

# Chapter 1

## Introduction

## 1.1 Nano Science, Nano Technology and Nano Materials: New Era of Science

### 1.1.1 Nano Technology

The miniaturization of all kind of electronic devices is much more needed in the technology of twenty first century. The ultimate performance of the device radically increases when the devices are sized into nano meter. This mechanism raises all fundamental issues concerning particular functionality and selectivity of new materials. The universalisation of nano science and technology is very important for the sustainable development of any nation. This development of nano technology has facilitated the society in several ways in the last few years. This intense and dedicated technique of nano technology lay concrete in the way of enhanced and revolutionized application in various divisions like environmental studies, power, drug, information technology, various kinds of delivery system and many more. Nanotechnology has the capability to design, fabricate and make the suitable and appropriate application of the micro or nano structured materials for the benefit of mankind. In the perspective of nano technology one can understand the fundamental relationship linking properties and dimension of the nanomaterial. Nanotechnology has immerged to be a new grassland of scientific domain. It manufactures many nano materials with meta stable phases. These materials have shown many special features like superconductivity, magnetism etc. Nanotechnology creates the significant importance in low current physics. The various equipments generated by nano technology will benefit the 21<sup>st</sup>

century human society. By nano technology we have designed computers of enormous power that compete with human brain in terms of algorithm. It has developed biosensors for detection of various life threatening diseases at the very early stage and develop drug delivery system that attack the disease-affected cells on spot as well. It has manufactured nano robots for repairing the interior damage of human bodies and removal of toxic materials from human bodies. In this way, we have nano scaled electronic instruments and devices continuously keeping an eye on our neighbouring environment.

### 1.1.2 Nano Science:

*"There's Plenty of Room at the Bottom : An  
Invitation to Enter a New Field of Physics"*

—Richard Feynman

Richard Feynman give this quotation while delivering a lecture at the annual meet by American Physical Society Meeting at Caltech by the date December 29, 1959. The lecture pursued the chances of direct manipulation of lone atoms as a powerful form. Nano technology has benifited people from various walks of life, viz. teachers, scientists, students and scholars as well as personnel from various science discipline, like physical science, chemical science and materials science. Though discoveries and innovations in research area are unpredictable, nano technology is likely to raise micro atomic system single new object to macro system with new properties and various function. For the promotion of knowledge based theoretical and experimental intense research in nano science government of India had announced Nano Mission

in 2007. The Department of Science and Technology (*DST*) has taken the responsibility as nodal agency in India. They build an international hub for this. The main objective of nano mission is to improve the end products of National Sustainable Development (*NSD*) as well as the inherent process of the development. The Nano Mission aims to introduce innovation in fields of national importance and human welfare, viz. clean drinking water, materials and sensor growth, drug delivery etc. This mission will connect industries with educational sectors and research institute on a much deeper level. This inter connections will promote *PPP* model in the Nano Science and Nano Technology in terms of research as well as in application for the betterment of human being on Earth. So we can say nano mission 2007 is an umbrella programmed for its capacity in many ways.

### **1.1.3 Nano Materials:**

Nano materials are the materials having dimensions 1 to 100 nano meters. They are of two types, viz. organic and inorganic materials. All the particles are neither crystalline nor amorphous in surface property [1]. They have further been categorised into a) Nanostructure Material (*NM*) and b) Nano Particles Materials (*NPM*). The nanostructure materials are also called condensed bulk materials. The grain size of bulk materials are in nano meter range. The nano phase or the nano particles materials are dispersive materials in nature [2]. Now a days it has been noticed the unique properties of nano phase materials and their huge impact on social, economic, science and technology and that is why discrimination of the nano materials from

bulk material has great importance. Fabrication of nanostructure materials is a complex technique in order to assemble nano particles. So many research groups all over the world has intensively involved themselves towards find out the low cost and easy synthesis methods to fabricate the nano structures materials. As synthesised nanostructure materials, have shown superior characteristics properties than nano particles in different device study.

The characteristics of atoms mainly take place because of their interrelation to each other's quantum mechanically. These interactions make them stable as a unit. The dissimilar interactional force between the carbon atoms are the main reasons for the different properties of diamond, graphite, fullerene, graphene, carbon nano tube though they are made of same building block, carbon atom. This difference in properties for the nano materials of the same parent atoms are also seen by some other means such as coarser-grained counterparts, smaller grain size [3]. Depending upon there electrical conductivity nano particles may classified as metals, semiconductors and superconductor. It may be dielectrics and magnetic materials. Nano materials are either inorganic or organic. Organic nano materials may be classified as organic small molecules or polymers. Among these nano materials we are interested on semiconductors heterostructure materials because it is the optimum material for the fabrication of opto electronic device, photonic nano devices etc. [4]. The size sensitivity of the particles attributes to the change in properties of nano materials [3]. If the particle size changes then it is obvious that the surface to volume ratio will also change. It is also proved that large surface area plays an important role for nano porous materials and huge number of atoms at the surface level tends to size induced properties

of nano materials. These surface chemical activity fits the material for the industrial application towards catalytic activity, absorption etc. [5, 6].

## 1.2 Classification of Nano Materials:

We have already discussed about the size dependence on properties of nano materials in the previous paragraph. From this size dependence we can classify nano materials into four categories. These are

**a) Zero dimensional (0-D) nano material:** It is also called quantum dots.

**b) One dimensional (1-D) nano material:** It is quantum wire. Here the free electrons move towards one direction.

**c) Two dimensional (2-D) nano material:** It behaves like thin film. Here the free electron moves in a plane.

**d) Three dimensional (3-D) nano material:** It is known as nano structured material. The free electrons can to and fro in all possible three direction such that x, y and z direction.

## 1.3 Different Types of Nano Materials:

### 1.3.1 Fractals:

Fractals are the nano materials which have similar atomic arrangements toward all magnification by self physical, chemical and biological augmentation technique. Coulomb repulsive force acts between charge particles, monomer which is suspended in liquid and are made to float by Brownian motion. If

the chemical composition of the liquid gets changed then a charge is induced, an interplay within the composition elements is started and cluster is formed. Lin et al. [7,8] conveys the widespread characteristics of the colloidal aggregation. This universal property does not depend on nature of any colloidal systems. In this context two things are very important for colloidal aggregation. One is *DLCA* and the other is *RLCA*. *DLCA* stands for Diffusion Limited Colloidal Aggregation and *RLCA* is for Reaction Limited Colloidal Aggregation (*RLCA*). When there is a feeble repulsion force among the colloidal particles then only *DLCA* comes into force. In *DLCA* the fast reaction rate is totally dependent on the time span of the aggregation to interact each other through the process of diffusion. In slow *RLCA* by the technique of thermal activation the cluster to cluster repulsive force will be overcome. The colloidal aggregation of silicon, gold and polystyrene has been established in many research articles [9,10].

### **1.3.2 Porous Materials:**

Porous materials, a special kind of nano materials, have great utilization in science and technology [11,12]. Porous materials has been categorized a huge number of voids on the surface as well as inside the materials. In nano porous material merely 5 to 25 percent void space are located as compared to the total volume of the material. The percentage of porosity is higher in oxide nano materials where as in metal nano materials it much less as compared to the previous. The voids in the materials can increase the diffusion probability in ceramics nano materials.

As per *IUPAC* (international union of pure and applied chemistry) porous material has been categorised according to size of pores as listed in the table 1.1 [13].

Table 1.1: Classification of porous materials

Sl no.	Name of materials	Pore size (x)
1	Microporous materials	$X < 2 \text{ nm}$
2	Mesoporous materials	$50\text{nm} < x < 2 \text{ nm}$
3	Macroporous materials	$X > 50 \text{ nm}$

The size of the porous determines the degree of absorption property of the nano materials. It may be absorption or it may be adsorption. One can prepare the Mesoporous nano material by some technique namely sol-gel, chemical etching, template assistance etc. These porous nano materials has caught great attention of all the scientific community for their greater application in the field of catalytic effect, filtration, opto electronics, adsorption etc. [14,15]. This type of materials can also be used for removal of different types of pollutant from the environment [16]. It has the capacity to store energy [17]. It has a very low dielectric constant. This property of low dielectric constant allows the material to be a befitting candidate for optoelectronic devices with minimum loss of energy.

### 1.3.2.1 Carbon Based Nano Materials:

Carbon is not just an element. It is also the basis of all life in this world. The element carbon has repeatedly surprised us from the very beginning of life in this universe. Few years ago only two solid phases of carbon were familiar to us, one is graphite and another is diamond. Both the materials



are 3 dimensional in structural organisation. Although these two well known solids have originated from the same element carbon but their respective properties are not the same. Diamond, an insulator, was the material of super hardness among all the hardest materials where graphite has very soft property and it is highly conducting in nature. The hybridization of carbon is  $sp^3$  in diamond where the hybridization is  $sp^2$  for graphite. So the mixing up of these two type of hybridization leads carbon to form various types of carbon allotropes. This could be only happen when the position of carbon atom changed. In the table no. 1.2, we have shown different types of carbon allotropes.

