2.1 Introduction

The present chapter is a detailed review of research works reported in the literature related to the preparation of reduced graphene oxide and its photocatalytic application. Their attractive and excellent properties make it a suitable candidate to be used as composite materials. Works on reduced graphene oxide-ZnO nano-composites (rGO-ZnO) with different structure of ZnO and its degradation rate of organic pollutant are also summarized. Finally, their characterizations techniques are reviewed. This brief literature review helped the accomplishment and planning of the research work for synthesizing of graphene oxide-based nanoceramic composites and its recent applications.

2.2 Graphite

Graphite is a well-known form of carbon and has a planer structure (Cooper, 1980; Russel, 1982). It consists of several graphene sheets stacked together and it may have flake like structure or a preferred orientation. In this structure, the carbon-carbon bond is strong, and bonding between planes is weak. Its interatomic distance (carbon-carbon) is 0.142nm, and interatomic planer spacing is 0.304nm, which is shown in figure 2.1. Graphite unit cell structure with their side view and plane view of layer stacking of graphite is shown in figure 2.2, 2.3 and 2.4(C.F. Cooper et al. 1982, P.P. Briseboisa et al. 2020, J.R.Gong , InTechOpen 2011)
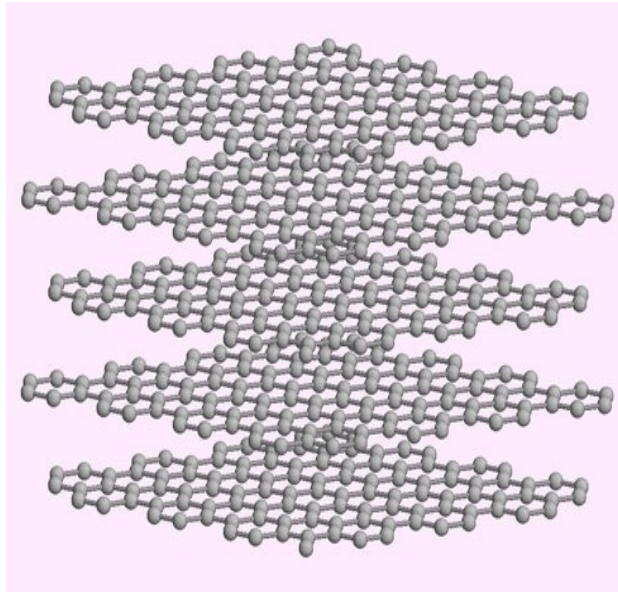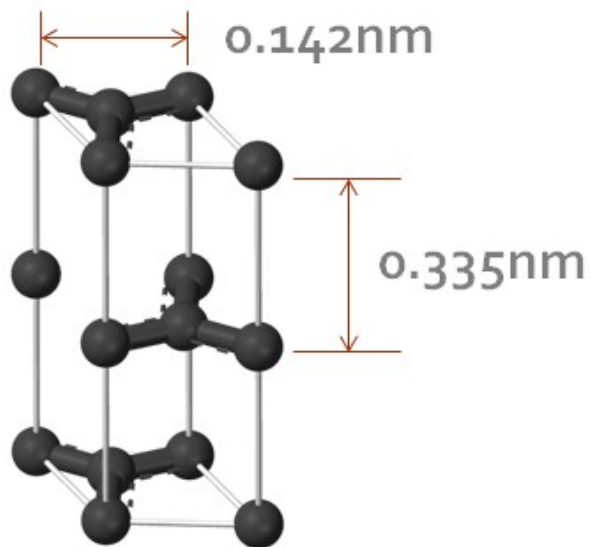
Figure 2.1 Crystal structure of graphite.
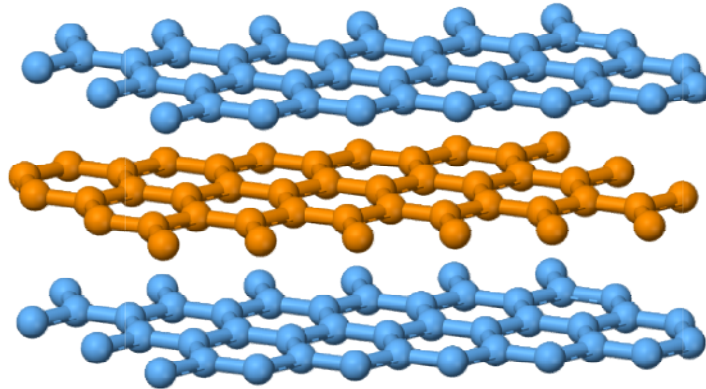

Figure 2.2 Graphite unit cell.

