

SYNTHESIS OF GRAPHENE FROM GRAPHITE OXIDE AND ITS
APPLICATION IN WATER PURIFICATIONChandrakant L. Tumbade¹ and Dr. G. R. Dhokane²¹Department of Physics, Shri. R.L.T. College of Science, Akola.²Department of Physics, Arts, Science and Commerce College, Chikhaldara Dist. Amravati.

ABSTRACT

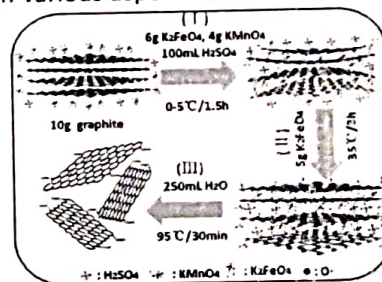
This paper describes method for the synthesis of graphene and Graphite oxide (GO) was effectively prepared by Hummers and Offeman method and it possesses different types of oxygen functionalities which allows GO. The GO was reduced by hydrazine hydrate and sodium borohydride as reducing agents to obtain graphene as end product. Characterization of both GO and G was carried out by SEM, TEM, UV-Vis spectroscopy and FTIR. Due to this the sp^3 hybridization of GO will convert to sp^2 hybridization by removing oxygen from GO. This quick and cost-effective technique used in water filter for purification of water.

KEYWORDS: carbon, graphite powder, composites, graphene, water purification .

INTRODUCTION

Materials determine our environment and their studies help in understanding the nature. Carbon being the prominent and quite easily available element is considered as the chemical basis of all known life. Carbon has been the most versatile material used for water purification in history [1-2]. Very early account of the use of charcoal in water purification is found in the Vedic literature [3]. It is believed that people of Indus valley civilization used carbon and porous materials, such as earthen vessels, for filtering and storing drinking water. The most widely used material for water purification today is activated carbon [4-8] derived from plant sources. It has the best possible surface area and could be produced at low cost, making it the most affordable adsorption medium in diverse applications. A number of other forms of carbon have appeared with very large adsorption capacities [9]. Advanced techniques such as membrane filtration, reverse osmosis and ion-exchange can be used in treatment and removal of contaminants from water [10-11]. However, higher cost limits the large scale application of such treatment techniques in developing countries.

One of the fascinating new additions into the carbon family is Graphene, the one-atom thick sheets of carbon [12]. Carbon materials, such as activated carbon, charcoal, carbon nanotubes [13-15], have been used extensively in water purification [16] and, hence, are indispensable components of all commercial water technologies [17-18]. It is natural to look at the application of graphene in various aspects of environmental remediation. Graphene is the first stable two-dimensional crystal, discovered in 2004. Since then, this new nanomaterial has been the object of a large interest due to its peculiar and intriguing properties [12]. It has attracted great interest because of its advantageous material properties, including high charge mobility, transparency, mechanical strength and flexibility [19]. An ideal graphene consists entirely of sp^2 -hybridized carbon atoms due to this reason graphene have emerged as a "shining star" in materials science [20]. When sp^2 -carbon atoms are arranged into two-dimensional fused hexagons, they form a single-



atom-thick allotrope of carbon called graphene. The covalent bonds between nearest-neighbour carbon atoms in graphene are formed by sp^2 -hybridised orbitals. These strong bonds give graphene its extraordinary mechanical strength, making it possible to have stable free-standing graphene, being only one atomic layer thick [21]. Various methods have been developed to prepare individual graphene, such as chemical vapor deposition (CVD), micromechanical exfoliation of graphite and epitaxial growth on electrically insulating surfaces and many more. However, chemical reduction of graphite oxide colloidal suspensions has been considered as an effective route to synthesize graphene sheets due to its simplicity, reliability, ability for large-scale production and exceptionally low price [22]. The method for production of graphene is the oxidation of graphite to graphite oxide which can be easily exfoliated into graphene oxide (GO) layers in solution [23] and readily converted back to graphene by chemical reduction [24-25]. A simple classification as followed using reducing agents as hydroquinone [26], dimethylhydrazine [23], sodium borohydride [27], sulfur containing compounds [28], aluminum powder [29], performing under various conditions *i.e.* acid/alkali [30], thermal treatment [31] and others like microwave [32], sonochemical [33] and so on. These different reduction methods result in graphene with different properties. For instance, large-scale production of aqueous graphene dispersion can be easily realized by using hydrazine [34] to reduced graphene oxide without the surfactant stabilizers [35].