Table 1.2: Different types Carbon allotropes

Sl no	Name	Nature	Shape	Year of invention
1	Fullerenes	0 D	Sphere	1985
2	Nano tubes	1 D	Tube	1991
3	Graphene	2 D	Plane /sheet	2004
4	Diamond , Graphite	3 D	—	—

Graphene is a material which have no band gap energy. It is nothing but mono layer of graphite. Graphite is an allotropes of carbon. Single or few layers of carbon atoms arranged in a sheet are called graphene. In graphene sheets one type of electron and holes are present. With the use of graphene sheet we can form all types of material as mentioned in the table 1.2. As an example, the 3D crystal like graphite is established when graphene layers are overlapped one after the other to a certain extent. For this reason the electrical nature increases quickly. Till now after the discovery of fullerene a huge number of nano structure have been produced by resembled the nature

of hybridization. Some of them are carbon onions, carbon nanorods, carbon nano horns (*CNHs*) etc.

### **1.3.3 Zeolites:**

Zeolites are known as “molecular sieves” by means of physical structure that allows material shifting. It belongs to the camp of micro porous materials. *Si, Al, O* and *Ti, Sn, Zn* are the main elements of Zeolite materials. In nano science Zeolite materials have great importance in various fields mainly in catalytic application for removal of pollutant from environment [18-19]. There are almost 100 types of different Zeolites structure formation in the world. In all this structures, Zeolites appear to be like nanoscopic galleries, controlled by nanoscopic voids.

### **1.3.4 Self Assembly Passivated Nanocrystals Superlattices:**

The nano particles that are self organised onto single layers, *2D* thin films and the particles which are protected by organic coating for encapsulating size driven nanoclusters are called self-assembly passivated nanocrystals superlattices. Formation of such type of materials controlled by size and shape has the super ability to assemble towards superlattice crystals for some nano technology based applications [20]. Size and shape driven nano materials act similar to a molecular particles and ideal template for *2D* or *3D* self assembled superlatttice structure [21-23]. This type of material has electronic, optical, transport phenomenon as well as magnetic properties. This property

depends on coupling and nano crystal interaction [24].

### 1.3.5 Micelles:

Micelles are another type of materials in nano particle category. When the limit of concentration of surfactant crossed the Critical Micelle Concentration (*CMC*) in water, Micelle formation takes place. Surfactants have two types of group in there structure. These are hydro carbon chain and hydrophilic chain. Former is arranged towards the inner section of micelle and the later is connected with the aqueous environment. *CMC* has a great role as far as physical property is concerned. Above it the physical state changes significantly and around it, the bulk properties such that cosmic pressure, surface tension, self diffusion and conductivity changes accordingly. When reverse action is created such that hydrophilic head-groups are focussed to the centre and the hydrophobic groups are concentrating superficial directions of the micelles then it is called reverse micelles. The property of reverse micelles does not depend on *CMC*. By the use of reverse micelles nano particles are synthesised. There are two ways for this nano particle formation. Firstly two reverse micelles have been mixed. For the coalescence of these micelles, material exchange takes place and then interaction between centres and the nano molecules occurs. Secondly mixing of two reactants generates nano particles. Among these two reactants one is soluble in reverse micelles and the other, dissolves in water. By this simple process metal nano particles have been synthesised. sodium borohydride ( $NaBH_4$ ), hydrazine mono hydrate ( $N_2H_4$ ) are used as the reducing agent [25-28].

### 1.3.6 Self Assembled Mono Layers (*SAM*):

*SAMs* are a special type of nano materials, very suitable in nano technology. Main significance of *SAM* is that it carries information with it for the generation of ordered nano crystal materials without any interference. From individual nm scale elements like molecule, colloid etc nano scale materials are fabricated by a typical model established by *SAMs*. *SAMs* assemble onto surface of nano sheet of any geometrical shape and size by controlling the wetness and electrostatic quality of each individual. They can organise huge assemblies of nanomaterial. Here one thing is to be remembered that the kinetics and the mechanics of assemblies may differ drastically. It can significantly modify the interface of nano structure materials and the surroundings of it. *SAMs* can generate macroscopic materials having different properties and functions. A very special feature of *SAMs* is that it can add chemical functionality to the surface of inorganic nanomaterial. It also makes surface stability thermodynamically. Thus this type of materials can connect to complex system of particles [29].

### 1.3.7 *NC* (Nano Crystal) Core/Shell Structures:

*NC* core /shell structure nano particles have caught the attention of scientific community of the world because of its application in catalysis, electro chemistry, biology and various other fields. Already the techniques of coating of one type of semiconductor material on another type of semiconductor are known to us. Till now, a huge number of *NC* core/shell structure have been synthesised. *CdSe/CdS*, *CdTe/CdSe*, *CdSe/ZnS*, *CdSe/ZnSe*,

*CdSe/ZnTe* and *FePt/Fe<sub>3</sub>O<sub>4</sub>* core/shell nanoparticles are some of them. The conditions to prepare this *NC* core/shell materials epitaxy growth are depicted bellow.

a) The similarity on the surface energy should be attained for better preparation of above said materials.

b) The *NC* materials have to resist the surroundings below which the 2<sup>nd</sup> type of materials is doping.

c) In 2<sup>nd</sup> phase material the heterogeneous nucleation is much less than that of homogeneous nucleation.

d) The probability of inter diffusion between two types of phase when deposition is undergoing is merely impossible. By this noble preparation technique one can also prepare Metal oxide nano particles [30-34].

### 1.3.8 Nature's Nanoparticle Factories:

By the law of god, we are quite lucky to have many numbers of nano particles which are naturally prepared in the suitable environment. One can see lot of nano particles namely *CdS*, *H<sub>2</sub>UO<sub>2</sub>PO<sub>4</sub>*, *Te*, *Fe<sub>3</sub>S<sub>4</sub>*, *Se*, *Ag*, *Fe<sub>3</sub>O<sub>4</sub>*, *La(NO<sub>3</sub>)<sub>2</sub>*, *Au*, *Tc* etc. We have also found that some cellular organism inventing and using *NC* particles. Now a days, one word has been very popular in bio science and that is bio magnetism. Some crystal like *Fe<sub>3</sub>O<sub>4</sub>* have shown moment of magnetisation and these materials can make our organ to navigate in earth magnetic field. Magnetic sensors bound the magneto tactic bacteria to swim downward against aqua –air interface which is full of oxygen [35,36].

### 1.3.9 Metal Based Nano Materials:

The tremendous application of metal based nano materials in science and technology have received preference in all scientific communities specially for material science researcher in the last few decades. Among all category of metal based nano materials, metal oxides and metal chalcogenide nano molecules are the two strong candidate of our basic concern because they have various types of application in so many fields. Synthesis of nano material has been experimented for several decades. But as year progresses the synthesis process of nano materials get better and simple. Now this preparation technique has reached its peak point of sophistication and for this reason large scale of quality production can be possible. In the following two sections some review of past research work about metal oxide and metal chalcogenide nano material have been discussed carefully.

#### 1.3.9.1 Metal Oxides:

Metal oxide is that type of material which have extended surface defect. This defect made the metal oxide, a transition group metal, a superior candidate in field of nano science [37]. This transitional oxide have transform itself to new kind of crystal structure from the present structure by controlling the temperature and pressure. This transition of crystal arrangement or phase transformation leads to atomic change as well as change in spin orientation. They behave like local and 'd' electron material [38]. The transition metal oxides basically have a structure of rock salt. *MnO*, *NiO* and *CoO* are some example of them. Here the 'd' orbital can split into two sub band. These

two sub bands are  $t_{2g}$  and  $e_g$ . The  $t_{2g}$  band is fully filled for  $3d^6$  orientation and leads  $FeO$  towards insulator and very surprisingly  $NiO$ ,  $MnO$  and  $CoO$  have shown anti ferromagnetism [39]. Material science has become rich to have metal oxide material in its category. Higher  $TC$  superconductivity is the exceptional property of layer  $CuO$  [40].

Metal oxide and transition metal oxide are used in different places of our daily life and science advancement like  $Ls$ ,  $Cs$  in  $LCR$  circuit,  $IC$  industry, gate material, memory material, ferroelectric material, material for non volatile memory, capacitor of decoupling properties, fuel cell and secondary cell materials [41-47].

