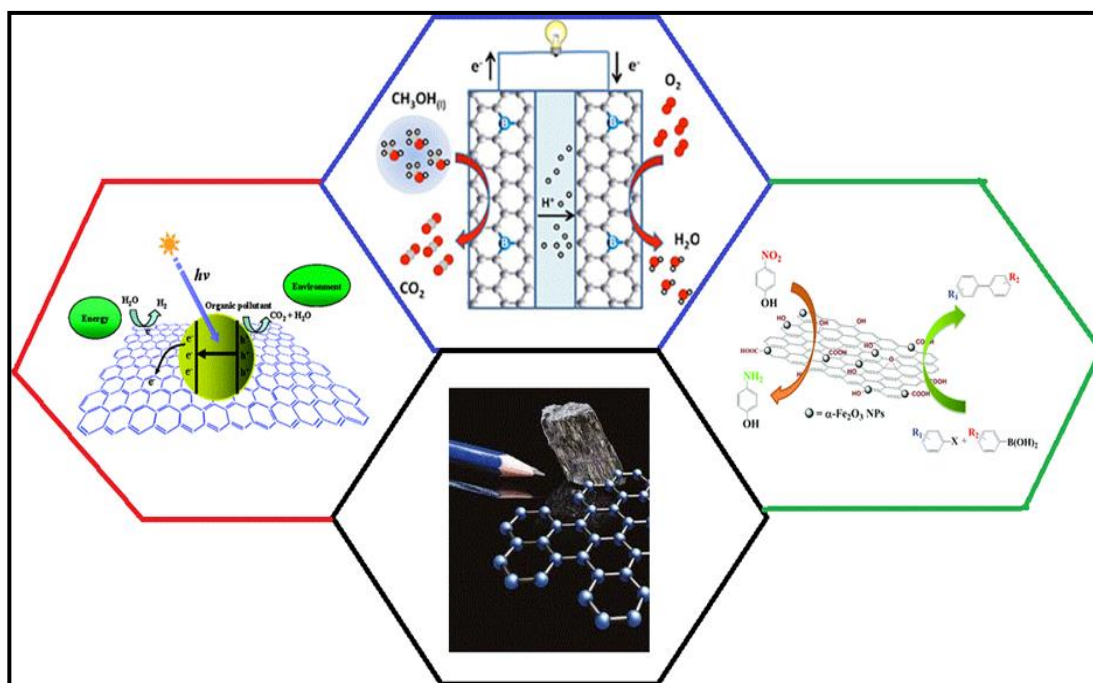
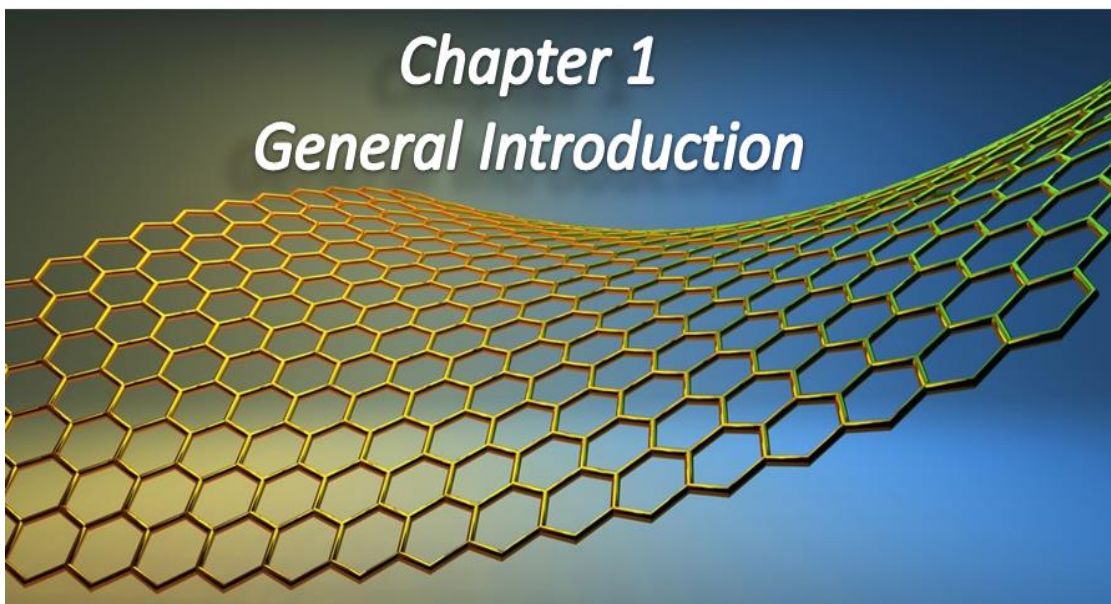


# Chapter 1

## General Introduction



The motivation and research background of the present investigation are discussed in this chapter along with brief literature review on catalytic properties of graphene based nanocomposites.

## 1.1 Motivation and background

Catalysis is the key to success in developing new processes for various industries as well as in academic research. They can speed up chemical reactions or improve the selectivity of reactions without consuming themselves [1]. They are extensively used in energy related systems, organic reactions and environmental protection. The practical applications of the conventional catalysts such as noble metals, metal oxides, enzymes, etc. are often limited by their high cost, low efficiency, toxicity or environmental issues. To tackle these problems, graphene and its derivatives have been studied broadly to replace conventional catalysts or as catalyst support for improving the catalytic performance [2]. The single layered structure of graphene provides a huge specific surface area for loading catalysts. In addition, its high conductivity, optical transparency, chemical, optical, thermal and electrochemical stability make it an attractive material for developing new catalysts with improved lifetime of catalysts. Thus, it has been regarded as an important component for functional materials.

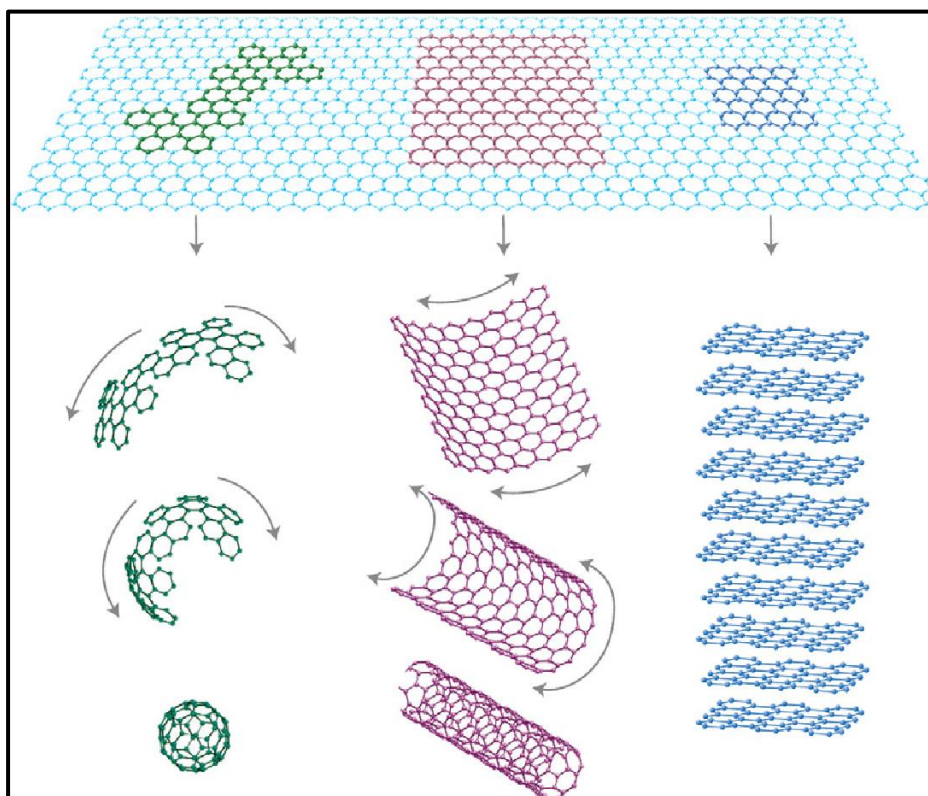
Graphene sheets can be functionalized with various active components such as metals, metal oxide, polymers, small organic molecules or even other carbon nanomaterials to furnish unique properties and possibly induce new functions based on synergetic effects, providing a new opportunity for designing and developing next-generation catalysts. Chemically modified graphene (CMG) materials such as graphene oxide (GO) and reduced graphene oxide (rGO) can be obtained at relatively low cost at large scale. They are widely explored as catalysts or catalyst support due to their ability to form stable dispersion in aqueous or organic media and can be blended with other nanomaterials to form functional composite. Therefore, they are promising catalysts and also attractive components for developing new catalysts.

This thesis represents my research efforts focused on developing new ideas on the preparation and characterization of some functionalized graphene based nanocomposites and their catalytic applications in organic transformations, energy related systems, photocatalysis and environmental protection.

## 1.2 Graphene

Graphene is a two-dimensional one atom thick single-layer of  $sp^2$ -hybridized carbon atoms packed densely into a honeycomb crystal lattice. It is the thinnest and strongest known material in the universe. Its extended honeycomb network is the basic

building block of other important allotropes of carbon, including graphite, carbon nanotubes (CNTs) and fullerenes (Fig. 1.1). It can be stacked to form graphite, rolled to form CNTs and wrapped to form fullerenes [3,4]. In October 2004, Andre Geim and Konstantin Novoselov have first isolated single layer graphene from naturally occurring graphite. They received Nobel Prize “for groundbreaking experiments regarding the two-dimensional material graphene” in 2010 [4, 5].



**Fig 1.1** Graphene, the basic building material for other allotropes of carbon, 0D fullerene, 1D carbon nanotube and 3D graphite

### 1.2.1 Properties of Graphene

Among different carbon nanomaterials, graphene has fascinated the most intense attention due to the fact that it has several genuine advantages over other carbon nanomaterials for developing new catalysts or catalyst support [6-8]. The specific surface area of graphene is much higher than any other carbon nanomaterials. It has a theoretical specific surface area ( $\sim 2630 \text{ m}^2 \text{ g}^{-1}$ ), twice that of single walled CNTs ( $1315 \text{ m}^2 \text{ g}^{-1}$ ) and much higher than those of carbon black, activated carbon and graphite. Therefore, graphene is highly desirable for potential application as a catalyst support. Graphene

based materials can be obtained from graphite at relatively low cost on a large scale. So, the production cost of graphene based materials is much lower compared to other nanomaterials [09-13]. Moreover, graphene shows superior electron mobility ( $15000 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ ) under ambient conditions [14]. The high electron mobility of graphene facilitates the electron transfer during the catalytic reaction. Hence improves its catalytic activity. Furthermore, graphene is found to have a high optical transparency due to its one atom thickness. Therefore, graphene based materials are extremely useful in transparent conducting electrodes [15]. In addition, graphene possess excellent chemical, electrochemical and thermal stabilities and mechanical strength which can possibly improve the lifetime of catalysts [16]. Its Young's modulus, elastic modulus, fracture strength and thermal conductivity values are 1.0 TPa, 0.25 TPa, 130 GPa and  $5000 \text{ W m}^{-1} \text{ K}^{-1}$ , respectively [17, 18]. Table 1.1 shows the superior physical properties of graphene compared to other carbon allotropes.

**Table 1.1** Physical properties of graphitic carbon materials

Properties	Fullerene	Carbon nanotube	Graphene
Structural dimension	0D	1D	2D
Young's modulus	15.9 GPa	$\sim 1.25 \text{ TPa (SWNT)}$	1TPa
Tensile strength	-----	13 $\sim$ 52 GPa (SWNT)	130 GPa
Band gap	1.5 $\sim$ 2.0 eV	0 $\sim$ 1.9 eV	0 eV
Electrical conductivity	$10^{-14} \sim 6 \times 10^{-8} \text{ S cm}^{-1}$	$0.17 \sim 2 \times 10^5 \text{ S cm}^{-1}$	$\sim 10^6 \text{ S cm}^{-1}$
Electron mobility	$0.5 \pm 0.2 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$	$1000 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$	$15000 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$
Thermal conductivity	$0.4 \text{ W m}^{-1} \text{ K}^{-1}$	$6600 \text{ W m}^{-1} \text{ K}^{-1}$ (SWNT)	$5000 \text{ W m}^{-1} \text{ K}^{-1}$
Thermal stability	1000 °C	$\sim 1800 \text{ °C}$	$\sim 2800 \text{ °C}$
Solubility (in NMP)	$890 \mu \text{ g mL}^{-1}$	$116 \mu \text{ g mL}^{-1}$	$4.7 \mu \text{ g mL}^{-1}$
Density	$1.65 \text{ g cm}^{-3}$	$1.33 \text{ g cm}^{-3}$	$2.2 \text{ g cm}^{-3}$

### 1.2.2 Synthesis of Graphene

Till now, tremendous efforts have been made for the synthesis of graphene and graphene based composites. The synthetic methods can be broadly classified as the bottom-up and top-down methods.

### *Bottom-up method*

In bottom-up method graphene materials are synthesized directly from carbon sources. This method includes chemical vapor deposition (CVD), plasma enhanced CVD (PECVD), epitaxial growth on electrically insulating surfaces (SiC), solvothermal, organic synthesis etc [19]. CVD method is used to grow large size, high quality, single and few-layered graphene sheets on metal surfaces such as Ni, Cu, Co, Pt, Ir and Ru [20]. In PECVD method, single-layered graphene is synthesized from a H<sub>2</sub>/CH<sub>4</sub> gas mixture on Cu surface at shorter reaction time and lower deposition temperature compared to CVD [21]. In epitaxial growth method, high-quality very large area few layer graphene sheets can be prepared by ultrahigh vacuum annealing of single-crystal SiC [22]. Graphene is also obtained from the wet chemical reaction of Na and ethanol followed by pyrolysis or by organic synthesis via thermal fusion of polycyclic aromatic hydrocarbons [23, 24].