EXPERIMENTAL

Graphite powder was received from Sigma-Aldrich. Concentrated sulfuric acid (98% H_2SO_4 , GR grade), potassium permanganate ($KMnO_4$ purified) and hydrogen peroxide solution (30% H_2O_2), sodium carbonate ($NaCO_3$, pure), hydrochloric acid (35% HCl, GR grade) were received from MERCK private limited. Sodium nitrite ($NaNO_2$, extrapure), sulphanic acid ($C_6H_5NO_3$, AR grade) was received from HIMEDIA Company. Sodium Borohydride ($NaBH_4$, AR grade) was received from RANKEM and hydrazine hydrate (80% N_2H_5OH , AR grade) was received from CDH private limited as reducing agent. Soap solution and aquaregia was used to clean the apparatus, while MilliQ water was used to rinse the apparatus and also used throughout the experiment.

SYNTHESIS OF GRAPHITE OXIDE

The synthesis of graphite oxide from graphite powder was carried out by using Hummers and Offeman method [36]. Briefly given as: 23 mL of 98% concentrated H_2SO_4 was cooled down below $0^\circ C$ in ice bath for 30-40 min. separately, 1 g of graphite powder and 0.5 g of $NaNO_2$ was mixed together. This mixture was then added to cool concentrated H_2SO_4 and kept on constant stirring in an ice bath for 50 min so that the chemicals get sufficient time to get mix with each other. Then after, 3 g of $KMnO_4$ was added slowly and gradually to solution, the solution color immediately turned greenish black in color from black, resulting in oxidation by maintaining the temperature of the solution below $20^\circ C$ with constant stirring for 15 min. removed the solution from the ice bath and allowed to attain the room temperature. After the room temperature was attained the solution was kept under oil-bath with constant stirring and the solution color changes to brown in color. 135 mL of MilliQ water was added followed by addition of 15 mL of 30% H_2O_2 solution to terminate the reaction and kept on stirring for 15 min where dark brown color was observed in the solution. The solution was kept to settle down for overnight and was centrifuged to obtain the product. Washed solid product several times with 5% of HCl solution to remove impurities and sulfate ions where absence of sulfate ions was detected by using 0.2 M $BaCl_2$ solution. The product was then vacuum dried using Rota vapor at 40 to $50^\circ C$ to obtain dried product as graphite oxide (GO).

SYNTHESIS OF GRAPHENE

70 mg of above prepared GO was dispersed in 70 g of MilliQ water, the dispersion was then sonicated for 1 h, clear brown colored solution was obtained. Then the pH of solution was adjusted by addition of 5% sodium carbonate solution up to 10. Separately, 600 mg of sodium borohydride solution was obtained by adding 600 mg of $NaBH_4$ in 15 gm of MilliQ water and was added to the above prepared

dispersion. And kept the aqueous mixture under oil-bath at 75 °C for 1 h with constant stirring. Centrifuged and washed the mixture repeatedly with MilliQ water. Partially reduced graphene solution and change in color from brown to black was observed. Again redispersed the above obtained product into 75 g of MilliQ water and sonicated for few minutes to get properly dispersed solution. Then 45 mg of sulphanic acid and 18 mg of sodium nitrite was mixed in 10 g of water in a beaker and 0.5 g of 1N HCl solution was taken in separate beaker. Both the beakers were kept in ice-bath to lower down the temperature of solutions. Then both solutions were mixed together and aryl diazonium salt of orange colored solution was obtained. This mixture was then added to the above dispersed solution which was kept in ice-bath with constant stirring for 2 h. Bubbles were expelled from the mixture after addition of diazonium salt solution. Again the mixture was centrifuged and washed several times with MilliQ water to remove impurities and redispersed in 75 g of MilliQ water. And in the last step 2 g of hydrazine hydrate in 5 g of MilliQ water was added to the dispersed solution and kept on stirring for 20 h at 90 °C. It was observed that after every 45 min of stirring and heating at 90 °C, the water starts evaporating so MilliQ water was added to maintain the required volume of mixture till the reaction was completed. Centrifuged the obtained product and washed several times with MilliQ water and complete removal of sulfate ions were confirmed till we get clear solution without turbidity using 5% sodium carbonate solution [37].

RESULTS AND DISCUSSION

In this work, we chemically synthesized GO using Hummers and Offeman method [36] with slight modification by using NaNO_2 . Among several chemical reductant reported [38-39] we choose hydrazine hydrate and sodium borohydride as reducing agents for the reduction of GO to G, which is the majority often used reductant due to its simple reduction procedure and generation of highly reduced graphene oxide with excellent physical properties [40].

Powder sample of GO was observed in brown color and of graphene were observed in black color. A scanning electron microscope (SEM) image of GO shows flakes like structures in Figure 1(B). The transmission electron microscope (TEM) in Figure 1(C) represents graphene sheets stacked on one another at lower resolution. At higher resolution Figure 1(D) shows the magnified TEM image of Figure 1(C) and HRTEM image of Figure 1(E) clearly shows crystal planes of graphene.

