Chapter 2

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A brief review of different types of covalent functionalization of GO has been included in this chapter. The methods used for the removal of contaminants from water have been discussed. Different dyes and their side effects on living organisms have been introduced. The metal oxide photocatalyst for the removal of dyes and the effect of pH, oxygen, catalyst dose etc. on photocatalysis has also been discussed. The properties and synthesis methods of TiO$_2$ and ZrO$_2$ is also included. A review on TiO$_2$/graphene and ZrO$_2$/graphene composites used as photocatalyst in the present work is also discussed.

2.1 Introduction

Graphene discovered in 2004 by Andre Geim and Konstantin Novoselov becomes an exciting material due to its stable 2D properties [1, 2]. In the same year, Berger et al. [3] produced ultrathin epitaxial films of graphite on (0001) surface of 6H–SiC in ultrahigh vacuum by thermal decomposition. Ultrathin epitaxial films of graphite possess remarkable 2D electron gas behavior but composed of few graphene layers of size 30–200 nm [4, 5]. Monolayer graphene films of large sizes were produced in an argon atmosphere at a pressure of about one bar by Emtsev et al. [6] using ex situ graphitization of Si–terminated SiC (0001). Li et al. [7] also prepared large size monolayer graphene films by using CVD method. They also deposited thin films of graphene on 25 μm thick copper foils at temperature up to 1000°C by CVD technique using a mixture of methane and hydrogen.

Micromechanical exfoliation, CVD and other techniques can be used to generate high quality graphene but does not yet suitable for large scale production [8-10]. Also, these methods do not allow control over the layer thickness and have poor process repeatability. Thus, to obtain large quantity of graphene, exfoliation of graphite in different solvents was studied by Hernandez et al. [11]. They dispersed graphite powder in different solvents like dimethylformamide (DMF) or N-Methyl-2-pyrrolidone (NMP) by high intensity ultrasonic waves to obtain individual layers of graphene [11]. But the yield obtained by this method was also very low.

After that, Liao et al. [12] demonstrated that the large quantity of graphene sheets (diameter 300 nm) can be produced by reduction of graphite oxide with deionized water (DI) at 95°C under atmospheric pressure. Subsequently, lots of work has been reported to
produce graphene by reduction of graphene oxide (GO) using different reducing agents. Mei et al. [13] and Dey et al. [14] described the use of zinc powder in reduction GO. Wu et al. [15] used copper metal nanoparticles in place of zinc to reduce GO. Shul’ga et al. [16] reported the reduction of GO by ultraviolet radiations in vacuum. Thermal reduction method has been used by Wei et al. [17] to carry out the reduction of GO. So, GO can be used as a cost–effective starting material for mass production of graphene–based materials. Hydroxyl, carbonyl and epoxy functional groups present on the GO sheet increase its use in many application such as passive mode–locking of lasers [18-20], sensing and energy storage devices [21], drug delivery [22] etc. These functional groups on the surface can also be replaced by various other functional groups that modify the thermal, electrical, chemical and physical properties of GO. Another use of GO is in forming nanocomposites with improved elastic modulus, tensile strength, electrical conductivity, thermal stability etc. In solid form, GO layers form thin and stable paper like structure. Such GO films can be used for ion conductors, hydrogen storage applications [23] and nanofiltration membranes [24-30] etc.

2.2 Functionalization of GO

Graphene is the most thrilling discovery of the last decade. While lots of efforts have been made to investigate its physics [31-33], but the chemistry of graphene is still unexplored. Current challenges include the controlled chemical functionalization of graphene with functional groups to achieve good processibility. The main purpose of functionalization is to improve the dispersibility of graphene in various solvents by attaching some hydrophilic or hydrophobic organic functional group on its surface. GO because of easier synthesis and process ability has become an emerging material for applications in nanoscience and nanotechnology [34]. GO can be obtained in large quantity by chemical oxidation of graphite [35]. The various oxygen containing functional groups at the edges and carbon atoms of the graphene basal planes can be used for the intercalation or adsorption of ions and molecules for covalent modification [36-37].

Various methods have been reported till date for the introducing nitrogen (N), boron (B), sulphur (S) and fluorine (F) atoms on GO viz. CVD, N–plasma or N⁺–ion irradiation, arc discharge, electrothermal reactions, chemical synthesis and pyrolysis [38]. But these methods have disadvantages such as:

- Requirement of temperatures greater than 100°C,
- Requirement of water sensitive reagents [39],
- Potentially degrade the GO [40] and
- Yield toxic byproducts.

Thus functionalization of GO at room temperature become an issue when water sensitive reagents such as isocyanates and acid chlorides are used [41, 42]. Moreover, unlike graphene GO is electrically insulating and this limits the applications of its composite. Several studies was performed to improve the conductivity of GO [43]. Reddy et al. [44] prepared composite films of poly (3, 4-ethylenedioxyppyrrrole) and reduced graphene oxide (GR) by using an ionic liquid to study the effect of modification on the polymer, structure, conduction properties, and redox chemistry of films. They reported the 2–fold increment in dc electronic conductivity, improved switching kinetics and an amplified charge insertion–extraction capacity of composite films. McGrail et al. [45] reported covalent functionalization of GO and GR using the reaction between alcohol moieties of the platelets and various small molecule of polymeric nitriles.

The covalent functionalization relies on:

(a) Heterogeneous atoms doping on the basal plane (form covalent bond directly with carbon atoms of graphene)

(b) Chemical functionalization with organic molecules (covalent bond formation between the functional groups of GO and the guest functional groups)

**Heterogeneous doping**

Heterogeneous atoms doping is one of the most studied approach to chemically functionalize the graphene and this alters the electric properties of graphene. Wehling et al. [46] experimentally and theoretically demonstrated the doping of graphene by nitrogen. They reported that the single, open shell NO₂ molecule was strong acceptor, whereas its closed shell dimer N₂O₄ causes weak doping. N, B, P, S and halogen doping on graphene convert it into semiconductor. Depending on the doping atom, it may be either n–type or p–type semiconductor.

Nitrogen doping gives rise to n–type graphene. The bonded nitrogen atoms improve the electronic conductivity and offer more active sites. Nitrogen doping has been proved to be an effective method to improve the microstructure and the electrochemical properties of graphene. So far, many chemical routes have been developed for the synthesis of N–doped
Jiang et al. [47] used nitrogen doped graphene as a support in palladium/palladium oxide (Pd/PdO) core–shell cluster by C–C coupling reaction. They suggested that N–doped graphene modifies nucleation and growth kinetics of Pd/PdO during catalyst deposition, which results in smaller Pd/PdO particles, uniform dispersion and enhanced catalyst durability. Wang et al. [48] described the formation of platinum nanowire on the S doped graphene for electrocatalyst application. Boopathi et al. [49] observed the electron transfer kinetics of fluorinated graphene derivatives. The study revealed that fluorine not only induces defects in graphitic lattice leading to heterogeneous electron transfer process but also alter the electronic structure of graphene surface.

(b) Chemical functionalization with organic molecules

The functionalization with complicated organic groups is an easier and more beneficial approach as compared to heterogeneous atoms doping. In this process wide spectrum of functional groups have been chemically anchored onto GO as it contain more process able functional groups. Such kind of functionalization brings change in the properties of GO such as thermal stability, mechanical strength, electrical conductivity, process ability and make a platform for fabricating 3D materials [38]. The covalent bonds are formed between GO and the organic molecules by:

(i) Reaction with diazonium salts,

(ii) Amidation,

(iii) Esterification, substitution and cycloaddition etc.