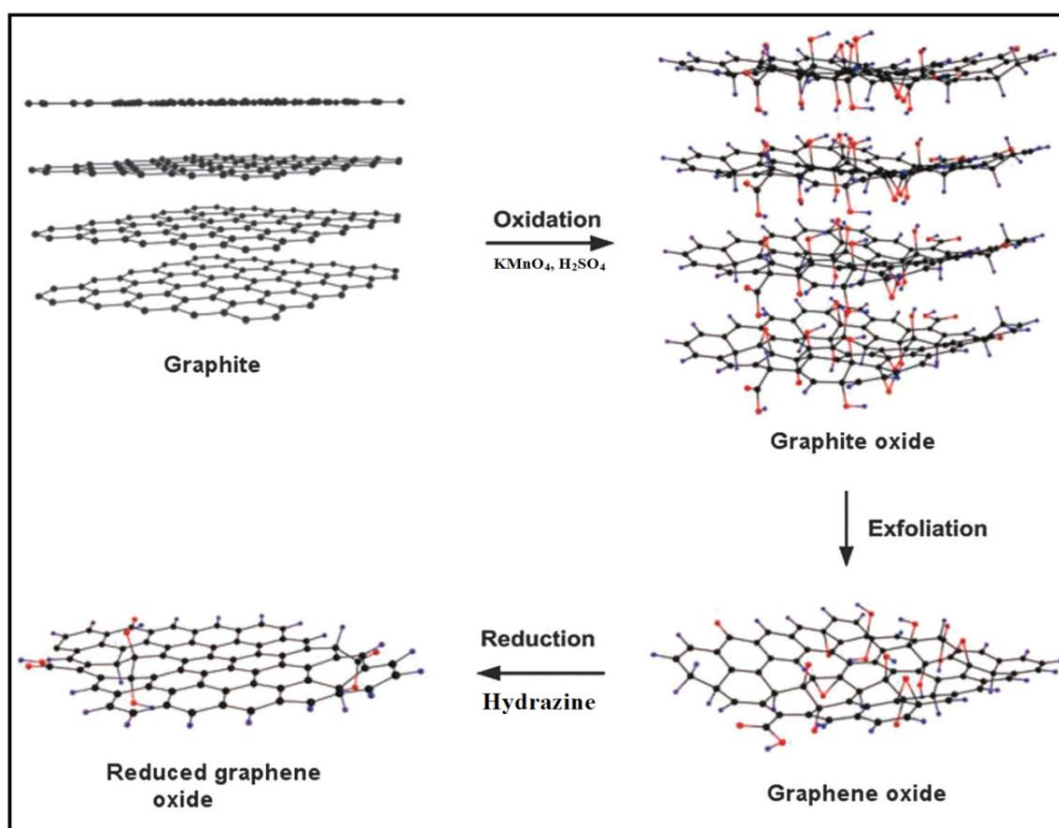
### *Top-down methods*

Top-down methods have several advantages compared to bottom-up methods. This include high yield, solution based processability and ease of implementation. These methods are used for large scale production of graphene. In this method, graphene is prepared by exfoliation or cleavage of graphite. Exfoliation use mechanical, chemical or thermal energy to break the week van der Waal bonds of graphite to separate out individual graphene sheets. In 2004, K. S. Novoselov *et al.* prepared single layered graphene films by mechanical exfoliation (repeated peeling) of small amount of highly oriented pyrolytic graphite [25]. They used scotch tape to peel off layers from graphite. Graphene sheets can also be prepared by liquid exfoliation of graphite by using intercalates such as N-methyl-pyrrolidine [26] and sodium dodecylbenzene sulfonate [27], thermal exfoliation and liquid intercalates (intercalates: oleum and tetrabutyl-ammonium hydroxide [28] and electrochemical exfoliation of graphite in ionic liquid [29]. Unfortunately, these methods face disadvantages such as low yields, expensive intercalates and low conductivity.

One of the most developed methods to obtain higher yields of graphene at low cost, facile preparation process, large sheet size and potential for functionalization is the chemical reduction of GO. In this method, initially graphite oxide is prepared by Brodie



[30] or Hummers [31] methods via the reaction of graphite with strong oxidizing agents such as potassium permanganate ( $\text{KMnO}_4$ ), sodium nitrate ( $\text{NaNO}_3$ ) in the presence of nitric ( $\text{HNO}_3$ ) or sulfuric acid ( $\text{H}_2\text{SO}_4$ ). Then it is exfoliated to GO sheets by ultrasonication which are highly oxidized and featured with oxygen functionalities on their surfaces. After chemical reduction of GO graphene with one to three layers are produced. Fig. 1.2 shows the illustration on the preparation of graphene. Commonly used reducing agents are hydrazine, dimethylhydrazine and sodiumborohydride etc [32, 33]. There are several other reduction methods for reduction of GO such as photochemical reduction, thermal reduction, photothermal reduction, sonolysis, microwave-assisted reduction and electrochemical reduction [34].

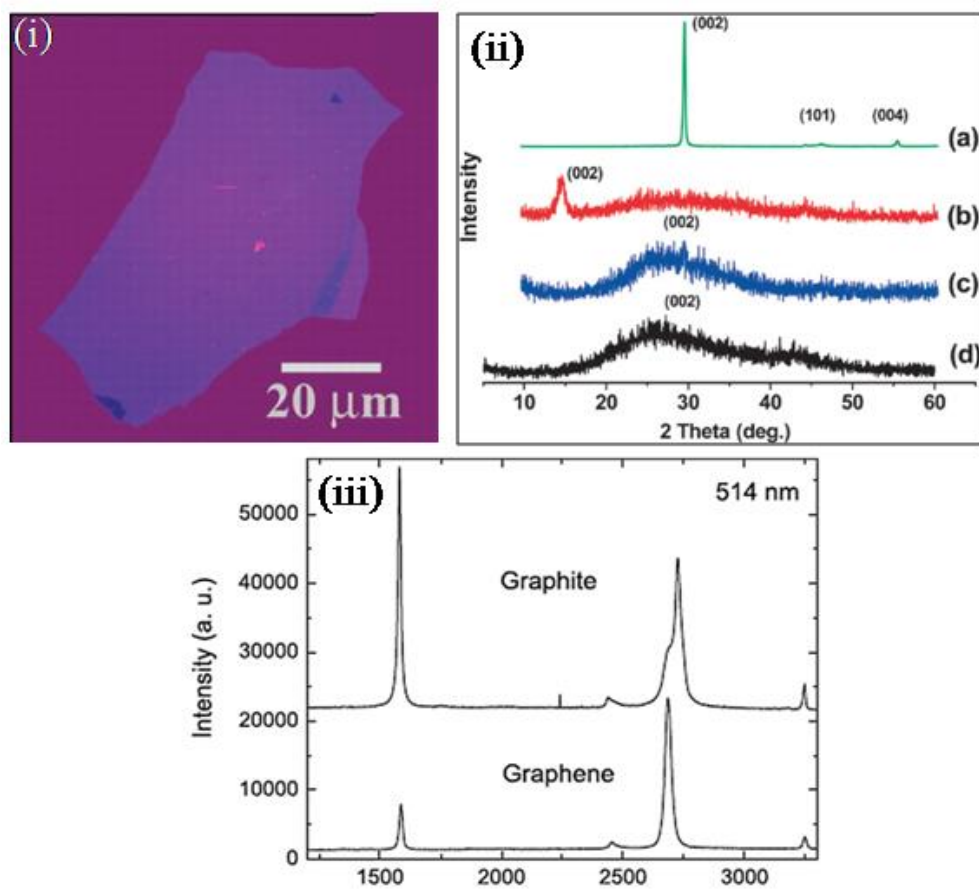


**Fig. 1.2** Illustration on the preparation of GO and rGO (adopted from ref. 36)

### 1.2.3 Characterization of Graphene

A variety of techniques can be used for the analysis of graphene and its derivatives. Among them X-ray diffraction (XRD), Raman spectroscopy, scanning electron microscopy (SEM), transmission electron microscopy (TEM) and atomic force microscopy (AFM) are frequently applied. The crystalline structure of graphene can be evaluated by XRD. Pristine graphite shows a sharp diffraction peak at  $2\theta = 26^\circ$

corresponding to the (002) reflection. This peak is shifted to  $2\theta = 11^\circ$  after the oxidation of the layers (Fig. 1.3 (ii)). The sharp peak of graphite becomes broadened as the number of layers decreases. The number of layers in graphene can be obtained by using Scherrer equation from the corresponding line broadening [35]. Raman spectroscopy is an important technique to characterize the ordered and disordered structure of graphene (Fig. 1.3 (iii)). It can also be used to determine the number of layers present in the graphene [36]. From SEM and TEM analyses structure and morphology of graphene and be obtained. AFM is another important method to analyze the topography of graphene. By using this technique mechanical, electrical, magnetic and even elastic properties of graphene can be studied [36].

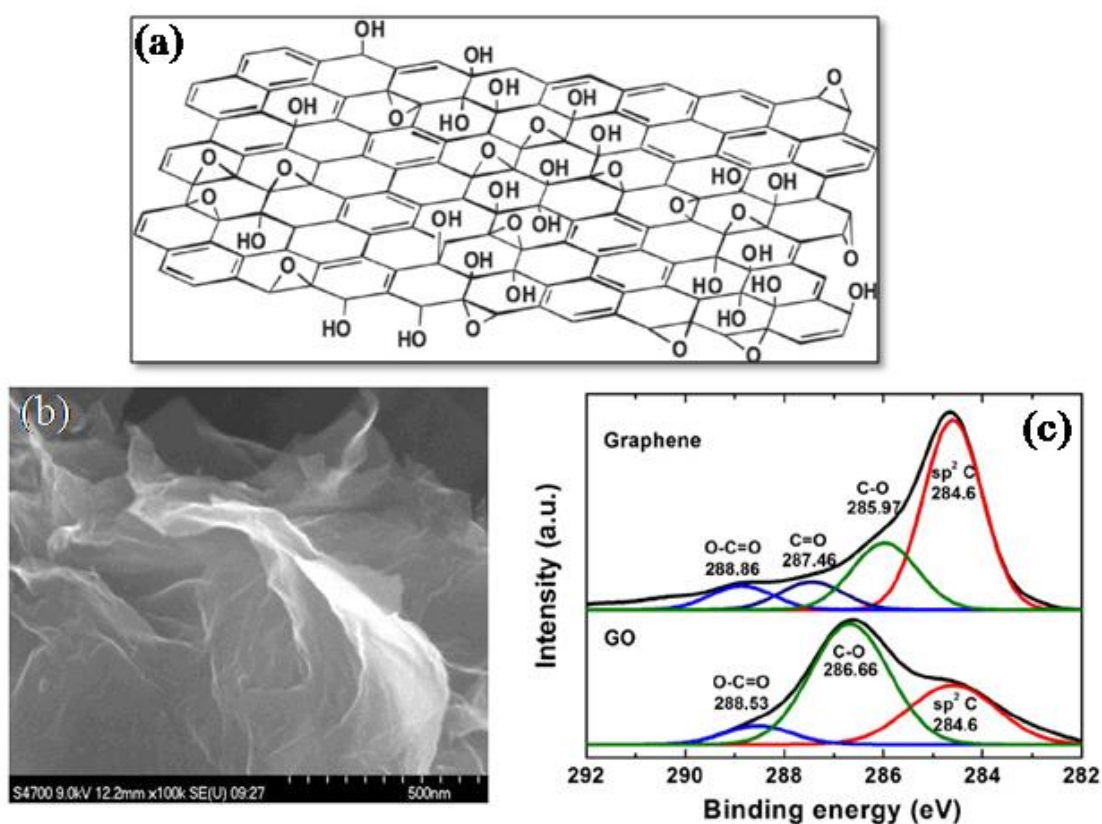


**Fig. 1.3** (i) Single layer graphene, first observed by Geim [5] (ii) XRD of (a) pristine graphite, (b) GO, (c) chemically reduced GO and (d) electrochemically reduced GO and (iii) Raman spectra for graphite and graphene (adopted from ref. 36).

### 1.3 Graphene oxide (GO)

GO can be derived from the chemical exfoliation of graphite oxide obtained from the oxidation of natural graphite powder in presence of various oxidants in acidic

medium. These synthetic protocols introduced a wide variety of oxygen functional groups such as carbonyl, carboxyl, hydroxyl, epoxy and a lot of water molecules into the materials. Due to the presence of these functional groups GO is hydrophilic, slightly acidic and function as a solid acid or green oxidant. Moreover, it contains both  $sp^2$  and  $sp^3$  carbons, which further increase the types of interactions that can occur with the surface. It can be characterized by using Fourier Transform infrared (FTIR) spectroscopy, XRD, SEM, TEM, Raman spectroscopy, X-ray photoelectron microscopy (XPS), nuclear magnetic resonance (NMR) and AFM techniques. The oxygen containing functional groups can be quantitatively and qualitatively described by the XPS and FTIR spectroscopy and presence of water can be studied by FTIR and NMR. SEM, TEM and AFM are used to investigate the morphology, structure and number of layers of GO sheets [37]. GO can be readily functionalized to improve its mechanical, thermal or electronic properties. It can be functionalized by adding small molecules and polymers through  $\pi$ - $\pi$  stacking or covalent C-C coupling reactions. Its properties can also be improved by chemical doping [38]. Fig. 1.4 shows the schematic model, TEM and XPS images of GO.



**Fig. 1.4** (a) Schematic Lef-Klinowski model of GO (b) TEM image of GO and (c) XPS of graphene and GO



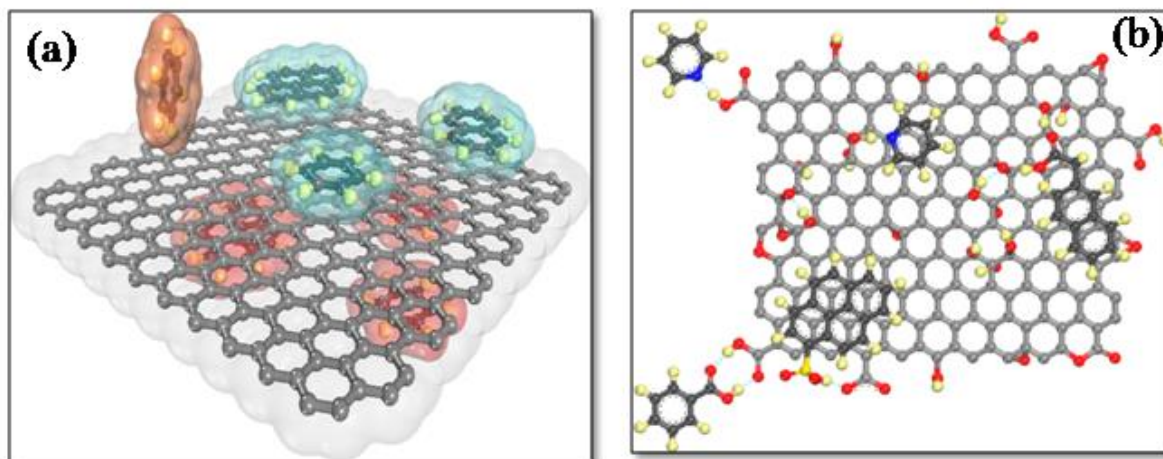
## 1.4 Functionalization of graphene

Functionalization is the best way to accomplish the greatest performance out of graphene. Functionalization and dispersion of graphene are very important for its applications

The functionalization of graphene can be done through covalent and non-covalent interactions. The covalent functionalization on graphene is achieved via atom doping or reaction with residual functional groups present on graphene which is formed during synthesis or destruction of graphene's conjugated structure. Thus, covalent functionalization results defects and loss of electronic properties of graphene. This method is required when the stability and the strong mechanical properties of functionalized graphene are needed. Modification via direct doping of heteroatoms into the graphene lattice is an effective method to tailor the electronic, mechanical and electrochemical properties of graphene [39, 40]. Nitrogen and boron atoms are considered as the best candidates for doping in graphene because of their similar atomic size with carbon [41].

