Review Article

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Recent advances in the catalytic applications of GO/rGO for green organic synthesis

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Abstract: Graphene is considered a promising catalyst candidate due to its 2D nature, single-atom thickness, zero bandgap and very high surface to volume ratio. Further, graphene oxide (GO) has been used as a catalytic support material for metal/metal oxide nanoparticles due to its tunable electrical properties. In addition, its high chemical stability and ultrahigh thermal conductivity may possibly promote high loading of catalytically active sites. This review article focuses on the recent progress in the catalytic applications of GO especially (i) as catalytic-support material (GO/reduced graphene oxide supported metal/metal oxide nanohybrids) for the green synthesis of biologically relevant molecules, (ii) for metal-free catalysis and (iii) for electrocatalysis, with special focus on graphene contribution to catalytic efficiency. The critical overview and future perspectives are also discussed.

Keywords: GO/rGO supported, green synthesis, biologically relevant, metal-free catalysis, electrocatalysis

1 Introduction

Researchers have been paying more attention to environmental issues in recent years because pollution is growing day by day, which poses a serious threat to the environment in particular, humans, plants and animals [1]. The design and development of cutting-edge environmentally friendly synthetic approaches using well-organized catalytic systems has gained significant attention in recent years to mitigate the toxic effects of pollutants [2]. Many interesting and attractive catalysts have recently been implemented in this context

and are rapidly growing at a faster pace to meet the ecological demands [3,4]. Although homogeneous catalysts bestow advantages of excellent selectivity and high catalytic activity and have been employed in petrochemical industry for the manufacture of several significant value-added consumer products, they still possess several disadvantages of low thermal stability, non-reusability and, hence, non-recyclability [5]. Application of selective, highly active and energy-efficient heterogeneous catalyst in organic synthesis is a thought-provoking area and is a key to sustainable development [6]. Among these are metal oxide nanoparticles (NPs) which are well-known to catalyze various organic transformations [7–9]. Further, variety of heterogeneous catalytic systems viz. metal-free carbon nanomaterials, including fullerene, carbon nanotube (CNT), graphite, graphene and carbon nanodots, have been explored either as an efficient carbocatalyst or as a metal oxide support for various catalytic applications [10–18]. However, there is still a huge scope for the expansion of suitable catalysts that not only provide high activity and selectivity but also provide a greener route to economic development. Graphene, a single layer of bonded sp^2 hybridized carbon atoms with a 2D flattened honeycomb-like structure discovered in 2004 [19], recently attracted considerable interest from researchers worldwide [20] (Figure 1). While its presence was predicted decades ago [21] and experimentally recognized in 1962 by Boehm et al., it was first isolated by Andre Geim and Konstantin Novoselov (2004) by the mechanical cleavage of graphite crystal at the University of Manchester. It is the basic building block of other carbon allotropes, and graphene can be wrapped to create 0D fullerenes, rolled up to form 1D CNTs and stacked to make 3D graphite [22]. It has excellent thermal, optical and mechanical properties that indicate its potential candidacy for many applications [23,24]. Other exceptional properties comprise superior thermal conductivity ($\sim 5,000$ W/m/K) [25], high planar surface ($2,630$ m²/g) [26], ultrahigh electron mobility ($2,00,000$ cm² V⁻¹ s⁻¹) [27], superlative mechanical strength (Young's modulus, $\sim 1,100$ GPa) [28] and outstanding electronic properties [29,30] which bestow

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Figure 1: Schematic depictions about the origin (presenting the transformation) of graphene from graphite and peculiar structure of graphite and graphene. Reproduced from [58].

graphene with great application prospects in a number of fields [31–33]. The number of investigations on graphene applications and its derivatives in heterogeneous catalysis has increased exponentially [34]. Since the last decade, graphene emerged as incomparable 2D supports and catalysts for various catalytic reactions due to its single-atom thickness and an incredibly high surface to volume ratio [20]. In addition, its high chemical stability and ultrahigh thermal conductivity may possibly promote high loading of catalytically active sites [20,25], and its high electrical conductivity renders it suitable for electrochemical processes. Because of these properties, graphene remains intact and resistant to degradation at high temperature, even in the presence of extremely acidic or alkaline media as well.

Graphene exhibits properties of zero bandgap and very low density of states around the Fermi level (E_F), which make graphene excellent material in catalytic applications among other 2D materials since the interactions between the graphene and the catalyst supported are highly tunable by physical or chemical method [20]. Chemical inertness of pristine graphene is well established from the small adsorption energies and limited charge transfer of the simulated adsorptions of various clusters and small gaseous molecules on it [20,35,36], and discovering effective ways of activating graphene is the major challenge in graphene-based catalysis that can be accomplished either by the introduction of defects [37,38] or by doping the substrate underneath epitaxial graphene [39] (Figure 2).

Graphene oxide (GO) is a single graphitic layer with randomly distributed sp^2 carbon atoms and sp^3 carbon atoms containing hydroxyl, epoxy, carbonyl and carboxyl functional groups. The epoxy and hydroxyl groups lie above and below each layer of graphene and the carboxylic groups typically reside at the edges of the

layers. The existence of various oxygen-containing groups on the GO surface offers outstanding hydrophilic character and analogous chemical reactivity [37]. In addition, the functional groups on the surface of GO serve as effective anchoring sites for immobilizing various catalytically active species. GO also possesses dynamic electronic properties and is usually insulated by the large portion of sp^3 hybridized carbon atoms bonded to oxygen-containing groups, resulting in sheet resistance of $\sim 1,012 \text{ sq}^{-1}$ or higher [40,41]. However, the sheet resistance of reduced GO (i.e., RGO) after GO reduction can be degraded by several orders of magnitude, thereby converting the material into a semiconductor or even a graphene-like assembly. It is well demonstrated that bandgap of GO can be tailored by controlling coverage, arrangement and relative ratio of the epoxy and hydroxyl groups [42–44]. The similar mechanical, optoelectronic or conductive graphene-like properties of reduced graphene make it highly desirable material to be used in a surfeit of application including catalysis due to its heterogeneous structure comprising graphene-like basal plane additionally decorated with structural defects and occupied with areas containing oxidized chemical groups [45].