(i) Reaction with diazonium salts

Diazonium salts can react in to two ways. In first type, replacement by an atom or group along with removal of N₂ and in second type nitrogen atom retained.

The reduction of diazonium salts has been widely employed for grafting aryl groups to the surface of sp² hybridized carbon materials like graphene, CNTs etc. Example includes the reaction of graphene with 4–nitrobenzene diazonium tetrafluoroborate (4–NBD) [50, 51], 4–bromobenzene diazonium tetrafluoroborate (4–BBD) [52, 53], 4–propargyloxybenzene diazonium tetrafluoroborate (4–PBD) [54] and 4–tert-butylphenyldiazonium tetrafluoroborate (4–TBD) to yield corresponding aryl grafted graphene. Reaction is initiated by the transfer of delocalized electron from the graphene to the aryl diazonium cation which results in the formation of aryl radical after releasing a
molecule of \( \text{N}_2 \). The aryl radical afterwards forms a covalent bond with a carbon atom of graphene lattice [55]. The diazonium coupling reaction of graphene strongly depends on the numbers of graphene layers. Sharma et al. [56] observed that single graphene layers were almost 10 times more reactive than bi– or multilayers of graphene. Additionally, Lim et al. [53] reported that the reactivity of edges was two times higher than the reactivity of the bulk single graphene layers. This type of functionalization results in the modulation of electronic properties of graphene and can be used as a sensor.

(ii) Amidation

Amidation is most effective way to chemically functionalize graphene and is most widely employed method than other methods. Stankovich et al. [57] treated GO with phenyl isocyanate. This reaction leads to the derivatization of both the edge carboxyl and surface hydroxyl functional groups via formation of amides or carbamate esters. It was observed that the functionalization can be controlled either by the reactivity of the isocyanate or by the reaction time.

Various \( -\text{NH}_2 \) terminated functional groups have been anchored onto graphene by the researchers reacting different amines with carbonyl group present on GO to the corresponding amide functionalization. Quintana et al. [58] demonstrated functionalization of graphene with polyamidoamine by the amide–bond condensation reaction. They reported that free terminal amino groups serve as ligands in the stabilization of gold nanostructures. Xu et al. [59] synthesized porphyrin–graphene nanohybrid, 5–(4–aminophenyl)–10,15,20–(triphenyl) porphyrin (TPP) in which GO was covalently bonded by amide bond with porphyrin amino group (TPP–\( \text{NH}_2 \)). Collins et al. [60] reported the conversion of alcohol groups directly to N, N–dimethylamide group by using N, N–dimethylacetaamide dimethyl acetal. Peng et al. [61] investigated electronic, magnetic and electron transport properties using density functional theory of covalently functionalized graphene by the amide groups. They found that if both sublattices of the graphene were evenly functionalized with the amide groups, the band gap of the modified graphene was large. Moreover, when the two sublattices of the graphene were unevenly functionalized, the decorated graphene exhibits magnetism. As the coverage of amide groups are increased, functionalized graphene can be transformed from semiconducting to half metallic or to metallic nature.

Liu et al. [62] functionalized GO with oligothiophene. They reported oligothiophene functionalized GO was more thermally stable and shows a superior optical limiting effect,
better than that of the benchmark optical limiting material C$_{60}$. Das et al. [63] synthesized amide–functionalized graphene nanoplatelets to enhance mechanical properties of polymethyl methacrylate. They noted that elastic modulus and the hardness of the composites increased by 70% and 10% respectively. Zhang et al. [64] prepared composite of pyrroldidine ring modified C$_{60}$ and GO. The amide bond was formed between carboxyl group of GO and pyrroldidine ring of C$_{60}$. Like CNTs these hybrids were useful in many optoelectronic applications due to their remarkable electronic and optical properties. Functionalization of GO by imidazolium derivatives has been reported by Karousis et al. [65]. In this, 1–(3–aminopropyl)–imidazole was attached to the carboxylic groups of GO through amide bonds. Recently Qu et al. [66] prepared N–doped graphene quantum dots by hydrothermal process using urea in order to investigate the optical properties. Hydrothermal conditions promote formation of amide bond between $\text{–NH}_2$ of urea and $\text{–COOH}$ of GO. N–doping results in an improvement in photoluminescence and yield of graphene quantum dots.

(iii) Esterification

The esterification is the reaction between $\text{–COOH}$ groups of GO with termination $\text{–OH}$ group of other substrate. There are a number of studies addressing this process. Yu et al. [67] reported functionalization of GO with $\text{–CH}_2\text{OH}$ terminated poly(3–hexylthiophene) (P3HT) through the formation of ester bonds with carboxyl groups of GO. They reported that P3HT–GO was soluble in common organic solvents due to the presence of hydroxyl groups and designed a photovoltaic device using a combination of P3HT/GO product with C$_{60}$. Salavagione et al. [68] performed esterification using the carboxylic groups of GO and the hydroxyl groups of poly vinyl alcohol (PVA). They demonstrated that the covalent linkages between the graphene layers and the PVA are responsible for altering the crsytallinity and thermal stability of the composite.

A wide range of organic compounds, such as porphyrins [67, 69], aromatic dyes, alkylamines [70], doxorubicin hydrochloride, ionic liquids [71], pyrene, perylenediimide [72], cyclodextrin [73] and aryl diazonium compounds [52-56] have all been noncovalently or covalently attached onto the GO nanosheets to generate functional organic nanocomposites for electrochemical applications.
2.3 Water treatment for removal of organic compounds

Fresh water is essential for living beings. On earth approximately 3% of fresh water is present in water bodies and rest is in ocean which is alkaline in nature. This small amount of fresh water is being polluted by human day by day. More than 80% of diseases that affects humankind are waterborne. Thus presence of wide variety of organic compounds, which are toxic and stable to decomposition in water supplies and industrial effluents, is an ever increasing problem for the global concern. High concentration of these compounds is introduced into water bodies by human beings by releasing:

- Municipal wastage
- Industrial waste chemicals, dyes, plastics etc.
- Pesticides, synthetic organics compound used in agricultural activities etc.

2.3.1 Conventional water treatment methods

Concern for the quality of water particularly for drinking and domestic purposes it has become necessary to remove contaminants from water. There are variety of conventional water treatment technologies that purify the water to varying degree.

The conventional methods so far used for water treatment are divided into three categories:

(a) Physical,
(b) Chemical and
(c) Biological methods

These methods can be used to degrade organic compounds present in water and have been further categorized as shown in Figure 2.1.

Depending on the contaminants present in water, these methods either alone or in combination with other type of treatment process are used. The greatest challenge in implementing a wastewater treatment technology is the cost of the process that will maximize the efficiency of water treatment and ensuring compliance with all health and safety standards regarding reuse of treated wastewater effluents.
(a) Physical methods

There are various types of physical methods used for waste water treatment. Adsorption method is a surface phenomenon for removal organic and inorganic pollutants. When a solution containing absorbable solute comes into contact with a solid with a highly porous surface structure, then liquid–solid intermolecular forces of attraction cause some of the solute molecules from the solution to be deposited at the solid surface [77]. Adsorption method is influenced by many physio–chemical factors such as:

- Dye/sorbent interaction
- Sorbent surface area
- Particle size
- Temperature
- pH and
- Contact time.
Adsorption has been found to be superior in terms of initial cost, flexibility, simplicity of design, ease of operation and insensitivity to toxic pollutants [76]. Adsorption techniques can be used for the removal of dissolved organic pollutants such as dyes but the efficiency of removal is very low. The other physical method for water treatment is membrane filtration. The particles that are removed from the water during filtration depend upon the size of filters. Moreover, membrane based method of waste water treatment have disadvantages like:

- Limited lifetime because of the membrane fouling.
- Costly due to periodic replacement of membrane.

