

Modified Hummers Method for Synthesis of Graphene Oxide - Solvent Influence

Neena.P

Department of Physics,

Sree Narayana Mangalam College, Maliankara, Ernakulam, Kerala, India.

Abstract: The aim of this study is to identify influence of different solvents on the properties of graphene oxide. In this work, Graphene Oxide (GO) was synthesized by treating graphite powder with KMnO_4 and a mixture of concentrated H_2SO_4 and H_3PO_4 . The experiment is carried out at room temperature without NaNO_3 . 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. Graphene oxide powders prepared were dissolved into different solvents, namely acetone and ethanol. Both the samples were characterized by UV-Visible spectroscopy and FT-IR spectroscopy. The results showed that treating graphite powder with KMnO_4 at 40°C for 12 h resulted in better degree of oxidation.

Key words: graphene oxide, modified hummers method, functional groups.

I. INTRODUCTION

Graphene is a one atom thick structure of sp^2 bonded carbon atoms. Graphene has attracted fabulous research interest in energy-storage techniques. It has great mechanical strength, large specific area and high electrical conductivity. Chemical method is the prominent method of producing graphene based materials in large quantity [1]. However, the well-known chemical synthesis methods such as Brodie method [2], Staudenmaier method [3] and Hummer's method [4] 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) [5]. 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, influence of 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 H_2SO_4 and H_3PO_4 as oxidants. To optimize the oxidation level, the effects of KMnO_4 , reaction time and reaction temperature were studied.

II. EXPERIMENTAL

CHEMICALS

Graphite powder and H_2SO_4 (98 wt %), Potassium Permanganate (KMnO_4), H_3PO_4 (85 wt %), Hydrochloric acid (35 wt%), Barium Chloride (BaCl_2) and H_2O_2 . All reactants and solvents have been used without further purification.

SYNTHESIS OF GRAPHITE OXIDE

In the synthesis of graphite oxide a mixture of 96 ml of concentrated H_2SO_4 and 10.7 ml of concentrated H_3PO_4 (9:1) Volume ratio was prepared. The mixture of these acids were poured slowly into the mixture of 0.6 g graphite powder and 4.8g Potassium Permanganate (1:8) in a beaker under stirring with glass rod and was continued for 12 Hours with a magnetic stirrer. Then the mixture was added into 250 ml of de-ionized water to stop the reaction. Following that 15ml of H_2O_2 was added into the mixture. The addition of H_2O_2 resulted in yellow colour, 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 SO_4 was removed completely. The removal of SO_4 was detected by the addition of Barium chloride where the presence of sulphate ion (SO_4) 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 hrs and a brown black sample was obtained.

PREPARATION OF GRAPHENE OXIDE SOLUTION

To produce acetone graphene oxide (A-GO) and ethanol graphene oxide (E-GO) samples, 1 mg of GO were dissolve in 1 ml of acetone/ethanol solution (volume ratio 1:1) under ultrasonic for 1 hour. 100 μl of A-GO/E-GO solution were then dropped on silicon wafer and spin at 2000 rpm for 20 second. The coated samples were then heated on the hot-plate with 80°C for 10 minutes. This step was repeated for 10 times.

III. CHARACTERISATION TECHNIQUES

3.1. UV-Vis spectroscopy was used in detection of the conjugation network and absorption of graphene oxide in acetone and ethanol. Double beam Lambda UV-Vis spectrophotometer (UV-2600 Shimadzu) was used to obtain the absorption spectra of graphene oxide in acetone and ethanol. The A-GO and E-GO solution samples were scanned for wavelength range from 200 to 800 nm.

3.2. FTIR

FTIR (Perkin Elmer, USA) was employed to analyze the presence/absence of functional groups on A-GO and E-GO. A-GO and E-GO samples were prepared using KBr and scanned in the range from 400 cm^{-1} to 4000 cm^{-1} to obtain the FTIR spectra.

III. RESULTS AND DISCUSSION

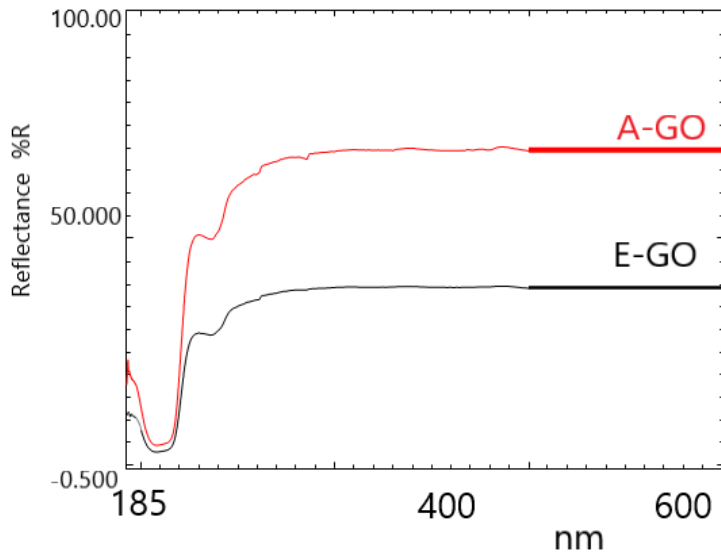


Figure 4.1. UV-Vis spectrum of graphene oxide samples

From figure 4.1, it is observed that graphene oxide shows maximum absorption peak at ~ 230 nm attributable to π - π^* transition of the atomic C-C bonds and shoulder peak at ~ 300 nm due to n - π^* transition of aromatic C-C bond [6].

