

Chemical Functionalization of Graphene and Graphene oxide -A review

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Abstract: Graphene is a material that has generated enormous research interest and activity in the past few vears due to its remarkable properties and wide applications in the fields, such as nanoelectronics, sensors, nanocomposites, batteries, supercapacitors, hydrogen storage, transparent conductors and energy storage materials. (Reduced) graphene oxides have a great potential as a functional chemical building block in fabrication of various carbon-based nanostructures and their composites, for which chemical functionalization of the materials is critically important. Functionalization of graphene is one of the key topics in graphene research. Graphene has found to be the best known transparent conductor or semiconductor. The graphene was synthesized by using chemical methods. This article aims to provide broad based coverage on the recent solution-based functionalization methods of graphene in a concise and mechanistic manner. This paper focuses on the reactions of the graphene sp^2 backbone, such as nucleophilic addition, cycloaddition, free radical addition, substitution and rearrangement, and reduction of graphene oxide and its various environmental applications.

I. INTRODUCTION

Functionalization of graphene is one of the key topics in graphene research. Generally, there are two main categories of functionalization viz. chemical and nonchemical. Chemical functionalization is realized through the formation of new covalent bonds between the atoms native to RGO/GO and the guest functional groups, in contrast, nonchemical functionalization is mainly based on π interaction between guest molecules and RGO/GO, i.e., mainly a physical interaction. Both types of functionalization can induce some property changes for graphene, but the chemical routes are more effective. So far, various chemical routes have been proposed, which successfully incorporate a large number of different atoms/organic groups into graphene, including heterogeneous atoms doping, diazonium amidation, silanization, esterization. coupling, substitution, cycloaddition, etc. The research also demonstrates that the size of graphene (particularly the thickness of the ribbons) strongly affects the reactivity of graphene and the application of the functionalized graphene¹⁻². Functionalization and dispersion of graphene sheets are of crucial importance for their applications. Dispersion of graphene enables processing

of this material by solvent-assisted techniques, such as layer-by-layer (LBL) assembly², spin coating³ and filtration. Soluble or dispersible graphene sheets are usually prepared by chemical modifications or noncovalent functionalization. For example, reduction of graphene oxide modified by alkyl amine produced stable dispersions of graphene sheets in organic solvents, and water-soluble graphenes were obtainable by inducing carboxylic or sulfonate groups onto their basal planes²⁻⁷ Non-covalent functionalization is considered to have less impact on the structure and properties of graphene. The reduction of graphite oxide in the presence of poly (sodium 4-styrenesulfonate) formed a stable aqueous dispersion of graphene sheets. Despite the great application potential, it is worth mentioning that graphene itself possesses zero band gap as well as inertness to reaction, which weakens the competitive strength of graphene in the field of semiconductors and sensors. This is one of the reasons for the huge increase in the number of research projects aimed at functionalization of graphene including reactions of graphene (and its derivatives) with organic and inorganic molecules, chemical modification of the large graphene surface, and the general description of various covalent and noncovalent interactions with graphene⁸⁻¹⁵. Band gap opening of graphene by doping, intercalation, and striping would be useful for functional nanoelectronic devices¹⁶⁻¹⁷. The organic covalent functionalization reactions of graphene include two general routes: (a) the formation of covalent bonds between free radicals or dienophiles and C=C bonds of pristine graphene and (b) the formation of covalent bonds between organic functional groups and the oxygen groups of GO. The most striking organic species for the reaction with sp² carbons of graphene are organic free radicals and dienophiles. Usually both are intermediary reactive components that are produced under certain conditions in the presence of graphene. This result is interpreted on the basis of the previous experimental and theoretical experience with fullerene and carbon nanotubes ¹⁸.

