Graphene Oxide (Study & Applications)

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ABSTRACT

Nanomaterials are developed to take the advantage of their small size and noble properties. Carbon based nanomaterials has attracted a large interest, due to their wide applications in technical, medical, environmental, agriculture and in astronomy. Carbon nanomaterials, (Graphene oxide and reduced graphene oxide are synthesised and their applications are studied. Graphene oxide one of the derivative of wonder material graphene has been synthesised by using modified Hummers method which is then reduced to rGO, by chemical reduction. Both GO and rGO were characterised using FTIR, Raman, XRD, SEM etc techniques then their various applications as studied which includes Sensor, Adsorbent property and catalytic property attributed by their unique properties.

Key Words: FTIR, XRD, SEM and rGO etc.

INTRODUCTION

Graphene Oxide

From last decades, graphene oxide has become the one of the most intensively studied material. It commercially found it’s applications as being promising in energy storage, fuel cells and catalysis when it’s nano-composites are formed with several other metals. As graphene is expensive and relatively hard to produce, great efforts are made to find an in-expensive method to form the derivative of graphene i.e Graphene oxide. Graphene oxide is a 2-D material, formed after the oxidation of graphene with ‘O’clock functional groups decorated at the sp² C basal plane.[1] Graphene oxide is hydrophilic due to presence of O functional group, where as graphene is hydrophobic. Size of graphene oxide can be modified from nm to mm. This modification of both in its composition and size of flakes makes it an appealing and useful material in
many areas, - electronics, (sensors and transparent conductive films), clean energy devices, composite materials, biology and medicine. In a single layer graphene sheet, a large no of ‘O’ clock containing functional groups are introduced on both the sides.[2] The introduction of functional groups enlarges the interlayer spacing by overcoming the van-der Waals interaction. The expanded sheet structure then can be easily pulled open by sonication which acts as an external force. GO contains many defects and the degree of defects are subjected to amount of oxidant added and oxidising time.

GO is produced after the oxidation of graphene by four method

1. Brodie
2. Hummers
3. Hofmann
4. Staudenmeir

Today the most studied and used way to synthesise GO is the Hummers method. Hummers method consists of treating graphite with a mixture of NaNO₃, potassium permanganate and sulphuric acid. GO can be easily dispersed in water but can also be dispersed in the organic solvents, where the negative charged GO sheets become suspension of colloids which is then stabilised by electrostatic forces.[3-5]

**Reduced Graphene Oxide**

Reduced graphene oxide (rGO) is the form of GO that is processed by chemical, thermal and other methods in order to reduce the oxygen content. rGO is a form of graphene having properties same as graphene, rGO usually have more defects and is of lesser quality than graphene produced directly from graphite. rGO contains residual oxygen and heteroatom, as well as having structural defects. But it is still an important material having qualities required for many application parts, in addition to attractive price and manufacturing processes. rGO can be used for various application, same as graphene like composite material, conductive inks, sensors etc.[6] Since effective yet inexpensive ways to make graphene (or closely related materials, such as rGO) are being intensively sought for, the reduction of graphene oxide (or graphite oxide) to rGO is popular and attractive. Several methods of reduction into rGO exist, and are rather cost-efficient and simple. Despite rGO’s less-than-perfect resemblance to pristine graphene, it is still an appealing material that can definitely be sufficient in quality for various applications, but for more attractive pricing and manufacturing processes. Reduced graphene oxide can be used (depending on the specific material’s quality) for the same various applications suitable for graphene use, like composite materials, conductive inks, sensors and more. Reduced GO is often a natural and understandable choice for applications that call for large amounts of material due to the relative ease in creating sufficient quantities of graphene in a relatively low cost[7-10]. The process of reducing graphene oxide to produce reduced graphene oxide is extremely important as it has a large impact on the quality of the rGO produced, and therefore will determine how close rGO will come, in terms of structure an properties, to pristine graphene. A number of processes exist for the reduction of GO, based on
chemical, thermal or electrochemical approaches. Some of these techniques are able to produce very high quality rGO, similar to high-quality graphene, but can be complex, expensive or time consuming to carry out. Once reduced graphene oxide has been produced, there are ways to functionalize the material for specific use in different applications. By treating rGO with various chemicals or by creating new compounds by combining rGO with other two-dimensional materials, it’s possible to enhance the properties of the compound to suit commercial applications[11]. In this research paper GO and reduced GO were characterised using different techniques and their applications were studied.