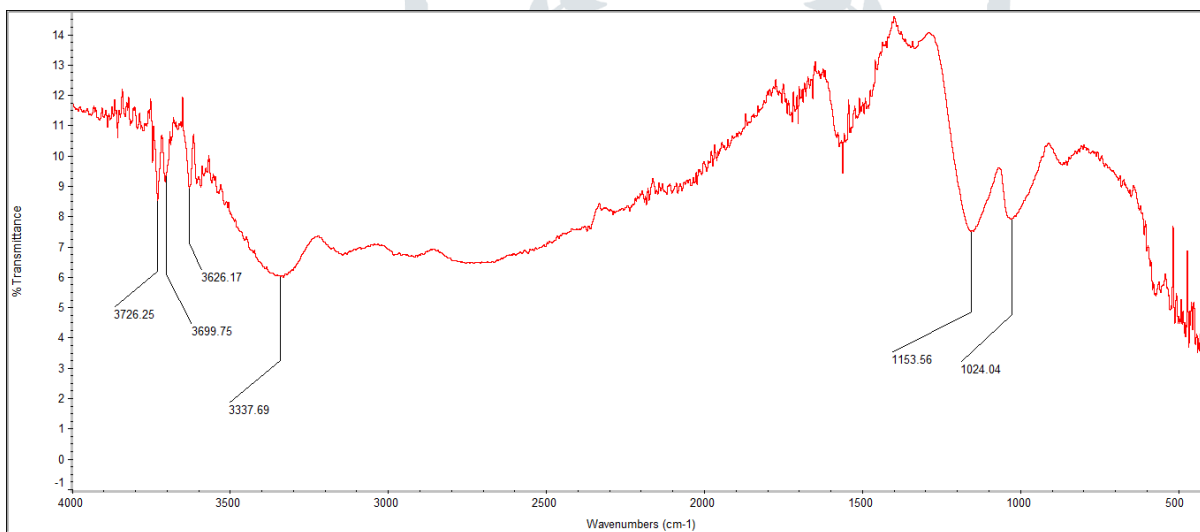


Figure 4.2.a. FTIR spectra of A-GO sample

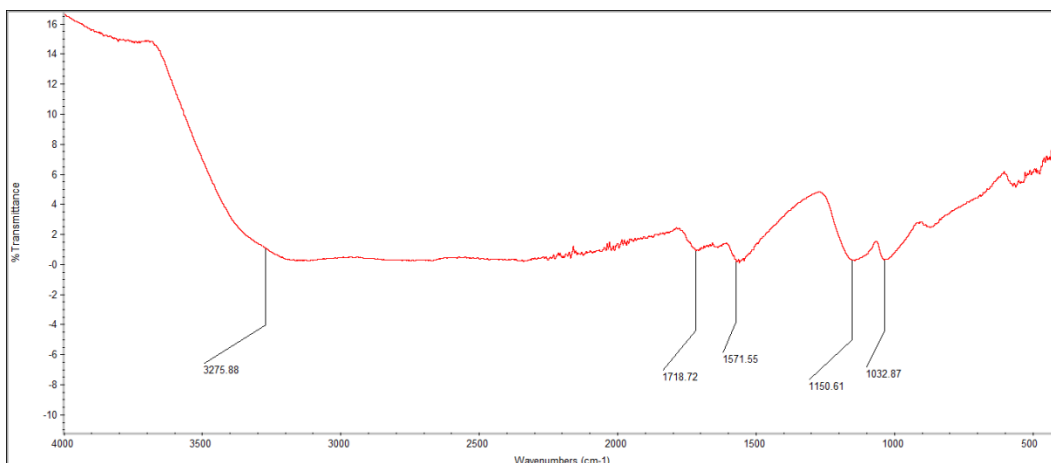


Figure 4.2.b. FTIR spectra of E-GO sample

FTIR spectra of A-GO and E-GO samples are shown in Figure.4.2a and 4.2.b. Investigation of bonding interactions in both samples is carried out by FTIR. The result clearly indicates that both A-GO and E-GO consist of carbonyl C=O, aromatic C=C, carboxyl CO, epoxy C-O-C and hydroxyl O-H [7,8]. The peak at 3275cm^{-1} corresponds to the O-H (hydroxyl) groups[9]. The band in between 2800cm^{-1} and 3275cm^{-1} represent the hydroxyl group in GO network. This reduces the intensity after a sulfanilic acid treatment[10]. The band between 3000cm^{-1} and 3800cm^{-1} represent as hydroxyl, as reported in previous work [11,12]. The peak between 2100cm^{-1} and 2300cm^{-1} relates to the peak for absorbed CO_2 molecules[13]. On the other hand, broad peak 1150.61cm^{-1} and 850.23cm^{-1} are corresponded to C=C bond (aromatic group)[7,13,14]. Moreover, the band between 1153.56cm^{-1} and 1024.04cm^{-1} corresponds to C-O-C (epoxy) groups [14]. All the peak shows the functional group existed in A-GO and E-GO samples.

V.CONCLUSION

The graphene oxide was synthesized by oxidizing purified natural flake graphite through modified Hummers method. UV-Vis spectrum of Graphene oxide shows maximum absorption peak at $\sim 257\text{nm}$ attributable to $\pi-\pi^*$ transition of the atomic C-C bonds. And the shoulder peak is at $\sim 300\text{nm}$ due to $n-\pi^*$ transitions of the aromatic C-C bonds. From FTIR studies, it has been proved that all peaks show the functional group existed in A-GO and E-GO samples. The graphite powder has been successfully oxidized with concentrated acid and KMnO_4 . In this approach an improved hummer's method is applied to produce graphene oxide, and is different from conventional hummer method of synthesis graphene oxide with NaNO_3 . It shows that, NaNO_3 does not affect the synthesis method to produce graphene oxide. Same characteristic of graphen oxide is obtained without using NaNO_3 . This method can decrease cost and further free toxic gases. Ethanol and acetone were used to perform the liquid medium of GO.

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