In contrast, non-covalent functionalization appears more versatile and promising as it does not affect the structure and electronic properties of graphene. Non-covalent functionalization includes  $\pi$ - $\pi$  interactions, van der Waals forces, hydrogen bonding, electrostatic interaction and coordinate bonds. Compared to covalent functionalization, non-covalent functionalizations are relatively weak but they are easy to achieve and when graphene's high surface area and electrical conductivity are required, these method are preferred [42].  $\pi$ - $\pi$  interactions is occurred between two components having  $\pi$  orbitals and planar geometry. Graphene monolayer has extended aromatic system and almost planar geometry. Therefore, it interacts strongly with small aromatic species. This interaction is comparable to covalent attachment in strength and provides a more stable alternative method where the conjugation of the graphene sheet does not disturb. Therefore, its electronic properties remain unchanged. Fig. 1.5 represents  $\pi$ - $\pi$  interactions of graphene with benzene, naphthalene and pyrene above and below the basal plane of graphene.  $\text{CH}\cdots\pi$  interactions are also possible between the edge of graphene and hydrogen atom of organic molecules oriented perpendicular to the surface of graphene. In GO, along with  $\pi$ - $\pi$  interactions, hydrogen bond occur due to the presence of various oxygen bearing functional groups [43]. Other non-covalent interactions are observed between graphene and hydrophobic organic molecules or

polymers. Since graphene is hydrophobic, it interacts with hydrophobic or partially hydrophobic organic molecules such as surfactants, ionic liquids and macromolecules. These interactions are used for dispersion of graphene in both aqueous and organic media or its incorporation in polymer matrix.



**Fig. 1.5** (a)  $\pi$ - $\pi$  or C-H $\cdots\pi$  interactions of graphene (b) both  $\pi$ - $\pi$  and hydrogen bonds with GO (adopted from ref. 43).

### 1.5 Functionalized graphene based nanocomposites

The 2D structure of graphene with high specific surface area and excellent physical and chemical properties make it an attractive functional material for incorporation of several nanomaterials to produce highly dispersed nanocomposites. By intercalating nanoparticles within the graphene sheets can also prevent aggregation of graphene layers. Graphene sheets can be blended with various components such as metal [44], metal oxide [45], polymer [46], small organic compound [47], biomaterial [48], metal-organic framework [49], or even other carbon nanomaterials like CNT [50] to furnish unique properties and possibly induce new functions based on synergetic effects, providing a new opportunity for designing and developing next-generation catalysts.

#### 1.5.1 Metal-nanoparticles graphene nanocomposites

Metal nanoparticles graphene based nanocomposites are widely employed in several applications. Most of the composites reported in literature include Au/graphene [51-58], Pt/graphene [59-67], Pd/graphene [44, 68-75], Ag/graphene [75-80], Ru/graphene [81-84], Rh/graphene [85,86], Ir/graphene [86], Fe/graphene [87-90],

Cu/graphene [91-93], Ni/graphene [94-98], Co/graphene [99], Ge/graphene [100, 101] and Sn/graphene [102].

There are several commonly used methods to synthesize well dispersed metal nanoparticles on basal plane of graphene. These methods include physical vapor deposition [68], atomic layer deposition [62, 66] and wet chemical synthesis. The wet-chemical synthesis methods have attracted significant attention because of their low cost, high yields, mass production and versatility. Till now, several wet-chemical synthetic methods have been reported, such as chemical reduction [69, 76, 84], photochemical reduction [52], microwave-assisted synthesis [103], sonochemical method [53, 70], electrochemical reduction [54] and electrodeless metallization [44]. One of the most popular approaches is the chemical reduction of metal precursors in the dispersion of graphene or its derivatives. For example, Iqbal et al. had prepared 3D mesoporous Pd nanoparticles tethered to surfactant modified rGO with an average diameter of 34 nm, where ascorbic acid was used to reduce metal precursor ( $H_2PdCl_4$ ) [69]. Table 1.2 shows a comparison between common preparation methods for metal-graphene nanocomposites.

**Table 1.2** Comparison of preparation methods for metal-graphene nanocomposites, accompanied by the corresponding metal precursors and particle size (adopted from ref. 36)

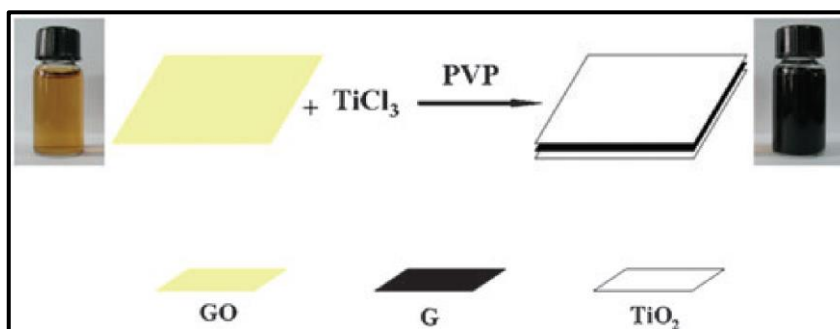
Nanocomposite	Metal precursor	Preparation method	Particle size/nm
Au/Graphene	Chloroauric acid	Reduction with sodium citrate	20
Au/ Graphene	Chloroauric acid	Photochemical reduction	<1
Pt/ Graphene	Potassium tetrachloroplatinate	Electrodeposition	As small as 2
Pt/ Graphene	Potassium hexachloroplatinate	Microwave synthesis	3.31
Pd/ Graphene	Tetraamminepalladium(II) nitrate	Gas-phase reduction	1–6
Pd/ Graphene	Palladium nitrate	Microwave assisted reduction	7–9
Ag/ Graphene	Silver nitrate	Hydrothermal synthesis	10

### 1.5.2 Metal oxide-nanoparticles graphene nanocomposites

The development of metal oxide graphene based nanocomposites provides an important milestone to improve the application of oxide nanomaterials in different fields.

Several metal oxide nanoparticles supported on graphene and its derivatives have been synthesized including TiO<sub>2</sub>/graphene [104-105, 108], Fe<sub>3</sub>O<sub>4</sub>/graphene [106], SnO<sub>2</sub>/graphene [107], ZnO/graphene [45, 109], ZrO<sub>2</sub>/graphene [110], MnO/graphene [111], Co<sub>3</sub>O<sub>4</sub>/graphene [112], Cu<sub>2</sub>O/graphene [113], CuO/graphene [114], Fe<sub>2</sub>O<sub>3</sub>/graphene [115], NiO/graphene [116], Al<sub>2</sub>O<sub>3</sub>/graphene [117, 118], RuO<sub>2</sub>/graphene [119] and MoO<sub>3</sub>/graphene [120].

Metal oxide nanoparticles are usually synthesized by using several techniques which includes sol-gel, hydrothermal/solvothermal process, electrochemical deposition, microwave-assisted growth, etc. The direct mixing approach is the most commonly used method to prepare the nanocomposites. In this method, the metal precursor is mixed with GO and converted to the corresponding metal oxides. After reduction of GO, graphene-metal oxide nanocomposites are obtained. For example, Zhu et al. has synthesized TiO<sub>2</sub>-graphene nanosheet using GO and TiCl<sub>3</sub> as the starting materials in the presence of polyvinylpyrrolidone (PVP), where TiCl<sub>3</sub> acts as a both reducing agent and a precursor (Scheme 1.1).



**Scheme 1.1** Procedure to design TiO<sub>2</sub>-graphene nanosheet (adopted from ref. 105)

The sol-gel process is a popular approach for preparation of metal oxide structures and film coatings. This method have been used to in situ prepared TiO<sub>2</sub> [104], Fe<sub>3</sub>O<sub>4</sub> [106] and SnO<sub>2</sub> [107] nanostructures on graphene. The key advantage of this process is the fact that the surface hydroxyl groups of the GO/rGO sheets act as nucleation sites for the hydrolysis step so that the resulting metal oxide nanostructure are chemically bonded to the GO/rGO surfaces.

Hydrothermal/solvothermal is a powerful method for the synthesis of inorganic nanocrystals, which operates at elevated temperature in a confined volume to create high pressure. This one-pot hydrothermal process can give rise to nanostructures with high crystallinity without post-synthetic annealing or calcination, and simultaneous reduction

of GO to rGO occurred [108,109]. For example, Low et al. has prepared ZnO-graphene nanocomposite by hydrothermal method, where the dispersion of GO and zinc nitrate heated in Teflon stainless steel autoclave at 90 °C at 12 pH [109].

The direct electrochemical deposition approach has been mainly developed for thin film based applications. This approach allows the decoration of inorganic crystals on graphene based materials without the requirement for post-synthetic transfer of the composite materials. Du et al. has synthesized ZrO<sub>2</sub>-graphene nanocomposite by one-step electrochemical deposition onto a glassy carbon electrode (GCE) from a mixture of ZrOCl<sub>2</sub>, rGO and chitosan [110] (Scheme 1.2).



**Scheme 1.2** Illustration of the one-step electro deposition of ZrO<sub>2</sub>-graphene nanocomposite and its application for the extraction and electrochemical detection of MP (adopted from ref. 110).

Microwave irradiation is a rapid and facile method to prepare metal oxide-rGO nanocomposites, such as MnO<sub>2</sub>-rGO [111] and Co<sub>3</sub>O<sub>4</sub>-rGO [112]. In spite of the ease of process and scalable production, this method does not show the fine control over the size uniformity and surface distribution of nanoparticles over rGO. Another important preparation method is the *ex situ* synthesis of metal oxide-graphene nanocomposites. In this method, pre-synthesized nanoparticles are added to the GO suspension, followed by chemical or thermal reduction to yield the final nanocomposites. This approach has more precise control over the particle size and surface properties of the nanoparticles as



compared to *in situ* method. However, the reduction process may change the nanoparticles surface properties and damage graphene lattice [36]. Table 1.3 shows a comparison between common preparation methods for graphene-metal oxide nanocomposites.

**Table 1.3** Comparison of preparation methods for graphene-metal oxide nanocomposites, accompanied by the corresponding metal precursors and particle size (adopted from ref. 36)

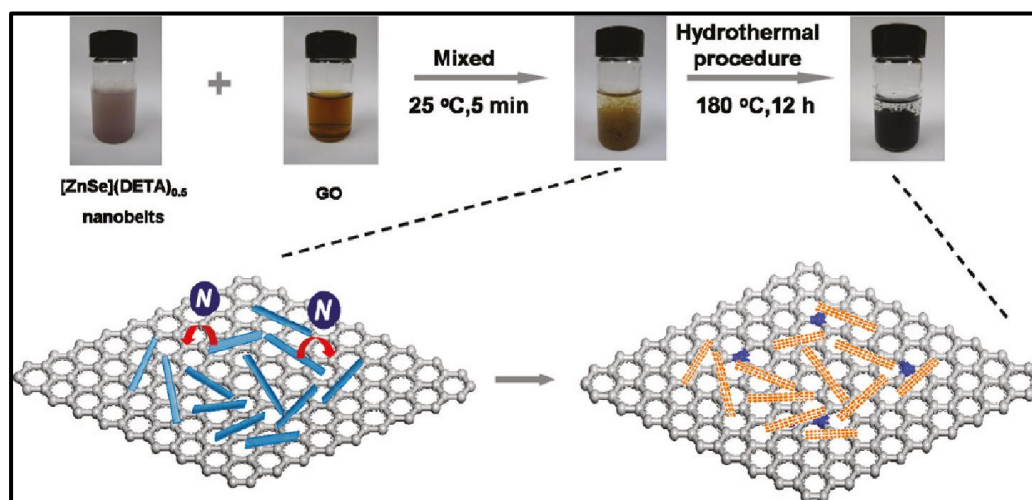
Nanocomposite	Metal precursor	Preparation method	Particle size/nm
Graphene-TiO <sub>2</sub> nanorod	Titanium isopropoxide	<i>Ex situ</i> synthesis	2-4 diameter 20-30 length
Graphene-TiO <sub>2</sub>	Tetrabutyl titanate	Hydrothermal synthesis	9
Graphene-ZnO	Zinc acetate	<i>Ex situ</i> synthesis	4.5
Graphene-SnO <sub>2</sub>	Tin(II) chloride dihydrate	Direct growth	~5-10
Graphene-MnO <sub>2</sub>	Potassium permanganate	Microwave irradiation	5-10
Graphene-Fe <sub>2</sub> O <sub>3</sub>	Iron(III) chloride	Direct growth	60
Graphene-Co <sub>3</sub> O <sub>4</sub>	Cobalt nitrate	Direct growth	10-30
Graphene-RuO <sub>2</sub>	Ruthenium (III) chloride	Sol-gel	5-20
Graphene-Al <sub>2</sub> O <sub>3</sub>	$\alpha$ - Aluminium oxide	Mechanical mixture	2.5-20

### 1.5.3 Other functionalized graphene based nanocomposites

Except metals and their oxides, a variety of other functional materials can also be immobilized onto graphene materials. Self-assembly is an effective method to prepare these materials. For example, Wang et al. prepared poly (diallyldimethylammonium chloride), PDDA functionalized graphene by reducing GO with NaBH<sub>4</sub> in the presence of PDDA. The electrostatic interaction between the positively charged PDDA and negatively charged rGO was the driving force for self-assembly [121].