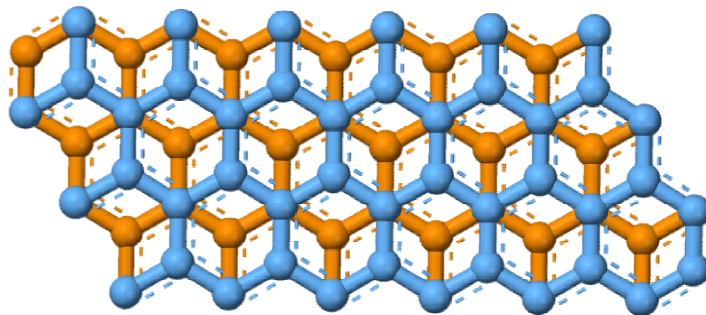**Figure 2.3** Side view of layer stacking of Graphite.

Figure2.4 Plane view of layer stacking of Graphite.

The physical properties of graphite, such as thermal expansion, thermal conductivity, and compressibility are dependenton its structure. Thermal expansion of graphite is 200 times more when planes are perpendicular to each other as compared to parallel planes. When the planes are in the perpendicular direction, its compressibility is 104-105 times greater. However, the random orientation of graphite structure decreases its degree of anisotropy.

2.3 Graphite oxide /Graphene oxide

Graphite oxide (GO) or graphene oxide is the oxygenated form of monolayer graphene which is produced by chemical oxidation of graphite. It isan unique material containing reactive oxygen functional groups, which is attributed for vast applications through chemical functionalization (W.K. Bai and E. Shen 2012; D.R.Dreyer, et al. 2010; M.Lubke et al. 2015; A. Safavi, et al. 2012). The graphene oxide synthesized by chemical modification of graphite having many biochemical and structural defects which create problems for some application but are an advantage for some others (Q. Xiao, et al. 2011). In this context, focus on its composites with other materials which are excellent water dispersibility (J.Liu, et al. 2014) would be more desirable. The dispersibility of GO only depends on polar and non-polar solvents (A.Romero, et al. 2015; J. Zhu, et al. 2010). In addition, controlled carbon to oxygen ratio of graphene oxide provides tunability to its properties from semi-metal to semiconductor (Q.Li, et al. 2010; J.Tian, et al. 2012). Generally, their property is dependent on carbon oxygen ratio of graphene oxide. Carbon to oxygen ratio of graphene oxide can be altered to change its properties from semi-metal to semiconductor (Q.Li, et al. 2010; J.Tianet al. 2012).

In addition, also the electronic and mechanical property of graphene oxide depends on carbon to oxygen ratio. It is possible to synthesis zero-band gap graphene by removing the C-O bond (A.K.Mkhoyan, et al. 2009). Various functional groups on the surface of GO makes it a platform for hybridizing with other materials. The route of graphene and graphite to graphene oxide and then to reduced graphene oxide are shown in figure 2.5 (a) and (b) respectively (E.J.C. Amieva, et al. 2016).
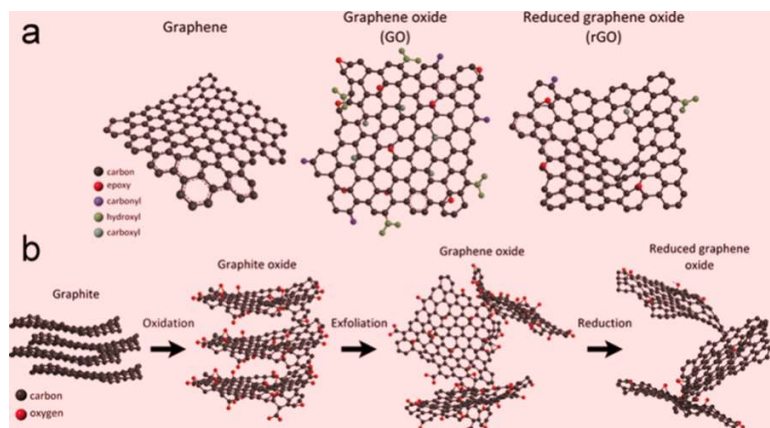
Figure 2.5 (a) Synthesisroute of Graphene, graphene oxide and reduced graphene oxide, (b) Synthesis route graphite to graphite oxide, graphene oxide, and reduced graphene oxide.

