



A Review on Common Methods for Characterizing Graphene Oxide (GO)

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Author's contribution

The sole author designed, analysed, interpreted and prepared the manuscript.

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ABSTRACT

Graphene oxide, two-dimensional material with the thickness of 1.1 ± 0.2 nm, has gained attention to a greater extent in the field of science for its radically distinctive properties: physical, chemical, optical as well as electrical etc. Graphene oxide (monolayer sheet) has been synthesized by oxidizing graphite (millions of layer) to graphite oxide (multilayers) which has been converted into graphene oxide via exfoliation followed by sonication and centrifugation - a method mentioned as Modified Hummer Method. I focus on the chemical structure of graphene oxide. However, I discuss the different analytical methods such as UV-Visible spectroscopy, Atomic Force Microscopy (AFM), X-ray Photoelectron Spectroscopy (XPS), Fourier Transform Infrared Spectroscopy (FTIR) as well as X-ray Diffraction pattern for characterizing the graphene oxide. Furthermore, this review covers the analytical evaluation of graphene oxide and discuss the past, present and future of graphene oxide in the scientific world.

Keywords: Graphene oxide; modified hummers method; spectroscopy; characterization.

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1. INTRODUCTION

Graphene, a hexagonal crystal lattice with sp^2 bonded structure, has recently recognized as a smart material in the field of material science [1-3]. Due to its remarkable physicochemical properties, graphene has become a unique material, and the usage of graphene is increasing day by day. As a result of having a two-dimensional structure, monolayer graphene has a large surface area; i.e. $2630 \text{ m}^2/\text{g}$ theoretically [4] and high thermal conductivity; i.e. $\sim 5000 \text{ Wm}^{-1}\text{K}^{-1}$ [5,6]. Graphene oxide has greater interactions with a lot of molecules for its high surface to volume ratio [7]. Owing to its special surface properties, graphene oxide can be modified in different ways to make it an imaging probe for biomedical applications [8,9]. Even, Graphene oxide has been appraised as a nano vector in the field of nanomedicine [8,9,10]. As a result of having oxygen functionalities, it has higher scope of dispersibility in water, but it works as an insulator unless otherwise it is converted into reduced graphene oxide (rGO) with some chemical reduction methods. To speak the truth, graphene oxide research is a certain branch of graphene research. So, GO is considered as a precursor of graphene. The one atomic thick layer of graphene oxide is produced by using Modified Hummers Method [11,12]. Graphene, prepared from natural graphite, contains epoxy bridges, hydroxyl groups and pairwise carboxyl groups as shown in the Fig. 1 [12]. The structural flaws are observed during oxidation process cited in Modified Hummers Method. These defects integrate the physical properties of GO from that of pure graphene. However, graphene oxide contains strong hydrophilic character for the presence of oxygen-containing functional groups which makes it readily dispersible in water [13,14].

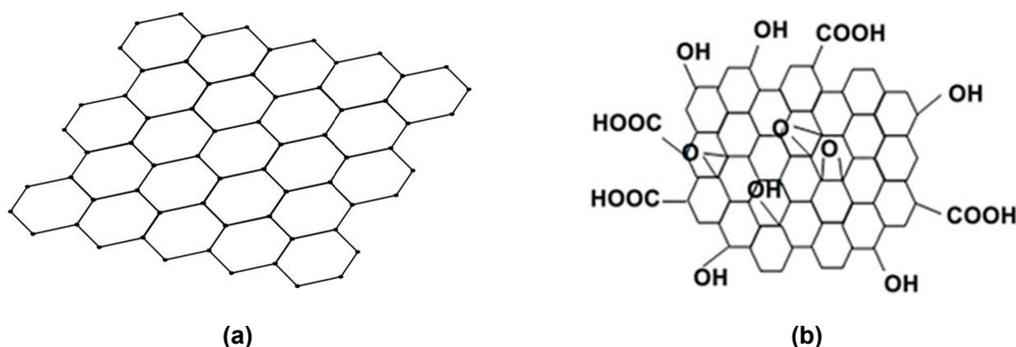


Fig. 1. Schematic structure of (a) A single layer graphene sheet (b) Graphene Oxide (GO)

Accordingly, it necessitates the exploration of properties of graphene oxide for its wide range of applications. That's why, successfully synthesized graphene oxide is characterized by using different analytical methods for different purposes. UV-Visible spectroscopy is used to study the absorbance of GO sheets. Atomic Force Microscopy (AFM) is used to study the topology of the thin films of graphene oxide, and the binding energies of the carbon atoms are analyzed by X-ray photoelectron spectroscopy (XPS).

