SYNTHESIS OF AMINO AND THIOL FUNCTIONALIZED REDUCED GRAPHENE OXIDE COMPOSITES

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A B S T R A C T

The world of nanotechnology has been transformed since graphene came into existence. Researchers all over the world have exploited graphene for its various potentials. Graphene find many applications in photo-devices, adsorption, food and medical industry, polymer fillers, sensors and energy storage devices etc. This has become possible due to unique layered structure of graphene and oxygen moieties present on graphene. These oxygen moieties have been tailored in many of its applications. Nitrogen and sulphur atoms are more nucleophilic than the oxygen atom in graphene. So, it is expected that thesubstitution of graphene with amine and thiol groups increase the nucleophilic properties of graphene. These interactions are expected to improve performance and functionality of the applications of graphene.

In this work of research,reduced graphene oxide is functionalized by amino and thiol groups by treating it with 4-aminothiophenol by two different methods to prepare adsorbing polymers.These composites are then characterized and confirmed by FTIR, XRD, TEM, SEM, and CHNS analysis. Keywords: Graphene oxide (GO); reduced Graphene oxide (rGO),4-Aminothiophenol

1.Introduction :

Graphene (Gr), a two dimensional structure of sp^2 hybridized carbon[1], shows extraordinary properties including high electron mobility at room temperature[2,3],exceptional thermal conductivity[3]and amazing mechanical properties.[4,5]Particularly, the electronic properties of this material has pulled in attention among lot of analysts. However, a significant number of these intriguing and one of a kind properties can be enhanced by means of synthetic functionalization of the surface or edge defects.[6-8] These preliminary adjustments empower chemical covalent bonding between the Gr and organic materials of interest and furthermore, make Gr as a perfect stage to anchor various functional moieties such as metal nanoparticles.[9]The addition of graphene to a host framework has accomplished various improved properties with promising applications in many industries such as aviation, electronics, energy, structural and mechanical, ecological, medicinal, nourishment and beverage. [8,10-17]

Functionalized Gr is usually easier to be dispersed in organic solvents and water, which can help the functionalization of Gr by various functional groups.[18-24]In this circumstance, synthetic functionalized Gr having utilities in polymer composites, energy-related materials[25] sensors, field impact transistors, photo-devices[26-32], transparent conductive electrodes[27], adsorption, separation, chemical synthesizes and biomedical frameworks, have been generally reviewed.[36] Graphene oxide (GO), itself have few sorts of oxygen carrying functional groups[28], hence, it has been specifically utilized as a platform for adsorption of metal ions in

aqueous solutions, solid-phase extraction, catalyst for many reactions and preparation of different Gr-based composites.[11] However, nitrogen in amine and sulfur in thiol are more nucleophilic than the oxygen atom. Along these lines, the substitution of Gr or GO with amine and thiol groups expands the nucleophilic properties of Gr and as an outcome, interfacial binding between Gr and the materials of interest can be accomplished. For instance such functionalization in carbon nanotube has been utilized to upgrade the controlled covalent binding to polymers or organic molecule.[28]More recently, different substituted amines have been inserted to GO to be used in energy storage, electro-catalytic oxygen reduction reactions (ORR),[29,30]electrochemical sensors, solid basic catalyst in organic chemistry, and optical Gr quantum dots[31]. These wide potential utilizations of functionalized-Gr require an effortless and controllable technique to embed a high fraction of functional groups in Gr sheets[9,10,29,30,32].In this proposed work of research, Graphene oxide was functionalized by amino and thiol groups by treating it with 4-aminothiophenol by two different methods to prepare adsorbing polymers.

2.Experimental:

2.1 Preparation of GO by modified Hummer's method[28-33]

Graphene oxide was prepared by a well-known and established Hummer's method by using Graphite flakes, $NaNO_3$ and Conc.H_2SO_4. $KMNO_4$ was used as an oxidising agent. It was washed with H_2O_2 and dil.HCl several times to obtain desired product.

