Chapter 1

Introduction

1.1 Nanomaterials

Particle is the small object which behaves as a whole unit with respect to its transport and properties. Particles are classified on the basis of diameter as Coarse (10,000-2500 nm), fine particles (2500-100 nm) and ultra fine or nanoparticles (1-100 nm). Nanoparticles may or may not exhibit size related properties that differs significantly from those observed in fine particle or bulk materials.\(^1\)\(^,\)\(^2\) Individual molecules are generally not referred as nanoparticles even though its size is in the range of nanoparticles. Nanoclusters have at least one dimension in the range 1-10 nm and narrow size distribution while, nanopowders are agglomerates of nanoparticles.\(^3\)

Nanoscience is the study of the material whose sizes are on the nanometer scale and Nanotechnology is the engineering of functional systems at the molecular scale, in other words it is the creation and exploitation of materials with structural features in between those of atoms and the bulk materials.\(^4\) Nanoscience and Technology emerged after the invention of Scanning Tunnelling Microscope (STM) in 1981.\(^5\) K. Eric Drexler encountered the Richard Feynman’s talk on *There is plenty of room at the bottom* and led foundation of molecular nanotechnology.\(^6\) In the emerging field of nanotechnology, a goal is to make nanostructured or nanoarrays with special properties with respect to those of bulk or single particle species.\(^7\)\(^,\)\(^8\)\(^,\)\(^9\)
1.1.1 Methods for Synthesis of Nanomaterials

One of the aspects of research on nanomaterial is based on its synthesis and assembly into 1, 2 or 3 dimensional architectures extending over several length scales with hierarchical construction principles. Synthesis techniques can be broadly classified into top down and bottom up approach methods.

Top down approach mainly includes milling technique by which macro or micro scale particles are grounded in planetary ball mill or other size reducing mechanism like photolithography.

Amongst the bottom up approach, synthesis methods can be grouped into liquid-solid transformation and Gas-solid transformation.

Liquid-solid transformation are the most commonly used to control the morphological characteristics with certain chemical versatility. The techniques developed under this category are mainly i) Co-precipitation method ii) Solvothermal method iii) Micro-emulsion techniques iv) template assisted techniques v) Spray Pyrolysis.

Gas Solid transformation method includes i) Chemical vapour Deposition (CVD) ii) Pulsed Laser Deposition (PLD).

The techniques related to synthesis method adopted for preparation of nanostructured zinc orthotitanates (ZOT) are discussed in brief.

1.1.1.1 Co-precipitation method:

Co precipitation means carrying down by the precipitate of the substance normally soluble under conditions employed. The coprecipitation of metal cations as carbonates, bicarbonates, hydroxides, oxalates followed by subsequent decomposition and calcination is the common method for synthesis of nanoparticles. This is simple and suitable method for synthesis of metal, metal-alloy and metal oxide nanoparticles. Co-precipitation method involves nucleation, growth, coarsening and agglomeration of the particles. During coprecipitation secondary processes such as Ostwald ripening and aggregation of the particle affect the morphology, size and other properties of the product. Therefore reaction conditions like rate of addition of reactant, stirring rate which influence the mixing process must be controlled to get the relevant size,
morphology and particle size distribution. However, Co-precipitation method doesn’t guarantee about formation of mono disper sed nanoparticles in all the cases. The process of nucleation and growth controls the particle size and morphology of the product. At the initial stage of the co-precipitation small crystallites formed (nucleation) tend to agglomerate quickly to form the larger and thermodynamically stable particle. Many research group synthesized nanoparticles of Fe, Au, Ag, Cu-Ni alloy, metal oxides such as ZnO, TiO2, Fe3O4, ZnTiO3. Jothimurugesan K. et al. synthesized Zn2TiO4 by co precipitation method at 700 °C and observed existence of secondary phases, while synthesis of bulk Zn2TiO4 by co-precipitation method was reported by Watanabe et al. Gu Y. et al. prepared Ce0.9Y0.2O1.9 a fluorite structured oxide by precipitating oxalates accompanying calcination at 300 °C.

Spinel nanostructures of Ni0.5Zn0.5Fe2O4, Mg2FeO4, Sm1-xSrxFeO3 have been synthesized by precipitation of respective hydroxides followed by calcination at desired temperature. H. Wang et al. reported synthesis of Indium Tin oxide (ITO) with particles size of ~ 12.6 nm and surface area 45.7 m2/g by coprecipitation method.

The synthesis of ternary metal oxides by direct precipitation has been observed to be rare and nevertheless possible in case of the ternary oxides possessing highly thermally stable structures such as spinel. In such case precipitation reactions are normally carried out at elevated temperatures (50-100 °C) so that hydroxide intermediates are condensed to form oxides. Then in this case calcination is not required. Nanoparticles of Fe2O3, MnFe2O4, CoFe2O4 etc. have been synthesized by this technique.