II. COVALENT FUNCTIONALIZATION OF GRAPHENE/GRAPHENE OXIDE

Niyogi and co-workers¹⁹ attached the graphene with nitrophenyls covalently. This shows that the introduction of a band gap, which can be controlled, by making the

functionalized graphenes which are potentially useful as semiconducting nanomaterials. He developed a facile and versatile method with Gao²⁰ for the introduction of various functional groups and polymeric chains onto graphene sheets via nitrene cycloaddition. This strategy allows various kinds of functional moieties and polymers to be covalently bonded to graphene, resulting in functional graphene sheets and 2-D macromolecular brushes, respectively. The functionalized graphene sheets show enhanced chemical and thermal stabilities compared with GO and can be further modified by different chemical reactions, including amidation, surface-initiated polymerization, and reduction of metal ions. The resulting functionalized graphene sheets are conductive electrically and display excellent dispersibility and processability in solvents. Yu et al.²¹ move a step forward designing and presenting a photovoltaic device using a combination of P₃HT/GO product with C60 which recorded a 200% increase in the power conversion efficiency in comparison with a pure P₃HT/C60 analogous system. This remarkable increase is attributed to an extended electron delocalization that occurred after the covalent attachment of P₃HT with GO in comparison to pure P₃HT. The formation of covalently bonded polymer-GO nanocomposites, where GO was initially functionalized with octadecylamine (ODA) has been reported by Pramoda et al.²². These ODA functionalized GO nanoplatelets were subsequently reacted with methacryloyl chloride to incorporate polymerizable -C=C- functionalities at the graphene surfaces. These intermediates were then employed in situ polymerization of methylmethacrylate to obtain covalently bonded PMMA/GO nanocomposites. Zhang et al. ²³ have reported on the formation of a hybrid material by covalent linking of C60 with GO. (Fig.1) In this synthesis an amide bond was formed between a pyrrolidine ring modified C60 and the carboxyl groups on the GO surface. Analogously to the fullerene derivatives of carbon nanotubes^{24, 25} GO-C60 hybrids could be useful in many optoelectronic applications due to their remarkable electronic and optical properties.



Fig. 1 Representation of formation of C₆₀-graphene oxide composite.

Avinash et al. ²⁶ reported covalently functionalized GO with ferrocene via a green chemistry approach at room temperature on solid phase alumina. The ferrocene/GO composite material exhibited interesting magnetic properties, with the magnetization of the composite material.

III. NONCOVALENT FUNCTIONALIZATION OF GRAPHENE

Wang et al.²⁷ reported the noncovalent functionalization of graphene with carboxylate-terminated perylene molecules. These functionalized graphene nanoplatelets were used to grow metal oxide via ALD methods. The ultrathin high dielectric integrated graphene is very useful to achieve high currents and ideal sub threshold swing without substantial gate leakage. Liu et al. 28 reported the deposition of gold nanoparticles on DNAfunctionalized graphene nanoplatelets. First thiolated DNA oligonucleotides were allowed to adsorb on GO nanoplatelets with the resulting DNA-coated GO DNA-RGO. reduced by hydrazine to Gold nanoparticles were then added to aqueous solutions of DNA-RGO and DNA-GO to form the related composites. These gold-decorated DNA-functionalized graphene nanoplatelets have potential application in catalysis, magnetism, battery materials, optoelectronics, field effect devices, and bio detection platforms. Functionalization of graphene through self-assembly of a hydrophobic backbone of Nafion has been reported by Choi et al.²⁹. Resulting graphene nanoplatelets were readily dispersible and displayed high conductivity and electrochemical bio sensing properties for organophosphates. Ansari et al. ³⁰ reported that a Nafion/ graphene nanocomposite can be produced by dispersion of Nafion in a GO aqueous solution and subsequent reduction with hydrazine. In their report, they showed that the presence of Nafion nanochannels dramatically increases the conductivity of graphene. Panchokarla et al. ³¹ prepared Nitrogen- or boron-doped graphene by using an arc discharge technique. N-doped graphene sheets are produced by carrying out the arc discharge between carbon electrodes in the presence of hydrogen and pyridine or ammonia. To produce borondoped graphene, it was necessary to use boron-stuffed graphite electrodes or a mixture of hydrogen and diborane vapour. The B-doped graphene showed p-type semiconductor behaviour.