(b) Chemical methods

Water treatment by chemical method involves the addition of chemicals to assist in the removal of particles from the water. There are several distinct chemical processes such as chemical coagulation, precipitation, oxidation, advanced oxidation, ion exchange, neutralization and stabilization which can be applied to wastewater treatment. Precipitation is used for removing dissolved metals from wastewater solution containing toxic metals. In coagulation process coagulants such as aluminum sulfate or iron (III) chloride was added to neutralize the particles. Metal hydroxides formed during the reaction adsorb the particles in suspension and facilitate their removal by subsequent processes of sedimentation and filtration [78]. Dyes can be removed using chemical techniques but addition of chemicals for their removal raise the possibility of secondary pollution. The water treatment using this method also faced the problem of disposal of sludge. Recently, advanced oxidation processes (AOP’s) which are based on the generation of powerful oxidizing agents such as hydroxyl radicals which is highly reactive having electrochemical oxidation potential equal to 2.8 V, have been used for the degradation of pollutant [79-81]. Alkaline chlorination uses chlorine as an oxidant against cyanide. However, alkaline chlorination as a chemical oxidation process lead to the creation of toxic chlorinated compounds and additional steps may be required for treatment. AOP’s method such as Fenton and Photo–Fenton catalytic reactions [79] uses hydrogen peroxide and iron catalyst solution to oxidize contaminants from wastewater in the presence of light. A complete oxidation of organic compound takes place into harmless products such as CO₂ and H₂O by Fenton and Photo–Fenton catalytic reactions. But the disadvantage of this process is the requirement of low pH values since iron precipitates at higher pH values. Thus among various AOP’s methods photocatalytic
(c) Biological methods

Biological treatment is an important part of any wastewater treatment plant. Biological wastewater treatment is the degradation of waste products from municipal or industrial sources by biological means. In this method, there is either small amount or no chemical addition is required and this reduces the cost of system. Bacteria and microorganism are mainly used to treat the wastewater. The large quantity of air is bubbled in to wastewater to live and grow the bacteria and microorganism which consume the dissolved organic food or pollutants from waste water. After several hours in a large holding tank, the water is separated from the sludge of bacteria. However, their application is often restricted because of technical constraints. According to Bhattacharyya and Sharma biological treatment requires [80]:

- Large land area,
- No effects toward diurnal variation,
- Flexibility in design and operation

Although many organic molecules are degraded, many others are recalcitrant due to their complex chemical structure [82]. In particular, due to their xenobiotic nature, dyes are not totally degraded by microorganisms. So, in the subsequent section various dyes polluting the water are being described.

2.3.2 Dyes

Dyes are soluble colored compounds applied on fiber from their aqueous solution. Synthetic dyes are used by many industries such as paper printing, food, pharmaceutical, leather and cosmetics. In the entire world approximately 800,000 tons of dyes is produced every year [83-85]. The dyes and their intermediates are the major pollutant of water because of their aromatic structure and non biodegradable nature. In the dyeing process approximately 10–15% of the dye remains unused. These unused dyes are released in to water by the textile or dyestuffs industries. Due to toxic nature [85], dyes become potential danger to both man and environment. As maximum number of dyes are non biodegradable so can not be removed from water naturally and impart harmful effects on entire food chain [83]. Some dyes when present even at very low concentrations may significantly affect
aquatic life. Robinson et al. [74] and Banat et al. [84] observed that presence of small amount of dye into water (<1 ppm for some dyes) cause allergy, skin irritation, respiratory problems and cancer to humans. Work has already been performed by researchers using conventional methods described earlier but all these method are time consuming, costly and not efficient.

(a) Types of dye

There are more than 10,000 dyes used in textile industries [83]. Some of the important categories of dyes used by textile industries are discussed below:

(i) Azo dyes

These dyes are characterized by the presence of an azo group (–N=N–) as the chromophore and their basic structure is R–N=N–R’, where R, R’ is aromatic moiety. The nature of the aromatic compound on both sides of the azo group controls the colours of the dye as well as the water-solubility and binding of it towards a particular fabric. Azo dyes are highly stable, soluble, toxic and less expensive in nature. These are the most widely used dyes in world (60 to 70% of total dye production per year) [86]. Some examples of it are methyl orange, C.I. Acid Red 74 and C.I. Acid Orange 7. Azo dyes and their intermediate degradation products are highly carcinogenic in nature.

(ii) Acid dyes

These are water soluble anionic dyes that are used to color fibers such as silk, wool, nylon and modified acrylic fibers. Most synthetic food colors fall in this category.

(iii) Basic dyes

These are water soluble cationic dyes that are mainly applied to acrylic fibers. Usually acetic acid is used to help the uptake of the dye onto the fiber. Basic dyes are used in the coloration of paper. Examples of these are methylene blue, crystal violet, rhodamin B and basic fuchsin safranin.

(iv) Direct or substantive dyes

These dyes are applied to cellulose fibers directly without the use of mordants. They are used for dyeing wool, silk, nylon, cotton, rayon etc. They are also used as pH indicators and as biological stains.

Other examples of the dyes are mordant dyes, vat dyes, reactive dyes, disperse dyes, sulphur dyes and aniline dyes.
(b) Important dyes used for present work

Textile industries consumed 60% of the dyes based on azo dyes. So in the present work most widely used methyl orange azo dye, methylene blue and rhodamine B basic dyes were chosen for detail discussion. As all of these are carcinogenic and used largely by many industries because of easy availability, water solubility, easy handling and low cost. These dyes are briefly discussed below.

(i) Methyl orange

Methyl orange is an anionic azo dye used in dyeing and printing textiles. It is also used as a pH indicator. It is also known by C.I. Acid Orange 52, C.I. 13025, helianthine B, Orange III, Gold orange and Tropaeolin D [87]. The structure of methyl orange is shown in Figure 2.2. The IUPAC name of it is 4–[4–(Dimethylamino) phenylazo] benzene sulfonic acid sodium salt [88]. The methyl orange dye have serious health impact such that ingestion of less than 40 gram may be fatal or may produce serious damage on the health of the individual e.g pneumoconiosis, skin disorder, eye conjunctival redness and high chronic doses cause congestion of the spleen and tumor formation etc [89]. Color change of methyl orange is observed in the pH range 3.1 to 4.4 from red to yellow respectively. Decolorization of MO is carried out in the presence of *OH radical group, which attacks on azo group of the methyl orange structure.

(ii) Methylene blue

It is a cationic dye used for dyeing cotton, wool, and silk. It is also known as C.I. basic blue 9, methylthioninium chloride and C.I. Solvent blue 8. The structure of it is shown in Figure 2.2. It has serious health impact if taken in excess such as eye burns in humans and animals, methemoglobinemia, cyanosis, convulsions, tachycardia, dyspnea, irritation to the skin, anameia, irritation to the gastrointestinal tract, nausea, vomiting and diarrhea [88].
(iii) Rhodamine B

Rhodamine B is a basic dye appears green in powder form but when added to water turns pink. The solubility of Rhodamine B in water is ~50 g/L. The structure of it is shown in Figure 2.3. It is commonly used to stain slides in laboratories, in the sewage industry to test for leakage in drains, wool, silk and polyamide fiber dyeing. Other names of Rhodamine B are C.I. Acid Red 52 and C.I. 45100. It is toxic to aquatic fauna and cause long term effects on the aquatic environment [90]. It is not a permitted food colour and is considered to be carcinogenic. If it is applied to the eyes causes severe eye damage. It has other side effect such as hepatotoxic (i.e. poisonous to the liver), skin infection, long term use or overdose has cause abdominal pain, diarrhoea, electrolyte imbalance (hypokalaemia or metabolic acidosis), dehydration, malabsorption, protein–losing gastroenteropathy, anorexia, weight loss, polyuria, cardiac arrhythmias, muscle weakness etc.