Synthesis of nano structured metal oxides by co precipitation in nonaqueous medium was also reported by many researchers. Hagenmullar et al. synthesized LiCoO2 by alcohol mediated simultaneous coprecipitation of hydroxides of Li(OH) and Co(OH)2 followed by calcination in the range 400-700 °C and yielded 12-41 nm size particles.

1.1.1.2 Solvothermal techniques:

In solvothermal synthesis chemical reactions performed in closed reaction vessel at temperatures higher than the boiling point of the solvent used. If water is used as solvent, it’s known as hydrothermal method. Solvothermal methods are mainly defined
by chemical parameters such as nature of the solvent and reagents, temperature and pressure. Solvothermal technique has been fundamental branch of nanoparticle synthesis and processing. This technique consumes less energy due to moderate reaction temperature and commonly inexpensive solvents can be used for the synthesis hence, it’s a greener technology approach. In solvothermal method only liquids having low boiling point can be used as solvents. In hydrothermal method homogenous or heterogeneous reaction takes place in aqueous medium at the temperature above the boiling point of water and at high pressure. Hydrothermal processing of materials encompasses processes like synthesis, crystal growth, treatment, fabrication, alteration, hot pressing, recycling, sintering etc. This technique offers a direct route to synthesize nanomaterials like oxides, chalcogenides having narrow size distribution. Generally, temperature in hydrothermal process fall between the boiling point of water and the critical temperature of water with pressure over 100 kPa. Mechanism of hydrothermal method follows liquid nucleation model. Detailed principles are comprised of theories of chemical equilibrium, chemical kinetics and thermodynamic properties of aqueous system under hydrothermal conditions. Furthermore in various cases, hydrothermal mechanisms are different. In many cases dissolution precipitation mechanism has been suggested by Overamenko et al and Eckert et al. However, authors observed that in-situ mechanism evolves from dissolution precipitation process at the beginning of the reaction for longer time. The stability and particle size of the product depend on pH of the reaction medium, concentration of precursors, reaction temperature and time. Moreover hydrothermal synthesis can be enhanced by coupling it with microwave, electrochemical, ultrasound, mechanochemical and optical radiation techniques. In few cases intermediate was formed instead of oxide then for such cases thermal decomposition has to be applied to get the desired oxide. Use of capping agents to control the particle size and shape has been reported by many researchers.

1.1.1.3 Sol-Gel Synthesis:

Sol Gel process is weight-chemical technique also known as chemical solution deposition. Nanomaterials typically metal oxides synthesized by this technique in which sol is a precursor for the formation of an integrated network of discrete particles.
or polymer known as a gel. Metal alkoxides or chlorides in the solution state undergo hydrolysis and polycondensation reaction to form network of either elastic solid or colloidal dispersion. A system composed of discrete sub micrometer particles dispersed to various degrees in a host fluid. Metal-oxy or metal-hydroxy polymer is formed in solution due to sol transformed into gel like diphasic system containing both liquid and solid phase by hydrolysis or a polycondensation reaction whose morphologies ranges from discrete particles to continuous polymer network.  

Hydrolysis lead to formation of sol and dispersion of colloidal particles in a liquid and further condensation results into gel which is an interconnected, rigid and porous inorganic network enclosing a continuous liquid phase. This transformation is called sol-gel transition. Gel drying can be performed in two ways, i) Removal of liquid trapped in pores under hypercritical conditions in which network does not collapse and arogels are produced. ii) The gel is dried under ambient condition due to this densification and shrinkage of pores occur yielding xerogel. Porosity generated in the gel depends upon the rate of solvent evaporation. The dried gel is fired or thermally treated at desired temperature to form metal oxides. The precursor sol can be deposited on a substrate to form a film by dip coating or spin coating. Precursor sol can also be casted into a suitable container with the desired shape to obtain monolithic ceramics, glasses, fibres, membranes and aerogels. The nanopowders can be synthesized from precursor gel. Sol gel synthesis is a low temperature and cheap technique which allows fine control over the chemical composition. Even small quantities of the dopant can be introduced into the sol and end up uniformly dispersed in the final product. The material synthesized by sol gel technique has diverse applications in optics, electronics, energy and space, sensors, medicines.  

The major drawback of sol gel method is control over the rate of hydrolysis and condensation of molecular precursors. These reactions are too fast, resulting in loss of morphological and structural control over the fine oxide materials. Besides, the different reactivity of metal oxides makes it difficult to control the composition and homogeneity of the complex multiple oxides by a sol gel process. The control over the reactivity of the precursors can be attempted by i) use of organic additives like carboxylic acids, β-diketones or functional alcohols, which acts as chelating ligands and modify the reactivity of the precursors and ii) control over the local water concentration and thus, over the hydrolysis of metal oxide precursors. In spite of all these efforts, the stronger
sensitivity of aqueous sol gel process towards any slight changes in the synthesis conditions and the simultaneous occurrence of hydrolysis and condensation reaction make it still impossible to complete control over the sol-gel processing of metal oxides in aqueous medium.