2.4 Electronic and Optical Properties of Graphene, Graphene oxide and Reduced Graphene oxide

The electronic and optical properties of carbon materials depend upon its electronic configuration. The electronic configuration of carbon atom is $1s^2$, $2s^2$, and $2p^2$. The 2s and 2p orbital have a very small difference in energy levels. One of the electrons in 2s orbital is energetically favourable to jump into the unoccupied 2p orbital. This is allowing for the creation of 4 equal bonds through the process called 'orbital hybridization.' In this process the 2s and 2p orbital hybridize to form sp^1, sp^2, and sp^3 orbital, depending on how many p orbital's are combining with the s orbital. This allows the carbon atoms to bond with multiple other elements such as organic or inorganic materials to form a variety of compounds. For this, the bond hybridization allows carbon atoms to bond to 2, 3 or more neighbouring atoms equally. The bond hybridization, for sp^2 and sp^3 carbon atoms, is demonstrated in figure 2.6.
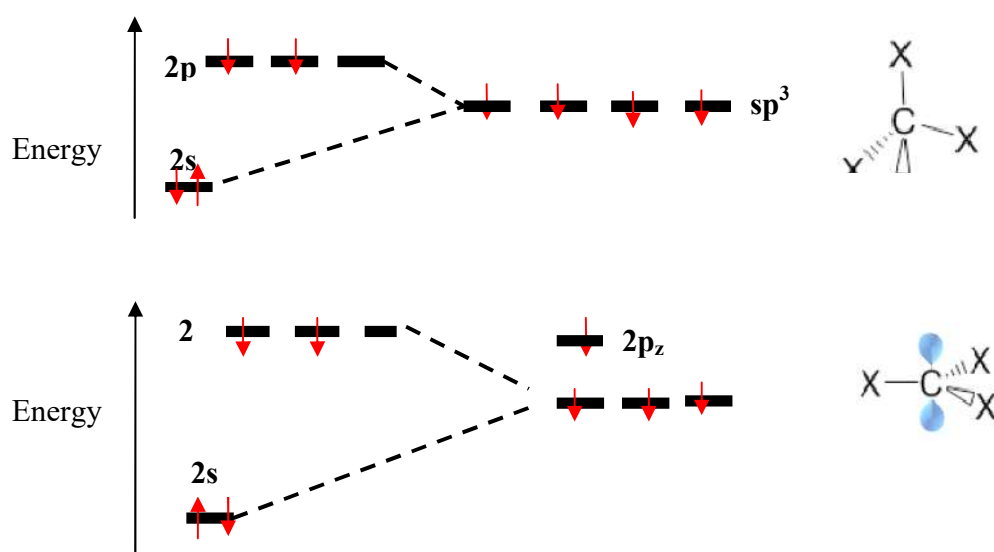
Figure 2.6 Orbital Hybridization for sp^2 and sp^3 orbital and their molecular diagram.

The sp^2 and sp^3 orbitals hybridization can be used to explain carbon allotropes such as diamond and graphite. In diamond, each carbon atom is bonded to 4 neighboring carbon atoms in a tetrahedral form through sp^3 hybridization, which is shown in figure 2.6. In graphite each carbon atom is bonded with three neighboring carbon atoms in a trigonal planar formation, forming a two-dimensional hexagonal lattice. A graphite sheet consists of multiple flat sheets of sp^2 carbon atoms stacked on top of each other. The electrically point of view, diamond is electrically insulator, and graphite is electrically conductive, although only in two dimensions. Graphite is a good electrical conductor due to its free electron in p_z orbitals which sits above and below the plane of sp^2 bonding which is shown in figure 2.6. The combination and delocalization of these p_z orbitals on each carbon atom allow for electrical conduction with the graphite sheet.

In the covalent chemical bonding between atoms, electrons must be shared by combining orbitals either via end to end overlap or side to side overlap. End to end overlap is known as sigma boning, and side to side overlap is known as pi (π) bonding. In the sp^3 carbon materials such as diamond, two sp^3 orbitals overlap to form a sigma bonding(σ) and a sigma anti-bonding(σ^*) orbital between each carbon atom. The electrons occupy the bonding orbital, which is of lower energy, thus creating a C-C σ bond. In the sp^2 carbon materials such as graphite, sp^2 orbitals overlap to form a C-C σ bond much like in diamond; however, the p_z orbitals can also form delocalized π bonds with neighboring carbon atoms shown in figure 2.7.
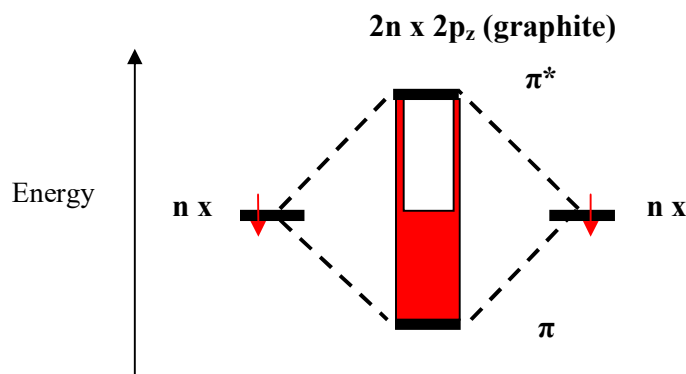

Figure 2.7 Molecular orbital diagram of graphite showing the increasing number of orbitals formed, resulting in the formation of a band of orbital when n approaches infinity. The red part of the band represents orbitals filled with electrons. The sp^2 C-C σ bonds are neglected for simplicity.

