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Graphene Oxide and N-Doped Graphene as Carbocatalysts in Organic Reactions

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Abstract: Due to promising merits such as nontoxicity, large surface area, high activity/selectivity, and good stability, graphene oxide (GO) and N-doped graphene (N-G) have attracted much attention as catalysts in various catalytic applications. Among other carbon materials such as carbon nanotube, fullerene like materials, 2D graphene oxide (GO) exhibited outstanding results in various organic reactions. Graphene oxide (GO), as a metal-free and readily available carbocatalyst, has been extensively studied in catalytic organic transformations. In this review, we will overview of the progress on the application of native GO and also N-doped carbon nanofibers as a catalyst for various organic transformations reported in the recent years.

Keywords: graphene oxide; N-doped graphene; organic reactions; oxidation; reduction; carbocatalyst; green

1. Introduction

In 80% of the chemical industrial processes are involved metal-catalysts.[1] Transition metals and or noble metals such as copper, nickel, palladium, platinum, cobalt, ruthenium, silver gold, and so on are dominated.[2-10] However, the metal-mediated catalytic systems are highly limited due to the high-cost and environmentally friendly. Recently, carbocatalysts which uses no metals are highly preferred catalytic systems for the organic transformation due to its positive views. Various carbon materials such as activated carbon, carbon nanotubes, heteroatoms doped carbon materials, graphene oxide, graphene with heteroatoms (N, O, S and so on) are employed as catalyst or support for active metal nanoparticles for these organic transformations.[11] Among them, graphene oxide and N-doped graphene is the most suitable and attractive candidates for the carbo-catalytic applications. Because of its acidic nature, the most common uses of GO are in organic reactions such as Michael addition, oxidation reactions, Friedel-Crafts reaction, aza-Michael addition, and ring opening polymerization.[12,13] In fact, the catalytic systems are green and environmentally friendly. Mass production of such 2D-graphene oxide and n-doped graphene is now possible.

This mini review aims to give an overview of the progress on the application of native GO and also N-doped carbon nanofibers as a catalyst for various organic transformations reported in the recent years.

2. Graphene Oxide as Carbocatalyst

Oxidation of alcohols is one of the key reactions in organic chemistry. The resultant carbonyl compounds such as aldehydes and ketones are essential in perfume industry. They can be used as an intermediate in C–C bond-forming reactions and in the synthesis of fine chemicals. These reactions are often performed with transition metal catalysts such as Pd, Au, Pt, and Ru. However, the most of the metal-catalyst mediated catalytic systems are often expensive, difficult to remove, toxic, and are frequently obtained from limited natural resources. It is found that the graphene oxide is demonstrated to be an efficient metal-free catalyst for the oxidation of alcohols. Fig. 1 shows the structure of graphene oxide.

Mirza-Aghayan and co-workers[14] used graphite oxide (GO) as an effective catalyst for the synthesis of aldehydes and ketones from various alcohols under ultrasonic irradiation. The GO displays several advantages, including low cost, ease of synthesis, and high stability to ambient conditions.

Sedrpoushan et al.,[15] utilized the nanoscale graphene oxide sheets as highly efficient carbocatalysts in green oxidation of benzylic alcohols and aromatic aldehydes. Overall, NGO is a powerful and environmental-friendly (metal-free) catalyst for oxidation of some benzyl alcohols, depending on the nature of the substituents, and all aromatic aldehydes (substituent-independent). NGO is promising for applications in environmental chemistry.