**Objective and Methodology**

In this paper, the graphene oxide is synthesized using modified Hummers method. And this GO is then reduced to rGO and then their properties are studied.

1 Synthesis of GO

1.1 History and principle

- In 1859, GO was first synthesized by Sir 2nd Baronet Benjamin Collins Brodie, by oxidising the graphite in bulk with nitric acid and potassium chlorate.
- But the nature and its structure was studied after more than a century by Lerf and Klinowsky through a C13 and NMR spectra.

It was then proposed that GO is made up of non oxidised aromatic patches of variable size, being separated from each other by aliphatic 6 membered ring having epoxide group, double bond and hydroxyl group. Here, the “o” functional group lie both above and below the basal plane, which give hydrophilic and polar nature to GO. Synthesised GO can be deposited by drop casting, dip coating, vacuum filtration, spin coating etc. By spin coating, large area of uniform deposition can be achieved.

Modified hummers method

Today the most popular and useful method for the synthesis of GO is modified Hummers method, in which graphite is treated with a mixture of sodium nitrate, potassium permanganate, and sulphuric acid. The older method involves the rapid heating of GO to 100 degrees in inert atmosphere inert atmosphere, which causes the explosive thermal reduction of materials and large amount of CO₂ and H₂O between the graphite layers. Difference between hummers’ method, modified hummers method and improved hummers method without NaNO₂ was studied by Marcano et al. So, in improved hummers’ method, the use of NaNO₃ is replaced by H₂SO₄, H₃PO₄ and amount of KMnO₄ is also doubled. and other advantages includes – hydrophilic carbon material, equivalent conductivity, no emission of toxic gases and finally attract by large production of GO.
Apparatus required

Volumetric flask (1000ml), beakers, conical flask, measuring cylinder, glass rod, centrifuge tubes, funnel, filter paper, watch glass, thermometer, litmus paper, watch glass, thermometer, litmus paper, pH strips.

Instruments

Weighing machine, magnetic stirrer, sonication bath, centrifuge machine (10,000rpm) , drying oven

Chemicals required

Graphite flakes(2gm), concentrated H₂SO₄ (50ml) ,KMnO₄ (6 gm) , Deionised water, H₂O₂ (30%)

PROCEDURE

1. In a volumetric flask, 2 gm of graphite flakes were mixed into 50 ml conc H₂SO₄.
2. Under continuous stirring on magnetic stirrer, mixture was cooled by using ice water bath and suspension was obtained.
3. The temperature was maintained below 10 degree centigrade and then 6 gm of oxidising agent was added moderately into suspension, with continuous stirring, the colour of suspension changes to green and then stirred or about 30 min in ice bath.
4. The suspension was then stirrered at room temperature for about 25 min and then followed by sonication in an ultrasonic bath for 8 min.
5. Then 250 ml DI was added into mixture with repeated interval of stirring and sonication for about 10-15 times, and the stirring was done at 450 rpm.
6. After that, 30 ml H₂O₂ (30%) was added to exfoliated GO achieved after ultrasonication of dispersed solution for about 1 hour.
7. Then centrifugation of solution was carried out at 10,000 rpm.
8. After this GO was washed with 2M HCl, to remove excess of metal ions or to neutralise it and also with DI water, a no of times, until the pH was 7.
9. Resulting Go precipitates were dried at room temperature for 24 hour and also in hot oven at 100 degree centigrade for few minutes.
10. The dried GO was then weighted and characterised.
2. Synthesis of Reduced Graphene Oxide

