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Carbon Nanocomposites: Preparation and Its Application in Catalytic Organic Transformations

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Abstract

Carbon nanocomposites have gained huge interest in catalysis due to their small size and shape-dependent physicochemical properties. Particularly, metal nanostructures/carbon materials (mainly graphene and carbon nanotubes) based nanocomposites demonstrated extraordinary catalytic activity in organic reactions. The catalytic products prepared by using carbon nanocomposites are found to be highly valuable in various fields including pharmaceutical, biomedical, agricultural, and material sciences. Hence, the demand of carbon nanocomposites has been increasing rapidly, and the development of novel preparation methods also deserve a special concern. In this chapter, we discuss the main advances in the field over the last few years and explore the novel preparation methods of carbon nanocomposites (metal nanostructures/carbon materials) and their applications in various catalytic organic transformations.

Keywords: carbon nanomaterials, metal nanostructures, nanocomposite, catalysis

1. Introduction

Carbon nanomaterials, including carbon nanotubes [both single-walled (SWCNTs) and multi-walled (MWCNTs)], graphene (G) or graphene oxide (GO), and carbon nanoparticles (CNPs), have attracted increasing attention owing to their unique structural regularity, high surface area, electrical conductivity, chemical inertness, biocompatibility, mechanical, and thermal stability [1, 2]. Graphene is a 2D single-atom-thick sheet of sp^2 -hybridized carbon, and it can be stacked to form 3D graphite and rolled to form 1D carbon nanotubes (CNTs). The long-range π -conjugation in graphene possesses astonishing thermal, mechanical, and electrical properties [3, 4]. Because of their outstanding physicochemical properties, researchers turned

straight away into the exploration and modification of graphene and CNTs. To date, the potential applications of graphene and CNTs are diverse, which include catalyst carrier, energy storage, absorbents, biomedical, textiles, and sensors and support in many areas. As a catalyst carrier, the role of graphene and CNTs is just outstanding [5]. Particularly, in heterogeneous catalysts, the carbon materials often employed as a support to disperse the metal nanoparticles [3, 6]. In fact, the metal nanoparticles can easily agglomerate to form big nanoparticles due to their high surface energy, and it can be avoided by using support materials. Generally, the activity of the heterogeneous catalyst is mainly due to the structure of the catalyst, size of the metal nanoparticles, nature of the support, metal-support interaction, and fine dispersion of catalyst in reaction medium [7, 8]. To date, there are several metal nanoparticles supported graphene or CNT catalysts developed and reported for various organic transformations. The catalytic products are highly valuable in various fields including pharmaceutical, biomedical, agricultural, and material sciences [9]. In recent days, the interest on carbon nanocomposites in organic reaction has been increased significantly due to their unexpected positive outcomes. In this chapter, we discuss the main advances in the field over the last few years and explore the novel preparation methods of carbon nanocomposites (metal nanostructures/carbon materials) and their applications in various catalytic organic transformations.

2. Preparation and characterization of carbon nanocomposites

2.1. Noncovalent functionalization

In general, the carbon nanomaterials are chemically inert and highly hydrophobic in nature [10]. Therefore, the dispersion/anchoring of metal nanoparticles on the surface of carbon materials is very challenging task [11]. The noncovalent functionalization is one of the very common methods for the preparation of metal nanoparticles supported carbon nanocomposites. The noncovalent functionalization is mainly referred as a physical absorption, which involves weak interactions (π -interactions) [12]. In general, the noncovalent functionalization method causes no change on the basal plane structure and the electronic properties of carbon materials. However, prior to metal dispersion, in most of the cases, the surface of carbon materials has been modified to improve the hydrophobic nature and better "metal-carbon interactions." There are two main methods for the preparation of metal nanoparticles supported carbon nanocomposites by using the noncovalent functionalization: (1) wet synthesis and (2) dry synthesis.

2.1.1. Wet synthesis

The wet synthesis method has been widely adopted for the preparation of metal nanoparticles supported carbon nanocomposites. The wet synthesis is quite simple and low time-consuming processing steps. Moreover, the uniform nucleation and the high possibility of the control of size and morphology of the metal nanoparticles are the key factors, which can be easily achieved through wet synthesis. So far, the researchers have developed numerous highly unique and efficient carbon nanocomposites. Particularly, in recent years, the numbers have been gradually increased due to the high demand of these useful materials in various fields such as catalysis, energy, sensors, biomedical, and textiles.

Noble metals such as silver (Ag), gold (Au), ruthenium (Ru), and palladium (Pd) nanoparticles have been widely employed as promoters and catalysts in various organic transformations. The carbon-based supports such as CNTs and graphene/graphene oxide (G/GO) are often used as support for the immobilization of Ag, Ru, Pd, and Au nanoparticles. It was found that the preparation method has huge influences on the structure and surface morphology of the carbon nanocomposites. Recently, Salam et al. [13] obtained a highly efficient silver-graphene nanocomposite (Ag-G) through a simple wet chemical route. They used silica-coated Ag nanoparticle solution as Ag sources. In a typical wet synthesis, the silica-coated Ag nanoparticle solution was added with aqueous GO solution under stirring for 15 min followed by the addition of hydrazine solution. The solution was heated at 80°C for 15–20 min, and the resultant precipitate (Ag-G) was filtered and dried. The Ag-G has been characterized by XRD, TEM, and Raman spectroscopy. The results confirmed the uniform dispersion of Ag nanoparticles with good attachment with GO. Well known that the NaBH_4 is a strong reducing agent and often used for the preparation of carbon nanocomposites. The Ag/graphene nanocomposites were prepared using NaBH_4 as a reducing agent [14]. In a typical procedure, GO was mixed with CH_3COOAg solution and stirred at 100°C, followed by the addition of aqueous NaBH_4 solution and stirred at 100°C. Finally, the Ag/G nanocomposites were obtained by centrifugation, washing, and freeze-drying. The SEM and TEM results confirmed that the Ag nanoparticles (ranging from 5 to 25 nm) were orderly decorated and closely attached on the graphene nanosheets.

Bozkurt [15] obtained Ag/graphene nanocomposite by the sonochemical method in situ reducing reaction of silver ions and GO with sodium citrate as a green reducing agent. At first, GO was well dispersed in distilled water, and an aqueous solution of AgNO_3 was gradually added to the above suspension under vigorous stirring condition. Finally, sodium citrate was added to the above mixture and sonicated for 1 h. The resultant black solid product (Ag/graphene nanocomposite) was centrifuged and dried in a vacuum. The authors have proposed mechanism for the formation of Ag nanoparticles on GO. Briefly, at first, silver nitrate precursor deposits on the surface of the GO nanosheets. Subsequently, the applied ultrasonic irradiation assists the deposited silver nitrate precursor to homogeneously disperse on the GO surface. The functional groups such as epoxy groups, hydroxyl groups ($-\text{OH}$), carbonyl groups ($\text{C}=\text{O}$), and carboxylic acid ($-\text{COOH}$) groups on the surface of GO would also act as the active sites for the metal cations. In general, the oxygen functional groups interact with the metal cations through electrostatic interactions. In the final step, the addition of sodium citrate reduces the GOAg^+ to Ag nanoparticles on the GO surface. In comparison with other methods, this ultrasonic irradiation method has advantages such as simplicity and high efficiency. The characterization results confirmed the merit of the ultrasonic irradiation method. TEM results showed the most of Ag nanoparticles deposited on the GO, which are spherical in shape with good attachment over GO surface.

A one-pot strategy was designed for forming the Au- SiO_2 -GO composite by Peng and coworkers [16]. To prepare Au- SiO_2 -GO composite, tetraethyl orthosilicate (TEOS) and HAuCl_4 were dissolved in TX-100 aqueous solution dispersed with GO, followed by the addition of compressed carbon dioxide (CO_2). Here the aim of utilizing compressed CO_2 is to form carbonic acid by reacting CO_2 with water. The carbonic acid can act as a catalyst for TEOS hydrolysis. Certainly, the compressed CO_2 can also promote the deposition of nanoparticles on a solid support. The solution mixture was stirred at room temperature for 7 hours. Finally, the CO_2 was released, and the product Au- SiO_2 -GO composite was obtained. The TEM observation confirmed the uniform

dispersion of Au nanoparticles on the GO with a narrow size distribution of 1.4–2.0 nm. The BET surface area and the total pore volume are 429 and 1.01 cm³ g⁻¹, respectively.

Binary Au-Ag catalyst has been widely demonstrated to be one of the highly efficient catalysts for organic reactions. Babu et al. [17] prepared Au-Ag/SLG nanocatalyst from H₂AuCl₄ × H₂O, Ag/DNA, and single-layer graphene (SLG). Negatively charged Salmon milt DNA was employed as Ag sources. In a typical wet synthesis, mixture of H₂AuCl₄ × H₂O and colloidal Ag/DNA was sonicated for 1 h at room temperature. Then, acid-treated single-layer graphene (*f*-SLG) was added to the above mixture and sonicated. Finally, the mixture was centrifuged to separate the Au-Ag/SLG and calcinated at 700°C for 3 h under inert atmosphere. Similarly, Pt-Ni bimetallic nanoparticles supported on CNTs nanocomposites (xPtNi/CNTs) with different compositions of Pt were synthesized [18]. Chemically modified CNTs were used for the decoration of nanocomposites. The solution phase reduction methods were adopted to prepare the nanocomposites in which ethylene glycol as a reducing agent in the polyol method or using poly (amidoamine) dendrimer as a platform and NaBH₄ as a reducing agent were used to deposit the Pt and Ni nanoparticles on the surface of modified CNTs. Recently, Yuan and coworkers [19] found that the bimetallic Pd-Ag nanoparticles supported MWCNTs (Pd-Ag/MWCNTs) are highly active catalyst for the electro-oxidation of ethanol, n-propanol, and *iso*-propanol. The Pd-Ag/MWCNTs was prepared by using the NaBH₄ reduction method in a mixed solvent of ethylene glycol and water. In a typical method, MWCNTs were first treated with conc. H₂SO₄ and conc. HNO₃ to create oxygen functional groups on the surface of MWCNTs. Subsequently, the acid-treated MWCNTs were added to a mixture of PdCl₂, AgNO₃, and ethylene glycol/water, and then the mixture was stirred for 30 min. Finally, NaBH₄ dissolved ethylene glycol was slowly added to the above mixture under vigorous stirring for 4 h. The Pd-Ag/MWCNT nanocomposite was characterized and applied for the electro-oxidation of ethanol, n-propanol, and *iso*-propanol.