2.3.3 Photocatalysis

Traditional methods used for dyes removal from water are not efficient as these methods have disadvantages like:

- Sludge formation,
- High operation cost,
- Time consuming and
- Ineffective in cases of complicated aromatic compounds [91].

Kim et al. [92] observed that the adsorption method has difficulties in the treatment of insoluble dyestuff in wastewater while the coagulation method is effective for treatment of insoluble dyestuff. Thus a new technique is required that resolve the above mention problems. Photocatalysis is a effective method that provides efficient degradation of soluble and insoluble dyes.

Photocatalysis is the acceleration of the reaction rate in the presence of light with the help of a photocatalyst. It is a fast, low operating cost method. Photocatalyst is a
substance that is able to produce chemical transformations of the reaction participants by absorption of light and these can be recovered and reuse. Photocatalytic degradation of dyes with metal oxide semiconductor become popular because metal oxide is a stable and low cost photosensitized material. Photocatalysis on semiconductor particles mainly take place in three steps [79, 93-95]:

(1) Absorption of photons with energy greater than the semiconductor band gap, leading to the generation of electron–hole pairs: The materials whose bottom level of conduction band is more negative than the redox potential of H⁺/H₂ (0 V vs. NHE), while the top level of the valence band is more positive than the redox potential of O₂/H₂O (1.23 V vs. NHE) can be used as a photocatalyst.

(2) Charge separation and migration of photo generated carriers: Crystal structure and particle size strongly affects this step. The large amount of defects reduces the photocatalytic activity of the semiconductor because defects act as trapping and recombination centers for photo generated electrons and holes.

(3) The surface chemical reactions: The important point for surface chemical reactions is available active sites and surface area of the catalyst. The photo generated electrons–holes pair recombines with each other if the active sites for reactions do not exist on the surface. Thus co–catalysts such as platinum [96] graphene [97-99] and ZrO₂ [100] are usually added to introduce active sites.

(a) Advantages of photocatalysis

Photocatalysis has various advantages such as:

- It is single step reaction and the results are obtained just by mixing the reactants and irradiating them.
- In photocatalytic reactions both oxidation and reduction reactions occurs simultaneously on the catalyst surface.
- Water can be used as a solvent and no special solvents are required which are expensive, difficult to dispose off and polluting in nature.
- Photocatalytic reactions occur at ambient temperature and pressure so need not to maintain drastic conditions as required in conventional reactions.
(b) Factors affecting photocatalysis

In photocatalysis process when light falls on the catalyst surface, the generated electron–hole pairs participates in reaction mechanism for desire application.

The rate of photocatalysis depends on various parameters such as:

- Presence of oxygen
- pH
- Catalyst dose
- Type of effluent
- Effluent concentration [101] etc.

In order to maintain an efficient photocatalysis reaction, it is essential to minimize the electron–hole recombination. Therefore, electron must be removed by an electron acceptor. Oxygen can act as effective electron scavenger as it dissolves easily in aqueous solution. Oxygen molecules adsorb electrons to produce superoxide radical $O_2^-$:

$$O_2 + e^- \rightarrow *O_2^-$$

When $H_2O_2$ is used as an additional oxidant, the rate of photo degradation significantly increased [95, 101-103] because of its valuable roles in both charge separation and oxidant formation. The addition of $H_2O_2$ improves the yield of the photocatalytic process.

$$H_2O_2 + hv \rightarrow 2*OH$$

The pH value is another important parameter in photo degradation. However, it is difficult to interpret the effect of pH on the photocatalytic degradation of dyes because it is related to the ionization state of the surfaces as well as of reactant dyes and products. Tunesi et al. [104] found that the positive holes are major oxidation species at low pH, whereas hydroxyl radicals were considered as the predominant species at neutral or high pH levels. Concalves et al. [105] observed that efficiency of the process was enhanced in alkaline solution because it was easier to produce hydroxyl radicals by oxidizing more hydroxide ions available on metal oxide surface in alkaline medium. Guillard et al. [106] and Reutergarth et al. [107] obtained similar results in the photocatalytic degradation of acidic azo dyes and triazine containing azo dyes. They reported columbic repulsion between the negative charged surface of photocatalyst and the hydroxide anions in alkaline solution. Jayant et al. [108] reported the rate of removal increases with increase in pH of the solutions up to 4.0 for malachite green and brilliant green dyes. It was observed that for pH
4.0 the semiconductor surface was slightly negatively charged and so the anionic dye molecule will experience a force of repulsion causing a decrease in the rate of the reaction.

Amount of catalyst in the solution also affects the degradation rate. Segne et al. [109] studied the effect of catalyst loading on the degradation of methylene blue using TiO$_2$ as a photocatalyst. It was found that rate of degradation increases with increase of catalyst loading up to a certain limit since the number of photons absorbed and the numbers of dye molecules adsorbed are increased with respect to increase in the catalyst concentration. However, after a certain limit further increase in catalyst amount did not increase dye absorption. Hence the additional catalyst powder was not effectively involved in the photocatalytic activity rather increase in the turbidity of the solution, which interfere with penetration of light into the solution [110].

(c) Applications of photocatalysis

Photocatalysis is effective, convenient and inexpensive method and have variety of applications such as:

(i) Removal of heavy metals

The heavy metals such as mercury (Hg), chromium (Cr), lead (Pb), cadmium (Cd), arsenic (As), nickel (Ni), copper (Cu) etc. are harmful for health. Heavy metals are generally considered to be those having density higher than 5 g/cm$^3$. Heavy metals in human cause severe disorder such as reduced growth and development, cancer, organ damage, nervous system damage, and in extreme cases death. Thus heavy metals are highly undesirable and it becomes necessary to remove them from water. The photocatalysis method can be used to remove these metals from water [111, 112]. Barakat et al. [113] reported the photocatalytic degradation of cyanide and copper using UV–irradiated TiO$_2$ suspension. Results show that free copper get completely removed in 3 hours. Mohapatra et al. [114] removed the hexavalent chromium from aqueous solution by TiO$_2$ modified with sulphate.

(ii) Removal of organic and inorganic compounds

Photocatalysis can be used in the degradation of organic and inorganic species from aqueous or gas phase using semiconductor photocatalyst. The semiconductor photocatalyst has ability to oxidize organic and inorganic compounds through redox processes [115]. Most organic compounds react with hydroxyl radical formed during reaction to form a carbon–centered radical. The resulting carbon–centred radical reacts with molecular oxygen
to form a peroxyl radical that undergoes subsequent reactions, ultimately producing harmless products such as carbon dioxide, water and simple mineral acids. [116]. In addition to it, inorganic species such as bromate, chlorate, azide, halide ions, nitric oxide, palladium, rhodium and sulfur can also be decomposed using photocatalysis process [117].

(iii) Degradation of dyes and pigments

The untreated dye from dyeing industries in water is a major source of water pollution. Chemical as well as biological changes occur in aquatic system due to dyes, as dyes consume dissolved O$_2$ and thus disturb the aquatic ecosystem [118-120]. Due to the complex aromatic structure and stability of these dyes, conventional methods are ineffective for degradation. But many of dyes are photoactive and therefore can be effectively removed by photocatalysis method [101].

