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# Covalently Functionalized Nano-Graphene Oxide for Fine Chemical Synthesis

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Additional information is available at the end of the chapter

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## Abstract

Nano-graphene, which is entirely composed of aromatic carbon atoms is relatively a new material, with two dimensional periodic structures and possess amazingly interesting chemical and mechanical properties. Graphene and graphene oxide (GO) materials have been explored widely as supports due to their tunable electrical properties and high surface area as well as different functional groups. The covalent modification of surface oxygen of carbon based materials, like graphene oxide and nano graphene oxide (NGO) with organo amine and other functional groups is very opt for various applications. Covalent immobilization of various organic functional moieties and metal modified organo functionalized species on nano-graphene oxide surface enables a robust immobilization of the reactive catalytic sites through strong binding on the support surfaces. Such materials prevent the leaching of active metals and improve their recyclability, when used as catalysts in solution phase. As the stability of metal depends also on the functionalization of the NGO support, metal modified/ covalently functionalized nano-graphene oxide materials are widely used in fine chemical synthesis. The functional group of NGO also prevents the aggregation of the catalytically active metal species during the reaction time. Both amine functionalized and metal (Pd) modified amine functionalized nano graphene oxide exhibit excellent activity towards fine chemical synthesis, such as with multicomponent reactions, oxidation reactions and C-C coupling reactions.

**Keywords:** graphene oxide, different amine functionalized, metal nanoparticles, oxidation reaction, one-pot reaction multicomponent reaction, coupling reactions