In nonaqueous sol-gel synthesis, the transformation of precursor takes place in an organic solvent under exclusion of water. The potential precursors include inorganic metal salts, metal alkoxides, metal acetates and metal acetylacetonates etc. Organometallic compounds are also frequently used, but the process is rather based on thermal decomposition than sol-gel.

1.1.1.4 Combustion Synthesis:

Combustion (CS) synthesis is facile and economically viable technique for the synthesis of ceramics, catalyst, composites, alloys and nanomaterials. In combustion synthesis exothermicity of the redox reaction is used to produce the material.

Depending upon the nature of the reactants, elements or compounds and exothermicity (adiabatic temperature), the CS is described as Self propagating High Temperature Synthesis (SHS), Low temperature Combustion Synthesis (LCS), Sol-Gel Combustion, Emulsion Combustion and Volume Combustion (Thermal explosion) Synthesis.

Combustion processes are generally characterized by high temperature, fast heating rate and short reaction time. These features make combustion synthesis an attractive, low cost method for manufacture of the nanomaterials. Other advantages are i) Use of simple equipment ii) Formation of high purity products iii) Stabilization of metastable phases iv) Formation of virtually any size and shape products.

Combustion Synthesis can be classified into three broad classes based on the physical nature of the precursors, namely i) Conventional Self propagating High temperature Synthesis (SHS) ii) Solution Combustion Synthesis iii) Gas phase Combustion Synthesis.41

**Conventional Self propagating High temperature Synthesis (SHS):** It is difficult to synthesize nanomaterials with high surface area and having low particle size distribution by conventional solid state method since it requires high temperature
Modified combustion synthesis methods are quite effective as compared to the conventional solid state synthesis. Modified methods are i) SHS followed by intensive milling ii) SHS along with mechanical activation iii) SHS followed by chemical treatment known as chemical dispersion iv) SHS with additives v) Carbon Combustion Synthesis. In SHS followed by chemical dispersion method, the synthesized powder is treated with dilute acid solution which dissolves defect rich layer followed by ball milling. Nanosized boron, aluminium and silicon nitrides were synthesized by this technique. Chemical dispersion treatment produces pure products and consumes less energy compared to ball milling. This technique cannot be applied effectively for a wide range of SHS products. The SHS with additives applied for nanomaterials synthesis is known as alkali molten salt assisted combustion. In this method reducing metal like Mg is allowed to react with transition metal oxide in a melt of alkali salt (e.g. NaCl) to form fine metal particle. Due to heat generated by combustion reaction, salts melt at 1083 K and further nucleation occurs in molten NaCl which inhibits agglomeration and growth of the particles. By product (MgO) formed in this process can easily be leached out by treatment with dilute acid.

Solution Combustion Synthesis: This technique is simple, versatile, simple and fast process compared to other combustion techniques. Variety of nanomaterials can be synthesized by this method. In this method self sustained reaction in homogeneous
solution of different oxidizers (metal nitrates) and fuels takes place. It is well known that fuel is an important part of the metal oxide synthesis. Urea and glycine are the most commonly used fuel for producing highly uniform complex oxide ceramic powder with precisely controlled stoichiometry. All these fuels used are source of C and H which on combustion form CO\textsubscript{2} and H\textsubscript{2}O along with heat liberation and they form complexes with metal ion facilitating homogeneous mixing of cations in the solution. The exothermicity varies from 1000 to 1800 K. The nature of the combustion may be flaming or non-flaming which depends upon the fuel used. Urea has been found to be most preferred fuel due to its high exothermicity and easy availability. This technique has been applied for preparation of alumina based oxides, ceria based oxides, solid oxide fuel cells and so many varieties of oxides. Apart from urea and glycine, other fuels like carbon hydrazides (CH), oxalyl dihydrazide (ODH), malonic acid dihydrazide (MDH), ammonium acetate, citric acid, ammonium citrate etc. also can be used in the SCS. The concept of mixture of fuel has also been attempted for synthesis of nanomaterials. The complex fuel favours formation of nanosized particles but further calcination may be required for the removal of organic content which depends on the nature of the fuel. Many books and reviews have been published on combustion synthesis in recent years.

1.1.1.5 Template Based Synthesis

In this technique the template simply serves as a scaffold against which other kinds of materials with similar morphologies are synthesized. Template base synthesis can be used to synthesize self assembled nanoparticles into 2 or 3-D nanostructures. The properties of such self assembled nanoparticles are different than individual particles. Many natural materials can be used as template to organize and interconnect assemblies of nanoparticles on surfaces. Natural materials which can be used as template have specific binding properties in molecular recognition. Template based synthesis of nanoparticles is simple and convenient route. In situ generated material is shaped into a nanostructure with its morphology complementary to that of the template. The materials such as zeolites, glasses, layered solids, molecular sieves, alumina membranes can be used as hard solid template. Nanoparticles can be synthesized by using 3D network of DNA as a template. In earlier studies,
twinned Zn$_2$TiO$_4$ spinel nanowires have been synthesized by using ZnO nanowires as template.\textsuperscript{65} Similarly Ga$_2$O$_3$, MgO nanowires have also been employed as template for synthesis of single crystal ternary oxide.\textsuperscript{66,67,68} Templates can be filled using solution route, sol-gel technique or electrochemical route. The organic or inorganic template can be removed by various techniques such as heat treatment,\textsuperscript{69} microwave irradiation,\textsuperscript{70} washing with the organic solvents,\textsuperscript{71} calcination,\textsuperscript{72} and dissolution of the core particles.\textsuperscript{73}

