loading of about 1 mg cm⁻². Meanwhile, another working electrode without carbon black (CB) was also prepared by substituting 10 wt.% of carbon black with active materials (few-layer graphene) via the same procedures described above. The electrolyte was 1.0 mol L⁻¹ LiPF₆ in ethylene carbonate/dimethyl carbonate (1:1 by vol.), and Celgard 2400 was used as the separator. The electrodes were chipped into disks of 10 mm in diameter and then were assembled in an argon-filled glove box (Super 1220/750, Shanghai Mikrouna Co. Ltd.) without oxygen and water (contents less than 0.1 ppm). The electrochemical performance was investigated on LAND CT-2001A at room temperature in the voltage window range 0–3.0 V versus Li/Li⁺ at different current densities. The first cycle began with the discharge process, corresponding to the intercalation of lithium ions into the electrodes.

3. Results and discussion

Wheat straw was selected as the starting material to synthesize few-layer graphene not only because it is widespread, abundant, and readily available, but also because it has a multilevel layered structure consisting of three different polymers that associate with each other; namely, cellulose, hemicellulose and lignin [17,18]. This natural multilayer structure gave us some inspiration for the preparation of graphene sheets via a combined hydrothermal and graphitization process that strips wheat straw directly. As shown by the images in Figure S1 (a and b) and S2a, a wheat straw stem is formed as concentric annulus leaving a lumen at the center. The outermost side of the stem is a dense layer of hydrophobic wax, which gives extra mechanical strength to the stem and protects the stem from degradation to moisture (Figure S1c and d). Beneath the epidermis is a loose layer mainly composed of lignin and hemicellulose that protects the crystalline cellulose inside (Figure S1e and f) [18,19]. The crystalline cellulose, which is the skeleton of wheat straw, is itself a layered structure consisting of cellulose microfibrils with a few nanometers in diameter and millimeters in length. These crystalline microfibrils with high tensile strength are the basic structure unit in the cell walls of wheat straw. The cellulose microfibrils are mostly independent and weakly bond together by hydrogen bonds and van der Waals forces [20,21].

Fig. 1 illustrates the overall evolution of synthetic processes (Figure S2 shows the digital photographs of the corresponding products for each step). Recycled wheat straws are firstly cut into small pieces and cleaned followed by a hydrothermal treatment under the basic solution. Given the treatments with alkali have been widely used in varieties of industrial productions, particularly in dyeing and printing industries, the use of KOH would not be an intractable issue for the scale up of our synthesis technology. Moreover, the dealing methods of the wastewater containing organic compounds, which are produced during the hydrothermal treatment, will be very easily implemented according to the literatures (such as electrochemical technologies, activated sludge processes, etc) [22,23]. During the hydrothermal process, high concentrated hot alkali solution can gradually saponify the wax and dissolve hemicellulose and lignin, while the crystalline cellulose is partly degraded but not dissolved [17–19]. After removal of hemicellulose and lignin, the links between the cellulose microfibrils are loosened. As shown in Figure S2b, it is clear to see wheat straws have converted to cellulose fibers mixed with some residual KOH. In the following

Download English Version:

<https://daneshyari.com/en/article/217958>

Download Persian Version:

<https://daneshyari.com/article/217958>

[Daneshyari.com](https://daneshyari.com)