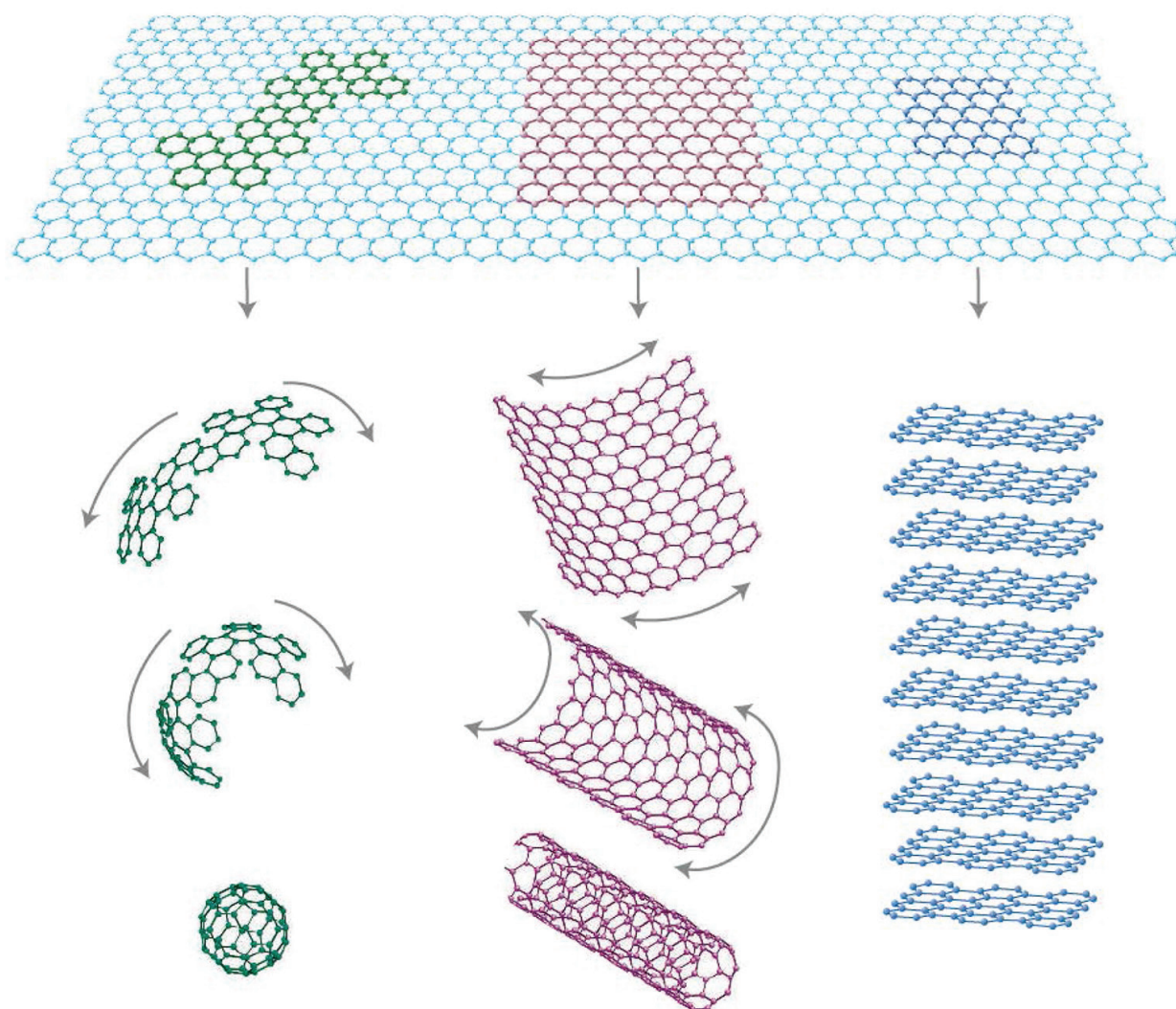
## 1. Introduction

High surface-to-volume ratio as well as distinctive thermal, electrical, mechanical, as well as optical characteristic can be named as the main advantages of the nano materials. Generally, carbon-based nanomaterials, with at least 1D in nanometer size, possess exceptional and innovative properties in their specific structure. Carbon allotropes, fullerene, carbon nanotube (CNT), graphene, graphite etc. exist in different forms in zero, one, two, or three dimensions. Some of the carbon based nanomaterials are preferred as a support for active materials in catalysis. Among these materials, nano-graphene oxide is preferred to be an ideal 2D catalytic support, because of its outstanding electrical and thermal conductivity as well as mechanical strength with high surface area [1–15]. The characteristics of graphene nanomaterials enable them to interact with organic molecules through both covalent and non-covalent bonds. H-bonding,  $\pi$ - $\pi$  stacking,  $\pi$ -cation interaction,  $\pi$ -anion interaction, hydrophobic interaction, and van-der Waals bonding etc. are examples of such non-covalent interactions. Covalent bonds happen between organic molecules and graphene based carbon nanomaterials with certain functional groups, such as carboxyl, hydroxyl, and epoxy group, facilitating the functionalization of graphene based nano materials. Pristine forms of these graphene based nanomaterials are water insoluble and in most of the organic solvents. Exploiting the exceptional property, a variety of plans have been established to obtain stable and uniform dispersions of active materials [16–18]. Chemical modification is an outstanding, alternative for the connection of organic group on the graphitic surface of these nanomaterials [4, 6, 19]. Metal modified functionalized graphene based nano materials prevent the leaching of the nano metals.

Many researchers contributed to the improvement in the activity and selectivity of functionalized graphene based nanomaterials in different applications, relative to the pristine material. This chapter provides an insight into the covalently functionalized nano-graphene oxide and metal modified covalently functionalized nano-graphene oxide materials and their versatile applications in the field of catalysis plus their applicability in fine chemical synthesis.

## 2. Carbon nanomaterials and their allotropes

Carbon receives its designation from the Latin word 'carbo' meaning charcoal, and forms the more well-known stable allotropes compared to other elements. While, the basic carbon atom builds up with tetrahedral lattice of  $sp^3$  hybridization in diamond, the  $sp^2$  hybridized extended networks are responsible for the formation of graphite. In past three decades, different allotropes of carbon have been discovered with periodic binding networks of alternate  $-sp^3$ ,  $-sp^2$  and  $sp$  hybridized carbon atoms. Among the allotropes, buckminsterfullerene (C<sub>60</sub>), carbon nanotubes (CNTs) and graphene are most famous. These carbon allotropes appear in zero, one, two, or three dimensions and in different forms (**Figure 1**). While many allotropes of carbon like carbon nanofibers, amorphous carbon etc. exist, depending on the type of hybridization and shape of the materials, these allotropes exhibit varied exciting properties. The reporting of first stable two dimensional graphene material with extraordinary properties in 2007 may be considered as a breakthrough in the Nano carbon chemistry arena [2].



**Figure 1.** Mother of all graphitic forms. Graphene is a 2D building material for carbon materials of all other dimensionalities. It can be wrapped up into 0D Bucky balls, rolled into 1D nanotubes or stacked into 3D graphite [reproduced with permission from Ref. [2]].

### 3. Graphene

Graphene is a tightly packed monolayer of  $sp^2$ -bonded carbon atoms into honeycomb two dimensional (2-D) crystal lattice. Graphene has fascinated both physicists and chemists due to its extraordinary properties such as thermal conductivity, an excellent electronic properties, high specific area etc. Graphene can be prepared by various methods and each process enjoys diverse advantages and limitations.

### 4. Synthesis of graphene

Literature survey reveals that graphene can be synthesized by using different techniques and starting materials. Quality of graphene synthesis can be achieved either by top-down or bottom-up approaches as summarized in the **Figure 2**.