2.2 Reduction of GO to reduced Graphene oxide (rGO):[27,35-37]

Graphene oxide (GO) prepared by modified Hummers method was reduced by $NaBH_4$. 1g GO was dispersed in 500ml beaker containing 250 ml distilled water by continuous stirring. 1g $NaBH_4$was added slowly while stirring. Addition of $NaBH_4$produces effervescence. This solution was kept stirring for about 20-30 mins. A dark brown colored solution turned black after reduction.

2.3 Preparation of rGO and 4-Aminothiophenol (PATP) polymer by dispersion method:

1g rGO was taken in a 500ml beaker containing 250 ml Distilled Water.1g 4-aminothiophenol (PATP)was added to it and kept stirring for 24 hrs. The beaker was then kept in a water bath containing ice. 3.312g ammonium persulphate (APS) was added to the above solution at the temperature of 5-10^{0}C as oxidant for oxidative polymerization.The above mixture was then filtered and dried. This polymer is denoted asAT-4. AT-4 was characterized by FTIR, TEM, SEM, XRD and CHN analysis.
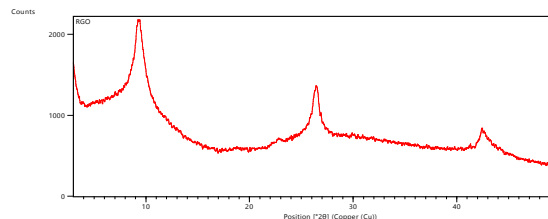
2.4 Alternative method to prepare rGO and 4-Aminothiophenol (PATP) polymer by Liquid-Solid interface method:

The aforementioned AT-4 polymer is prepared by liquid-solid interface as follows-1g rGO was taken directly in a mortar-pastel. 1g PATP was added to it and grinded together for 30 mins. A paste like substance formed at room temperature. After 30 mins, 3.312gm APS was added to it for further liquid-solid interface.A black compound was obtained. For comparison this polymer was denoted as AT-4G and was also characterized by FTIR, TEM, XRD, SEM and CHN analysis. PATP and APS were used as obtained.
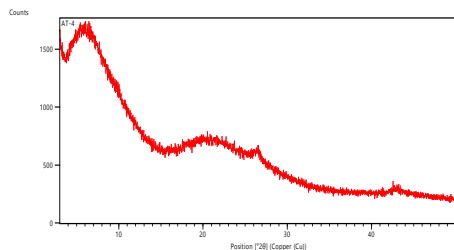
3. Results& Discussions :

On account of GO functionalization process, the initial reactants have a high dispersibility in aqueous solution while, after amine and thiol functionalization the resultant product is relatively insoluble, even its dispersibility in water is definitely diminished when contrasted with GO.
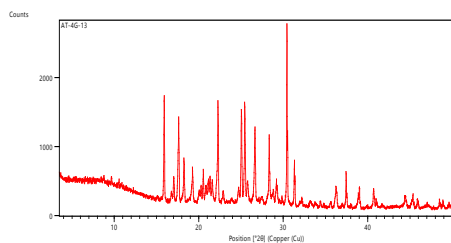
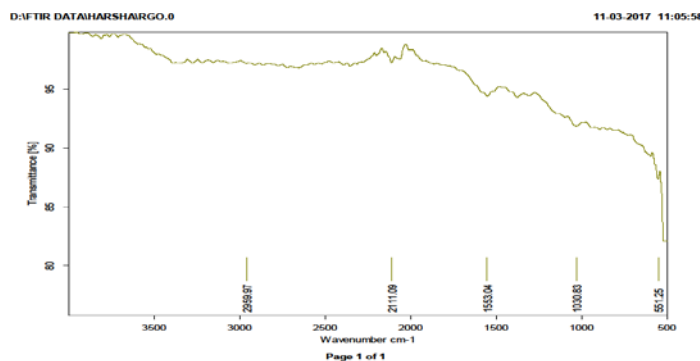Fig. 1. a. : XRD of reduced graphene oxide(rGO)