Apparatus required

Volumetric flask, conical flask, test tubes, filter paper, funnel, thermometer, measuring cylinder, dropper

Chemicals required

Hydrazine hydrate, 1M HCl, Graphene oxide

Procedure

1. For rGO, graphene oxide was sonicated for 2 hours.

2. Hydrazine hydrate was added dropwise to the exfoliated graphene oxide suspension at room temperature.

3. The reduction was carried out at 100 degree centigrade for 1 hour.
4. Ratio for hydrazine hydrate and graphene oxide was maintained at 9:7 for this sample according to weight.

5. Black precipitate is obtained at last, which is being filtered by filter paper made of cellulose.

6. Then washing is given with 1M HCl solution and distilled water to obtain a neutral pH.

7. Finally this filtrate was dried for 24 hours at room temperature to obtain reduced graphene.

Result and Discussion

1. Graphene Oxide

1.1. XPS Photoemission Spectroscopy

To study the chemical composition of graphene oxide, XPS is the most proffered method. Functional groups can be identified from XPS spectra present in graphene oxide by deconvolving the C 1s and O 1s core level spectra into components, each one assisted to a particular functional group. The C 1s spectra of GO is typically fitted by the sum of five components - aromatic rings and hydrogenated (C=C/C-C, C-H, 284.6-284.9 eV), hydroxyl groups (C-OH, 285.9 eV), epoxy groups (C-O-C, 286.9 eV), carbonyl groups (C=O, 288.2 eV), and carboxyl groups (C=O(OH), 289.3 eV). Some functional groups like those corresponding to the epoxy and hydroxyl groups, are entangled due to the large number of configurations that can be found in GO, which led to n intrinsic spectral broadening. As far as O 1s spectrum is concerned, it is not sufficiently resolved to be deconvolved, the assignment of components is a very complex task in it.
1.2. **Raman spectrum analysis**

![Raman spectrum graph](image)

Raman spectroscopy is a widely used tool for the characterization of carbon products, especially considering the fact that conjugated and double carbon-carbon bonds lead to high Raman intensities. In Raman spectrum of GO, where the in-phase vibration (G band) of GO is at 1567.04 nm and the disorder band (D band) of GO is at 1339.22 nm.

1.3. **SEM analysis**

![SEM image](image)

Structure and morphology study of nanomaterials can be done by Scanning electron microscopy. From SEM image it is clear that how the sheets are stalked together in fig 1.3. Fig shows the SEM image of exfoliated GO. It clearly shows that how graphene sheets re exfoliated.
1.4XRD Analysis

General crystalline material characterization is mostly achieved by X-ray diffraction (XRD). It is used to measure the average spacing between layers or rows of atoms, and determine the crystal.

Fig 1.4 shows that diffraction peak is at 2 theta = 10 degree, which is mainly due to the orientation of graphite. The diffraction peak of pure graphite is found at 26 degree, corresponding to the highly organized layer structure with an interlayer distance of 0.34 nm along the (002) orientation.

The disappearance of peak at 26 degree and appearance of peak at 10 degree, shows that the product is completely oxidized after the chemical oxidation and exfoliation, indicating an change and increase of d spacing from 0.34 nm to 0.82 nm.
1.5 FT-IR analysis

Fig 1.5 shows that synthesized GO has a peak at 1081 1/cm, which is attributed to the C-O bond, which confirms the presence of oxide functional group after the oxidation process. Peaks in the range of 1630 1/cm to 1650 1/cm show that the C=C bond still remained before and after the oxidation process. A broad peak is observed at 2885 1/cm to 3715 1/cm by the absorbed water, contributed by the O-H stretch of water molecule. From this it can be concluded that GO is a highly absorptive material, as verified by its ability to become a gel-like solution.
2 Reduced graphene oxide -

2.1 UV-Visible spectroscopy

The UV–Visible spectrum of the reduced graphene oxide nanoparticles solution recorded was plotted as shown in Fig. 2.1, which clearly showed an increase in intensity with time. The UV–Vis spectrum in Fig. 1.1 showed an SPR peak of nanoparticles. The size and shape of the graphene nanoparticles reflects the absorbance peak.

