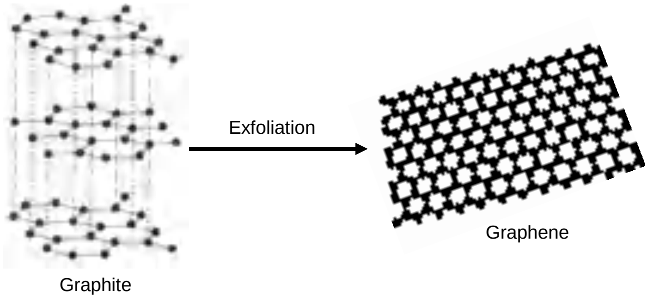
Chapter I

Section A

A brief introduction on carbonaceous nanomaterial graphene and its derivative

I.A.1. Introduction to graphene

Graphene, single-layered 2D carbonaceous material mainly contains a honeycomb C (carbon) network and is prevalent in several carbon-based nanomaterials. Novoselov and his co-workers prepared single-layer graphene and few-layer graphene by peeling of graphite layer repeatedly (Scheme I.A.1). In general, single and few-layer graphene nanosheets are obtained by the mechanical exfoliation (“Scotch-tape” method) [1] and by epitaxial chemical vapour deposition of bulk graphite [2]. The exfoliation of graphene sheets from graphite has attracted much attention as it enhances the quality of graphene and enables large scale synthesis. Many researchers have been focusing on graphene owing to its unique electrical, optical, mechanical properties and its modified form CMG (chemically modified graphene) is used in catalysis and catalytic support [3]. There are two methods for the graphene functionalization covalent and non-covalent method, although the first one is mainly used by chemists for reaction purposes [4]. The covalent functionalization is achieved mainly through a few techniques, such as reaction with residual functional groups present on graphene during the production, atom doping, etc [4]. The non-covalent functionalization of graphene involves π-π interaction and van der waals forces of interaction with polymers and various organic molecules with hydrophobic properties. Due to non-covalent functionalization, the extended π system of graphene is not disturbed, which indicates that the mechanical strength and electrical conductivity of functionalized graphene remain unaffected [5]. In the covalent modification, graphene loses some of the conjugation systems, and thereby compromising some of its properties. Covalent functionalization produces some lattice defects in the nanosheets due to the interruption of π-π conjugation whereas the conjugation is not disturbed in non-covalent functionalization. The covalent functionalization of graphene increases its dispersibility in organic solvents. Generally, the organic covalent functionalization reaction of graphene involves the covalent bond formation between dienophiles or free radicals and the C=C bonds of pristine graphene [6]. Graphene possesses a large surface area of up to 2600 m^2 g^{-1}, which is a significant factor that affects its use as support in a heterogeneous catalytic system [3]. The chemical modification and chemical production of graphene is a great challenge for synthetic chemists. Hydrogenated, fluorinated and oxygenated derivatives of graphene possesses interesting properties and are so called graphane, fluorographene and graphene oxide respectively [9]. Among them, graphene oxide (GO) has been regarded as the outcome of the oxidation and chemical exfoliation of natural graphite [10-12]. The application of metal-free carbon materials as heterogeneous catalysts replaces hazardous liquid BrØnsted and Lewis acid catalysts in organic synthesis [7, 8]. This accounts for the use of functionalized graphene in catalysis as a rich class of nonpolluting and reusable solid-state material.

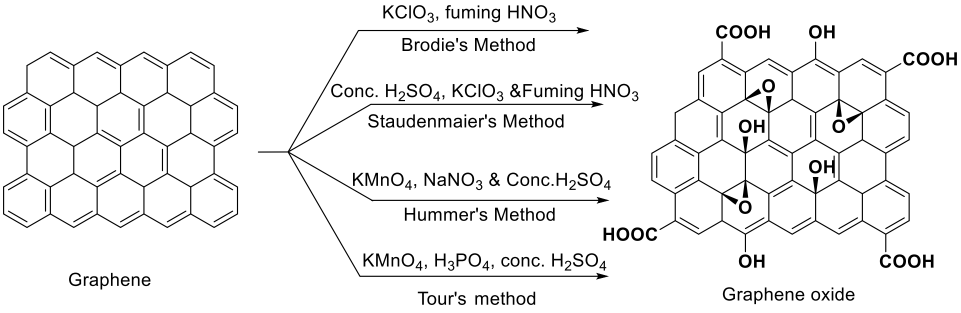


Scheme I.A.1. *Single-layer of graphene extraction by exfoliating graphite.*

I.A.2. Introduction to graphene oxide (GO)

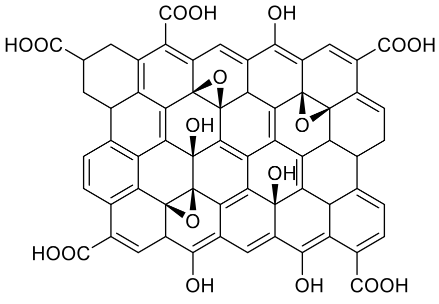
GO is a single layer of graphite oxide and is obtained from the oxidation of graphite powder. The properties of GO are far from those of graphene, although both of them are two-dimentional carbon materials. In 1855, graphite oxide (a bulk form of GO) was first synthesized by Brodie from graphite powder using a strong oxidizing agent like $KMnO_4$, $NaNO_3$, $KClO_3$, and H_2SO_4 [13]. Graphite oxide can be readily exfoliated through ultrasonication in water and other organic solvents owing to its hydrophilic nature and greater interlayer distance than graphite. The single and multi-layer GO make a stable dispersion in these solvents [14]. GO behaves as an acid catalyst due to the presence of extrinsic oxygenated groups on its basal plane. Thus the structural difference between graphene (possesses only hexagonal sp^2 carbon network) and graphene oxide (GO) have a huge influence on their properties. In 1898, a modification of Brodie's method, was described by Staudenmeir [15]. This method eliminates the demerits of Brodie's method and concentrated H_2SO_4 was added to graphite powder along with $KClO_3$ and fuming HNO_3 and resulted in highly oxidized GO in a single step. However, the most widely used method for the synthesis of GO was developed by Hummers in the year 1958. This method involves the addition of $NaNO_3$, conc. H_2SO_4 and $KMnO_4$ for the oxidation of graphite to GO. However, $NaNO_3$ evolves some toxic gases like NO_2/N_2O_4 during GO synthesis and dissolves Na^+ and NO^{3-} ions in the water waste. Later, a few modifications are made to the modified Hummers method. After that, Tour *et al.* (2010) refurnished the Hummers method by eliminating $NaNO_3$, increasing the amount of $KMnO_4$, and introducing the reaction mixture of H_2SO_4/H_3PO_4 in a 9:1 volume ratio for a prolonged time. The environmental issues of the

Hummers method was addressed by Tour and reported a better method to synthesize heavily oxidized GO (Scheme I.A.2) [16].