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. b. : XRD AT- 4

c. XRD of AT-4

Fig. 2 a.   FTIRreduced graphene oxide(rGO)

Fig. 2. b :   FTIR of 4 aminothiophenol- rGO polymer (AT-4)

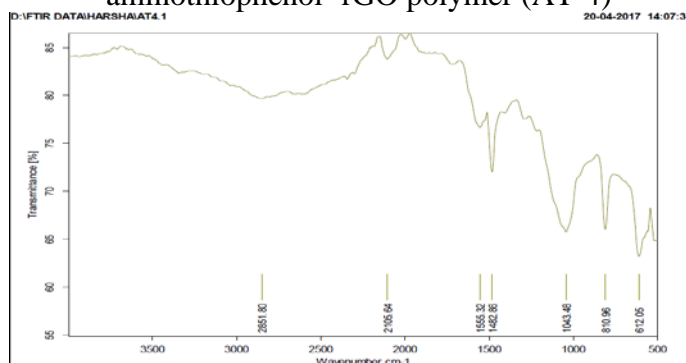Fig. c. : FTIR of 4aminothiophenol – rGO polymer AT-4G

With a specific goal to examine the structure, rGO and functionalized rGO were described by XRD. In fig. 1.a the strong diffraction peak of GO is located at a $2\theta=10.7°$, indicating the layer-to-layer distance of 0.83 nm in view of the Bragg equation, owing to the introduction of various oxygen-containing groups and water molecules. Whereas, the diffraction peak of the functionalized-rGO (fig. 1.b.) moves to a lower 2θ angle with a d-spacing of 1.10 nm, which is 0.27 nm larger than that of GO, and 0.77 nm larger than the lattice spacing of graphite (d-spacing=0.334 nm). In fig.1.b & 1.c the increase in the layer-to-layer distance signifies the fact that $-NH_2$ and S-H groups are covalently attached to therGO surface and many of layers are well separated. Now the polymers become more appropriate for embedding the desired materials.

TheXRD patterns show that crytallinity of the rGO is significantly influenced by PATP in both the techniques of dispersion and liquid-solid interface .
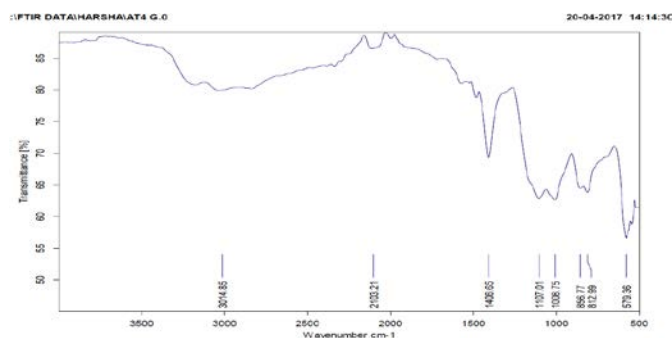
FTIR spectra of GO demonstrate clear bending and stretching vibrations of OH hydroxy, C=Ocarbonyl/carboxyl, C-O epoxy and alkoxy, and C=C aromatic groups, as indicated in various refrences.The FTIR spectrum ofrGO(fig. 2 .a) &functionalized-rGO (fig. 2.b. & 2.c.)shows a clear decrease in both OH and C-O epoxy groups. The functionalization of the GO material causes a decreaseof its hygroscopic nature, and thus the noticeable decrease inhydrogen-bonded

