

## CHAPTER 2

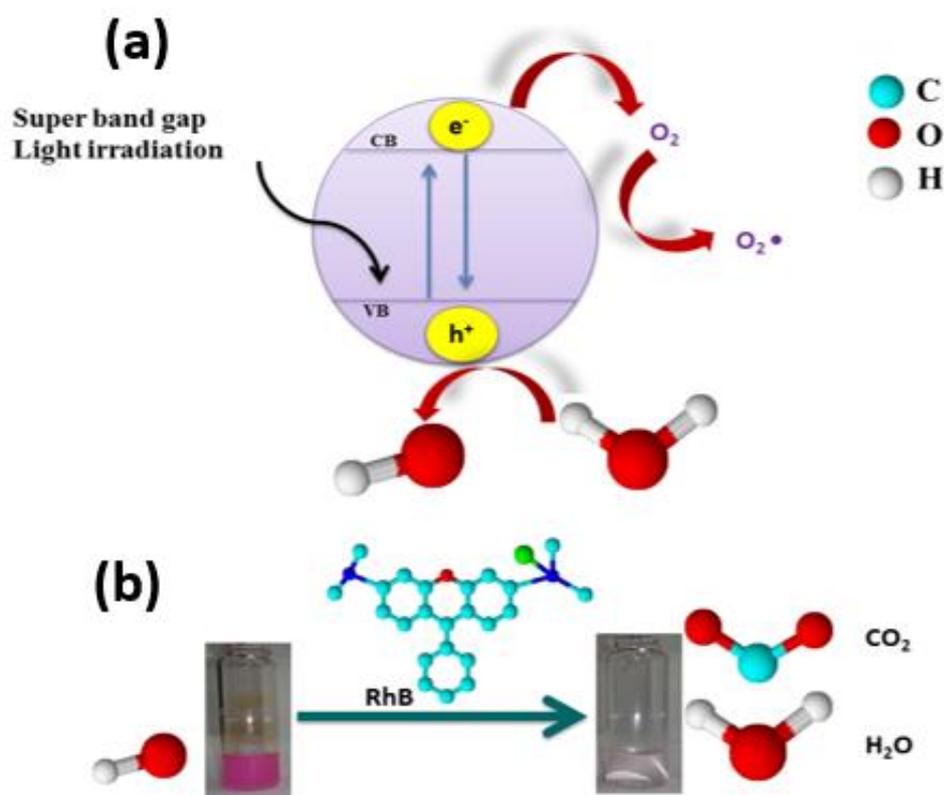
### LITERATURE REVIEW

#### 2.1 HISTORY OF PHOTOCATALYST

A term “photocatalyst” has various definitions however, in short, we can define that “a chemical reaction induced by photo-absorption of solid material”. The photocatalyst are unchanged before and after the reaction. Most of the research articles indicate that Honda–Fujishima effect is the first discovery of the photocatalytic effect which was published in Nature 1972<sup>1</sup>. Actually, photocatalytic decomposition of organic compound by TiO<sub>2</sub> already reported before discovery of this effect. TiO<sub>2</sub> was used as white pigment in earlier days since it is a low-cost material, light stable (visible light) with eco-friendly nature. In 20<sup>th</sup> century, TiO<sub>2</sub> incorporated with fabric and it was used for degradation propose. In 1938, Vacuo “et al.” discovered the photobleaching of dye by TiO<sub>2</sub>. Further, the degradation mechanism also describes that UV absorbed TiO<sub>2</sub> produce the surface reactive oxygen species which are known as photosensitizers. Subsequently, in 1956, Mashio “et al.” reported on “Auto-oxidation by TiO<sub>2</sub> photocatalyst”<sup>2</sup>. It has been found that the H<sub>2</sub>O<sub>2</sub> is produced during the photocatalytic reaction. As said in the beginning of this paragraph, Honda–Fujishima effect was published in 1972. The main outcome of this effect is “water is decomposed by TiO<sub>2</sub> electrode while irradiated with UV light”. After the discovery of these incredible effects, the photocatalytic research was exponentially geared up which has been evident from recent scientific publications.

## 2.2 MECHANISM OF PHOTOCATALYSIS

When the surface of the semiconductor irradiated with super-band light, the loosely bonded valence bond electrons move to the conduction band. The electron undergoes the reduction reaction with surface adsorbed  $O_2$  and the holes subjected to oxidation reaction with water molecules to produce free reactive radicals. In mean time, the electron-hole pair recombination takes place via radiative transition<sup>3</sup>. The schematic mechanism of semiconductor photocatalysis was shown in fig 2.1. The overall process and reactions are happened in femto seconds interval.