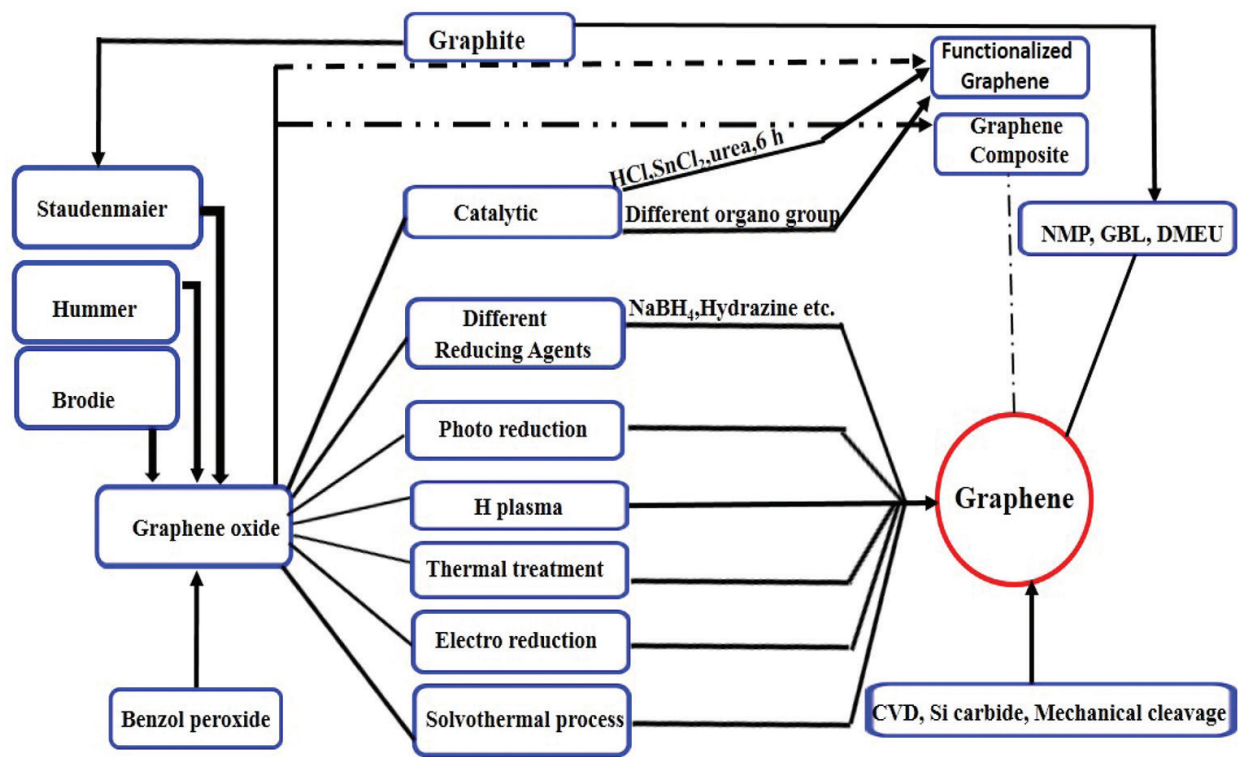


Figure 2. Road map to high quality graphene.

4.1. Top-down Synthesis

In top-down method, the graphene oxide and reduced graphene oxide are produced from the graphite powder. Generally using a large quantities of graphite, graphene oxide (GO) was obtained through oxidation process, while graphene was generated by reduction or exfoliation process of GO. Although reduced graphene oxide and graphene have similar properties, the surface of reduced graphene oxide possess some functional groups and carbon vacancies. Due to the similarity in properties, many researchers have used reduced graphene oxide in place of graphene. The different methods were developed by Brodie (1860) [20], Staudenmaier (1898) [21], and Hummers and Hoffeman (1958) [22] for the preparation of graphene. Out of these Hummers and Hoffeman Method gained more popularity and this method involves stoichiometry amounts of numerous strong acids and oxidizing agents such as con. nitric acid, con. sulfuric acid, sodium nitrite, and  $\text{KMnO}_4$  for oxidation. The synthesis of graphene oxide (GO), followed by modified Hummers method with sonication method for exfoliation of few-layer stacked graphite oxide to graphene oxide. Successful exfoliation totally depends on the sonication time, energy and solvents used. The advantages of this process are easy preparation in short reaction times and lower generation of toxic gases.

4.2. Bottom-Up process

In bottom up process for synthesis of graphene sheets by pyrolyzation is called as solvothermal method. In this method sodium and ethanol are used for sodium ethoxide, and sodium ethoxide was pyrolyzed into stacked layers of graphene. The stacked layered graphene is

converted into single layered graphene sheet by sonication. This method is highly cost-effective, but provides defective graphene. Another approach for synthesis of graphene is by unzipping or unwrapping of CNTs. Chemical vapor deposition (CVD) is also an alternate method for synthesis of graphene [23–27]. The main advantages of CVD are the quality parameters, such as size, shape, and morphology of anticipated material which can be tuned by controlling the conditions of chemical vapor decomposition.

## 5. Functionalized Graphene Oxide

Surface functionalization is fundamental technique in material science, in which new functional groups are added onto the surface of the materials by chemical methods. Modification and functionalization of graphene oxide surface is possible only due to presence of different oxygen containing functional groups. Covalent and non-covalent methods are the two ways for functionalization of carbon based graphene oxide materials with different advantages and drawbacks. The final characteristics of the materials will be dependent on the nature of functionalization.

