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Recent Advances in Synthetic Methods to Prepare Graphene Oxide

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Abstract: This article reviews most essential ongoing advances in engineered strategies to create graphene oxide through wet science. In such methods, graphene sheets functionalized with various oxide gatherings: hydroxyl, carboxyl, epoxide, peroxide and ketone. Brodie-Staudenmaier-Tours-Hummers, Modified Hummers and Improved Hummers methods are discussed. The influence of synthesis on the graphene oxide structure is discussed. Physical - Chemical characterization such as Raman Spectroscopy and Fourier-transform infrared spectroscopy (FTIR) is additionally examined toward the end of article.

Keywords: Graphene Oxide, Synthesis, Physical-chemical characterization, Raman Spectroscopy

I. INTRODUCTION

Graphene has turned out to be a standout amongst the most imperative materials of the 21st century because of its tremendous properties like chemical reactivity, excellent conductivity, thermal, mechanical and many more. There are a wide range of applications of graphene and its functionalized product graphene oxide (GO). The GO acts as base material for the future application of water purification, super capacitors, sensor materials, adsorbent materials, as a catalyst carrier, as a biological drug, as a composite in antibacterial activity, coatings in and many more applications At first, the most ideal method for making a lot of graphene was through a wet substance technique that initially made graphene oxide and from that returned to graphene by different reduced strategies. Wet substance techniques fells behind in light of the fact that they were explosive, costly and required practice to get right. Fundamentally, graphene oxide is characterized as a layer of graphene enhanced with oxygen containing useful gatherings, for example, hydroxyl (OH), carbonyl (C=O), and alkoxy (C-O-C) gatherings. For all intents and purposes, graphene oxide is made when a perfect graphene is oxidized. The span of the GO is controlled by the chips of graphite. The most extreme hypothetical estimation of oxidation for graphene can't be more than 50 at.%O in view of the sp^2 hybridization of carbon atoms in the graphene hexagons. An oxidation over the 50 at.%O may happen with a completely oxidation by peroxide gatherings, however this oxidation review isn't yet examined.

II. SYNTHETIC METHODS FOR GRAPHENE OXIDE

Graphene oxide can be produced by mainly two kinds of methodologies/medium either by dry medium or wet medium. The dry medium approach comprises an oxidation response of graphene through nuclear oxygen in ultrahigh vacuum conditions [1,2] , and its introduction to sub-atomic oxygen[3,4], after that treating it with ozone under ultraviolet light [5,6]. By differentiate; another approach which is wet amalgamation is most appropriate. In this approach, graphite is normally utilized as graphene source, on account of its characteristic abundance and cheap cost.

In the past, a few techniques were proposed and the three noteworthy strategies to prepare GO are Brodie [7], Staudenmaier [8] and Hummers [9]. From these three essential techniques various varieties were inferred to enhance the general yield and nature of the acquired item, for example the Tour strategy [10]. Later on, one of the the best method till now was given by Pendolino and co-workers [11]. As of late, a "crude" approach was embraced by various scientists which comprises in a free-water peeling and oxidation of graphite through solid oxidizing operator in a solid protic medium (like H_2SO_4) [12,13].

A. Brodie - Staudenmaier –Hummers Based Methods

1) *Brodie Method.* The first documented synthesis of graphitic oxide materialis attributed to Brodie in 1859 [7]. His study was focused on finding the weight of graphite and, as common at that time, a series of chemical reactions were investigated to elucidate the properties of this novel material that is graphene oxide. Thus, graphite was mixed with potassium chloride ($KClO_3$) and solubilized in fumic nitric acid to oxide the sample. Further oxidation processes were carried out on the sample till

any changes were visible. The elemental analysis revealed a composition of circa 60% C, 2 % H and 38 % O. The resulting product, gives a mixture of graphene and graphite oxide, which is soluble in pure water.