Chemical analysis of GO and G was carried out by using UV-Vis spectroscopy and fourier transform infrared spectroscopy (FTIR). The UV-Vis spectra of obtained GO as shown in Figure 1(A) shows band in the wavelength region of 990-1010 nm for GO and shows strongest band at 265 nm, medium band at 810 nm and weak band at 1075 nm. From SEM images *i.e.* Figure 1(B) flakes of GO was observed.

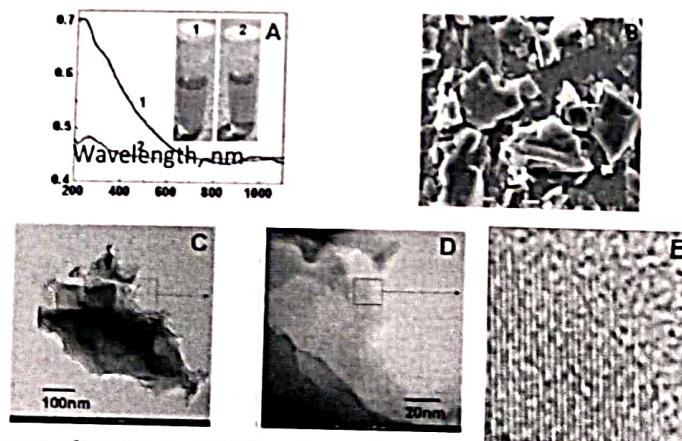


Figure 1. (A) UV-Vis spectra of GO (1) and G (2) and inset images shows digital pictures of GO (1) and G (2), (B) shows SEM image of GO, (C) represents lower resolution TEM image of G, (D) higher resolution of (C) and (E) shows HRTEM of (D)

From figure 2. (A) and (B) show the FTIR spectrum for the obtained GO (black) and G (red) in full range of wavenumbers (400-4000 cm^{-1}) and Close window (800-4000 cm^{-1}) respectively. The presence of different types of oxygen functionalities in GO was confirmed at 3425.90 cm^{-1} due to O-H stretching vibrations, at 1730.65 cm^{-1} observed stretching vibrations from C=O, at 1620.30 cm^{-1} , skeletal vibrations from unoxidized graphitic domains were observed and at 1058 cm^{-1} C-O stretching vibrations were analyzed [41]. Two strong peaks were observed in G, the one at 3430.40 cm^{-1} were due to O-H stretching vibrations of absorbed water molecules and structural OH groups, the other at 1164.11 cm^{-1} was of the C-O on the graphene[42].

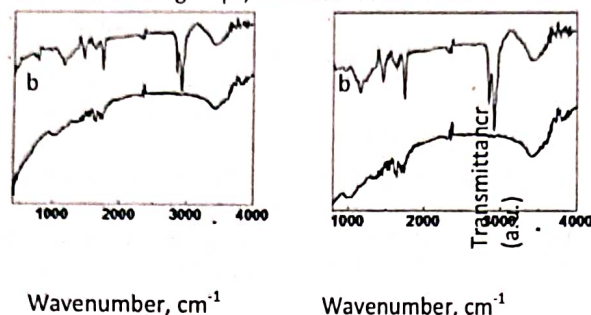


Figure 2. (A) Full range (400-4000 cm^{-1}) FTIR spectra of GO (black) and G (red), (B) Close window (800-4000 cm^{-1}) of FTIR spectra of GO (black) and G (red)

These observations indicated that oxygen-containing groups existed on the surface of graphene and during the oxidation process of the graphite powder in the concentrated sulfuric acid with potassium permanganate, the original extended conjugated *p*-orbital system of the graphite were destroyed and oxygen containing functional groups such as hydroxyl, carbonyl and carboxyl groups were inserted into the carbon skeleton [43]. Moreover, only the broad O-H and the C-O stretching bands were indicating that after a hydrazine reduction process, the GO had been successfully restored to graphene [44].

CONCLUSIONS

We prepared graphite oxide (GO) using Hummers and Offeman method [37] in which we changed in sodium nitrate. The preparation of graphene from graphite oxide was done by reduction of hydrazine hydrate instead of hydrazine as it is not stable compound and we obtained stacked graphene. This method is cheap to prepare graphene on large scale. Characterization was approved by using SEM, TEM, UV-Vis spectroscopy and FTIR where SEM gives clear image of formation of GO flakes. TEM images shows stacked graphene sheets and planes, UV-Vis spectra shows the peak at 265 nm and FTIR confirms the shifting of groups to form graphene from graphite oxide. Due to its versatility in properties it gives promising results for further application such as water purification used in water purifier. We expect that this work will add to understanding of next generation membranes for water purification.

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