The graphene-like materials were obtained by chemical modification of graphite known as reduced graphene oxide (rGO). Graphene is considered as the building block for sp^2 bonded carbon atom, much like graphite materials. In graphene, each atom is connected to 3 other carbon atoms on the two-dimensional plane and leaving one electron freely available in the third dimension for electronic

conduction. The electronic properties of materials define the energy difference between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) which is known as bang gap of materials. The band-gap of graphene is zero, which is shown in figure 2.8 and behaves as like metals and its electronic properties is directed by π-π* bands. In pure graphene, Fermi energy is at charge neutrality point, so its electronic properties depend on the k-point (Dirac point). The band-gap of graphene oxide is 2eVand for rGO band-gap can vary from~1.00 to 1.69eV depending on the degree of reduction (Abid et al.2018). Therefore properties of GO and rGO behaves as semi-metal to semiconductor, which is shown in figure 2.8(Abid et al.2018).
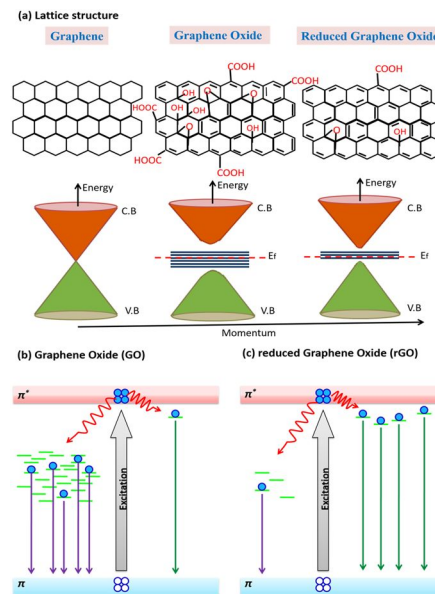

Figure 2.8 Schematic representation of: (**a**) Lattice structure and corresponding energy band diagrams of Graphene, GO and rGO; and electronic transitions in (**b**) GO and (**c**) rGO.

The optoelectronic properties of GO and rGO depend on the combination of sp^2 and sp^3 bonding. π-π^* states of sp^2 locations primarily control its optoelectronic properties, lying in σ-σ^* gap (C.T.Chien et al.2012; J. A.Yan et al.2009). In GO π bonding is weaker with lower formation energy, and many disorder-induced localized states may appear within the 2D network (Abid et al.2018). These disorder-induced localized states might be present in the band tail of π-π^* gap or lie deep inside this gap which may cause wide absorption or emission bands (C.T.Chien, et al. 2012; J.A.Yan, etal.2009). The reduction process leads to increased carrier mobility, higher absorption, a tunable band-gap where photo responsibility can be controlled by controlling the defects and oxygen groups (Y. Zhang, et al. 2013; C.T.Chien, et al. 2012).

2.5 Synthesis of Graphene oxide and reduce graphene oxide

Synthesis of graphene in mass production is major problem. Lot of method for synthesis of graphene like mechanical exploration, epitaxial growth, chemical vapor deposition (CVD), and chemical exfoliation has been reported in the literature. Among them one of the major routes for mass production of graphene material synthesis is the chemical exfoliation of graphite. This requires overcoming graphite's interlayer bonding energy, allowing for separation of individual sheets. The graphene oxide (GO) is a chemically modified material made from natural graphite, which can be reduced in various ways to give graphene like platelets, commonly known as reduced graphene oxide (rGO), which is a solution processable in environmentally friendly solvents (i.e. water). However, the chemical modification required to form both GO and rGO platelet causes a reduction in some of the favorable properties of

graphene. Dreyer et al. 2010 has been developing a method for synthesis of graphene oxide. The reaction between graphite and $KClO_3$ in fuming $HNO_3$was performed by B.C. Brodie at that time resulted with an increasing mass of flake graphite.Later, Staudenmier in year 1898 modified this method by using concentrated H_2SO_4. In this, Dreyer et al., 2010 were aliquot added the chlorate over the course of reaction. After that, Hummer and offeman using the alternate oxidation such as concentrated H_2SO_4; KMnO4has further improved the above method. This method is mostly used until now with some modification and improvement.

H.Yang et al. 2014 developed a facile synthesis method by some modification on Hummer's method. This method acutely promote the lesser use of acid, extremely time saving, minimum energy consuming, and high efficiency without releasing toxic gas. Until now, a continuous rapid research is evolving to develop a simple and environment friendly methods to prepare GO.A. T. Smith, et al. 2019 has developed synthesis method that improves the efficiency of the oxidation process.T. D.Artur,et al.2019 has split GO preparation process into two stages. Firstly soft chemical exfoliation of initial graphite into graphene flakes in liquid media and secondary oxidation of resulting product in mild conditions. H.Chen,et al.2019 has prepared GO in three different procedures: a modified Charpy- Hummer method, modified Hummer method at room temperature, and low temperature modified Hummer method. These methods produced mass production of high-quality graphene materials.