A one-pot hydrothermal or solvothermal process can also be used for the functionalization of graphene based nanocomposites. For example, Chen et al. prepared a nitrogen-doped graphene/ZnSe nanocomposite by hydrothermal treatment at low temperature from GO nanosheets and ZnSe-(diethylenetriamine)<sub>0.5</sub> nanobelts (Scheme

1.3). In this method, ZnSe(DETA)<sub>0.5</sub> nanobelts were used not only as the sources of ZnSe but also as the nitrogen source [122].



**Scheme 1.3** Schematic illustration of the preparation of GN-ZnSe nanocomposites (adopted from ref. 122)

## 1.6 Applications of graphene based nanocomposites in catalysis

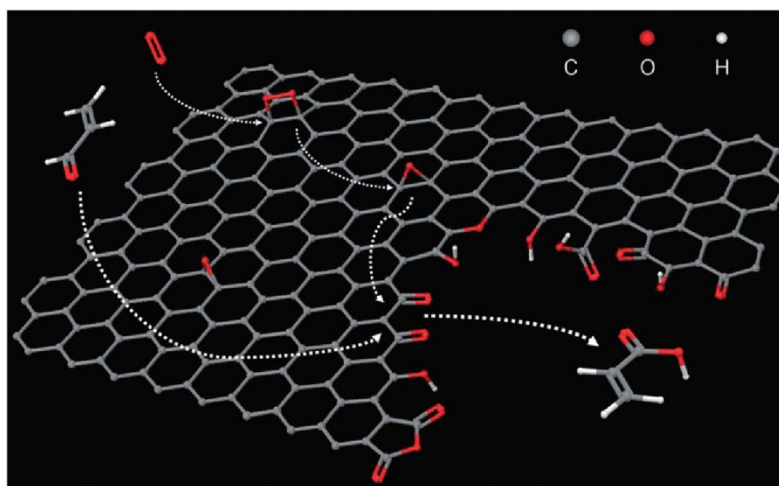
Graphene based materials have a deep impact on electronic and optoelectronic devices, chemical sensors, energy conversion and storage, catalysis and biomedical applications. They have been explored for catalyzing organic, electrochemical, and photochemical reactions. Some of the catalytic applications graphene and functionalized graphene based materials are summarized below.

### 1.6.1 Catalysts for organic reactions

#### (i) Metal-free graphene based catalysts

The use of metal-free carbon catalysts i.e. carbocatalysts instead of metal-supported catalysts in organic synthesis has largely progressed. This results the discovery and development of novel carbon forms as fullerenes, CNTs, graphene and others. The catalytic performance of a catalyst depends on the nature, concentration and accessibility of the active sites that are capable of chemisorbing the reactants and form surface intermediates. It has been observed that functionalized carbons are more proficient catalysts than unfunctionalized one. Pristine graphene has weak catalytic activity due to its zero band gap and lack of functional groups. In contrast, functional group rich materials, such as GO, exhibits high reactivity under mild conditions and are potential

catalysts for various organic reactions. In pristine graphene, the basal planes are not very reactive. The only active sites present at the edge of the graphene layers as unsaturated carbon atoms [36]. Yet it can still find catalytic applications that make use of its delocalized  $\pi$ -electron system, such as complexation reactions of chromium [123]. Graphene could be a selective catalyst for model chemical reactions involving the insertion of oxygen into organic molecules with high productivity e.g. the selective oxidation of acrolein to acrylic acid (Fig. 1.6) [124].

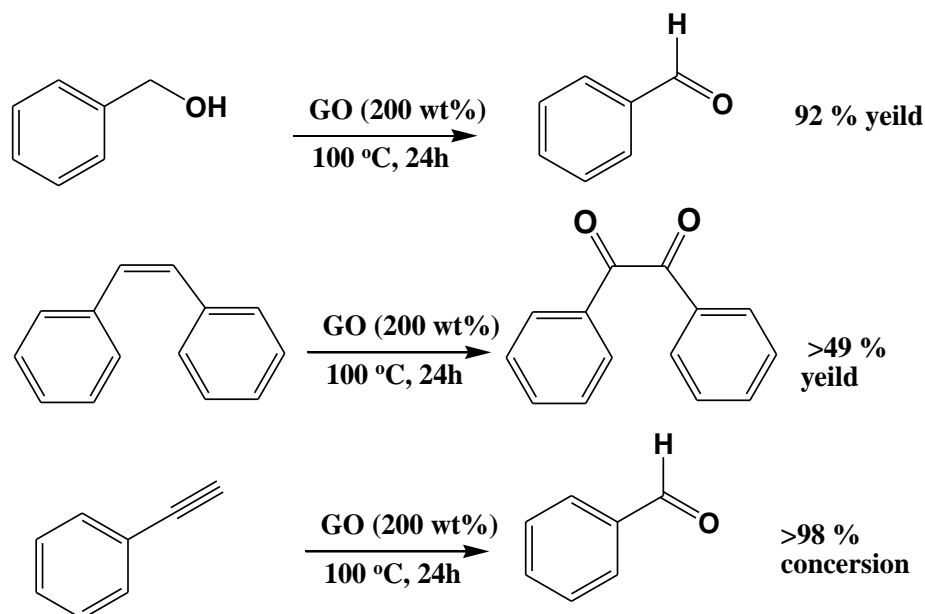


**Fig. 1.6** Suggested reaction pathway for the oxidation of acrolein to acrylic acid at the graphitic carbon surface (adopted from ref. 124)

As a highly oxidized and thermodynamically unstable materials, GO has been commonly used as a precursor to graphene. It not only showed high catalytic activities for various chemical reactions, but can also be conveniently recycled and reused. Bielawski *et al.* [125] has used GO as a mild and efficient carbocatalyst for the generation of various aldehydes or ketones from various alcohols, alkenes and alkynes with high yield and good selectivity (Fig. 1.7). Due to its excellent dispersion in aqueous medium and convenient reactivity for functionalization via covalent anchoring of catalytically active units, GO has been widely used as a carbocatalysts to promote various oxidation, C-C coupling, polymerization, and acid base reactions [126].

Reduction of GO makes rGO, which is hydrophobic with low solubility in water and polar solvents and also it has a tendency to undergo stacking. Therefore, some stabilizers or functionalization of rGO is required. The functionalized rGO has been used as a carbocatalysts in various oxidation, reduction, acid base, and thermal decomposition reactions [126]. For example, sulfonated rGO was used as a solid acid catalyst in the

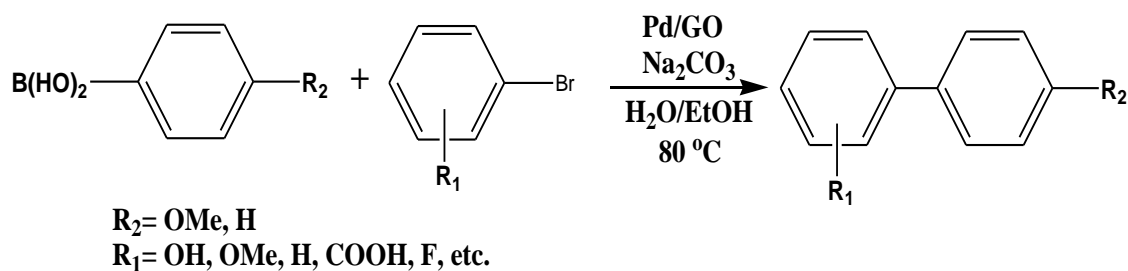
hydrolysis reaction of ethyl acetate [127]. Again, the presence of heteroatoms in the graphene layer can enhance the catalytic activity of graphene. Garcia et al. [128] has used N and B doped graphene as carbocatalysts for the activation of molecular oxygen in selective aerobic oxidation of benzylic hydrocarbons, cyclooctane and styrene.



**Fig. 1.7** Oxidation of benzyl alcohol and *cis*-stilbene and hydration of 1-ethynylbenzene catalyzed by GO

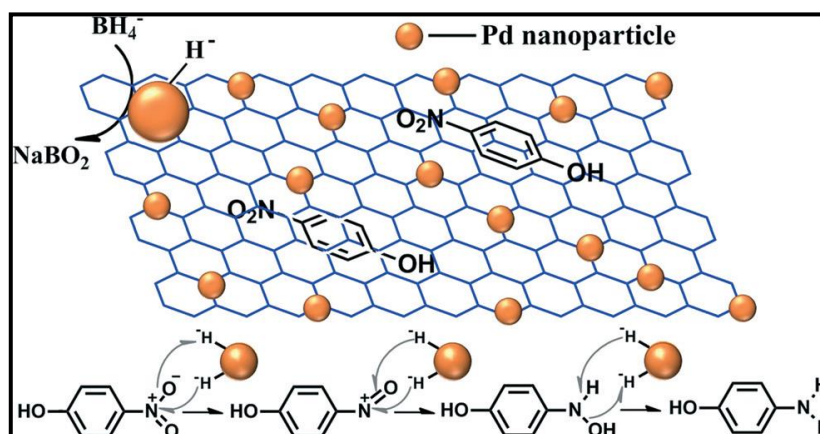
**(ii) Metal supported graphene-based catalysts**

C-C cross coupling reactions is generally catalyzed by Pd catalysts. The immobilization of Pd on an appropriate support is favorable for improving their catalytic activities. Graphene and GO has been considered as a potential support for Pd-catalyzed C-C cross coupling reactions. Mulhaupt et al. [70] prepared Pd/GO nanocomposite and used as a highly active catalyst for Suzuki-Miyaura coupling reaction (Fig.1.8). These catalysts showed much higher activities with turnover frequencies exceeding 39000 h<sup>-1</sup> and very low palladium leaching (<1 ppm).



**Fig. 1.8** Suzuki-Miyaura reactions of aryl bromides with Pd/GO

Pd/graphene nanocomposites were also used for the catalytic hydrogenation reactions of nitrophenols and nitrotoluenes [72]. The Pd/graphene catalyst exhibited much higher activity and stability compared to the commercial Pd/carbon catalyst. The plausible mechanism for the hydrogenation of 4-nitrophenol (4-NP) in presence of  $\text{NaBH}_4$  is shown in scheme 1.4. In another work, Das et al. [79] used Ag/rGO nanocomposite as catalyst towards 4-NP reduction. They have reported a green synthetic approach for reduction of GO to rGO by using L-Arginine amino acid.



**Scheme 1.4** A plausible mechanism for the reduction of 4-nitrophenol catalyzed by the Pd/graphene catalyst in the presence of  $\text{NaBH}_4$  (adopted from ref. 72).

### 1.6.2 Catalysts for electrochemical reactions

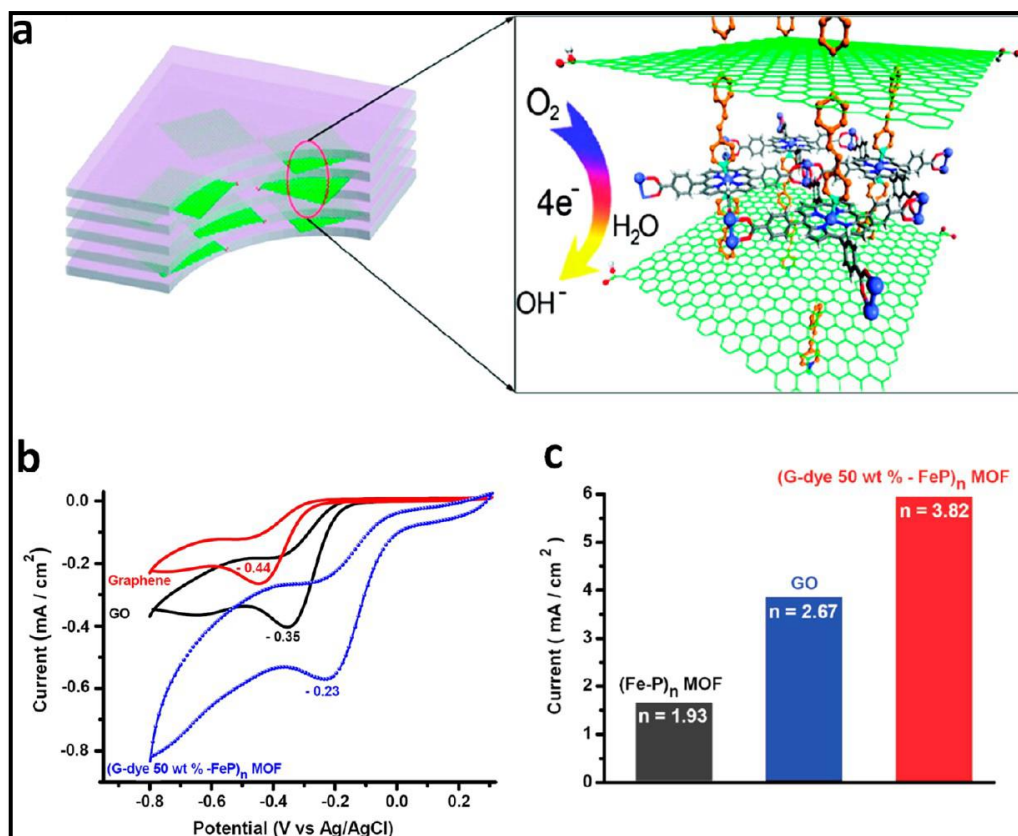
Graphene and its derivatives have been utilized as templates for the synthesis of different graphene-based nanocomposites used as electrocatalysts in various energy-conversion applications such as hydrogen evolution reaction (HER), oxygen reduction reaction (ORR), alcohol oxidation reaction, and  $\text{CO}_2$  reduction reaction. Tremendous researches have been carried out to enhance the electrocatalytic performance of these nanocomposites. The high electrocatalytic performance of these electro-catalysts is due to the synergistic effect between the noble metals and the graphene support. Pt is the most studied noble metal active center due to its intrinsic activity towards HER, ORR, and alcohol oxidation reaction. However, solely utilization of Pt as an electro-catalyst is limited due to its high cost, CO poisoning, poor durability and agglomeration of catalysts. One of the most widely methods for improving the activity of Pt catalyst is immobilizing Pt onto graphene surface [129].