Ru was found to be an excellent catalyst for organic reactions due to its wide chemical states (II to +VIII) and tunable properties [20]. Particularly, the Ru catalyst has shown an excellent activity in oxidation reactions because of its redox properties. Interconnected RuO₂ nanoparticles anchored GO nanocatalyst (RuO₂/GO) with very good BET surface area (285 m²/g) were obtained by Yuan and coworkers [21]. Very simple method was adopted for the preparation of RuO₂/GO. Briefly, Ru(acac)₃ and GO were dispersed in methanol and sonicated for several hours followed by heating at 65°C to evaporate the methanol. The obtained slurry was grinded well with mortar and pestle until the homogeneous mixture was obtained, and then, it was calcinated in the muffle furnace under N₂ atmosphere at 600°C (heating rate of 5°C/min) for 3 h. The RuO₂/GO was completely characterized by various spectroscopic and microscopic techniques.

Wang et al. [22] obtained Pd nanoparticles immobilized GO nanocomposite by a very simple wet chemical method. PdCl₂ and hydrazine hydrate were used as Pd sources and reducing agent, respectively. Initially, an aqueous suspension of GO was prepared, and then, PdCl₂ was added under the assistant of mild ultrasound. The hydrazine hydrate was then added to the above mixture and the solution heated at 100°C for 1 h. The black solid of Pd/GO was isolated by filtration and washed copiously with water and methanol. TEM image of the Pd/graphene composite showed that the Pd nanoparticles were supported on the surface of the GO sheets without any agglomeration of the Pd nanoparticles. The Pd nanoparticles are composed of spherical particles. The size of the Pd particles calculated to be 2–6 nm. The metal surface area of Pd/graphene measured to be 161 m²/g.

Recently, a facile and green method was developed to synthesize a new type of catalyst by coating Pd nanoparticles on reduced graphene oxide (rGO)-CNT nanocomposite [23]. At first, the three-dimensional microstructure of an rGO-CNT nanocomposite was obtained by hydrothermal treatment. The homogeneous mixture of GO and CNTs was prepared under sonication conditions, and the mixture was subsequently sealed in a 50-ml Teflon-lined autoclave and maintained at 180°C for 12 h. A black gel-like 3D cylinder of rGO-CNT composite was obtained. The resultant rGO-CNT composite was dispersed in aqueous solution, and subsequently, K_2PdCl_4 was added. The mixture was vigorously stirred for 30 min in an ice bath. Then, the reaction mixture was washed well with pure water to obtain Pd-rGO-CNT nanocomposite.

Similarly, CuO nanoparticles were decorated on the surface of GO to obtain CuO/GO catalyst [24]. In a typical procedure, GO was dispersed in methanol and sonicated for 1 h. Then, the $Cu(acac)_2$ added to the above mixture was refluxed for 5 h (Step 1), and the MeOH was slowly evaporated. The resultant slurry was mixed well by a mortar and pestle, and obtained homogeneous mixture of GO and $Cu(acac)_2$ was calcinated under inert atmosphere at 350°C for 3 h. **Figure 1(a)** shows a schematic illustration for the preparation of CuO/GNS. The CuO/GNS was completely characterized by TEM, SEM-EDS, XPS, Raman, and XRD (**Figure 1**). The TEM images showed the strong attachment of CuO nanoparticles on the GNS with particle size distribution of 12–35 nm. Raman and XPS results indicated the strong attachment of CuO on GNS through covalent bonding (Cu—C). The Cu 2p XPS spectrum of CuO/GNS showed shakeup satellite peaks of the Cu $2p_{3/2}$ at 942.4 eV and Cu $2p_{1/2}$ at 962.6 eV, which confirmed the presence of Cu(II) species (CuO).

2.1.2. Dry synthesis

The dry synthesis is found to be highly efficient and suitable method for the synthesis of carbon nanocomposite. The main advantages of this method are its simplicity, better adhesion, and advantages of least parameters to be controlled [25]. It was found that the dry synthesis is the method, which is highly suitable for the decoration of metal nanoparticles on carbon

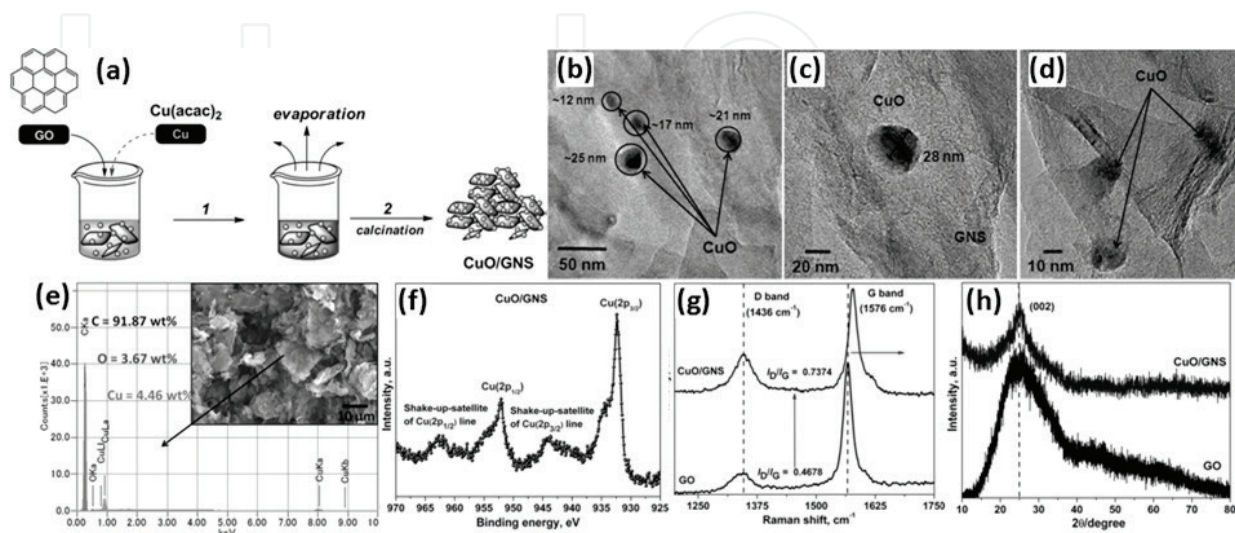


Figure 1. (a) Schematic illustration of the procedure for the preparation of CuO/GNS, (b–d) TEM images, (e) SEM-EDS, (f) XPS, (g) Raman, and (h) XRD patterns of CuO/GNS (from Gopiraman et al. [24]).

nanomaterials when compared with wet synthesis method. In fact, several drawbacks of the wet synthesis method have been resolved by the dry synthesis method. Moreover, the carbon materials are highly hydrophobic, and it needs surface modification (with oxygen functional groups ($C-OH$, $C-O-C$, $C=O$, and $COOH$ or amine groups) prior to the decoration of metal nanoparticles [26]. The oxygen functional groups could play a bridging role between the metal nanoparticles and the carbon materials. However, the creation of the oxygen functional groups is very difficult in case of activated carbon, carbon nanofibers, and carbon black. Interestingly, carbon materials without any surface functional groups could also be utilized successfully for the preparation of carbon nanocomposites. However, the large-scale production of the carbon nanocomposites through dry synthesis is limited.

A rapid and solventless dry synthesis method was described for the preparation of carbon nanocomposites by Lin and coworkers [27]. This straightforward two-step process involves the dry mixing of a precursor metal salt with carbon materials (CNTs or GO) followed by heating in an inert atmosphere. They found that the dry synthesis procedure is scalable and applicable to various other carbon substrates (e.g., CNFs, expanded graphite, CNTs, activated carbon, and carbon black) and many metal salts (e.g., Ag, Au, Co, Ni, and Pd acetates). The Ag nanoparticles decorated CNTs have been reported as a model system, and the composites were prepared under various mixing techniques, metal loading levels, thermal treatment temperatures, and nanotube oxidative acid treatments. The TEM and SEM observation confirmed the uniform and strong attachment of Ag nanoparticles on the surface of the CNTs. However, in a wet synthesis, many factors such as solvent, concentration of metal precursor, reducing agent, deposition time, and temperature need to be controlled very carefully. Similarly, Ag nanoparticles of small average diameter (<5 nm) were decorated on the surface of MWCNTs by a simple mechanochemical process [28]. In a typical preparation, the silver acetate and MWCNTs were placed in a zirconia vial. Then, two zirconia balls were placed in a vial, and the set-up was secured in a SPEX CertiPrep 8000D high energy shaker mill and subjected to mechanical shaking for a desired period of time to yield the Ag/MWCNTs nanocomposite. The mechanochemical process requires no solvent, no additional reducing agents, or no applied electrical current. They demonstrated that the mechanochemical process was found to be readily applicable to not only CNTs, but also other carbon materials that are thermally conductive such as graphene, GO, and activated carbon (**Figure 2**). Moreover, different organic metal salts (e.g., Au and Pd acetates and Pt acetylacetonate) were also successfully applied in