OH groups may be due to aloss ofadsorbed water, or might be the result of reduction. GO displays a broad FTIR peak at 3500-2500 cm^{-1} attributed to the stretching of adsorbed water molecules andstructural O–H groups (such as alcohol and carboxylic acid) which do not allow distinction between C–OH and H$_2$O peaks. The sharp peak at 1715 cm^{-1} is attributed to the C=O stretchingof carboxylic acid group, 1614 cm^{-1} to the sp^{2}C=C and conjugated C=O stretching, 1213 cm^{-1}and 1040 cm^{-1} to C–O stretching of phenolic and epoxy groups, respectively. In the case offunctionalized -rGO, two almost distinct sharp peaks at 3345cm^{-1} and 1580cm^{-1} attributed to N-H stretching,which overlapped with a broad peak arisen from carboxylic acid stretching, can be seen.Moreover, compared to GO, the bandwidth at 3500-2500 cm^{-1}and the intensity of all peaksattributed to oxygen functional groups are remarkably decreased, indicating that most of GOoxygen species are reduced or substituted with amino and thiol groups during the functionalization process. Hence, FTIR analysis confirms the amino & thiol functionalization of rGO.
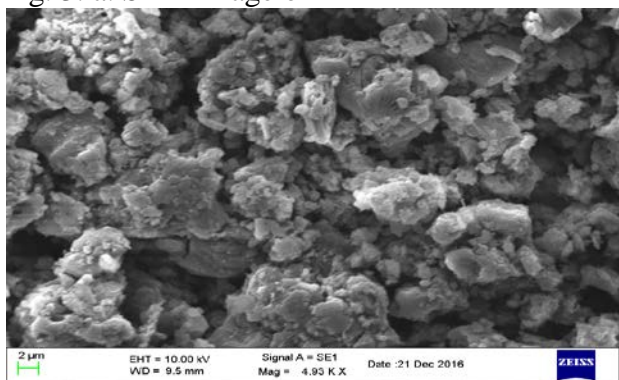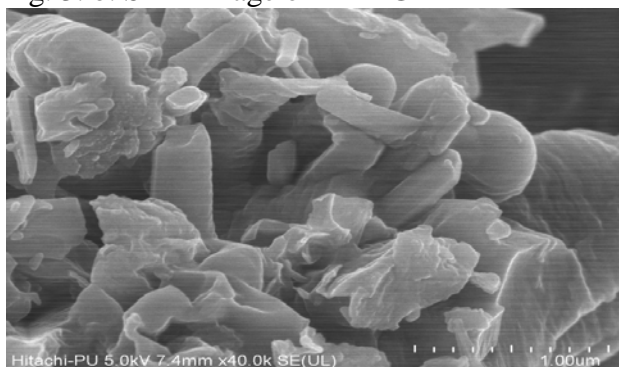
Fig. 3. a. SEM image of AT-4

Fig. 3. b. SEM image of AT-4G

The SEM images of functionalized-rGO (fig. 3.a & 3.b.) showing the respectable exfoliation of graphite during oxidation process.
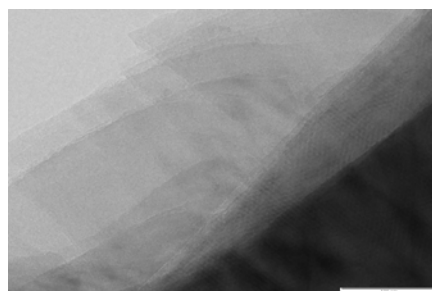
Fig. 4. a. : TEM AT 4
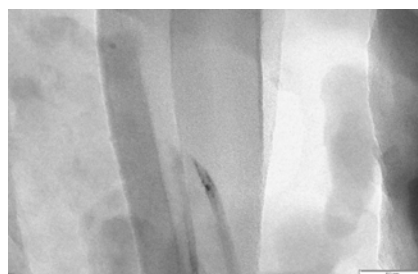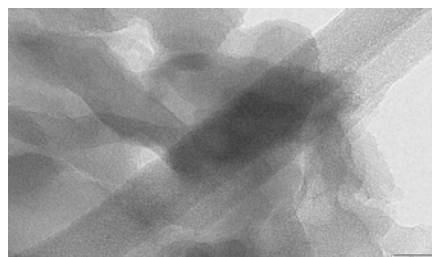

Fig. 4.b. : TEM AT 4

Fig. 4.c.: TEM AT 4G

Fig. 4. d. : TEM AT 4G

The TEM images of AT- 4 are shown in Figure 4a and 4b. whereas fig.4c & 4d. represent TEM images of AT- 4G.
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The TEM Images of functionalized-rGO showed that the sheets are informally folded on each other with many ripples and seem to form the tangled patches. Between the crosswise edges of the multi-layer of functionalized-rGO a porous network with a size ranging from 100 to 500 nm, is clearly observable. These specifications could be related to the amino and thiol surface functional groups.