2) *Staudenmaier Method*. In 1898 Staudenmaier [8] improved the Brodie's reaction by adding sulfuric acid (H_2SO_4), to increase the acidity of mixture, and several aliquots of solid $KClO_3$, over the course of reaction. Despite that, Brodie and Staudenmaier method generates toxic gas ($ClO_{2)}$ toxic gas which rapidly decomposes in air giving explosions. These modifications led to a more oxidized graphitic material and a simplification of the reaction.
3) *Hummers Method.* In 1958, Hummers and Offeman [9] proposed an alternative way to oxide graphite improving the safe operational conditions with a very good reducing time, from 10 to 2 days. They mix graphite with concentrated sulfuric acid (H_2SO_4), sodium nitrate ($NaNO_3$) and potassium permanganate ($KMnO_4$) to obtain a brownish grey paste. The suspension is diluted with water and hydrogen peroxide (H_2O_2) is added to get a higher oxidation degree and to eliminate manganese from the dispersion (yellow-brown mixture). Finally, the sample was filtered and washed with water. They achieved the same degree of oxidation reported by Staudenmaier, however, the yield of Graphene Oxide (GO) results very less. The weakness of this method includes a time-consuming of the separation and purification process. From Hummers method a large number of variation approaches has been developed and a typical GO product is made by flakes of about 1nm and a lateral size of 1µm.
4) *Tour Method.* In 2010, at Rice University [10], an improved version of Hummers method was proposed by Tour's group. They have replaced the sodium nitride ($NaNO_3$) with ortho-phosphoric acid (H_3PO_4) in a mixture of H_2SO_4/H_3PO_4 (9:1) and increasing the amount of $KMnO_4$. There is no generation of toxic gases, such as NO_2, N_2O_4 or ClO_2, this is considered as the advantage of this method and temperature is also easily controllable in Tour Method. The authors claim that the presence of ortho- phosphoric acid generates a more intact graphitic basal plane. A comparison of this improved method with other two above mentioned methods can be seen in Figure 1.

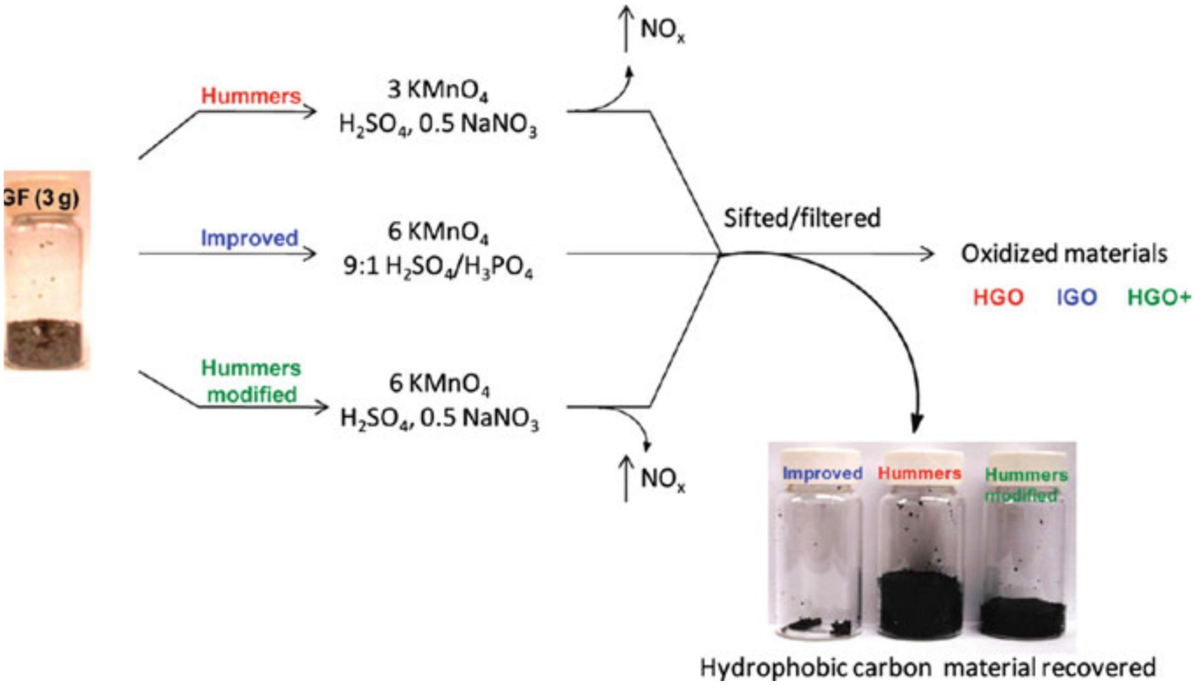

Fig. 1 . Showing Comparison of Hummers(HGO), Hummers Modified(HGO+) and Improved Method(IGO) [17]

B. *Free –Water Oxidation Method*

The Free-Water Oxidation strategies exploit a response between extended graphite and oxidizing reagents in a free-water medium. Due to inorganic carbon which is basically latent at room temperature, its scattering in a dissolvable needs extremely solid protic acid or blend of warm acids, for example, sulfuric (H_2SO_4) or nitric acid (HNO_3). In addition, a solid oxidizing reagent, for example, potassium permanganate ($KMnO_4$), guarantees the obligations of oxygen functionalities in to inorganic carbons. In view of recorded reason, the free-water oxidation strategies got from adjustment of the Hummers technique in which a few constraints, for example, dangerous reagents, were moved forward. Some altered/enhanced strategies are