Despite the aforementioned fascinating properties, GO and RGO do have some disadvantages for practical applications. The combination of structural defects, poor dispersion, restacking and multilayer thickness can affect the electrical properties and high surface area of GO materials [46]. The insulating nature of regular GO also limits its applications in electronic devices and energy storage. Furthermore, the residual defects and holes degrade the electronic quality of RGO [47]. The oxygenated groups will extend GO's structural/chemical diversity to a large extent through more chemical modification or functionalization, providing an efficient

Figure 2: Different forms of graphene: (a) graphene oxide, (b) pristine graphene, (c) functionalized graphene, (d) graphene quantum dot and (e) reduced graphene oxide. Reproduced from [58].

way to tailor GO's physical and chemical properties to planned rates. Consequently, GO and GO-based composites have demonstrated great potential in the energy storage/conversion and environmental protection applications [48].

GO, an oxidized form of pristine graphene, carries negative charge due to the presence of oxygen-containing functional groups on the surfaces and hydrophilic GO can be further reduced to form hydrophobic rGO. Graphene has further attracted great interest as a promising nanomaterial for a variety of bioapplications because of its extraordinary properties. However, both GO and rGO are known to induce cytotoxicity, DNA damage and oxidative stress in mammalian cells. *In vitro* studies show that graphene induces cytotoxicity as a result of increased formation of reactive oxygen species and also as a result of disrupted mitochondrial membrane potential eventually leads cells to apoptosis while surface modifications can significantly reduce their toxic interactions with living systems [49].

The discovery of graphene has brought a massive development and new dimension to material science and

nanotechnology. In fact, graphene has shown great talent in all fields of science and technology and has a wide variety of applications, from health to aerospace including catalysis. Hence, modern graphene work has concentrated on exploring new graphene derivatives for their use in product and device development and heterogeneous catalysis through functionalization or surface modification, due to their multidisciplinary capabilities.

Many interesting studies related to the multiple applications of graphene-based nanocomposites have been reported in the field of energy and environmental science [50], biomedical engineering [51], drug delivery and tissue engineering [52], agricultural production and crop protection [53], water treatment, supercapacitor electrodes [54], high-performance sensor applications [55], biosensors and bioelectronics [56] and many more [57]. Besides the above applications, recent research update on graphene/graphene-related materials and their engineering applications in different fields of science and technology is reported by Tiwari et al. [58]. Some fundamental aspects of graphene, GO, graphene

quantum dots, graphene nanoribbon, etc., are also discussed followed by progress in materials engineering concerning graphene covering materials fabrication, detailed properties and applications. Navalón et al. [59] highlighted the achievements of graphene-based materials in green catalytic processes. The synthesis and features in carbocatalysis including hydrocarbon conversions and environmental purification, covering advanced oxidation processes, organic synthesis, selective oxidation and hydrogenation reactions have also been elucidated. In a review article published by Yu et al. [60], the basic structure, preparation methods and properties of graphene and GO, methods for the reduction of GO, functionalization of graphene and GO consisting of covalent binding modification, noncovalent binding modification and elemental doping are described.

Despite excellent research on the use of graphene-based heterogeneous catalysts in organic transformations of simple and complex molecules [18,20,34], there are only a few literature reports [61–63] related to the investigations based on the use of GO/rGO as a catalyst/catalyst support for the green synthesis of biologically relevant molecules. The use of a number of oxygenated groups in particular, viz. hydroxyl (OH), alkoxy (C–O–C), carbonyl (C=O), carboxylic acid (COOH) and other oxygen-based functional groups necessary for surface functionality; a large number of defects; and a special 2D structure have made GO the perfect material in catalytic field [64–67]. In addition, the negatively charged surface of GO can be easily exploited to spread other catalytically active materials on its surface, including NPs of metal and metal oxide, to enhance their resultant properties [68,69]. For this purpose, many metal and/or metal oxide NPs such as Cu [70], Ni [71], Au [72,73], Ag/CeO₂ [74], Pd [75] and Pt [76] have been incorporated into the GO/rGO. Furthermore, properties similar to that of pristine graphene can be achieved by rGO, which has been further examined for manifold catalytic applications [77–80]. Recently, many environmentally sound alternative green protocols for the synthesis of biologically active heterocyclic compounds using nanocatalysts [81,82] have been researched. Keeping in view the multiple role of graphene in catalysis and the importance of pharmacologically active compounds in medicinal field, it became a necessity to write a review article on expeditious protocols involving graphene-based nanocomposites as catalyst for the synthesis of biologically significant molecules. The present review article is aimed at supporting the scientific community on this subject. Today's main challenge is to achieve sustainable chemical production with lower energy usage and less

effects on the environment, and nanocatalysis contributes significantly to the implementation of green chemistry principles. In this context, academic and industrial scientists need a timely update on recent advances in the graphene-based nanocatalysis. Although several research articles have been published on the catalytic applications of GO and reduced nanosheets of GO as effective carbocatalyst, the current review article summarizes the detailed investigation on GO as (i) an excellent catalytic support material (GO/rGO-supported metal/metal oxide nanohybrids) for the synthesis of diverse bioactive heterocyclic compounds, (ii) a green metal-free catalyst and (iii) an electrocatalyst for some reactions of industrial importance and also offers an insight on critical overview and future perspectives. An overview of catalysis followed by important properties of graphene and varied applications of graphene-based nanocomposites in different fields of science and technology is outlined in the beginning of this review. Applications of GO/rGO as a catalyst support (CuO-GO/rGO, Cu@Cu₂ONPs-RGO, PtNPs@rGO, RGO/ZnO, sulfonated rGO, pyrene tagged metal complex/N-heterocyclic carbene metal complex/Ionic liquid supported onto GO) in organic synthesis, GO/rGO as a green metal-free catalyst and GO/rGO as an electrocatalyst are then described in detail. Lastly, challenges and opportunities are explored for the potential production of graphene-based nanomaterial in sustainable catalysis. This analysis offers crucial details for the catalysis community with great success in designing and manufacturing graphene-based novel nanomaterials as heterogeneous catalysts for organic synthesis.