**Figure. 2.1** (a) Schematic mechanism of semiconductor photocatalysis for organic dye degradation (b) colour change is observed during dye degradation.

The produced free radicals have been utilized for organic molecule degradation, biological inactivation and fine chemical product synthesis so on.

### **2.3 FACTORS AFFECTING THE SEMICONDUCTOR PHOTOCATALYSIS EFFICIENCY**

At present, the semiconductor photocatalytic efficiency is not par with expectation level. Since, the catalytic efficiency dependence on several factors such as surface area of the catalyst, crystalline nature, availability of the active sites, band gap, band position, light absorbance efficiency (quantum efficiency)<sup>4</sup>, production and separation of charge carriers. Further, the natural sun light contains 45% of visible region, which is much higher than to UV. Nevertheless, the pioneer photocatalyst materials like TiO<sub>2</sub> and ZnO are performed well at UV region<sup>5</sup>. Therefore, most of the research groups are intensively working to solve the each challenge; the separation of charge carrier is one of an important issue in semiconductor photocatalytic field. A number of efforts have been made towards to decrease the recombination of photo-induced electro-hole. In which metal doped and hybrid semiconductor structures were developed to curtail the issues. The hybrid structures are classified as semiconductor–semiconductor (S-S), semiconductor–metal (S-M), the semiconductor–carbon (S-C) and the multicomponent hybrid. The hybrid structure forms a heterojunction between two components, so it is called as hybrid structures or heterojunctions. The S-S heterojunction can be categorized into two types i.e. p-n heterojunction and non p-n heterojunction. Another important heterostructure is S-M heterojunction. Till today, there are many heterojunctions reported such as Au/TiO<sub>2</sub>, Ag/AgCl, Ag/AgBr. The S-C heterojunction includes activated carbon, carbon nanotubes

(CNTs) and graphene heterostructures. The latest developed structure is multicomponent heterojunction which is composed of S-metal-S structure<sup>4</sup>.

Dye is a solid colored compound which has been used in many applications like textiles, plastics and paint industries<sup>6</sup>. Dye can be classified as natural and synthetic dye, in which natural dye can be obtained from natural plant, leafs and fruits extract. The brief classification of dye and their applications are given in table 1.

**Table: 2.1.** Classification of organic dye and their applications

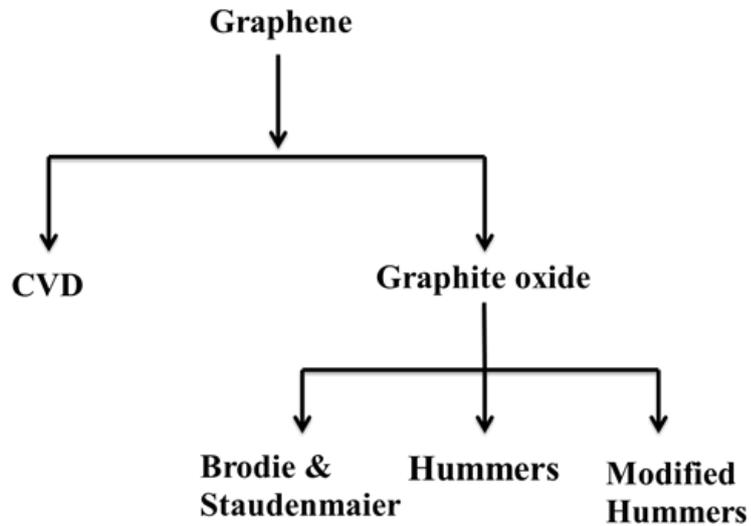
<b>Classification of dyes</b>	<b>Description of dyes</b>	<b>Application</b>	<b>Example of dyes</b>
Natural	Synthesis from plant	Textiles	Indigo
Synthetic	Human made organic compounds	Plastics, paint	~
Acid	Anionic charge compound	Colour basic tissue proteins	Acid yellow
Basic	Cationic charge compound	dyeing Acrylic Fibres	Methyl violet
Reactive	Chromospheres contain substituent	Cotton dyeing	Reactive Red 120
Sulfur	Sulfur compound was attached with chromospheres	Fabric dyeing	Sulfur Black 1
Disperse	Disperse dyes are less soluble in water	Dyeing of Polyester Fabric	Disperse Yellow 26

The usage of dyes increased exponentially every year; hence the water contamination also linearly increasing day to day. Consequently, the elimination of dye from waste water is an essential issue. Plenty of traditional waste water processes have been reported so far such as adsorption, oxidation degradation, photo-fenton, photocatalysis, sonocatalysis, nano-filtration electro-coagulation and desalination<sup>7,8</sup>. Each method has its individual merit and demerit. Compared with other methods, semiconductor photocatalysis has some unique features such as environmental friendly, low cost and it has complete ability to eliminate the pollutants.