(iv) Air purification

Photocatalysis is a promising technique to reduce air contaminants such as NO$_x$, hydrocarbons, carbon monoxide etc. Photochemical reaction resulting from the action of sunlight on NO$_2$ and volatile organic compounds (VOC’s) leads to the formation of photochemical smog or ozone as a secondary pollutant [121]. Heterogeneous photocatalysis is a promising method for NO$_x$ removal. In the presence of UV–light, catalysts such as TiO$_2$, ZnO etc. present at the surface of the material get activated, enabling the degradation of pollutants in the air. Boonen et al. [121] and Ifang et al. [122] studied the kinetics of degradation of pollutants of air by photocatalysis process.

(v) Desalination of seawater

Desalination of sea water is an important use of photocatalysis process. Since there is abundant amount of water on the surface of earth, but a major part of water lies in ocean that is alkaline in nature and therefore of no use. Thus, the water is not a major issue in the world but its saline nature is main disadvantage. To make saline water drinkable lot of techniques have been devised so far like multi stage flash distillation, multiple effect distillation, vapor compression, ion exchange, reverse osmosis, electro dialysis, solar distillation [123, 124] etc. But these techniques have poor efficiency and expensive too. Solar distillation is a most attractive and simple technique as compared to other techniques, but it is especially suited to regions where solar energy is available in huge amount. Thus because of limitations of existing methods it become necessary to improve the desalination process. Recently photocatalysis is used in the desalination of sea water. Sharma et al.
[124] used nickel sulphide (NiS) as a photocatalyst for the solar desalination. Better quality and increases in the rate of production of desalinated water was observed. NiS also lowers chloride, fluoride, nitrate, calcium, magnesium, iron, cadmium contents and hardness of water. So far different semiconducting oxides like CuO, PbO₂ and MnO₂ have been utilized as photocatalysts for the desalination. It is observed that metal oxides not only improve the efficiency of the process but the rate of production of desalinate water is also increased to a remarkable extent [125].

2.3.4 Metal oxide semiconductor as a photocatalysts

Different metal oxide semiconductor has been used as a photocatalyst. Gauvea et al. [95] reported photocatalytic activity of ZnO for degradation of different reactive dyes viz. Remazol Brilliant Blue R, Remazol Black B, Reactive Blue 221 and Reactive Blue 222 and found that mineralization higher than 80% for all the dyes takes place. It was observed that ZnO semiconductor exhibits better efficiency than that observed with anatase TiO₂. Because of good photocatalytic properties of ZnO it becomes a hot topic and lots of work has been done in this area. Lizama et al. [118] reported degradation of reactive blue 19 using ZnO and TiO₂. They observed that ZnO showed greater degradation activity than TiO₂ and reported that the acute toxicity evolved from zero to around 50 toxicity units in the initial stages of irradiation, further deplete to minimal values after 30 minutes of reaction for both the catalyst. Amisha et al. [119] studied this material for degradation of reactive black 5 and the influences of hydrogen peroxide, ammonium persulphate and isopropanol on the degradation rate. They reported interesting results that 99.91% degradation of dye took place in the presence of UV light whereas only 55.25% degradation occurred under solar light after 80 minutes of irradiation. Mijin et al. [120] used ZnO to remove dyes from water because it absorbs larger fraction of the UV light having threshold wavelength of 387 nm. Li et al. [126] demonstrated microwave assisted method for the synthesis of bismuth phosphate nanostructures and used it in photocatalytic application for the degradation of methyl orange under UV and visible light irradiation. They suggested that the photocatalytic activity was closely related with the crystalline phase, band gap of bismuth phosphate and observed that hexagonal bismuth phosphate nanoparticles with narrow band gap showed the highest photocatalytic performance. Zhang et al. [127] demonstrated hydrothermal synthesized SnS₂ nanoparticles in photocatalytic degradation of methyl orange. Recently, photocatalysis method has becomes so popular
that different types of dyes have been removed using various catalysts [128-130]. Munusamy et al. [131] studied photocatalytic effect of TiO₂ on degradation of brilliant green dyes and using Zn, Cu doped TiO₂. They showed TiO₂ has excellent result on degradation of brilliant green as compared to doped TiO₂. They obtained 99% degradation in presence of TiO₂, 87% for TiO₂/Zn and 46% for TiO₂/Cu. Jingfei et al. [132] discovered new materials Gd₂InSbO₇ and Gd₂FeSbO₇ that degrade dyes under visible light. They observed that complete removal of rhodamine B took place in visible light after 225 min/260 min with Gd₂FeSbO₇/Gd₂FeSbO₇ respectively.

Other metal oxide semiconductor systems used for the photocatalytic degradation of aromatic dyes are WO₃ [110], SrO₂ [134], Fe₂O₃, CeO₂ [134], Cds [108], SrTiO₃ [134], ZnS [135] and ZrO₂ [110]. Out of these TiO₂ and ZnO are most widely used semiconductor photocatalysts because of their high photosensitivity, photochemical stability, large band gap, strong oxidizing power and non–toxic nature [93-95,118,119]. Anatase TiO₂ and surface modified TiO₂ have attracted much interest in recent years because of its ability to decompose chemical compounds and dye components [93-95]. In present work titanium dioxide and zirconium dioxide are selected as a photocatalyst to remove dyes from water.

The advantages of TiO₂ as a photocatalyst are:

- Reaction takes place at room temperature.
- Intermediate products are usually completely degraded in to non–toxic substances such as CO₂ and water [93-95, 131].
- Supported on various substrates such as glass, fibers, stainless steel, inorganic materials, sand and activated carbons.
- Photogenerated holes are extremely oxidizing and photogenerated electrons reduce sufficiently to produce superoxides anions.

### 2.4 Titanium oxide (TiO₂) Photocatalyst

Titanium (Ti) is the ninth most abundant element on the earth crust [136]. It does not exist in metallic state because of its great affinity for oxygen and other elements. It exists in +4, +3 and +2 oxidation state [136].

#### 2.4.1 Properties of TiO₂

TiO₂ is thermally stable and non–flammable oxide of titanium. It is also known as titanium (IV) oxide, titania, titanic acid anhydride or Ti white. It is odorless powder
having molecular weight of 79.9 g/mol. TiO₂ is considered very close to an ideal semiconductor for photocatalysis because of its high stability and safety toward both humans and the environment. Table 2.1 shows the chemical, physical and thermal properties of TiO₂ [137].

Table 2.1 Chemical, physical and thermal properties of TiO₂

<table>
<thead>
<tr>
<th>Chemical properties</th>
<th>Physical properties</th>
<th>Thermal properties</th>
</tr>
</thead>
<tbody>
<tr>
<td>Symbol</td>
<td>Density</td>
<td>Melting point</td>
</tr>
<tr>
<td>TiO₂</td>
<td>4.23 g/cm³</td>
<td>1,843°C</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Chemical composition</th>
<th>Molar</th>
<th>Mass</th>
<th>Boiling point</th>
</tr>
</thead>
<tbody>
<tr>
<td>Titanium</td>
<td>59.93%</td>
<td>79.94 g/mol</td>
<td>2,972°C</td>
</tr>
<tr>
<td>Oxygen</td>
<td>40.55%</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

There are four commonly known natural polymorphs of TiO₂ in nature:

1. Anatase (tetragonal)
2. Rutile (tetragonal)
3. Brookite (orthorhombic)
4. TiO₂ (B) (monoclinic)

Data related to crystal structure of rutile, anatase and brookite polymorphs is given in Table 2.2.