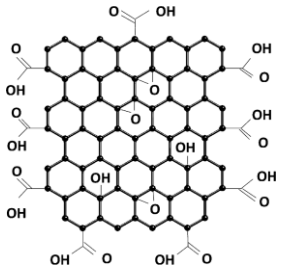
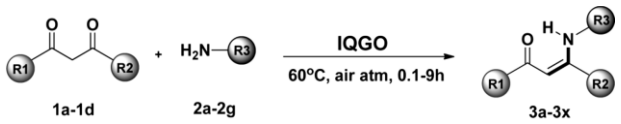


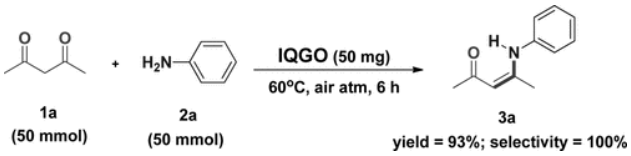
Fig. 1. Graphene oxide with oxygen-functional groups (C═O, −COOH, C—OH, and −C—O—C−).



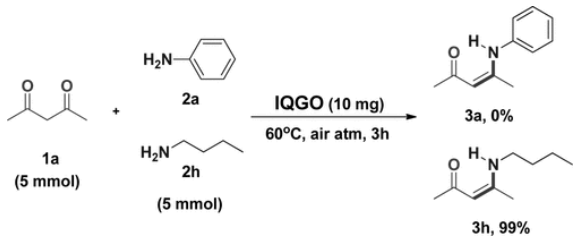
R_1 = CH_3, OCH_3, OCH_2CH_3 or CF_3 and R_2 = CH_3

R_3 = C_6H_5, C_6H_4-CH_3, C_6H_4-Cl, C_6H_4-OCH_3, C_6H_4-F, C_6H_{11} or C_4H_9

Scheme 1. Industrial-quality graphene oxide (IQGO) catalysed metal and solvent-free synthesis of β-ketoenamines under feasible conditions.[16]

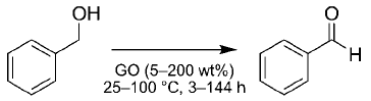


Scheme 2. Scale reaction of IQGO catalyzed condensation of acetylaceton (1a) and aniline (2a).[16]

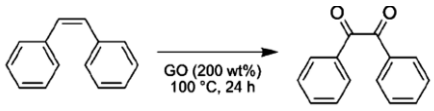


Scheme 3. Chemoselectivity of IQGO system.[16]

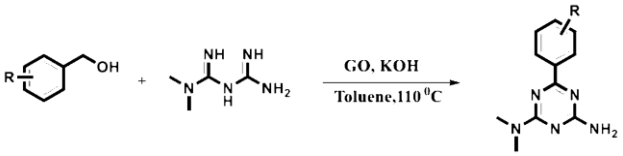
The β-enamino ketones and esters are essential basic units for the formation of biologically active motifs such as peptides, β-amino esters and alcohols, γ-amino alcohols and alkaloids. The β-ketoenamines are highly efficient antitumor, antibacterial, and anti-inflammatory agents. There are several metal catalysts mediated direct condensation of β-dicarbonyl compounds with amines are demonstrated. Metal catalysts such as $NaAuCl_4$, Ag nanoparticles, $Mg(ClO_4)_2$, $CoCl_2{\cdot}6H_2O$, $Zn(OAc)_2{\cdot}2H_2O$, $CeCl_3{\cdot}7H_2O$, $Zn(ClO_4)_2{\cdot}6H_2O$, $ZrCl_4$, $SnCl_4$, Cu nanoparticles, Cu(II) nitrate trihydrate, $ZrOCl_2{\cdot}8H_2O$, and $InBr_3$ reported to date. However, Gopiraman et al., used industrial-quality graphene oxide (IQGO) as catalyst for the synthesis of β-ketoenamines under feasible conditions. They found that the IQGO is highly active for the synthesis of β-ketoenamines under feasible conditions. Scheme 1 shows industrial-quality graphene oxide (IQGO) catalysed metal and solvent-free synthesis of β -ketoenamines under feasible conditions.[16] Scheme 2 shows scale reaction of IQGO catalyzed condensation of acetylaceton (1a) and aniline (2a). Scheme 3 depicts the chemoselectivity of IQGO system. The IQGO is not only efficient but also reusable and selective.