### 1.3.9.2 Metal Chalcogenides:

Chalcogenide materials are formed by using at least one chalcogen anion like  $Se$ ,  $Te$ ,  $S$  etc and one electropositive component. Chalcogenide is actually a chemical compound in structure. Metal chalcogenides nano structure have the potential to behave as a fittest candidate for opto electronic device, display instrument because of their fabulous electronic and optical behaviour [48]. Sulphur ( $S$ ) named chalcogenide nano material are comprehensively scrutinised for the reason that they have exclusive carrier mobility, extended band gap and superior photovoltaic property [48]. To add this without using any toxic material one can tune the bang gap of ternary, quaternary or pentenary metal chalcogenide material leads to use as catalytic materials [49]. In metal chalcogenide material the recombination of  $e^-/h^+$  pairs are restricted very rapidly because this material experiences photo corrosion even if in illumination phase [50-52].

The sulfide based nano chalcogenide material exhibits very interesting properties. The properties are namely size dependence band gap [53], temperature of melting point [54], phase transition among solids [55] and pressure [56]. On review on synthesis technique we have go through the preparation of different metal chalcogenide nano crystal [57-62].

### **1.3.10 Polymer Based Nano Materials:**

Conjugated polymer (*CPs*) have shown very crucial role in material science and nano technology. It exhibits various important characteristics. In the field of bio technology, polymer nano materials have enormous uses. Their drug delivery capability makes them famous in the field of nano medicine science as they deliver therapeutic mediator straight to the affective spot. Behaviour like insulator gives mechanical strength to metallic cables. The biocompatibility characteristics make polymers as bio sensors and catalyst. The chemical property, electrical behaviour, stability in air medium, doping and dedoping technique and easy processable feature have granted polymer-based nanomaterial research status in nano science and technology [63-65]. Polypyrrole (*PPY*), Poly(p-Phenylenevinylene) (*PPV*), Polythiophene (*PTh*) derivatives, Polyaniline (*PANI*), Polyacetylene (*PA*), Polyfuran (*PF*) poly(3,4-ethylene dioxythiophene) (*PEDOT*) etc fall into *CPs* category [63-65]. We have noticed that the optical property of *CPs* shows important role in photonic device [66]. Easy modification skill like chalk and cheese needs and minimising processing cost input allows the possibility to work *CPs* for photovoltaic (*PV*) battery for next generation. Noh and co-workers in 2008



designed a ultra thin top-gate FET made of polymers at room temperature [67]. In 2015 Mircea Chipara and group give the theory, synthesis technique, property and modification of polymer-driven nano composites [68]. Jinyu Han *et.al* in 2018 investigate about polymer based nanocomposites and their vast application in the field of vaccine and drug delivery [69].

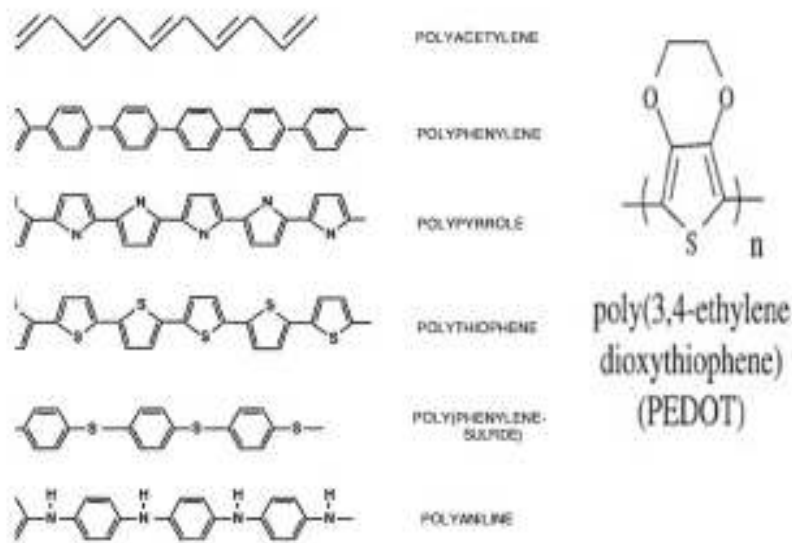


Figure 1.3.1: Structure of some polymer

The metal oxide–polymer hybrid nano composites towards the photo-voltaic applications were deeply sensed by Boucle et al. in 2007 [70]. Hamilton group in 2004 has given an eye view on organic phototransistor made of polymers for study of its electrical properties under solar light simulation (*SSL*) [71].

Monomers are the unit block of formation of polymers. In the molecular level the monomers are connected through carbon single bond. Basically

polymers are insulator or merely semiconductor in structure. They have poor electrical conductance because in their  $sp^3$  hybridized bonding the contribution of  $\sigma$  bond electron are very less. The alteration of single bond and double bond in the centre chain of polymer also support low conductivity. This low electrical conductivity transforms into high conductivity nano materials only by oxidation or reduction and thus some amount of ionization potential have incorporated via less sharing of conjugated  $\pi$  electron. Without making any noise to the  $\sigma$  bonding of polymer through oxidation and reduction electrons easily debarred and included respectively for making participation in increasing electrical conductance. This is the technique by which one can easily tune the insulating polymer into conducting polymers [72-75]. The newly incorporation of electrical conductivity more or less depends on defect states. These defects are situated in between the conduction band ( $CB$ ) and valence band ( $VB$ ) of the polymer nano material. The researcher will now discuss about one noble polymer namely zinc tetra tert-butyl phthalocyanines ( $ZnTTBPc$ ).

#### 1.3.10.1 Zinc tetra tert-butyl phthalocyanines ( $ZnTTBPc$ ):

Phthalocyanine ( $Pc$ ) belongs to the category of organic polymer semiconductor. Easily solution processable low cost semiconducting polymers have potential application in the field of organic optoelectronics, viz. solar cell, organic thin film transistors ( $OTFTs$ ), organic photo transistors [76-79] etc. To this end, because of their ease of  $\pi$  electron conjugated disk type molecules, the  $Pc$ 's has enjoyed a lead role in the synthetic modification due to its ultra high electronic delocalization ( $UHED$ ), great photo-chemical and thermal

durability [80-82]. *Pc*'s are *p* type stable aromatic semiconductor with the low mobility and fewer carrier concentration. Physicochemical and optoelectronic properties of *Pc*'s can be tuned by altering the central atoms. It is also capable of introducing substituents atom at the axial as well as peripheral position [80]. *Pc*'s are potential candidate in solar cell applications because it has the beauty to avail the absorption peak in red or near-Infra red (*Q* band) domain [83-86]. Among *Pc*'s, metal phthalocyanine (*MPC*) exhibits excellent potentialities towards the formation of best order thin film. *MPC*'s further has the ability to absorb light of all region from ultra violet (*UV*) region to visible region (*Vis*).



Figure 1.3.2: Chemical Structure of *ZnTTBPC*

*MPC*'s is the fittest candidate for its application in optical logic display device, solar cell, photo catalytic degradation of different dyes or pollutants,

non linear opto electronics, organic *LED*, schottky diodes etc [82] due to its unique characteristics. *MPC's* are nothing but semiconductor of extrinsic type. Among *MPC's* zinc phthalocyanine (*ZnPc*) is considered as the superior candidate due to its high photo sensitivity, reproducibility and high optical absorption range [82]. In tetra-tert-butyl zinc (*II*) phthalocyanine (*ZnTTBPc*) there are four periphery benzene rings are adjoined by four tert-butyl (*tBu*) groups, which increases better solubility and chemical stability [87]. H. B. Y. Smida and B. Jamoussi reported degradation of nitro aromatic pollutant by Titanium Dioxide/Zinc Phthalocyanine (*TiO<sub>2</sub>/ZnPc*) [88]. People have synthesised different *ZnPc* based composites and showed its photocatalytic capabilities, non linear optical properties and photo-induced charge generation [89,90].

## 1.4 World of 2D materials:

Two dimensional materials (*2D*) are the material with a depth of few nano meters or less than that. They are single atomic layer structure. *2D* materials are totally made up of surface of their own. This type of layered materials has grown up very quickly in the world because they have a very distinct application in nano science and nano technology. They are flexible to a very high extent. *2D* materials have porosity in their surface as well as quite rigid and stronger than other material. Two dimensional materials have the potential application in the field of nano technology mainly in photovoltaics, semiconductors, electrode, catalysis and water cleaning. *2D* materials are made up of two or more elements of covalent bond [91]. It is categorised

by  $2D$  allotropes of different element or compound. When  $2D$  materials are formed from element then it carries – ene in suffix position in the name and as it is derived from compounds, the name would be referred to as –ana, -ide in the suffix position. These layered materials are also popular as Van der Waals heterostructure.