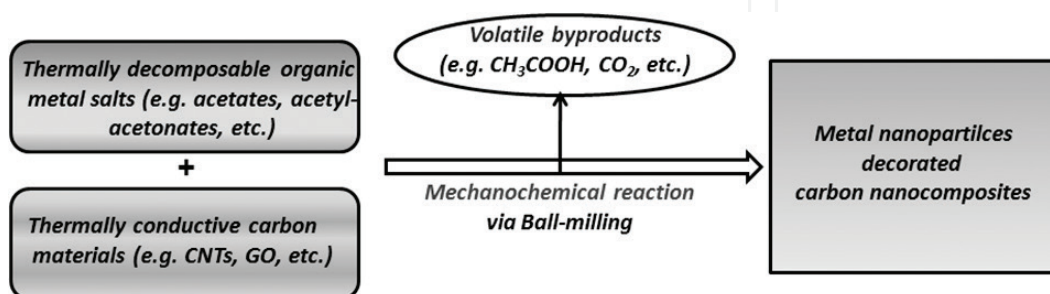
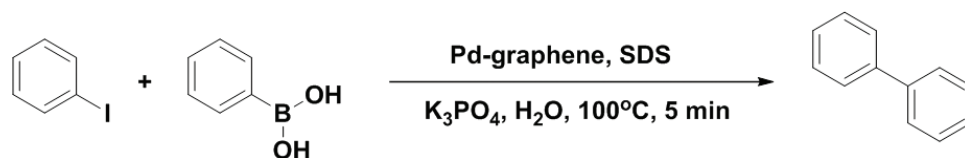


Figure 2. General procedure for preparation of carbon nanocomposites by mechanochemical synthesis (from Lin et al. [28]).



Scheme 1. Suzuki reaction of iodobenzene with phenylboronic acid catalyzed by Pd-graphene nanocomposites (from Li et al. [39]).

similar procedures to obtain the corresponding carbon nanocomposites. The mechanochemical process is found to be rapid, versatile, and potentially scalable, making it useful for further exploitation in various applications. **Scheme 1** shows the general procedure for the preparation of carbon nanocomposites by mechanochemical process.

Later, Kim's group [29–33] developed various carbon nanocomposites by using the dry synthesis method also called “mix-and-heat” method. The prepared carbon nanocomposites were utilized as heterogeneous catalysts in various organic reactions. The metallic Ru nanoparticles were decorated on graphene nanosheets (GNSs) by “mix-and-heat” method [29]. Initially, the bi- and few-layered graphene nanosheets (GNSs) were obtained from graphene nanoplatelets (GNPs) by a solution-phase exfoliation method. The obtained GNSs were chemically treated with concentrated H_2SO_4 and HNO_3 to create oxygen functional groups ($-\text{COOH}$, $-\text{C}=\text{O}$, $-\text{C}-\text{O}-\text{C}-$, and $-\text{OH}$) on the surface of GNSs. The resultant *f*-GNSs were used for the decoration of Ru nanoparticles. In a typical preparation, $\text{Ru}(\text{acac})_3$ was added into *f*-GNS and mixed well by a mortar and pestle under ambient conditions. Then, the homogeneous mixture of *f*-GNS and $\text{Ru}(\text{acac})_3$ was calcinated at 300°C for 3 h under an argon atmosphere. The morphology of the resultant nanocomposite (GNS-RuNPs) was found to be excellent. Ultrafine Ru nanoparticles were homogeneously dispersed on the surface of GNSs. Interestingly, the size of these attached Ru nanoparticles was found to be below 3.0 nm. Similarly, GNSs-RuO₂NPs was prepared by a simple “mix-and-heat” method. **Figure 3** shows the schematic illustration for the preparation of GNSs-RuO₂NPs, TEM images, RuO₂ particle distribution, XPS, XRD patterns, and Raman spectra of GNSs-RuO₂NPs (from Gopiraman et al. [32]).

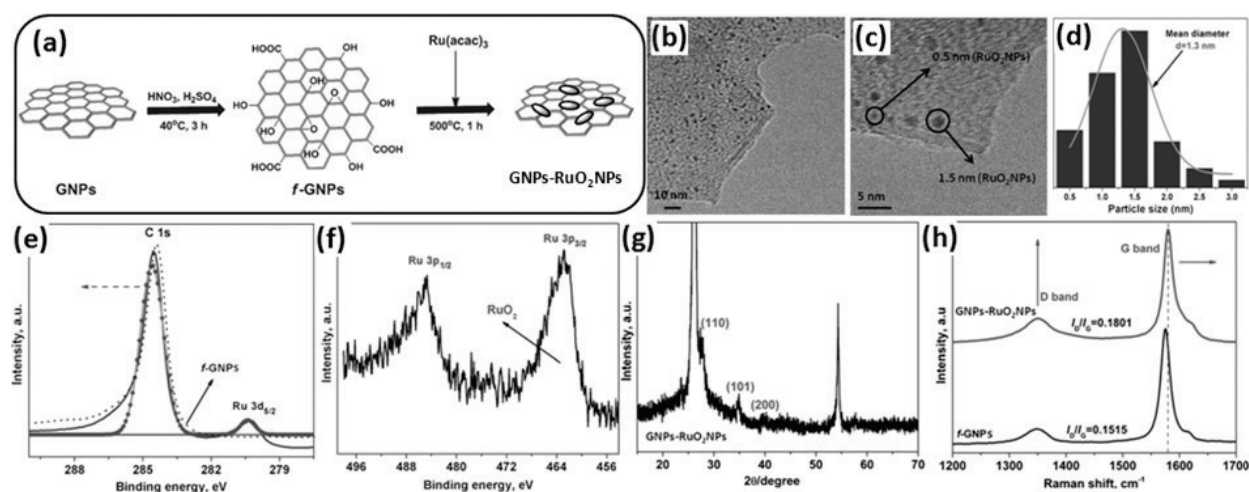


Figure 3. (a) Schematic illustration for the preparation of GNSs-RuO₂NPs, (b and c) TEM images, (d) RuO₂ particle distribution, (e and f) XPS, (g) XRD patterns, and (h) Raman spectra of GNSs-RuO₂NPs (from Gopiraman et al. [32]).

XRD patterns, and Raman of GNPs-RuO₂NPs. Later, CuO/MWCNTs [30], RuO₂/MWCNTs [31], and GNPs-RuO₂NPs [32] were synthesized by the dry synthesis method. It was demonstrated that the SWCNTs were also utilized to successfully decorate the RuO₂ via dry synthesis method [33]. Astonishingly, the mean diameter of the RuO₂ nanoparticles attached to SWCNTs was found to be about 0.9 nm. The BET surface area of RuO₂/SWCNT was found to be 416 m² g⁻¹. Moreover, Raman and XPS results confirmed that the RuO₂ nanoparticles were strongly attached on the surface of SWCNTs.

3. Carbon nanocomposites catalyzed organic reactions

Recently, carbon nanocomposites have been widely used as heterogeneous catalysts in various organic transformations. Less than 10% of the chemical processes in chemical industries are still conducted without the addition of catalyst [34]. The catalytic products such as organic building blocks, pharmaceuticals, natural products, and agricultural derivatives are very valuable in chemical industries [35]. Numerous metal catalysts (supported and unsupported) are reported for the industrially important organic transformations. Carbon nanocomposites, particularly structural carbon (graphene and CNTs) based materials, are recently being used as heterogeneous catalysts in organic transformations. In fact, the high surface area, fine dispersion, stability, reusability, and easy recovery are the key factors. Moreover, the immobilization of metal nanoparticles onto the carbon support has revealed more versatility in carrying out the highly selective catalytic processes [36]. In comparison with CNTs, graphene or GO has been preferred due to its low cost, large-scale preparation, and less health risk.

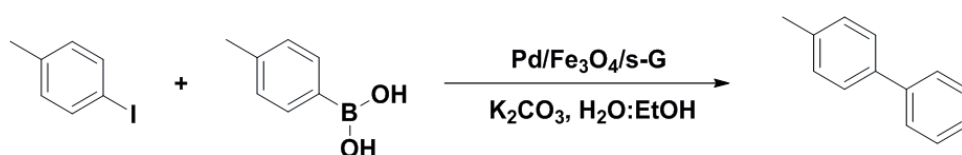
3.1. Noble metals supported carbon catalysts

Pd nanoparticles supported carbon materials have been widely used as heterogeneous or semi-heterogeneous catalysts for C—C coupling reactions, such as Mizoroki-Heck, Suzuki-Miyaura, and Sonogashira reactions [37]. These cross-coupling reactions are the most efficient methods for the construction of C—C bonds. The Pd as a catalyst can assemble C—C bonds between various functionalized substrates allowed researcher to achieve the reactions that were previously impossible (or possible with multiple steps) [38]. Hence, these methodologies have found extensive use in organic synthesis and material science. Moreover, these cross-coupling reactions found to play an important role in pharmaceutical, fine chemical, and agrochemical industries.

Li et al. [39] demonstrated Pd-graphene nanocomposites as an efficient nanocatalyst for Suzuki reaction. The Pd-graphene nanocomposites showed an efficient catalytic activity toward Suzuki reaction in water under aerobic condition for a short time. **Scheme 1** shows the Suzuki reaction of iodobenzene with phenylboronic acid catalyzed by Pd-graphene nanocomposites. The catalyst is not only efficient but also easily recovered and reused several times for the low-cost and environmentally friendly synthesis of biaryls. Using 1.1 mol% of Pd-graphene nanocomposite with sodium dodecyl sulfate (SDS) at 100°C, the catalytic system affords 100% of yield with 95.5% selectivity. Interestingly, the catalyst can be reused at least for 10 times (at 10th cycle, the yield was 78.6%).