IV. APPLICATION OF FUNCTIONALIZED GRAPHENE

Huang et al. ³² have shown that graphene can be used to absorb Pb(II) cations from aqueous solution. The authors noted that the adsorption capacity was strongly dependent on solution pH. In a similar way, Vasudevan and

Lakshmi ³³ have demonstrated that phosphate anions can be removed from aqueous solutions by graphene at an optimal pH value of nearly 7. They concluded that the absorption kinetics followed a second-order kinetic model, suggesting that the absorption was chemically controlled. GO has been shown by Zhao et al.³⁴ to be an effective absorbent of both Cd(II) and Co(II) from large volumes of water. Yang and co-workers ³⁵ further showed that methylene blue can be effectively removed from aqueous solutions using GO. The authors recorded a removal efficiency higher than 99%. Zhao and

colleagues ³⁶ prepared sulphonated graphene nanosheets from GO which is highly effective for the removal of naphthalene and 1-naphthol, with very high absorption capacities. Chandra and Kim³⁷ functionalized graphene sheets with polypyrole (PPy), with the resulting composite material showing high and selective absorption capacity for Hg(II) cations. The presence of graphene in PPy enhances the charge density of the pyrrolic nitrogen, thus increasing the electrostatic interaction between adsorbate and adsorbent. In a recent article, Chen et al. ³⁸ showed that upon irradiation of CdSe/ZnS nanocrystals deposited on graphene, an efficient energy transfer occurs from the individual NPs to the graphene surface. This energy transfer is indicated by a fluorescence intensity quenching of the CdSe/ZnS nanocrystals by a factor of 70. The CdSe/ZnS nanocrystals were deposited by spin casting onto the graphene sample deposited on quartz substrates at a low Under illumination. fluorescence density. from individual nanocrystals located on the graphene layer or on the quartz substrate could be observed, with strong fluorescence quenching observed for particles deposited on the graphene sheets. A similar fluorescence quenching was observed when CdS and CdSe NPs were dispersed on GO nanoplatelets ³⁹.

V. CONCLUSION

New methodology has been developed in environmental and electrochemical aspect. Apart from developing new methodologies, it is equally important to improve current methods to increase the ease of functionalization as well as to reduce possible chemisorbed or physisorbed contaminants from the introduction of new functional adducts. Lastly, the improvement in synthetic modifications on graphene is definitely to stay and to bring promising opportunities to graphene.

REFERENCES

- R. Sharma, J. Baik, C.Perera, "Anomalously Larg Reactivity of Single Graphene Layers and Edges toward Electron Transfer Chemistries." Nano Letters, vol. 10, pp.398-405, (2010).
- [2] H, Lim, J, Lee, H. Shin, "Spatially Resolved Spontaneous Reactivity of Diazonium Salt on Edge and Basal Plane of Graphene without Surfactant and its Doping Effect." Langmuir, vol.26, pp. 12278-12284, (2010).
- [3] D. Li, M. B. Muller, S. Gilje, R. B. Kaner, G. G. Wallace, "Processable aqueous dispersions of graphene nanosheets". Nature Nanotech. Vol.3 pp.101-105, (2008)
- [4] W. Hong, Y.Xu, G. Lu, C. Li G. Shi, "Transparent graphene/PEDOT- PSS composite films as counter electrodes of dye-sensitized solar

cells." Electrochem. Commun. vol.10, pp.1555-1558, (2008).

- [5] H. Chen, M. B. Muller, K. J. Gilmore, G. G. Wallace, D. Li. "Mechanically strong, electrically conductive, and biocompatible graphene paper." Adv. Mater. Vol.20, pp. 3557-3561, (2008).
- [6] S. Niyogi, E. Bekyarova, M. E. Itkis, J. L. McWilliams, M. A. Hamon, R. C. Haddon, "Solution properties of graphite and graphene." Am.Chem. Soc, vol. 128, pp.7720-7721, (2006).
- Y. Si and E. T. Samulski, "Synthesis of water soluble graphene Nano Lett. Vol.8, pp.1679-1682, (2008).S. Stankovich, R. D. Piner, X. Q. Chen, N. Q. Wu, S. T. Nguyen, R. S. Ruoff, "Stable aqueous dispersions of graphitic nanoplatelets via the reduction of exfoliated graphite oxide in the presence of poly (sodium 4styrenesulfonate)."J. Mater.Chem.vol.16, pp.155-158 (2006).
- [8] Q. H. Wang, M. C. Hersam, "Room-temperature molecular-resolution characterization of selfassembled organic monolayer on epitaxial graphene." Nat. Chem, vol.1, pp.206-211, (2009).
- [9] A. Bostwick, T. Ohta, T. Seyller, K. Horn, E. Rotenberg, "Quasiparticle dynamics in graphene." Nat.Phys. vol.3, pp. 36-40, (2007).
- [10] T. Ohta, A. Bostwick, T. Seyller, K. Horn, E. Rotenberg, "Controlling the electronic structure of bilayer graphene". Science, vol. 313, pp. 951-954, (2006).
- [11] D. C. Elias, R. R Nair, T. M. G. Mohiuddin, S. V. Morozov, P. Blake, M. P. Halsall, A. C. Ferrari, D. W. Boukhvalov, M. I. Katsneltson, A. K. Geim, K. S. Novoselov, "Control of graphene's properties by reversible hydrogenation: evidence for graphane". Science, vol.323, pp 610-613, (2009).
- [12] X. R. Wang, X. L. Li, L. Zhang, Y. Yoon, P. K. Weber, H. L. Wang, J. Guo, H. J. Dai, "N-Doping of Graphene Through Electrothermal. Reactions with Ammonia," Science, vol.324, pp.768-771, (2009).
- [13] D. V. Kosynkin, A. L. Higginbotham, A. Sinitskii, J. R. Lomeda, A. Dimiev, B. K. Price, J. M. Tour, "Longitudinal unzipping of carbon