Mazzaro et al. [60] synthesized monodispersed Pt nanoparticles supported on high-quality graphene nanosheets via an easy, low cost and reproducible procedure. The nanocomposite exhibited a remarkable electrocatalytic HER activity in 0.1 M phosphate buffer achieving a turnover frequency of  $4600 \text{ h}^{-1}$  at zero overpotential, which is almost three times that of the commercial Pt/C electrocatalyst. In another work, Ojani et al. [61] fabricated graphene-supported hollow Pt nanospheres using Co nanoparticles as the sacrificial template for HER. The electro-catalyst exhibited superior electrocatalytic performance towards HER compared to the solid Pt nanoparticles supported graphene.

Pt-graphene based catalysts are also used for electrocatalytic ORR. For example, Kou et al. [130] prepared Pt-graphene nanocomposite via the impregnation method where Pt nanoparticles with average diameter of 2 nm were uniformly distributed on graphene surface. The catalyst showed higher electrochemically active surface area, ORR activity, and enhanced stability compared with the commercial catalyst. The electrocatalytic applications of different metal oxide-graphene based nanocomposites were also carried out for ORR. Dai et al. [131] studied the electrocatalytic performance of  $\text{Co}_3\text{O}_4/\text{rGO}$  and  $\text{Co}_3\text{O}_4/\text{N-rGO}$  for ORR. Both the electro-catalysts have higher catalytic activities for ORR in an alkaline solution through 4-electron process as compared to that of commercial Pt/C catalyst.

Jahan et al. [49] synthesized a hybrid MOF by adding pyridinium dye-functionalized rGO sheets to metalloporphyrin MOF with enhanced catalytic activity for ORR. rGO and pyridinium acted synergistically with the porphyrin catalysts to afford facile 4-electron ORR which is also useful for DMFC. The composite had higher selectivity for ORR and significantly reduced methanol crossover effects compared to Pt catalyst. Fig. 1.9 shows the schematic of chemical structure, CVs of ORR and electrochemical activity of the composite.

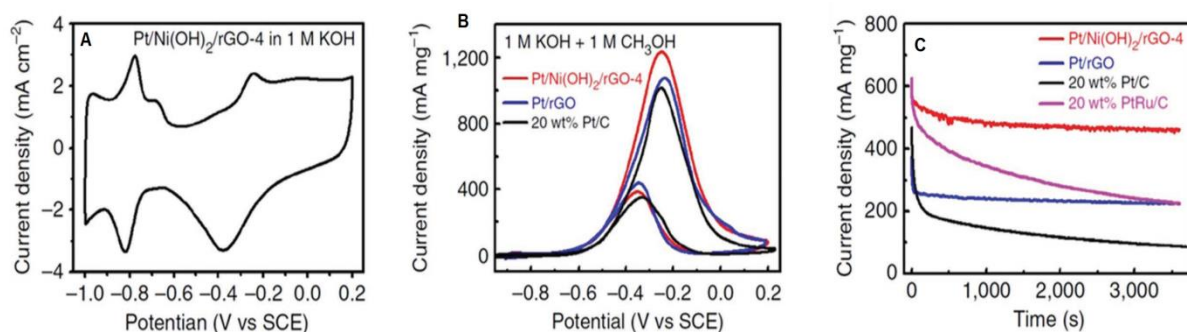


**Fig. 1.9** (a) Schematic of the chemical structures of the composite (b) CV of ORR on exfoliated graphene, GO, and composite (c) Electrochemical activity for (Fe-P)<sub>n</sub> MOF, GO and the composite(adopted from ref. 49)

Electro-catalytic methanol oxidation is an important reaction in direct methanol fuel cells (DMFCs). Li et al. [59] synthesized graphene composites decorated with Pt nanoparticles with higher electrochemically active surface area (ECSA) and better electrocatalytic performance for methanol oxidation than a commercial Pt/carbon catalyst. The lower oxidation potential, higher current density and better stability of Pt/graphene indicated a higher catalytic activity for the methanol electro-oxidation, which is due to the higher ECSA and good dispersion of Pt on graphene surface. In another work, Yoo et al. [132] also reported the same reaction using Pt/graphene with Pt size smaller than 0.5 nm. The smaller particle size of Pt enhanced the electrocatalytic activity for DMFCs due to the strong interaction between graphene and small Pt atoms.

Recently, Ni has been reported as a promising candidate for methanol oxidation. Huang et al. [133] prepared ternary Pt/Ni(OH)<sub>2</sub>/rGO hybrid by a two-step solution method. The incorporation of Ni(OH)<sub>2</sub>, promoted the dissociative adsorption of water molecules and subsequent oxidative removal of carbonaceous poison on neighboring Pt

sites. Thus, the hybrid exhibited exceptional activity and durability towards methanol oxidation reaction. Fig. 1.10 shows the CV curves of the composites in KOH, methanol/KOH and their durability tests. Table 1.4 shows comparison of the methanol oxidation reaction performances with graphene-based noble-metal nanocomposites as electrocatalysts.



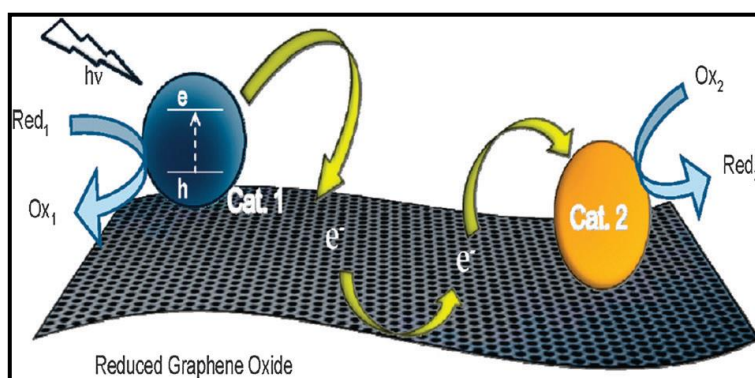
**Fig. 1.10** CV curve of Pt/Ni(OH)<sub>2</sub>/rGO in 1 M KOH. (b) CV curves of Pt/Ni(OH)<sub>2</sub>/rGO, Pt/rGO hybrid and standard 20 wt% Pt/C in 1 M methanol/1 M KOH. (c) Short-term durability measurement of the materials (adopted from ref. 133)

**Table 1.4** Comparison of the methanol oxidation reaction performances with graphene-based noble-metal nanocomposites as electrocatalysts (adopted from ref. 129)

Electrocatalyst	Electrolyte	Peak current from CV curves	Durability
Pt/Ni(OH) <sub>2</sub> /rGO	1 M KOH + 1 M methanol	1070 mA mg <sup>-1</sup>	90% activity retention after 3600s
Rh nanosheets/rGO	1 M KOH + 1 M methanol	264 mA mg <sup>-1</sup>	<20% activity retention after 6000 s
PtNi/graphene	0.1M HClO <sub>4</sub> + 1 M methanol	2.065 mA cm <sup>-2</sup>	N.A.
Pt/graphene	0.5 M H <sub>2</sub> SO <sub>4</sub> + 0.5 M methanol	199.6 mA mg <sup>-1</sup>	≈53% activity retention after 500 s
Pd/N, S-doped graphene	0.5 N NaOH + 1 M methanol	11.3 mA cm <sup>-2</sup>	41.6% activity retention after 3000 s
Pt <sub>9</sub> Rh <sub>1</sub> /graphene	0.1 M HClO <sub>4</sub> + 0.1 M ethanol	≈1.3 mA cm <sup>-2</sup>	N.A.
Ni <sub>75</sub> Pd <sub>25</sub> /graphene	1 M KOH + 0.1 M ethanol	614 mA mg <sup>-1</sup>	21.7% activity retention after 10000 s

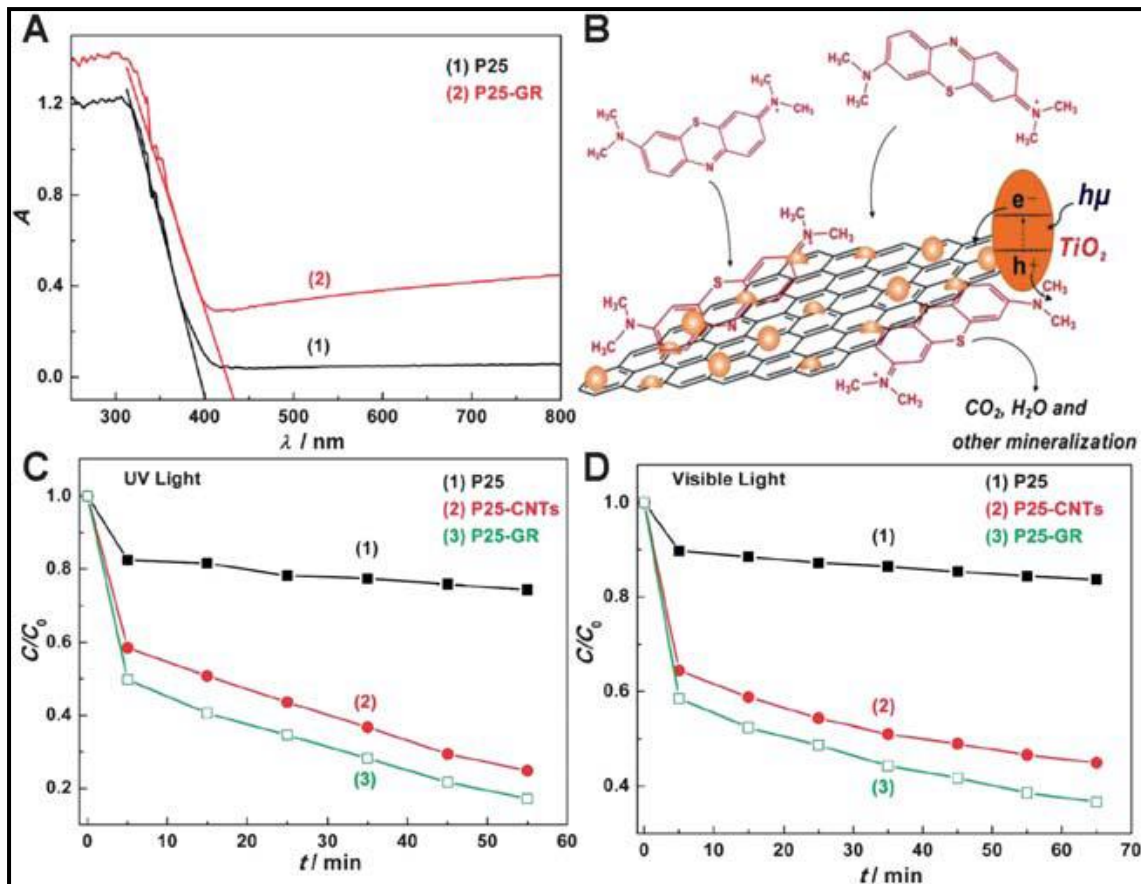
### 1.6.3 Catalysts for photo chemical conversion

In the photochemical conversion reaction, photo-generated electron-hole pairs are formed on the catalyst surface. In the excited state the photo-generated electron-hole pairs are very unstable and can be recombined. Graphene can act as a high performance support for photocatalysis due to its superior electron mobility and conductivity, high specific surface area, high adsorption capacity and high transparency. Lightcap et al. [134] has demonstrated the feasibility of graphene to store and transport electrons through a stepwise electron transfer process (Fig. 1.11), where it can prevent electron-hole recombination by accepting and transporting photoelectrons. Thus graphene could be regarded as an efficient photocatalytic support for the development of next generation catalyst systems.



**Fig. 1.11** Illustration of the three-step electron transfer process involved in making graphene a 2D conducting support (adopted from ref. 134)

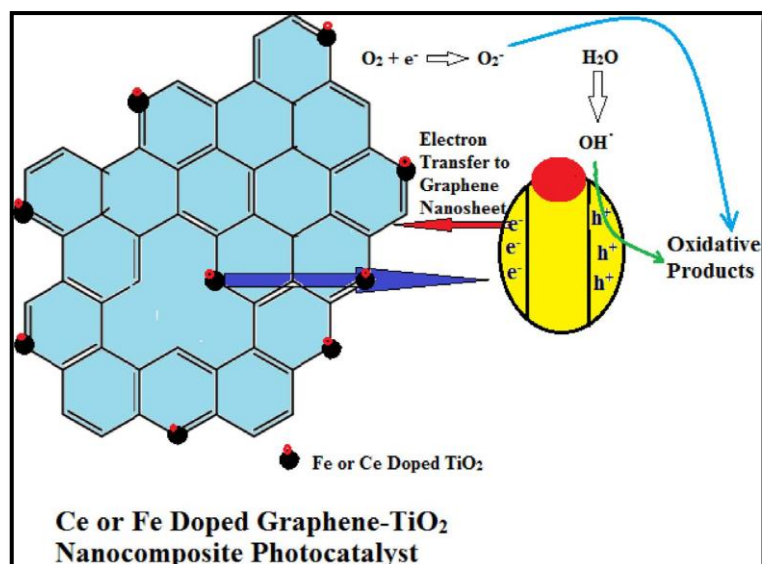
Zhang et al. [135] synthesized chemically bonded a graphene-P25 TiO<sub>2</sub> nanocomposite through one-step hydrothermal process from GO and P25 and applied to the photocatalytic degradation of organic dye. Incorporation of graphene causes the bandgap narrowing of P25 (Fig. 1.12). The nanocomposite was found to have high dye adsorption capacity, enhanced charge separation and transportation properties. The results demonstrated that the graphene-P25 TiO<sub>2</sub> nanocomposite exhibited enhanced photocatalytic activity towards the degradation of methylene blue compared to bare P25 and P25-CNTs under UV and visible lights.



**Fig. 1.12** (a) Diffuse reflectance absorption spectra of P25-graphene, (b) structure of P25-graphene and possible process of photo-degradation; comparison of photocatalytic activity under (c) UV light and (d) visible light (adopted from ref. 135)

Recently, Shende et al. [136] prepared ternary hybrid nanocomposites graphene-Ce-TiO<sub>2</sub> and graphene-Fe-TiO<sub>2</sub> by using one step in-situ ultrasound assisted method and applied in photo-degradation of crystal violet dye. They found that the degradation efficiency was enhanced with doping of Ce or Fe in graphene-TiO<sub>2</sub>. Also, graphene-Fe-TiO<sub>2</sub> showed better efficacy towards the photo-degradation of the dye. Fig. 1.13 shows the proposed charge transfer mechanism of the photocatalytic dye degradation.