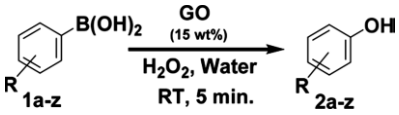
Scheme 4. Oxidation of benzyl alcohol using graphene oxide (GO).[17]



Scheme 5. Oxidation of cis-stilbene using GO.[17]



Scheme 6. GO as a carbo-catalyst for the synthesis of tri-substituted 1,3,5-triazines using biguanides and alcohols.[18]



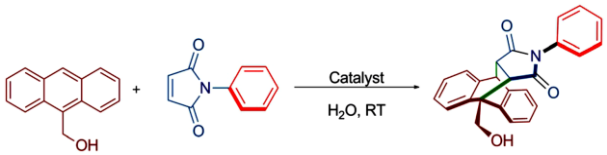
Scheme 7. GO catalyzed ipso-hydroxylation of boronic acids.

Dreyer et al.,[17] developed GO-based catalytic system for the oxidation of various alcohols and cis-stilbene, and the hydration of various alkynes. These reactions were found to proceed under relatively mild conditions and afforded the desired product (aldehyde, acid, or ketone) in good to excellent yields. Moreover, catalyst recovery was found to be both convenient and effective using simple filtration techniques. The results constitute the first examples of using graphene-based materials as (metal-free) carbocatalysts to facilitate synthetically useful transformations. In a broader perspective, the promise of GO and other 2D arrays of carbon materials now extends beyond the utilization of their remarkable electronic and mechanical properties. Scheme 4 shows the oxidation of benzyl alcohol and Scheme 5 shows the oxidation of cis-stilbene using GO.

Chaurasia et al.,[18] developed a simple, metal free and cost-effective protocol for the preparation of tri substituted 1,3,5 triazine using graphene oxide as a carbo-catalyst. Substituted triazine can be synthesized in good to excellent yields under mild reaction conditions (Scheme 6). Furthermore, the use of graphene oxide as a catalyst results in a product free from metal traces. Recyclability study shows that it can be recycled up to six cycles without significant loss in catalytic activity. To show the scalability of the developed methodology, gram scale synthesis was also carried out.

Karthik et al.,[19] employed graphene oxide as a carbocatalyst for sustainable ipso-hydroxylation of arylboronic acids as a simple and straightforward strategy to access phenols (Scheme 7).

Scheme 8 shows the GO-catalyzed Diels–Alder reaction at room temperature. The Diels–Alder (DA) reaction, a [4+2] cycloaddition reaction, is highly important in synthetic organic chemistry and is frequently used in the synthesis of natural products containing six-membered rings. They found that high yields, a wide substrate scope, low temperature, excellent functional group tolerance, atom



Scheme 8. GO-catalyzed Diels–Alder reaction at room temperature.[20]

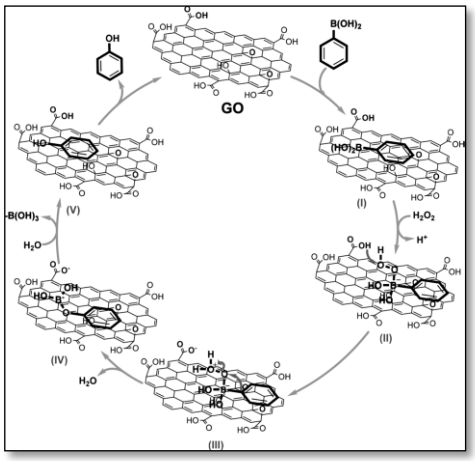


Fig. 2. Plausible mechanism of GO catalyzed ipso-hydroxylation of boronic acid.[20]

economy, and water as a green solvent are noteworthy features of this protocol. The heterogeneous GO catalyst was easily recovered and used multiple times without any significant loss in catalytic activity.[20] Fig. 2 shows the proposed mechanism for the system.