### 1.1.2 Properties of nanomaterials

Material when reduced to nanoscale, exhibits different properties compared to material in macro state. This transformation enables drastic change in properties like some opaque substances become transparent, some stable materials turn into combustible, and some materials which are insoluble in one solvent become soluble in that particular solvent, some chemically inert materials becomes chemically active.

#### 1.1.2.1 Bulk and Nanomaterial

Bulk material possesses well defined physical properties which are not susceptible to their size, but nanomaterials can display wealth of novel properties as their size changes from bulk to nanoscale. These emerging novel properties of nanomaterial appear from two main aspects, surface and quantum effect. As material downsizes, more and more surface atoms are exposed. The surface properties previously overwhelmed by bulk material become dominating in nano system. On the other hand physical properties may become quantized as electrons are spatially confined in quantum wells of the nanostructure. Both lead to general acceptance that size variation of the nanostructure can provide one of the most powerful means to tune the electrical, optical and magnetic properties of the functional materials.\textsuperscript{74}

#### 1.1.2.2 Properties of metal oxides nanoparticles

Metal oxides are one of the attractive materials from scientific as well as technological point of view amongst all functional materials. Versatile structures and properties of metal oxides makes them primary target in solid state chemistry. It possesses variety of
crystal structures ranging from simple rock salt to highly complex incommensurately modulated structures. The nanoscale metal oxides can exhibit unique physical and chemical properties due to their limited size and high density at corner and edge surface sites. Particle size affects on three important groups of basic properties of any material. These are namely i) structural characteristics ii) electronic properties and iii) physical and chemical properties.

i) Structural Characteristics: Bulk metal oxides are generally strong and stable systems with defined crystallographic structures. Decrease in particle size influence on the surface free energy and stress. The changes in thermodynamic stability due to size reduction can induce structural transformation and cell parameter modification. In extreme cases the nanoparticles can disappear due to interaction with its surrounding and high surface free energy. In order to display mechanical and structural stability, nanoparticles must have low surface free energy. Size induced structural distortions have been observed in case of metal oxides. Decrease in particle size increases the number of surface and interface atoms which generates intrinsic strain and affiliated with structural perturbations. There is possibility of existing extrinsic strain along with intrinsic strain associated with a particular type of synthesis. Existing strain may be partially relieved by annealing or calcination. On the other hand interactions with substrate on which nanoparticles are supported can complicate the situation and induce structural perturbations or phases which is not observed for bulk state of metal oxide.

Nanostructures of metal oxides can take on geometries not seen in the bulk state. Along with this oxygen to metal ratio can vary due to increases in oxygen vacancies in nanostructured metal oxides which are not observed commonly in bulk state. Hence, enhancement in chemical reactivity takes place in nanostructured state. In other extreme, nanoparticles could have larger oxygen/metal ratio than in bulk metal oxides. This could lead to perturbation in chemical activity as a result of i) higher positive charge on metal oxides and smaller negative charge on oxygen anion (ligand effect). ii) Variation in the relative number of cation and anion centres exposed on the surface (ensemble effect). From an electronic viewpoint, perturbations in chemical reactivity may arise from changes in size of the band gap or from redistribution of atomic charges when transforming from macrostructures to nanostructures.
ii) Electronic properties: The size reduction produces quantum size or confinement effect which arises from presence of discrete, atom like electronic state. From solid state point of view, these states can be considered as being superposition of bulk like states with simultaneous increases in oscillator strength.\(^8\) Besides this, quantum confinement effect influence on optical band gap and energy shift of exciton level.\(^8\),\(^9\) Long range effect of Medulang field which deals with electronic properties of bulk metal oxide surfaces is limited or absent in nanostructured oxides.\(^8\),\(^9\) Theoretical studies on metal oxides show that redistribution of charges takes place during transformation of large periodic structures to small clusters or aggregates which is significant in case of covalent compare to ionic solids.\(^8\),\(^9\) Covalent or ionic character in metal oxygen bond depends on size of the particle. Theoretical study interpreted that, ionic character in M-O bond increases with decrease in size of the particle.\(^9\)

iii) Physical and chemical properties: Structural and electronics properties affect on physical and chemical properties of the solid. Many oxides in bulk state have wide band gap and low reactivity.\(^8\) A decrease in average particle size affects on the magnitude of band gap as well as surface properties, which strongly influence on conductivity and chemical reactivity.\(^8\),\(^9\),\(^9\),\(^8\) Solid-gas or Solid-liquid chemical reactions take place on surface of the solid or sub-surface region of the solid. In case of nanostructured metal oxides, surface properties are strongly modified with respect to 2-D infinite surface, producing solids with unprecedented sorption or acid-base characteristics.\(^9\) Furthermore, the presence of co-ordinated atoms (like corner or edges) or O vacancies in an oxide nanoparticle should produce specific geometrical rearrangements as well as occupied electronics state located above the valence band of the corresponding bulk material.\(^9\),\(^9\),\(^8\) All these surface changes causes enhancement in the chemical reactivity of the system.\(^9\),\(^9\),\(^9\),\(^9\),\(^9\)