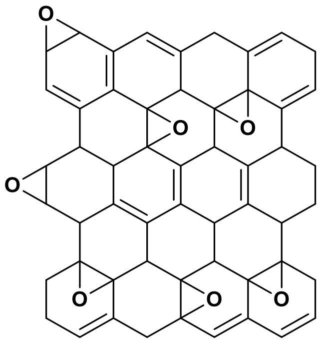


Scheme I.A.2. *Different methods for graphene oxide (GO) synthesis.*

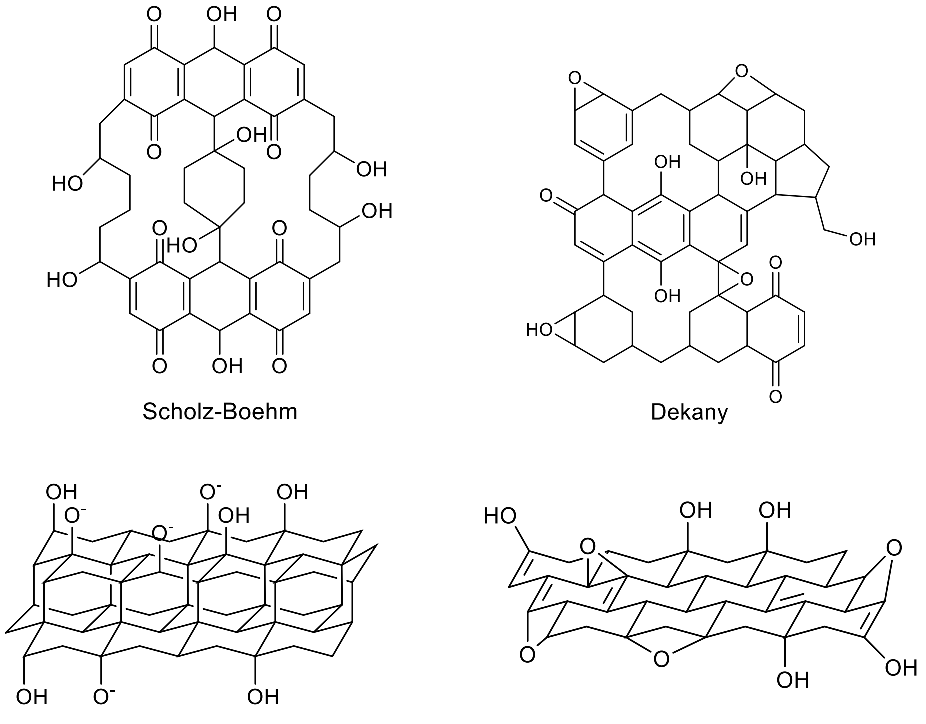
Dimiev *et al.* proposed the structural formula of GO which clearly describes its acidic property in an aqueous solution [17]. Although the exact structure of GO is uncertain, Klinowski *et al.* proposed the structural model of GO which has been widely accepted, shows only the chemical connectivity (Figure I.A.3). Some other proposed structural models of GO are shown in the following figure I.A.1.



Lerf-Klinowski model



Hofmann



Scholz-Boehm

Dekany

Nakajima-Matsuo

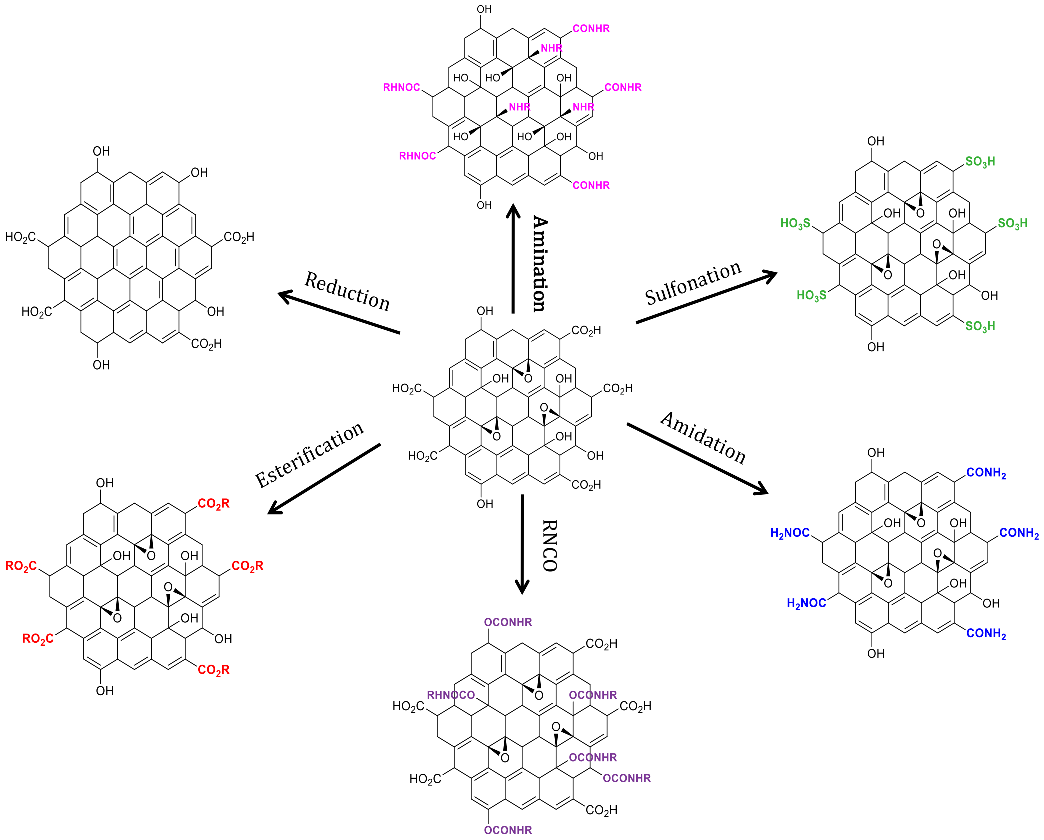
Ruess

Figure I.A.1. *Proposed structural models of GO.*

Since GO is an oxidized form of natural graphite, it is an inexpensive and abundant source of carbocatalyst. GO is built on a C grid forming a graphite plane, and the layers are terminated with -OH and -COOH groups. The acidic property of GO is due to the presence of extrinsic oxygen functionalities on the GO basal plane. Due to the presence of a large number of oxygen-containing functional groups in GO, such as carbonyl (C=O), carboxyl (–COOH), epoxy (–O–), and hydroxyl (–OH), GO has been considered as an acid catalyst as well as an oxidant (pH 4.5 at 0.1 mg mL^{-1}) [18].

I.A.2.1. Preparation of graphene oxide derivatives

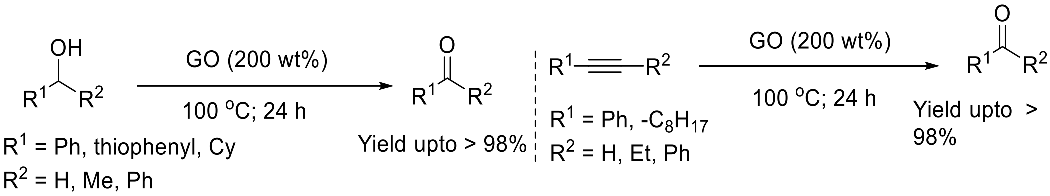
Since GO has epoxide rings, they can participate in epoxide ring opening reaction by amine. Therefore, a new acid-base bifunctional solid catalyst is formed where the amino group is covalently bonded to the acidic GO surface (Scheme I.A.3) [19]. The modification in GO through amination enhances the material stability and is widely used in the chemical industry and in organic transformations. Similarly, the incorporation of imidazolium [20], dopamine [21], and *p*-nitrophenyl [22] on the GO surface by covalent attachment increases the physicochemical properties. For example, isocyanate functionalized GO makes a stable dispersion in a polar protic solvent and has been used for organic field effect transistors [23]. Sing *et al.* developed another interesting graphene-based materials, where amines are grafted with carboxyl group to form amide functionality onto the surface of GO [24]. Amide functionalized GO (AGO) achieved enhanced thermal stability as compared to GO and its dispersibility in polar solvents is stable more than two months. Another GO derivative reduced graphene oxide (rGO) is obtained by the reduction of the oxygen content of GO chemically, thermally or electrochemically [25]. GO is highly dispersible in water and other solvents whereas rGO is less. As the property of rGO is similar to that of graphene, it is used in the production of batteries, printable graphene electronics and in biomedical applications. Due to the presence of oxygen functionality on the surface of graphene oxide, surface modification through covalent attachment can be achieved for the synthesis of various graphene oxide derivatives (Scheme I.A.3). Kumar *et al.* performed covalent functionalization of GO using esterification reaction by m-Toluic acid. GO modified via esterification was soluble in polar organic solvents and have various application in gas sensors [26]. The mineral-acid catalyzed reaction using H_2SO_4, HNO_3, HCl used in industry and laboratory has several drawbacks severe reaction condition, catalyst reusability problem and corrosion problem. Thereby, solid acid catalysts effectively erase the problems regarding corrosion and reusability and securing environmental sustainability. Bazarganipour *et al.* synthesized sulfonated graphene oxide (SGO) using chlorosulfonic acid and investigated its catalytic activity for the hydrolysis of cellulosic substrates [27].