The complete recovery and excellent reusability are the major advantages of using heterogeneous catalysts [40]. However, in most of the heterogeneous catalytic systems, the isolation of catalysts from the reaction mixture by conventional filtration methods is inefficient and time consuming. Therefore, magnetically recoverable carbon nanocomposites have gained much attention due to it easily and complete recovery of the catalyst from reaction mixture. Fe_3O_4 and Pd nanoparticles were decorated on sulfonated graphene (s-G) by a facile chemical approach [41]. The prepared carbon nanocomposite Pd/ Fe_3O_4 /s-G was used as an excellent semi-heterogeneous catalyst for the Suzuki-Miyaura cross-coupling reaction in an environmentally friendly solvent (water/ethanol (1:1)) under ligand-free ambient conditions (**Scheme 2**). It was found that even a low amount of catalyst Pd/ Fe_3O_4 /s-G (0.15 mol% Pd) is also enough to achieve 97% of the product after 30 min of the reaction time. The small size and homogeneous distribution of Pd nanoparticles on the Fe_3O_4 /s-G matrix are the main reason for the excellent catalytic activity. The activity of Pd/ Fe_3O_4 /s-G did not deteriorate even after 10th cycle, which may be due to the easy and efficient magnetic separation of the catalyst and the high dispersion and stability of the catalyst in an aqueous solution. At 10th cycle, the Pd/ Fe_3O_4 /s-G catalyst gave 84% of the product. Similarly, magnetically recoverable Pd/ Fe_3O_4 nanoparticles supported graphene nanosheets (Pd/ Fe_3O_4 /G) were prepared for Suzuki and Heck coupling reactions (**Figure 4**) [42]. The Pd/ Fe_3O_4 /G system gave excellent yields over a broad range of highly functionalized substrates in both Suzuki and Heck coupling reactions. With 7.6 wt% of Pd, the Pd/ Fe_3O_4 /G worked well in Suzuki cross-coupling reaction with a high turnover number (TON) of 9250 and turnover frequency (TOF) of $111,000 \text{ h}^{-1}$. Due to the good magnetic property of the Pd/ Fe_3O_4 /G, it was easily recovered using a simple magnet and reused for 10 times (**Figure 4**).

Similarly, various Pd nanoparticles supported graphene nanocomposites were prepared and used as an excellent nanocatalyst for the cross-coupling reaction. Pd nanoparticles supported graphitic carbon nitride (Pd/g- C_3N_4) was prepared through a one-step photodeposition strategy, and it was used for Suzuki-Miyaura coupling reactions by Sun and coworkers [43]. They found that the Pd/g- C_3N_4 was worked well at room temperature without any phase transfer agents, toxic solvents, and inert atmosphere. Under the optimized conditions, the Pd/g- C_3N_4 achieved a complete conversion (100%) of the reactant and a high yield of 97% for biphenyl. Unlike other supports, the g- C_3N_4 with plenty of nitrogen-containing anchor sites was a suitable platform for Pd atoms, which could favor fine dispersion and stabilization of the ultrafine Pd nanoparticles on g- C_3N_4 . Siamak et al. [44] used single- or multi-walled carbon nanotubes (SWCNTs and MWCNTs) as a support for the decoration of Pd nanoparticles. Both the supported catalysts (Pd/MWCNT)M and (Pd/SWCNT)M were successfully employed in Suzuki cross-coupling reactions with a wide variety of functionalized substrates. Interestingly, they noticed that the MWCNTs supported Pd nanoparticles catalyst (Pd/MWCNT)M showed slightly better yield



Scheme 2. Suzuki-Miyaura cross-coupling reaction catalyzed by Pd/ Fe_3O_4 /s-G catalyst (from Elazab et al. [41]).

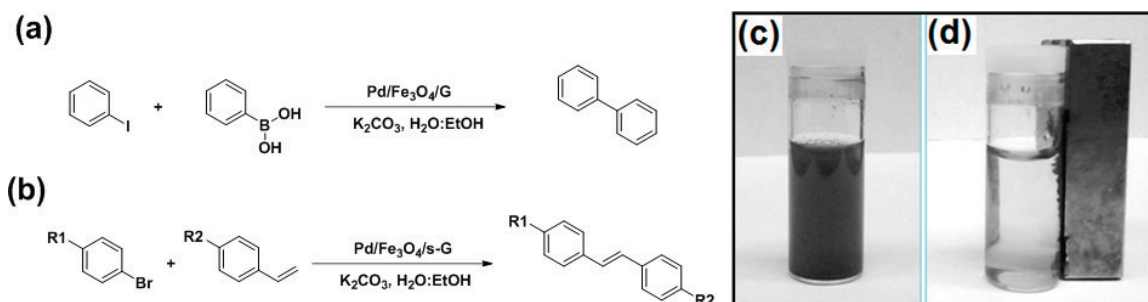
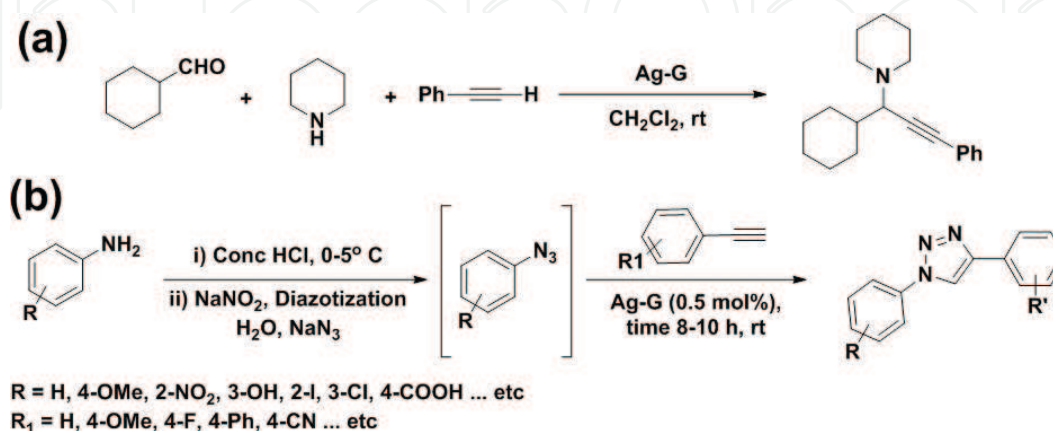


Figure 4. Pd/Fe₃O₄/G catalyzed (a) Suzuki cross coupling, (b) Heck coupling reactions, (c) the reaction mixture with Pd/Fe₃O₄/G, and (d) separation of spent catalyst from reaction mixture using a simple magnet (from Hu et al. [42]).

when compared with SWCNTs supported Pd catalyst (Pd/SWCNT)M). They concluded that the superior catalytic activity and excellent reusability of (Pd/MWCNT)M mainly due to the larger diameter of the MWCNTs (20–150 nm) offer stronger surface interactions and provide large number of anchoring sites for the Pd nanoparticles, thus facilitating the deposition of the greater number of Pd nanoparticles on the surface of MWCNTs with strong attachment.

In organic synthesis, multi-component reactions (MCRs) are very important and essential for the synthesis of diverse complex molecules through a combination of three or more starting materials in a one-pot reaction [45]. For instance, synthesis of propargylamine through coupling reaction of aldehydes, amines, and alkynes (A³ coupling) is one of the important MCRs. The propargylamines are highly valuable in the synthesis of various biologically active compounds and natural products [46]. To synthesis the propargylamines, graphene-based composite with silver nanoparticles (Ag-G) was prepared *through* a simple chemical route by Salam and coworkers [13]. After being optimized the reaction conditions, the scope of the catalytic was extended. The catalytic system worked well for a wide range of substrates including aromatic and aliphatic aldehydes, including those bearing functional groups such as —OH, —Cl, and —Br additions. The Ag-G is air-stable, heterogeneous, cost-effective, easily recoverable, and reusable without loss in activity and selectivity. **Scheme 3(a)** shows three-component (A³) coupling reaction catalyzed by the Ag-G. Moreover, the Ag-G catalyst is also suitable for



Scheme 3. Ag-G catalyzed (a) three-component (A³) coupling reaction and (b) synthesis of triazoles from anilines (from Salam et al. [13]).

the synthesis of triazoles from anilines by one-pot two-step click reaction in water medium at room temperature (**Scheme 3(b)**). The excellent catalytic activity is due to the synergistic effect of GO. In fact, GO has high adsorption nature toward reactants through p-p stacking interactions. Hence, the GO could help the reactant to go closer to the Ag nanoparticles on GO, leading to good contact between the reactant and Ag on GO. In addition, electron transfer from the GO to Ag nanoparticles increases the local electron concentration, facilitating the uptake of electrons by reactant molecules [13].

The catalytic conversion of nitrophenols to valuable aminophenols in water by using NaBH_4 is one of the important organic conversions [47]. In general, the nitrophenols are the major organic pollutants, which can be found in industrial and agricultural wastewaters. They are highly water soluble and stable in the soil and thus cause harmful effects to human beings, animals, and agricultural plants [48]. Very recently, a simple and efficient method for the reduction of nitrophenols to aminophenols was developed by using carbon nanocomposites as a catalyst. The catalytic products (aminophenols) can be used as anticorrosion-lubricant, corrosion inhibitor, photographic developer, and analgesic and antipyretic drugs [49]. Ag nanoparticles supported carbon nanofiber composites (CNFs/AgNPs) were fabricated for the reduction of 4-nitrophenol with NaBH_4 in water [50]. The TEM images confirmed that very fine Ag nanoparticles were homogeneously dispersed on the CNFs (**Figure 5**). The results showed an excellent catalytic activity of CNFs/AgNPs in the reduction of 4-nitrophenol. The reason for the superior catalytic activity of CNFs/AgNPs is mainly due to the high surface areas and synergistic effect on delivery of electrons between CNFs and Ag nanoparticles. Notably, the CNFs catalyst could be easily recycled at least for three times without loss in its activity. Possible catalytic mechanism is elucidated schematically in **Figure 5(e)**. Similarly, Wang et al. [51] found that Au nanoparticles supported functionalized CNTs [with cyclotriphosphazene-containing polyphosphazenes (PZS)] (Au@PZS@CNTs nanohybrids) are highly suitable catalyst for the reduction of 4-nitrophenol.

