

Full Length Article

Synthesis of graphene oxide and reduced graphene oxide by needle platy natural vein graphite



R.M.N.M. Rathnayake^{a,c}, H.W.M.A.C. Wijayasinghe^{a,*}, H.M.T.G.A. Pitawala^b, Masamichi Yoshimura^c, Hsin-Hui Huang^c

^a National Institute of Fundamental Studies, Kandy, Sri Lanka

^b Department of Geology, University of Peradeniya, Peradeniya, Sri Lanka

^c Graduate School of Engineering, Toyota Technological Institute, 2-12-1 Hisakata, Tempaku, Nagoya 468-8511, Japan

ARTICLE INFO

Article history:

Received 7 August 2016

Received in revised form

14 September 2016

Accepted 3 October 2016

Available online 5 October 2016

Keyword:

Needle platy graphite

Reduced graphene oxide

Graphene oxide

Chemical oxidation

Chemical reduction

ABSTRACT

Among natural graphite varieties, needle platy vein graphite (NPG) has very high purity. Therefore, it is readily used to prepare graphene oxide (GO) and reduced graphene oxide (rGO). In this study, GO and rGO were prepared using chemical oxidation and reduction process, respectively. The synthesized materials were characterized by X-ray diffraction (XRD), atomic force microscopy (AFM), scanning electron microscopy (SEM), high-resolution transmission electron microscopy (HRTEM), X-ray photoelectron spectroscopy (XPS), and Fourier transform infrared (FTIR) spectroscopy. XRD studies confirmed the increase of the interlayer spacing of GO and rGO in between 3.35 to 8.66 Å. AFM studies showed the layer height of rGO to be 1.05 nm after the reduction process. TEM micrographs clearly illustrated that the prepared GO has more than 25 layers, while the rGO has only less than 15 layers. Furthermore, the effect of chemical oxidation and reduction processes on surface morphology of graphite were clearly observed in FESEM micrographs. The calculated $R_{O/C}$ of GO and rGO using XPS analysis are 5.37% and 1.77%, respectively. The present study revealed the successful and cost effective nature of the chemical oxidation, and the reduction processes for the production of GO and rGO out of natural vein graphite.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

Natural graphite is an important raw material that can be used for many industrial applications [1,2]. At present, most of these industries still use expensive synthetic graphite, rather than natural graphite resources. This is possibly due to the fact that there is less awareness of the possibilities and practical procedures for the use of these natural resources. However, the recent studies carried out in the recent past revealed the possibility of producing high performing materials from natural graphite, or even as carbon-based nanomaterials, such as graphene oxide [2,3]. Among the countries possessing natural graphite resources, Sri Lanka is renowned for its highly crystalline vein graphite with high natural purity, in the range of 95–99% carbon. Therefore, there is a high potential for the production of different industrial products at low cost from these natural graphite resources [4,5]. The graphite has a

hexagonal layered arrangement of carbon atoms in the crystal structure. In a plane, the C–C spacing is 1.42 Å and the planes are stacked in ABA Bernal stacking order with a layer distance of 3.34 Å [6]. In this crystalline structure, sp^2 hybridized carbon atoms are connected to each other by covalent bonds while the van der Waals interaction act between the adjacent planes [7]. This outer-plane weak interaction was allowed to slip on an adjacent plane in the presence of mechanical stress. This property has made the graphite suitable to use in many components which require high lubricating properties [7]. Furthermore, due to its hexagonal arrangement of carbon atoms the unhybridized p -orbitals can form an electron cloud throughout the lattice, which results in higher electrical conductivity. The electrical conductivity can reach 25,000 S/cm and in the range of 1000 S/cm for the plane of a single-crystal and dense polycrystalline graphite [7,8]. From this material, expanded graphite can be produced using a chemical oxidation process, and it is considered as a graphite intercalation compound [8–10]. Graphite can be expanded by the processes such as intercalation of strong acids with microwave irradiation, chemical oxidation and ultrasound irradiation [10,11]. In this study, expansion of graphite was carried out with a chemical oxidation technique, using 98% H_2SO_4 , 85% H_3PO_4 and $KMnO_4$ [9]. This process is highly effective

* Corresponding author at: National Institute of Fundamental Studies, Hanatana road, Kandy, Sri Lanka.

