Materials Research Bulletin 61 (2015) 383–390

Contents lists available at ScienceDirect

Materials Research Bulletin

journal homepage: www.elsevier.com/locate/matresbu

Green synthesis of boron doped graphene and its application as high performance anode material in Li ion battery

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ARTICLE INFO

Article history:
Received 23 August 2014
Received in revised form 27 September 2014
Accepted 17 October 2014
Available online 18 October 2014

Keywords:
Lithium ion battery
Boron doping
Electronic states
Specific capacity

ABSTRACT

The present work demonstrates a facile route for the large-scale, catalyst free, and green synthesis approach of boron doped graphene (B-G) and its use as high performance anode material for Li ion battery (LIB) application. Boron atoms were doped into graphene framework with an atomic percentage of 5.93% via hydrogen induced thermal reduction technique using graphite oxide and boric acid as precursors. Various characterization techniques were used to confirm the boron doping in graphene sheets. B-G as anode material shows a discharge capacity of 548 mAh g^{-1} at 100 mA g^{-1} after 30th cycles. At high current density value of 1 A g^{-1}, B-G as anode material enhances the specific capacity by about 1.7 times compared to pristine graphene. The present study shows a simplistic way of boron doping in graphene leading to an enhanced Li ion adsorption due to the change in electronic states.

1. Introduction

Lithium ion batteries (LIBs) are the most popular and promising electrochemical energy conversion and storage device because of their portability, conversion efficiency, and no gaseous exhaust. The main targets of present LIBs are to achieve high energy density and power density with extensive chemical stability and higher service life at low cost. These criteria demand of an anode electrode material with higher specific capacity than the existing conventional graphite (372 mAh g^{-1}). Graphene, a single sheet of sp^2 bonded carbon atoms in the shape of a honeycomb network, has opened up a new direction in the field of electrochemical energy devices [1–3]. The two-dimensional structure of graphene sheets gives high aspect ratio and good electrical conductivity with high surface area [4]. 2D morphology of graphene sheet also enhances the current rates in an electrochemical cell by reducing the diffusion time. Since the discovery of graphene in 2004, from highly ordered pyrolytic graphite (HOPG) using 'peeling off' technique by Geim and Novoselov [5], it has been used widely in energy applications, nanoelectronics, biosensors, and gas sensors [1,2,4,6,7]. Chemical impurities such as boron (B) or nitrogen (N), when doped in carbon materials, can give '*p*' or '*n*' type semiconducting material due to the transfer of electrons between the dopants and the host material. The transition occurs as a result of the modification of electronic band structure through the bonding between carbon atoms and analogous atomic sized three or five valence electron containing dopant atoms [8]. Electrochemical studies of doped graphene with various dopants such as B, N, P, and S have been reported recently [9]. Theoretical study shows the possibility of lowest potential barrier for lithium diffusion on boron-doped graphene compared to other doped graphene [10]. To synthesize heteroatoms-doped graphene, various routes have been implemented till date with mainly two diversions. One is via in-situ method, in which doping is done during the synthesis of the host material itself and the other one is to treat the synthesized material with a particular precursor material of nitrogen or boron at elevated temperatures or plasma treatment in particular environment (NH_3, B_2H_6). Plasma treatment is an efficient way for heteroatom doping but there is a possibility of creating more defects within the sample and thereby decreasing the electrical conductivity also. The problem with in-situ techniques is that the catalyst metal precursor impurity hampers the study of the contribution solely from the doped material, while that for ex-situ method is the need of high temperature and more time or steps involved. When the chemical stability of the doped graphene is reduced, the dopant leaves the host surface [11].

There are only few reports on synthesis of boron-doped graphene samples, and in these studies, the source material involved such as BBr_3 [12] or B_2H_6 [13] are toxic and they need special concern for the handling. Greener approach was done by Sheng et al. in the presence of B_2O_3 vapor, but at elevated

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http://dx.doi.org/10.1016/j.materresbull.2014.10.049
0025-5408/

temperature of 1200 °C [14]. Controlled boron doping on monolayer graphene film by CVD technique using polystyrene and boric acid as carbon and boron precursor, respectively, was reported by Wu et al. [15]. This synthesis procedure involves many steps before achieving small quantity of B-G and cannot be used for energy related applications where large quantity of materials are required. Xu et al. reported boron doped graphene synthesis by calcination process at three different temperatures in argon atmosphere using thrice amount of boric acid with respect to graphite oxide to achieve a maximum of 1.92% doping [16].

In the present study, we reported a large scale, catalyst free, and green synthesis of boron-doped graphene (B-G) with higher doping level (5.93%) using less quantity of boron precursor. Electrochemical study shows its application as effective anode material in LIB with high current rate capability.

2. Experimental

2.1. Synthesis

Graphite oxide (GO) was prepared by modified Hummer's method [17]. In this method, 2 g of graphite powder was added to concentrate H_2SO_4 solution in an ice bath under vigorous stirring. $NaNO_3$ was added gently into the solution followed by $KMnO_4$. This unit was then allowed to come to room temperature after removing from ice bath. The suspension was made dilute by adding warm water. H_2O_2 (3%) was further added to it until the solution becomes bright yellow in color. This solution was washed multiple times with water. The diluted suspension was then centrifuged and dried at 60 °C. This as-synthesized material was named as graphite oxide (GO) and mixed properly with boric acid in a ratio of 2:1 using a mortar and pestle. The combination was evenly grinded for some time and sprinkled over a quartz boat. The boat was placed at the center of a parallel quartz cylinder inside a tubular furnace. The quartz tube was designed to have the provision of gas flow with end coupling finishing. The inner space was first flushed with argon gas for 15 min at room temperature. Hydrogen (99.99%) gas was then allowed and temperature was increased to 500 °C for 0.5 h. The temperature was further raised to 700 °C for 0.5 h in argon atmosphere. After that, heating was switched off and the sample was furnace cooled to room temperature. Boron atoms get doped into the vacancies created by the removal of oxygen groups or defects in the structure of graphene sheets. The as-synthesized material was collected and washed with copious amount of ethanol and warm de-ionized water. The washed sample was dried at 60 °C in vacuum oven and named as B-G.