Finally the chemical modification is to oxidize the graphite into graphite oxide, which can easily be exfoliated into individual GO sheets and then reduced back to a graphene like materials. However, chemically reduced graphene oxide has some oxygen functionality, as well as defects in the lattice structure (C.K. Chua, and M. Pumera 2014). It can not be considered the same as pure graphene and is therefore called reduced graphene oxide (rGO). In the literature, there are many different methods of reducing GO to rGO (S. Stankovich, et al.2007). The hydrazine (N_2H_4) is a reducing agent which is most commonly used in reduction method (S. Stankovich, et al.2007). The reaction mechanism of hydrazine with the present functional groups of GO is very difficult to determine that which functional groups are affected by the hydrazine. X. Gao et al. 2010 suggest that hydrazine removes epoxide groups on the surface of GO sheets as well as forming the hydrozone groups by reacting with carbonyl groups. The effect of hydrazine and thermal reduction on oxygen containing functional groups of GO has been determined using the density functional theory which are listed in table 2.1(X. Gao, et al. 2010). The schematic diagram for reduction method reduced graphene oxide is shown in figure 2.9.

Table 2.1 Reduction of oxygen functional groups after hydrazine and thermal reduction.

| Oxygen Containing Functional Group	Hydrazine at Room Temperature	Thermal Treatment $(700\text{-}120^0C)$	Combined Hydrazine and Thermal Treatment
Epoxide(C-O-C	Removed	Not Removed	Removed
Edge Epoxide (C-O-C)	Converted	Not Removed	Not Removed
Alcohol(C-OH)	Removed	Removed	Removed
EdgeAlcohol (C-OH)	Not Removed	Removed	Removed
Corboxyle(C=O)	Not Removed	Not Removed	Not Removed
Corboxylic acid (C=O)	Partially Removed	Removed	Removed
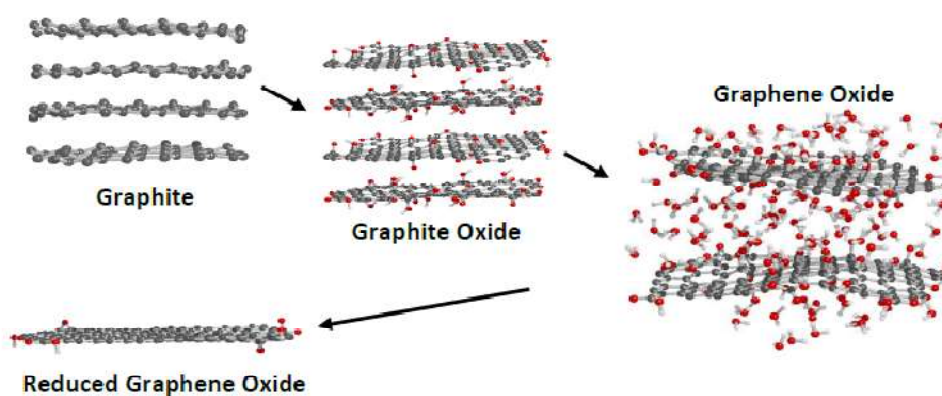
Figure 2.9 Schematic diagram represent the reduction process of graphite into reduced graphene oxide.

2.6 Synthesis of Graphene oxide-based nanoceramic composite

GO-based Nano ceramic material composite plays an important role in wide range of applications. It can be prepared by different processing routes such as sol-gel method (A.E.Danks, et al.2016;Z.Durmus, et al.2019), hydrothermal method (Y.Li, et al. 2015;J. Ding, et al.2015, X.Wu, et al.2018,)assisted solution route (M.Darwish, et al.2016), aqueous chemical route (M. R. Parra, et al.2014), chemical precipitation method(Q.Yang, et al.2010), and electrochemical deposition (Y. Li, et al. 2015;F.Khurshid, et al.2019).In GO-based nanoceramic composite, the composites materials such as Cds, SnO_2,Sio_2, WO_3, ZnO, Nb_2O_3 etc. embedded or hybridized or on the GO sheets with functional components of GO (P.V. Kamat et al.2010; X.Zhao, et al. 2014; Quek J.A. et al. 2018, Ning Z. et al. 2019; Lin Z. et al. 2018; Wu Z., et al. 2019; Yosefi L., et al. 2019). Therefore in the present section discussion on the preparations method of GO-based composites materials that have been predicted by some researchers.

