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Full Length Article

Controlled synthesis, characterization and reduction of graphene oxide:
A convenient method for large scale productionTarko Fentaw Emiru^a, Delele Worku Ayele^{a,b,c,*}^a Material Science and Engineering Program, College of Science, Bahir Dar University, P.O. Box 79, Bahir Dar, Ethiopia^b Department of Chemistry, College of Science, Bahir Dar University, P.O. Box 79, Bahir Dar, Ethiopia^c Energy Research Center, Bahir Dar Institute of Technology, Bahir Dar University, P.O. Box 79, Bahir Dar, Ethiopia

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ABSTRACT

In this work, graphene oxide was synthesized by treating graphite powder with KMnO_4 and a mixture of concentrated $\text{H}_2\text{SO}_4/\text{H}_3\text{PO}_4$ and reduced with ascorbic acid to produce reduced graphene oxide. The effects of reaction parameters such as reaction time, reaction temperature and amount of KMnO_4 on the degree of oxidation of graphite powder to graphene oxide were studied. The prepared graphene oxide and reduced graphene oxide were characterized by UV-Visible spectroscopy, FT-IR spectroscopy, and XRD. The results showed that treating graphite powder with KMnO_4 at 40 °C for 12 h resulted in better degree of oxidation. The designed synthesis strategy could be simple/convenient, easily controlled and an alternative approach for large scale production of graphene oxide (GO) and reduced graphene oxide (rGO).

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Introduction

Graphene related materials have so many potential applications such as light weight, thin, flexible, durable display screens and electric circuits, super capacitors [1], transistors [2], transparent conducting electrodes for the replacement of ITO, conductive polymer composite [3], energy storage materials due to having an extremely high surface area [4], and solar cells [5]. However, there is a challenge of producing high quality graphene in large quantity using low cost and environmental friendly method. Among graphene synthesizing mechanisms, mechanical exfoliation [6] can produce the pristine graphene. But, the process is complicated and the product is small size, which is limited for large scale quantities. CVD [7,8] also allows production of large area graphene films of single to few-layers. However, it requires high temperature up to 1000 °C along with a hydrocarbon gas flow as precursor and pure hydrogen as a carrier gas, which limits the application range. Epitaxial growth [9] can also produce graphene with perfect structure (defect free) and excellent properties but the products are small-size and are difficult to assemble into films. In addition, requirement of high energy limits its application for large scale production. Chemical method is the prominent method of produc-

ing graphene based materials in large quantity [10]. However, the well-known chemical synthesis methods such as Brodie method [11], Staudenmaier method [12] and Hummer's method [13] were hazardous and toxic since ClO_2 and NO_2 evolves during the process. The Tour method (improved green synthesis method) is the one that is relatively safe (environmental friendly) [14]. In addition, the final yield is much higher than the former methods. This method describes that GO is synthesized by treating graphite powder with H_3PO_4 , H_2SO_4 and high quantity of KMnO_4 . However, the influence of the quantity of KMnO_4 , reaction time, and the temperature on graphite oxide preparation was not clear.

In this work, we prepared graphene oxide by easy, cost effective and convenient method via treating graphite powder with KMnO_4 and a 9:1 mixture of concentrated $\text{H}_2\text{SO}_4/\text{H}_3\text{PO}_4$ as oxidant. Moreover, reduction of graphene oxide (GO) to produce reduced graphene oxide (rGO) was carried out using anon-toxic reducing agent, ascorbic acid (AA). To optimize the oxidation level, the effects of KMnO_4 , reaction time and reaction temperature were studied. Graphene oxide and reduced graphene oxide were characterized by visual inspection, UV-Visible spectroscopy, FT-IR spectroscopy, and XRD.

The route to prepare rGO involves three steps. Firstly, graphite powder is oxidized to graphite oxide, which can be dispersed in water or another polar solvent due to the presence of hydroxyl and epoxide groups across the basal planes of graphite oxide and carboxyl groups located at the edges [13]. Secondly, graphite oxide

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can be exfoliated either by sonication or mechanical stirring to form few or single layer graphene oxide sheets [6]. Thirdly, graphene oxide is reduced by removing oxygen containing functional groups.

Experimental

Chemicals

Graphite powder and H₂SO₄ (98 wt%), Potassium Permanganate (KMnO₄), H₃PO₄ (85 wt%), Hydrochloric acid (HC 35 wt%), barium chloride (BaCl₂), (C₆H₈O₆) and H₂O₂ (30%), CH₃CH₂OH (Assay; 97%). All reactants and solvents have been used without further purification.