Pristine graphene (P-G) was synthesized by hydrogen reduction technique under similar experimental condition without boron precursor as reported by us earlier [18].

2.2. Characterization

X-ray diffraction (XRD) measurements were carried out in a PANalytical X'Pert Pro X-ray diffractometer with Cu-Kα source of radiation ($\lambda = 0.15406$ nm) and Ni as filter at 40 kV and 30 mA. The diffraction data was recorded with a step size of 0.016° in the range of 5–90° (2θ). X-ray photoelectron spectroscopy (XPS) study was done using SPECS instrument with Mg-Kα as the X-ray source and PHOIBOS 100MCD as the analyser at ultrahigh vacuum (10^{-10} mbar) for the confirmation of boron doping in graphene framework. Raman spectroscopy readings were taken using LabRAM HP 800 UV Raman spectrometer with 632 nm, He–Ne laser as excitation source to study the vibrational modes in the range 800–3200 cm^{-1}. Sample damaging was prevented using low intense laser power. Functional group identification was done in a PerkinElmer FT-IR spectrometer using KBr pellet within the range of 600–4000 cm^{-1}. Brunauer–Emmett–Teller (B–E–T) surface area analysis was done using a Micromeritics ASAP 2020 instrument by nitrogen adsorption–desorption isotherms at liquid nitrogen temperature of 77 K. Field emission scanning electron microscopy (FESEM, FEI QUANTA 3D) and high-resolution transmission electron microscopy (HRTEM, Technai G20 S-Twin (200 kV)) instruments were utilized to study the morphology of the synthesized samples. For HRTEM, the samples were dispersed in ethanol by ultrasonication and drop casted on a holey carbon coated 200 mesh copper grid. After drying in ambient atmosphere, the coated grids were used to study the texture of the samples.

2.3. Electrochemical measurements

The electrode material slurry was prepared by combination of the material i.e., P-G or B-G (75%) with polyvinylidene fluoride (PVDF) as binder (15%) and conductive carbon (10%) in *N*-methyl 2 pyrrolidone (NMP) solvent using a mortar and pestle. Using doctor blade technique, this slurry was spread over a copper foil of thickness 0.009 mm and dried overnight at 120 °C. Dried coated foil was then shaped into 12 mm diameter coins. Swagelok type cells were assembled inside argon (99.999%) filled glove box (H_2O and $O_2 < 0.1$ ppm) with lithium foil as reference electrode and celgard 2400 as separator. The separator soaked with 1 M lithium hexafluorophosphate ($LiPF_6$) dissolved in ethylene carbonate and dimethyl carbonate (1:1 v/v) was used as the electrolyte. Galvanostatic charge discharge studies had been done using a Solartron electrochemical workstation, in the voltage range of 3–0.01 V (vs. Li/Li^+) for different current densities at room temperature. The ac impedance spectra were recorded in the range 100 kH_Z–0.01 H_Z by applying a sine wave of amplitude 5 mV.

3. Results and discussion

Schematic illustration of the synthesis of boron-doped graphene with contrast to pristine graphene is shown in Fig. 1. Boric acid was used as boron precursor. The oxygen containing functional groups present in the GO such as, —OH, —COOH, and =CO groups react intensely with the allowed hydrogen gas at the experimental temperature of 500 °C. This aggressive exothermic reaction gives sufficient strength for the exfoliation of graphene planes and reduction of oxygen functional groups by the formation of carbon dioxide gas and water vapor simultaneously. Also, boric acid gets decomposed at this environment and doped within the few layer graphene structure.

Fig. 2 shows the diffraction patterns of graphite (Gr), graphite oxide (GO), pristine graphene (P-G), and boron-doped graphene (B-G). Sharp (0 0 2) peak at ~26° in Fig. 2(a) exhibits high crystalline nature of the used graphite. The forward shift of this peak to 11° in Fig. 2(b) emphasizes on the expansion of carbon basal plane with the incorporation of oxygen containing functional groups. This implies the increase of the interlayer spacing from graphitic 0.34 nm to 0.84 nm and thereby formation of GO. Fig. 2(c) shows the diffraction pattern for pristine graphene having d spacing of 0.36 nm. The broadening of C (0 0 2) peak in Fig. 2(c) and (d) indicates the amorphous nature of synthesized P-G and B-G. No additional peak around $\sim 2\theta = 14°$ and 28° for Fig. 2(d) suggests the absence of B_2O_3.

XPS analysis has been done for boron-doped graphene in the binding energy range 0–600 eV to study the surface elemental composition of the material. The survey spectrum in Fig. 3 shows the presence of carbon, oxygen, and boron. The substitution level of boron into carbon framework was calculated from the relative intensities of B1s, O1s, and C1s within the XPS survey spectrum (Fig. 3). It shows almost ~5.93% atomic percentage of boron doped