It is well known that, the nature of metal-oxygen bonding in metal oxides varies from covalent or metallic to ionic.\(^1\)\(^\text{02, 03}\) Metal oxides demonstrate fascinating electronic and magnetic properties due to bonding and structural changes. Oxides like RuO\(_2\)\(^1\)\(^\text{04}\) and ReO\(_3\)\(^1\)\(^\text{05}\) are metallic, while BaTiO\(_3\) is insulator,\(^1\)\(^\text{06}\) ZnTiO\(_3\) is semiconductor.\(^1\)\(^\text{17}\) The ferro-, ferri- and antiferromagnetic properties are associated with metal oxides like titanates,\(^1\)\(^\text{07}\) niobates, and tantalates.\(^1\)\(^\text{08}\) Metal oxides like cuprate are superconductor\(^1\)\(^\text{09}\) and mangnites shows massive magneto-resistance or
multiferroics combining ferroelectricity and ferromagnetism within the same material.\(^{110}\)

The exceptionally broad spectrum of properties makes bulk metal oxides a vital constituent in technological applications like gas sensing, medical science, electronics, ceramics, energy conversion and storage and surface coating etc.

1.1.3 Multiple component oxides

Multicomponent oxides contain two or more metals. Multicomponent metal oxides may have pervoskite or spinel type structure.

1.1.3.1 Pervoskite Structure

The class of metal oxides with the empirical formula ABO\(_3\) known as pervoskite structures which was derived from the rare mineral of CaTiO\(_3\) known as pervoskite.\(^{111}\) Pervoskite may possess cubic or orthorhombic crystal structure. Cubic form of the material is ideal form of the pervoskite as shown in Figure 1.1. A (blue) cations are shown at corners of the cube and Oxygen (red) in face centre position while B cation (yellow) at centre of the cube. In pervoskite structure A cation is coordinated to 12 oxygen ions to form cuboctahedral coordination environment while B cation is coordinated to six oxygen ions in an octahedral array. Therefore, A cation should be normally larger than B cation. The simple cubic structure emphasising the coordination environment of A cation is shown in Figure 1.1. The chemical composition of these pervoskite oxides can vary depending upon the valences of the cation A and B which give rise to A\(^{+1}\)B\(^{+5}\)O\(_3\), A\(^{+2}\)B\(^{+4}\)O\(_3\) and A\(^{+3}\)B\(^{+3}\)O\(_3\) types.\(^{112}\) Pervoskite type oxides exhibit variety of physical properties like ferroelectric, dielectric, pyroelectric and piezoelectric properties.\(^{113}\)
1.1.3.2 $A_2BO_4$ type spinel oxides

Spinels are complex oxides displaying a regular structure in which oxygen ion array consists of face centered cubic structure in which one third of the metal ions are located at tetrahedral sites and remaining at octahedral sites. The spinels can be formed by association of two trivalent cations with one bivalent cation (II-III type) or two bivalent cations with one tetravalent cation (II-IV type) or one hexavalent cation with two monovalent cations (I-VI type).

The $A_2BO_4$ spinel oxide form family of about 120 compounds having significant range of properties like ferro and antiferromagnetism, coexistence of transparency and conductivity, superconductivity and ferroelectricity. $A_2BO_4$ type spinels are classified as either normal or inverse, representing different distribution of A and B cations over tetrahedrally and octahedrally coordinated cation sites. These structures undergo characteristic structural changes as a function of temperature.
structural changes are (i) normally disordered inverse structure orders crystallographically at low T and (ii) at finite temperatures in inverse and normal spinels, develop characteristic distribution of cation associated with order-disorder structural changes. In the spinel structure A and B metal atoms are distributed over the interstitial sites of a distorted f.c.c. of oxygen sublattice. Half of the octahedrally coordinated f.c.c. sites (Oh) and eighth of tetrahedrally coordinated interstitials (Td) are populated by the A and B cations. Degree of inversion (\(\lambda\)) dimensionless quantity describe relative concentration of A cations on Td sites. In terms of \(\lambda\), the spinel chemical formula can be written as \([A_{2-\lambda}B_{\lambda}](A_{\lambda}B_{1-\lambda})O_4\) with brackets and parenthesis representing Oh and Td sites respectively. Depending upon \(\lambda\) value spinels are sorted into (i) normal spinel (\(\lambda=0\)) an ordered phase with cubic (F\(_{3dm}\)) symmetry having Oh sites occupied by exclusively by A cations and Td sites by B cations. (Figure 1.2a) (ii) inverse spinel (\(\lambda=1\)) having half of the cation A occupying the Td sites and other of half of A together with all B atoms occupying Oh sites much as in a 50-50% binary alloy on Oh sites (Figure 1.2b). Therefore inverse spinel corresponds to a class of configurations rather than single crystallographic structure. In such cases one can expect ordering at low temperature. It is reported that tetragonal crystal structure with space group P4\(_1\)2\(_2\) has been observed experimentally for A\(_2\)TiO\(_4\), (A = Mg, Zn, Mn) inverse spinels. Compounds having tetragonal P4\(_1\)2\(_2\) structures are observed to undergo first order transition to the disordered inverse state with \(\lambda=1\) with cubic crystal structure having space group F3dm (Figure 1.2c)
Figure 1.2: a) Ordered normal spinels ($\lambda = 0$, F3dm)  
  b) Ordered inverse spinels ($\lambda = 1$, P4$_1$22)  
  c) Disordered inverse state ($\lambda = 1$, F3dm)  
  d) disordered –disordered state (F3dm)$^{123}$  
  Red: Oxygen, Blue: Cation A, Gray: Cation B