2. GRAPHENE OXIDE FABRICATION METHOD

2.1 Materials

Analytical grade chemicals such as natural graphite (crystalline, briquette), concentrated sulfuric acid (H_2SO_4), sodium nitrate (NaNO_3), potassium permanganate (KMnO_4) and hydrogen peroxide (H_2O_2) etc. are used for graphene oxide synthesis.

2.2 Common Synthesis Techniques of Graphene Oxide

Graphene oxide is prepared according to Modified Hummer's Method where natural graphite is used a starting material [12]. This review depicts the most common synthetic methods such as Brodie (1859), Staudenmaier (1898), Hummers (1958) and Tour (2010) which have become fashionable after the late discovery of graphene in 2004. Brodie, the chemist who synthesized GO for the first time, used potassium chlorate (oxidizing agent) and fuming nitric acid (intercalating agent-aids in oxidation) to produce GO with the thickness of 0.05 mm. Staudenmaier utilized sulfuric acid with the chemicals used by

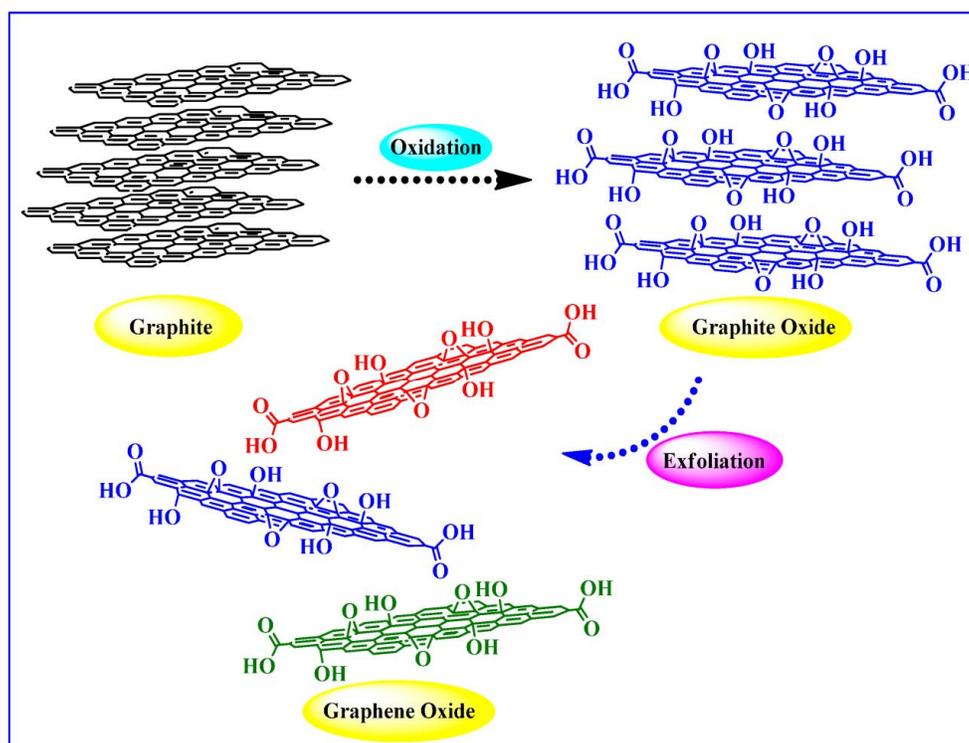


Fig. 2. Chemical route for the oxidation and exfoliation of graphite resulting in GO as depicted by Garg et al. [16]

Brodie giving a favor over Brodie method because of having no repeated use of nitric acid to reduce the production of NO_x gases during chemical reaction. Hummers then developed the technique after half of a century of the time of Staudenmaier replacing nitric acid by sodium nitrate as well as potassium chlorate by potassium permanganate as an oxidizing agent. The improvements developed by Hummers only for removing toxic gases produced in Brodie and Staudenmaier made it a promising candidate for GO production. Tour and Kosynkin has lately developed the Hummer's method by replacing sodium nitrate with phosphoric acid (chelating agent) to protect the GO surface from undesirable defects and fragmentation through inhibiting conversion of vicinal hydroxyl into vicinal oxygen groups [15]. The chemical scheme for synthesizing GO is shown in Fig. 2.