3. N-Doped Graphene - Catalysis

Fig. 3 shows the structure of N-doped graphene. The most common nitrogen configurations that are usually found in N-doped carbon nanoparticles are pyridinic, pyrrolic and quaternary (graphitic) nitrogen. There are several methods are available for the doping of N-atom into the carbon matrix. [21]

Kong et al.,[22] used N-doped graphene nanosheets as metal-free carbocatalyst for the reduction of 4-nitrophenol (Nip) to 4-aminophenol (Amp) without any by-product generation. They found that the NG sheet catalyzed reaction follows pseudo-zero-order kinetics, while all the metallic catalysts follow pseudo-first-order kinetics. The in situ FTIR experiment demonstrated that Nip ions will combine with NG via the O atoms of their hydroxyl groups. Moreover, only the carbon atoms next to the doped N atoms on NG surface can be activated, serving as the active sites. As expected, all four kinds of the doped N atoms are beneficial to the adsorption and activation of Nip, contributing to the catalytic reduction reaction.

Rizescu et al.,[23] used N-Doped graphene as a metal-free catalyst for glucose oxidation to succinic acid. N-Containing graphene obtained either by simultaneous amination and reduction of graphene oxide or by pyrolysis of chitosan under an inert atmosphere have been found to act as catalysts for the selective wet oxidation of glucose to succinic acid. Selectivity values over 60% at complete glucose conversion have been achieved by performing the reaction at 160 °C and 18 atm O_2 pressure for 20 h.

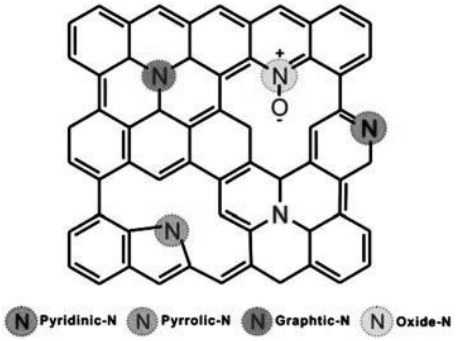


Fig. 3. N-doped graphene with N-functionalities (pyridinic-N. pyrrolic-N, graphitic-N and oxide-N).

Ren and co-workers[24] prepared 3D porous N-doped reduced graphene oxide (N-rGO) aerogels by a hydrothermal reduction of graphene oxide (GO) with urea and following freeze-drying process. N-rGO aerogels have a high BET surface of 499.70 m^2/g and a high N doping content (5.93–7.46 at%) including three kinds of N (graphitic, pyridinic and pyrrolic). Their high catalytic performance for phenol oxidation in aqueous solution was investigated by catalytic activation of persulfate (PS). We have demonstrated that N-rGO aerogels are promising metal-free catalysts for phenol removal.

Candu and group[25] developed N-doped defective graphene [(N)G] obtained by pyrolysis at 900 °C of chitosan contains about 3.7% of residual N atoms, distributed as pyridinic, pyrrolic and graphitic N atoms. They found that (N)G acts as basic catalyst promoting two classical C single bond C bond forming nucleophilic additions in organic chemistry, such as the Michael and the Henry additions. N as dopant changes the reactivity of the neighbour C atoms. The noticed that the general activity of N-doped graphene as base catalysts and illustrate the potential of carbocatalysis to promote reactions of general interest in organic synthesis.

4. Conclusions

In summary, carbocatalytic activity of the graphene oxide in organic reactions and the usefulness of N-doped graphene as metal-free catalyst in organic transformations are also studied. The advantages of the metal-free graphene based carboncatalytic system are also outlined.

Conflicts of Interest

The authors declare no conflict of interest.