Scheme I.A.3. *Functionalization of graphene oxide (GO) using different approaches.*

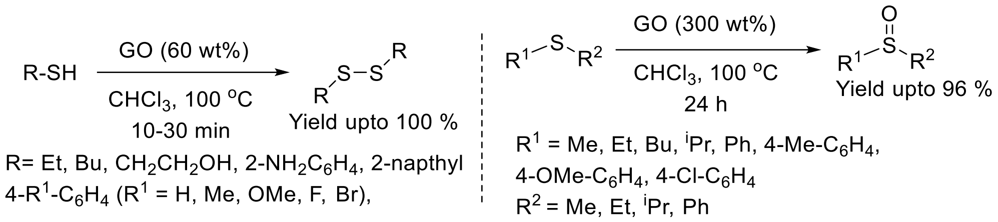
I.A.2.2. Graphene oxide (GO)- catalyzed organic reactions

GO has been emerging as a solid heterogeneous carbocatalyst that shows activity and selectivity like a homogeneous one [28]. Some organic transformations using GO as carbocatalyst are shown below which depicts the versatility of this carbonaceous nanomaterial. In 2010, Dreyer *et al.* demonstrated GO as a metal-free inexpensive carbocatalyst to facilitate the oxidation of various alcohols, alkenes, and alkynes (Scheme I.A.4). These organic transformations afforded the desired product (aldehyde or ketone) in excellent yield and proceeded under mild reaction conditions [29].



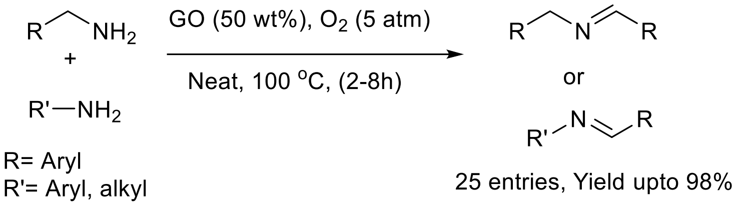
Scheme I.A.4. *GO catalyzed oxidation of various alcohols and hydration of alkynes.*

In 2011, the same group described graphene oxide catalyzed selective oxidation of thiols and sulfides to disulfides and sulfoxides (Scheme I.A.5) [30]. They observed that this oxidative transformation efficiently produced thiols and sulfoxides with good to excellent yield (51- 100 %) in a short reaction time (within 10 min in most cases). However, there was no case of over-oxidation of the substrate and the heterogeneous nature of GO has a profound effect to facilitate the above transformation and isolation of the target product.



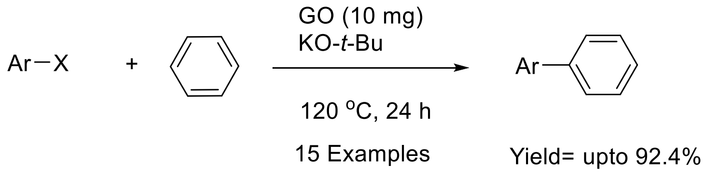
Scheme I.A.5. *Selective oxidation of thiols and sulfides to disulfides and sulfoxides using GO as heterogeneous catalyst.*

Huang *et al.* described GO as a durable and efficient catalyst for the transformation of various amines to their corresponding imines via a metal-free route (Scheme I.A.6) [31]. This method proceeds under neat reaction conditions with molecular O_2. GO was found to be highly efficient to produce symmetrical, asymmetrical, and cyclic imines through an eco-friendly reaction protocol. Here, GO was prepared by the Hummers method and characterized by a range of spectroscopic tools.



Scheme I.A.6. *Aerobic oxidative coupling of various amines to imines catalyzed by GO.*

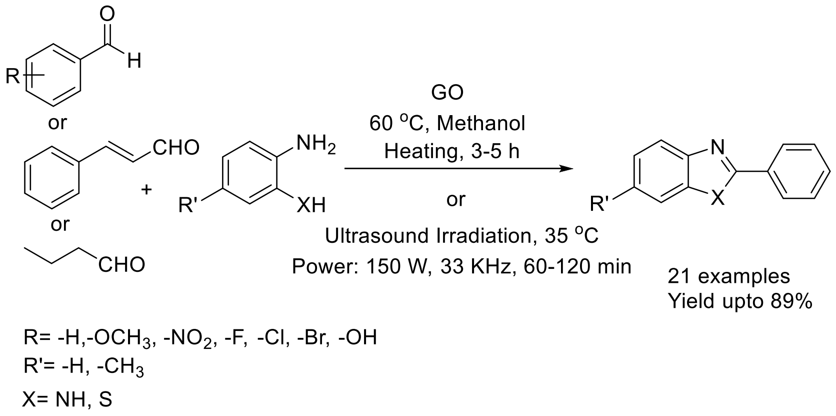
Gao *et al.* observed C-C bond formation reaction via C-H bond activation using graphene oxide (GO) as a reusable and inexpensive heterogeneous catalyst (Scheme I.A.7) [32]. Herein, the target product biaryls were obtained in presence of *tert*-BuOK at 120 °C using GO as a metal-free catalyst. Aryl iodides with electron-donating groups are more reactive in this reaction than electron-neutral aryl iodides. Aryl chlorides and bromides are also employed in this reaction but resulted low yield.



Ar= C_6H_5, 4-MeO-C_6H_4, 4-Me-C_6H_4, 4-Et-C_6H_4, 1-napthyl, 4-Cl-C_6H_4 etc
X= I, Br, Cl

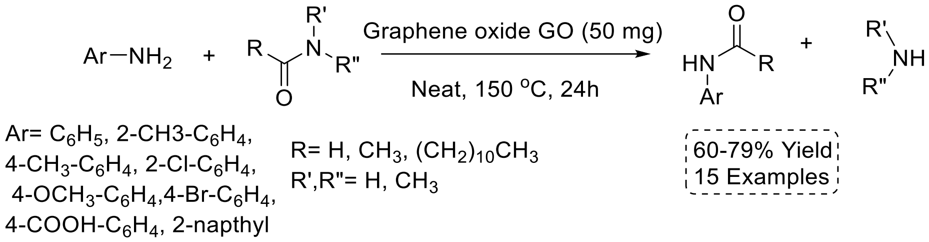
Scheme I.A.7. *Graphene oxide catalyzed C-C bond formation reaction.*

Dhopte *et al.* investigated the catalytic activity of graphene oxide (GO) for the synthesis of benzimidazoles/benzothiazoles from the mixture of *o*-phenylenediamine/*o*-aminothiophenol, aromatic and aliphatic aldehydes in methanol solvent at 60 °C/35 °C under heating as well as microwave irradiation (Scheme I.A.8) [33]. The excellent yield of desired product benzimidazoles/benzothiazoles was observed under microwave irradiation at a short reaction time (within 1 hour) at room temperature. Here, GO plays a dual role as an oxidizing agent and solid acid catalyst. The yield of the target product is higher in the polar solvent than in the non-polar solvent and the reason may be owing to the better dispersibility of GO in polar solvents. The heterogenous catalyst GO produced the target product with diverse functionality via an eco-benign process.



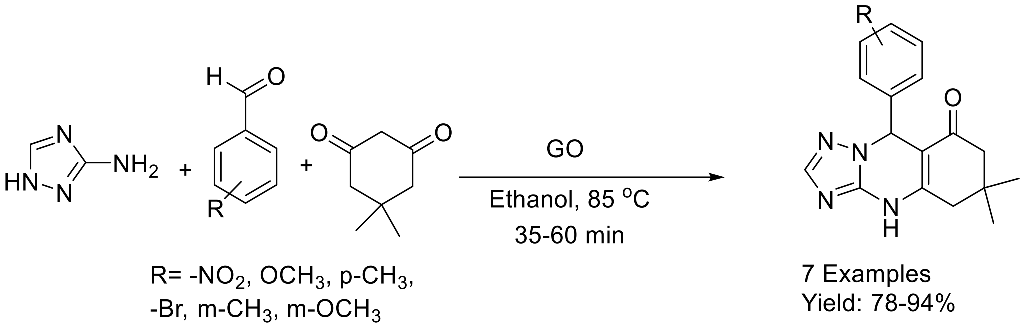
Scheme I.A.8. *The synthesis of benzimidazoles/benzothiazoles from o-phenylenediamine/o-aminothiophenol using GO as solid heterogeneous catalyst.*

Bhattacharya *et al.* reported GO catalyzed transamidation of aliphatic amides (Scheme I.A.9) [34]. Generally, transamidation involves the interconversion of the amide with amines which is a common alternative to the amide formation from amines and carboxylic acids. A wide variety of functional groups ranging from electron-donating to withdrawing exerted the target product with good to excellent yield. However, aliphatic amines and aromatic amides did not produce any kind of target product.