3. CHARACTERIZATION

3.1 UV-visible Spectroscopic Analysis of Graphene Oxide

UV-Visible study of graphene oxide lattice shows that the predominant absorption maxima occurs

at ~230 nm for its $\pi-\pi^*$ sp² clustered C=C chromophore units and there is a shoulder located at ~300 nm for its n- π^* plasmon peak of autochrome's containing carboxyl, carbonyl and hydroxyl functional groups. Besides, another absorption will occur at approximately 212 nm for $\pi-\pi^*$ aromatic transition for C-C bonds which corresponds to sp³ character in GO. The above absorptions will not change despite having different mass ratios of oxidizer potassium permanganate (KMNO₄) to graphite, for example, Fig. 3(a) reported by Q Lai et al. [17]. But it can be changed such a way that the samples others than above under UV-visible analysis will not show these behaviors due to reduction of oxygen functionalities in graphene oxide sample, for instance, Fig. 3 (b) reported by E. Aliev et al. [18].

As sonication and centrifugation are the two ways for getting exfoliated graphene oxide, these two methods have different impacts on graphene oxide. Tindall scattering effect is seen after centrifugation. Besides, sonication has also greater effects on graphene oxide. However, the absorbance of graphene oxide dispersions increases with increasing sonication time.

Furthermore, Beer-lambert law aids in determining the concentration of graphene dispersions.

3.2 Atomic Force Microscopic Analysis of Graphene Oxide

AFM is viewed as the straightforward method for the topological studies of graphene oxide sheets [19]. To observe the thickness of different layers of graphene oxide, graphene oxides are placed on some inert substrate (e.g., Si) dropwise and air dried at room temperature. Exfoliation has a profound effect on the dispersion of graphene oxide layers. If exfoliation time is increased, graphene oxide layers are properly dispersed. AFM analysis shows that the thicknesses of single, double and triple layer graphene sheets after chemical oxidation are approximately 0.57,

1.25 and 1.83 nm respectively [20]. The interlayer distance between layers of graphite is 0.335 nm which is larger than that of 0.5 nm in layers of graphene oxide. Graphite platelets are measured at the central parts when placed in the substrate of 2.7 nm which is probably equal to eight layers of graphene isolated by the 0.34 nm Vander Waals distance. Graphite platelets tends to fold in some places and the surface contains nanoparticles attached to it Fig. 4(a) and nanoparticles evaporate mostly from the surface after oxidation Fig. 4(b) [21].

3.3 X-ray Photoelectron Spectroscopic Analysis of Graphene Oxide

X-ray photoelectron is a quantitative surface analytical technique used to find elemental as well as chemical composition of the material

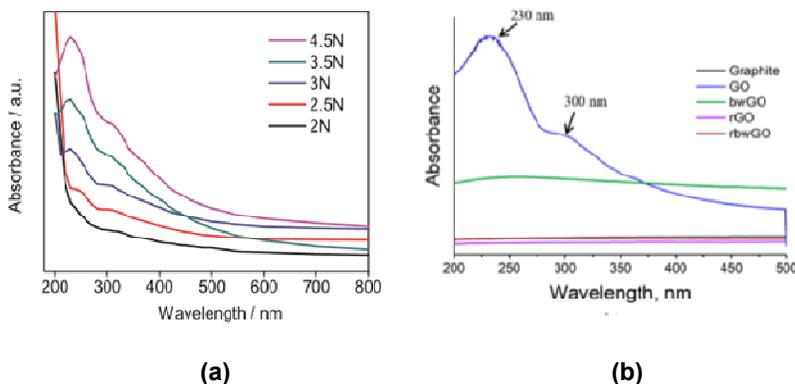


Fig. 3. (a) UV-visible absorbance of samples of different mass ratios of KMnO_4 to Graphite (N=10 g and graphite=10 g); (b) UV-Visible absorbance of samples of GO and base washed GO & their reduced forms