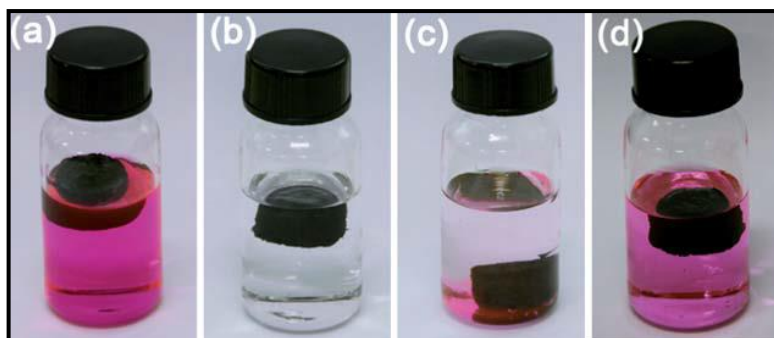




**Fig. 1.13** The proposed charge transfer mechanism during the photo degradation of dye in the presence of Ce or Fe doped graphene-TiO<sub>2</sub> nanocomposite (adopted from ref. 136).

#### 1.6.4 Environmental and other applications

Due to the high specific surface area and good chemical stability graphene can also be used as an adsorbent for adsorption treatment of polluted water. Iqbal and Abdala [137] produced thermally reduced graphene by thermal exfoliation of GO and used as an adsorbent to remove methyl orange (MO) dye from aqueous solution. They found that graphene could be a very proficient adsorbent with 98% removal efficiency and can also be regenerated and reused with no significant change in its adsorption capacity. Zhao et al. [138] reported graphene sponge (GS) as an efficient and reusable adsorption and desorption material for contaminated water. GS showed a tunable pore structure and surface properties and were mechanically tough. They showed high adsorption and desorption ability for various water contaminations such as dyes, oils and many other organic solvents. Fig. 1.14 shows the adsorption and desorption of rhodamine B dye in GSs.



**Fig. 1.14** (a) and (b) A GS in rhodamine B solution (a) at the beginning and (b) for 180 min (c) and (d) The same GS adsorbed with rhodamine B in ethanol for (c) 2 min and (d) 10 min (adopted from ref. 138)

Graphene is also used as an ideal platform for the high sensitive detection of various species. Wang et al. [139] chemically functionalized GO with p-phenylenediamine which showed ultra-high sensitivity for the detection of  $\text{Pb}^{2+}$ . By using anodic stripping voltammetry method on the amine functionalized GO modified electrode, the detection limit for  $\text{Pb}^{2+}$  in aqueous solution was 0.1 pM.

Graphene materials have also been utilized usefully as promising alternate electrode materials in energy storage devices. For example, Xia et al. [140] designed a ternary nanocomposite of graphene/ $\text{Fe}_2\text{O}_3$ /polyaniline and used for high-performance supercapacitors. The nanocomposite exhibited improved energy density, high specific capacitance, and long electrochemical life due to the synergistic effects from the combination of the three components. Ye et al. [141] reported a 3D graphene aerogel on Ni foam hybrid material prepared through a two-step process and explored its energy storage application as a binder-free supercapacitor electrode. The nanocomposite exhibited excellent electrical double-layer capacitance behavior including high rate capability, good electrochemical cyclic stability and high specific capacitance value at low current density.

### 1.7 Objective of the present investigation

The discovery of graphene has opened a new route for the use of two-dimensional carbon materials as catalysts or catalytic supports. Graphene materials not only have inherent catalytic properties, but can also enhance the performance of other catalysts by forming functional composites. This has allowed researchers to design and develop new functionalized graphene based materials. The aim of this work is to

functionalize graphene based nanocomposites and to investigate their catalytic properties for different applications.

Main objectives of the work are listed below:

- i. To synthesize graphene and functionalized graphene-based nanocomposites.
- ii. Functionalization of graphene based nanocomposites with metal, metal oxides, polymers, small organic molecules and CNTs.
- iii. To explore the applications of the functionalized graphene-based nanocomposites in catalysis including organic transformations, energy related systems, photocatalysis and environmental protection.

### **1.8 Plan of the present work**

To fulfill the above mentioned objectives, the following plan of work has been adopted:

- i. Synthesis of graphene and graphene oxide from natural graphite by modified Hummer's method.
- ii. Preparation of functionalized graphene based nanocomposites with CuO, Ni-polypyrrole, ZrO<sub>2</sub>-chlorosulfonic acid and *p*-phenylenediamine-MWCNT.
- iii. Characterizations of the nanocomposites by fourier transform infrared (FTIR) spectroscopy, X-ray diffraction (XRD), scanning electron microscope (SEM), and energy dispersive X-ray (EDX), Raman spectroscopy, dynamic light scattering (DLS), transmission electron microscope (TEM).
- iv. Study of absorption and photo-degradation of some of the nanocomposites by UV visible spectroscopy.
- v. Study of the electrochemical properties of some the nanocomposite by using cyclic voltammetry (CV), galvanostatic charge/discharge and electrochemical impedance spectroscopy tests.
- vi. Applications of the nanocomposites as catalyst for reduction of 4-nitrophenol, as electrocatalyst for electro-oxidation of methanol, as supercapacitor, as photocatalyst for dye degradation and dye adsorbent.

## 1.9 References

- [1] Ball, P. *Designing the molecular world: Chemistry at the frontier*, Princeton University Press, 1996.
- [2] Huang, C., Li, C., and Shi, G. Graphene based catalysts. *Energy & Environmental Science*, 5(10):8848-8868, 2012.
- [3] Geim, A. K. Graphene: status and prospects. *Science*, 324(5934):1530-1534, 2009.
- [4] Allen, M. J., Tung, V. C., and Kaner, R. B. Honeycomb carbon: A review of graphene. *Chemical reviews*, 110(1):132-145, 2009.
- [5] Geim, A. K. and Novoselov, K. S. The rise of graphene. In *Nanoscience and Technology: A Collection of Reviews from Nature Journals*, 11-19, 2010.
- [6] Antolini, E. Graphene as a new carbon support for low-temperature fuel cell catalysts. *Applied Catalysis B: Environmental*, 123:52-68, 2012.
- [7] Hu, H., Xin, J. H., Hu, H., Wang, X. and Kong, Y. Metal-free graphene-based catalyst-Insight into the catalytic activity: A short review. *Applied Catalysis A: General*, 492:1-9, 2015.
- [8] Jariwala, D., Srivastava, A., and Ajayan, P. M. Graphene synthesis and band gap opening. *Journal of nanoscience and nanotechnology*, 11(8):6621-6641, 2011.
- [9] Loh, K. P., Bao, Q., Ang, P. K. and Yang, J. The chemistry of graphene. *Journal of Materials Chemistry*, 20(12):2277-2289, 2010.
- [10] Pumera, M. Electrochemistry of graphene: new horizons for sensing and energy storage. *The Chemical Record*, 9(4):211-223, 2009.
- [11] Rao, C. N. R. and Sood, A. K. *Graphene: synthesis, properties, and phenomena*. John Wiley & Sons, 2013.
- [12] An, X. and Jimmy, C. Y. Graphene-based photocatalytic composites. *RSC Advances*, 1(8):1426-1434, 2011.
- [13] Huang, X., Qi, X., Boey, F., and Zhang, H. Graphene-based composites. *Chemical Society Reviews*, 41(2):666-686, 2012.
- [14] Novoselov, K. S. Two-dimensional gas of massless Dirac fermions in graphene. *Nature*, 438:197-200, 2005.
- [15] Hong, T. K., Lee, D. W., Choi, H. J., Shin, H. S., and Kim, B. S. Transparent, flexible conducting hybrid multilayer thin films of multiwalled carbon

- nanotubes with graphene nanosheets. *ACS Nano*, 4(7):3861-3868, 2010.
- [16] Zhu, Y., Murali, S., Cai, W., Li, X., Suk, J. W., Potts, J. R., and Ruoff, R. S. Graphene and graphene oxide: synthesis, properties, and applications. *Advanced materials*, 22(35):3906-3924, 2010.
- [17] Lee, C., Wei, X., Kysar, J. W. and Hone, J. Measurement of the elastic properties and intrinsic strength of monolayer graphene. *Science*, 321(5887):385-388, 2008.
- [18] Bai, S. and Shen, X. Graphene-inorganic nanocomposites. *RSC Advances*, 2:64-98, 2012.
- [19] Huang X, Qi X, Boey F, Zhang H. Graphene-based composites. *Chemical Society Reviews*, 41(2):666-86, 2012.
- [20] Wang, X., You, H., Liu, F., Li, M., Wan, L., Li, S., Li, Q., Xu, Y., Tian, R., Yu, Z., and Xiang, D. Large-scale synthesis of few-layered graphene using CVD. *Chemical Vapor Deposition*, 15(1-3):53-56, 2009.
- [21] Wang, Y., Xu, X., Lu, J., Lin, M., Bao, Q., Ozyilmaz, B., and Loh, K. P. Toward high throughput interconvertible graphane-to-graphene growth and patterning. *ACS nano*, 4(10):6146-6152, 2010.
- [22] Rollings, E., Gweon, G. H., Zhou, S. Y., Mun, B. S., McChesney, J. L., Hussain, B. S., Fedorov, A. V., First, P. N., De Heer, W. A., and Lanzara, A. Synthesis and characterization of atomically thin graphite films on a silicon carbide substrate. *Journal of Physics and Chemistry of Solids*, 67(9-10):2172-2177, 2006.
- [23] Choucair, M., Thordarson, P., and Stride, J. A. Gram-scale production of graphene based on solvothermal synthesis and sonication. *Nature nanotechnology*, 4(1):30-33, 2009.
- [24] Wang, X., Zhi, L., Tsao, N., Tomović, Ž., Li, J., and Müllen, K. Transparent carbon films as electrodes in organic solar cells. *Angewandte Chemie International Edition*, 47(16):2990-2992, 2008.
- [25] Novoselov, K. S., Geim, A. K., Morozov, S. V., Jiang, D., Zhang, Y., Dubonos, S. V., Grigorieva, I. V., and Firsov, A. A. Electric field effect in atomically thin carbon films. *Science*, 306(5696):666-669, 2004.
- [26] Hernandez, Y., Nicolosi, V., Lotya, M., Blighe, F. M., Sun, Z., De, S., McGovern, I. T., Holland, B., Byrne, M., Gun'Ko, Y. K., and Boland, J. J.



- High-yield production of graphene by liquid-phase exfoliation of graphite. *Nature nanotechnology*, 3(9):563-568, 2008.
- [27] Lotya, M., Hernandez, Y., King, P. J., Smith, R. J., Nicolosi, V., Karlsson, L. S., Blighe, F. M., De, S., Wang, Z., McGovern, I. T. and Duesberg, G. S. Liquid phase production of graphene by exfoliation of graphite in surfactant/water solutions. *Journal of the American Chemical Society*, 131(10):3611-3620, 2009.
- [28] Li, X., Zhang, G., Bai, X., Sun, X., Wang, X., Wang, E., and Dai, H. Highly conducting graphene sheets and Langmuir-Blodgett films. *Nature nanotechnology*, 3(9): 538–542, 2008.
- [29] Liu, N., Luo, F., Wu, H., Liu, Y., Zhang, C., and Chen, J. One-step ionic-liquid-assisted electrochemical synthesis of ionic-liquid-functionalized graphene sheets directly from graphite. *Advanced Functional Materials*, 18(10):1518-1525, 2008.
- [30] Brodie, B. C. XIII. On the atomic weight of graphite. *Philosophical Transactions of the Royal Society of London*, 149:249-259, 1859.
- [31] Hummers Jr, W. S., and Offeman, R.E. Preparation of graphitic oxide. *Journal of the American Chemical Society*, 80(6):1339-1339, 1958.
- [32] Lomeda, J. R., Doyle, C. D., Kosynkin, D. V., Hwang, W. F., and Tour, J. M. Diazonium functionalization of surfactant-wrapped chemically converted graphene sheets. *Journal of the American Chemical Society*, 130(48):16201-16206, 2008.
- [33] Si, Y. and Samulski, E. T. Synthesis of water soluble graphene. *Nano letters*, 8(6):1679-1682, 2008.
- [34] Huang, X., Qi, X., Boey, F., and Zhang, H. Graphene-based composites. *Chemical Society Reviews*, 41(2):666-686, 2012.
- [35] Rao, C. N. R., Biswas, K., Subrahmanyam, K. S., and Govindaraj, A. Graphene, the new nanocarbon. *Journal of Materials Chemistry*, 19(17):2457-2469, 2009.
- [36] Machado, B. F. and Serp, P. Graphene-based materials for catalysis. *Catalysis Science & Technology*, 2(1):54-75, 2012.
- [37] Stobinski, L., Lesiak, B., Malolepszy, A., Mazurkiewicz, M., Mierzwa, B., Zemek, J., Jiricek, P., and Bieloshapka, I. Graphene oxide and reduced