Almost plenty of  $2D$  materials are predicted as stable material on Earth. Many of them are supposed to be synthesised [92-93]. The commercial market for  $2D$  materials specially for graphene will be about \$390 million *US* as per our expectation by 2025. Graphene is the first  $2D$  material discovered in 2004. It is nothing but single layer of graphite. After graphene a huge number of single layer  $2D$  material were identified. 2011 was the year of discovery of first MXene. In 2012 silicene, 1<sup>st</sup> post-graphene substance was identified. After that Germanene in 2014, Stanene in 2015 and Plumbene in 2018 were noticed. Some other type of  $2D$  materials have been given in the table 1.3.

Table 1.3: Different types of  $2D$  materials

Sl.	2D material	Origin	Remarks
1	Graphene	Graphite	Discovered in 2004
2	Graphyne	carbon	hybridization, where $1 < n < 2$
3	Borophene	Boron	Discovered in 2015
4	Silicene	silicon	Hexagonal honeycomb structure
5	Stanene	Tin	Hexagonal honeycomb structure
6	Plumbene	Lead	—————
7	Phosphorene	Phosphoru	nonzero band gap
8	Antimonene	Antimony	—————
9	Germanene	Germanium	Honeycomb structure
10	Bismuthene	Bismuth	Discovered in 2016

Now in this context I want to discuss about Graphene, the noble material to match my thesis topic.

### 1.4.1 Graphene:

*“Much like the world described in Abbott’s Flatland, graphene is a two-dimensional object. And, as ‘Flatland’ is “a romance of many dimensions”, graphene is much more than just a flat crystal. It possesses a number of unusual properties which are often unique or superior to those in other materials. In this brief lecture I would like to explain the reason for my (and many other people’s) fascination with this material, and invite the reader to share some of the excitement I have experienced while researching it.” .....Konstantin S. Novoselov (Nobel lecture, December 8, 2010)*

On 5<sup>th</sup> of October, 2010 at Joseph’s Primary School, Kolkata, a little girl borrowed a pencil to scribble in her note book. She had absolutely no idea that the pencil, she had just borrowed, has a material that has made science advance in leaps and bounds. The material was graphene which awarded Andre Geim and Konstantin Novoselov with the Nobel prize in physics 2010. The discovery of graphene was in fact an accidental one. Both Andre Geim and Konstantin Novoselov, two Russian Scientists, were doing trial on graphite about its electrical properties. Surprisingly they found that using a sticky tape they can extract a thin layer of graphite from the bulk, repeated peel-

ing helped the scientists to achieve one atomic thickness i.e. 2-*D* graphite or graphene.

*“A playful idea is perfect to start things but then you need a really good scientific intuition that your playful experiment will lead to something, or it will stay as a joke forever”.....Novosolev*

Alan Usher, director of the Centre for Graphene Research in the UK, says.

*‘For decades graphene was seen as a purely theoretical interest because in the 1930s it was predicted that it couldn’t be stable.’ He says. ‘But Geim and Novoselov decided not to believe the theory and just tried it for themselves.’ He adds that the simplicity of the ‘sticky-tape’ technique they employed only makes the discovery more remarkable: ‘that’s the kind of science that really deserves recognition.’ It was a ‘fun Friday afternoon project’ Novoselev said. Novoselev also says ‘Graphene is a marvellous material to work with. Anybody can do it - which is probably why it has spread so widely so quickly.’*

Graphene is zero band gap two dimensional material. It is monolayer of graphite. A carbon monolayer designed a honeycomb shaped lattice. Each carbon has  $sp^2$  bonded. It is not only the thinnest ever but also the strongest. Though absolutely transparent, it is too dense to let even the smallest gas atom of Helium to pass through it. As a conductor of electricity it performs

as good as copper. In terms of thermal conductivity, it excels all materials on earth.

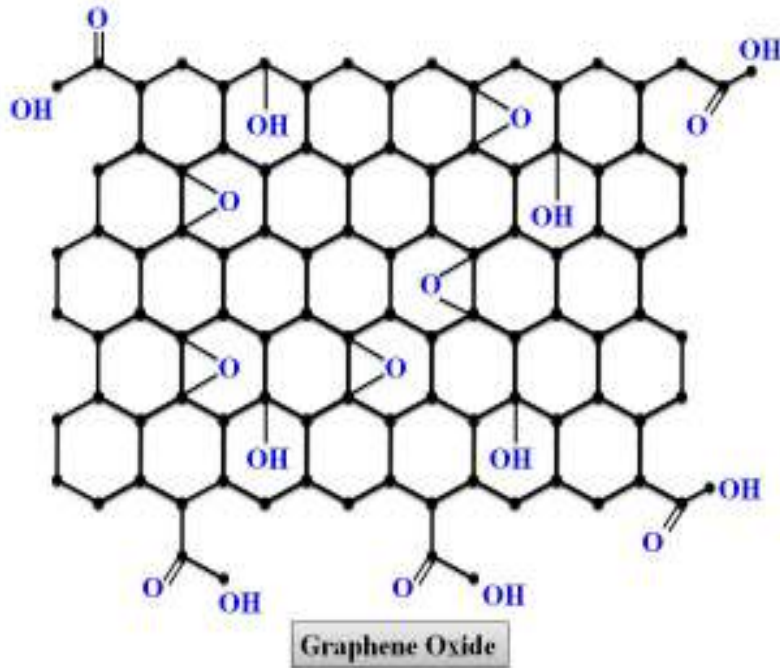


Figure 1.4.1: Structural representation of Graphene Oxide (*GO*)

Carbon, the elementary particles of all life on earth has to surprise us once again. The main logic of our surprising factor is that the atoms which connected with the edge of graphene are chemically more reactive than other carbon allotropes as a huge number of defects are present in it. These defects are the key factor of enhancement of chemical properties. Among all the allotropes, graphene have been honoured with maximum number of atom situated at edge.



#### 1.4.1.1 Properties of Graphene:

Graphene, the noble material has some extraordinary properties by which it have the confidence to live in the various zone of science and technology. Graphene is a zero band gap semi-metallic material. The gap in band can be produced with the introduction of external electric and magnetic field. The optical properties can be tuned by thr number of graphene sheets. A single layer graphene sheet can absorb almost 2.4 % of incident photonic energy. The rest huge amount of optical signal can pass through it and transparency can change towards least amount accordingly. Graphene can absorb the photons ranging from visible to near infra red region. The minimum band gap energy, Dirac fermions on the surface of graphene and the mutual correlation with electromagnetic radiation, makes the saturation effect over the wide spread of absorption. This radiation absorbance is independent of wavelength. These optical properties make graphene applicable in the field of fast microwave, tetrahertz photonics etc. Graphene makes its prominent place in the field of electronic industry. It shows  $4.5 \times 10^3$  times larger electronic conductivity than copper [94]. Electrical conductivity of graphene increases with its layer number. In room temperatures, it is noticed that the coefficient of thermal conduction of graphene in suspension condition is much better than the pristine graphite. Like electrical conductivity, thermal conductivity of the graphene changes with the number of layers or by the impurity doping in it. According to the measure value of co-efficient of elasticity ( young's-modulus), tensile strength, graphene has emerged to be the strongest material in the world.

### 1.4.2 Why Graphene is so special?

Before discovery of graphene we are familiar with steel as being the strongest material in the world. But now graphene has been proven that it is almost 200 times stronger than steel.. In this category graphene has reached the first position and forced diamond to stay behind it. As we all know, graphene of zero energy band gap material with electrical resistance is likely to zero which leads graphene as 250 times better

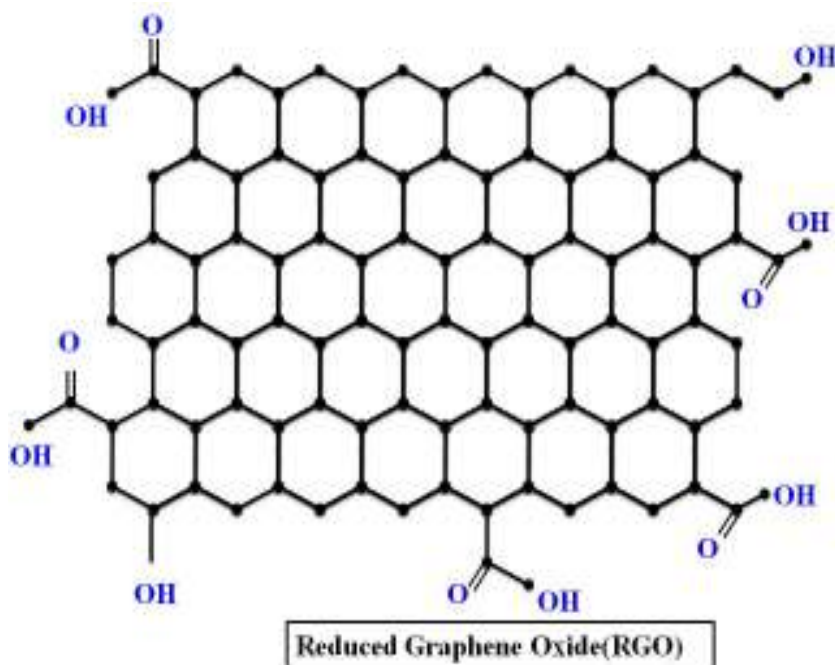


Figure 1.4.2: Structural representation of Reduced Graphene Oxide (*RGO*)

electrical conductivity than silicon. The oxidation of graphene makes it super impermeable material. That is why smallest particle helium cannot pass through it. One amazing thing of graphene in this context is that the water molecule can penetrate the graphene oxide (*GO*) surface [95, 96]. Thus graphene can also works as a water purifier.

