NEW CARBON MATERIALS
Volume 32, Issue 2, Apr 2017
Online English edition of the Chinese language journal

Available online at www.sciencedirect.com
ScienceDirect

Cite this article as: New Carbon Materials, 2017, 32(2): 174-187

RESEARCH PAPER

Effect of graphite/sodium nitrate ratio and reaction time on the physicochemical properties of graphene oxide

Edwin T. Mombeshora[1], Patrick G. Ndungu[2], Vincent O. Nyamori[1,*]

[1] School Chemistry and Physics, University of KwaZulu-Natal, Westville Campus, Private Bag X54001, Durban, 4000, South Africa;

[2] Department of Applied Chemistry, University of Johannesburg, P.O. Box 17011, Doornfontein, Johannesburg, 2028, South Africa

Abstract: Graphene oxide (GO) was synthesized by the reaction of graphite with sodium nitrate and the graphite/sodium nitrate mass ratio and the reaction time were varied in order to obtain the highest oxygen content. The GO was characterized by TEM, SEM, AFM, XRD, FT-IR, TGA, elemental analysis, and UV-vis and Raman spectroscopy. The effect of oxygen content on the physicochemical properties of GO was investigated. Results indicate that increasing the graphite to sodium nitrate ratio increases the oxygen content, BET surface area, pore volume and pore size but reduces the crystallite size of the GO samples. However, the oxygen content of GO is not directly related to the reaction time. Physicochemical properties such as d-spacing and defect density increase with increasing oxygen content while the thermal stability decreases. The physicochemical properties such as oxygen content, crystallinity, thermal stability and structure can be tailored by varying the graphite/sodium nitrate ratio and reaction time.

Key Words: Graphene oxide; Oxygen content; Reaction time; Carbon; Hummer's method

1 Introduction

Graphene, a two dimensional single atomic layer of sp^2 carbon atoms, is one of the thinnest material and there have been numerous reports in the literatures since its discovery [1,2]. The most focused aspect of graphene in these reports is electronic properties even though there are some biomedical [3] and hydrogen storage [4] applications in literatures. Graphene has found numerous applications as both electron and hole transport layer in solar cells [5-13], as additives in batteries [14-16], components for field emission cathodes [17-19], transistors [20] and as electrochemical capacitors [2]. Single layer of graphene was initially made via mechanical separation of graphite sheets [1]. However, availability of graphene oxide in solution has enabled functionalization, characterization and processing of graphene layers through numerous solution-based techniques [21]. This is facilitated by ionizability and hydrophilicity of most oxygen moieties on GO sheets [22].

The chemical routes, especially the modified Hummers methods, are the most popularly utilized in graphene synthesis [1,23-26]. The chemical route is easy, scalable and associated with reasonable costs [24,27-29]. The structural properties of graphene from GO has attracted much attention owing to their influence on quantum Hall effect, sensitivity, mechanical hardness, hydrophilicity, sheet size, defects and electrical conductivity amongst others [23,24,27,30,31]. For instance, even though GO from chemical oxidation is a suitable precursor of graphene, oxidation reduces conductivity but enhances exfoliation in water under ultrasonic condition [24]. Additionally, in practice GO can only be partially reduced to form graphene-like sheets, i.e. only partial restoration of the conjugation system is achieved [25]. Therefore, it is critical to select suitable graphene synthesis parameters on the basis of intended applications.

The main role of $NaNO_3$ in the Hummers methods is oxidizing effect [32], it aids H_2SO_4 and $KMnO_4$. Additionally, H_2O_2 also has an oxidizing effect via its decomposition to active oxygen atoms that oxidize graphite in the presence of H_2SO_4 [32]. Also, H_2O_2 reduces residual permanganate and manganese dioxide to a colourless manganese sulfate during the reactions. More research is still needed in understanding the synthesis routes for a number of reasons such as the exact GO structure elucidation [23,33] and the elimination of sodium nitrate because it generates toxic gases, NO_2 and N_2O_2. The main reason, amongst others, is the sample variation due to different synthesis parameters and therefore lack of standardized products [33]. This study brings out some insights into controllable oxidation of graphite to GO. Also, a few studies have been dedicated to synthesis conditions. Similar studies were done on effect of oxidation time on graphite exfoliation using perchloric and nitric acids, and potassium chromate [29]. Wu [28] investigated the effect of sodium nitrate to potassium permanganate ratio on GO yield under a fixed

Received date: 10 Dec. 2016; **Revised date:** 10 Feb. 2017
***Corresponding author.** E-mail: nyamori@ukzn.ac.za
Copyright©2017, Institute of Coal Chemistry, Chinese Academy of Sciences. Published by Elsevier Limited. All rights reserved.
Supplementary data associated with this article can be found in the online version.
DOI: 10.1016/S1872-5805(17)60114-8

graphite amount. They proposed that to form GO, Na^+ and NO_3^- are initially intercalated (equation 1) followed by reaction of expandable graphite with diamanganese heptoxide i.e. oxygen containing moieties from the $KMnO_4$ hydrolysis [33] (equation 3).

$$C_{(graphite)} + NaNO_3 \rightarrow C_{NaNO_3} \qquad (1)$$

$$4\,KMnO_4 + 2H_2O \rightarrow 4KOH + 4MnO_2 + 3O_2 \qquad (2)$$

$$C_{NaNO_3} + nO_2 \rightarrow GO \qquad (3)$$

This hints on the importance of the ratio of graphite to sodium nitrate in the synthesis of GO. This work highlights that the initial step in GO synthesis is affected by graphite to sodium nitrate ratio. Hence, the study elaborates the outcomes when either sodium nitrate or graphite mass was in excess or when it was the same. The influence of reaction duration on the physicochemical properties of GO is also explained.