nanotubes to form graphene nanoribbons," Nature, vol.458, pp. 872-876, (2009).

- [14] K. P. Loh, Q. Bao, P. K. Ang, J.Yang, "The chemistry of graphene, J. Mater. Chem, vol. 20, pp. 2277-2289, (2010).
- [15] J. Park, W. H. Lee, S. Huh, S. H. Sim, S. B. Kim, K. Cho, B. H. Hong, K.S. Kim, "Work-Function Engineering of Graphene Electrodes by Selfassembled Monolayers for High-Performance Organic Field-Effect Transistors," J. Phys. Chem. Lett.vol. 2, pp. 841-845, (2011).
- [16] J. Park, S. B. Jo, Y. J. Yu, Y. Kim, J. W. Yang, W. H. Lee, H. H. Kim, B. H. Hong, P. Kim, K. Cho, K. S. Kim, "Single-Gate Bandgap Opening of Bilayer Graphene by Dual Molecular Doping" Adv. Mater. Vol.24, pp. 407-411, (2012).
- [17] V. Georgakilas, M.Otyepka, A. B. Bourlinos, V. Chandra, N. Kim, K. C. Kemp, P. Hobza, R. Zboril, K.S. Kim, "Functionalization of graphene: covalent and non-covalent approaches, derivatives and applications." Chem. Rev. vol.112, pp. 6156-6214, (2012).
- S. Niyogi, E. Bekyarova, M. E. Itkis, H.Zhang, K. Shepperd, J. Hicks, M.Sprinkle, C. Berger, N. Lau, C. De, W. A. Heer, E. H. Conrad, R. C Haddon, Nano Lett. 10 4061. (2010)
- [19] H. He, C. Gao, General Approach to Individually Dispersed, Highly Soluble, and Conductive Graphene Nanosheets Functionalized by Nitrene Chemistry Chem. Mater.vol. 22, pp.5054-5064, (2010).
- [20]] D.Yu, Y.Yang, M. Durstock, J. B. Baek, L.Dai, Soluble P3HT-grafted graphene for efficient bilayer-heterojunction photovoltaic devices.ACS Nano.vol. 4, pp. 5633-5640, (2010).
- [21] K. P. Pramoda, H. Hussain, H. M. Koh, H. R. Tan, C. B. He, Covalent bonded polymergraphene nanocomposites," J. Polym. Sci.,Part A Polym Chem.vol. 48, pp.4262-4267, (2010).
- [22] Zhang, X., Y. Huang, Y. Wang, Y. Ma, Z. Liu and Y. Chen, "Synthesis and characterization of a graphene-C₆₀ hybrid material". Carbon, Vol.47 pp.334-337, (2009).