Table 2.2 Crystal structure data of TiO₂ [137]

<table>
<thead>
<tr>
<th>Properties</th>
<th>Rutile</th>
<th>Anatase</th>
<th>Brookite</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lattice constant (Å)</td>
<td>a = 4.5936</td>
<td>a = 3.784</td>
<td>a = 9.184</td>
</tr>
<tr>
<td>(Å)</td>
<td>c = 2.9587</td>
<td>c = 9.515</td>
<td>b = 5.447</td>
</tr>
<tr>
<td>Volume/molecule (Å³)</td>
<td>31.2160</td>
<td>34.061</td>
<td>32.172</td>
</tr>
<tr>
<td>Molecule (cell)</td>
<td>2</td>
<td>2</td>
<td>4</td>
</tr>
<tr>
<td>Ti–O bond length (Å)</td>
<td>1.949 (4)</td>
<td>1.937(4)</td>
<td>1.87–2.04</td>
</tr>
<tr>
<td>O–Ti–O bond angle</td>
<td>81.2°</td>
<td>77.7°</td>
<td>77.0°–105°</td>
</tr>
<tr>
<td>angle</td>
<td>90.0°</td>
<td>92.6°</td>
<td></td>
</tr>
</tbody>
</table>

Though both rutile and anatase belong to the tetragonal crystal system but rutile has a denser arrangement of atoms. The luster and hardness of anatase and rutile are similar, but their cleavages are different.
Zhang et al. [138] found that anatase and brookite structures transformed to the rutile phase after reaching a certain particle size, rutile phase becoming more stable than anatase for particle sizes greater than 14 nm. Once the rutile phase formed, it grew much faster than the anatase. The activity of the rutile phase as a photocatalyst is generally less than anatase phase. Sclafani et al. [139] suggested that the rutile phase can be active or inactive in photocatalysis, depending on its preparation conditions. They observed that absorption of light by the particles was affected by the particle size distribution, texture, amount and the nature of the adsorbed reactant species. They found that final level of photoactivity is determined not only by semiconducting properties but also by the physicochemical properties.

Brookite TiO₂ is insoluble in acids and is chemically inert. Powdered rutile is used in paints, plastics, paper, foods and other applications. Rutile nano particles are transparent to visible light but effectively absorb the UV light and hence used in sunscreens to protect against UV–induced skin damage. Shi et al. [140] found anatase phase is more chemically reactive and has a greater potential than rutile structure. It is preferred over other polymorphs for catalytic applications because of slightly higher Fermi level, lower capacity to absorb oxygen and higher degree of hydroxylation.

### 2.4.2 Photoactivity of TiO₂

TiO₂ is a large band semiconductor with band gaps of 3.2 eV, 3.02 eV, and 2.96 eV for the anatase, rutile and brookite phase respectively [141]. The valence band of TiO₂ is
composed of the 2p orbitals of oxygen hybridized with the 3d orbitals of titanium, while in the conduction band there are only 3d orbitals of titanium [142]. The photochemical oxidation reaction on the TiO₂ surface occurs by:

(i) **Charge–carrier generation**

When UV light of energy greater than the band gap of TiO₂ falls on it, the electrons (e⁻) present in the valence band are excited to the conduction band leaving behind holes (h⁺) as shown in Figure 2.6.

\[ \text{TiO}_2 + \text{hv} \rightarrow e^- + h^+ \]

(ii) **Charge–carrier trapping**

In charge carrier trapping, valence band hole successfully migrates to surface and initiates oxidation reaction [143] and produce hydroxyl radicals:

\[ \text{H}_2\text{O} + h^+ \rightarrow \text{HOH} + \text{H}^+ \]

Electron present in conduction band successfully migrates to surface and initiating reduction reaction to produce superoxide anion:

\[ \text{O}_2 + e^- \rightarrow \text{O}_2^- \]

(iii) **Charge–carrier recombination**

The recombination of electron hole pairs is found to be a main factor for limiting the oxidation rate of organic substrates.

\[ e^- + h^+ \rightarrow \text{TiO}_2 + \text{heat} \]

(iv) **Photocatalytic degradation**

Hydroxyl radicals and superoxide ions attack on any dye through chemical redox reactions and convert it in to degradable products.

\[ \text{Dye} + \text{OH} \rightarrow \text{CO}_2 + \text{H}_2\text{O} \]

The excited e⁻'s in the conduction band of TiO₂ is free and in 3d state. Because of dissimilar parity between valance band and conduction band, the transition probability of e⁻'s present in conduction band to the valence band decreases, this leads to decrease in the recombination of e⁻/h⁺ [142]. Anatase TiO₂ can be considered as the active photocatalytic phase based on the

![Figure 2.6 Photocatalysis in TiO₂](image)
charge carrier dynamics, chemical properties and the activity of photocatalytic degradation of organic compounds.

2.4.3 Synthesis of TiO$_2$ photocatalyst

TiO$_2$ nanoparticles can be synthesized by using various methods such as sol–gel method, sulfate and chloride process [144], impregnation [145], oxidation of TiCl$_4$ [146], hydrothermal method [147, 148] co–precipitation [149] etc. Sol–gel method [150] is most widely method to synthesize various metal oxides due to ease of fabrication and low processing temperatures. It is used to prepare TiO$_2$ particles and films.

(A) Sol–gel process

Sol–gel process involves the transition of a system from colloidal suspension of solid particles in a liquid known as sol to the gel. The homogeneity of the gels depends on the solubility of reagents in the solvent, the sequence of addition of reactants, temperature and the pH of the system [149]. It is a wet–chemical technique used for the synthesis of metal oxide. The precursors used in the preparation of the “sol” are usually inorganic metal salts or metal organic compounds such as metal chlorides and metal alkoxides. Alkoxides are very reactive and not commercially available which limits the use of types of materials that can be prepared by them. The sol gel thin film coatings are used extensively for different applications as protective and optical coatings, sensors, high or low dielectric constant films, inorganic membranes, electro–optic and nonlinear optical films, electrochromics and ferroelectrics.

The sol-gel method was developed in the 1960s mainly due to the need of new synthesis methods. The metal salts, metal chlorides and metal alkoxides can be used as precursors. The sol–gel process involves the following steps:

(i) Hydrolysis:

In hydrolysis a suspension of sol is formed by mixing colloidal particles in water at a pH that prevents precipitation [150]. The reaction occurs by the addition of water which results in the replacement of alkoxide groups (–OR) with hydroxyl groups (–OH). To increase the reaction rate ammonia or HCl can be used as a catalyst. During hydrolysis, hydroxyl ions get attached to the metal atom. The reaction is given below [151]:

$$\text{M–OR} + \text{OH}^- \rightarrow \text{M–OH} + \text{ROH}$$
M represents the metal, ROH an alcohol. Hydrolysis is completed depending upon the availability of sufficient amount of water and catalyst.

(ii) Condensation and polymerization:

In condensation reaction two partially hydrolyzed molecules condense together to loss of water or ROH molecules. The reaction is shown below [151]:

\[
\begin{align*}
M-\text{O-H} & \quad + \quad \text{HO}-M \quad \rightarrow \quad M-\text{O-M} + \text{H}_2\text{O} \quad \text{(Water condensation)} \\
M-\text{O-R} & \quad + \quad \text{HO}-M \quad \rightarrow \quad M-\text{O-M} + \text{R-OH} \quad \text{(Alcohol condensation)}
\end{align*}
\]

This reaction can be continued to build larger and larger metal containing molecules by the process of polymerization. The condensation is a dynamic process. Parameters which influence the condensation process are:

- Type of precursor,
- The ratio between alkoxide and water,
- Type of catalyst,
- Type of solvent,
- Temperature and pH,
- Relative and absolute concentrations of the reactants.