### 5.1. Non covalent Functionalization

In noncovalent modification can be achieved through van-der Waals force between planer groups and the carbon atom. Noncovalent modification avoids disrupting the construction of the carbon materials, allowing their original characteristics to be reserved. Non covalent functionalization is a type of physical adsorption, just likes the weak interactions, which does not affect the basal plan structure of carbon based graphene sheets. Sometime metal modified carbon based materials and also some heteroatoms such as N, O, and S doped on to the carbon based materials have also been used to support metal nano particles to enhance the reactivity as well as stability through the interactions of active metal clusters and carbon vacancies. The main approaches for the non-covalent modification/functionalization of carbon based materials to form metal nano particles are wet impregnation and dry synthesis [28].

Many researchers have proposed non covalent functionalization of metal nano particles over carbon based materials by wet synthesis method. Wet synthesis procedure often undergoes from several drawbacks, such as non-homogeneous distribution and adhesion and many sources such as the type of organic solvents, reducing agents, metal precursors concentration and temperature also influence the quality of the product. Thus, this method is less used.

The dry synthesis method has been receiving vital consideration due to its simplicity and advantage of controlling parameters plus enhanced adhesion. Generally, carbon based materials are of hydrophobic nature, which can be lessened through decoration with metal nano particles via dry synthesis method. In this method to creates bridging of functional groups of support materials with nano metals [29, 30]. Thus the problems associated with wet synthesis procedure have been resolved by dry synthesis approach for preparation of carbon based materials loaded with metal Nano particles.

## 5.2. Covalent Functionalization

Covalent modification/functionalization makes covalent linkage of chemical bonds or functional groups onto the surface. The chemical bond is formed between different chosen functional groups such as carboxylic, hydroxyl and epoxy groups with oxides of the graphene oxide. The covalent modification of carbon based materials mainly changes the hybridization of carbons in  $sp^2$  to  $sp^3$ . Not only functionalization with mono-, di- or tri- amine groups [4, 31], different hetero atoms such as P, B, and O also can be introduced to the carbon network of graphene oxide. The inorganic complexes/nano composites have also been introduced on to the carbon based graphene through covalent modification. The covalent modification enhances both physical and chemical properties of nano graphene such as solubility, catalytic activity, electron mobility and introduces hydrophilicity to the materials. Co-precipitation method is one of the techniques to achieve covalent functionalization of carbon based materials which enhances activity, selectivity and stability of materials. Hydrothermal method is the other method for covalent functionalization of Nano graphene oxide, which not only improves the activity, selectivity and stability of materials, but also affords good morphology. In hydrothermal method, Specific temperature and pressure with constant rate are maintained to facilitate the morphology of the materials. Thus, hydrothermal method is considered the ideal technique for preparation of covalent functionalization of carbon based Nano graphene oxide.

## 6. Catalytic Applications

Catalyzed organic transformation reactions display an important role in industries for the synthesis of natural products, pharmaceuticals product, and agricultural derivatives [32, 33]. Carbon based materials such as graphitic carbon and their functionalization and metal modified functionalized graphitic carbon based compounds have been used as catalysts for fine chemical synthesis. Functionalized carbons based materials are often more active and/or more selective catalysts than the un-functionalized carbon based materials. Nitrogen insertion into the graphene materials is one of the interesting modifications, which includes the pyrrolic N, pyridinic N, graphitic N, or different of amino groups in to graphene structures. Functionalized carbon based graphene materials are active for a different reactions including selective oxidative oxidation of aromatic compounds [34], dehydrogenation of hydrocarbons [35, 36], decarboxylation of fatty acids [37], base catalyzed reactions and one-pot multicomponent reactions [12].

### 6.1. Catalysis by GO based materials

Graphene oxide (GO) based materials have been festooned with different oxygen functional groups, including carbonyl, epoxy, hydroxyl, and carboxylic acids. These functional groups impart graphene oxide inherent acidity, and oxidative properties, chemical and catalytic activity. Due to the oxygen containing groups, GO based materials have been successfully explored as catalysts for a variety of fine chemical syntheses reactions involving oxidation, epoxidation, oxidative coupling, dehydrative polymerization, Claisen–Schmidt coupling and

hydrogenation. Bielawski and coworkers have reported [38] the oxidation reaction of alcohols to ketones and aldehydes, as well as alkenes to diketones using graphene oxide catalyst at 150 °C. GO itself a solid acid catalyst, so it has been employed for the synthesis of dipyrromethane and calix-4-pyrroles [39]. GO was found to be good to catalyze the Aza-Michael additions [40], Claisen–Schmidt coupling reactions [41], ring opening polymerization [42] and Friedel-Crafts reactions [43]. Some fine chemical syntheses using graphene oxide based catalysts are summarized in **Table 1**.