The EDX elemental mapping of carbon and nitrogen of a large area of functionalised-rGodispersed powder illustrate a homogeneous distribution of N and S functionalities on the graphene structure. The EDX elemental analysis, whichis

Fig5. a. : CHNS Analysis of AT-4.
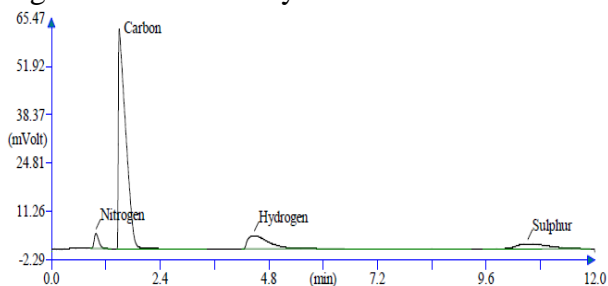
Retention Time (min)	Component Name	Element %
0.983	Nitrogen	5.819
1.500	Carbon	52.296
4.483	Hydrogen	3.336
10.525	Sulphur	14.338
		75.788

Fig.5. b : CHNS Analysis of AT-4G.
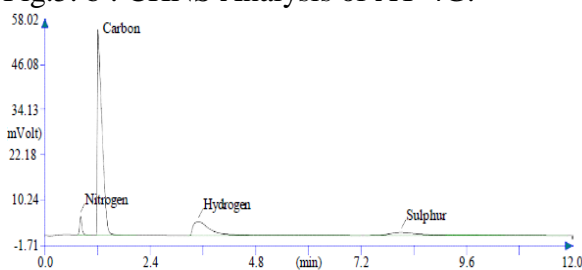
RetentionTime (min)	Component Name	Element %
0.817	Nitrogen	3.983
1.208	Carbon	38.321
3.500	Hydrogen	2.895
8.125	Sulphur	9.586
		54.785

CHNS analysis also confirmed the presence of nitrogen and sulphur in the polymers AT-4 and AT-4G indicating the amine and thiol functionalization of rGO.

4. Conclusions:

This amino and thiol functionalized-rGO is so important to future research for the extension of various graphene-based composites. More recently, different substituted amines have been embedded to rGO to be applied in various fields of physics, chemistry, biology, biochemistry and energy related materials. These wide potential applications of such functionalized-Gr need a facile and controllable method to implant a high fraction of functional groups in Gr sheets. These amine and thiol groups can assist the immobilization of inorganic molecules and organic materials or high loading metal nanoparticles to obtain graphene-based composite materials for development of high performance and flexible electro-catalyst for fuel cells and bio-electronic devices.

5. Acknowledgements:

6. References:

1. AmerKhudairHussien Al-Nafiey, (2016). Reduced graphene oxide-based nanocomposites. Synthesis, characterization & applications. Lille 1,
2. C. Lee , X. D. Wei , J. W. Kysar , J. Hone, (2008)Measurement of Elastic Properties andIntrinsic Strength of Monolayer Graphene.Science;Vol. 321 , 385-389.
3. A. A. Balandin, S. Ghosh, W. Z. Bao, I. Calizo, D. Teweldebrhan,F. Miao, C. N. Lau, (2008) Superior Thermal Conductivity Property of Single Layer Graphene.Nano Letter,8, 902.
4. VenkatesanTharanitharan and Rajesh Kalaivani, (2014) Adsorption of Heavy Metal ions from Water and Wastewater

Using Modified Acrylic Ester Polymeric Resin.CheSci Rev Lett, 2(5), 393-401

5. K. I. Bolotin , K. J. Sikes , Z. Jiang , M. Klima , G. Fudenberg , J. Hone ,P. Kim, H. L. Stormer, (2008), Ultrahigh electron mobility in suspended graphene.Solid State Commun. 146,351.