2.6.1 Hydrothermal method

The hydrothermal or solvothermal method is a method in which materials synthesized at high temperature and pressure. It is carried out in Teflon-line autoclave and the temperature used is between 160-180^{0}C (L.Sun, et al.2015; X. Xu, et al., 2014). It is an effective and very low-cost method which could be favorable to synthesis GO-based nano-composites materials. F.Lorestani et al, 2015; X.Wu et al.2018, using this method and synthesized reduced graphene oxide in excessive

amount.X. Xu, et al., 2014 using this method and synthesized rGO/COWO$_4$ composites.

Similarly, L.Dong, et at. 2014 has been synthesized rGO/TiO$_2$ nano-composites as anode material for lithium-ion batteries using the same method. B.Pan et al.2019 also synthesis Ag$_2$CO$_3$-TiO$_2$ loaded reduced graphene oxide nanocomposites. This method reduction of GO is achieved at 130^0C for 4h. Junwei D. et al.2015 is also using hydrothermal method for synthesis of rGO-ZnO at 120^0C for 10h.

Later, this method has been modified as a microwave-assisted hydrothermal method. Y. Gui et al. 2015 has been used this method and to synthesize graphene/WO$_3$ by employing GO as a starting material. This method was again modified by L.Tang, et al. 2015 to prepare rGO/SnO$_2$ nano-composite, which was assisted by ionic liquid that acts as a reaction medium in order to enhance the microwave-assisted hydrothermal method.

2.6.2 Electrochemical Deposition

The electrochemical deposition, also known electroplating is a deposition method in which a material is deposited onto a conducting surface or electrode from the solution containing ionic species (salts). In this technique is mostly used employed for deposition of thin films of materials to the surface of an object. F.Rahmanabandi et al.2019 utilizing this technique and deposited nano-composite material onto an electrode for application of novel glucose sensor and GO-based super-capacitor. Similarly, Y. Li et al. 2015 have synthesized GO/ZnO nano-

composite film on Fluorine doped tin oxide (FTO) coated glass substrate using the same method. N.R.L. Maria, et al. 2019 synthesized ZnO/Cu$_2$O heterojunction solar cells by electrodeposition technique. In this method, ZnO and Cu$_2$O films were deposited by a conventional three-electrode ECD method using a potentiost at (PGSTAT 101AUTOLAB) and NOVA software. For modification, the films were coated with GO film by dip-coating method.

2.6.3 Sol-gel Technique

The sol-gel process is a method that has been involved the transition of a solution system from a colloidal liquid "sol '' into a solid '' gel'' phage. In the sol-gel process, sol behaves as the precursor for the formation of the gel network. In this method, metals oxide, inorganic metal salts, or metal organic compound such as metal alkoxides used for preparation of the "sol". The "Sol" precursor is hydrolyzing through polymerization reaction and forms a colloidal suspension or a "sol". Further processing of the "sol" makes it possible to make materials in different forms. The sol-gel method is a desirable and low-cost method for preparation of controlled shape and morphology of the elements with low processing temperature which directly obtained from the gel state.

Recently, GO-based material nanocomposites have been synthesized by using the sol-gel technique (Chan Zheng, et al., 2015; M. Li, et al., 2016; D. Zehra, et al.2019). P.K. Labhane, et al.2019 has also been synthesized RGO-ZnO nanocomposites using a similar method. In this concentration of ZnO is added in the solution of RGO for preparation of RGO-ZnO nanocomposites. In the sol-gel

process, different types of biomolecules also encapsulated with reduced graphene oxides.