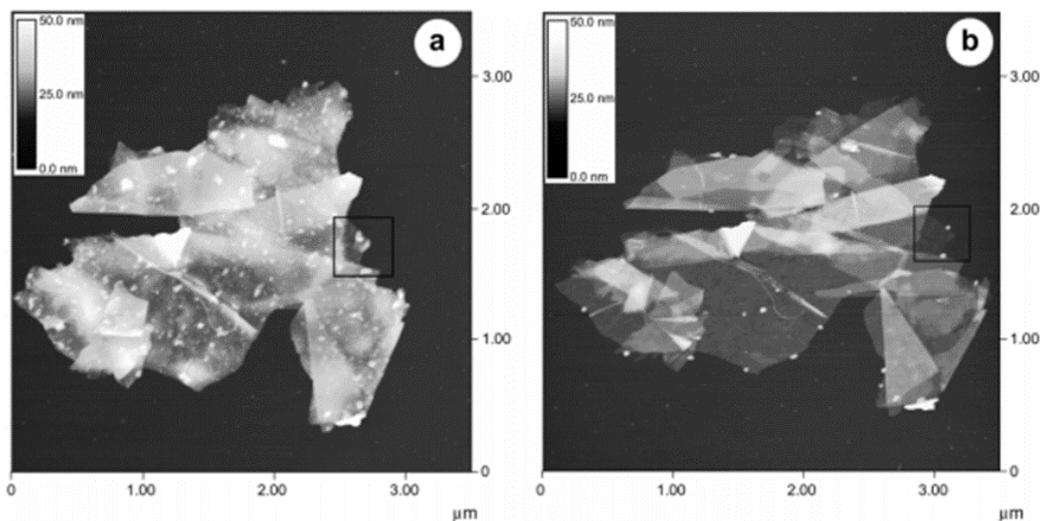


Fig. 4. AFM images of a few layer graphite (a) Before oxidation and (b) After oxidation [21]

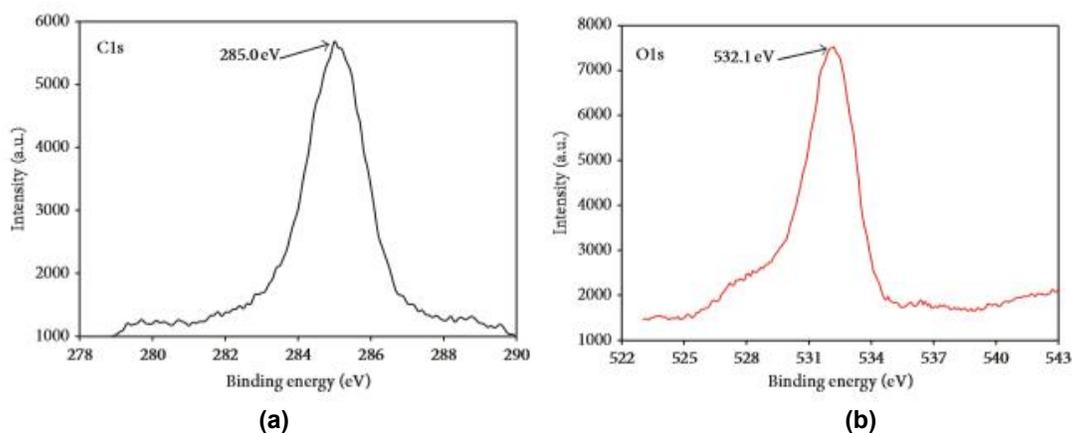


Fig. 5. (a) The XPS spectra of GO sheet (a) C 1s and (b) O 1s

under study [22]. I observe the elemental analysis of graphene oxide (GO) from literature study, and XPS shows the characteristic signal of C 1s at ~ 285 eV which corresponds to C=C, C-C and C-H functional groups and characteristic signal of O 1s at ~ 533 eV which corresponds to C-O and C=O bond groups [23,24]. The characteristic signal for the binding energies are follows Fig. 5 (a) & 5(b) [25].