## 6.2. Catalysis by Functionalized nano GO Catalysts

Although graphene oxide is a solid acid catalyst, researchers have modified its surface characteristics through functionalization according to their requirements. Modifying the GO by covalent modification of its surface silanol groups with different nitrogen containing organo amines increase the basicity of this materials making them suitable for base catalyzed reactions such as Knoevenagel condensation and MCRs. Rana et al have reported a method for covalent modification of organo-functionalized graphene oxide which showed excellent activity towards one-pot synthesis of pyrazolo-pyranopyrimidine derivatives [12]. Graphene-based solid acid materials anchored with both amine and sulfonic acid containing groups proved good for both acid and base catalyzed reactions, such as decarboxylation of nitro aldol reactions [44]. The graphene-based solid acid catalyst prepared by anchoring with sulfonic acid-containing group to a graphene oxide/reduced graphene oxide surface reportedly exhibited excellent activity towards acid catalyzed reactions of esterification of acetic acid with cyclohexanol gave 58.9% yields [47]. Details of various reactions catalyzed by functionalized GO based materials are shown in **Table 2**.

## 6.3. Catalysis by metal modified amine functionalized nano carbon based catalysts

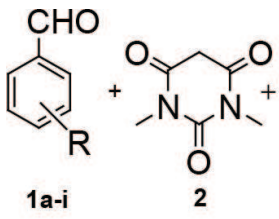
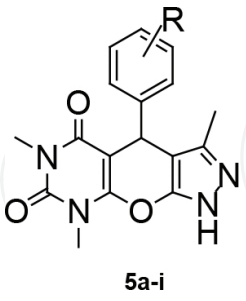
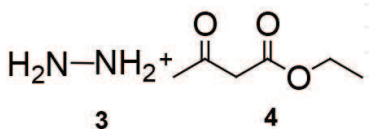
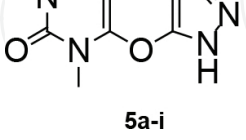
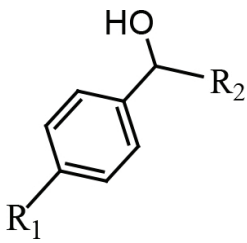
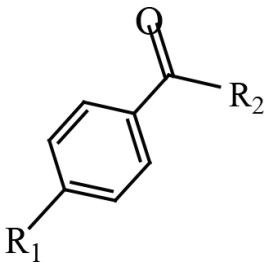
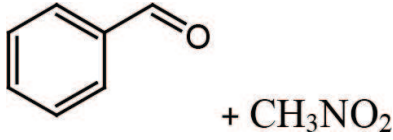
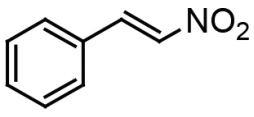
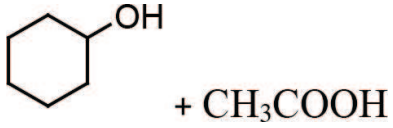
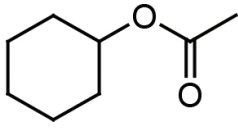
Hybrid materials involving inorganic graphene oxide and organo amine groups have an extra advantage in binding the metal atom strongly as compared to un-functionalized GO. The amine functionalized graphene oxide as support material has high surface area to enhance catalytic activity as well as dispersion capacity. The metal remains strongly covalently bounded to the support of graphene oxide and also it does not leach in the reaction medium. Hence it will be reusable for several cycles. Furthermore, the functionalized amine possess external binding capacity, which will readily provide more number of active sites. Generally, metal modified amine functionalized graphene oxide (GO)/reduced graphene oxide/ graphene based materials are also decorated with selective oxygen functional groups, including carbonyl, epoxy, carboxylic acids and nitrogen containing group as well as metal particles. These groups impart graphene oxide their inherent acidity, basicity and oxidative properties and their chemical and catalytic activity.

The activity of the metal modified amine functionalized carbon based graphene materials depends on type of metal and also on the oxidation state of the metal particles. Among the noble metals particles, generally, palladium metal particles have been more promising in nanotechnology and catalysis. Palladium having zero oxidation state will be more active towards coupling reactions, while the bivalent palladium metal particles will be active for oxidative



Starting Material	Product	Conditions	Catalyst (wt% GO)	Yield (%)	Ref.
		24 h, 100 °C	200	92	[38]
		RT	-	≥85	[39, 40, 42]
	<p>R=H, CH<sub>3</sub> R<sub>1</sub>=Et, n-Pr, n-Bu, Bz R<sub>2</sub>=Et, n-Pr, n-Bu, Bz X=CN, CONH<sub>2</sub>, COOC</p>				
		80–100 °C, 14–24 h	200	R or R': Electron donating group >50 R or R': Electron withdrawing group <30	[41]
		1–6 h, RT	10–50	52–94	[43]
<p>R<sub>1</sub>=COCH<sub>3</sub>, NO<sub>2</sub> R<sub>2</sub>=CH<sub>3</sub>, Aryl</p>					