- [23] A.G.Nasibulin, P. V. Pikhitsa, H. Jiang, D. P. Brown, A. V. Krasheninnikov, A. S. Anisimov, P. Queipo, A. Moisala, M.Choi, D. Tomanek, E. I. Kauppinen, etal. A novel hybrid carbon material Nat. Nanotechnol. Vol.2, pp.156-161, (2007).
- [24] J. L. Delgado, P. Cruz, A. Urbina, J. T. Navarrte, J.Casado, F. Langa, "Synthesis and characterization of a graphene–C60 hybrid material," Carbon, Vol.45, pp.2250-2252, (2007).
- [25] M. B. Avinash, K. S. Subrahmanyam, Y. Sundarayya, T. Govindaraj "Covalent modification and exfoliation of graphene oxide using ferrocene," Nanoscale, vol. 2, pp. 1762-1766, (2010).
- [26] X. Wang, S. M. Tabakman, H. Dai, "Atomic layer deposition of metal oxides on pristine and functionalized graphene," J.Am. Chem. Soc. vol.130, pp. 8152-8153, (2008).
- [27] J. Liu, Y. Li, Y. Li, J. Li, Z. Deng, "Noncovalent DNA decorations of graphene oxide and reduced graphene oxide toward water-soluble metal carbon hybrid nanostructure via selfassembly", J. Mater. Chem. vol. 20, pp.900-906, (2010).
- [28] B. G. Choi, H. Park, T. J. Park, M. H. Yang, J. S. Kim, S.Y.Jang, N. S. Heo, S. Y. Lee, J. Kong, W. H. Hong, "Solution chemistry of selfassembled graphene nanohybrids for highperformance flexible biosensors," A CS Nano,vol. 4, pp.2910-2918, (2010).
- [29] S. Ansari, A. Kelarakis, L. Estevez, E. P. Giannelis, "Oriented arrays of graphene in a polymer matrix by in situ reduction of graphite oxide nanosheets," Small,vol. 6, pp. 205-209, (2010).
- [30] L. S. Panchokarla, K. S. Subrahmanyam, S. K. Saha, A. Govindaraj, H. R. Krishnamurthy, U. V. Waghmare, C. N. Rao, "Synthesis, Structure, and Properties of Boron- and Nitrogen-Doped Graphene," R. Adv. Mater. Vol.21, pp. 4726-4730, (2009).
- [31] Z. H. Huang, X. Zheng, W. Lv, M. Wang, Q. H. Yang, F. Kang. Adsorption of lead (II) ions from aqueous solution on loe temperature

exfoliated graphene nanosheets." Langmuir, vol.27, pp.7558-7562 (2011).

- [32] S. Vasudevan, J. Lakshmi, "The adsorption of phosphate by graphene from aqueous solution". RSC Adv. Vol. 2, pp.5234-5242, (2012).
- [33] G. Zhao, J. Li, X.Ren, C.Chen, X. Wang, "Fewlayered graphene oxide nanosheets as superior sorbents for heavy metal ion pollution management." Environ. Sci. Technol. Vol.45, pp.10454-10462, (2011).
- S. T. Yang, S. Chen, Y. Chang, A. Cao, Y. Liu, [34] H. J.Wang. Removal of methylene blue from aqueous solution by graphene oxide. Colloid Interface Sci. 359 (2011) .
- [35] G. Zhao, L. Jiang, Y. He, J. Li, H. Dong, X. Wang, W. Hu, "Sulfonated graphene for persistent aromatic pollutant management". Adv. Mater.vol. 23, pp.3959-3963, (2011).

- V.Chandra, K. S. Kim, "Highly selective [36] adsorption of Hg²⁺ by a polypyrrole-reduced graphene oxide composite Chem. Commun, vol. 47, pp. 3942-3944 (2011).
- [37] Z. Chen, S. Berciaud, C. Nuckolls, T. F. Heinz, L. E. Brus, "Energy transfer from individual semiconductor nanocrystals to graphene," ACS Nano, vol. 4, pp.2964-2968, (2010).
- A. Cao, Z. Liu, S. Chu, M. Wu, Z. Ye, Z. Cai, Y. [38] Chang, S. Wang, Q.Gong, Y. Liu, "A Facile One-step Method to Produce Graphene-CdS Quantum Dot Nanocomposites as Promising Optoelectronic Materials," Adv. Mater.vol. 22,pp.103-106, (2010).
- Y. T. Kim, J. H. Han, B. H. Hong, Y. U. Kwon, [39] "Electrochemical Synthesis of CdSe quantum-Dot arrays on a graphene," Adv. Mater. vol.22, pp. 515-518, (2010).

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