1.1.3.3 Zinc Titanates

Zinc titanates are well known for their applications in the fields such as paint and pigments,$^{124}$ gas sensors,$^{125}$ catalytic sorbents,$^{126,127}$ electrode of solid oxide fuel (SOFC),$^{128}$ metal-air barriers,$^{129}$ microelectronics,$^{130}$ high performance catalyst for CO and NO reduction.$^{131}$ Zinc titanates and modified zinc titanates are found to be good candidates for microwave resonators materials.$^{132}$
ZnO based compounds are technologically more important since they exhibit specific functions that are unachievable by pure ZnO phase. ZnO can form spinel type ternary compounds with other oxides in the form of ZnM$_2$O$_4$ or Zn$_2$MO$_4$ (M=Al, Cr, Fe, Ga, In, Sn, Ti, Mn, V) as well as it can form pervoskite compounds with other oxides in the form of ZnMO$_3$.

ZnO-TiO$_2$ system generates series of compounds known as zinc titanates which includes zinc orthotitanate (Zn$_2$TiO$_4$), zinc metatitanate (ZnTiO$_3$), Zn$_2$Ti$_2$O$_6$, Zn$_2$Ti$_3$O$_8$ and Zn$_4$Ti$_5$O$_{16}$. After the work of Dulin and Rase, Bartram Slepetys and Yamaguchi et al., three zinc titanate compounds have been confirmed to exist in ZnO-TiO$_2$ system, namely ZnTiO$_3$(h), Zn$_2$TiO$_4$(c and t) and Zn$_2$Ti$_3$O$_8$(c). ZnTiO$_3$ decomposes to into rutile and Zn$_2$TiO$_4$ at 925 ± 25 °C under condition of solid state dry reactions. Amongst all zinc titanates, only zinc orthotitanate is found to be thermodynamically stable in sintered form. Phase transition of ZnO-TiO$_2$ system is complex which depends on precursors used, method of synthesis, Zn/Ti ratio, additives used and temperature employed. Formation temperature of zinc titanates varies with preparation method and Zn/Ti ratio of the precursors used. G. Krylova et al. synthesized Zn$_2$TiO$_4$ and ZnTiO$_3$ from stoichiometric proportion of Zn/Ti to be 2 and 1 respectively by sol-gel method. Literature survey reveals that many researchers have synthesized nanostructured Zn$_2$TiO$_4$ from ZnO and TiO$_2$ by various methods like ball milling, solid state reaction route. Liang Li et al. reported the growth of high quality Zn$_2$TiO$_4$ crystal by optical floating zone method. The author determined optical interband transitions as indirect transitions and hence, reported Zn$_2$TiO$_4$ as indirect band gap materials with band gap 2.29 eV. Birnbaum et al. synthesized Zn$_2$TiO$_4$ by thermal combination of ZnO and TiO$_2$ at 1200 °C and observed that about 45% NiO can be substituted for ZnO as per Vegard’s law. The Zn$_2$TiO$_4$ spinel having disordered cubic structure was synthesized by grinding of stoichiometric mixture of ZnO and TiO$_2$ followed by heat treatment at 1100 °C for 7 h. The structure of Zn$_2$TiO$_4$ and other similar compounds were refined using neutron diffraction analysis technique by Marine et al. U. Steinike and B wallis showed that double oxides of Zn and Ti can be synthesized form solid state reaction of ZnO and TiO$_2$. Moreover kind of double oxide depend on TiO$_2$ structural modification since there exist structural similarity between Zn$_2$TiO$_4$ (spinel) and TiO$_2$...
(anatase), ZnTiO₃ (Pervoskite) and TiO₂ (rutile). While the Zn₂Ti₃O₈ is formed only on the basis of Zn₂TiO₄ phase and its structure was derived as defect spinel. Yi Yang et al. synthesized twined Zn₂TiO₄ spinel nanowires using ZnO nanowires as template by employing three stage synthesis including vapour phase transport method, magnetron sputtering technique and solid state deposition at 800 °C. Y. Yang also studied the formation of multi twinned Zn₂TiO₄ nanowires based on solid-solid reaction of ZnO nanowires with conformal shell of TiO₂ which is deposited by atomic layer deposition (ALD). They found that multi twinned Zn₂TiO₄ developed through an oriented attachment of initially separated spinel nanobricks and simultaneous Ostwald ripening process. Toberar et al. obtained porous rutile TiO₂ through reduction and vapour phase leaching of Zn from macroporous monolith of Zn₂TiO₄ at high temperature. Kim et al. reported microwave dielectric properties of titanium incorporated Zn₂TiO₄. Accordingly, TiO₂ forms solid solution within Zn₂TiO₄ matrix that improves dielectric properties of Zn₂TiO₄. But this requires high sintering temperature ~ 1100 °C.