References

1 Schlögl R. Heterogeneous Catalysis. *Angew. Chem. Int. Ed.*, 2015, **54**, 3465-3520. [CrossRef]
2 Gopiraman M.; Karvembu R.; Kim I.S. Highly Active, Selective, and Reusable RuO_2/SWCNT Catalyst for Heck Olefination of Aryl Halides. *ACS Catal.*, 2014, **4**, 2118-2129. [CrossRef]
3 Gopiraman M.; Deng D.; Ganesh Babu S.; Hayashi T.; Karvembu R.; Kim I.S. Sustainable and Versatile Cuo/GNS Nanocatalyst for Highly Efficient Base Free Coupling Reactions. *ACS Sustainable Chem. Eng*, 2015, **3**, 2478-2488. [CrossRef]

4 Gopiraman M.; Babu S.G.; Khatri Z.; Kai W.; Kim Y.A.; Endo M.; Karvembu R.; Kim I.S. An Efficient, Reusable Copper-oxide/Carbon-nanotube Catalyst for N-arylation of Imidazole. *Carbon*, 2013, **62**, 135-148. [CrossRef]
5 Gopiraman M.; Ganesh Babu S.; Khatri Z.; Kai W.; Kim Y.A.; Endo M.; Karvembu R.; Kim I.S. Dry Synthesis of Easily Tunable Nano Ruthenium Supported on Graphene: Novel Nanocatalysts for Aerial Oxidation of Alcohols and Transfer Hydrogenation of Ketones. *J. Phys. Chem. C*, 2013, **117**, 23582-23596. [CrossRef]
6 Gopiraman M.; Bang H.; Babu S.G.; Wei K.; Karvembu R.; Kim I.S. Catalytic N-oxidation of Tertiary Amines on RuO_2 NPs Anchored Graphene Nanoplatelets. *Catal. Sci. Technol.*, 2014, **4**, 2099-2106. [CrossRef]
7 Somasundaram S.; Ill-Min C.; Vanaraj R.; Ramaganthan B.; Mayakrishnan G. Highly Active and Reducing Agent-free Preparation of Cost-Effective NiO-based Carbon Nanocomposite and its Application in Reduction Reactions under Mild Conditions. *J. Ind. Eng. Chem.*, **60**, 91-101. [CrossRef]
8 Gopiraman M.; Deng D.; Saravanamoorthy S.; Chung I.M.; Kim I.S. Gold, Silver and Nickel Nanoparticle Anchored Cellulose Nanofiber Composites as Highly Active Catalysts for the Rapid and Selective Reduction of Nitrophenols in Water. *RSC Adv.*, 2018, **8**, 3014-3023. [CrossRef]
9 Gopiraman M.; Muneeswaran M.; Kim I.S. Highly Porous Ru/C and Cu/C Nanocatalysts Derived from Custard Apple for Rapid and Selective Reduction of p-nitrophenol. *Nano Prog.*, 2019, **1**, 30-36. [Link]
10 Saravanamoorthy S.; Vijayakumar E.; Jemimah S.; Ilangovan A. Catalytic Reduction of p-Nitrophenol and Carbonyl Compounds by NiO-Nanoparticles Fastened Graphene Oxide. *Chem. Sci. Eng. Res*, 2019, **1**, 1-7. [Link]
11 Liu L.; Liu S.; Li L.; Qi H.; Yang H.; Huang Y.; Wei Z.; Li L.; Xu J.; Liu B. A General Method to Construct Single-Atom Catalysts Supported on N-Doped Graphene for Energy Applications. *J. Mater. Chem. A*, 2020, **8**, 6190-6195. [CrossRef]
12 Tian Y.; Cao Y.Y.; Pang F.; Chen G.Q.; Zhang X. Ag Nanoparticles Supported on N-Doped Graphene Hybrids for Catalytic Reduction of 4-Nitrophenol. *RSC Adv.*, 2014, **4**, 43204-43211. [CrossRef]