(iii) Gelation:

The term gel can be defined as interconnection of 3-D network by the simultaneous hydrolysis and polycondensation of an organometallic precursor. In this state, the sol particle aggregate to give viscous solution. The process continues until a gel is formed [152]. A continuous network is formed when sol–gel transition (gel–point) is reached. From the classic theory of polymerization to modern fractal geometry and percolation theory [151, 152] there have been a variety of explanations offered for sol gel transition. In the gelation the surface charge develops on the sol particle either by differential dissociation of one of its lattice ions or adsorption of charged species from solution. An equal and oppositely charged diffused layer formed in the solution. As a result when two sol particles comes closer, the diffused layer surrounding to sol particles act as an energy barrier due to repulsive forces.

Apart from the repulsion, there is an attractive force between individual sol particles arising from the van der Waals interactions and a very short range repulsive force. If the particle crosses the energy barrier, the total energy become negative and can ultimately lead
to the formation of aggregates, and it grows in size until they extend throughout the sol and this is called sol–gel transition or gelation.

(iv) Aging:

When the gel is formed, a large number of sol particles and clusters are still in unreacted form. Ageing of the gel is therefore a very important stage in the process [152]. The aging process occurs by:

- Continuing polymerization,
- Syneresis,
- Coarsening and
- Phase transformation

Polymerization is the increase in connectivity of the gel network by condensation of unreacted hydroxyl groups. Syneresis is the spontaneous and irreversible shrinkage of the gel network, resulting in expulsion of liquid from the pores. Coarsening is a process of dissolution and re-precipitation driven by the difference in solubility. The phase transformation consists of segregation of liquid phase into two or more phases included solid phase.

(v) Drying:

In drying process liquid evaporates resulting in the shrinkage of the gel network. It is difficult to expel the water from gel and at the critical point the liquid recedes into the interior leaving pores near the surface. This results in the formation of Xero–gel.

(vi) Heat Treatment:

The gel after drying contains residual structural water mainly in the form of adsorbed hydroxyl, residual organics either adsorbed or chemically bonded after drying. Thus material should be annealed to remove the residues for obtaining the desired material.

(B) Advantages of Sol–Gel Technique

Sol gel process is a simple, economic and effective method to produce high quality materials. It has lots of advantages:

- It does not require vacuum ambient.
- High purity products can be produced by it.
- It can have low temperature heat treatment capability, usually 200–600°C.
- Can produce thick coating to provide corrosion protection performance.
Easily allow to shape the materials into complex geometries in a gel state such as films on curved surfaces.

(C) Limitations of Sol–Gel Technique

Sol–gel technique has many advantages but has some limitations such as:

- It is a time consuming process
- Some of the solvents are toxic which are used as a precursor for the preparation of the sol
- It is not stable.

2.4.4 TiO₂/graphene photocatalyst

TiO₂ is a dense nonporous material with low surface areas. Thus, to enhance its photocatalytic properties some supporting substrate is required. Graphene has large surface area thus can be used as a supporting material to enhance its photocatalytic properties. Zhou et al. [97] prepared TiO₂/graphene composites by solvothermal reaction using graphite oxide and tetrabutyl titanate to enhance photocatalytic activity of TiO₂ towards methylene blue under irradiation of sunlight. They reported that anatase TiO₂ particles were dispersed on the surface of graphene sheets uniformly and degrade methylene blue more efficiently. Zhang et al. [98] improved the photocatalytic performance of TiO₂/graphene nano composites by decreasing defects of graphene and increasing interfacial contact between graphene and TiO₂. They prepared defect free graphene by exfoliation method in the organic solvent. Huang et al. [99] observed TiO₂/graphene composites exhibit enhanced photodegradation of formaldehyde in air and the concentration of graphene has influence on the photocatalytic activity of TiO₂. It was reported that enhanced photocatalytic activity was caused by C–Ti bond, which decreased the recombination of electron–hole pairs. The prepared TiO₂/graphene hybrid by Liang et al. [153] has 3–fold superior photocatalytic activity in degradation of rhodamine B over TiO₂ (P25) materials. Ping et al. [154] found that TiO₂ (P25) degussa/graphene hybrids were much better than the bare TiO₂ (P25). Stengl et al. [155] prepared TiO₂/graphene oxide nanocomposite by thermal hydrolysis of graphene oxide nanosheets and titania peroxo–complex for photocatalytic degradation of butane in gas phase. Jung et al. [156] used PVA–TiO₂/graphene nano composite for methylene blue dye removal and found long term stability of composite. Gao et al. [157] modified the surface of water filtration membranes with TiO₂/graphene oxide to enhance their photocatalytic activities under both UV and sunlight irradiations. TiO₂ particles were
deposited on the graphene oxide sheet using layer by layer approach method followed by reduction of graphene oxide. They observed improvement in methylene blue degradation.

2.4.5 Applications of TiO$_2$

TiO$_2$ has a wide range of applications due to its excellent photocatalytic, optical, biocompatibility, strength, machineability, whitening, resistance to corrosion [158] properties.

TiO$_2$ in anatase phase acts as a photocatalyst under ultraviolet light. The strong oxidation potential of hydroxyl radical helps in waste water and air purification [93-95]. Because having large refractive index ($n = 2.7$) and a good reflector of visible light it is used as a white pigment. It is added to paints, cements, tile or other products because of its brightness. It is also used as a pigment in paints, paper industries, toothpastes, foods, medicines etc. [152, 158].

TiO$_2$ is also used in self cleaning or antifogging applications. When the building materials are coated with TiO$_2$ in anatase phase the buildings remain clean at all the times because the hydrocarbons wastage gets oxidized and dirt on the walls washes away in rain water. Other field of its application is sensors such as humidity and gas sensors. TiO$_2$ particles have high sensitivity and response time to the different gases. Moreover, it is used in ceramics, in electric devices such as voltage dependent resistor, electrochromic devices, plays a role in the bone implants, gate insulator for the new generation of MOSFETs and as a spacer material in magnetic spin–valve systems. Other applications of TiO$_2$ include cosmetic products such as sunscreen creams, whitening creams, morning and night creams, skin milks etc.

2.5 Zirconium Oxide (ZrO$_2$)

ZrO$_2$ is an inorganic metal oxide also referred as zirconium oxide or zirconia. Zirconium is one of the oldest mineral of the earth.

2.5.1 Properties of ZrO$_2$

ZrO$_2$ has great hardness, chemical inertness, high melting point, high density and lack of toxicity [159-161]. ZrO$_2$ does not melt below 2680°C. Because of its high thermal stability it is used in high–temperature ceramics such as crucibles or furnaces [161]. The band gap of ZrO$_2$ ranges from 3.25–5.1eV depending on the phase (cubic, tetragonal, monoclinic) and preparation methods [162]. The most frequent accepted value is 5 eV, with
the conduction band potential of $-1.0 \text{ V vs. normal hydrogen electrode}$ at zero pH. The wide band gap and high negative value of conduction band potential allowed its use as a photocatalyst in the production of hydrogen in water decomposition [163]. Molecular stability of ZrO$_2$ can be enhanced by mixing it with metallic oxides, such as MgO, CaO, or Y$_2$O$_3$. Zirconia consists of seven-coordinate zirconium centres unlike TiO$_2$ which features octahedral Ti in all phases. This is due to the larger size of Zr atom relative to the Ti atom [161]. ZrO$_2$ exits in three forms $vi$z. Monoclinic (M), Cubic (C) and Tetragonal (T) shown in Figure 2.7.