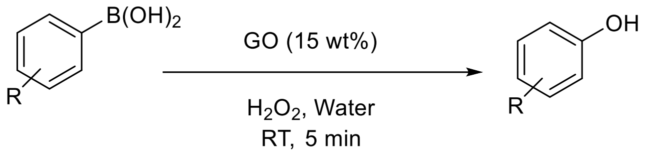
Scheme I.A.9. *GO catalyzedtransamidation reaction of aliphatic amides.*

In 2019, Ebajo Jr. *et al.* demonstrated GO catalyzed eco-friendly pathway for the synthesis of bioactive heterocyclic compound tetrazoloquinazolinone starting from 3-amino-1,2,4-triazole, benzaldehyde, and dimidone (Scheme I.A.10) [35]. This GO catalyzed reaction is not influenced by the nature of substituents present in the aromatic aldehyde. It was assumed that this reaction was accelerated by the BrØnsted acid edges and lewis acidic sites of GO.



Scheme I.A.10. *The multicomponent reaction of tetrazoloquinazolinone derivatives using GO.*

In 2019, the synthesis of phenols through ipso-Hydroxylation of arylboronic acids using GO as sustainable carbocatalyst was demonstrated by Karthik *et al.* (Scheme I.A.11) [36]. The outstanding catalytic activity of GO was observed in water and this may be due to the better dispersibility of GO in a polar solvent. GO mediated oxidation redaction generally requires high catalyst loading but in presence of H_2O_2, this reaction is completed with a minimum GO loading. The oxygen functionalities mainly carboxylic acid groups of GO played a vital role inipso-Hydroxylation of arylboronic acids.

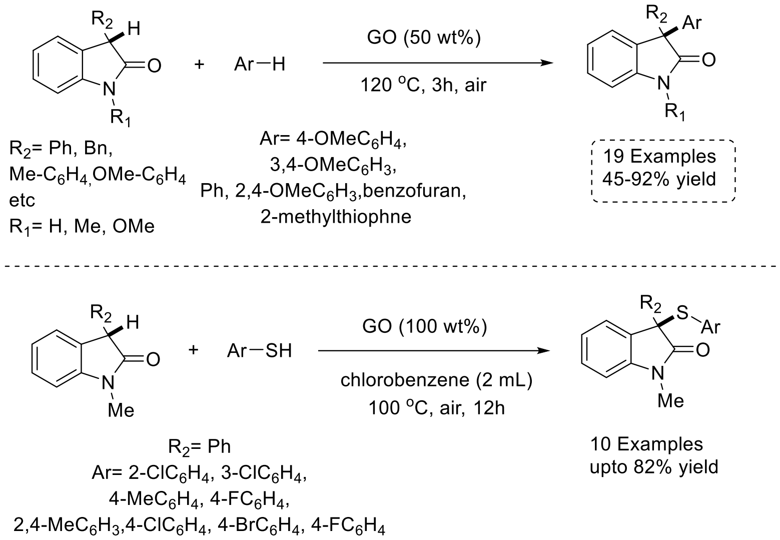


R= *p*-Cl, *p*-Br,*p*-I, *p*-NO_2, *p*-CH_3,*p*-OCH_3, *p*-OH, *m*-CN, napthyl, isopropyl, Ph, *O*-Ph, cyclohexyl imidazoyl, 4-pyridyl, 3-pyridyl, terphenyl, phenyloxy phenyl, 4-pyrazolyl

26 Examples
Yield: 78-96%

Scheme I.A.11. *Graphene oxide catalyzedipso-Hydroxylation of boronic acids.*

CDC (Cross-dehydrogenative coupling) is a class of reaction that results in the direct formation of C-C and C-N bonds from two unmodified C-H bonds or C-H and N-H bonds. Wu *et al.* demonstrated the metal-free synthesis of 3-aryloxindoles and 3-sulfenylated oxindoles via CDC (cross dehydrogenative coupling) reaction of oxindoles with arenes and thiophenols using commercially available robust catalyst GO (Scheme I.A.12) [37]. In absence of GO catalyst the reaction did not take place and the best result was obtained with 50 wt % of GO. This reaction is highly regioselective and produced only one regioisomer. A wide variety of substituted oxindoles produced the target coupling product with excellent yield.



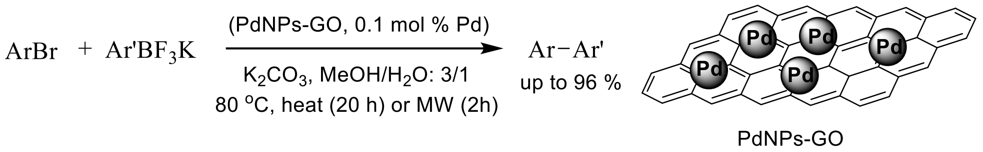
Scheme I.A.12. *GO catalyzed cross dehydrogenative coupling of oxindoles with arenes and thiophenols to yield 3-aryloxindoles and 3-sulfenylated oxindoles.*

The emergence of GO as a heterogeneous catalyst has also found application in Fridel craft alkylation [38], selective hydrogen transfer [39], oxidation of glutaraldehyde to glutaric acid [40], Fisher esterification [41], oxidation of 5-hydroxymethylfurfural into 2, 5-diformylfuran [42] and many more have also been reported [43-46]. With growing interest in green chemistry, multicomponent reaction (MCR) has been considered an important tool of green chemistry. Concerning the environmental factors, the carbocatalyst graphene oxide has been exclusively utilized in MCR for the expedient synthesis of a different heterocyclic motif. Apart from the numerous application in diverse organic transformation GO can be employed as solid support for different NPs via the simple synthetic procedure. From the sustainable perspective, high chemical and thermal stability, high surface area, high recyclability, and easy separation are the most desirable attributes of a heterogeneous solid supported metal catalyst [47, 48].

I.A.3. Graphene oxide as catalyst support: Formation of various metal composites

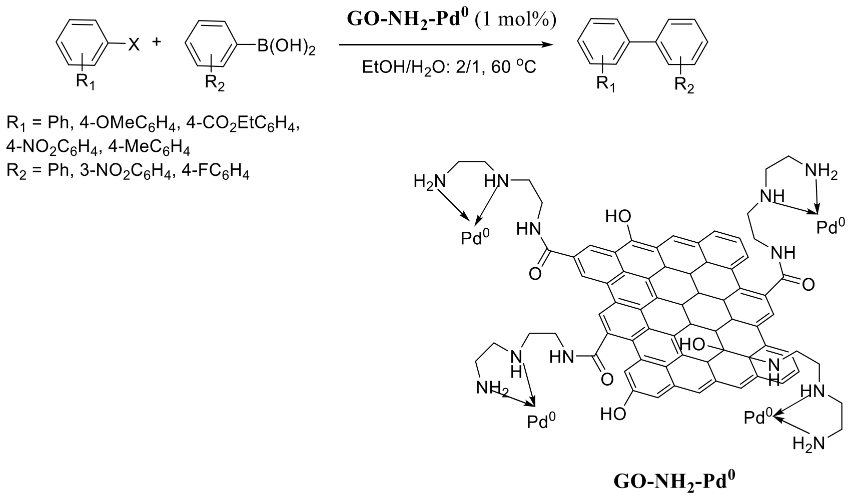
The activity of the supported catalysts mainly depends on the interaction between the catalyst and the support. GO has been proved to be more advantageous as support of catalyst than pristine graphene owing to the presence of functional groups and inherent structural defects which enables catalysts to bond easily through surface functionalization [49]. GO is cheap and easily available, along with this its amphiphilic nature and better dispersibility in aqueous as well as in organic solvents make the supported catalyst accessible to different reactants in the reaction. GO has a high range of binding energy with different metals, which leads to higher stability with a lower reaction barrier [50-51]. Metal nanoparticles (NPs) can be assumed as the intermediate of homogeneous and heterogeneous catalysts [52]. The main difficulty in NPs application is their agglomeration, that deactivates the catalyst after reaction and causes trouble in the regeneration process. Due to the small size of the NPs, they are not easily removed from the reaction mixture. Therefore, there is a need for heterogeneous catalysts via immobilization of metal NPs on solid supports to achieve high catalytic activity, high mechanical and thermal stability, easy regeneration, and separation procedure [53-62]. Among the other metals, palladium (Pd) has attracted special attention [63-64] as it catalyzes a wide variety of organic reactions. Among the reactions, oxidative cyclization [65], cross-coupling reactions, especially Suzuki coupling [66], Negishi coupling [67], Stille coupling [68], Stille-Kelly coupling [69], Kumada coupling [70], Hiyama coupling [71], and Sonogashira coupling [72] are noteworthy to mention. Usually, these cross-coupling reactions involve mostly soluble Pd organic complex under homogeneous conditions [73]. However, the high cost and low efficiency in the separation of homogeneous catalysts at successive runs always remains a challenge. To overcome this more attention has been given to the development of heterogeneous catalysts where palladium ions or palladium nanoparticles are immobilized on the solid support. The novel graphene-based materials are promising candidates for catalyst support due to the large specificsurface area and delocalized π-electron system. Over the recent years, PdNPs supported on GO has been successfully employed as a catalyst for different organic transformation reaction [74-76]. Generally, it is a very difficult process to remove Pd metal (poisoned) from the convenient inorganic supports such as silicates, alumina, and zeolites, but GO can be burned simply to evolve CO, pure Pd, and ash. GO covers its surface with a nearly monoatomic layer of Pd atoms through binding with oxygen functionalities via a coordinate-covalent bonding mechanism [77]. Another advantage of using GO as catalyst support is the recycling experiment of the used catalyst.