Among noble metals, Ru has shown the ability to catalyze a remarkable range of organic transformations because of its wide range of oxidation states (-2 to +8) and tunable properties [52]. The Ru metal is well known for oxidation-reduction and cross-coupling reactions. The catalytic products are high-functional components in the perfume industry and pharmaceuticals.

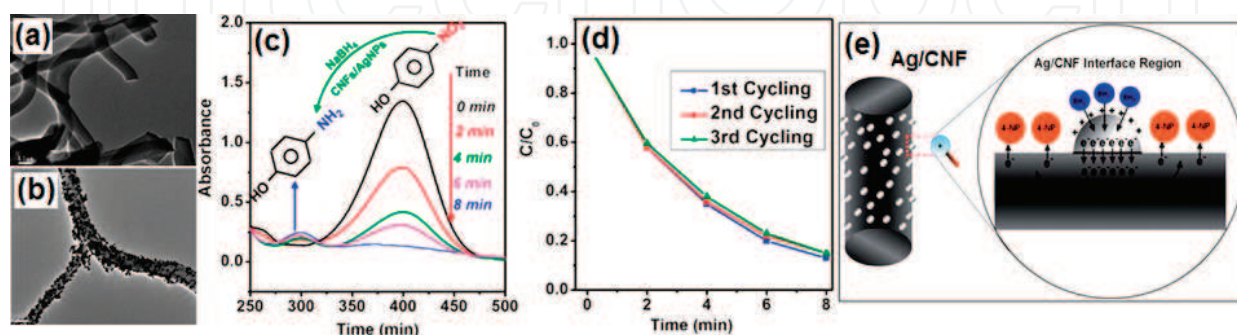
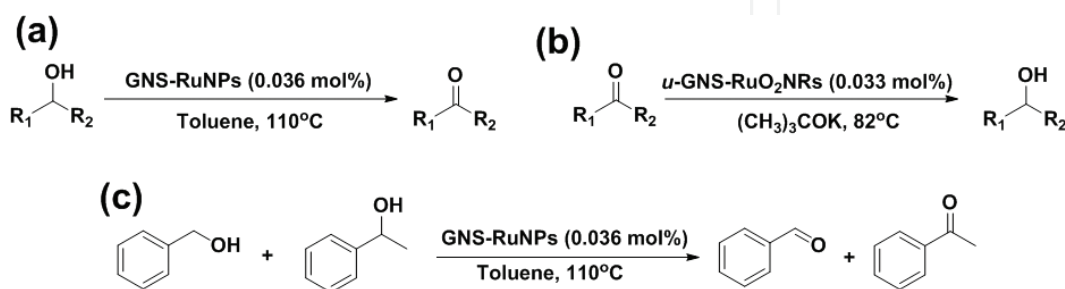


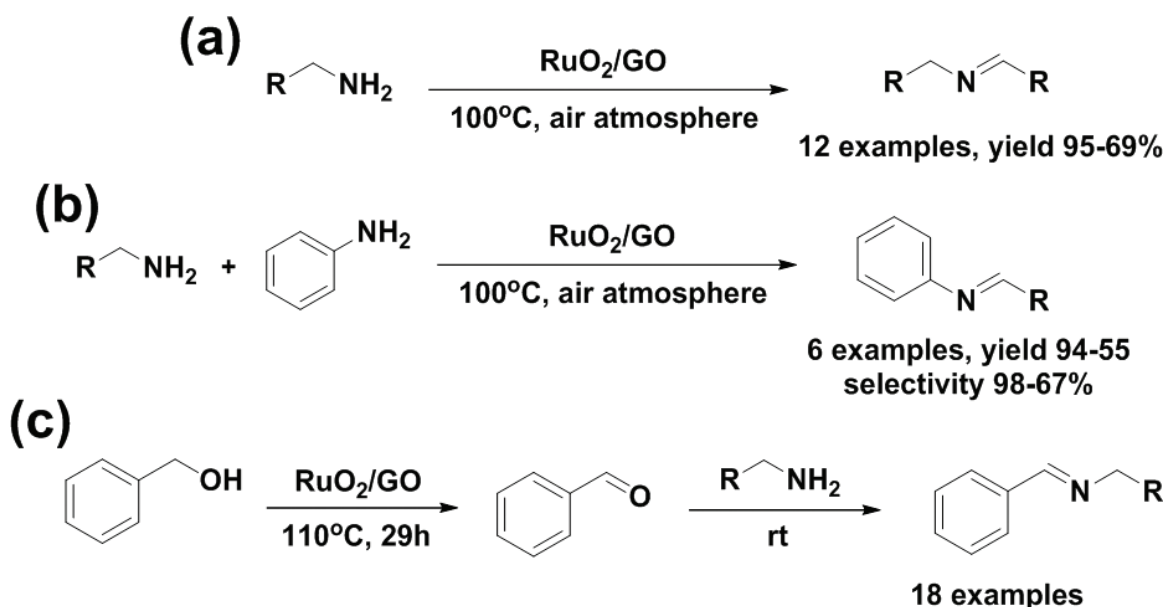
Figure 5. (a and b) TEM images of CNFs/AgNPs, (c) UV-vis absorption spectra during the catalytic reduction of 4-NP over CNFs/AgNPs, (d) reusability test, and (e) postulate mechanism of the catalytic reduction of 4-NP with the CNFs/AgNPs (from Zhang et al. [50]).

So far, several Ru nanoparticles supported CNTs or GO catalyst are developed for the organic transformations [53, 54]. Kim's group prepared various Ru or RuO₂ nanoparticles supported carbon nanocomposites and used as heterogeneous catalysts in organic transformation [29, 31–33]. For example, 0.5–3 nm size of metallic Ru nanoparticles decorated graphene nanosheets (GNSs) was used for the oxidation of alcohols [29]. Results revealed that various alcohols (aliphatic, aromatic, alicyclic, benzylic, allylic, amino, and heterocyclic alcohols) can be oxidized into their corresponding carbonyl compounds in good to excellent yields with high selectivity (**Scheme 4**). Very interestingly, a 0.036 mol% Ru (5 mg) of catalyst (GNS-RuNPs) was more than enough for complete oxidation of alcohols (the lowest amount of catalyst so far reported), which shows the merit of the GNS support. The formation of active Ru-oxo species during the reaction was confirmed. The GNS-RuNPs was found to be highly efficient, chemoselective, heterogeneous, stable, and reusable. The GNS-RuNPs catalyst was reused for four times without significant loss in its catalytic activity. After 4th cycle, the used GNS-RuNPs were calcinated at high temperature and used for transfer hydrogenation of carbonyl compounds. It was concluded that the excellent catalytic activity of GNS-RuNPs is due to the smaller size of the Ru nanoparticles, higher surface area, strong interaction between Ru nanoparticles and GNSs, and an effective dispersion of the catalyst in the reaction medium. Similarly, RuO₂NPs/MWCNTs [31] and RuO₂NRs/GNPs [55] were prepared and used for both aerial oxidation of alcohols and transfer hydrogenation of carbonyl compounds. Aliphatic and aromatic tert-amine oxides (amine N-oxides) are essential and key components in the formulation of several cosmetic products as well as in biomedical applications. The GNPs-RuO₂NPs demonstrated excellent catalytic activity toward oxidation of tertiary amines to their corresponding N-oxides in good to excellent yields [32]. The results showed that the scope of the reaction can be extended to various aliphatic, alicyclic, and aromatic tertiary amines.

Imines are very important moieties for the formation of fine chemicals, biologically active compounds, and their intermediates [56]. Interconnected ruthenium dioxide nanoparticles (RuO₂NPs) anchored graphite oxide nanocatalyst (RuO₂/GO) with good BET surface area (285 m²/g) were prepared and used as a catalyst for the synthesis of imines (**Scheme 5**) [21]. Generally, the graphene-based nanocomposites are often suffered from the lower BET surface area due to the face-to-face aggregation of graphene sheets. However, in case of RuO₂/GO, the interconnected RuO₂ network strongly prevented the further aggregation of GO, leading to the high-specific surface area of RuO₂/GO. It was noticed that a broad range of

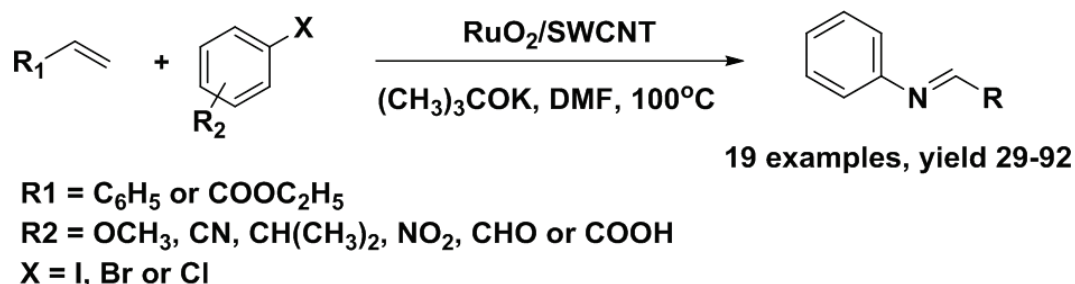


Scheme 4. Ru-graphene catalyzed (a) oxidation of alcohols, (b) transfer hydrogenation of carbonyl compounds, and (c) chemoselectivity oxidation of alcohols (from Gopiraman et al. [29]).