## 1.5 2D Material Beyond Graphene:

Although graphene has been considered as the most promising material in 21<sup>st</sup> century, but beyond graphene there exist numbers of 2D material of great importance with wide range of special properties. Such as 2D oxides, hexagonal boron nitride, transition metal dichalcogenide (*TMDCs*) etc. Among them *TMDCs* has received great interest due to its special features.

### 1.5.1 Transition Metal Dichalcogenide (TMDCs):

Now-a-days, 2-D transition metal dichalcogenide (*TMDCs*) nano materials have fascinated the scientific community and have emerged to be the fittest candidate for next generation nano electronic devices [97-102]. This promising new class of isolated mono layer of *TMDCs* have been widely used in the field of optoelectronics, photocatalysis and electronics [103-104]. It has enjoyed several important features like thickness dependent electronic band structure, high transparency [103], remarkable mechanical strength and outstanding electrical and optical properties [105].

*TMDCs* are basically semiconductor in nature.  $MX_2$  is the type of chemical symbol of *TMDCs*, where  $M$  stands for transition metal atom,  $X$  denotes chalcogen atom shown in periodic table. *TM's* (Transition metals) are  $Mo$ ,  $W$  etc and chalcogens are namely  $S$ ,  $Se$  and  $Te$ . In formation of *TMDCs*,  $M$  atoms are sandwiched with two thin layers of  $X$  atom. Mono-layer of 2-D *TMDCs* are very thin. As an example the thickness of  $MoS_2$  mono layer is about  $6.5\text{\AA}$ . If we stack layers of *TMDCs* one after one, a bulk crystal is formed. The mono layers are bonded by weak Van-der-Waals

force of attraction. Some special features of *TMDCs* are listed below.

Figure 1.5.1: Two- dimensional transition metal dichalcogenide (*TMDC's*)

a) Monolayer of *TMDCs* are direct band gap nano material. These materials are mainly performed in electronic zone, specially in fabrication of transistor.

b) *TMDCs* have no centre of inversion. So the concern material can have new degrees of freedom. The name of this degree of freedom is *K*-valley index and this is the beginning of Valleytronics.

c) They are the key materials of spintronic.

d) *TMDCs* have the very tight spin-orbit coupling. This leads them towards spin-orbital split mechanism. A huge number of *TMDCs* have been synthesised in recent times. Molybdenum disulfide ( $MoS_2$ ), tungsten disulfide ( $WS_2$ ), cobalt disulfide ( $CoS_2$ ), molybdenum diselenide ( $MoSe_2$ ) etc. are of them. Our interest is focussed only on  $MoS_2$ .

### 1.5.1.1 Molybdenum disulfide ( $MoS_2$ )

Among this various *TMDCs* nano materials,  $2D-MoS_2$  took the light from all the researcher as a photo *FET* [106-108], photocatalytic agency, lithium ion batteries, sensing and hydrogen production and many other field of applications [109, 110].  $MoS_2$  nano structure facilitates itself to act as excellent materials. In  $MoS_2$  the weak Van der Waals interaction holds together. The metal *Mo* layer is stacked by two *S* layers [111]. The co-relation between electrons of *Mo* atom would aid in enhancing planar electric transportation properties [112]. Monolayer of  $MoS_2$  shows direct band gap and the value is  $1.8\text{ eV}$ , whereas bulk  $MoS_2$  is an indirect band gap material with energy band gap is  $1.2\text{ eV}$  [113-115]. This laid mono or few layer  $MoS_2$  nano sheet towards designing transistor, logic circuit, memory device, sensor, photo transistor [116-119] etc.  $MoS_2$  has kept its promise for its optoelectronic and photocatalytic experience because of its structural characteristics as well as electrical and optical features. The direct band gap energy of monolayer's (*ML*) or few layers (*FL*) of  $MoS_2$  convey that it can be a gifted material for opto electronic applications. For instance,  $MoS_2$  mono layer shows mobility of  $200\text{ cm}^2/Vs$ . It shows photo responsivity as high as  $800\text{ A/W}$ . It has weak absorption only at  $620\text{ nm}$  and  $670\text{ nm}$ . So it is important to synthesize different  $MoS_2$  based composite to extent its absorption spectral range in the higher wavelength range that can further improve the optical properties of  $MoS_2$ .

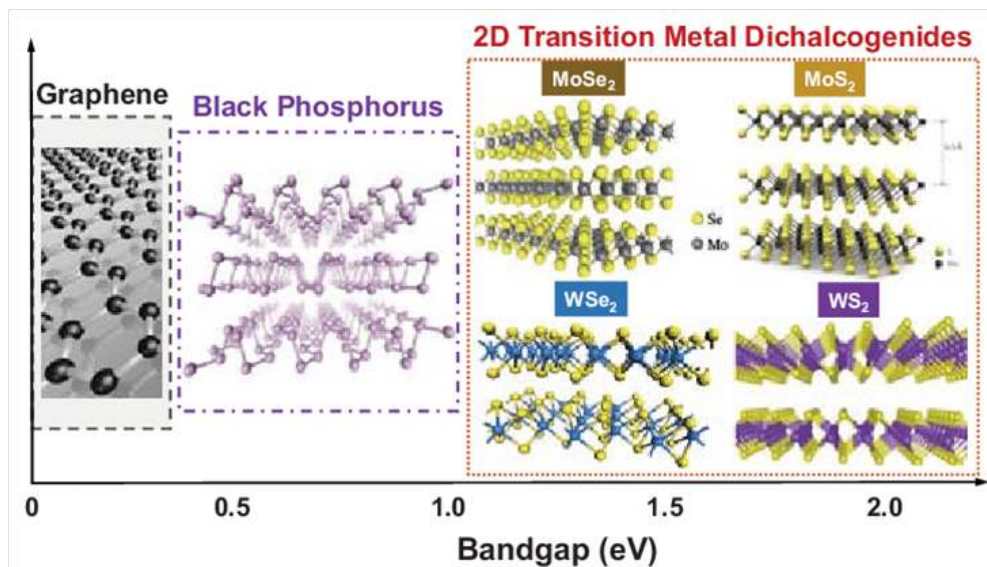


Figure 1.5.2: Band Gap of different *TMDC'S*

## 1.6 Some application of Graphene and $MoS_2$ based nano composite materials:

### 1.6.1 Removal of pollutant by Photo Catalysis:

To get clean environment it is important to remove the pollutant like antibiotics, dyes or different phenolic compound from the air, water or land. To this end degradation of organic or inorganic pollutants by photocatalytic technique is considered as a low-cost, eco-friendly and most viable technology. The degradation process is occurred by the oxidation or reduction of the pollutant by the photogenerated charge carriers. When solar light of suitable wavelength is illuminated on the pollutant in presence of the catalyst the electrons can jump to the conduction band (*CB*) and subsequently

left a hole in valence band ( $VB$ ) of the catalyst. These electrons react with the oxygen present in the solution and transformed into super-oxide radicals ( $O_2^{\bullet-}$ ). These radicals oxygen species can work in two ways. First off all it reacts directly with the pollutant and ended at degraded product. Secondly with the interaction with  $H^+$  the oxygen species transforms into  $HO_2^-$ .

This unstable species further reacts with  $H^+$  and form  $H_2O_2$ . This  $H_2O_2$  dissociates into hydroxyl radicals ( $OH^{\bullet}$ ). These radicals can further react with the pollutant and degrade it. On the other hand electron can directly degrade the pollutant. ( $OH^{\bullet}$ ) radicals can also be formed with another technique when holes react with water. They also have the potential to degrade the pollutant. The photo generated holes can directly interact with the antibiotic pollutant and conclude with the degraded product.