**Table 1.** Some reactions catalyzed by graphene oxide (GO).

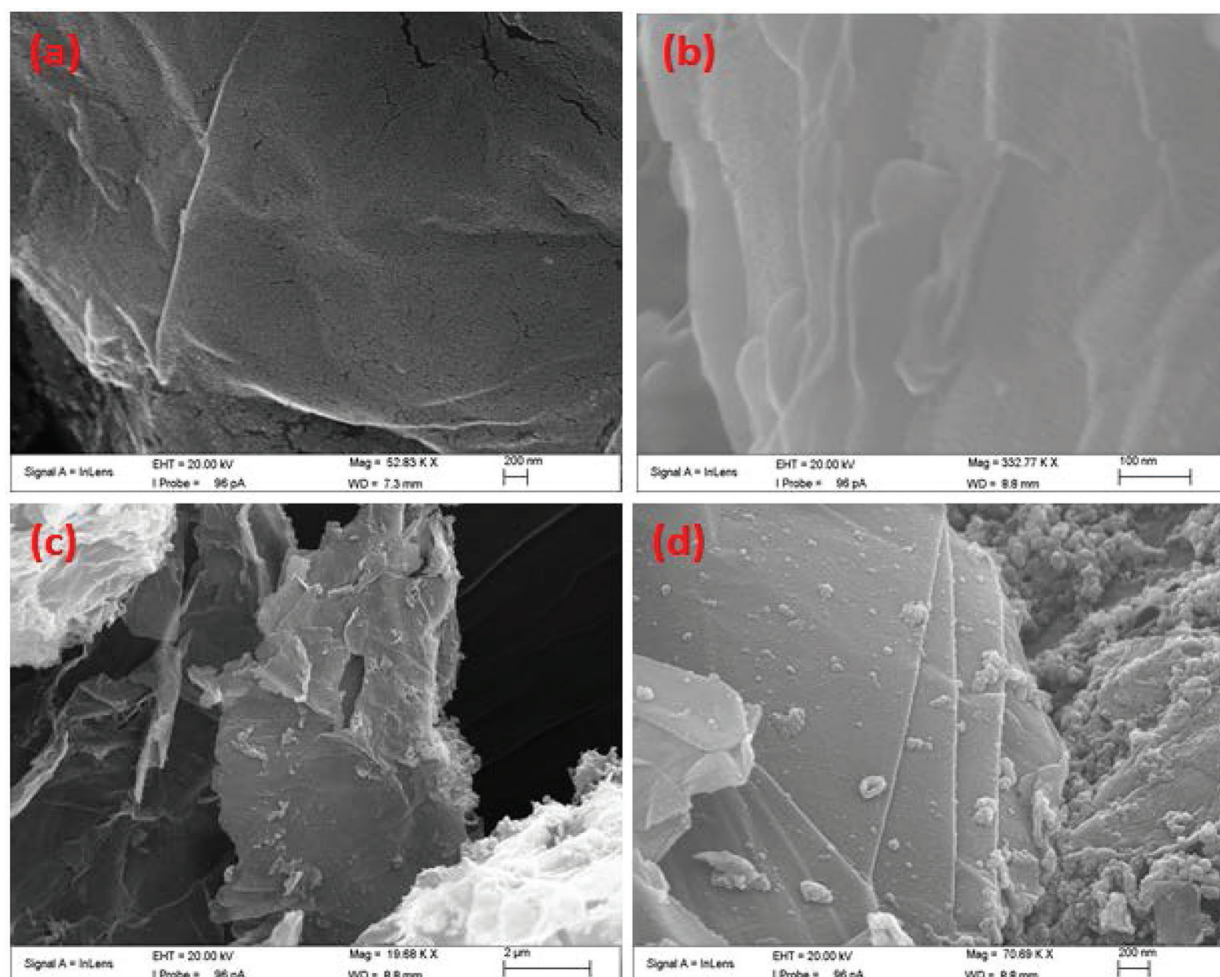
Starting Materials	Product	Conditions	Catalyst	Yield (%)	Ref.
 <p>1a-i + 2</p>	 <p>5a-i</p>	45–60 min,	Diamine functionalized GO	<93	[12]
 <p>3 + 4</p>	 <p>5a-i</p>				
		10 h 1atm O <sub>2</sub> , 40–70 °C	N-doped graphene		[45]
		10 h 100 °C	1° and 3° amine 100 functionalized graphene oxide		[46]
		100 °C	Sulfated graphene	58.9	[47]