Gómez-Martínez *et al.* demonstrated an efficient pathway for the Suzuki-Miyaura coupling reaction between aryl bromides and potassium aryltrifluoroborates using PdNPs supported on graphene oxide (GO) and reduced graphene oxide (rGO) (Scheme I.A.13) [78]. Both catalysts disperse properly in a mixture of $MeOH/H_2O$ (3:1) and proved to be very active at 80 ^oC under conventional heating and microwave irradiation technique. The catalyst can be reused upto 8 cycles under microwave irradiation due to the lower aggregation of PdNPs. However, the higher agglomeration of metal nanoparticles under heating conditions may be the reason for the deactivation of the catalyst. A dissolution/re-deposition mechanism has been proposed based on Pd leaching during the reaction and again re-deposited after the reaction.



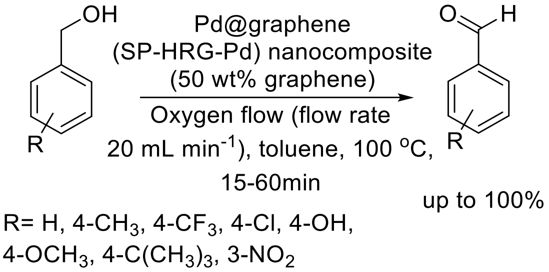
Scheme I.A.13. *PdNPs-GO catalyzed Suzuki–Miyaura reaction of potassium aryltrifluoroborates.*

In 2013, N. Shang *et al.* reported the synthesis of palladium supported on polyamine modified graphene oxide (GO-NH_2-Pd^{2+}) and investigated its catalytic activity in the Suzuki-Miyaura reaction (Scheme I.A.14) [79]. The catalyst was characterized by TEM, X-raydiffraction spectroscopy (XRD), X-ray photoelectron spectroscopy (XPS), and infrared spectroscopy (IR). It was found that the prepared catalyst retains the reactivity characteristics of a homogeneous catalyst, but at the same time, it can be easily recovered and reused up to 10 successive runs without significant loss of its catalytic activity.



Scheme I.A.14. *The Suzuki–Miyaura coupling of aryl halides and arylboronic acids catalyzed by GO-NH_2-Pd^{2+}.*

Al-Marri *et al.* described a single pot, environmental friendly, and facile synthesis of palladium (Pd)@graphene nanocomposites (SP-HRG-Pd) by the in situ reductions of graphene oxide (GO) and $PdCl_2$ using miswak (Salvadora persica L.) root extract as bioreductant (Scheme I.A.15) [80]. The flavonoids (polyphenolic) and terpenoids moieties of the miswak root extract facilitated the reduction of GO and $PdCl_2$ as well as confirmed the homogeneous binding of PdNPs on the graphene layer. Due to the high dispersibility of SP-HRG-Pd nanocomposite by the stabilization of phytomolecules, the synthesized nanocomposite catalyst showed excellent catalytic activity towards the selective oxidation of aromatic alcohols.



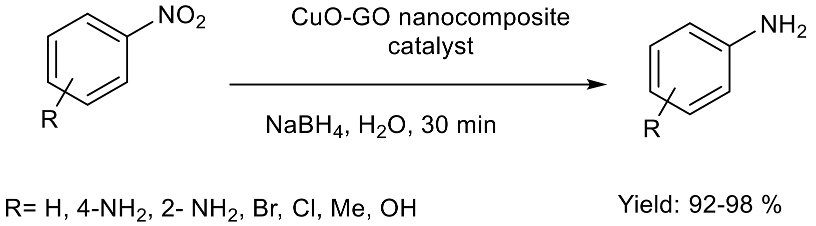
up to 100%

R= H, 4-CH_3, 4-CF_3, 4-Cl, 4-OH, 4-OCH_3, 4-$C(CH_3)_3$, 3-NO_2

Scheme I.A.15. *Pd@graphene nanocomposite catalyst mediated selective oxidation of alcohols.*

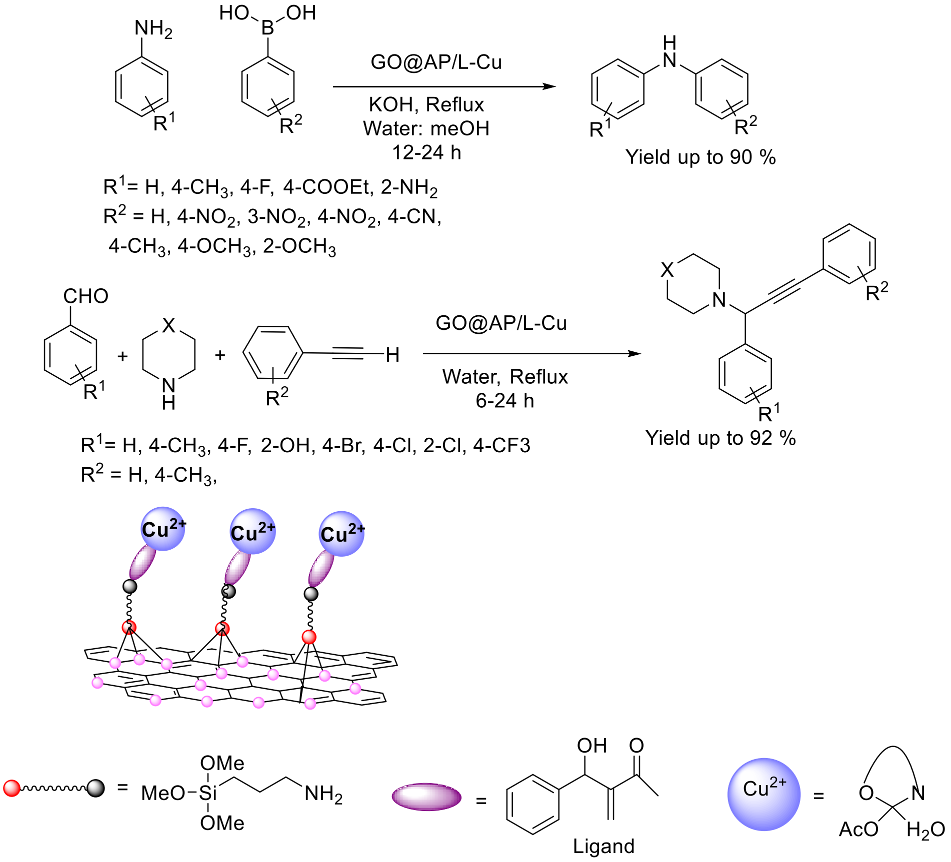
The application of Cu-based nanoparticles has generated great attention in recent years because Cu is inexpensive and earth-abundant. The possible modification of these nanoparticles using different synthetic methods, post-synthetic chemical treatments and the development of novel supports has also been largely responsible for the growing interest in this field. Cu-based materials undergo a wide variety of organic reactions due to Cu's variable oxidation states (Cu0, CuI, CuII, and CuIII) [81-84]. The most economical way to create advance Cu-based nanomaterials is to anchor CuNPs on carbon-based catalytic support.