Chuan-Feng Shih et al. attempted to achieve low temperature sintered Zn₂TiO₄ with near zero temperature coefficient by incorporating TiO₂. Due to the high crystallinity, the Zn₂TiO₄:TiO₂ showed good dielectric properties even at low sintering temperature. Earlier to this the author synthesized high quality Zn₂TiO₄ from nanowires of ZnO and TiO₂, which showed promising microwave properties at low temperature < 1000 °C. Liyuan Wan et al. synthesized ZnO/Zn₂TiO₄ core shell nanowires by solid state reaction of ZnO nanowires with conformal shell of TiO₂ at 800 °C. Conformal core shells of TiO₂ were deposited on ZnO nanowires by sol-gel method. Photocatalytic degradation of acetone studied under UV light irritation which fractionates to formates, carbonates and CO₂. Chen-chun synthesized Zn₂TiO₄-ZnO nanowires by two stage fabrication process. Zn₂TiO₄ synthesized possess cubic structure with two different orientation relationships with ZnO. They also pointed out that unilateral surface diffusion of ZnO into TiO₂ played important role in the formation of Zn₂TiO₄. Dongfi Sun et al. synthesized Zn₂TiO₄ and TiN nanofibres by facile combination of electrospinning and thermolysis under different atmospheres. Nicolas T. Nolan et al. synthesized zinc titanates by sol gel method in the temperature range 400-1000 °C and investigated effect of ratio Zn/Ti on phase of the zinc titanates. It was observed that, when precursor concentration of Titanium is excess over the zinc precursor, formation of metastable zinc metatitanate is favoured which
gets almost transformed into zinc orthotitanate at temperature < 900 °C while if concentration of zinc precursor is excess, unstable Zn₂Ti₃O₈ is formed which is transformed into zinc orthotitanates at 1000 °C.