![Figure 2.7 Structure of tetragonal, monoclinic and cubic ZrO$_2$](image)

The Zr$^{4+}$ ion in tetragonal and cubic phase of ZrO$_2$ has eight-fold coordination. It exists in tetragonal structure in the temperature range of 1170°C to 2370°C [161]. At very high temperature ($>2370^\circ \text{C}$) the ZrO$_2$ has a cubic structure. Zhao et al. [164] showed that the t–ZrO$_2$ phase can be obtained from the cubic phase by alternate displacements of oxygen atoms in c axis. For the tetragonal structure, cell dimensions are a=5.05 Å, c=5.18 Å, and d$_z$=0.0574.

In monoclinic phase of ZrO$_2$ the Zr$^{4+}$ ion has seven-fold coordination $i.e.$ surrounded by seven oxygen atoms as shown in Figure 2.8. ZrO$_2$ exist in monoclinic phase below 1170°C. For the monoclinic structure, cell dimensions are $a = 5.15$ Å, $b = 5.21$ Å, $c = 5.31$ Å and $\theta = 99.23^\circ$.

ZrO$_2$ has large number of excellent properties such as it has high mechanical strength, fracture toughness, thermal insulation, wear and erosion resistance, chemical durability and alkali resistance. Table 2.3 lists the chemical, physical and thermal properties
of ZrO₂. So, due to these properties it is used in a variety of applications like in constructional ceramics, biological ceramics and heterogeneous catalytic processes.

### Table 2.3 Chemical, physical and thermal properties of ZrO₂

<table>
<thead>
<tr>
<th>Chemical properties</th>
<th>Physical properties</th>
<th>Thermal properties</th>
</tr>
</thead>
<tbody>
<tr>
<td>Symbol</td>
<td>Density</td>
<td>Melting point</td>
</tr>
<tr>
<td>ZrO₂</td>
<td>5.68 g/cm³</td>
<td>2715°C</td>
</tr>
<tr>
<td>Chemical composition</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Zirconium</td>
<td>Molar mass</td>
<td></td>
</tr>
<tr>
<td>91.22%</td>
<td>123.22 g/mol</td>
<td></td>
</tr>
<tr>
<td>Oxygen</td>
<td>Boiling point</td>
<td></td>
</tr>
<tr>
<td>40.55%</td>
<td>4300°C</td>
<td></td>
</tr>
</tbody>
</table>

#### 2.5.2 Synthesis of ZrO₂ photocatalyst

Several chemical and physical methods used to synthesize ZrO₂ are:

- Thermal decomposition [165]
- Chemical evaporation [166]
- Sol–gel method [167]
- Hydrothermal technique [168].
- Emulsion method [169] and
- Combustion method

Bahari et al. [167] synthesized tetragonal phase zirconia (t–ZrO₂) at room temperature by the sol–gel method. They prepared zirconium dioxide by the hydrolysis and condensation of zirconium propoxide under acidic conditions. Tetragonal phase zirconia prepared using the sol–gel method can be stabilized at low temperatures depending on pH and the hydrolysis catalysts used in the synthesis. Hydrothermal route is extensively employed method in the synthesis of metal oxide nanostructures [168, 170]. Siu et al. [171] and Matos et al. [170] used hydrothermal method to prepare ZrO₂ particles. They observed that size of particles in the region 5–120 nm at room temperature and have larger surface area. Another important method of ZrO₂ synthesis is combustion method also known as self–propagating high–temperature synthesis (SHS). It is an effective, low–cost method to obtain fine particles of various industrially useful oxides that can be used as supports as well as catalyst materials. The catalysts and nanocarriers prepared by combustion method have better properties than those of prepared by traditional method. Depending on the physical nature of the initial reaction medium combustion method is classified in to:
(a) Conventional SHS \(\rightarrow\) initial reactants are in solid state

(b) Solution–combustion SHS \(\rightarrow\) initial reaction medium is aqueous solution.

(c) Gas–phase combustion \(\rightarrow\) Synthesis of nanoparticles in flame

It is difficult to produce nano materials by conventional SHS, where the initial reactants are in solid phase and having size of particles in the range of 10–100μm. The solid reactant was heated at high reaction temperatures (>2000 K). This makes difficult to synthesize nanosize structures with high surface area [172]. However, nanomaterials can be synthesized after heat treatment following by other process such as:

- Intensive milling,
- Mechanical activation (MA),
- Chemical treatment, so–called chemical dispersion,

Solution combustion synthesis (SCS) is a simple and quick process which allows effective synthesis of a variety of nanosize materials. In this process reactants in desired concentrations were dissolved in water and stirred until homogeneous solution was not received. The solution was slowly heated to evaporate water and concentrate reactants under constant stirring. This process not only yields nanosize oxide materials but also allows uniform doping. Complex catalysts like combinations of copper, zinc, zirconium and palladium oxides were prepared by SCS routes [173].

Sahu et al. [174] synthesized fine zirconium dioxide powder using zirconyl nitrate by combustion method. They studied the catalytic activity of the zirconia samples by hydrogenation of cyclohexanone with isopropyl alcohol. Schuyten et al. [173] reported volume combustion synthesis of catalysts and concluded catalysts prepared by conventional volume combustion synthesis techniques were highly sensitive to the fuel/oxidizer ratio. The solution combustion synthesized catalysts was used for air and water pollutants remediation.

### 2.5.3 ZrO\(_2\) as a photocatalyst

ZrO\(_2\) is an element of same group and almost have same properties as that of TiO\(_2\). TiO\(_2\) is water soluble and cannot be reused on the other hand ZrO\(_2\) is not soluble in water. It behaves as an n–type semiconductor. Some researchers have used ZrO\(_2\) in photocatalysis as a photocatalyst. Silvia et al. [133] synthesized ZrO\(_2\) and ZrO\(_2\)/Fe semiconductors by a sol–gel technique. The prepared catalyst was used to degrade nitrite, EDTA and Cr(VI) using
photocatalysis process. They found that its efficiency was lower as compared to that of TiO$_2$ (P25). Cai et al. [175] used ZrO$_2$ to modify the photocatalytic properties of TiO$_2$. They observed that addition of ZrO$_2$ not only significantly improved the catalytic activity, but also increase the thermal stability of TiO$_2$. They used this binary composite in the removal of methanol. Yan et al. [100] used ZrO$_2$/CuO composite as a photocatalyst under simulated sunlight irradiation. Das et al. [176] used ZrO$_2$ in TiO$_2$ for the degradation of phenol. Othman et al. [177] studied photocatalytic activity of sulphated ZrO$_2$/V$_2$O$_5$ catalysts for the degradation of direct blue–1 dye. Kadi et al. [96] enhanced the photocatalytic properties of ZrO$_2$/SiO$_2$ nanoparticles by platinum doping. Thus, ZrO$_2$ was used to enhance the photocatalytic properties of various catalysts, but alone ZrO$_2$ was not used as a catalyst in the photocatalysis process. Here ZrO$_2$ used as a photocatalyst and effect of graphene on its photocatalytic properties is also examined.

2.5.4 Applications of ZrO$_2$

ZrO$_2$ has advantages over other ceramics in different fields because of its high mechanical strength and fracture toughness. ZrO$_2$ have clinical applications such as: arthroplasty, dental crowns but with limitation of fatigue failure in some cases. It has applications in optical coating, protective coating and thermal–barrier coating, catalysis or catalyst support and fuel–cell technology. Zirconia based ceramics are also used in engineering applications such as in manufacture cutting tools, gas sensors, oxygen sensor, piezoelectric, electro optic, dielectric and nanoelectronic devices. It can be used in detection of pesticides e.g. Nitroaromatic pesticides, asmethyl parathion and paraoxon [172-174].
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