Zhang *et al.* described the synthesis of graphene oxide (GO) supported by CuO nanoparticles (CuO-GO) by a facile hydrothermal self-assembly process, (Scheme I.A.16) [85]. The synergetic coupling effect of copper oxide nanoparticles with GO in this hybrid nanocomposite presented an excellent performance in aqueous $NaBH_4$ for the reduction of a variety of nitroaromatics. Although CuONPs and GO separately displayed negligible catalytic activity for the above reduction at room temperature. The CuO-GO can be easily recovered from the reaction mixture and reused up to the 6th consecutive cycle.



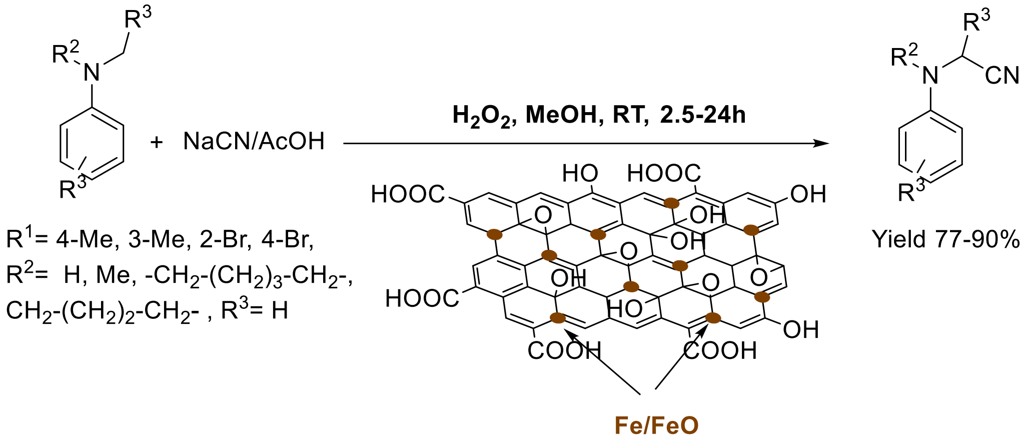
Scheme I.A.16. *CuO–GO nanocomposite catalyzed heterogeneous reduction of substituted nitroaromatics in aqueous solution.*

The Chan-Lam coupling is the most powerful synthetic route for carbon-heteroatom bond formation through the oxidative coupling of aryl boronic acids, organostannanes or siloxanes with N-H or O-H containing compounds in the air [86]. In 2019, Mittal *et al.* synthesized graphene oxide (GO) supported Cu (II) Schiff's base complex (GO@AP/L-Cu) and examined its catalytic activity in the cases of Chan-Lam coupling and C-H activation reaction (Scheme I.A.17) [87]. Both the reaction was found to be simple, efficient and a higher yield of the product was obtained (~90%). (GO@AP/L-Cu) was characterized by Raman, FT-IR, UV–Visible, PXRD, FESEM, TEM, EDAX, TGA, XPS, Elemental mapping, BET, CHNS, and AAS analysis.



Scheme I.A.17. *Graphene oxide supported Cu (II) ligand complex (GO@AP/L-Cu) catalyst for N-arylation and C-H activation reactions.*

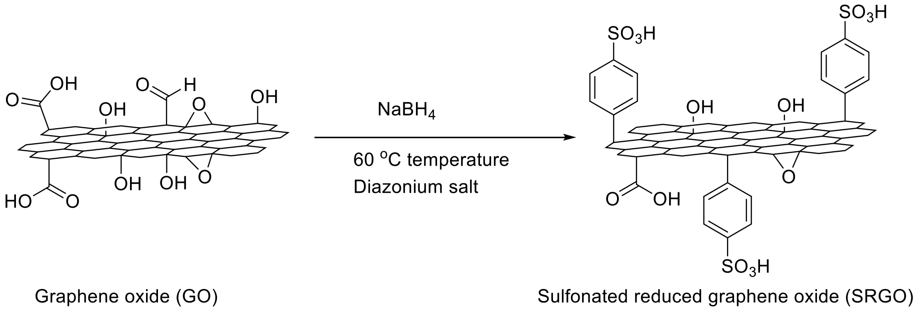
Transition metal-catalyzed C-H activation, especially cyanation of tertiary amines at α-position is a powerful synthetic tool due to the importance of α-aminonitriles as very useful synthetic intermidiates [88-90]. These compounds can be easily converted into a wide variety of biologically active compounds such as α-amino acids and 1,2-diamino compounds, among others (Scheme I.A.18) [91]. Verma *et al.* developed a cheap, simple, and highly efficient composite of iron (Fe) nanoparticles supported on graphene oxide (GO) for the oxidative cyanation of tertiary amines to biologically important α-aminonitriles in high yields. Moreover, they reported a magnetically separable graphene oxide (GO) supported catalyst for the first time and it was recycled successfully several times without significant loss of its catalytic activity [91].



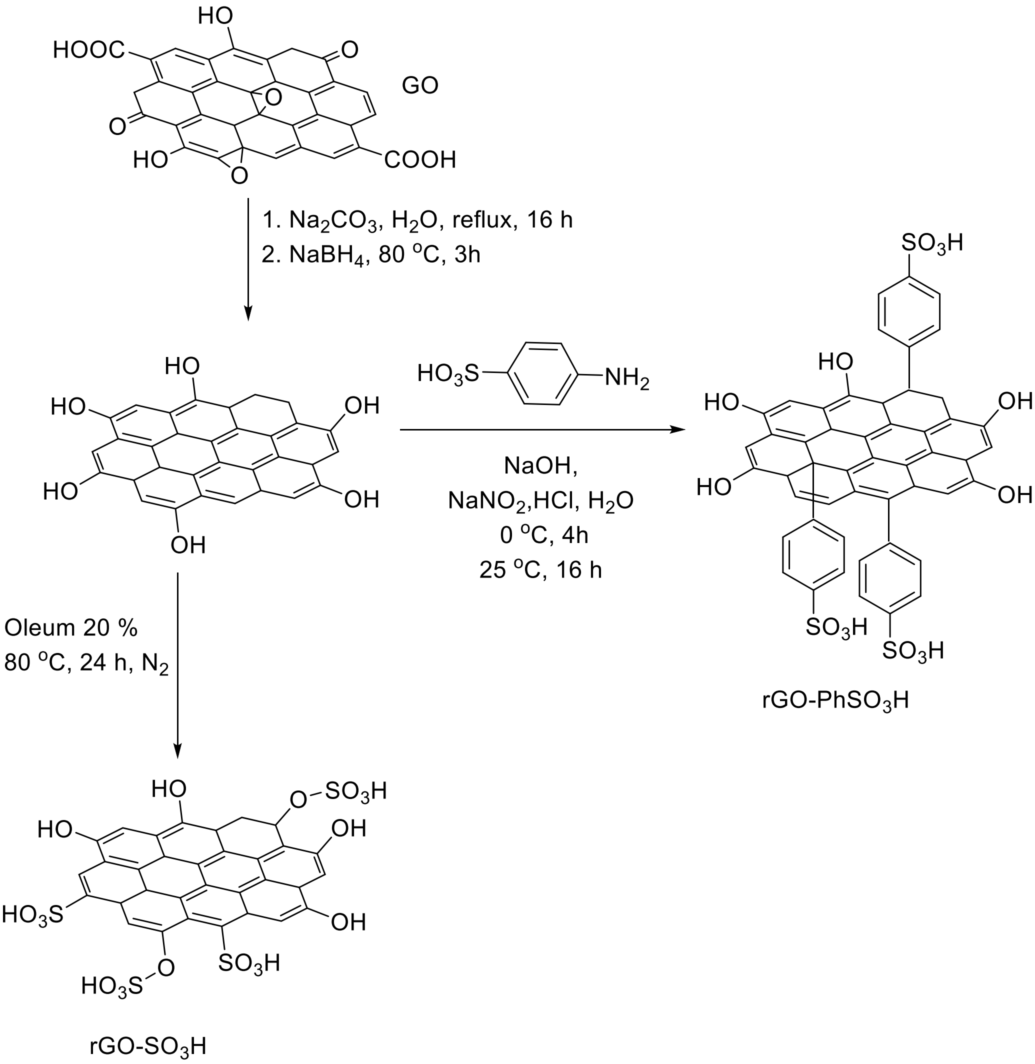
Scheme I.A.18. *Oxidative cyanation of tertiary amines catalyzed by magnetically separable iron nanoparticles supported on graphene oxide.*