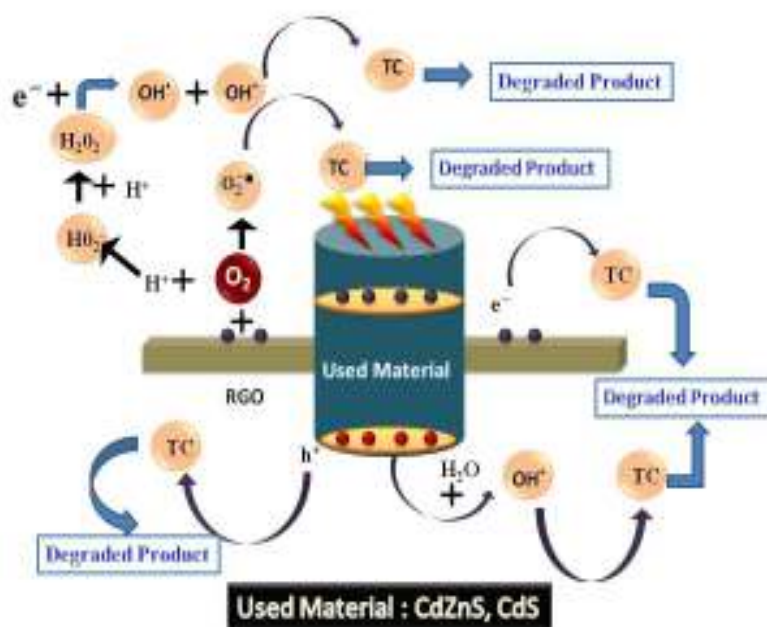


Figure 1.6.1: Mechanism of photocatalytic degradation

Under different types of light illumination such that *UV* lamp, *UV-A* lamp and solarium lamp, the noble material  $TiO_2$  can perform photocatalytic activity on urgent basis, as observed by Reyes and his group in the year 2006 [120].

Zhigang et.al in 2010 synthesised graphene–gold nano particles composites for their tremendous catalytic application in the field of aquatic dye degradation under visible light illumination [121].

In 2011 krishnamoorthy et. al reported that pure *GO* can have the great capability working as catalyst under *SSL* for resazurin degradation [122].

Jintao Zhang and his team in the year of 2011 were able to synthesized graphene-metal-oxide nanocomposite and open up a new canvas for the removal of Rhodamine *B* (*RhB*) dyes under simulated solar light (*SSL*). The authors also noticed that the charge generation and charge separation take place through the interface of the junction which leads the great electrical characterisation [123].

In 2011, Wang and his group synthesized *C – N – S* tridoped  $TiO_2$  by sol-gel technique and observed tetracycline (*TC*) antibiotics removal from the environment under *SSL* [124].

Yanhui Zhang in 2012 created some special technique to use graphene based semiconductor material as a photo degradation agent which is superior to the controlled semiconductor nano material. They have given the identity of graphene as a photo sensitizer. They have synthesised *RGO – ZnS* nano composite for better performance towards the photocatalytic removal of different aquatic pollutant under *SSL* [117].

In 2012 Ping Chen and the group have also explained the enhancement



of photocatalytic performance of  $N_2$  doped graphene /  $ZnSe$  nano materials over controlled-  $ZnSe$  nano material [125].

In 2012 Wang et al. have synthesised  $RGO$  linked  $ZnO$  nano particles ( $NPs$ ) through the method of photo reduction. They have studied the removal of aqueous organic pollutant  $RhB$  with the as-synthesised  $RGO-ZnO$  nano composite. The recycling performance of the catalyst showed up to 99 % capability even after several times of application [126].

Shah et.al in 2012 have synthesised several types of  $RGO@TiO_2$  nano composite through an easy mono step hydrothermal green synthesis technique.  $RGO@TiO_2$  nano composite have shown better photocatalytic performance than controlled- $RGO$  sheet and controlled- $TiO_2$  nano particles for  $RhB$  dye degradation under  $SSL$  [127].

Jing Li et.al in 2012 addressed the synthesis technique, structural behaviour and catalytic degradation of 4-nitro phenol (4 -  $NP$  ) by graphene based  $Au$  hydro gel sample. They also mentioned that the introduction of graphene enhance the performance of  $Au$  particle [128].

In 2013 Pradhan and his group fabricated  $\alpha-Fe_2O_3 / RGO$  composite by hydrothermal route. They used the composite material as a catalyst of phenol degradation under solar light illumination. The aim of improvement of photocatalytic efficiency of  $\alpha-Fe_2O_3$  was fulfilled only after the introduction of graphene sheet to it [129].

In 2013 Xiang and his group have focussed their mind and work towards the  $H_2$  evolution from water splitting by graphene decorated photo catalyst and compared its performance with the nano catalyst without graphene incorporation [130].

Au et al. in 2014 scrutinized the photocatalytic effect towards  $CO_2$  reduction, with the help of  $Cu_2O$ /reduced graphene oxide ( $RGO$ ) composite where the composite was synthesised by single step electro chemical process [131].

Chakraborty et.al in 2014 synthesised  $RGO - Cd_{0.75}Zn_{0.25}S$  nano rod composite in single step low cost solvothermal process. They concluded that the degradation efficiency of controlled- $Cd_{0.75}Zn_{0.25}S$  nano rod increased after successive attachment of the nanorod on the basal plane  $RGO$  sheet. Here  $RGO$  does a crucial performance for hindering the recombination process of photo generated electrons and holes enhance the catalytic efficiency thereby [132].

Yan Liu in 2014 described the synthesis protocol of  $TiO_2-RGO$  nano layered structure material by hydrothermal route and explained the photocatalytic degradation mechanism towards the reduction of Methyl Orange ( $MO$ ) by  $TiO_2-RGO$  under visible light illumination. They have also reported that  $TiO_2-RGO$  showed better efficiency compare to controlled- $TiO_2$  NP or  $RGO$  sheet [133].

In 2015 Changchang Ma et.al has described facile single step one pot hydrothermal preparation of  $CdSe$  quantum dot material with doping of cobalt ( $Co$ ) and potassium( $K$ ) as a strong photo catalysts. They have further synthesised the above concerned material with a different percentage of  $Co$  and  $K$  . It was observed that that 3%  $Co$ -4%  $K/CdSe$  quantum dot materials showed the maximum efficiency of photo catalysis under visible solar light irradiation for tetracycline hydrochloride degradation [134].

In 2018 Juan Wen et. al described the synthesis pattern of graphene

based  $Ce - Ti$  nano composite material for the photo catalytic degradation of  $RhB$ . They have synthesised 7 different types of graphene based  $Ce - Ti$  nano composite with different  $wt\%$  of loading of  $Ce$ ,  $Ti$  as well as graphene. Among them 10 %  $CeO_2 - TiO_2/10\%$   $RGO$  nano composite have shown best performance for the photocatalytic  $RhB$  degradation [135].

Fengmin Wu et. al in 2018 explained how the catalytic efficiency of controlled- $MgFe_2O_4$  binary oxide nano particles have been enhanced by the incorporation of graphene sheet towards the dies out of methyl orange ( $MO$ ), a organic water pollutant under  $SSL$ . They reported that the efficiency of the catalyst for the photo degradation of  $MO$  reaches almost 90% within 60  $min$  [136].

In 2018 Basith and the group reported the enhancement of photocatalytic behaviour of  $Bi_{25}FeO_{40} - RGO$  nano-composite compared to controlled  $Bi_{25}FeO_{40}$  nano materials for  $RhB$  degradation and hydrogen evolution reaction ( $HER$ ) by water-splitting. They have used hydrothermal technique for the synthesis of materials. The possible degradation mechanism has also been discussed throughly [137].

Mitra and her group in 2019 synthesized of  $PANI - RGO$  composite by sample oxidative polymerization process and used it as a photo catalyst of organic dyes namely  $RhB$ , malachite green and congo red under  $SSL$ . The degradation efficiency of synthesised composite sample was 99.68% for malachite green in 15 minutes, where as 99.35% is for  $RhB$  in 30  $min$ . The  $PANI - RGO$  composite showed 98.73 % degradation efficiency for congo red in 45  $min$  [138].

The photocatalytic performance of  $MoS_2$ -based composites have been

reported by several group of scientists.

Qian Liu et.al in the year of 2013 have synthesized  $MoS_2/TiO_2$  nano hybrid materials for the enhanced catalytic  $H_2$  production under light [139].

Yongtao Lu et.al in 2014 reported the coupling of  $Zn_xCd_{1-x}S$  NPs with  $MoS_2$  nano layers via easy exfoliation technique. They observed that as-synthesised composites was superior catalyst for the water splitting and  $H_2$  production [140].