Scheme 5. RuO₂/GO catalyzed (a) self-coupling of amines, (b) cross coupling of aniline with substituted primary amines, and (c) oxidative coupling of benzyl alcohol and substituted primary amines (from Yuan et al. [21]).

amines including less reactive aliphatic amines can be transformed by the RuO₂/GO to obtain the corresponding imines in good yields (98–58%) with an excellent selectivity (100%). In addition, an indirect two-step protocol was adopted for the coupling of alcohols and amines to obtain imines, and the results were found to be excellent. The reusability, stability, and heterogeneity of RuO₂/GO were also investigated. The authors claimed that this is the most efficient RuO₂-based nanocatalyst for the synthesis of imines among those reported to date. Similarly, ultrafine RuO₂ nanoparticles (RuO₂NPs) with 0.9 nm in size were immobilized on SWCNTs by a straightforward “dry synthesis” method and used it for Heck olefination of aryl halides (**Scheme 6**) [33]. Although Ru has showed good catalytic activity toward Heck reaction, the bromo- and chloroarenes are less reactive. Interestingly, the SWCNTs supported RuO₂ catalyst worked well for the olefination of less reactive chloro- and bromoarenes. In case of supported heterogeneous catalysts, the activity is dependent on the nature of the support, metal-support interaction, and the particle size. It was believed that the inert SWCNTs might be transformed to a very active catalyst through the strong interactions between RuO₂ and carbon vacancies.

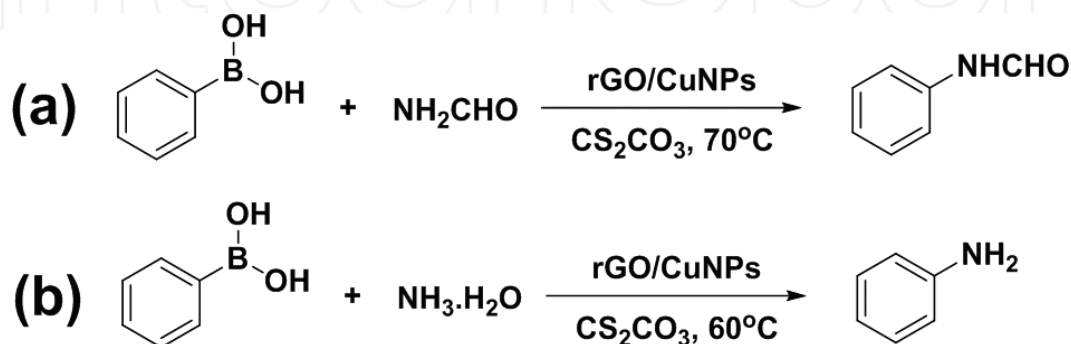


Scheme 6. RuO₂/SWCNT catalyzed Heck type olefination of aryl halides (from Gopiraman et al. [33]).

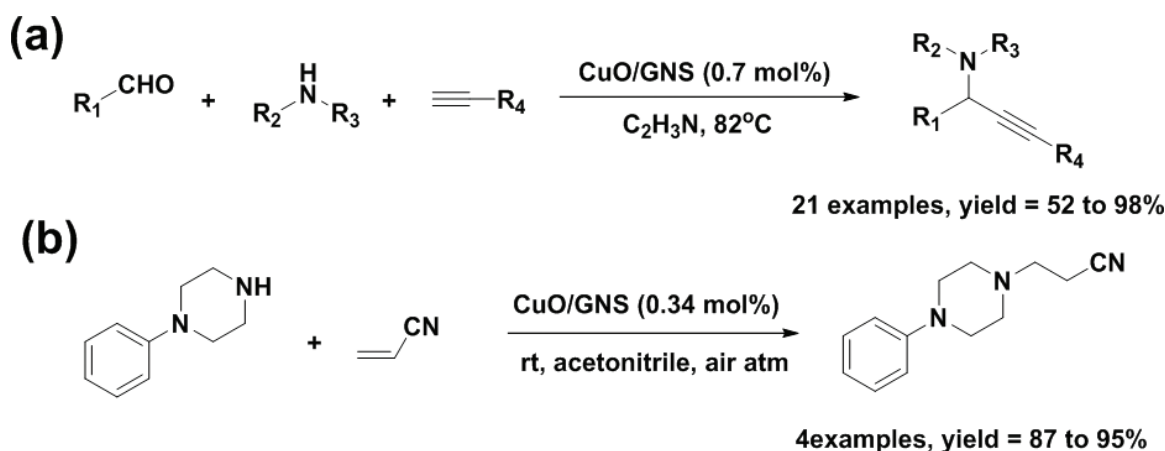
3.2. Non-noble metal supported carbon nanocomposites

Due to less cost, high activity, and less toxic nature, non-noble (Ni, Cu, Fe, Al, V, Ce, and Mn) nanoparticles are extensively employed studied as efficient catalysts for the organic transformations [57]. Particularly, Ni, Cu, and Fe nanoparticles have been widely studied for the organic conversion. Formamides are valuable intermediates in the synthesis of pharmaceutically important compounds [58]. Fakhri et al. [59] prepared Cu nanoparticles supported GO catalyst (rGO/CuNPs), and it was used for the synthesis of formamides and primary amines (**Scheme 7**). It was demonstrated that the rGO/CuNPs are highly efficient and reusable. Similarly, highly sustainable and versatile carbon nanocomposite CuO/GNS was prepared and used as catalysts for base-free coupling reactions (**Scheme 8**) [24]. Under very mild reaction conditions (CuO/GNS 0.7 mol%, acetonitrile 5 mL, air atmosphere, 3.5–12 h, 82°C), the CuO/GNS demonstrated outstanding catalytic activity in terms of yield (52–98%) and TON/TOF under base-free reaction conditions. A wide range of aromatic aldehydes, amines, and alkynes were employed to extend the scope of the catalytic system. In addition to the heterogeneous, stable, and reusable nature, the versatility of CuO/GNS was realized from the higher yield in aza-Michael reaction (**Scheme 7(b)**). After use, the GNS and CuO NPs (as CuCl₂) were successfully recovered from the u-CuO/GNS (**Figure 6**). The recovered GNS and CuCl₂ can be used for other applications. Recently, a highly efficient and cost-effective CuO/carbon-nanoparticle catalyst (CuO/CNP) was prepared by a simple “mix-and-heat” method and used for the self-coupling of amines [24]. The CuO/CNP demonstrated excellent catalytic activity toward the synthesis of imines under optimal reaction conditions involving 12 h of reaction time, 25 mg of catalyst, air atmosphere, and 110°C. A wide range of amines (aromatic, aliphatic, alicyclic, and heterocyclic amines) were efficiently catalyzed by CuO/GNS. Heterogeneity, stability, and reusability of CuO/CNP were found to be excellent.

Nitrogen-containing heterocycles including imidazole and its derivatives are prevalent structural motifs in various fields such as biological, pharmaceutical, and material sciences [60]. They are highly efficient antibacterial, antimalarial, antiviral, antimycobacterial, and antifungal compounds. Gopiraman and coworkers [30] have prepared highly efficient and reusable CuO/MWCNT catalyst for N-arylation of imidazole (**Scheme 9**). It was found that a 0.98 mol% (5 mg) of the CuO/MWCNT was sufficient for the efficient N-arylation of imidazole. The results



Scheme 7. rGO/Cu NPs catalyzed (a) formylation of different arylboronic acids and (b) amination of different arylboronic acids (from Fakhri et al. [59]).



Scheme 8. CuO/GNS catalyzed (a) three-component coupling of aldehyde, amine, and alkyne and (b) aza-Michael reaction of amines with acrylonitrile (from Gopiraman et al. [24]).

showed that this is the smallest amount of catalyst used for N-arylation of imidazole reported to date. Chemical and physical stability, heterogeneity, and reusability of CuO/MWCNT were found to be excellent. After 4th cycle, MWCNTs were successfully separated from the used CuO/MWCNT, and it was confirmed. Based on the results obtained, it was concluded that the good catalytic activity of CuO/MWCNT is due to high surface area and effective dispersion of the CuO/MWCNT in the reaction medium.

Formic acid is often produced from biomass cellulose as well as from fats and oils. This simple acid can be used for storage of hydrogen for different applications [61]. Several metal catalysts including Pt and Cu were employed to decompose formic acid [62]. However, the stability and reusability of the catalysts are limited because the sintering of Cu leads to deactivation in catalytic reactions. Bulushev et al. [63] Cu nanoparticles supported N-doped expanded graphite oxide for the decomposition of formic acid. They showed that the problem of sintering of Cu leaching could be resolved by N-doping of the carbon support. The N-doping leads to a strong interaction of the Cu species with the support by pyridinic nitrogen atoms present in the carbon support. The results showed that the N-doped Cu catalyst has good stability in the formic acid decomposition even at 478 K for at least 7 h on-stream and a significantly higher catalytic activity.