**Table 2.** Reaction catalyzed by functionalized GO and hetero atom doped.

reactions. Researchers have described the C-C coupling reactions with inert conditions and various type of organic solvents by different catalysts loaded on acidic supports. For example, the palladium modified montmorillonite as catalyst for C-C coupling reaction with 92% yield was reported at 150 °C and reaction time of 2–3 h [48]. A 35 % conversion towards C-C coupling reaction with organic solvent at 3 h reported by Corral et al., [49]. Melania et al. have published the C-C coupling reaction with Pd@GO/Pd@RGO catalysts and using organic solvents at 80 °C >90% yield after 20 h [50]. Rumi et al. presented that, GO-PdNPs gave C-C coupling products (85% yield) with toluene at 110 °C in 24 h [51]. Xiang et al. reported that, Pd<sup>2+</sup>/GO gave C-C coupling products (85.5% yield) with DMA/H<sub>2</sub>O at 80 °C in 24 h [52]. Li et al. have employed Pd–Ni/RGO catalyst with ethanol and water solvent at 300 °C for 5 h and reported 98.6% yield towards C-C coupling products [53].

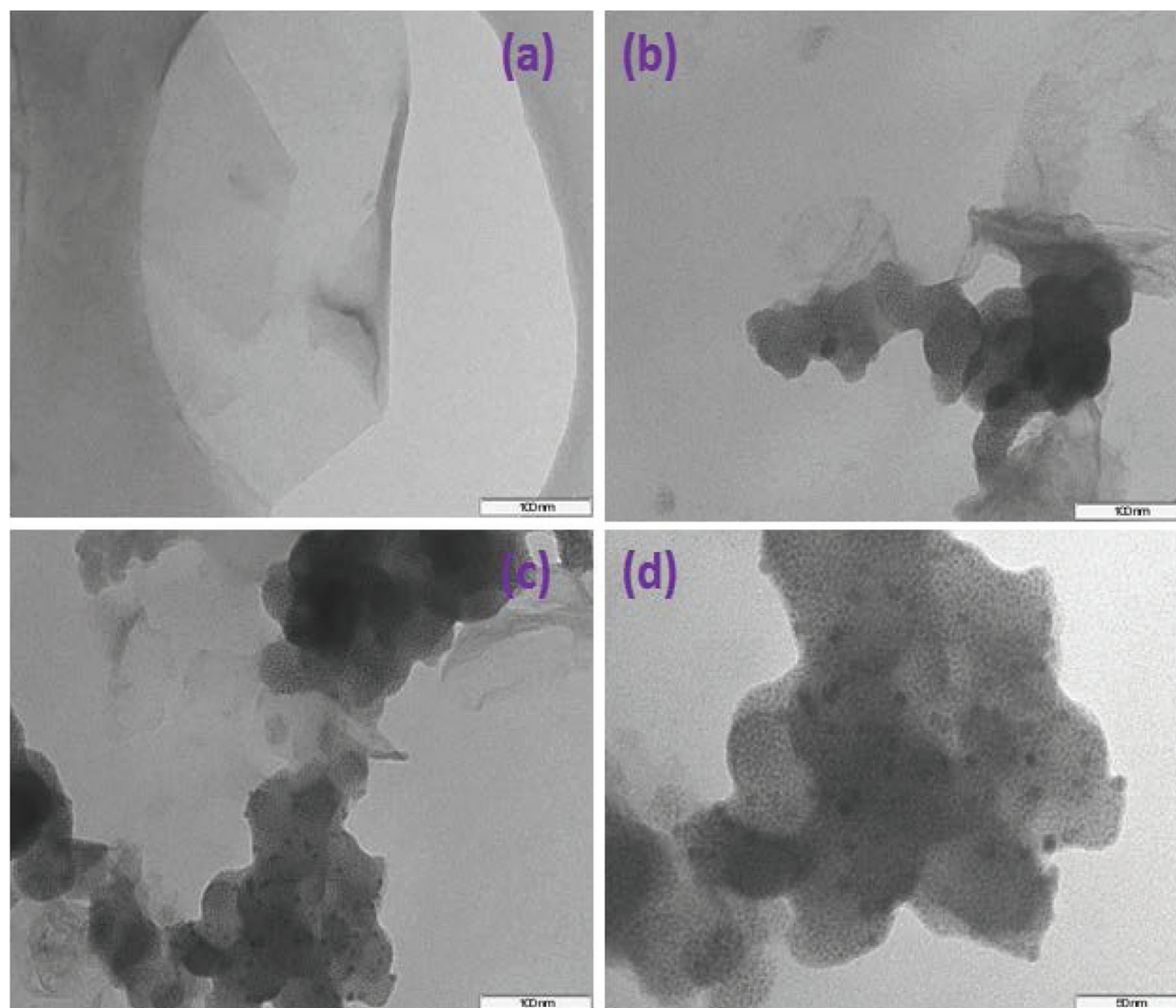
Siamaki et al. have reported the C-C coupling by Pd/G catalyst gave excellent yields with Turnover frequency (TOF) =  $108,000 \text{ h}^{-1}$  [54]. Nie et al., have reported that C-C reaction with Pd-Ni/RGO catalyst gave TOF =  $38,750 \text{ h}^{-1}$  [55]. Turnover frequency (TOF) provides the clear information about the efficiency of catalyst, which will be necessary for any applications. The TOF totally depends on the metal concentration of the materials. Mulhaupt et al. have reported a coupling reaction over  $\text{Pd}^{2+}$  exchanged graphite oxide with turnover frequency of TOF =  $39000 \text{ h}^{-1}$  [56].