1) *Sun Method*. Sun and Fugetsu at Hokkaido University [13], in 2013 acquainted an immediate technique which creates graphene oxide. Extended graphite was utilized as carbon precursor. The potassium permanganate ($KMnO_4$) had two-fold impacts: it can be utilized as intercalating operator and also oxidizing specialist. The intercalation of $KMnO_4$ between graphitic layers delivered a further unconstrained development which resembles a froth of graphitic material, as appeared in Figure 2. The proportion Graphite: H_2SO_4 is diminished to 1:20 and extra reagents were eliminated from the response procedure. Response happens in acidic medium of sulfuric acid. Due to this lessened proportion, Sun's technique can be considered as one of the primary green strategy among all the wet synthetic strategies.
2) *Peng Method*. Peng and his associates [14] proposed an adaptable and green technique to deliver GO, utilizing potassium ferrate (K_2FeO_4) as solid oxidant in 2015.This strategy keeps away from the presentation of substantial metals or the development of dangerous gases during the preparation of this compound. In this technique, graphitic flakes with potassium ferrate dispersed in concentrated sulfuric acid, were stacked into a reactor and mixed for 1h at room temperature. The item was water-washed by repeated centrifugation to acquire an exceedingly water solvent graphene oxide.
3) *4Steps Method* . This strategy is derived from the essential exfoliation – oxidation methodology and was enhanced by Pendolino and his colleagues [11,15]. This strategy comprises of four response steps that are controlled by temperature, which influences the last product firmly. In the initial step the oxidation procedure for the blend graphite-$KMnO_4$ dispersed in concentrated sulfuric acid (H_2SO_4) get pale slurry. The second step (warm) comprises the exfoliation of graphite and is the most basic one stage. The creation of GO is constrained by temperature and just happens when the temperature of water bath was around 30^0C. At that point hydrolysis for 1h at 90^0C finishes the third step. The cleaning of sample is finished by centrifugation, up to the neutrality of the solution, at forth step.

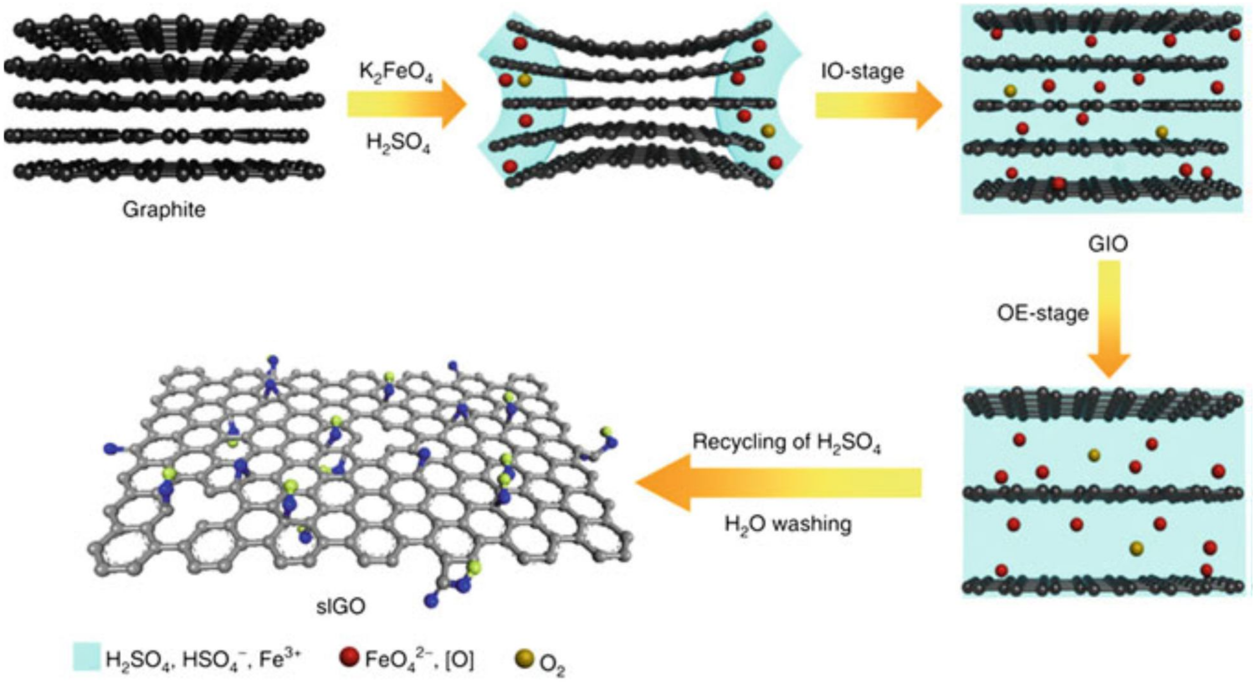

Fig. 2. Synthesis of graphene oxide by using K_2FeO_4 as oxidizing reagent by Peng and his co-workers [14].