2 GO/rGO as catalyst support

Carbon materials have attracted great attention as support materials used in heterogeneous catalysis because of their large surface area and chemical stability by virtue of which high loading of active sites is facilitated [34]. Among carbon materials, graphene and its derivatives (GO/rGO) have extraordinary properties, comparatively activated carbon, carbon black and CNTs that make it a promising candidate for catalysis [70–72,83–85]. Metal atoms are well recognized for catalyzing the growth of CNTs, and this was the basis for the study of metal–carbon interactions that encouraged applications focused on graphene-supported metals [86]. Although unsupported NPs have been reported as catalysts for organic transformations [7–9],

agglomeration of NPs leads to reduced active surface area, resulting in poor catalytic performance. This can be circumvented by loading various metal/metal oxide NPs onto GO/rGO for many catalytic applications to improve the conversion efficiency, and several researchers have studied the subject extensively [78–80]. Recently, a review article on the utilization of four categories of carbon-based materials, viz. graphene (including, GO and RGO), graphitic carbon nitride, CNTs and activated carbon as supports in organic transformations including hydrogenation, oxidation, reduction, condensation, and multi-component reactions, is reported in detail by Bahuguna et al. [87].

The role of metal oxide NPs/pyrene tagged metal complexes/N-heterocyclic carbene metal complex/sulfonated groups/ionic liquid supported on GO/rGO as catalytic support for the synthesis of bioactive molecules is comprehensively reviewed in terms of catalytic performance, activity, selectivity and greenness of the process.

2.1 Metal oxide NPs supported on GO/rGO catalyzed organic transformations

In recent years, CuO-GO/rGO nanocomposite has been extensively used as a catalyst for various organic transformations, viz. synthesis of coumarin-based triazoles [88], CO oxidation [89], nitroaromatics hydrogenations [90], imidazo[1,2-*a*]pyridines syntheses [91], ynones, 1,3-diynes, 1,5-benzodiazepines [92] syntheses, etc. Further, it can also be utilized as a catalyst for *N*-arylation of *N*-heterocycles [77], decomposition reaction of dye molecules [93], synthesis of alkylaminophenols via Petasis-Borono-Mannich (PBM) reaction [94], synthesis of flavanones [95], etc. In one such study, Movahed et al. [77] carried out the synthesis of core-shell Cu@Cu₂O NPs on RGO (Cu@Cu₂O NPs-RGO) by *in situ* reduction of GO and copper sulfate using L-ascorbic acid as a reducing agent and applied it as a heterogeneous catalyst in the *N*-arylation of *N*-heterocycles. In another study, the CuO_x nanocomposites based on rGO revealed a far higher catalytic activity against the decomposition reaction of dye molecules under visible light illumination compared to the unembellished CuO_x NPs [93]. Choi and coworkers [93] performed the synthesis of CuO_x/rGO nanocomposites by controlling the impregnation condition of a copper precursor (Cu(NO₃)₂·3H₂O) on GO and explored for catalytic activity toward the dye molecules' decomposition reaction under visible light illumination. Among CuO_x/rGO nanocomposites, CuO/rGO showed excellent

photocatalytic activity that can be credited to the synergistic combination of dye adsorptivity and electron acceptability of the rGO, the surface hydroxyl species in the CuO/rGO, the narrow bandgap and smaller size of the CuO NPs.

It is well-known that the PBM reaction, reported by Nicos Petasis in 1993, may be used in combinatorial chemistry and drug development [96]. It can also be used to access highly functionalized amines and amino esters with a high diastereoselectivity as well as enantioselectivity [97,98]. In yet another research, the composite CuO NPs/rGO acts as a catalyst as well as a susceptor and improves the overall potential of the reaction mixture to absorb microwave irradiation (MW) [94]. In this research, Dandia et al. [94] developed CuO NPs/rGO composite catalyzed green method for selective synthesis of alkylaminophenols in 73–93% yield through the PBM reaction of boronic acids, salicylaldehyde and amines under MW (Scheme 1).

CuO NPs/rGO was recovered from the reaction mixture and recycled eight times without any noticeable loss of activity. The catalytic activity was found to be around sevenfold higher at 400 W power output under microwaves compared to traditional methods. Nanocomposite was synthesized using GO, Cu(OAc)₂

Scheme 1: A CuO NPs/rGO composite catalyzed Petasis-Borono-Mannich reaction. Reproduced by permission of The Royal Society of Chemistry. RSC Advances 2018;8(53):30280–8. doi: 10.1039/C8RA05203D.

monohydrate and hydrazine hydrate as a reducing agent; and GO reduction, protection and functionalization occur in a single step (Scheme 2). The CuO NPs/rGO composite X-ray diffraction (XRD) pattern revealed diffraction peaks for the CuO NP phase and rGO crystallographic planes which indicated the positive modification of CuO NPs on the rGO sheets. Transmission electron microscopy (TEM) imaging verified that the rGO sheet had been updated with a lot of the CuO NPs (about 23 nm). The overlap of CuO NPs, for transparent rGO sheet, demonstrated that the particles could adsorb on both sides of the rGO. The PBM reaction was even studied using various catalyst concentrations and in the presence of different solvents such as CH₃CN, MeOH, 1,4-dioxane, THF, DMF and DCM. Excellent product yield (92% yield) was achieved with 10 wt% of the CuO NPs/rGO composite containing 2% CuO load in the presence of DCM. In this connection, a sustainable approach has further been developed by Gupta et al. [95] toward the synthesis of hybrid molecules containing versatile heterocyclic moiety, flavanone, possessing numerous biological activities such as antioxidant, antitumor, anti-inflammatory, anticancer, antidiabetic and antiulcer [99–102] with bioactive triazole [103] by combining Michael addition and click reaction using CuO/rGO nanocomposite as a catalyst (Scheme 3). The GO powder XRD (PXRD) pattern revealed characteristic diffraction

peaks at 2θ corresponding to 9.33 and 42.20 due to [001] and [100] planes, suggesting graphite oxidation to GO. In the CuO/rGO nanocomposite PXRD pattern, the absence of the [100] plane at $2\theta \sim 42.20$ and the appearance of a peak at $2\theta \sim 24.90$ suggested that GO was reduced to rGO during CuO NPs doping on GO. Catalyst could be recycled and reused up to seven repeated runs without losing activity as compared with the reported methodologies [104–107]. Other prominent features of the process include water as a green solvent, good to excellent yields (87–96%), low catalyst loading, high atom efficiency, high substrate variation and good gram scale reaction. In addition, polar protic solvents, such as water and ethanol, showed improved conversion (92 and 94%, respectively) in the presence of 8 mg nanocomposite under refluxing conditions of 30 min (Scheme 4).