Tan et. al in 2014 synthesised  $MoS_2 - ZnO$  nano-composite. They have studied the adsorption and photocatalytic activity of  $MoS_2 - ZnO$  composite and compared it with controlled- $MoS_2$  towards the degradation of of Methylene blue ( $MB$ ). With respect to the capability of  $MoS_2$  nano flowers the composite sample have shown better performance at adsorption in dark and catalytic activity in presence of  $SSL$ . They have noticed that the photocatalytic efficiency is almost 92.7 % for 100 *min* [141].

In 2015 Zehong Cheng and his group explained how graphene like  $MoS_2$  decorated nano hybrids materials opened up new possibilities in many technological aspects. They have synthesised  $MoS_2$  nanosheet decorated with inorganic  $NP$  via one step protocol technique for the photodegradation of 4 -  $NP$  [142].

In 2015 Yong-Jun Yuan et.al published simple but noble hydrothermal preparation technique of  $MoS_2$  coated  $ZnO$  nano structure having enhanced  $H_2$  productions capability [143].

In 2013 W. L Ong and his group focused their work to develop inorganic  $M - RGO - TiO_2$  composite and its application towards the photocatalytic  $H_2$  production [144].

In 2014 Zhu and group has given the potential fingerprint for preparation of catalyst for the  $H_2$  production from water splitting. They have successfully synthesised  $MoS_2$ -  $RGO$  loaded  $ZnS$  composite via one pot single step hydrothermal route and used it as catalyst for the hydrogen production [145].

### 1.6.2 Photocurrent generation:

Now a days, reduced graphene oxide ( $RGO$ ) based composite materials are considered as building blocks for optoelectronic application owing to its excellent photo induced charge generation in solid phase as well as in the solution phase [146-150]. In these systems  $RGO$  provides an excellent support to anchor different optical materials on its basal plane, which facilitates the separation of photoinduced charge efficiently and subsequently increases the optoelectronic activity of the composite [151-153]. In  $RGO$  based composites, the photo induced electrons migrate to  $RGO$  sheets from the conduction band of the attached optical materials that hinder the electron-hole recombination possibility and increases the photogenerated charge carrier concentration. Several approaches have been proposed to tailor different  $RGO$  based composites to cater the active material for optoelectronic devising. Most of the reports focus on  $RGO$  based oxide semiconductors composite, whose performance is strongly impaired by the oxygen vacancies and surface absorption-desorption processes which causes photocurrent instability [153].

Generally for opto electronic measurement a thin film of concern graphene based material have developed on a substrate probably in silicon substrate by some different technique. After developing the film two or many electrodes

are drawn by some conductive solution. The different procedure of thin film fabrication method using solution process are discussed below:

Formation of thin film from the solution mainly used for the polymer materials. In this process a solution of the concerned polymer material is prepared in suitable solvent. The film are prepared from the solution either drop casting, dip coating or spin coating method.

**i) Drop casting method:**

It is a simple and easy method for thin film preparation. Here we turn our concerned sample into its homogeneous solution phase with a particular solvent. This solution of nano materials allows to fall drop wise on a pre-cleaned substrate which placed on the warm platform for dry the film. After the formation of thin film two electrodes are drawn on it by some conducting adhesive.

**ii) Dip coating method:**

This technique takes more time to prepare the thin film compared to the previous one. This is a very easy method to develop thin film. In this technique we generally coat the pre-cleaned substrate on the both side of it. This method is suitable for large area thin film preparation.

**iii) Spin Coating technique:**

In this process uniform film can be prepared. The film thickness can be controlled by changing the spinning rate and time of the spin coating unit.

In 2010 Chang et.al described noble synthesis process of graphene/ $TiO_2$  nanocomposite material by the technique of solution growth. They have shown that efficiency enhancement in graphene/ $TiO_2$  composite material is greater than graphene sheet for solar cell [154].

Eda et. al in 2010 synthesized the graphene by chemical process. They used this material for electrical and opto electrical applications. They clearly explained the origin of the electrical and opto electrical properties of chemical synthesized graphene [155].

In 2010 Bonaccorso et.al have mentioned that graphene has the photonics as well as opto electrical behaviour. Graphene proved itself as the fittest candidate in terms of solar cell , *LEDs*, touch screen, detector of photon, laser materials etc. [156].

In 2010 Cao et. al depicted a single step one pot synthesis technique of graphene/*CdS* nano materials for photo electrical applications. They were able to anchored *CdS* quantum dot on the basal plane of graphene mono layer with great accuracy [157].

In 2011 Huang et.al explained the synthesis of mono and few layer *GO* via low cost, easily proceceble inkjet print technique. They printed *RGO* on a plastic substrate for the measurement of electrical and thermal properties. They also fabricated sensor device which showed high efficiency as a chemical sensor [158].

In 2012 Konstantatos et.al consider graphene as an optoelectronic materials because of its large surface area and wide spread bandwidth [159].

In 2012 Liu et.al extended their work towards synthesis of energy hervest-ing material based on graphene analougus materials. Their research work highlights on tremendous progress of graphene composite material for the device supported to energy, solar cell and fuel management [160].

Zhang et.al in 2012 fabricated photonic device based on single layer of graphene. The device showed an exellent opto electrical behaviour with wide

optical range and the photoresponsivity of the device was  $8.61AW^{-1}$  [117].

In the same year Kuila and his group depicted the carbonaceous method for the fabrication of graphene thin film on silicon substrate . It showed the *p*-type semiconducting property with the mobility of  $90\text{ cm}^2V^{-1}S^{-1}$ . Thus it can be used as FET materials and photodetectors [161].

Zhang and his group in 2013 have made favourable matching between  $TiO_2$  nano tube and *RGO* by electrophoretic deposition to synthesized *RGO*– $TiO_2$  nanocomposites. They have also given an experimental conclusion that the synthesized nanocomposite can be used as a dye – sensitized solar cell (*DSSC*). The efficiency of nano composite materials is very much greater than the controlled  $TiO_2$  nanotube [162].

Khare et.al in 2013 synthesized *RGO/ZnO* nanocomposite hybrid material. They observed that the composite materials have great possibility to used as solar cell material of solar cell material with greatest efficiency compared to their counter part [163].

Nagashio and his group profoundly explained the transport mechanism of graphene/  $SiO_2$  (Silicon dioxide) nano phase materials and the materials was synthesised by  $O_2$  plasma technique [164].



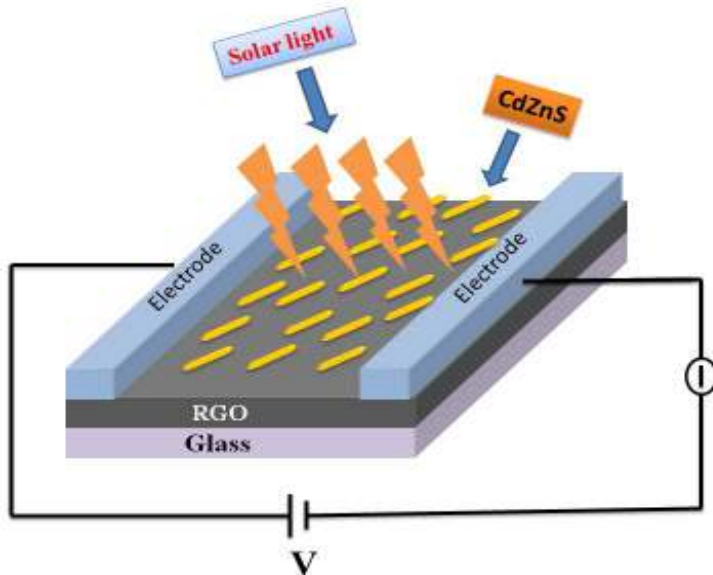


Figure 1.6.2: Cartoon of Photocurrent Generation

In very recent, Heshmatynezhad et.al have synthesised bismuth sulfide/reduced graphene oxide ( $Bi_2S_3/RGO$ ) composite material by sonication technique under  $UV$  light irradiation [165]. They have thoroughly investigated the electronic and optical behaviours. These properties depend on calcination temperature and the percentage of  $RGO$  present on it. The result also indicate of  $n$  type behaviour of the synthesised material.

Hsin-Chia ho and his group in 2019 have demonstrated that the graphene decorated  $TiO_2$  nano composite material. It have shown the enhance photo current generation compared to controlled- $TiO_2$  [166].

In 2019 Khurshid et.al demonstrated the application of photo-electro chemical behaviour of  $RGO/ZnO$  composite with the doping of  $Ag$  nano particles [167]. They explained the recombination behaviour of photo induced

excitons. The incorporation of *Ag* particle and *RGO* sheet have retarded the recombination probability and as a result the photo current increases in *Ag* doped *RGO/ZnO* nano composite material compared to controlled samples. The current density of the as synthesised *Ag – RGO/ZnO* based device was investigated and the value was as  $206 \text{ nAcm}^{-2}$ .