Synthesis of graphite oxide

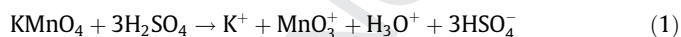
For a typical synthesis of graphite oxide, a mixture of 96 ml of concentrated H₂SO₄ and 10.7 ml of concentrated H₃PO₄ (9:1 volume ratio) was prepared. The mixture of these acids was poured slowly into the mixture of 0.6 g graphite powder and 4.8 g potassium permanganate (1:8) in a beaker under stirring with glass rod. The reaction was then heated to 40 °C controlled by water bath and stirred for 12 h. Then, the mixture was added into 250 ml of de-ionized water to stop the reaction. Following that 15 ml of H₂O₂ was added into the mixture. The addition of H₂O₂ resulted in yellow color, indicating high level of oxidation. The solution was then filtered to remove metal ions using filter paper and funnel. A yellow paste was produced. The paste was washed with 5% HCl aqueous solution using centrifuge until SO₄²⁻ was removed completely. The removal of SO₄²⁻ was detected by addition of barium chloride where the presence of sulfate ion showed a white precipitate when barium chloride was added to the supernatant. The supernatant was decanted away and the remaining solid material was collected. Then the mixture was washed multiple times with de-ionized water using centrifuge until the pH of the supernatant was neutral. Finally the material was dried at 50 °C for 24 h and a brown black sample was obtained.

Preparation of graphene oxide

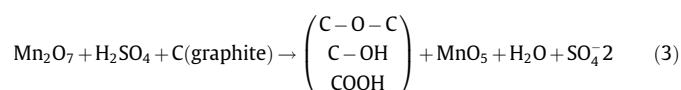
For a typical preparation of graphene oxide solution, 0.5 g of graphene oxide solid sample was grounded with mortar and pestle. The powder was dispersed in de-ionized water and stirred with magnetic stirrer at 60 °C for 12 h.

Formation mechanism of grapheneoxide

The active species to oxidize graphite is diamanganese heptoxide (Mn₂O₇) which is obtained via the reaction of monometallic tetra oxide and MnO₃⁺ as shown in the reaction 1 below [15].



The transformation of MnO₄⁻ into a more reactive form Mn₂O₇ will certainly help oxidize graphite powder as shown in the reaction below [16].



But the bimetallic form of manganese oxide has been reported to detonate when heated up to 55 °C temperature or when reacted with organic compounds [15].

Reduction of graphene oxide

Graphene oxide was reduced by using ascorbic acid (C₆H₈O₆). 5 g ascorbic acid was added to the GO solution and stirred with magnetic stirrer for 30 min at 60 °C. The product was centrifuged to remove the supernatant. Then, excess H₂O₂ was added to the black paste to oxidize the unreacted ascorbic acid by stirring for 30 min at 60 °C. After stirring, the resulted black product was collected by centrifugation and washed with ethanol and water 3 times respectively and then dried at 100 °C for 24 h.

The proposed mechanism for reduction of GO by ascorbic acid

The epoxy groups of GO can be easily attacked by nucleophilic reagents, resulting in a nucleophilic substitution reaction to open the epoxy rings [17]. It is supposed that ascorbic acid donates proton and electron to graphene oxide. It opens the epoxide rings and converts to easily leaving group (OH) and finally dehydrates, leaving a graphene sheet. To remove the OH group it is believed that ascorbic acid donates one proton to the OH group and finally dehydrates.

Designation of the prepared samples

GO1, GO2, GO3 and GO4 were graphene oxide samples. These samples were synthesized by taking the same amount of graphene powder, for the same reaction time and at the same reaction temperature. But, the concentration of KMnO₄ was varied.

GO5 and GO6 were graphene oxide samples. These samples were synthesized by taking the same amount of graphene powder, the same amount of KMnO₄ and for the same reaction time. But the reaction temperature was varied.

GO7, GO8, GO9 and GO10 were graphene oxide samples synthesized by taking the same amount of graphene powder, the same amount of KMnO₄ and at the same reaction temperature. But the reaction time was varied. The parameters and designations of the prepared samples are shown in the Table 1 below.

Characterization techniques

UV-Visible spectroscopy was used in detection of the conjugation network and absorption of GO and rGO. Double beam Lambda 35 UV-Vis spectrophotometer (Perkin Elmer, USA) was used to obtain the absorption spectra of GO and rGO. The GO and rGO solution samples were scanned for wavelength range from 200 to 800 nm. FTIR (Perkin Elmer, USA) was employed to analyze the presence/absence of functional groups on GO and rGO sheets. GO and rGO pellets were prepared using KBr and the samples were scanned in the range from 400 cm⁻¹ to 4000 cm⁻¹ to obtain the FTIR spectra. The X-ray diffraction (XRD) patterns of graphene, GO and rGO powders were recorded with a scanning rate of 1° per minute in a 2θ range from 10° to 80° with Cu Kα radiation (λ = 1.5418 Å) to characterize the inter layer spacing. It was done at 40 keV and 30 mA.

Result and discussion

Visual observations

Formation of graphene oxide was preliminarily well known by changing of color as shown in Fig. 1(E). Initially, when the mixture of acids was added slowly into the mixture of graphene powder and potassium permanganate, it produced a dark green color with a slight exothermic to 30–40 °C as shown in the Fig. 1(A). The dark green color seems to indicate that Mn₂O₇ was formed. As the reac-

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