Another important aspect of the technique is the adaptation of various functional groups to the conditions of the reaction (Scheme 4). Reported plausible mechanism for CuO/rGO nanocomposite catalyzed reaction is outlined in Scheme 5. Similarly, flavanones containing a moiety of 1,2,3-triazole (4a–j) were also synthesized in a single step in magnificent yield (90–97%; Scheme 6). Further studies with different functional groups attached to phenyl azide were also carried out and reported to provide desired flavanone enclosed triazoles in excellent yield.

Scheme 2: Synthesis of the CuO NPs/rGO composite. Reproduced by permission of The Royal Society of Chemistry. RSC Advances 2018;8(53):30280–8. doi: 10.1039/C8RA05203D.

Scheme 3: Synthesis of CuO/rGO nanocomposites. Reproduced by permission of The American Chemical Society. ACS Omega 2018;3(7):7288–99, <https://pubs.acs.org/doi/10.1021/acsomega.8b00334>. Notice to readers: further permissions related to the material excerpted should be directed to the ACS.

Scheme 4: General scheme for the cyclization of chalcones to flavanones. Reproduced by permission of The American Chemical Society. ACS Omega 2018;3(7):7288–99, <https://pubs.acs.org/doi/10.1021/acsomega.8b00334>. Notice to readers: further permissions related to the material excerpted should be directed to the ACS.

Scheme 5: Plausible mechanism for the CuO/rGO nanocomposite catalyzed reaction. Reproduced by permission of The American Chemical Society. ACS Omega 2018;3(7):7288–99, <https://pubs.acs.org/doi/10.1021/acsomega.8b00334>. Notice to readers: further permissions related to the material excerpted should be directed to the ACS.

Scheme 6: General scheme for 1,2,3-triazoles. Reproduced by permission of The American Chemical Society. ACS Omega 2018;3(7):7288–99, <https://pubs.acs.org/doi/10.1021/acsomega.8b00334>. Notice to readers: further permissions related to the material excerpted should be directed to the ACS.

Recently, nitrogen-doped graphene encapsulated Cu NPs are reported to act as an efficient and durable catalyst in selective oxidation of 5-hydroxymethylfurfural to 2,5-furandicarboxylic acid as a bioplastic monomer under mild conditions [108].

Moreover, catalytic applications of Pt NPs supported onto graphene are well established, which include its use as electrocatalyst for methanol oxidation reaction (Pt/graphene nanosheet surface [GNS]) [109] and for proton exchange membrane fuel cell (PEMFC) (Pt/rGO) [110], electrochemical sensors (Pt/G) [111], alcohol oxidation (Pt/rGO) [112], styrene hydrogenation (PtNPs/G) [113], etc. Aday et al. [114] reported the development of highly crystalline, colloidally stable and highly monodisperse Pt NPs@rGO and its use as a catalyst for the synthesis of acridinedione derivatives which are well recognized to possess numerous biological activities such as anticancer, antimicrobial, myorelaxant, free radical scavenging, etc. [115–117]. The synthesis of acridinedione derivatives was carried out in 94–96% via single-pot, multicomponent condensation of dimedone, various aromatic aldehydes and several aromatic amines in the presence of water/ethanol as a green solvent using Pt NPs@rGO as a recyclable heterogeneous catalyst [114] (Scheme 7).

Characterization of the synthesized catalyst was done on the basis of high-resolution electron microscopy,

TEM, X-ray diffraction, Raman and X-ray photoelectron spectroscopy techniques. The results obtained using Pt NPs@rGO were compared to those obtained using other catalysts such as Pt NPs, glacial acetic acid, P-Dodecylbenzenesulfonic acid, H_2SO_4 and hydrochloric acid; and it was found that Pt NPs@rGO delivered the highest yield. It has been shown that no special care need to be taken in processing or handling the catalyst because it is not prone to air or moisture [114].

Metal oxide NPs supported on RGO has further been investigated for the green synthesis of the substituted indole derivatives [118] especially the 3-substituted indoles [119,120] that are established medicinally potent lead molecules and key intermediates for the synthesis of various therapeutic agents [121]. Green method for efficient synthesis of biologically active 3-substituted indoles using RGO/ZnO nanocomposite as recyclable heterogeneous catalyst in water (Scheme 8) has been developed by Rajesh et al. [122]. It is demonstrated that nanocomposite can act as amphiphilic heterogeneous catalyst in water, as the RGO surface is hydrophobic and the surface polarity of ZnO NPs is hydrophilic in nature [123] and can be recycled six times without substantial loss in catalytic activity. Other advantageous features of the methodology are higher environmental

Scheme 7: Synthesis of acridinedione derivatives in the presence of Pt NPs@rGO.

Scheme 8: RGO/ZnO-catalyzed synthesis of 3-amino alkylated indoles.

compatibility, sustainability factors such as smaller E-factor and higher atom economy.

Khatun et al. [124] reported zinc metal containing aminically modified GO catalyzed CO₂ fixation through *N*-formylation and carbamate formation reactions of amines. It was found that *N*-formylation of both aromatic and aliphatic amines gave high yield of the corresponding formylated products in the presence of polymethylhydrosiloxane as reducing agent under 1 bar CO₂ pressure and mild temperature. Formation of carbamates from aniline or its derivatives and alkyl/aryl bromide was achieved with good product selectivity under the same CO₂ pressure at room temperature under solvent-free condition. The catalyst can be reusable even after six consecutive runs, further making it a green catalytic process.

Variety of indole derivatives, aromatic aldehydes and secondary amines were employed to obtain good yields (83–92%) of a series of 3-amino alkylated indoles. RGO/ZnO was reported to be the best catalytic system for the synthesis of 3-amino alkylated indoles in terms of

activity, selectivity and greenness of the protocol, with negligible waste generation from the reaction mixture [122]. Further investigations on indole with active methylene compounds and various aromatic aldehydes were also carried out to give the corresponding 3-substituted indoles in excellent yields via Knoevenagel condensation followed by Michael addition. It was established that the aromatic aldehydes bearing electron-donating substituents such as –OMe and –OH at meta and para positions showed less reactivity over electron withdrawing substituents such as –NO₂ and chloro at *ortho* and *para* positions [122].