C-C and C=C graphene lattices show characteristic signal at approximately ~ 284.4 eV while carbons attached to epoxy and phenolic groups exhibit their relative binding energies at around ~ 286.5 eV. However, carbons attached to ketone and carboxylic groups show characteristic signal in between ~ 288 - 290 eV. O 1s spectra from GO sample confirms the strong oxidation of graphite and contains different oxygen functionalities. Carboxyl groups containing C=O and O-C=O show characteristic signal at about

~ 532 eV and phenolic -OH and epoxy groups show their corresponding signals at ~ 533 eV [26].

3.4 Fourier Transform Infrared Spectroscopy of Graphene Oxide

Oxygen functionalities are observed through analyzing FTIR spectrum. The spectrum (Fig. 6) depicts the broad peak between 3000 - 3700 cm^{-1} for the presence of stretching and bending vibrations due to the OH group of water molecules attached on the GO surface [27,28]. Symmetric and anti-symmetric vibrations of CH_2 occurs at 2930 and 2850 cm^{-1} respectively. Edges of GO contains carboxylic and carbonyl functional groups where C=C and C=O stretching vibrations of both functional groups occur at 1630 and 740 cm^{-1} respectively. The peaks at 1385 and 1110 cm^{-1} are likely to be noticed for the

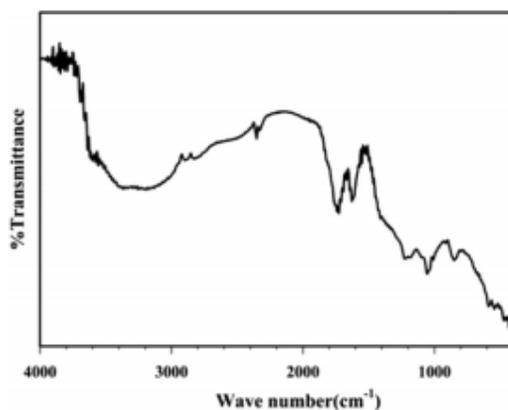


Fig. 6. FTIR spectrum of GO [28]

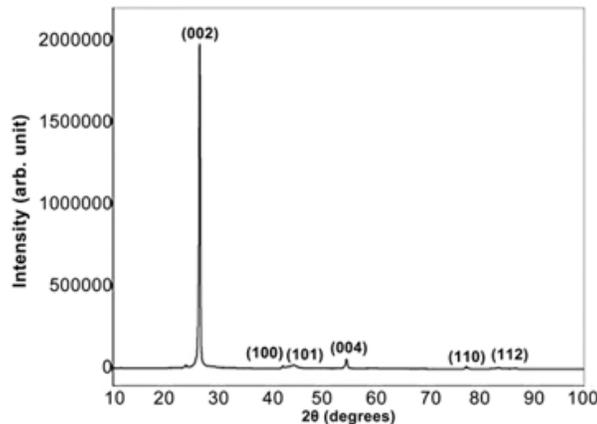


Fig. 7(a). XRD plot of natural graphite

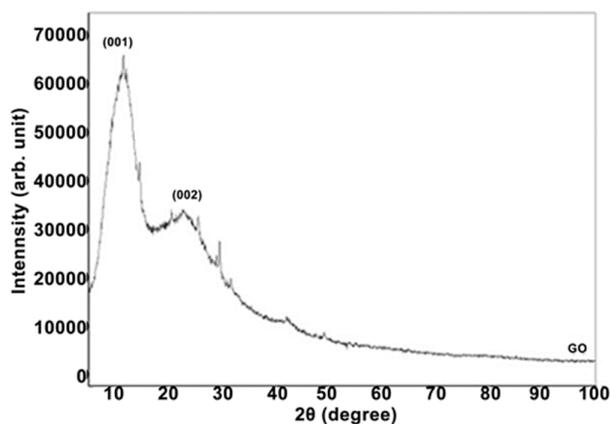


Fig. 7(b). XRD plot of Graphene Oxide

occurrence of stretching vibrations of C-O carboxylic acid and C-OH alcohol groups which ultimately state the hydrophilic character of GO [29].