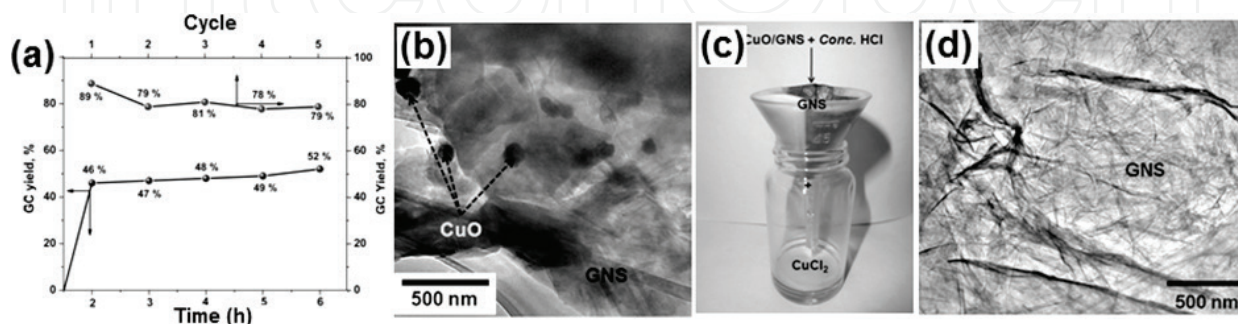
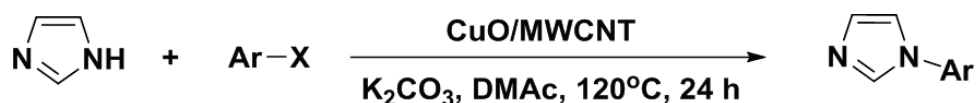
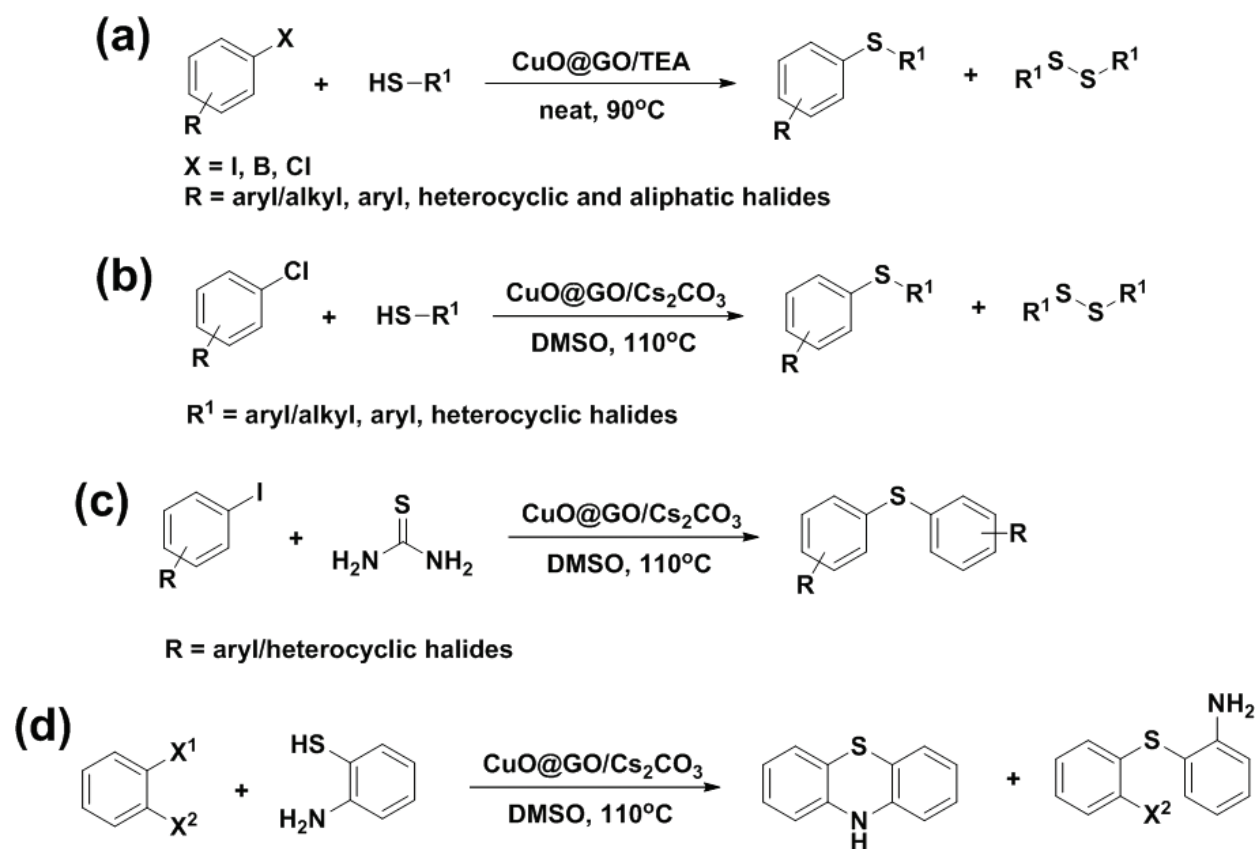


Figure 6. (a) Reusability and heterogeneity tests of CuO/GNS, (b) TEM images of used CuO/GNS, (c) photographic image showing the recovery of GNS and CuCl₂ from used CuO/GNS, and (d) TEM images of recovered GNS (from Gopiraman et al. [24]).

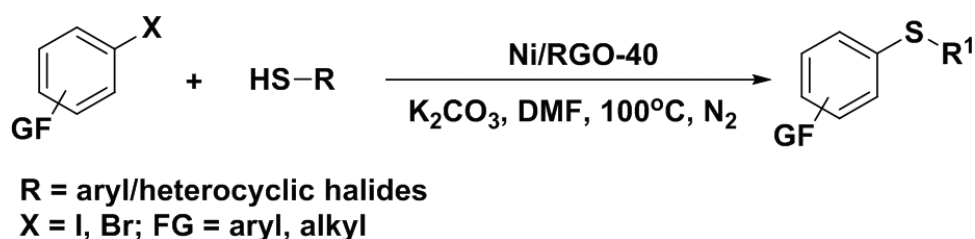


Scheme 9. CuO/MWCNT catalyzed N-arylation of imidazole with various aryl halides (from Gopiraman et al. [30]).

Kamal et al. [64] prepared GO-based nanocomposite (CuO@GO), and it was utilized for ligand-free and solvent-free C—N and C—S cross-coupling reactions with weak bases such as triethylamine (**Scheme 10**). They found that the CuO@GO is a simple and efficient catalyst for solvent- and ligand-free C—S cross-coupling reactions in the presence of weak bases and relatively mild reaction conditions by using the CuO@GO catalytic system. In addition, the CuO@GO was readily separated by centrifugation and could be reused six times under the solvent-free conditions with only a marginal loss of catalytic activity. Catalytic conversion of biomass-derived acids to valuable products is an important process in various chemical industries. Similarly, Ni nanoparticles supported reduced graphene oxide (Ni/RGO) was prepared and used as a heterogeneous catalyst for the C—S cross-coupling reaction between aryl halides and thiols (**Scheme 11**) [65]. They found that the catalytic performance is mainly dependent on the sizes of the Ni nanoparticles. Moreover, the electron-rich planar surface of RGO helps in stabilizing the nanoparticles and prevents agglomeration.



Scheme 10. CuO@GO catalyzed (a) S-arylation of various thiols with different aryl halides, (b) S-arylation of various thiols with different aryl chlorides, (c) reactions of various iodobenzenes with thiourea, and (d) cascade C—S and C—N cross coupling of aryl ortho-dihalides and ortho-aminobenzenethiols (from Kamal et al. [64]).



Scheme 11. Ni/RGO-40 catalyzed C—S cross coupling between aryl halide and thiol (from Sengupta et al. [65]).

Very recently, carbon black (CB) supported Ni catalyst (Ni/CB) has been prepared by a facile method using NiCl₂ as the nickel source and hydrazine hydrate as the reducing agent [66]. The Ni/CB catalyst showed excellent activity toward hydrogenation of nitrophenols in water at room temperature. Results showed that the synergistic effect of nano-Ni and carbon black, the presence of oxygen functional groups on carbon black for anchoring Ni atoms, strong adsorption ability for organic molecules, and good conductivity for electron transfer from the carbon black to Ni nanoparticles are the main reason of the superior catalytic activity of the Ni/CB. Moreover, the Ni/CB catalyst is not only cheap but also magnetically separable, and therefore, this approach facilitates achieving the cost-effective reduction of nitrophenols to aminophenols. Similarly, Saravanamoorthy et al. [67] prepared highly efficient and cost-effective NiO-based carbon nanocomposite (NiO/CNP) by a simple “mix-and-heat” method. The NiO/CNP exhibited that high-rate constant (k_{app}) values of $4.2 \times 10^{-2} \text{ s}^{-1}$ and $3.06 \times 10^{-2} \text{ s}^{-1}$ were calculated for the reduction of 4- and 2-nitrophenols. Interestingly, the catalyst worked well for the transfer hydrogenation of carbonyl compounds under mild reaction conditions (5 mg of NiO/CNP, 9 h of reaction time, 2 mmol of NaOH, air atmosphere, and room temperature). It was found that the NiO/CNP composite is chemoselectivity and heterogeneous in nature, stable, and reusable.

Nitrogen-doped carbon materials are found to be highly efficient support for metal nanoparticles [68]. In fact, the N-dopants in the carbon matrix act as efficient anchoring sites or defects for enhancing the nanoparticle nucleation and reducing the nanoparticle size [69]. Interestingly, the N-dopants can modify the electronic structure of the carbon matrix and tune the activity of the sp² carbon and metal nanoparticles, thus promoting the higher catalytic activity. In addition, the hydrophilicity and basicity of carbon supports can be improved by N-doping; therefore, the N-doped carbon materials could be effectively used to prepare catalysts in the aqueous phase. However, the recent studies on the N-doped carbon supports are mainly focused on noble metals. Very recently, Nie et al. [70] prepared porous N-doped carbon black supported Ni catalyst (Ni/NCB) by a simple chemical method. The prepared Ni/NCB catalyst showed high performance in the hydrogenation of vanillin (4-hydroxy-3-methoxybenzaldehyde) to 2-methoxy-4-methylphenol under mild conditions at low hydrogen pressure (0.5 MPa) and mild temperature (<150°C), which is significantly superior to other frequently used Ni catalysts. The nanostructure of Ni/NCB, intimate interaction between the Ni nanoparticles and the N species, and lower oxidation state are the main reason for higher catalytic activity of Ni/NCB. Moreover, the Ni/NCB catalyst is cost-effective and easily separable.