2.2 Pyrene-tagged metal complexes supported onto GO as catalyst

Although noncovalent methods for the immobilization of catalysts on solid surface are easy approaches, the drawback may be that the link between catalyst and

solid is often not too strong [125]. Because of the intrinsic ability of pyrene to afford π stacking interactions with graphitic surfaces [126], pyrene-tagged metal complexes have been effectively supported on graphitized solids [127] and some have even been used in catalysis to reveal excellent recyclability properties [128]. It is demonstrated that noncovalently immobilized pyrene-tagged N-heterocyclic carbene (NHC)-based catalyst onto graphene surface modified important properties of the catalyst that can be related to π - π stacking interactions established between aromatic reactant and pyrene functionalities [129,130]. Ruiz-Botella and Peris [125] prepared two pyrene-tagged NHC complexes of rhodium(I) and immobilized these complexes onto rGO support and studied their catalytic activity in the 1,4-addition of phenylboronic acid to cyclohex-2-one and in the hydrosilylation of terminal alkynes. It was reported that bimetallic catalyst with the two pyrene tags supported on to reduced graphene exhibited improved catalytic activity against the monometallic one with only one pyrene tag for both the reactions that was further correlated to earlier studies demonstrating significant reduction in leaching when the metal complex is anchored to the surface of solid with more than one pyrene tag [129]. While the monometallic catalyst quickly became inactive, the solid containing bimetallic catalyst could be recycled up to five times with no noticeable loss of activity in the case of the addition of phenylboronic acid to cyclohexanone. Moreover, better selectivity toward β -(Z)-vinylsilane was observed in the hydrosilylation of terminal alkynes in case the immobilized bimetallic catalyst was used although the catalyst could only be reused upto two runs. Interesting results indicate that rGO-supported catalysts offer not only better catalytic performance but also improved selectivity. In yet another study, Sabater et al. [131] developed

highly efficient catalyst by co-immobilizing Pd and Ru complexes with pyrene-tagged NHC ligands onto rGO surface and examined for its catalytic activity in the hydrodefluorination of a series of fluoroarenes with catalytic system recycled up to 12 times without the measurable loss of activity (Figure 3).

Many organic transformations like the cyclization of acetylenic carboxylic acid and the coupling of diphenylcyclopropenone with substituted phenylacetylenes, hydrogenation of alkenes and alcohol oxidation have also been carried out using pyrene-tagged metal complexes supported on rGO with excellent recyclability [132,133].

2.3 NHC metal complex supported on GO as catalyst

N-heterocyclic carbenes [134] are among the most widely studied group of ligands, with applications in various fields including catalysis. The silylation modification technique reported on GO may provide catalytic activity for graphene nanocomposites [135]. In one such study, ionic liquid framework-modified GO (GO-IL)-supported NHC palladium complex (NHC-Pd/GO-IL) was synthesized by GO modification via a silylation reaction and used as an effective and recyclable catalyst for Suzuki reaction by Movahed et al. [136] (Scheme 9). The nanocomposite demonstrated strong catalytic activity in EtOH-H₂O (1:1) for the Suzuki coupling of a variety of activated and deactivated aryl halides with aryl boronic acid. Further, the catalyst could be reused several times without significant decrease in its catalytic activity. Leaching experiments such as hot filtration and atomic absorption spectrometry analysis confirmed the

Figure 3: Immobilization of pyrene-tagged palladium and ruthenium complexes onto reduced graphene oxide for hydrodefluorination. Reprinted (adapted) with permission from American Chemical Society” ref. [131] *Organometallics* 2015;34(7):1186–90. <https://doi.org/10.1021/om501040x>. Copyright ©2014 American Chemical Society.

Scheme 9: GO NHC-Pd/GO-IL catalyzed Suzuki reaction.

heterogeneous nature of the catalytic reaction. In addition, the TEM image of the recovered catalyst showed the existence of well-distributed Pd NPs without any accumulation on the GO-IL sheets. It is shown that imidazolium IL plays a significant role in improving the dispersibility of Pd NPs found inside the GO-IL sheets, thereby avoiding the agglomeration of Pd NPs on the sheets of GO-IL. Evaluation by quantitative energy-dispersive X-ray spectroscopy (EDS) mapping indicated that the elements N, Pd and Si were found to be uniformly distributed across the entire surface of NHC-Pd/GO-IL nanocomposite, rather than only being localized at the edges of graphene sheets.

In yet another research, Shang and coworkers [137] immobilized NHC–palladium complex (NHC-Pd^{2+}) onto the surface of GO via a chemical bonding method for the first time and employed as an effectual catalyst for Suzuki–Miyaura coupling reactions with yields of the products ranging between 83 and 96%. Recyclability of the catalyst was checked and it was found that it could be reused for at least six consecutive cycles without significantly losing its catalytic activity. GO-supported NHC-Pd^{2+} catalyst was characterized by TEM, X-ray diffraction spectroscopy, X-ray photoelectron

spectroscopy and infrared (IR) spectroscopy. Several other investigations have also been carried out using the NHC-supported rGo nanocomposite catalyzed transformations. Recently, Page and coworkers [138] covalently modified partially rGO with 3-methyl-4-phenyl-1,2,3-triazolium salts, making use of epoxy functionalities on the carbon nanomaterial. Hydroxyl-triazolium-functionalized materials thus formed were used to prepare graphene-oxide-supported rhodium–triazolylidene hybrid catalysts which displayed outstanding activity for the hydrosilylation of terminal and internal alkynes. Furthermore, catalysts showed good selectivity toward β -(Z)-vinylsilane isomers (for the terminal substrates not hindered) or syn additions (Figure 4).