Earlier, we have reported the design and fabrication of hybrid materials such as amine functionalized nano graphene oxide materials and metal modification with Pd(II)/Pd(0) [1–3]. We have also studied the C-C Suzuki reaction with Pd(0)-AAPTMS@G catalyst and observed an impressive TOF =  $185\,078 \text{ h}^{-1}$  with recyclability of catalyst up to 6<sup>th</sup> run using eco-friendly water as solvent [4] In this review, we include our latest results on the scope of GO and amine functionalized GO-based materials/ metal modified amine functionalized GO based materials in selective coupling reactions. We evaluated the activity of different graphene based vtmaterials catalysts in C-C coupling of idobenzene with phenylboronic acid and different



**Figure 3.** SEM Image of (a) graphene oxide, Scale bar = 200 nm (b) amine functionalized graphene oxide, Scale bar = 100 nm, (c) Pd(0) modified amine functionalized graphene, Scale bar = 2  $\mu\text{m}$  and (d) Higher magnification of Pd(0) modified amine functionalized graphene, Scale bar = 200 nm [reproduced with permission from Ref. [4]].





**Figure 4.** TEM Image of (a) graphene oxide, scale bar = 100 nm (b) amine functionalized graphene oxide, scale bar = 100 nm (c) Pd(0) modified amine functionalized graphene, scale bar = 100 nm and (d) Higher magnification of Pd(0) modified amine functionalized graphene, scale bar = 50 nm. [reproduced with permission from Ref. [4]].

halo benzenes with varied halo pyridines. Considering the bond energies of C–I, C–Br and C–Cl, bonds are 222.6, 281.4 and 340.2 kJmol<sup>–1</sup> respectively, the C–I bond breaks easily to form C–C coupling product then others. Thus, iodobenzene benzene gave excellent yields (98%) in short reaction time (25 min) with Pd (0)-AAPTMS@G material. The organo amine modified GO sheets serve to stabilize the Pd metal nanoparticles as well as to supply suitable electron density to the metal species. The catalyst is stable in aqueous medium due to strong interaction of amino group and metal particles. Up to the 6<sup>th</sup> cycle the recycled catalyst showed full efficacy with minimal loss of activity and 7<sup>th</sup> onwards some reduction in its efficiency was observed.

Al-Marri et al reported that, Pd@graphene nanocomposite gives 100% conversion towards oxidation of benzyl alcohol with toluene solvent at 100 °C [57]. MnO<sub>2</sub>/graphene oxide at 80 °C and in 3 h gave 91 % yield towards conversion of benzyl alcohol to benzaldehyde reported by Kadam et al. [58].



Earlier we reported the controlled oxidation of benzyl alcohol to benzaldehyde with Pd(II)-AAPTMS@GO as the catalyst, which showed excellent (95%) conversion and 99% selectivity in 1 h under eco-friendly room temperature and solvent free conditions [6]. It is also observed that metal modified amine functionalized nano graphene oxide materials showed excellent activity and stability then metal modified graphene materials. Scanning/ Transmitted electron microscopy gave the clear evidence about the nano graphene sheet and metal nano particles. SEM/ TEM Image of graphene oxide (a) amine functionalized graphene oxide (b) Pd(0) modified amine functionalized graphene (c) and Higher magnification of Pd(0) modified amine functionalized graphene (d) are illustrated in **Figures 3** and **4**. In these figures, the net-like structure performed after functionalization over the graphene oxide surface and graphene oxide sheets get converted to Nano graphene sheets. A perusal of the **Figure 4** confirms the uniform distribution of metal Nano particles on the surface. Solvents used and sonication process play important role in the changes in building blocks and stacking modes between graphene oxides based composites and covalent functionalization of different nano structures of final materials obtained.

## 7. Conclusions

Although metal deficient, GO is used in many catalytic reactions due to its surface oxy groups. To overcome the deficiency, covalently functionalized nano-graphene oxide/ metal modified functionalized nano-graphene oxides of metal have been developed, which are ideal to catalyze the C-C coupling and oxidation reactions. The surface functionalized/ metal modified surface functionalized materials proved superb with increased stability, reusability as well as activity towards fine chemical synthesis. With various potential applications, these surface functionalized materials have opened new opportunities in the fields of nanotechnology and catalysis. In this book chapter, we have summarized the recent advances in covalent functionalization of Nano graphene oxides, plus the stability and activity relationship in the in the field towards fine chemical synthesis.

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