6. Jian Bao, You Fu and Zhihao Bao. (2013)Thiol-functionalized magnetite/graphene oxide hybrid as a reusable adsorbent for Hg2+ removal. Nanoscale Research Letters, 8:486

7. Da Chen, Hongbin Feng, and Jinghong Li.(2012)Graphene Oxide: Preparation, Functionalization, and ElectrochemicalApplications.Chem. Rev., 112, 6027−6053

8. S. V. Morozov , K. S. Novoselov , M. I. Katsnelson , F. Schedin , D. C.Elias, J. A. Jaszczak , A. K. Geim. (2000). Ultraviolet Raman microscopy of single and multilayer graphene,Phys. Rev. Lett,100, 016602.

9. VivekDhand, KyongYop Rhee, Hyun Ju Kim, and Dong Ho Jung (2013) A Comprehensive Review of Graphene nanocomposites: Journal of NanomaterialsVolume, Article ID 763953, 14 pages

10. Na Zhou, Jinhua Li, Hao Chen, Chunyang Liao, Zhaopeng Chen, Lingxin ChenA functional graphene oxide-ionic liquid composites/gold nanoparticles sensing platform for ultrasensitive electrochemical detection ofHg2+DOI: 5 10.1039/b000000x

11. AsoNavaee,AbdollahSalimi,(2015)Efficient amine functionalization of graphene oxide through Bucherer reaction: An extraordinary metal-free electrocatalyst for oxygen reduction reaction RSC Advances Page 2-25DOI: 10.1039/C5RA07892J

12. D.R. Dreyer, S. Park, C.W. Bielawski and R.S. Ruoff, (2010) The chemistry of Graphene Oxide.Chem. Soc. Rev., 39, 228–240.

13. V. Singh, D. Joung, L. Zhai, S. Das, S.I. Khondaker and S. Seal, (2011) Graphene Based Materials-Past, Present and Future.Prog. Mater. Sci.56, 1178–1271.

14. V. Georgakilas, M. Otyepka, A.B. Bourlinos, V. Chandra, N. Kim, K.C. Kemp, P.Hobza, R. Zboril and K.S. Kim, (2012) Functionalization of Graphene: Covalent and Non-Covalent Approaches;Chem. Rev., 112, 6156–6214.

15. A. Schlierf, P. Samori and V. Palermo, (2014) Graphene-organic composites for electronics;optical & electronic interaction in vacuum, liquids &thin solid films; J. Mater. Chem. C, 2, 3129-3143.

16. M. Bacon, S.J. Bradley, T. (2014) Graphene Quantum Dots. Nann, Part. Part. Syst. Charact., 31, 415–428.

17. S. Eigler and A. Hirsch, (2014) Chemistry with Graphene & Graphene oxide- Challenges for synthetic chemists.Angew. Chem. Int. Ed 53, 2-21.

18. Ilayda Duru, Duygu Ege, and Ali Reza Kamali Graphene oxides for removal of heavy and preciousmetals from wastewater.10.1007/s10853-016-9913-8

19. Xiangto Wan, Yifei Guo, Li Yang, Meihua Han, Jing Zhao and Xiaoliang Cheng(2012)Nanomaterials as Sorbents to Remove Heavy Metal Ions in Wastewater TreatmentJ Environ Anal Toxicol. Volume 2 • Issue 7 • 1000154

20. Layek RK, Nandi AK, (2013) A Review on Synthesis and Properties of Polymer FunctionalizedGraphenePolymer, doi: 10.1016/j.polymer.2013.06.027

21. T.S. Sreeprasad, Shihabudheen M. Maliyekka, K.P. Lisha, T. Pradeep(2011) Reduced graphene oxide–metal/metal oxide composites: Facile synthesis and application in water purificationJournal of Hazardous Materials 186, 921–931.