I.A.4. Sulphonated graphene oxide synthesis and its application

Solid acid has attracted much attention as an environmentally safe catalyst due to its great potential to replace homogeneous liquid acid [92-94]. Among solid acids, sulfonated-based materials of carbon are noteworthy for mention [95-99]. A large series of sulfonated catalysts of carbon were synthesized by the carbonization of sugar, cellulose [100-101] followed by direct sulfonation of the resulting carbon. However, these sulfonated based carbon materials have a low surface area (approx 2 m^2 g^{-1}), do not swell up, and exhibited higher thermal stability [93]. During the last two decades, GO has been employed as a catalyst as well as catalyst support due to its outstanding properties like appropriate chemical and thermal stability, high surface area, easy synthesis, low cost, and surface functionalization possibility. Due to the interesting properties of GO as catalyst support for heterogeneous catalytic systems, many synthetic routes have been discovered for the attachment of sulfonated groups on the surface of GO nanosheets. Sulfonated graphene oxide (SGO) can be synthesized by various sulfonating agents such as H_2SO_4 [102], chlorosulfonic acid [103], 2-chlorosulfonic acids [104], sulfanilic acids [105]. In 2014, Naeimi and Golestanzadeh prepared sulphonated reduced graphene oxide, sulfonated graphene oxide, and sulfonated propylsilane graphene oxide nanosheets and used them for the eco-friendly synthesis of bisphenolic antioxidants [105]. Some previous work showed that the catalytic efficiency of sulphonated graphene oxide (SGO) is higher than GO owing to the presence of sulphonic acid groups on the surface [106-108]. So far, some organic reactions have been conducted using sulfonic acid functionalized reduced graphene oxide (rGO-$PhSO_3H$) [109-111]. These procedures however involve the reduction of graphene oxide (GO) to reduced graphene oxide (rGO) using $NaBH_4$ as a reducing agent (Scheme I.A.19).



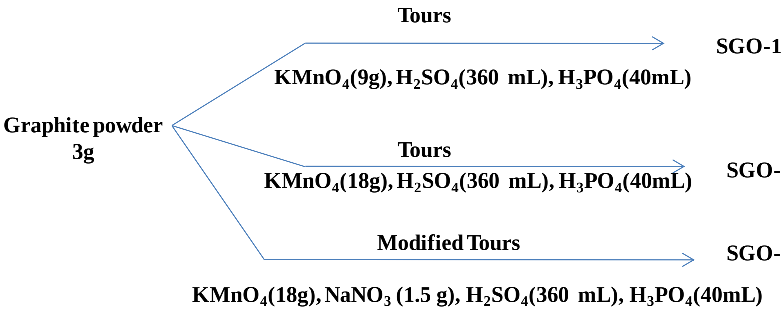
Scheme I.A.19. *Preparation of sulfonated reduced graphene oxide (SRGO) from GO.*



Scheme I.A.20. *Schematic diagram for the synthesis of rGO-PhSO$_3$H and rGO-SO$_3$H from graphene oxide.*

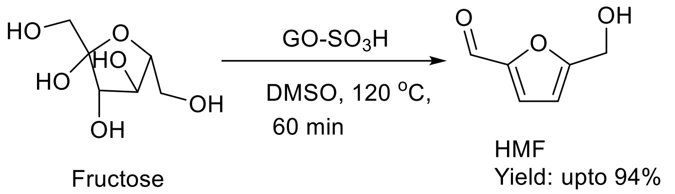
After that, there are two chemical methods for the immobilization of sulfonic acid groups on the surface of rGO. Chemical modification of reduced graphene oxide (rGO) involved the grafting of diazonium salt of sulfanilic acid on the rGO surface to produce rGO-PhSO$_3$H [112]. Another sulfonation process involves simple stirring and heating with oleum containing free SO_3 (20 %) species to produce rGO-SO_3H (Scheme I.A.20) [102]. A covalent bond is formed between carbon and sulfur atoms that are further confirmed by FT-IR and Raman spectroscopic analysis. This covalent functionalization allows stability to the material against leaching when they are employed in liquid phase catalytic reaction.

In 2016, Hou *et al.* reported the one-pot synthesis of sulfonated graphene oxide (SGO) and used it for the efficient conversion of fructose to 5-hydroxymethylfurfural (HMF) [113]. Their synthesized SGO catalysts were named as SGO-1, SGO-2 and SGO-3, however, SGO-1, SGO-2, SGO-3 were synthesized by Tours method and Modified Tours method respectively (Scheme I.A.21).



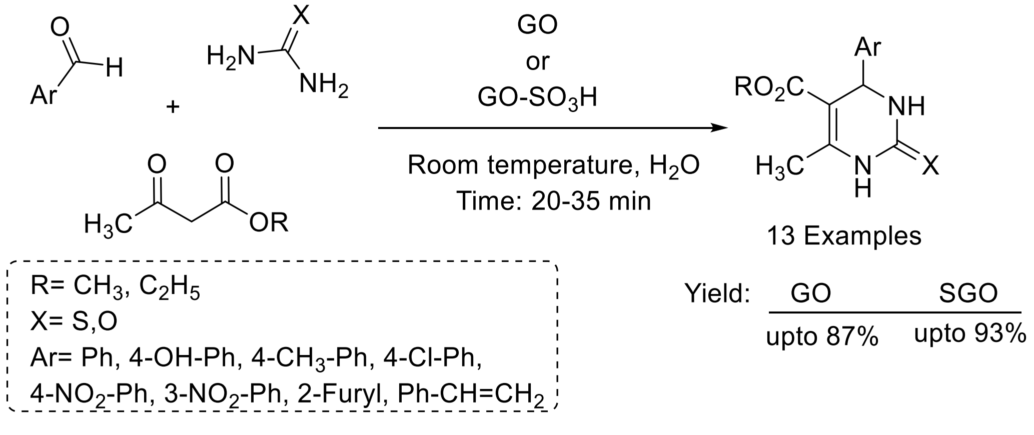
Scheme I.A.21. *Sulfonated graphene oxide synthesis by Hou et al.*

SGO-3 showed the maximum yield (85 %) for the conversion of fructose to HMF whereas SGO-1 and SGO-2 exerted relatively low yield of HMF. The catalytic activity of sulfonated graphene oxide (SGO) depends on the density of the active sites and on its accessibility (Scheme I.A.22) [114]. They showed SGO catalyst for fructose degradation can be recycled upto 5th run with slightly loss of its catalytic activity.



Scheme I.A.22. *SGO catalyzed one-pot conversion of fructose to HMF.*

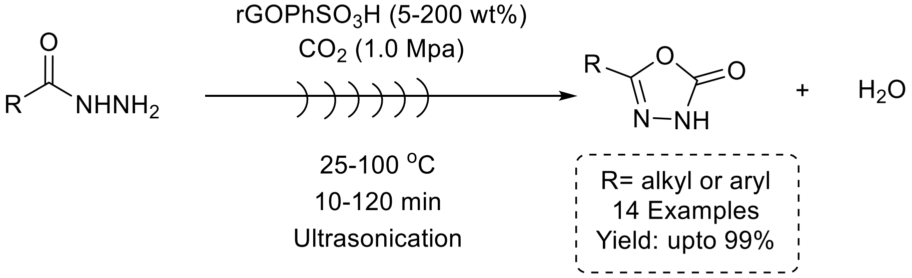
Vessally *et al.* demonstrated an efficient synthesis of 3,4-dihydropyrimidine-2(1H)-ones/thiones from ethyl acetoacetate, urea or thiourea and aldehydes in presence of sulfonated graphene oxide/graphene oxide in aqueous solvent at room temperature (Scheme I.A.23) [115]. The dihydropyrimidones (DHPMs) can be easily separated from the reaction mixture without workup. The reactants with diverse functionalities successfully reacted and exerted the corresponding DHPMs with high purity. In this reaction SGO has been found to be more suitable than GO.