The upside of this technique is that this confines the hazardous response because of Mn_2O_7 in concentrated Sulfuric acid for temperature above than 55^0C and thus create a kind of GO which contains a measure of oxygen areas lower to around 20-30 at.%O. This sort of GO can be utilized for ultrafilteration or biosystems because of the low harmful impact.

III. CHARACTERIZATION

The physical chemical characterization of GO isn't frequently of simple interpretation since this material is made of carbon and oxygen as the greater part of natural particles. In the accompanying section, the most general strategies and the representative interpretation to recognize the GO are shown.

A. Ftir.

The FTIR is efficient for quick characterization of carbon containing mixes. It turns out to be particularly basic to interpret FTIR signals as indicated to hydroxyl (OH), epoxy (C-O-C) and ketone (C=O) gatherings. The comparing vibrational frequencies for the extending mode are around 3420 cm^{-1}, 1080 cm^{-1} and a doublet at 1700 cm^{-1}, individually. An average FTIR range is appeared in Figure 3 a. It is clear from assume that the unique finger impression locale of IR-range of GO differs. The plots a and b in the Figure 3a is demonstrating the range of two different synthesis of GO having an oxygen substance of 20 at.%O, while plot c speaks to a commercial GO having 50 at.%O. The majority of the distinction has been found for tops at 1090 cm^{-1} and first peak of the doublet is around 1700cm^{-1}.

B. Raman Spectroscopy

Raman range for GO demonstrates just two widen crests which indicates G and D band (Fig 3 b.). The main band is found around 1590cm^{-1} and was credited to in-stage vibrations of ordered crystal structure while D band was around 1350cm^{-1} and is assigned to disordered structure. This reality connects the G band to the sp^2 carbon and D band to the nearness of sp^3 hybridized, consequently, to oxygen spaces.

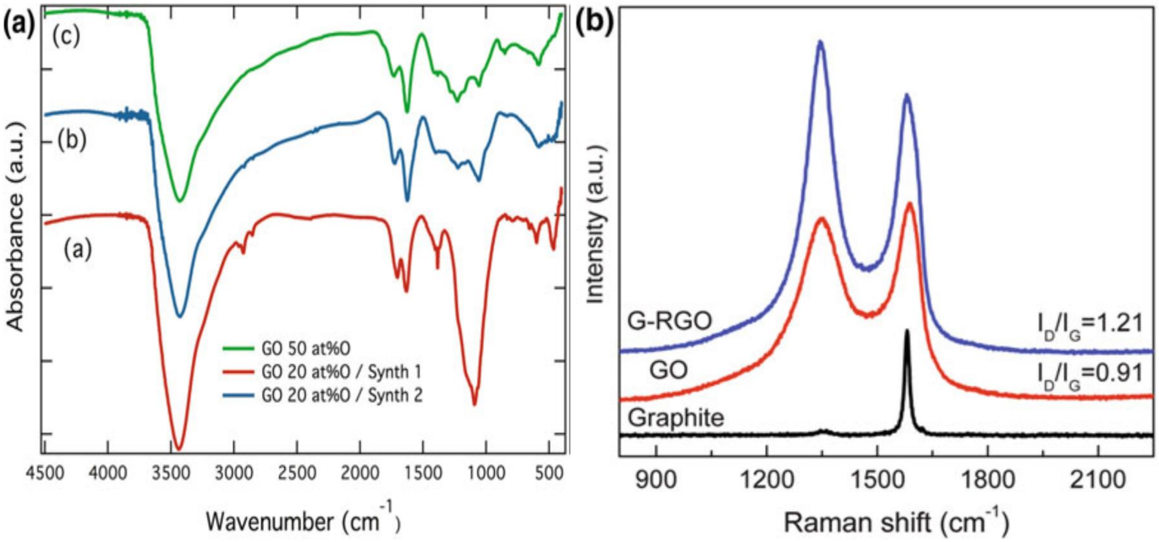

Fig 3 a. FTIR spectra showing the different oxygen content from the 4-step synthetic method. b. Raman spectra of graphite, GO and RGO [18]

IV. CONCLUSION

In all previously mentioned techniques to get GO, a few constraints are experienced. Essential, lab security is affected by harmful reagents. The utilization of sodium nitrate ($NaNO_3$) or potassium chlorate ($KClO_3$) in Brodie or Staudenmaier techniques may comes about hazardous, while sodium nitrate ($NaNO_3$) (Hummers) or fuming nitric acid (HNO_3), present heteroatoms and imperfections in the GO structure that unquestionably influences the reactivity. Next, the presence of Mn_2O_7 in a solution of sulphuric acid explodes with a temperature more than 55^{0}C. Another vital factor that matters is the quality and grain size of graphite. In fact, more work is needed to produce defect free high quality GO.

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