2.4 Sulfonated rGO catalyzed organic transformations

Among solid acid catalysts, sulfonated graphene has emerged as an interesting environmentally benign water-tolerant solid-acid catalyst [139]. Since the last decade, sulfonated graphene has been discovered for various catalytic applications such as acid-catalyzed liquid reactions [140], hydrolysis of cellulose [141], conversion of 5-(hydroxymethyl)-2-furfural into bio-fuels [142], synthesis of 6,6'-(aryl(alkyl)methylene) bis (2,4-dialkylphenol) antioxidants [143], etherification of glycerol with isobutene [144], etc. 1,3,4-Oxadiazole moiety is a key intermediate for the synthesis of many antibacterial, antiviral, antiparasitic and other drugs [145,146]; and hence several methods were reported for the synthesis of 1,3,4-oxadiazoles [147,148]. Owing to the drawbacks such as requirement of large amount of solvent, strong basic medium and a long reaction time associated with 1,3,4-oxadiazole cyclization process with hydrazides [149], Brahmaya et al. [150] reported the direct synthesis of 1,3,4-oxadiazoles from hydrazides with carbon dioxide (1.0 MPa) using nano sulfonated rGO ($\text{rGOPhSO}_3\text{H}$) as an efficient and mild carbon catalyst under ultrasonic irradiations (Scheme 10).

Figure 4: Graphene modified with rhodium-based N-heterocyclic carbenes for alkyne hydrosilylation. Reprinted (adapted) with permission from American Chemical Society. Ref. [138] ACS Applied Nano Materials 2020;3(2):1640–55. <https://doi.org/10.1021/acsanm.9b02398>. Copyright ©2020 American Chemical Society.

Scheme 10: Direct synthesis of 1,3,4-oxadiazoles from hydrazides using rGO/PhSO₃H catalyst.

Scheme 11: rGO-SO₃H catalyzed direct amidation of carboxylic acids with amines.

In other investigation, RGO-SO₃H was used as an effective catalyst for one-pot synthesis of a series of 2-amino-3-cyano-7-hydroxy-4*H*-chromene derivatives using multicomponent reaction of phenols, aldehydes and malononitrile under mild and green conditions [151]. The reaction was performed in water as a green solvent providing good to excellent yield of the product, and the catalyst RGO-SO₃H was reusable at least five times without measurable decrease in its catalytic activity. The synthesized compounds were characterized using IR, ¹H NMR and mass spectral studies. The rGO-SO₃H was even successfully applied as a reusable solid acid catalyst for direct amidation of carboxylic acids with amines using ultrasonic irradiation [152] affording the corresponding amides in good to high yields (56–95%) in short reaction time (Scheme 11). Sulfonic acid-containing aryl radicals were grafted onto chemically rGO under sonochemical conditions to prepare sulfonated rGO nano-sheets (rGO-SO₃H), which were characterized by fourier-transform infrared spectroscopy (FT-IR) spectroscopy, Raman spectroscopy, scanning electron microscope (SEM), XRD, thermogravimetric analysis (TGA), differential scanning calorimetry and X-ray photoelectron spectroscopy (XPS).

2.5 Ionic liquid supported on GO as catalyst

Owing to their high thermal and chemical stability, low volatility, very high ability to dissolve a wide variety of compounds and more significantly, their environmentally friendly behavior [153], surface functionalization of G and GO using ionic liquids is gaining particular

importance recently. The ionic liquid-functionalized graphene (G-IL/GO-IL) has been extensively used in pollutant decontamination, enhancement of styrene-butadiene rubber nanocomposites, high-temperature proton exchange membrane fuel cell, sensing and biosensing, lubrication, catalysis and carbon dioxide capturing and hydrogen production [154–159]. Moreover, ionic liquids interact strongly with the sp²-hybridized G and GO sheet carbon networks because of their high dipolar nature and make them more dispersible compared to their native networks [153]. It is established that acylation, isocyanate formation, esterification, amide formation, nucleophilic ring opening, diazotization and cycloaddition reactions generally facilitate the covalent functionalization of G and GO [33,160]. In one such investigation, Nakhate and Yadav [161] synthesized GO-supported functionalized ionic liquid (PTS-Im-3@GO) by anchoring 1-(4-sulfobutyl)-3-(3-propyltriethoxysilyl) imidazolium hydrogen sulfate onto GO via covalent bonds and used it for styrene oxide ring opening reaction with isopropyl alcohol, giving 95% conversion and 100% regioselectivity toward 2-isopropoxy-2-phenylethan-1-ol at 50°C. Among various heterogeneous catalysts used, viz. GO, PTS-Im-1@GO, PTS-Im-2@GO, PTS-Im-1, PTS-Im-2, PTS-Im-3, H β -zeolite and montmorillonite K-10, PTS-Im-3@GO showed good conversion toward the desired product. Characterization of PTS-Im-3@GO was done by FT-IR, SEM, EDS, TGA, XRD, silicon-29 magnetic resonance spectroscopy, XPS and carbon hydrogen nitrogen sulphur analysis. Likewise, Garkoti et al. [162] developed heterogenization of amine-functionalized ionic liquids via covalent immobilization of 2-chloroethylamine on GO sheets modified by imidazole. The prepared material was characterized by FTIR, XRD, TGA, TEM, SEM and EDX spectroscopy and used as a catalyst for the synthesis of 3-substituted indoles via Yonemitsu-type reaction. After recovery from the reaction mixture, the catalyst was reused seven times without any significant loss of activity. Hanoon et al. [163] reported an efficient method for the facile synthesis of biologically relevant benzimidazole derivatives [164] using an acidic ionic liquid covalently supported on graphene sheets (A-FGO). The catalyst was efficiently synthesized and characterized using FTIR, SEM, X-ray photoelectron spectroscopy, EDS and X-ray diffraction techniques. The catalyst was removed by filtration, washed with dichloromethane and reused in the next cycles (up to five runs). Shorter reaction times, high yields, safer reaction conditions, the eco-friendly nature and possible reuse of the catalyst are the salient features of the present methodology.