Scheme I.A.23. *SGO catalyzed synthesis of 3,4-dihydropyrimidine.*

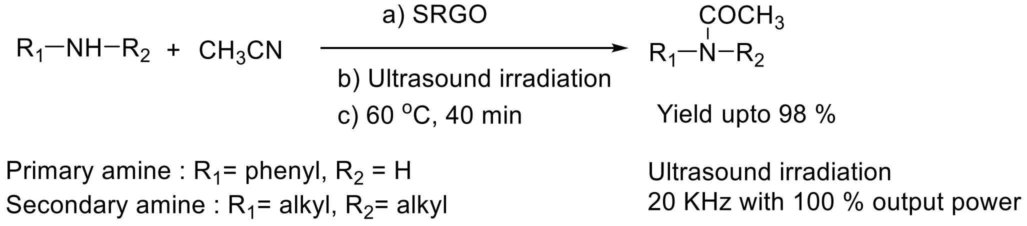
The SGO catalyst was recycled upto 6th run and characterized by XRD, Raman, FT-IR. After 6th run no structural change in SGO catalyst was observed but slight decrease in the yield of the reaction may be due to the reduction of oxygen functionalities and covering the SGO surface with some impurity.

Brahmayya *et al.* described the cyclization of hydrazides to 1,3,4-oxadiazole synthesis using sulfonated reduced graphene oxide ($rGOPhSO_3H$) shown in scheme I.A.24 [116]. They observed the direct cyclization of 4-methyl benzoyl hydrazide with carbon dioxide (CO_2) under room temperature as well as ultrasonic irradiation. Although, the percentage of conversion under ultrasonic irradiation was 84 % using 5 wt % of $rGOPhSO_3H$ in just 50 min and the best yield was obtained with 200 wt% of this nanocatalyst. The product yield was found to be same upto 4th run and the yield decreases from 5-7th run and the reason may be due to the leaching of some SO_3H group from the catalyst surface.



Scheme I.A.24. *The synthesis of 5-susbstituted-1,3,4-oxadiazole-2-ones using sulfonated reduced graphene oxide ($rGOPhSO_3H$).*

In 2017 Brahmayya *et al.* synthesized amides through N-acetylation of amines with acetonitrile using sulfonated reduced graphene oxide (SRGO) as catalyst under sonication (Scheme I.A.25) [117]. SRGO was found to be more favourable than GO in this catalytic reaction. The highest yield was observed in presence of 60 mg of SRGO within 40 min at 60 °C temperature. Electron withdrawing group containing aromatic amines afforded the corresponding amide with slightly lower yield than electron donating group containing aromatic amines (96-99 %). Interestingly, some sensitive substrates like phenol and thiophenol produced the corresponding *N*-acetylation product in good to excellent yield without protecting –OH, -SH groups. The catalytic activity of sulfonated reduced graphene oxide (SRGO) was nearly constant upto 4th cycle and reused easily without inactiveness.

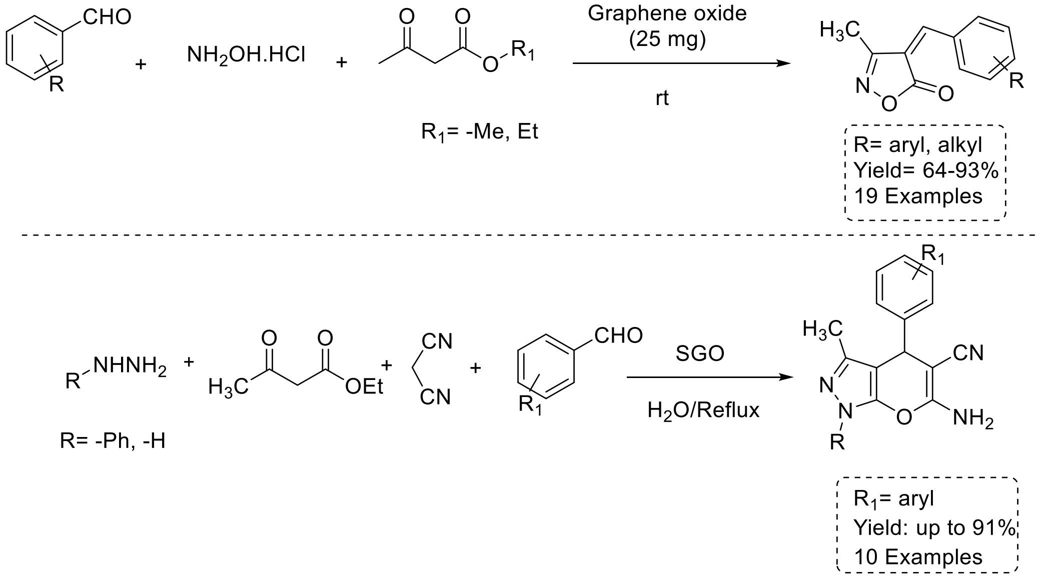


Scheme I.A.25. *Sonochemical N-acetylation with various amine compounds.*

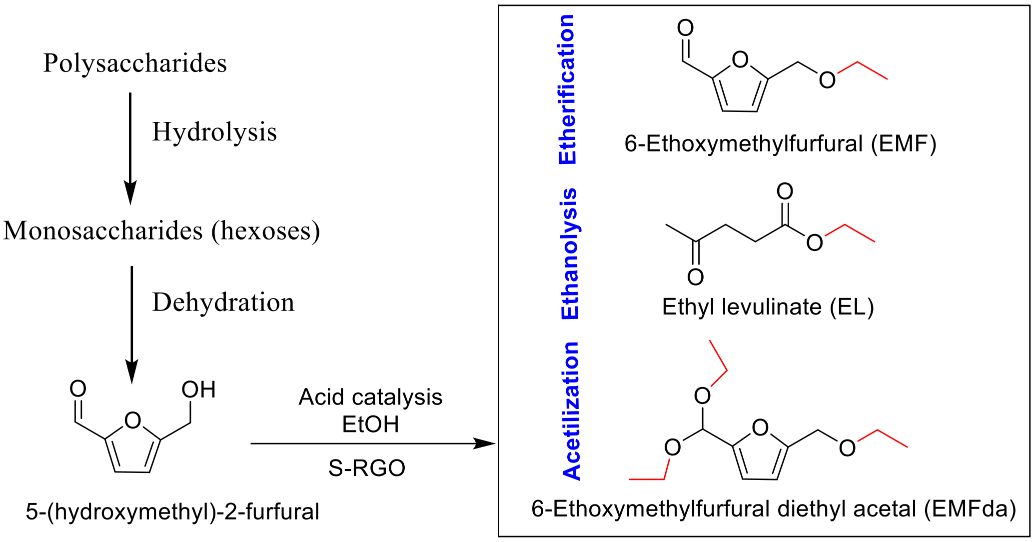
In 2020 Ghosh *et al.* employed sulfonated graphene oxide (SGO) as metal-free catalyst for the synthesis of 3-methyl-4-(hetero)arylmethylene isoxazole-5(4H)-ones and 6-Amino-3-methyl-4-phenyl-1,4-dihydropyrano[2,3-c]pyrazole-5-carbonitriles (Scheme I.A.26) [118]. Substituted isoxazoles were prepared from aldehyde, ethyl acetoacetate and hydroxylamine hydrochloride at room temperature under solvent free condition using of SGO. The catalytic potential of SGO was investigated for another important heterocyclic moiety substituted pyranopyrazole using reactants such as phenyl hydrazine, ethyl acetoacetate, malononitrile and aromatic aldehyde in H_2O medium at refluxed condition. The catalyst can be reused upto five consecutive cycles without lose of its catalytic activity.

In the year 2014, Antunes *et al.* reported the synthesis of biofuels or fuel additives in the carbohydrate platform from 5-(hydroxymethyl)-2-furfural and ethanol using sulfonated graphene oxide as effective catalyst (Scheme I.A.27)

[119]. They synthesized rGO from GO by the treatment of benzyl alcohol at 190 °C for 20 min under microwave irradiation. To collect the solid the solution was centrifuged and washed with ethanol repeatedly and then dried at 65 °C. After that rGO was heated in presence of H_2SO_4 (30 mL, 97 wt%) at 160 °C for 5 h under N_2 atmosphere to obtain sulfonated, partially reduced graphene oxide (S-rGO). The incorporation of the sulfur on H_2SO_4 treatment was confirmed by energy dispersive spectroscopy (EDS).



Scheme I.A.26. *SGO catalyzed benign synthesis of isoxazoles and pyranopyrazoles.*



Scheme I.A.27. *Conversion of HMF to the products for biofuel application using S-rGO.*

I.A.5. References

References are given in Bibliography under Chapter I, Section A