13 Wang C.; Kang J.; Sun H.; Ang H.M.; Tadé M.O.; Wang S. One-Pot Synthesis of N-Doped Graphene for Metal-Free Advanced Oxidation Processes. *Carbon*, 2016, **102**, 279-287. [CrossRef]
14 Mirza-Aghayan M.; Kashef-Azar E.; Boukherroub R. Graphite Oxide: An Efficient Reagent for Oxidation of Alcohols under Sonication. *Tetrahedron Lett.*, 2012, **53**, 4962-4965. [CrossRef]
15 Sedrpoushan A.; Heidari M.; Akhavan O. Nanoscale Graphene Oxide Sheets as Highly Efficient Carbocatalysts in Green Oxidation of Benzylic Alcohols and Aromatic Aldehydes. *Chinese J. Catal.*, 2017, **38**, 745-757. [CrossRef]
16 Deng D.; Xiao L.; Chung I.M.; Kim I.S.; Gopiraman M. Industrial-Quality Graphene Oxide Switched Highly Efficient Metal-And Solvent-Free Synthesis of β-ketoenamines under Feasible Conditions. *ACS Sustainable Chem. Eng.*, 2017, **5**, 1253-1259. [CrossRef]
17 Dreyer D.R.; Jia H.P.; Bielawski C.W. Graphene Oxide: A Convenient Carbocatalyst for Facilitating Oxidation and Hydration Reactions. *Angew. Chem.*, 2010, **122**, 6965-6968. [CrossRef]
18 Chaurasia S.R.; Dange R.; Bhanage B.M. Graphene Oxide as a Carbo-Catalyst for the Synthesis of Tri-substituted 1, 3, 5-triazines using Biguanides and Aalcohols. *Catal. Commun.*, 2020, **137**, 105933. [CrossRef]
19 Karthik M.; Suresh P. Graphene Oxide as a Carbocatalyst for Sustainable Ipso-Hydroxylation of Arylboronic Acids: A Simple and Straightforward Strategy to Access Phenols. *ACS Sustainable Chem. Eng.*, 2019, **7**, 9028-9034. [CrossRef]
20 Girish Y.R.; Pandit S.; Pandit S.; De M. Graphene Oxide as a Carbocatalyst for a Diels–Alder Reaction in an Aqueous Medium. *Chem. Asian J.*, 2017, **12**, 2393-2398. [CrossRef]
21 Zhao A.; Masa J.; Muhler M.; Schuhmann W.; Xia W. N-Doped Carbon Synthesized from N-Containing Polymers as Metal-Free Catalysts for the Oxygen Reduction under Alkaline Conditions. *Electrochim. Acta*, 2013, **98**, 139-145. [CrossRef]
22 Kong X.K.; Sun Z.Y.; Chen M.; Chen Q.W. Metal-Free Catalytic Reduction of 4-nitrophenol to 4-aminophenol by N-doped Graphene. *Energy Environ. Sci.*, 2013, **6**, 3260-3266. [CrossRef]
23 Rizescu C.; Podolean I.; Albero J.; Parvulescu V.I.; Coman S.M.; Bucur C.; Puche M.; Garcia H. N-Doped Graphene as a Metal-Free Catalyst for Glucose Oxidation to Succinic Acid. *Green Chem.*, 2017, **19**, 1999-2005. [CrossRef]
24 Ren X.; Guo H.; Feng J.; Si P.; Zhang L.; Ci L. Synergic Mechanism of Adsorption and Metal-Free Catalysis for Phenol Degradation by N-doped Graphene Aerogel. *Chemosphere*, 2018, **191**, 389-399. [CrossRef]
25 Candu N.; Man I.; Simion A.; Cojocaru B.; Coman S.M.; Bucur C.; Primo A.; Garcia H.; Parvulescu V.I. Nitrogen-Doped Graphene as Metal Free Basic Catalyst for Coupling Reactions. *J. Catal.*, 2019, **376**, 238-247. [CrossRef]