2.7 Application of Graphene Oxide –based Material nanoceramic composite

2.7.1 Wastewater Treatment

In the country, rapid increasing the industry has led to an increase in discharge wastewater. It is a huge source of organic pollution which produces pollutants that are extremely harmful to people and the environment. The Pollutants have been contained heavy metals (Hou Wang, et al. 2015) and organic dyes (Xiao Huang, et al. 2011). The major pollutants in wastewater could be organics, such as dyes, phenolic compounds, oils, etc. There are number of method for treatment of water Pollution such as sedimentation, coagulation, filtration, biotechnology (K. N. M.Bernard, et al.2019, S.Ali, et al. 2019), Osmosis, chemical oxidation, photocatalytic degradation (Y. Mokhbil et al. 2019), absorption (S.Taghipour, et al.2019), membrane process (A.Mona et al.2018), dialysis (R.Lafi et al.2018), foam flotation (L.Chang, et al.2019). Water treatment method such as sedimentation, coagulation, filtration, biotechnology, Osmosis, chemical, and oxidation were suffering from some disadvantage such as incomplete removal, high treatment cost, time consuming and generation of toxic secondary pollutants (P.Krzeminski, et al. 2019,Z. Chen et al. 2019).
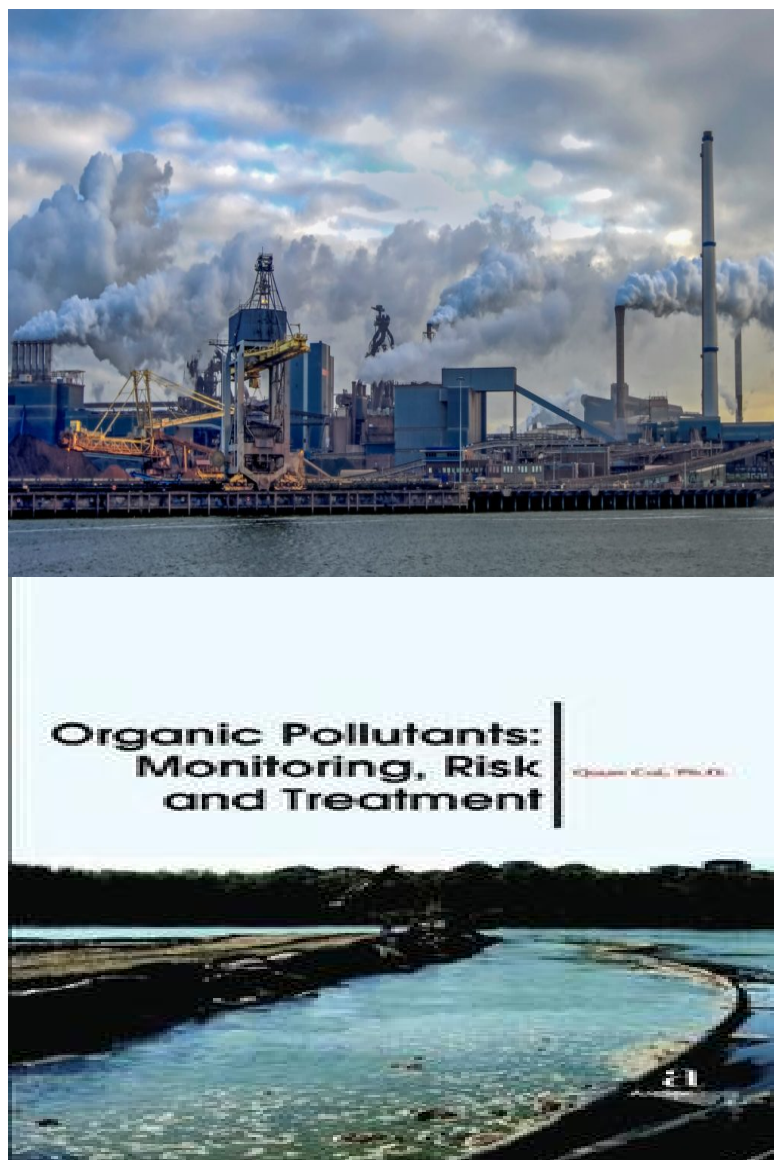
Figure2.10 Industrial Organic Pollutants.

Recently researchers try to reduce organic pollutant from wastewater using the various GO-based photocatalytic materials such as TiO_2, ZnO, etc. (P.K. Boruah, et al. 2015; Wang, et al. 2018; S. K. Mandal, et al. 2019). GO and rGO having the large surface area and grapes of functional groups which makes it a strong candidate for adsorption/absorption and photocatalyst application in wastewater treatment.

2.7.2 Photocatalysis

The GO-based nano-composite photocatalytic materials such as TiO_2, ZnO, ZnS, and WO_3 have a great interest in degrading the insecticides, organic dyes, heavy metals, and other carcinogenic chemicals. It is reusable and self-regenerated properties (V.K.Gupta, et al. 2015; M. Li, et al. 2016; Hou Wang, et al., 2015). However, GO, and rGO has a large surface area which is beneficial for rapid recombination of photogenerated electrons and holes within photocatalyst (L. Hu, et al. 2013). Being the excellent physical and mechanical properties of reduced graphene oxide can be utilized as an effectual electron acceptor to boost the photoinduced charge transfer for improved photocatalytic activity (V.K. Gupta et al. 2015; L. Hu et al. 2013).

2.7.3 Parameters effecting the photocatalytic activity

There are different types of parameters such as pH of the solution, initial concentration of dyes, photocatalyst particle size and morphology and its concentration, reaction temperature, light intensity, and the presence of electron acceptors. The degradation mechanism of organic pollutant influences these parameters. The effect of the above parameters is discussed in the following paragraphs.

2.7.4 The effect of pH

The Degradation of the organic pollutant from the wastewater highly depends on the pH. It is a challenging task to explain the effect of pH on the photocatalytic degradation. The reason behind it that in the reaction mechanism formation of hydroxyl radicals, which are attracted to the organic pollutant by direct oxidation with the positive hole, and immediate reduction by the electron in the conducting band. In this mechanism, hydroxyl radicals can contribute to the degradation of organic pollutants, and it depends on the substrate nature and pH. ZnO is having either a positive or a negative charge on its surface, which is influence adsorption of organic pollutants with pH variation. The effect of different pH and catalyst concentration has been reported by X.Du, et al.2019. He observed that increasing the pH from 3 to 9 of hybrid catalyst Cu@C_2ORGOCE exhibited high catalytic activity in acidic solution.