2 Experimental

2.1 Materials

The procurement of graphite powder (< 150 μm, 99.99%) was from Sigma Aldrich, USA. $KMnO_4$ (99%) and NaNO3 (99%) were both purchased from Associated Chemical Enterprise, South Africa. H_2SO_4 (98.37%, C.C. Imelmann Ltd, South Africa) was used as-received without dilution and H_2O_2 (30%, Merck ltd, South Africa) was diluted to the required concentrations in the respective methods as stated in the subsequent procedures. The product was washed with double deionized water (DI).

2.2 Method

In the general procedure, graphite was added to a round-bottomed flask with H_2SO_4 (98%, 12 mL) cooled in an ice water bath and stirred. After the mixture was stirred for a few minutes, sodium nitrate was added and stirred further for 30 min. Thereafter, to the mixture, $KMnO_4$ (1.5 g) was slowly added while maintaining the temperature below 10 °C. Afterwards, the reaction mixture was further stirred at room temperature for the required duration and DI (15 mL) was added slowly. The reaction temperature was raised to 98 °C and maintained for a specified time under stirring. H_2O_2 (30%, 50 mL) was added to the mixture prior to several cycles of washing using DI until the filtrate was neutral. The samples were dried at 50 °C for 48 h. The samples used to investigate effect of graphite/sodium nitrate ratios, i.e. 2:1, 1:1 and 1:2, were named as G2N1-$t_{12,24}$, G1N1-$t_{12,24}$ and G1N2-$t_{12,24}$, respectively. Where $t_{12,24}$ in this case means each sample was stirred for 12 h at room temperature and 24 h at 98 °C. Another series of samples with graphite/sodium nitrate ratios of 1:1 were synthesised and used to study the effect of reaction times. They were named as G1N1-$t_{3,3}$, G1N1-$t_{6,12}$, G1N1-$t_{12,12}$, G1N1-$t_{12,24}$, where the subscript t and the two sets of numbers refers to the reaction time in mimutes at room temperature and at 98 °C, respectively.

Similarly, samples G2N1-$t_{0,0.25}$ and G1N1-$t_{3,0}$ were synthesised as above, however with some slight variations, i.e. as for G1N1-$t_{3,0}$, the graphite/sodium nitrate ratio was 1:1 and the mixture was heated for 3 h at 35 °C. Thereafter, 3% H_2O_2 (150 mL) was added slowly followed by stirring for 30 min. This was done to investigate outcomes when reaction at room temperature in the previous series was changed to 35 °C, a lower temperature without ramping to 98 °C. Whereas for G2N1-$t_{0,0.25}$, the graphite/sodium nitrate ratio was 2:1 and the temperature of the mixture was raised to 50 °C. Thereafter, it was ramped to 98 °C and maintained at this temperature for 15 min. The reason for this case was to determine outcomes when reaction at room temperature in the previous series was changed to 50 °C, an intermediate temperature before reaction at 98 °C for a short time of 15 min.

2.3 Materials characterization

Structures of the GO were examined with transmission electron microscopy (TEM, JEOL TEM 1010 transmission electron microscope) and scanning electron microscopy (SEM, JEOL JSM 6100 microscope). The GO sheet roughness was analysed using an atomic force microscopy (AFM, Bruker Inova) in the tapping mode and in the micron level using as-synthesized sheets without use of a substrate. Images were captured and processed using the Nano Drive software and Nanoscope analysis, respectively. The crystal structures of the GO samples were characterized by means of an X-ray diffractometer (Rigaku MiniFlex 600). The graphitic crystal quality was analyzed by Raman spectroscopy (100 mW Delta Nu Advantage 532TM spectrometer of 10 cm^{-1} resolution with a 2D CCD detector and grating lines were 1 800 mm^{-1} with a laser source (Nd:YAG) at wavelength of 532 nm). Thermal stability analyses were done with a TGA thermal analyser (TA Instruments Q seriesTM Thermal Analyser DSC/TGA (Q600) with TA instruments Universal Analysis 2 000 software for data acquisition and analysis) from room temperature to 1 000 °C. Absorption characteristics were investigated with a UV-Vis spectrometer (Perkin Elmer Lambda 35 double beam spectrometer with FL Winlab software) and infra-red transmission spectra were taken by a Perkin Elmer spectrometer (Perkin Elmer spectrum 100 series with universal ATR accessory). Samples were prepared for textural characterization by degassing at 90 °C for one hour then at 200 °C for 10 h. Nitrogen sorption analyses were done using a Micrometrics TRI STAR 3020V1.03 (V1.03) instrument at 77 K in nitrogen. Elemental compositions were determined by use of a LECO CHNS-932 elemental analyzer standardized with acetanilide.

Download English Version:

https://daneshyari.com/en/article/7954316

Download Persian Version:

https://daneshyari.com/article/7954316

Daneshyari.com