- graphene oxide studied by the XRD, TEM and electron spectroscopy methods. *Journal of Electron Spectroscopy and Related Phenomena*, 195:145-154, 2014.
- [38] Dreyer, D. R., Park, S., Bielawski, C. W., and Ruoff, R. S. The chemistry of graphene oxide. *Chemical society reviews*, 39(1):228-240, 2010.
- [39] Zhang, W., Wu, L., Li, Z., and Liu, Y. Doped graphene: synthesis, properties and bioanalysis. *RSC Advances*, 5(61):49521-49533, 2015.
- [40] Shi, L., Niu, X., Liu, T., Zhao, H., and Lan, M. Electrocatalytic sensing of hydrogen peroxide using a screen printed carbon electrode modified with nitrogen-doped graphene nanoribbons. *Microchimica Acta*, 182(15-16):2485-2493, 2015.
- [41] Liu, H., Liu, Y., and Zhu, D. Chemical doping of graphene. *Journal of materials chemistry*, 21(10):3335-3345, 2011.
- [42] Liu, J., Tang, J., and Gooding, J. J. Strategies for chemical modification of graphene and applications of chemically modified graphene. *Journal of Materials Chemistry*, 22(25):12435-12452, 2012.
- [43] Georgakilas, V., Tiwari, J. N., Kemp, K. C., Perman, J. A., Bourlinos, A. B., Kim, K. S., and Zboril, R. Noncovalent functionalization of graphene and graphene oxide for energy materials, biosensing, catalytic, and biomedical applications. *Chemical reviews*, 116(9):5464-5519, 2016.
- [44] Chen, X., Wu, G., Chen, J., Chen, X., Xie, Z., and Wang, X. Synthesis of “clean” and well-dispersive Pd nanoparticles with excellent electrocatalytic property on graphene oxide. *Journal of the American Chemical Society*, 133(11):3693-3695, 2011.
- [45] Chen, Y. L., Hu, Z. A., Chang, Y. Q., Wang, H. W., Zhang, Z. Y., Yang, Y. Y., and Wu, H. Y. Zinc oxide/reduced graphene oxide composites and electrochemical capacitance enhanced by homogeneous incorporation of reduced graphene oxide sheets in zinc oxide matrix. *The Journal of Physical Chemistry C*, 115(5):2563-2571, 2011.
- [46] Kim, H., Abdala, A. A., and Macosko, C. W. Graphene/polymer nanocomposites. *Macromolecules*, 43(16):6515-6530, 2010.
- [47] Wang, S., Goh, B. M., Manga, K. K., Bao, Q., Yang, P. and Loh, K. P. Graphene as atomic template and structural scaffold in the synthesis of

- graphene-organic hybrid wire with photovoltaic properties. *ACS Nano*, 4(10):6180-6186, 2010.
- [48] Wang, Y., Li, Z., Hu, D., Lin, C. T., Li, J. and Lin, Y. Aptamer/graphene oxide nanocomplex for in situ molecular probing in living cells. *Journal of the American Chemical Society*, 132(27):9274-9276, 2010.
- [49] Jahan, M., Bao, Q., and Loh, K. P. Electrocatalytically active graphene-porphyrin MOF composite for oxygen reduction reaction. *Journal of the American Chemical Society*, 134(15):6707-6713, 2012.
- [50] Yu, D. and Dai, L. Self-assembled graphene/carbon nanotube hybrid films for supercapacitors. *The Journal of Physical Chemistry Letters*, 1(2):467-470, 2009.
- [51] Vinodgopal, K., Neppolian, B., Lightcap, I. V., Grieser, F., Ashokkumar, M., and Kamat, P. V. Sonolytic design of graphene-Au nanocomposites. Simultaneous and sequential reduction of graphene oxide and Au (III). *The Journal of Physical Chemistry Letters*, 1(13):1987-1993, 2010.
- [52] Chen, J., Cui, X., Wang, Q., Wang, H., Zheng, X., Liu, C., Xue, T., Wang, S. and Zheng, W. One-pot photochemical synthesis of ultrathin Au nanocrystals on co-reduced graphene oxide and its application. *Journal of colloid and interface science*, 383(1):140-147, 2012.
- [53] Bai, R. G., Muthoosamy, K., Zhou, M., Ashokkumar, M., Huang, N. M., and Manickam, S. Sonochemical and sustainable synthesis of graphene-gold (G-Au) nanocomposites for enzymeless and selective electrochemical detection of nitric oxide. *Biosensors and Bioelectronics*, 87:622-629, 2017.
- [54] Zou, C. E., Yang, B., Bin, D., Wang, J., Li, S., Yang, P., Wang, C., Shiraishi, Y. and Du, Y. Electrochemical synthesis of gold nanoparticles decorated flower-like graphene for high sensitivity detection of nitrite. *Journal of colloid and interface science*, 488:135-141, 2017.
- [55] Huang, J., Zhang, L., Chen, B., Ji, N., Chen, F., Zhang, Y., and Zhang, Z. Nanocomposites of size-controlled gold nanoparticles and graphene oxide: formation and applications in SERS and catalysis. *Nanoscale*, 2(12):2733-2738, 2010.
- [56] Zhang, N., Qiu, H., Liu, Y., Wang, W., Li, Y., Wang, X., and Gao, J. Fabrication of gold nanoparticle/graphene oxide nanocomposites and their

- excellent catalytic performance. *Journal of Materials Chemistry*, 21(30):11080-11083, 2011.
- [57] Ramazani, A., Abrvash, M., Sadighian, S., Rostamizadeh, K., and Fathi, M. Preparation and characterization of curcumin loaded gold/graphene oxide nanocomposite for potential breast cancer therapy. *Research on Chemical Intermediates*, 44(12):7891-7904, 2018.
- [58] Yu, Y., Si, J., Yan, L., Li, M., and Hou, X. Enhanced nonlinear absorption and ultrafast carrier dynamics in graphene/gold nanoparticles nanocomposites. *Carbon*, 148:72-79, 2019.
- [59] Li, Y., Tang, L., and Li, J. Preparation and electrochemical performance for methanol oxidation of Pt/graphene nanocomposites. *Electrochemistry Communications*, 11(4):846-849, 2009.
- [60] Mazzaro, R., Boni, A., Valenti, G., Marcaccio, M., Paolucci, F., Ortolani, L., Morandi, V., Ceroni, P., and Bergamini, G. Uniform Functionalization of High-Quality Graphene with Platinum Nanoparticles for Electrocatalytic Water Reduction. *ChemistryOpen*, 4(3):268-273, 2015.
- [61] Ojani, R., Valiollahi, R., and Raoof, J. B. Comparison between graphene supported Pt hollow nanospheres and graphene supported Pt solid nanoparticles for hydrogen evolution reaction. *Energy*, 74:871-876, 2014.
- [62] Kim, K., Johnson, R. W., Tanskanen, J. T., Liu, N., Kim, M. G., Pang, C., Ahn, C., Bent, S. F., and Bao, Z. Selective metal deposition at graphene line defects by atomic layer deposition. *Nature communications*, 5:4781, 2014.
- [63] Que, L., Zhang, L., Wu, C., Zhang, Y., Pei, C., and Nie, F. Pt-decorated graphene network materials for supercapacitors with enhanced power density. *Carbon*, 145:281-289, 2019.
- [64] Liao, F., Shen, W., Sun, Y., Li, Y., Shi, H., and Shao, M. Nanosponge Pt modified graphene nanocomposites using silicon monoxides as a reducing agent: High efficient electrocatalysts for hydrogen evolution. *ACS Sustainable Chemistry & Engineering*, 6(11):15238-15244, 2018.
- [65] Feng, H., Liu, Y., and Li, J. Highly reduced graphene oxide supported Pt nanocomposites as highly efficient catalysts for methanol oxidation. *Chemical Communications*, 51(12):2418-2420, 2015.

- [66] Sun, S., Zhang, G., Gauquelin, N., Chen, N., Zhou, J., Yang, S., Chen, W., Meng, X., Geng, D., Banis, M. N., and Li, R. Single-atom catalysis using Pt/graphene achieved through atomic layer deposition. *Scientific reports*, 3:1775, 2013.
- [67] Woo, S., Lee, J., Park, S. K., Kim, H., Chung, T. D., and Piao, Y. Electrochemical codeposition of Pt/graphene catalyst for improved methanol oxidation. *Current Applied Physics*, 15(3):219-225, 2015.
- [68] Jiang, Y., Yan, Y., Chen, W., Khan, Y., Wu, J., Zhang, H., and Yang, D. Single-crystalline Pd square nanoplates enclosed by {100} facets on reduced graphene oxide for formic acid electro-oxidation. *Chemical Communications*, 52(99):14204-14207, 2016.
- [69] Iqbal, M., Li, C., Jiang, B., Hossain, M. S. A., Islam, M. T., Henzie, J., and Yamauchi, Y. Tethering mesoporous Pd nanoparticles to reduced graphene oxide sheets forms highly efficient electrooxidation catalysts. *Journal of Materials Chemistry A*, 5(40):21249-21256, 2017.
- [70] Scheuermann, G. M., Rumi, L., Steurer, P., Bannwarth, W., and Mülhaupt, R. Palladium nanoparticles on graphite oxide and its functionalized graphene derivatives as highly active catalysts for the Suzuki–Miyaura coupling reaction. *Journal of the American Chemical Society*, 131(23):8262-8270, 2009.
- [71] Johnson, J. L., Behnam, A., Pearton, S. J., and Ural, A. Hydrogen sensing using Pd-functionalized multi-layer graphene nanoribbon networks. *Advanced materials*, 22(43):4877-4880, 2010.
- [72] Sun, J., Fu, Y., He, G., Sun, X., and Wang, X. Catalytic hydrogenation of nitrophenols and nitrotoluenes over a palladium/graphene nanocomposite. *Catalysis Science & Technology*, 4(6):1742-1748, 2014.
- [73] Jiang, Y., Lu, Y., Li, F., Wu, T., Niu, L. and Chen, W. Facile electrochemical codeposition of “clean” graphene-Pd nanocomposite as an anode catalyst for formic acid electrooxidation. *Electrochemistry Communications*, 19:21-24, 2012.
- [74] Li, H., Chang, G., Zhang, Y., Tian, J., Liu, S., Luo, Y., Asiri, A. M., Al-Youbi, A. O., and Sun, X. Photocatalytic synthesis of highly dispersed Pd nanoparticles on reduced graphene oxide and their application in methanol



- electro-oxidation. *Catalysis Science & Technology*, 2(6):1153-1156, 2012.
- [75] Pasricha, R., Gupta, S., and Srivastava, A. K. A facile and novel synthesis of Ag-graphene-based nanocomposites. *Small*, 5(20):2253-2259, 2009.
- [76] Zheng, H., Ni, D., Yu, Z., and Liang, P. Preparation of SERS-active substrates based on graphene oxide/silver nanocomposites for rapid detection of L-Theanine. *Food chemistry*, 217:511-516, 2017.
- [77] Zhang, Y., Liu, S., Wang, L., Qin, X., Tian, J., Lu, W., Chang, G., and Sun, X. One-pot green synthesis of Ag nanoparticles-graphene nanocomposites and their applications in SERS, H<sub>2</sub>O<sub>2</sub>, and glucose sensing. *RSC Advances*, 2(2):538-545, 2012.
- [78] He, K., Zeng, Z., Chen, A., Zeng, G., Xiao, R., Xu, P., Huang, Z., Shi, J., Hu, L., and Chen, G. Advancement of Ag-graphene based nanocomposites: an overview of synthesis and its applications. *Small*, 14(32):1800871, 2018.
- [79] Das, T. K., Bhawal, P., Ganguly, S., Mondal, S., and Das, N. C. A facile green synthesis of amino acid boosted Ag decorated reduced graphene oxide nanocomposites and its catalytic activity towards 4-nitrophenol reduction. *Surfaces and Interfaces*, 13:79-91, 2018.
- [80] Jaworski, S., Wierzbicki, M., Sawosz, E., Jung, A., Gielerak, G., Biernat, J., Jaremek, H., Łojkowski, W., Woźniak, B., Wojnarowicz, J. and Stobiński, L. Graphene oxide-based nanocomposites decorated with silver nanoparticles as an antibacterial agent. *Nanoscale research letters*, 13(1):116, 2018.
- [81] Liu, X., Yao, K. X., Meng, C., and Han, Y. Graphene substrate-mediated catalytic performance enhancement of Ru nanoparticles: a first-principles study. *Dalton Transactions*, 41(4):1289-1296, 2012.
- [82] Li, G., Nagasawa, H., Kanezashi, M., Yoshioka, T., and Tsuru, T. Graphene nanosheets supporting Ru nanoparticles with controlled nanoarchitectures form a high-performance catalyst for CO<sub>x</sub>-free hydrogen production from ammonia. *Journal of Materials Chemistry A*, 2(24):9185-9192, 2014.
- [83] Li, G., Kanezashi, M., and Tsuru, T. Catalytic ammonia decomposition over high-performance Ru/Graphene nanocomposites for efficient CO<sub>x</sub>-free hydrogen production. *Catalysts*, 7(1):23, 2017.
- [84] Upare, P. P., Lee, M., Lee, S. K., Yoon, J. W., Bae, J., Hwang, D. W., Lee, U. H., Chang, J. S., and Hwang, Y. K. Ru nanoparticles supported graphene oxide

- catalyst for hydrogenation of bio-based levulinic acid to cyclic ethers. *Catalysis Today*, 265:174-183, 2016.
- [85] Chandra, S., Bag, S., Bhar, R., and Pramanik, P. Sonochemical synthesis and application of rhodium-graphene nanocomposite. *Journal of Nanoparticle Research*, 13(7):2769-2777, 2011.
- [86] Tang, Z., Shen, S., Zhuang, J., and Wang, X. Noble-metal-promoted three-dimensional macroassembly of single-layered graphene oxide. *Angewandte Chemie International Edition*, 49(27):4603-4607, 2010.
- [87] Chen, Y., Lei, Z., Wu, H., Zhu, C., Gao, P., Ouyang, Q., Qi, L. H. and Qin, W. Electromagnetic absorption properties of graphene/Fe nanocomposites. *Materials Research Bulletin*, 48(9):3362-3366, 2013.
- [88] Guo, J., Wang, R., Tjiu, W. W., Pan, J., and Liu, T. Synthesis of Fe nanoparticles@ graphene composites for environmental applications. *Journal of hazardous materials*, 225:63-73, 2012.
- [89] Stein, M., Wieland, J., Steurer, P., Tölle, F., Mülhaupt, R., and Breit, B. Iron Nanoparticles Supported on Chemically-Derived Graphene: Catalytic Hydrogenation with Magnetic Catalyst Separation. *Advanced Synthesis & Catalysis*, 353(4):523-527, 2011.
- [90] Zou, Y. H., Liu, H. B., Yang, L., and Chen, Z. Z. The influence of temperature on magnetic and microwave absorption properties of Fe/graphite oxide nanocomposites. *Journal of magnetism and magnetic materials*, 302(2):343-347, 2006.
- [91] Luo, J., Jiang, S., Zhang, H., Jiang, J., and Liu, X. A novel non-enzymatic glucose sensor based on Cu nanoparticle modified graphene sheets electrode. *Analytica chimica acta*, 709:47-53, 2012.
- [92] Pavithra, C. L., Sarada, B. V., Rajulapati, K. V., Rao, T. N., and Sundararajan, G. A new electrochemical approach for the synthesis of copper-graphene nanocomposite foils with high hardness. *Scientific reports*, 4:4049, 2014.
- [93] Hwang, J., Yoon, T., Jin, S. H., Lee, J., Kim, T. S., Hong, S. H., and Jeon, S. Enhanced mechanical properties of graphene/copper nanocomposites using a molecular-level mixing process. *Advanced materials*, 25(46):6724-6729, 2013.
- [94] Zhou, C., Szpunar, J. A., and Cui, X. Synthesis of Ni/graphene nanocomposite for hydrogen storage. *ACS applied materials & interfaces*, 8(24):15232-15241,