3.5 X-ray Diffraction Pattern of Graphene Oxide

The crystalline properties of natural graphite and graphene oxide is analyzed by XRD. The intense peak (002) is observed at $2\theta=26.42^\circ$ which depicts the higher crystalline properties of natural graphite with d-spacing of 3.37 \AA as shown in Fig. 7 (a). A sharp diffraction peak is observed at $2\theta=11.95^\circ$ with d-spacing of 7.4 \AA for Modified Hummers Method synthesized GO as shown in Fig. 7 (b). The larger interlayer spacing in GO is due to the presence of oxygen functionalities [30-32].

4. CONCLUSION AND PERSPECTIVES

Due to its higher electrochemical properties, graphene oxide has captured a large field in electroanalytical chemistry as well as electrochemical applications; for instance, electrocatalysts, electrochemical biosensors, enzyme biosensors, electrochemiluminescence etc. Even, graphene oxide likely to dominate over other carbon-based materials such as fullerene, carbon nanotubes (CNT), graphite and diamond for higher physicochemical properties. Scientists and researchers have designed the graphene oxide easily due to its superior structural properties and applied it for electrochemical sensor. These types of developments have been progressed recently. Furthermore, developments are advancing day by day to make it available for different applications and much more works must be done for further improvement. Modified

Hummer's method has achieved the highest favor over the most common synthesis techniques because of selecting the chemicals for synthesizing GO in the perspective of toxic gases. The method produces the GO with high surface to volume ratio to make it applicable for a diverse range of applications. Several common analytical methods such as UV-visible, AFM, XPS, XRD and FTIR have been used to study the properties of graphene oxide though there are other analytical methods; for example, EDX, TGA, etc. to analyze the properties of GO.

COMPETING INTERESTS

Author has declared that no competing interests exist.

REFERENCES

1. Geim AK, Novoselov KS. The rise of graphene. *Nature Materials*. 2007;6(3): 183–191.
2. Sykes ECH. Graphene goes undercover. *Nat. Chem*. 2009;1:175.
3. Stoller MD, Park S, Zhu Y, An J, Ruoff RS. Graphene-Based Ultracapacitors. *Nano Letters*. 2008;8(10):3498–3502.
4. Balandin AA, Ghosh S, Bao W, Calizo I, Teweldebrhan D, Miao F, Lau CN. Superior Thermal Conductivity of Single-Layer Graphene. *Nano Letters*. 2008;8(3): 902–907.
5. Ghosh S, Calizo I, Teweldebrhan D, Pokatilov EP, Nika DL, Balandin AA, Bao W, Miao F, Lau CN. Extremely high thermal conductivity of graphene: Prospects for thermal management applications in nanoelectronics circuits. *Applied Physics Letters*. 2008;92(15):151911.
6. Kostaleros K, Novoselov KS. Graphene devices for life, *Nat. Nanotechnol*. 2014;9:744-5.
7. Bitounis D, Ali-Boucetta H, Hong BH, Min DH, Kostarelos K. Prospects and Challenges of Graphene in Biomedical Applications. *Advanced Materials*. 2013;25(16):2258–2268.
8. Georgakilas V, Otyepka M, Bourlinos AB, Chandra V, Kim N, Kemp KC, Hobza P, Zboril R, Kim KS. Functionalization of graphene: Covalent and non-covalent approaches, derivatives and applications. *Chemical Reviews*. 2012;112(11):6156–6214.
9. Rodrigues AF, Newman L, Lozano N, Mukherjee SP, Fadeel B, Bussy C, Kostarelos K. A blueprint for the synthesis and characterisation of thin graphene oxide with controlled lateral dimensions for biomedicine. *2D Materials*. 2018;5(3): 035020.
10. Yang K, Feng L, Shi X, Liu Z. Nanographene in biomedicine: therapeutic applications, *Chem. Soc. Rev*. 2013;42: 530-47.
11. Hummers WS, Offeman RE. Preparation of graphitic oxide. *Journal of the American Chemical Society*. 1958;80(6):1339–1339.
12. Alam SN, Sharma N, Kumar L. Synthesis of Graphene Oxide (GO) by Modified Hummers Method and Its Thermal Reduction to Obtain Reduced Graphene Oxide (RGO)*. *Graphene*. 2017;06(01):1–18.
13. Pei S, Cheng HM. The reduction of graphene oxide. *Carbon*. 2012;50(9): 3210–3228.
14. Wang G, Yang J, Park J, Gou X, Wang B, Liu H, Yao J. Facile synthesis and characterization of graphene nanosheets. *The Journal of Physical Chemistry C*. 2008;112(22):8192–8195.
15. Tour JM, Kosynkin DV. Highly oxidized graphene oxide and methods for production thereof; 2012. US20120112929736A1
16. Garg B, Bisht T, Ling YC. Graphene-based nanomaterials as heterogeneous acid catalysts: A comprehensive perspective. *Molecules*. 2014;19(9): 14582–14614.
17. Lai Q, Zhu S, Luo X, Zou M, Huang S. Ultraviolet-visible spectroscopy of graphene oxides. *AIP Advances*. 2012;2(3):032146.
18. Aliyev E, Filiz V, Khan MM, Lee YJ, Abetz C, Abetz V. Structural characterization of graphene oxide: Surface functional groups and fractionated oxidative debris. *Nanomaterials*. 2019;9(8):1180.
19. Tao H, Zhang Y, Gao Y, Sun Z, Yan C, Texter J. Scalable exfoliation and dispersion of two-dimensional materials – An update. *Physical Chemistry Chemical Physics*. 2017;19(2):921–960.
20. Wu ZS, Ren W, Gao L, Liu B, Jiang C, Cheng HM. Synthesis of high-quality graphene with a pre-determined number of layers. *Carbon*. 2009;47(2):493–499.
21. Osváth Z, Darabont A, Nemes-Incz P, Horváth E, Horváth Z, Biró L. Graphene