## **2.4 TWO DIMENSIONAL CARBON MATERIALS**

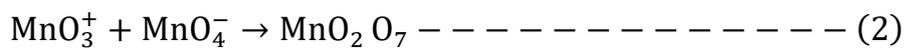
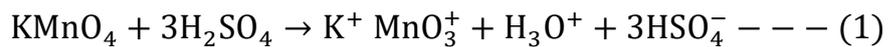
More than 70 years ago, a theory was proposed on low dimensional crystals by Landau and Peierls. “Thermodynamically two dimensional materials are unstable due to the thermal fluctuation since the melting point has been reduced when decreasing the thin film thickness and became an unstable while reducing thinfilm thickness furthers too few atomic”. In 2004, Prof. Andre Geim and Prof. Konstantin Novoselov (Manchester University) won the Noble prize for the successful isolation of a single layer of graphite at room temperature which is called as graphene<sup>9</sup>. Graphene (GR) is made up of a single layer of graphite in which carbon atoms were arranged in a hexagonal lattice of honeycomb structure<sup>10</sup>. In GR, carbon atoms have  $sp^2$  hybridization which shows anomalous physical properties than that of all three dimensional carbon allotropes at room temperature. As a rising star, GR has been rapidly growing in the field of electronics, biotechnology, energy and environmental sectors<sup>11</sup>. There are few methods which for synthesizing the high crystalline graphene sheet which includes chemical vapor deposition (CVD), oxidation-exfoliation of graphite and reduction of graphene

oxide via reducing agent and so on<sup>12</sup>. In CVD process methane ( $\text{CH}_4$ ) is used as a hydrocarbon source and copper (Cu) foil has been used as a substrate for graphene growing. The growth mechanism of graphene depends on certain features such as nature and thickness of the substrate (copper or nickel), and the growth temperature. There are some limitation in this process (i.e.) CVD preparation process involves high cost and limited size substrate. Amongst, graphene oxide (GO) is the chief precursor for graphene preparation and it can be synthesized using simple graphite oxidization-exfoliation process<sup>13</sup>. Graphene oxide is stable and hydrophilic compound which exhibits black color in nature. GO has strong functional groups at the edges as well as plane carbon atoms on the either side of the sheet, which is the responsible for exciting properties<sup>12</sup>. Physicist found that from theoretical as well as experimental evidence, GO acts as a wide band gap semiconductor (insulator) at room temperature and its optical band gap is tunable (insulator- semiconductor) by varying the oxidation level. Graphene oxide has been synthesized from graphite by different routes like Brodie, Staudenmaier, Hummers, modified Hummers and improved synthesized methods<sup>14</sup>. The former methods use  $\text{KClO}_3$  (Potassium chloride) and  $\text{HNO}_3$  (Nitric oxide) as oxidant to oxidize the graphite. In Hummers method  $\text{H}_2\text{SO}_4$  and  $\text{KMnO}_4$  are used as oxidizing agents. Recently Marcano 'et.al.' (2010) reported an alternative method for Hummers route which is claimed as an environmental friendly method. Herein 9:1 ratio of  $\text{H}_2\text{SO}_4/\text{H}_3\text{PO}_4$  mixture is used as oxidizing agent resulting highly oxidized graphite material than to any other methods<sup>15</sup>. However, most of the research group is following the modified Hummers method due to the gram scale production and utility of low cost<sup>16</sup>. The various preparation method of graphene was given in following flow chart.