22. Chuyen V. Phama, Michael Ecka, and Michael Kruegera (2013) Thiol functionalized reduced graphene oxide as abase material for novel graphene-nanoparticle hybrid composites. Chemical Engineering Journaldoi: http://dx.doi.org/10.1016/j.cej.2013.07.007

23. Y. Huang, J. Tang, L. Gai, Y. Gong, H. Guan, R. He, H. Lyu,(2013), Chemical

Engineering Journal (2017),Different approaches for preparing a novel thiol-functionalized graphene oxide/Fe-Mn and its application for aqueous methylmercury removal doi: http://dx.doi.org/10.1016/j.cej.2017.03.015

24. Helen R. Thomas, Alexander J. Marsden, Marc Walker, Neil R. Wilson, andJonathan P. Rourke. (2014)Sulfur-Functionalized Graphene Oxide by Epoxide Ring-Opening;Angew. Chem, 126, 1 – 7

25. Dr. Y. Zhu , S. Murali , Dr. W. Cai , Dr. X. Li , J. W. Suk , J. R. Potts ,Prof. R. S. Ruoff (2010)Graphene and Graphene Oxide: Synthesis, Properties,and ApplicationsAdv. Mater., 22, 3906–3924

26. Won-Chun OhAndFeng-Jun Zhang(2011)Preparation and Characterization of Graphene Oxide Reduced From a Mild Chemical Method Asian Journal of Chemistry; Vol. 23, No. 2, 875-879

27. Jianguo Song, Xinzhi Wang, and Chang-Tang Chang(2014) Preparation and Characterization of Graphene Oxide Journal of NanomaterialsVolume 2014, Article ID 276143, 6 pageshttp://dx.doi.org/10.1155/2014/276143

28. Zhao J, Pei S, Ren W, Gao L, Cheng HM, ACS Nano. 2010. Efficient preparation of large-area graphene oxide sheets for transparent conductive films.Sep 28; 4(9):5245-52.

29. Paulchamy et al., (2015).A Simple Approach to Stepwise Synthesis of Graphene OxideNanomaterial; J NanomedNanotechnol, 6: 1

30. Narasimharao K, Venkata RamanaG, Sreedhar D and Vasudevarao V(2016).Synthesis of Graphene Oxide by Modified Hummers Method and Hydrothermal Synthesis of Graphene-NiO Nano Composite for Supercapacitor Application J Material SciEng, 5:6

31. YanwuZhu, ShanthiMurali, WeiweiCa Xuesong Li, Ji Won Suk , Jeffrey R. Potts ,AndRodney S. Ruoff (2010))Graphene and Graphene Oxide: Synthesis, Properties, and Applications Adv. Mater., 22, 3906–3924

32. Y. Si, E. T. Samulski, (2008).Synthesis of Water Soluble GrapheneNano Lett, 8, 1679.

33. H.-J. Shin, K. K. Kim, A. Benayad , S.-M. Yoon, H.K.Park,I.-S. Jung,M. H. Jin, H.-K.Jeong , J. M. Kim , J.-Y. Choi, Y. H. Lee, (2009)Efficient Reduction of Graphite Oxide by SodiumBorohydride and Its Effect on Electrical Conductance Adv. Funct.Mater.,19, 1987.

34. SinaAbdolhosseinzadeh, Hamed Asgharzadeh & HyoungSeopKimFast and fully-scalable synthesis of reduced graphene oxideScientificReports | 5:10160 | DOI: 10.1038/srep10160

35. Vandana Sharma, AveshGarg, Suresh ChanderSood (2015). Graphene Synthesis via Exfoliation of Graphite by Ultrasonication .International Journal of Engineering Trends and Technology (IJETT) – Volume 26 Number 1- ISSN: 2231

36. Zhen-zhen Yang et al, (2015).A simple method for the reduction ofGraphene oxide by sodium borohydride with $CaCl_2$ as a catalyst; New Carbon Materials,30(1): 41–47

37. A. K. Geim and K. S. Novoselov (2007).The Rise of Graphene. Nature Material, 6(3), 183-91.