3 GO/rGO as a green metal-free catalyst

Carbocatalysis is a form of catalysis for the transformation or synthesis of organic or inorganic substrates using heterogeneous carbon materials. The introduction of GO as a new class of metal-free catalysts based on carbonaceous materials opens up a range of potential application possibilities in chemical synthesis. For the first time, Dreyer and his coworkers [165] reported GO as a carbocatalyst to catalyze the oxidation of various alcohols and alkenes, and the hydration of different alkynes into their respective aldehydes and ketones in good to excellent yields. Several experiments have since been conducted to investigate GO as a carbocatalyst. In one test, Basu and coworkers [166] produced for the first time from a mixture of secondary aryl alcohols and thiols an effective and mild one-pot GO catalyzed sequential dehydration–hydrothiolation reaction. The resultant unsymmetrical thioethers were synthesized under metal-free conditions and the catalyst could be reused for five cycles without losing any appreciable activity. Patel and coworkers [167] employed GO as metal-free carbocatalyst to promote amidation of esters with amines in good to superb yields without using any additives. It is demonstrated that the enhanced catalytic activity can be due to the oxygen functionalities on the GO surface that form H-bonds with the reactants, thereby speeding up the reaction. Improved yields and a wide range of functional group tolerance are some of the important features of the developed protocol. In yet another research, Karthik and Suresh [168] reported sustainable metal-free approach using GO as a benign solid-acid catalyst to synthesize phenols from aryl and heteroaryl boronic acids, *ipso*-hydroxylation occurs in a short reaction time by using aqueous H_2O_2 as an oxidant in the presence of water. The presence of carboxyl groups boosts *ipso*-hydroxylation as revealed by the control experiments, and GO can be reused several times without losing its activity.

Furthermore, GO has been successfully utilized as a green carbocatalyst for the synthesis of numerous biologically relevant scaffolds such as benzylbarbiturocoumarin

derivatives [169], 3-dihydroquinazolinones and quinoxalin-4-(3*H*)-ones [170] and benzylpyrazolyl coumarin derivatives [171], 2,5-dimethyl-*N*-phenyl pyrrole [172], poly heterocyclic spiro-indeno quinoxaline pyrrolizidines quinoxalin and spiro-oxindoles pyrrolizidines [173], 3-sulphenylimidazo[1,2-*a*]pyridines [174], dihydro-2-oxopyrroles [175], etc. Roy et al. [176] developed an eco-friendly method for the synthesis of library of bioactive nitrogen containing heterocycles, quinoxalines [177] from 2-nitroanilines under entirely metal-free conditions using GO or rGO as a green catalyst (Scheme 12).

A wide range of functional groups such as methyl, methoxy, furyl or bromide present with either nitroaniline or dicarbonyl compounds, along with ketone or aldehyde, provided excellent quinoxaline transformation (Scheme 12). Initially, GO or rGO catalyzed the reduction of nitroaniline with hydrazine hydrate takes place followed by the reaction with 1,2-dicarbonyl compounds or with α -hydroxy ketones in one-pot tandem way to afford quinoxalines in good yields (83–95%). After being recovered from the reaction mixture, the catalyst was recycled without any appreciable loss of activity for four uninterrupted runs.

Ebajo et al. [178] reported the synthesis of triazoloquinazolinone compounds by utilizing Brønsted acidic edges and Lewis-acid sites in GO as heterogeneous promoters. GOs with the maximum number of Lewis acid sites possess the highest degree of oxidation resulting in the best yields (up to 95%) under moderate reaction conditions (85°C in EtOH). According to them, the perceived Lewis acidity through the opening of basal plane epoxide ring in addition to the saturated Brønsted acidic carboxylic groups is responsible for the increased carbocatalytic activities as revealed by the results of FT-IR spectroscopy, temperature-programmed decomposition mass spectrometry and X-ray photoelectron spectroscopy. In one more investigation, the identification of GO as pseudocatalyst in organic transformations is further supported by the fact that recycled GO can be successfully regenerated to hold 97% activity of new GO [179]. It is demonstrated that graphene's structural features can

Scheme 12: GO/rGO catalyzed synthesis of quinoxalines from 2-nitroaniline.

provide a broad range of conversion and selectivity by tailoring the surface morphology and functionalities [83]. In this sense, several review articles and accounts have been published on carbocatalytic activity of graphene [34,85,180]. Such eco-friendly approaches built by researchers opened the door to more studies focused on GO as a metal-free catalyst for sustainable organic synthesis. Further investigations toward the catalytic activity of GO can be done by manipulating surface modification and edge defects which may lead to the development of novel green synthetic protocols involving GO as a metal-free catalyst.

4 GO/rGO as electrocatalyst

Electrocatalytic activity of graphene-based nanomaterials was first reported in 2009 for methanol oxidation reaction with an unprecedented high activity in Pt subnanoclusters supported onto graphene nanosheets by Yoo et al. [181]. Since then several studies based on electrocatalytic property of graphene-based materials have been carried out by researchers all over the world. Owing to the fascinating properties of graphene such as chemical stability, electrical conductivity, tunable surface area and excellent mechanical behavior, graphene-based materials have outstanding applications as electrode materials in electrochemical devices such as supercapacitors, rechargeable lithium ion batteries, fuel cells and solar cells [182–185]. Among these devices, future-generation energy devices for clean power production include PEMFCs and rechargeable metal–air batteries [186,187]. Technically, precious Pt-based nanomaterials are the commercial electrocatalysts for the oxygen reduction reaction (ORR), which reports 36–56% of the cost of the PEMFCs [188]. Various heteroatom-doped carbon materials [189], sulfur-doped graphene (SG) [190], phosphorous-doped graphite layers [191], iodine-doped graphene [192] and edge-halogenated (Cl, Br, or I) graphene nanoplatelets [193] and mesoporous nitrogen-doped carbons prepared from ionic liquids and nucleobases for productive metal-free oxygen reductions [194] are investigated. An article published by Iqbal et al. [195] outlines graphene-based materials for fuel cell technology applications such as electrodes additives, bipolar plates and proton conducting electrolyte membrane. The graphene dispersed electrodes show improved electrocatalytic activity toward fuel oxidation and oxidant reduction reactions. In addition, graphene as an electrolyte has displayed an excellent performance

toward high ionic conductivity and power density in proton exchange membrane devices. The integration of graphene into fuel cell systems has shown commendable efficiency and has promising future for commercial applications.