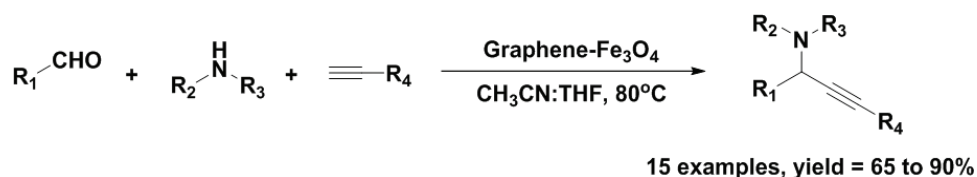
The Fe₃O₄ nanoparticles have played a crucial role as a heterogeneous catalyst due to its environmentally benign, high catalytic activity, good magnetic separation performance, and

high chemical stability [71]. Huo et al. [72] prepared graphene-Fe₃O₄ nanocomposite for the A³ coupling of aldehydes, alkynes, and amines (**Scheme 12**). The catalytic system produced a diverse range of propargylamines in a moderate to high yield under mild conditions. Interestingly, this catalyst could be reused up to eight times with essentially no loss of activity. Moreover, the separation and reuse of graphene-Fe₃O₄ were very simple, effective, and economical. Similarly, Stein and coworkers [58] prepared Fe nanoparticles supported GO for the preparation of hydrogenation of different olefins and alkynes with H₂.

3.3. Bimetallic carbon nanocomposites

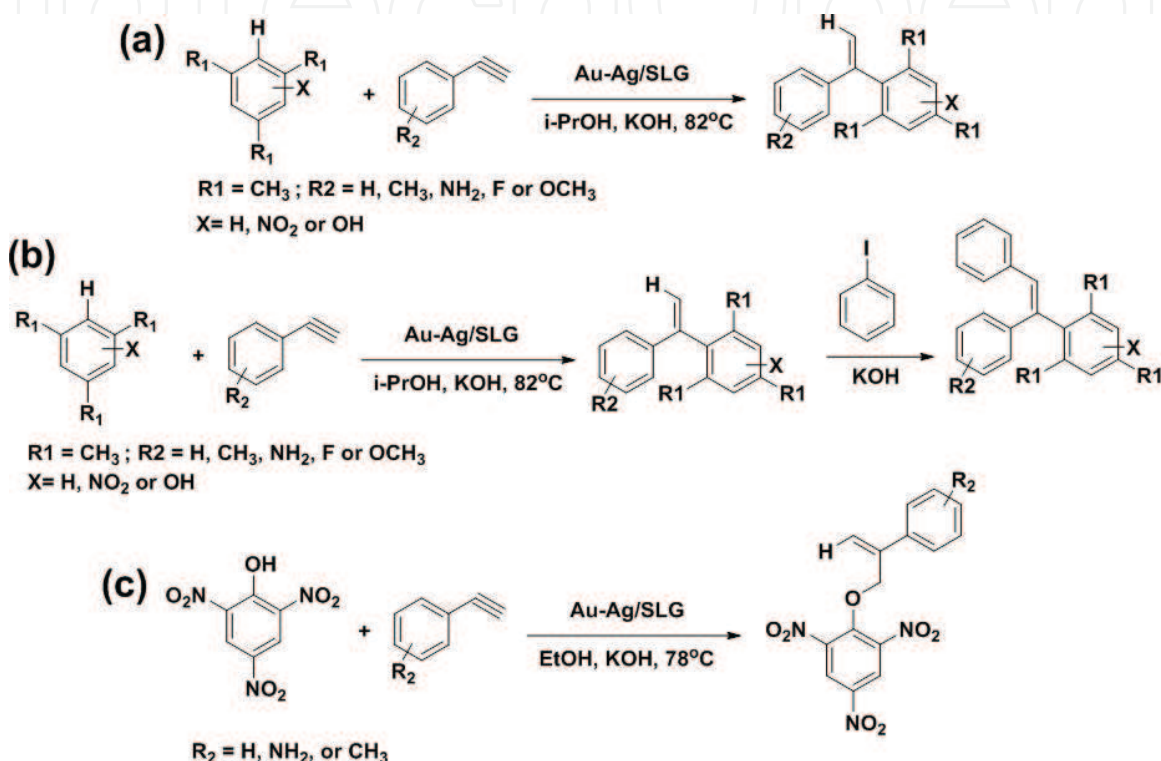
Bimetallic alloy nanoparticles show an enhancement in the catalytic properties owing to the synergistic effects between the two or more distinct metals [73]. In particular, carbon materials supported bi- or multi-metallic nanocomposites are often show dramatic change in the catalytic activity when compared with the mono metallic carbon supported catalysts. Babu et al. [17] prepared bimetallic Au-Ag nanoparticles supported single-layer graphene (SLG) nanocomposites (Au-Ag/SLG) for the hydroarylation, C-arylation, and hydrophenoxylation reactions under mild and ligand-free conditions (**Scheme 13**). They found that the catalytic activity of the Au-Ag/SLG found to be better than the mixture of monometallic nanocatalysts (Au/SLG and Ag/SLG). Interestingly, more than twofold synergy was obtained by this bimetallic nanocatalyst (Au-Ag/SLG). Usage of meager amount of precious metals (0.09 mol% of Au and 0.22 mol% of Ag) and very good reusability made this catalytic system economically feasible. Similarly, Lv and coworkers [74] prepared porous Pt-Au nanodendrites supported on reduced graphene oxide nanosheets (Pt-Au pNDs/RGOs) for the reduction of 4-nitrophenol. They found that the Pt-Au pNDs/RGOs exhibited significantly enhanced catalytic performance toward the reduction of 4-nitrophenol, as compared to commercial Pt black and home-made Au nanocrystals. The reason for the enhancement in the catalytic activity of the Pt-Au pNDs/RGOs is due to its unique interconnected nanostructures of Pt-Au pNDs, which provide more available active sites and the improved mass transport by using RGOs as a support, along with the synergistic effects between Pt and Au.

Aryl-substituted alkynes are versatile intermediates in the formation of various agrochemicals, medicines, and functional organic molecules [75]. Sonogashira cross-coupling reaction of terminal alkynes with aryl halides is one of the most efficient routes for the construction of substituted aryl alkynes. Supported Pd-Cu catalyst has been found to be highly efficient for the Sonogashira cross-coupling reaction in good yield. Diyarbakir et al. [76] prepared Cu-Pd alloy nanoparticles immobilized GO catalyst (rGO-CuPd) for the Sonogashira cross-coupling reactions of various aryl halides with phenylacetylene (**Scheme 14**). The rGO-CuPd catalyst worked well for both electron-rich and electron deficient aryl iodides and aryl bromides,

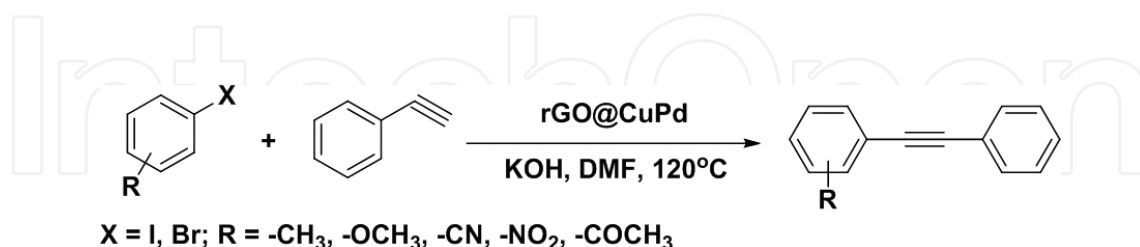


Scheme 12. Graphene-Fe₃O₄ nanocomposite catalyzed A³ coupling of aldehydes, alkynes, and amines (from Huo et al. [72]).

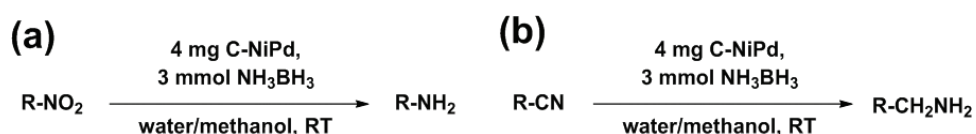
affording the targeted biaryl products in high yields. They concluded that the rGO-CuPd catalytic system has obvious advantages such as recyclable, easy to operate, and environmentally friendly over the conventional Sonogashira couplings. Goksu et al. [77] developed bimetallic Ni-Pd nanoparticles supported GO catalytic system for the tandem dehydrogenation of ammonia borane and hydrogenation of nitro/nitrile compounds (**Scheme 15**). They found that the G-NiPd catalyst is highly active and reusable. Moreover, the reaction can be performed in an environmentally friendly process with short-reaction times and high yields.



Scheme 13. Au-Ag/SLG catalyzed (a) hydroarylation of alkynes with arenes, (b) direct arylation of 1,1-diphenylethylenes with iodobenzene, and (c) hydrophenoxylation of alkynes with substituted phenols (from Babu et al. [17]).



Scheme 14. rGO-CuPd catalyzed Sonogashira couplings of various aryl halides and phenyl acetylene (from Diyarbakir et al. [76]).



Scheme 15. G-NiPd catalyzed tandem reaction of (a) various R-NO₂ compounds and (b) nitrile and/or nitro compounds (from Goksu et al. [77]).

4. Conclusion

In recent days, the metal nanoparticles supported carbon nanocomposites are found to play a significant role in a wide range of potential applications. Due to unique properties including high surface area, the carbon nanocomposites are often used as an efficient heterogeneous catalyst for industrially important organic reactions. In order to achieve carbon nanocomposites with excellent physicochemical properties, several methods have been developed so far. In this chapter, we have summarized the recent progress in the research on the preparation methods of carbon nanocomposites (mainly, graphene or graphene oxide and CNTs) and its uses in organic reactions.

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