Fig. 2.1 UV–Visible spectrum of the graphene
2.2 Fourier-transform infrared spectroscopy

![FTIR Spectrum](image.png)

The FTIR spectrum of reduced graphene oxide nanoparticles showed three distinct peaks, 3398, 1613 and 1106 cm\(^{-1}\) as shown in the Fig. 2.2. The pick at 3398 cm\(^{-1}\) show the O-H stretch and 1613 pick show the C=C stretch and 1106 pick are show O-H stretch.

2.3 Scanning Electron Microscope

SEM images revealed that the reduced GO material consists of randomly aggregated, thin, crumpled sheets closely associated with each other and forming a disordered solid. The folded regions of the sheets were found to have widths of nanometer by high-resolution Fig. 2.3.
2.4 X-ray diffraction

A comparison of the obtained XRD spectrum with the standard confirmed that the Graphene particles formed in the experiments were in the form of nanocrystals, corresponding to [100], [110], [200], [211] and [222].

Table no 1 XRD data of Graphene, Average crystalline size of the graphene nano particles is 22.03nm show in the table.

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<th>2-theta(deg)</th>
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Applications of Carbon Nanomaterials

Due to exponential population growth and limited availability of fossil fuels, we are facing the crisis of energy sources. Carbon, one of the most abundant materials found on earth, and its allotrope forms such as fullerenes, carbon nanotubes and graphene have been proposed as sources of energy storage and production because of their wonder properties. Various methods for the synthesis and incorporation of carbon nanomaterials in various applications like sensors, waste water treatment, battery, hydrogen storage cells, adsorbents, supercapacitors etc have been discussed by highlighting their benefits. Fullerenes, carbon nanotubes and graphene have all been included in solar cells with interesting results, although a number of problems are still to be overcome in order to achieve high efficiency and stability. However, the flexibility and the low cost of these materials provide the opportunity for many applications such as wearable and disposable electronics or mobile charging. Graphene oxide and reduced graphene oxide in combination with various composites, can create a more porous film with extraordinary capacitive performance, opening the way to many practical applications from mobile phones to electric cars. In conclusion, we show that carbon nanomaterials especially graphene oxide and reduced graphene oxide, developed by inexpensive synthesis and process are the boom for future of nanomaterials applications and provides us with so many potential applications which are very useful for the mankind and can be performed efficiently at low cost.

Conclusion

Nanomaterials are development to take the advantage of their small size and nobel properties Carbon based nanomaterial has attracted a large interest, due to their wide applications in technical, medical, environmental, agriculture and in astronomy. Carbon is well known for its distinct solid state allotropes with viable structures and properties ranging from sp² hybridized graphite. Various allotropes of carbon are – Diamond, Fullerene, Lonsdaleite, Carbon nano tubes, Graphene oxide and reduced graphene oxide. Graphene is the most useful and common allotrope of carbon, as it has a special set of properties that makes it unique – About 100 times stronger than strongest steel. Tensile strength – 130 GPa and good conductor heat and electricity. GO and rGO are the important useful derivatives of graphene. Graphene oxide has become one of the most intensively studied material. It commercially found its applications as being promising in energy storage, fuelcells and catalysis. Nanomaterials are prepared from various methods like Physical, Chemical and Biological method. GO is prepared by various methods but among these Modified Hummers is used. It is being prepared by modified Hummers method and then it is reduced to rGO by chemical reduction methods. Both GO and rGO are characterized by various methods like SEM, TEM, XRD, FTIR, Raman etc and then their various applications are studied – like in sensors, as adsorbent and as a catalyst.
References