Rising demand for renewable energy has driven extensive work into powerful, cost-effective and eco-friendly energy conversion and storage systems. In this context, nanomaterials based on graphene have been used in fuel cell applications as gifted electrocatalysts for ORR [196–198]. Kumar et al. [199] developed extendable and benign method by using N-doped reduced graphene oxide (NrGO) for the metal-free oxygen reduction reaction. Characterization of NrGOs was carried out by XPS, Raman, FT-IR, HR-SEM, atomic force microscopy, XRD and UV-Vis techniques. Based on XPS, the highest degree of nitrogen doping was obtained at 4.3 atom percent at 450°C with an atomic ratio of C/O as high as 16. This NrGO's electrocatalytic behavior against the ORR in alkaline electrolytes has been verified by electrochemical characterizations with a high reaction onset potential of 0.78 V vs reversible hydrogen electrode. Recent review article by Ali and Shen [200] emphasized efforts to expand the nanoscale synthesis of graphene-supported electrocatalysts and their electrocatalytic characteristics for a remarkable hydrogen evolution reaction (HER). HER has tremendous potential for the future renewable technologies in terms of energy storage and energy conversion. The effect of graphene for HER in alkaline medium is researched by Huang et al. [201]. Currently, the efficiency of water electrolysis producing hydrogen is too poor to compete economically for real energy requirements [202]. The best catalysts are the elements from the Pt group metals which are perfect from thermodynamics and kinetics point of view, but their lack and high cost hinder their large-scale use, requiring cheaper and more viable catalysts [203,204]. In this context, Luis-Sunga et al. [205] recently reviewed nonprecious metal graphene-based catalysts for HER.

5 Critical overview and future perspectives

While graphene-based materials are in their evolving stages, they have excessive potential to facilitate a wide range of organic transformations and can offer amazing talent in the design of new catalytic systems. Brilliant physicochemical properties associated with graphene

combined with excellent catalytic performance in terms of high activity, selectivity, stability, recyclability and greenness of the synthetic process (by lowering energy consumption) of graphene-based nanocatalysts makes them superior over other heterogeneous catalysts in solving today's major problems of sustainable development. Further, the variety of functional oxygenated groups on graphene oxide makes it an desirable medium for anchoring other catalytically active groups. Furthermore, nanosized materials exhibit additional unique properties compared to the macroscale as demonstrated by unexpected catalytic activity of gold NPs not found in bulk gold. Taking into account the added value, as catalysts these materials can provide affordability and the durability of their use as opposed to metal catalysts, and it can be expected that this field will continue to expand in the years to come. Consequently, it empowers us with abundant future applications as demonstrated by the growing number of research publications and patents in recent years.

Although the past decade has brought much progress, there are still challenges, which include loss of catalytic activity due to metal leaching under severe conditions. Another major concern is the lack of control over distinct morphologies that must be addressed during scale-up synthesis of nanocomposites. A uniform distribution over the support surface is not always an easy task, and implementation of large-scale production in industry is the biggest challenge. Further, supported metal NPs face consequences of deactivation associated with their extended usage under conditions of reactions, such as coke forming, aggregation, coarsening and sintering. Despite the ideas of a promising future, threats to both the environment and human health are still not clearly understood based on the evidences presently existed. To overcome these challenges, it is suggested that toxicity and long-standing effects of nanomaterials and by-products required to be studied while designing the catalyst more widely as soon as possible keeping in view the human health and environmental impacts. Thoughtful strategy for the development of highly active and enantioselective recyclable nanocomposite catalyst for the green and sustainable organic synthesis is the need of hour.

6 Conclusions

Graphene-based nanocomposites act as talented catalysts for facilitating wide range of organic transformations and

have amazing potential in designing novel catalytic systems. In this review article, first the use of GO/rGO supported metal/metal oxide nanocomposite as excellent catalytic support material for the synthesis of diverse bioactive molecules is broadly reviewed. The use of GO/rGO as metal-free catalyst for various organic transformations and as electrocatalyst for reactions of industrial relevance is then briefly summarized. Finally, an insight is also presented into the critical overview and future perspectives for the future development of graphene-based nanocomposite catalysts. The most relevant literature including green synthetic strategies for the synthesis of pharmacologically active compounds using graphene-based nanocomposite as catalyst have been summarized, which will surely help the scientists in preparing novel graphene-based nanocatalysts for satisfactory chemical manufacture. It will provide a greener and more sustainable alternative pathway as the catalyst can be easily separated from the reaction mixture on most routes and can be recycled and reused without apparent loss of activity making it economic.

Besides the abovementioned catalytic applications, graphene-based nano spinel ferrites (GNSFs) hold great potential in remediating contaminated aquatic environments. In this context, introduction of magnetic spinel ferrites into 2-D graphene family nanomaterials conveys various benefits of inhibited particle agglomeration, enhanced active surface area and easier magnetic separation for reuse, making the GNSFs highly efficient and eco-friendly materials, which in turn have the potential of removing several unmanageable contaminants including organic dyes, antibiotics and heavy metal ions [206]. Further, introducing graphene materials into hierarchical catalysts can enhance the removal of gaseous HCHO, which is one of the most abundant indoor pollutant, and potentially other indoor pollutants. The Pt/NiFe-LDH/rGO showed excellent catalytic performance for HCHO degradation at room temperature, which are because of better dispersion of both NiFe-LDH and rGO in the composite [207]. Graphene-based materials through hybridization or fabrication of various functionalities on their large surface open up new avenues for the adsorptive removal of volatile organic compounds (e.g., through the buildup of efficient air purification systems) [208]. A biosensor based on the $\text{CeO}_{2-x}/\text{C}/\text{rGO}$ nanocomposites exploited for the detection of uric acid, an important molecule in the biological and medical fields. The biosensor based on the $\text{CeO}_{2-x}/\text{C}/\text{rGO}$ nanocomposites shows a great potential for practical applications by presenting a high sensitivity of $284.5 \mu\text{A cm}^{-2} \text{mM}^{-1}$ at -0.4 V (vs saturated calomel

electrode), a wide linear range between 49.8 and 1050.0 μM and a low detection limit of 2.0 μM [209].

Considering the practical utility of GBMs in various fields of science and technology and the sustainability of their use compared to metal-based catalysts in organic synthesis, it is easy to predict that this area will grow extensively in the years to come; and further research is needed to identify an optimized catalyst in various organic transformations and to develop an environmentally friendly, energy-efficient and cost-effective method for graphene-based nanocomposites synthesis.

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