- layers from thermal oxidation of exfoliated graphite plates. Carbon. 2007;45(15): 3022–3026.
22. Hauffe WDJ, Oconnor BA, Sexton R, St. C. Smart (Eds). Surface analysis methods in materials science. (Bd. 23 springer series in surface sciences). Springer-verlag berlin, Heidelberg, New York. 453 S., 250 Abb., 18 Tab. Crystal Research and Technology. 1992;27(8):1078–1078. [ISBN: 3–540–53611–6]
 23. Dubin S, Gilje S, Wang K, Tung VC, Cha K, Hall AS, Farrar J, Varshneya R, Yang Y, Kaner RB. A one-step, solvothermal reduction method for producing reduced graphene oxide dispersions in organic solvents. ACS Nano. 2010;4(7):3845–3852.
 24. Rourke JP, Pandey PA, Moore JJ, Bates M, Kinloch IA, Young RJ, Wilson NR. The real graphene oxide revealed: Stripping the oxidative debris from the graphene-like sheets. Angewandte Chemie International Edition. 2011;50(14):3173–3177.
 25. Song J, Wang X, Chang CT. Preparation and characterization of graphene oxide. Journal of Nanomaterials. 2014:1–6.
 26. Fujimoto A, Yamada Y, Koinuma M, Sato S. Origins of sp³C peaks in C1s X-Ray photoelectron spectra of carbon materials. Analytical Chemistry. 2016;88(12):6110–6114.
 27. Scholz W, Boehm H. Investigations on graphite oxide. VI. Reflections on the structure of Graphite Z, Anorg. Allg. Chem. 1969;369:327-340.
 28. Shariary L, Athawale AA. Graphene oxide synthesized by using modified hummers approach. Int. J. Renew. Energy Environ. Eng. 2014;2:58-63.
 29. Wei N, Peng X, Xu Z. Understanding water permeation in graphene oxide membranes. ACS Applied Materials & Interfaces. 2014;6(8):5877–5883.
 30. Nasrollahzadeh M, Babaei F, Fakhri P, Jaleh B. Synthesis, characterization, structural, optical properties and catalytic activity of reduced graphene oxide/copper nanocomposites. RSC Advances. 2015;5(14):10782–10789.
 31. Huh SH, Ju HM, Choi SH. X-ray diffraction patterns of thermally reduced graphenes. Journal of the Korean Physical Society. 2010;57(61):1649–1652.
 32. Chen J, Yao B, Li C, Shi G. An improved hummers method for eco-friendly synthesis of graphene oxide. Carbon. 2013;64:225–229.

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