E-mail addresses: athulawijaya@gmail.com, athula@ifs.ac.lk (H.W.M.A.C. Wijayasinghe).

to reduce the van der Waals interaction in between planes, which is inversely proportional to the interlayer spacing, thus increasing the interlayer distances [10]. A single layer of graphite has excellent mechanical, electrical, thermal and optical properties, and a high specific surface area. Chemically modified graphene (CMGs) and their colloidal suspensions allow them to be used in polymer composites, ultra-high capacitors, hydrogen storage materials, rechargeable batteries, conducting inks, thermal management, and chemical/biosensors [2,12].

Natural vein graphite can be categorized into four main structurally distinct varieties, which are namely: needle platy graphite (NPG); shiny slippery fibrous (SSF); coarse flake of radial (CFR); and coarse striated flaky (CSF) graphite [4,5]. Among these four varieties, NPG has the highest natural purity of around 99% [1]. NPG graphite typically exists in the mid-area of graphite veins and it can easily be separated manually.

While the production of graphene oxide (GO) and reduced graphene oxide (rGO) have been typically created from synthetic and flake graphite, high purity natural vein graphite has yet to be utilized fully. Therefore, the objective of the present study was to synthesize GO and rGO from high purity NPG variety of natural vein graphite by developing feasible and cost-effective methods.

2. Experimental

For the present study, improved Hummer's method was used to produce GO [3]. NPG variety of Sri Lankan vein graphite was used as the starting material. All the acids (98% H_2SO_4 and 85% H_3PO_4), oxidizing agents (KMnO_4 and 40% H_2O_2), 99.8% *N,N*-dimethylformamide (DMF) and 65% hydrazine monohydrate used for this study were purchased from Sigma-Aldrich.

Preparation of graphene oxide (GO) was carried out using chemical oxidation method, and for that 3 g of NPG were mixed with 18 g of KMnO_4 , and 360 ml of 98% H_2SO_4 and 40 ml of 85% H_3PO_4 [9,13]. Then the mixture was stirred at 60 °C for 12 h and allowed to cool down to 30 °C. Then 4 ml of H_2O_2 was added into a separate beaker with 250 ml of deionized water and the prepared graphite mixture was added slowly into this beaker while stirring. The mixture was allowed to settle by keeping for six hours. Finally, the prepared sample was filtered and dried in a vacuum oven at 60 °C for 2 h [14,15]. Reduced graphene oxide (rGO) was prepared using 1 g of GO synthesized under the previous step. The GO sample was sonicated with 40 ml of *N,N*-dimethylformamide (DMF) for 1 h. Then it was stirred with 10 ml of hydrazine monohydrate at 80 °C for 12 h. Finally, the sample was washed with distilled water until the pH became 7 and then dried in a vacuum oven at 60 °C for 2 h.

The prepared materials were characterized by powder X-ray diffraction (XRD) (Rigaku-Ultima IV X-ray diffractometer) with a step size 0.02° and Cu $\text{K}\alpha 1$ radiation to evaluate the expansion of graphite layers. The morphology of the samples was analyzed by atomic force microscope (AFM) (Nanoscope Multimode 8) with the silicon nitride cantilevers with the ring constant of 0.4 N/m. The surface of the samples was studied by EVO/LS 15 ZEISS scanning electron microscopy (SEM). High-resolution transmittance electron microscopy (HRTEM) images were obtained by a JEM-2100 electron microscope, at an accelerating voltage of 200 kV. Specimens were prepared by dispersing powders in ethanol to form a suspension, and followed by ultrasonication for 1 h. The high-resolution images of periodic structures were analyzed and filtered by the fast Fourier transformation (FFT) method. The FTIR spectra were measured using Fourier transform infrared (FTIR) spectrophotometer (Nicolet 6700) with attenuated total reflectance to analyze functional groups attached to graphite surface. The elemental composition of the material surface was studied by PHI 5000 X-ray