- 2016.
- [95] Cao, Y., Su, Q., Che, R., Du, G., and Xu, B. One-step chemical vapor synthesis of Ni/graphene nanocomposites with excellent electromagnetic and electrocatalytic properties. *Synthetic Metals*, 162(11-12):968-973, 2012.
- [96] Wu, Y. G., Wen, M., Wu, Q. S., and Fang, H. Ni/graphene nanostructure and its electron-enhanced catalytic action for hydrogenation reaction of nitrophenol. *The Journal of Physical Chemistry C*, 118(12):6307-6313, 2014.
- [97] Li, N., Cao, M., Wu, Q., and Hu, C. A facile one-step method to produce Ni/graphene nanocomposites and their application to the thermal decomposition of ammonium perchlorate. *CrystEngComm*, 14(2):428-434, 2012.
- [98] Yeh, C. C. and Chen, D. H. Ni/reduced graphene oxide nanocomposite as a magnetically recoverable catalyst with near infrared photothermally enhanced activity. *Applied Catalysis B: Environmental*, 150:298-304, 2014.
- [99] Yang, S., Cui, G., Pang, S., Cao, Q., Kolb, U., Feng, X., Maier, J., and Müllen, K. Fabrication of cobalt and cobalt oxide/graphene composites: Towards high-performance anode materials for lithium ion batteries. *ChemSusChem: Chemistry & Sustainability Energy & Materials*, 3(2):236-239, 2010.
- [100] Paul, H. and Mohanta, D. Hydrazine reduced exfoliated graphene/graphene oxide layers and magnetoconductance measurements of Ge-supported graphene layers. *Applied Physics A*, 103(2):395-402, 2011.
- [101] Ren, J. G., Wu, Q. H., Tang, H., Hong, G., Zhang, W., and Lee, S. T. Germanium-graphene composite anode for high-energy lithium batteries with long cycle life. *Journal of Materials Chemistry A*, 1(5):1821-1826, 2013.
- [102] Wang, G., Wang, B., Wang, X., Park, J., Dou, S., Ahn, H., and Kim, K. Sn/graphene nanocomposite with 3D architecture for enhanced reversible lithium storage in lithium ion batteries. *Journal of Materials Chemistry*, 19(44):8378-8384, 2009.
- [103] Hassan, H. M., Abdelsayed, V., Abd El Rahman, S. K., AbouZeid, K. M., Turner, J., El-Shall, M. S., Al-Resayes, S. I., and El-Azhary, A. A. Microwave synthesis of graphene sheets supporting metal nanocrystals in aqueous and organic media. *Journal of Materials Chemistry*, 19(23):3832-3837, 2009.

- [104] Du, J., Lai, X., Yang, N., Zhai, J., Kisailus, D., Su, F., Wang, D., and Jiang, L. Hierarchically ordered macro-mesoporous TiO<sub>2</sub>-graphene composite films: improved mass transfer, reduced charge recombination, and their enhanced photocatalytic activities. *ACS nano*, 5(1):590-596, 2010.
- [105] Zhu, C., Guo, S., Wang, P., Xing, L., Fang, Y., Zhai, Y., and Dong, S. One-pot, water-phase approach to high-quality graphene/TiO<sub>2</sub> composite nanosheets. *Chemical communications*, 46(38):7148-7150, 2010.
- [106] Zhou, G., Wang, D. W., Li, F., Zhang, L., Li, N., Wu, Z. S., Wen, L., Lu, G. Q., and Cheng, H. M. Graphene-wrapped Fe<sub>3</sub>O<sub>4</sub> anode material with improved reversible capacity and cyclic stability for lithium ion batteries. *Chemistry of Materials*, 22(18):5306-5313, 2010.
- [107] Wang, D., Kou, R., Choi, D., Yang, Z., Nie, Z., Li, J., Saraf, L. V., Hu, D., Zhang, J., Graff, G. L., and Liu, J. Ternary self-assembly of ordered metal oxide-graphene nanocomposites for electrochemical energy storage. *ACS nano*, 4(3):1587-1595, 2010.
- [108] Perera, S. D., Mariano, R. G., Vu, K., Nour, N., Seitz, O., Chabal, Y., and Balkus Jr, K. J. Hydrothermal synthesis of graphene-TiO<sub>2</sub> nanotube composites with enhanced photocatalytic activity. *ACS Catalysis*, 2(6):949-956, 2012.
- [109] Low, S. S., Tan, M. T., Loh, H. S., Khiew, P. S., and Chiu, W. S. Facile hydrothermal growth graphene/ZnO nanocomposite for development of enhanced biosensor. *Analytica chimica acta*, 903:131-141, 2016.
- [110] Du, D., Liu, J., Zhang, X., Cui, X., and Lin, Y. One-step electrochemical deposition of a graphene-ZrO<sub>2</sub> nanocomposite: Preparation, characterization and application for detection of organophosphorus agents. *Journal of Materials Chemistry*, 21(22):8032-8037, 2011.
- [111] Yan, J., Fan, Z., Wei, T., Qian, W., Zhang, M., and Wei, F. Fast and reversible surface redox reaction of graphene-MnO<sub>2</sub> composites as supercapacitor electrodes. *Carbon*, 48(13):3825-3833, 2010.
- [112] Yan, J., Wei, T., Qiao, W., Shao, B., Zhao, Q., Zhang, L., and Fan, Z. Rapid microwave-assisted synthesis of graphene nanosheet/Co<sub>3</sub>O<sub>4</sub> composite for supercapacitors. *Electrochimica Acta*, 55(23):6973-6978, 2010.

- [113] Yang, Z., Hao, X., Chen, S., Ma, Z., Wang, W., Wang, C., Yue, L., Sun, H., Shao, Q., Murugadoss, V., and Guo, Z. Long-term antibacterial stable reduced graphene oxide nanocomposites loaded with cuprous oxide nanoparticles. *Journal of colloid and interface science*, 533:13-23, 2019.
- [114] Zhao, Y., Song, X., Song, Q., and Yin, Z. A facile route to the synthesis copper oxide/reduced graphene oxide nanocomposites and electrochemical detection of catechol organic pollutant. *CrystEngComm*, 14(20):6710-6719, 2012.
- [115] Zhu, X., Zhu, Y., Murali, S., Stoller, M. D., and Ruoff, R. S. Nanostructured reduced graphene oxide/Fe<sub>2</sub>O<sub>3</sub> composite as a high-performance anode material for lithium ion batteries. *ACS nano*, 5(4):3333-3338, 2011.
- [116] Zhang, K., Li, H., Xu, X., and Yu, H. Synthesis of reduced graphene oxide/NiO nanocomposites for the removal of Cr (VI) from aqueous water by adsorption. *Microporous and Mesoporous Materials*, 255:7-14, 2018.
- [117] Fan, Y., Wang, L., Li, J., Li, J., Sun, S., Chen, F., Chen, L., and Jiang, W. Preparation and electrical properties of graphene nanosheet/Al<sub>2</sub>O<sub>3</sub> composites. *Carbon*, 48(6):1743-1749, 2010.
- [118] Liu, C., Zang, J., Yan, S., Yuan, Y., Xu, H., Yang, G., Wang, Y., Lu, J., and Xu, X. Uniform dispersion of nano-Al<sub>2</sub>O<sub>3</sub> particles in the 3D graphene network of ternary nanocomposites. *Ceramics International*, 45(3):3407-3413, 2019.
- [119] Wu, Z. S., Wang, D. W., Ren, W., Zhao, J., Zhou, G., Li, F., and Cheng, H. M. Anchoring hydrous RuO<sub>2</sub> on graphene sheets for high-performance electrochemical capacitors. *Advanced Functional Materials*, 20(20):3595-3602, 2010.
- [120] Cui, Y., Zhao, Y., Chen, H., Wei, K., Ni, S., Cui, Y., and Shi, S. First-principles study of MoO<sub>3</sub>/graphene composite as cathode material for high-performance lithium-ion batteries. *Applied Surface Science*, 433:1083-1093, 2018.
- [121] Wang, S., Yu, D., Dai, L., Chang, D. W., and Baek, J. B. Polyelectrolyte-functionalized graphene as metal-free electrocatalysts for oxygen reduction. *ACS nano*, 5(8):6202-6209, 2011.



- [122] Chen, P., Xiao, T. Y., Li, H. H., Yang, J. J., Wang, Z., Yao, H. B., and Yu, S. H. Nitrogen-doped graphene/ZnSe nanocomposites: hydrothermal synthesis and their enhanced electrochemical and photocatalytic activities. *ACS Nano*, 6(1):712-719, 2011.
- [123] Sarkar, S., Niyogi, S., Bekyarova, E., and Haddon, R. C. Organometallic chemistry of extended periodic  $\pi$ -electron systems: hexahapto-chromium complexes of graphene and single-walled carbon nanotubes. *Chemical Science*, 2(7):1326-1333, 2011.
- [124] Frank, B., Blume, R., Rinaldi, A., Trunschke, A. and Schlögl, R. Oxygen insertion catalysis by  $sp^2$  carbon. *Angewandte Chemie International Edition*, 50(43):10226-10230, 2011.
- [125] Dreyer, D. R., Jia, H. P., and Bielawski, C. W. Graphene oxide: a convenient carbocatalyst for facilitating oxidation and hydration reactions. *Angewandte Chemie International Edition*, 49(38):6813-6816, 2010.
- [126] Navalon, S., Dhakshinamoorthy, A., Alvaro, M., and Garcia, H. Carbocatalysis by graphene-based materials. *Chemical reviews*, 114(12):6179-6212, 2014.
- [127] Ji, J., Zhang, G., Chen, H., Wang, S., Zhang, G., Zhang, F., and Fan, X. Sulfonated graphene as water-tolerant solid acid catalyst. *Chemical Science*, 2(3):484-487, 2011.
- [128] Dhakshinamoorthy, A., Primo, A., Concepcion, P., Alvaro, M., and Garcia, H. Doped graphene as a metal-free carbocatalyst for the selective aerobic oxidation of benzylic hydrocarbons, cyclooctane and styrene. *Chemistry—A European Journal*, 19(23):7547-7554, 2013.
- [129] Liu, J., Ma, Q., Huang, Z., Liu, G. and Zhang, H. Recent Progress in Graphene-Based Noble-Metal Nanocomposites for Electrocatalytic Applications. *Advanced Materials*, 31(9):1800696, 2019.
- [130] Kou, R., Shao, Y., Wang, D., Engelhard, M. H., Kwak, J. H., Wang, J., Viswanathan, V. V., Wang, C., Lin, Y., Wang, Y., and Aksay, I. A. Enhanced activity and stability of Pt catalysts on functionalized graphene sheets for electrocatalytic oxygen reduction. *Electrochemistry Communications*, 11(5):954-957, 2009.

- [131] Liang, Y., Li, Y., Wang, H., Zhou, J., Wang, J., Regier, T., and Dai, H. Co<sub>3</sub>O<sub>4</sub> nanocrystals on graphene as a synergistic catalyst for oxygen reduction reaction. *Nature materials*, 10(10):780, 2011.
- [132] Yoo, E., Okata, T., Akita, T., Kohyama, M., Nakamura, J., and Honma, I. Enhanced electrocatalytic activity of Pt subnanoclusters on graphene nanosheet surface. *Nano letters*, 9(6):2255-2259, 2009.
- [133] Huang, W., Wang, H., Zhou, J., Wang, J., Duchesne, P. N., Muir, D., Zhang, P., Han, N., Zhao, F., Zeng, M., and Zhong, J. Highly active and durable methanol oxidation electrocatalyst based on the synergy of platinum-nickel hydroxide-graphene. *Nature communications*, 6:10035, 2015.
- [134] Lightcap, I. V., Kosel, T. H., and Kamat, P. V. Anchoring semiconductor and metal nanoparticles on a two-dimensional catalyst mat. Storing and shuttling electrons with reduced graphene oxide. *Nano letters*, 10(2):577-583, 2010.
- [135] Zhang, H., Lv, X., Li, Y., Wang, Y., and Li, J. P25-graphene composite as a high performance photocatalyst. *ACS nano*, 4(1):380-386, 2009.
- [136] Shende, T. P., Bhanvase, B. A., Rathod, A. P., Pinjari, D. V., and Sonawane, S. H. Sonochemical synthesis of Graphene-Ce-TiO<sub>2</sub> and Graphene-Fe-TiO<sub>2</sub> ternary hybrid photocatalyst nanocomposite and its application in degradation of Crystal Violet Dye. *Ultrasonics sonochemistry*, 41:582-589, 2018.
- [137] Iqbal, M. Z., and Abdala, A. A. Thermally reduced graphene: synthesis, characterization and dye removal applications. *RSC Advances*, 3(46):24455-24464, 2013.
- [138] Zhao, J., Ren, W., and Cheng, H. M. Graphene sponge for efficient and repeatable adsorption and desorption of water contaminations. *Journal of Materials Chemistry*, 22(38):20197-20202, 2012.
- [139] Wang, B., Luo, B., Liang, M., Wang, A., Wang, J., Fang, Y., Chang, Y., and Zhi, L. Chemical amination of graphene oxides and their extraordinary properties in the detection of lead ions. *Nanoscale*, 3(12):5059-5066, 2011.
- [140] Xia, X., Hao, Q., Lei, W., Wang, W., Sun, D., and Wang, X. Nanostructured ternary composites of graphene/Fe<sub>2</sub>O<sub>3</sub>/polyaniline for high-performance supercapacitors. *Journal of Materials Chemistry*, 22(33):16844-16850, 2012.
- [141] Ye, S., Feng, J., and Wu, P. Deposition of three-dimensional graphene aerogel on nickel foam as a binder-free supercapacitor electrode. *ACS applied*

*materials & interfaces*, 5(15):7122-7129, 2013