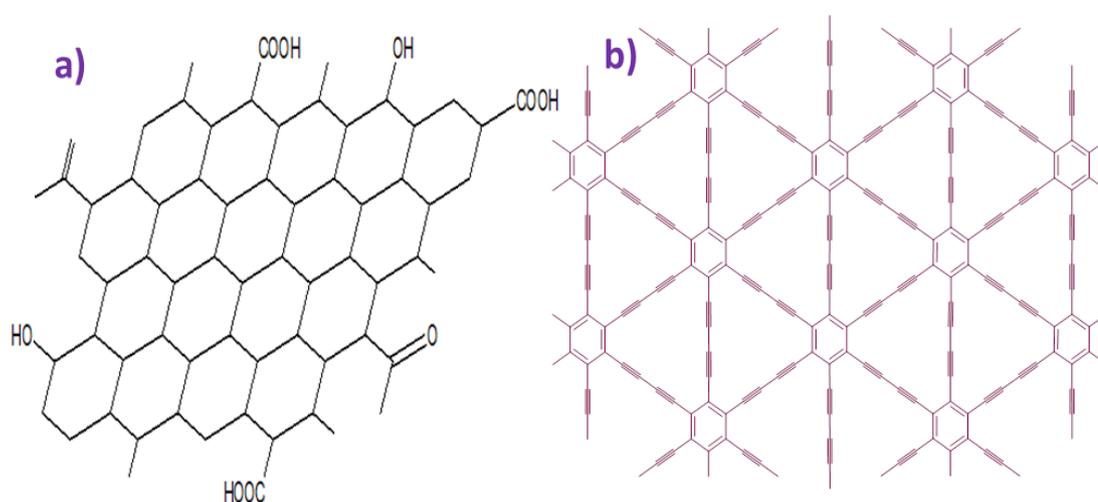
**Figure. 2.2** Flow chart of various preparation route of graphene nanosheets.

On the other hand, different mechanisms were proposed for graphite oxidation via Hummer’s method<sup>17</sup>. D.R. Dreyer ‘et al.’ in his review clarified that the basic reaction of Hummer’s method is given as follows:



Till today, the structure of GO is controversial due to the different structure and models proposed by diverse research groups namely Hofmann, Ruess, Scholz-bohem, Nakajima-Matsuo, Lurf-kinowski and Dekany ‘et al.’ However, the GO structure is highly depends on source of graphite and the oxidation material. Apart from that, the synthesis and identifying the new properties of a novel stable form of 2D carbon is the main goal for developing a new technology. Carbon has three different hybridization, including  $sp$ ,  $sp^2$  and  $sp^3$ . Using these important

factors, new different properties of a carbon allotrope are to be discovered. Graphdiyne (GD) was proposed several years ago and considerable effort has been made for constructing the GD structure<sup>18</sup>. GD is one of the leading 2D carbon allotrope. Herein  $sp$  and  $sp^2$  hybridize carbon atoms and diacetylenic linkages between the two adjacent carbons are formed, which makes them a hexagonal GD structure<sup>19</sup>.



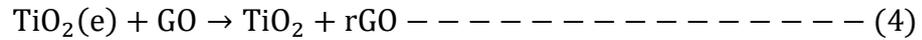
**Figure. 2.3** Chemical structure of (a) Graphene and (b) Graphdiyne.

The DFT coupled with Boltzmann transport equation found that GD has the bandgap in the range of 0.47-1.12 eV and the electrical conductivity is similar to silicon ( $2.56 \times 10^{-1} \text{ S}\cdot\text{m}^{-1}$ ), in-plane electron mobility on the order of  $10^5 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  at room temperature which are evidently proving that GD shows semiconductor behavior. Recently, GD has been synthesized via Glaser-hay coupling mechanism over the copper surface like as thin film (Li 2010). After discovery of graphene, the considerable attention paid for the preparation of other

two-dimensional materials. Non-carbon based materials also being explored. The low-dimensional nanostructures attracted much because these materials provide high surface area to volume ratio, good thermal conductivity, strongest, ultrathin with excellent optical transmittance, high chemical stability, strong electron affinity and ballistic carrier transport. The above said unique properties of two-dimensional materials (graphene and graphdiyne) made it a rising star material for most of the scientific field. Chemical structure of graphene and graphdiyne was shown in fig 2.3.

## **2.5 REDUCTION OF GRAPHENE OXIDE**

Reduction of GO is highly important process for using conventional application and the reduced form of GO is called as reduced graphene-oxide or graphene (rGO). Ample of methods has been reported in the view of high conductivity, low edge defect sheet, low cost and environmental eco-friendly techniques. One of most important process is photocatalytic reduction of GO in the presence of light<sup>20</sup>. UV assisted rGO synthesis is a less toxic method compared to other chemical approaches so that it called as green approach for GR synthesis. Some of the other methods have fewer drawbacks such as releasing of toxic gas, high temperature and huge economical cost. Considering these aspects, UV assisted GO reduction is a good replacement method. The brief mechanism of the photocatalytic graphene synthesis is when semiconductor excited by the light photon with equal or higher than to the band gap energy, the valence band electrons in the semiconductor gets excited and the same is injected into the GO lattice which will reduce the GO into rGO. From that, physical contacts occur due to the electron transition between semiconductor to GO. The reduction mechanism is given as follows (Y.P. Zhang 'et al.' 2011)<sup>21</sup>.