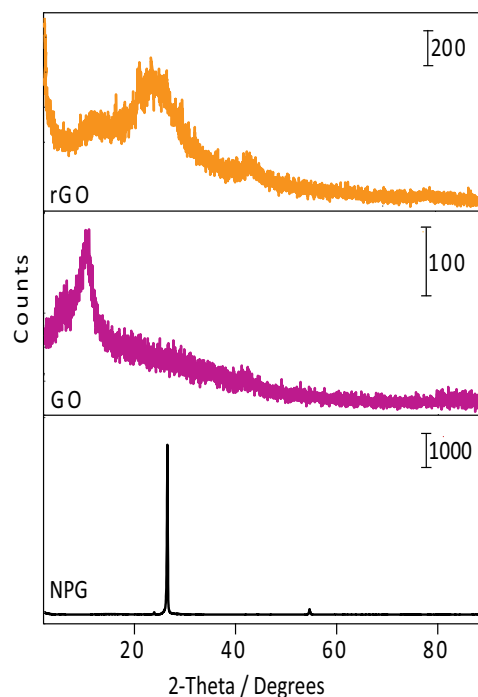


Fig. 1. X-ray diffractograms obtained on rGO, GO, and NPG.

photoelectron spectroscopy (XPS) Al-Mg anode. The samples were dried in vacuum before obtaining measurements.

3. Results and discussion

The X-ray diffractograms (XRD) obtained for NPG, GO, and rGO samples are shown in Fig. 1. The corresponding diffraction peaks were identified by comparing with the standard JCPDS data of graphite (JCPDS no. 23-64) [16,17].

The sharp diffraction peak appeared at $2\theta = 26.6^\circ$ of NPG vein graphite variety confirms the existence of graphite phase [17,18]. Further, the existence of a sharp, narrow peak with the absence of any residual phase seen in this diffractogram of NPG, indicates that this graphite is highly crystalline, and has very high purity, and lacks of mineral inclusions [19]. This can be due to the fact that the NPG is found in the middle part of the graphite vein. Thus, there is a high possibility for the existence of highly crystalline graphite with higher purity, because of less influence from the wall rock. Formation of GO leads to the expansion of graphite layers during the oxidation process [20–22]. Once the oxidation process is completed, the crystal structure has changed while oxygen-containing functional groups have been introduced into interlayers [23].

As seen in Fig. 1, the major peak of GO has shifted to the left compared to that of NPG, indicating an expansion of the interlayer space of graphite. It indicates that the method used in the present study can produce highly oxidized GO from NPG. Our resulted GO exhibits its major peak at $2\theta = 10.23^\circ$ with the interlayer spacing of 0.866 nm of (001) plane [21,23,24]. This major peak is a broad peak typical to GO and this type of peak broadening in the diffractograms can be observed in GO and rGO, due to the decrease of the crystal size into the nanoscale during the synthesis process. Further, in the X-ray diffractogram of the rGO sample, the main diffraction peak appears at $2\theta = 25.36^\circ$ with a corresponding interlayer spacing of 0.350 nm. It indicates a successful reduction of GO into rGO. This broad peak indicated that the rGO nanosheets are exfoliated into a monolayer or of few layers of rGO and resulted in a new lattice structure which is significantly different from the NPG and GO [18,25]. These results indicate that the pre-exfoliation of vein graphite directed to the dif-

Download English Version:

<https://daneshyari.com/en/article/5348267>

Download Persian Version:

<https://daneshyari.com/article/5348267>

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