The photo current generation in the field of electronics and opto electronics, graphene like *MoS<sub>2</sub>*-based nano composites have been reported by several group of scientists.

In 2014 J. Dattatray et.al reported the photo response behaviour by pulsed laser-deposited (*PLD*) *MoS<sub>2</sub>* Thin Films on *W*-tip and *Si* substrate. They have shown that the *PLD MoS<sub>2</sub>* Thin film can be used for a variety of field emission-based applications [168].

R. Cheng and his group in 2014 described how the *WSe<sub>2</sub> / MoS<sub>2</sub>* nano composite material can give photocurrent generation. For this they have synthesised p-type tungsten diselenide (*WSe<sub>2</sub>*) and n-type molybdenum disulfide (*MoS<sub>2</sub>*) of mono or few layer. They reported that the photocurrent efficiency was up to 12 % over the whole overlapping region [169].

In 2016 L. Zheng and his research team elaborately announce the photocurrent generation in *MoS<sub>2</sub> – TiO<sub>2</sub>* nano composite, where they have concluded that the photo response increases when *MoS<sub>2</sub>* nano sheet anchored with *TiO<sub>2</sub>* nano material than the current generation by controlled *TiO<sub>2</sub>* [170].

In 2017 X. Wang et.al synthesised *MoS<sub>2</sub> /polymer* nanocomposites with greater accuracy, characterise them by different technique and made them applicable in the field of opto electronic devices. The exceptional properties

facilitate  $MoS_2$  show immense possible applications in the optoelectronic area [171].

## 1.7 Frame work of my thesis:

The major intension of my thesis is to give emphasis on synthesis, characterization and applications of  $RGO$ - based nano composite and  $MoS_2$  based nano composite in different field. These applications are mainly concern with adsorption, photocatalytic and photocurrent generation. We have mainly focused on the low cost, noble facile preferably one pot single step synthesis process. After the synthesis of the samples the structural characterization and morphological behaviour have been scrutinize thoroughly by different technique. From the literature survey it has been noticed that the properties of the nano composites are strongly depends on the size and shape of the nano materials. We have synthesized  $RGO$  based composite materials like  $RGO - ZnS$ ,  $RGO - CdS$ ,  $RGO-CdZnS$  and graphene like  $MoS_2$  based materials like  $MoS_2 - ZnTTBPC$  . We have specially chosen inorganic semiconductor of nanorod morphology and extend our work to the organic small molequle to get a clear conception of size dependency of the molecule in terms of morphology and applications in different field. The content of my thesis are as follows:

Chapter 1 deals with the idea about the advantage of nanotechnology, the significance of nanoscience and the importance of different types of nanomaterials. When a material is on the nanoscale then the property of the component gives significantly better results. So, the technology in nanoscale

gives always a special inspiration to the research domain. A special emphasis is given on carbon-based materials i.e., graphene, *GO*, *RGO* and transition metal dichalcogenide (mainly *MoS<sub>2</sub>*) and small organic molecules (like *ZnTTBPc*) in this chapter. After a brief review of the interesting properties of the carbon-based nanomaterials and its successful applications in the field of nanotechnology, the chapter describes the special features in optoelectronics of metal-based nanomaterial specially *CdS*, *ZnS* and their mixed form. After the basic outlook, photocurrent generation, photocatalytic activity, and surface adsorption in *RGO* and *MoS<sub>2</sub>* based nanocomposite material are explained thoroughly with the help of some review articles. After all the discussion, this section, at last, gives an overview of my total work in this period. A brief discussion on synthesis and characterization of *RGO* - zinc sulfide (*ZnS*) composite and its application as solar light-responsive photocurrent generation and photocatalytic 4-nitrophenol reduction are addressed in chapter 2. In chapter 3, synthesis and characterization of *RGO* - cadmium sulfide (*CdS*) composite and its solar light-responsive photocurrent generation and photocatalytic degradation of tetracycline are discussed in detail. In chapter 4, solution-processable *RGO* - cadmium zinc sulfide (*CdZnS*) nanocomposite for large area thin film optoelectronic device application and solar light-responsive photocatalytic degradation of 4-nitrophenol are addressed. Sonochemical functionalization of *MoS<sub>2</sub>* by zinc phthalocyanine (*ZnTTBPc*) and its visible-light-induced photocatalytic activity is discussed in chapter 5.

In chapter 2, solution processable reduced graphene oxide - zinc sulfide (*RGO* - *ZnS*) composite has been synthesized via a simple, single step, one-

pot solvothermal route. As-synthesized composite was characterized structurally and optically. The photo induced charge generation of *RGO – ZnS* in solid phase as well as in solution phase has been investigated under simulated solar light illumination. *RGO – ZnS* thin film photo detector shows an excellent photocurrent generation with a high degree of reproducibility. The photosensitivity (ratio of photo to dark current) of the detector varies linearly with the light intensity, which is advantageous to tune the optoelectronic device performance and paves the way for its application. A remarkable increase of photo reduction efficiency of *RGO – ZnS* composite compare to controlled-*ZnS* / controlled-*RGO* towards the reduction of 4-Nitrophenol was observed.

Chapter 3 reports the photocatalytic performance of *RGO – CdS* composite towards the degradation of tetracycline (*TC*) antibiotics under solar light irradiation. The optoelectronics applications of *RGO – CdS* are also addressed here. We have synthesized the *RGO – CdS* composite through one pot single step solvothermal technique. The as-prepared composite was characterized structurally, morphologically and optically by *XRD*, *TEM*, *UV – vis* and *PL* spectroscopy. The reduction of *GO* was confirmed by *XPS* and Raman spectroscopy. The optical properties of controlled-*CdS* and *RGO – CdS* nanomaterials are studied by *UV-vis*, and *PL* spectroscopy. The room temperature photocatalytic performance of the *RGO – CdS* nanocomposite and controlled-*CdS* towards the degradation of tetracycline (*TC*) antibiotics in aqueous solution, under visible light, was studied extensively. The *RGO – CdS* nano composite shows a notable photocatalytic performance towards the degradation of *TC* in compared to *CdS* nanorods under solar light

irradiation. The current-voltage characteristics of  $RGO - CdS$  nanocomposite for different intensity of solar light ( $100\text{ mW/cm}^2$  to  $165\text{ mW/cm}^2$ ) and in darkness are investigated. A linear variation of current with the applied voltage is observed. Different optoelectronic parameters like photosensitivity  $P$  (the ratio of photocurrent to dark current), responsivity ( $R$ ) have been studied.  $P$  of our device varies linearly with the intensity of the light which is also advantageous for making different optoelectronic devices.

In chapter 4, we have reported the one pot single step solvothermal synthesis of reduced graphene oxide - cadmium zinc sulfide ( $RGO - Cd_{0.5}Zn_{0.5}S$ ) composite. The reduction of graphene oxide ( $GO$ ), synthesis of  $Cd_{0.5}Zn_{0.5}S$  nano rod and decoration of  $CdZnS$  nanorods onto  $RGO$  sheet was done simultaneously. The structural, morphological and optical properties were studied thoroughly by different techniques, such as  $XRD$ ,  $TEM$ ,  $UV - vis$ ,  $PL$ , Raman spectroscopy and  $XPS$ . The  $PL$  intensity of  $CdZnS$  nanorods quench significantly after the attachment of  $RGO$ , confirms photo induced charge transformation from  $CdZnS$  nanorods to  $RGO$  sheet through the interface of  $RGO - CdZnS$ . An excellent photo current generation in  $RGO - CdZnS$  thin film device has been observed under simulated solar light irradiation. The photocatalytic activity of the  $RGO - CdZnS$  composite was investigated towards the degradation of 4-Nitrophenol. A notable increase of photocatalytic efficiency of  $RGO - CdZnS$  compare to controlled- $CdZnS$  was observed.

In chapter 5, we have reported the synthesis of graphene like molybdenum disulfide-zinc phthalocyanine ( $MoS_2 - ZnTTBPC$ ) composite by sono chemical attachment of  $ZnTTBPC$  to  $MoS_2$  sheet. The  $MoS_2$  nano sheets were

synthesized via solvothermal route. Raman study gives sufficient evidence of existence mono-layer  $MoS_2$  in the  $MoS_2 - ZnTTBPc$  composite. The structural morphology of all synthesised nano materials are characterised by  $XRD$ ,  $PL$ ,  $UV - vis$ ,  $TEM$ ,  $SEM$  etc. The high energy transfer efficiency, authenticated by the steady-state photoluminescence and time-correlated single photon counting studies ( $TCSPC$ ) makes  $MoS_2 - ZnTTBPc$  (3 : 1) composite as a promising optoelectronic and photocatalytic material. It could thus present a promise as a new photo catalyst towards removing different pollutants and other optoelectronic devising.