Hydrothermal is a facile technique for synthesizing different metal oxides, metal sulphide nanoparticles with desirable shape and size. The hydrothermal process is carried out in closed container, so that the water goes to the boiling point under high pressure and heating. When the water attains the supercritical stage and it can reduce the GO sheet. Dubin ‘et al.’ proposed a revised hydrothermal method in which N-methyl-2-pyrrolidinone used as solvent. The resultant reduced material C/O ratio is 5.15. On the contrary, Wang et al received a highest C/O ratio 14.3 by using N, N-dimethyl-formamide as a solvent. D. Yang ‘et al.’ proposed the thermal reduction of GO where oxygen containing functional groups are reduced and decomposed into gas. Apart from that, thermal annealing can also reduce the GO powder at the temperature less than 2000 °C (Wu Z. S, 2009). Later, the microwave heating was used for reduction of GO powder which has been achieved within 1 min in ambient conditions (Y. Zhu ‘et al.’ 2010). Electrochemical reduction is proposed for GO reduction without any chemical agent. The electrochemical reduction was carried out with water buffer solution where the electron exchange occurs between electrode and GO resulting reduction of GO into rGO (M. Zhou ‘et al.’ 2009).

## **2.6 SYNTHESIS OF GRAPHENE METAL OXIDE NANOHYBRID**

Graphene-metal oxide nanohybrid has been synthesized by using various techniques including hydrothermal, microwave assisted, UV-assisted, sonochemical, mechanical mixing, simple chemical, combination of sonochemical and hydrothermal method. Amongst, the hydrothermal and microwave methods

reduce the graphene oxide into graphene and can ensure good binding between the components. In case of mechanical mixing, additional reducing agent is used for reduction.

## **2.7. HYDROTHERMAL/SOLVOTHERMAL METHOD**

Hydrothermal is a facile technique for synthesizing different types of metal oxides, metal sulfide nanoparticles in past few years. In this approach, we can control the temperature as well as the pressure, so that the morphology can be tuned. Apart from hydrothermal process, microwave and ultra-sonication irradiation can be combined to generate graphene-semiconductor hybrid. Ahmad et al. demonstrated that the hydrothermally synthesized ZnO-graphene composite showed less band gap in comparison with pure ZnO and found improved visible light absorption than bare ZnO. Some recent and important hydrothermally based synthesized graphene-metal oxide composite's parameters such as reaction time, particle size and the reaction temperatures are given in table 2.2.

## **2.8 SONOCHEMICAL SYNTHESIS OF GRAPHENE METAL OXIDE HYBRID**

The sonochemical method is a prime technique which has been used for the synthesis of nanoparticle in gram scale production. Sonochemical approach is one of the green methods utilized for the synthesis of graphene-metal oxide composite. As per earlier report, GO can be reduced in the presence of ultrasound without any additives. During irradiation, the hotspot reaction and bubble formation produce local temperature up to 1000 °C and high pressure 1000 atm due to which the chemical reaction is much faster. This high temperature and pressure produce

the several chemical and physical effects which results the existing morphology. Some of the interesting morphology of rGO-ZnO composite via sonochemical approach reported by Q.P. Luo et al.<sup>27</sup>. In sonochemical technique, hollow sphere ZnO-rGO hybrid was prepared within 15 min using ultrasound irradiation.

**Table.2.2** Some recent and important hydrothermally prepared graphene-metal oxide hybrid with reaction time and particle size.

S.NO	Composite	Temperture (°C)	Reaction time (h)	Particle size (nm)	Reference
1	ZnO-GR	160	24-160	20	22
2	TiO <sub>2</sub> - GR	120	3-120	20-200	23
3	TiO <sub>2</sub> - GR	180	180-8	12-16	24
4	TiO <sub>2</sub> - GR	180	180-8	15	25
5	Ag-TiO <sub>2</sub> - GR	200	200-18	10-25	26
6	CuO- FGR	-	24	200-500	26

## 2.9 MICROWAVE IRRADIATION APPROACH

Microwave irradiation (MI) is one of the best approaches to synthesis graphene-metal oxide nanocomposite or hybrid. MI is a flexible, inexpensive process and requires low time span for rapid uniform heating throughout the

samples. X. Liu et al. investigated the efficiency of microwave synthesized  $\text{TiO}_2$ -GO composite towards the reduction of Cr metal in water<sup>28</sup>. Y. Yen et al. recently reported that MI-assisted insitu synthesis of rGO- $\text{BiVO}_4$  composite using one-step synthesis technique<sup>29</sup>. The MI performed the dual role in graphene based composite preparation, which allowed the growth of nanoparticle as well as the reduction of GO to rGO.