2.7.5 Effect of Graphene oxide content on Photocatalyst

Recently, there are a few researchers performance the experiment for degradation of organic pollutant with the help of the photodegradation process using the various GO-based photocatalytic materials. L. Sun, et al. 2015 and X.Du,et al.2019 have been reported the low concentration of GO (0-0.5%) in the semiconductor to enhance their photocatalytic activity under visible light irradiation. However, further increased GO content which decreases the photocatalytic activity that resulted in low photocatalytic activity.

2.7.6 Effect of Catalyst loading, Size and structure of the photocatalyst

In the photocatalytic degradation process, amount of catalyst, its size and morphology have effected the degradation of organic pollutants. In the literature, the researchers were worked on the ZnO-rGO nanocomposites system for photocatalytic application. Dongying Fu et al. 2012 have been reported that low content of ZnO-rGO composites could not absorb the light completely, and an excess amount of ZnO-rGO reflects the light. Fengzhi Wang et al. 2018 have been reported that nanorods like morphology of ZnO- rGO composites enhanced the photocatalytic performance. H. N.Tien, et al. 2013 has been reported that sphere ZnOSPs-rGO enhanced the degradation of methylene blue. S. K. Mandal, et al. 2019 have been reported that quantum dots ZnO- rGO completely degraded the organic pollutants. Shaouhua Xu, et al.2014 have reported that flower-like ZnO-rGO enhanced the photogenerated carrier's recombination rate. X.Du, et al.2019 have been reported the effect of different pH and catalyst dosage on the photocatalytic activity. From the above literature study, we conclude that for the degradation of organic pollutant, the morphology of ZnO is significant. A few recent rGO-ZnO nanocomposites materials and their photocatalytic application have been listed in Table 2.1.

Table 2.2 Comparative study of degradation efficiency of rGO-ZnO based Photocatalyst.

Photocatalysts	Synthesis Method	Catalyst loading (mg-L^{-1})	Dye	Light source	Irradiation times (min)	Degradation efficiency (%)	Reff.
rGO –ZnO	Dispersion	50	Methylene blue	Xe lamp 200W	50min	80%	Fu D. et al.2012
rGO –ZnO nanorods	Hydrothermal	50	Rhodamine B& phenol	300 W Xe arc lamp	12min	97.2%	Wang, F. et al.2018
rGO –ZnO sphere	Facile &microwave	0.2	Methylene blue	Visible irradiation	90min		Tien H.N. et al. 2013
rGO –ZnO nanowire	Facile	20	Rhodamine 6G	Mercury lamp 150W	10min	98%	Zhang, C. et al. 2014
rGO –ZnO Quantum dots	Chemical Route	3	Rhodamine 6G	100W UV lamp	45min	100 %	Mandals S.K. et al. 2019
ZnO flower/RGO	One-Pot Hydrothermal	50	Methylene blue	UV lamp 100W& Sunlight	150min	97%	Xu, S. et al. 2014
ZnO hierarchical Mesoporousflower /rGO	Hydrothermal	50	Methylene blue	300W Mercury-Xenon lamp		99%	A.Shanmugas-undaram, et al. 2018

2.7.7 Reaction temperature

Photocatalytic degradation of organic pollutants is influenced by the reaction temperature. D.R.Paul, et al.2019 has been reported the temperature of the catalyst has an effect on the photodegradation process. Similarly, J.Zhu, et al. 2019 also has been declared the results of reaction temperature on acetaminophen degradation in PMS/MgCuFe-LDH system. He was found the acetaminophen degradation change at varying temperature.

2.7.8 Concentration and nature of pollutants

The organic pollutant of the wastewater is content the dyes, phenolic compounds, oils, etc. The degradation rate of organic pollutants is dependent on the nature and concentration of the contaminant. In this chemical structure and quality of the target, the compound has been influencing the degradation rate of the organic pollutant.

2.8 Summary

In the summary of this chapter, the research work on the synthesis of graphene oxide and their composites with nanoceramic material is going rapidly. The excellent physical and mechanical properties, researchers have been competed to develop structure morphology of novel nano-composite materials with various synthesis methods. The synthesis method plays an essential role to produce a more extensive scale production of reduced graphene oxide and control the specific structural morphology of rGO-ZnO nano-composite and other composites. These nanocomposites also give a great contribution toward enhancing the performance of photocatalytic degradation process of organic pollutant containing wastewater. Therefore, there a lot more work needs to be done to manipulate the GO-based nanocomposites for future advanced technology.