1.1.3.4 Doped zinc orthotitanates

Very few reports are available on Metal doped Zn₂TiO₄. S. Butee et al. synthesized Cu doped Zinc orthotitanates [(Zn₁₋ₓCuₓ)₂TiO₄, 0 ≤ x ≤ 0.20] spinels by solid state reaction and sintering at 1060 °C. The synthesized material has been used as microwave dielectric material whose microwave resonator quality factor found to be increased remarkably with respect to Zn₂TiO₄.¹⁶¹ The particle size was observed to be in the range 2-20 µm. Polymeric complex method was employed for synthesis of Zn₂Ti₁₋ₓFeₓO₄ by Jum Sung Jang et al. The obtained Fe doped Zn₂TiO₄ was used as visible light photocatalyst for H₂ generation from water-methanol solution.¹⁶² S. C. Souza et al. Synthesized Cobalt, Nickel and Manganese doped Zn₂TiO₄ spinel structures by polymeric precursor method known as Pinchi method.¹⁶³ The composition of Metal doped zinc orthotitanates was observed to be Zn₁₋ₓM₀ₓTiO₄. A.C. Chaves et al. studied photoluminescence in disordered Zn₂TiO₄ and M⁺ⁿ doped Zn₂TiO₄ (M⁺ⁿ : Cr⁺³, V⁺⁵ and Sn⁺⁴). These compounds were synthesized by polymeric precursor method (Soft solution method) and found maximum 8 times enhancement in PL in doped Zn₂TiO₄.¹⁶⁴ Substitutional doping was performed at the site of Ti⁺⁴ ion to get the composition of doped zinc orthotitanates as Zn₂Ti₁₋ₓMₓO₄. Chawarat Siriwong et al synthesized single phase Pt doped and undoped cubic phase Zn₂TiO₄ by flame spray pyrolysis technique using precursors zinc naphthenate and titanium tetraisopropoxides.¹⁶⁵ Jan Mrazek et al. synthesized rare earth metal (Eu, Er, Tm) doped Zn₂TiO₄ and undoped Zn₂TiO₄ by sol gel method using zinc acetate and titanium (IV) butoxide at 1200 °C.¹⁶⁶ The Zn₂TiO₄ obtained contains ZnO as well as Eu₂Ti₂O₇ as additional phases. P. Borse et al.¹⁶⁷ synthesized Fe and Cr doped/co doped zinc orthotitanates by solid state method in which doping and co-doping was done at Ti⁺⁴ site with various proportions of Cr and Fe by solid state reaction for tuning band gap of zinc orthotitanate into visible region. The synthesized compounds were employed for photocatalytic splitting of H₂O. Zinc orthotitanate having composition Zn₂Ti₀.₉Fe₀.₀₅Cr₀.₀₅O₄ produced maximum H₂ production.
Zn$_2$TiO$_4$ has been effectively used for removal of multiple constituents of hot stream gases being an efficient adsorbent of gases at high temperature.\textsuperscript{168} It is regenerable with negligible loss and having higher thermal stability than single metal oxides.\textsuperscript{169} Shiqiang Hao et al reported surface reactions of AsH$_3$, H$_2$Se and H$_2$S on (010) surface of Zn$_2$TiO$_4$ on the basis of DFT calculation and showed that 010 surface is having large fraction of the total surface area of Zn$_2$TiO$_4$ and having two distinct terminations, one oxygen rich and other metal rich. AsH$_3$ preferably forms bond with oxygen atom while H$_2$Se and H$_2$S forms bond with metal and hence adsorbed on (010) surface which is oxygen as well metal rich.\textsuperscript{170} The adsorption energy of H$_2$S at the Zn site is -0.75 eV so adsorbed effectively at Zn sites leading to dissociation of H$_2$S due to low adsorption energy. These theoretical finding suggest that Zn$_2$TiO$_4$ in tetrahedral form can be used as visible light photo catalyst for dissociation of H$_2$S to generate H$_2$ if band gap tuned to visible region. These findings led us to attempt H$_2$S splitting using zinc orthotitanate. Hence zinc orthotitanates can be acceptable solution to the environment as well as energy crises.

Summary of zinc orthotitanates with respect to method, particle size and morphology has been given in Table 1.1
Table 1.1: Summary of synthesis method and morphologies of zinc orthotitanate.

<table>
<thead>
<tr>
<th>Method</th>
<th>Size</th>
<th>Morphology/Structural</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solid State Reaction and sintering at 1150 °C</td>
<td>15-45 μm (Grain size)</td>
<td>__</td>
<td>171</td>
</tr>
<tr>
<td>Solid State Reaction sintering at 1100 °C</td>
<td></td>
<td></td>
<td>172</td>
</tr>
<tr>
<td>Sol Gel method</td>
<td>No report on size</td>
<td>Zn₂TiO₄(c) and TiO₂(r)</td>
<td>173</td>
</tr>
<tr>
<td>Polymeric precursor method</td>
<td>Un-doped Zn₂TiO₄ 4.1 nm,</td>
<td>Nanocrystals</td>
<td>174</td>
</tr>
<tr>
<td></td>
<td>Cr-doped Zn₂TiO₄ 3.9 nm,</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Sn-doped Zn₂TiO₄ 4.5 nm, and</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>V-doped Zn₂TiO₄ 4.5 nm</td>
<td></td>
<td></td>
</tr>
<tr>
<td>High energy ball milling</td>
<td>9.1 nm (α-Zn₂TiO₄) and</td>
<td>Nanocrystals after 6 h of ball</td>
<td>175</td>
</tr>
<tr>
<td></td>
<td>9.0 nm (ZnTiO₃)</td>
<td>milling</td>
<td></td>
</tr>
<tr>
<td>Electrospinning/sol–gel process/calcining</td>
<td>Diameter: 400–800 nm</td>
<td>Nanofibers composing of ZnTiO₃,</td>
<td>176</td>
</tr>
<tr>
<td></td>
<td>Length: ~μm</td>
<td>Zn₂TiO₄ and rutile TiO₂</td>
<td></td>
</tr>
<tr>
<td>Flame spray pyrolysis</td>
<td>5-10 nm</td>
<td>nanospheres</td>
<td>177</td>
</tr>
<tr>
<td>Floating zone method</td>
<td>6 mm (φ) x 30 mm(L)</td>
<td>Crystal (yellow)</td>
<td>178</td>
</tr>
<tr>
<td>Bridgman method</td>
<td></td>
<td></td>
<td>179</td>
</tr>
<tr>
<td>Solid state reaction and sintering at 1060 °C</td>
<td>~15 μm ( Zn₂TiO₄)</td>
<td>Grains</td>
<td>161</td>
</tr>
<tr>
<td></td>
<td>2-3 μm ( Cu@(Zn₁₋ₓCuₓ)₂TiO₄)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Method</td>
<td>Size</td>
<td>Morphology/Structural</td>
<td>References</td>
</tr>
<tr>
<td>-------------------------------------------------------------</td>
<td>-----------------------------</td>
<td>---------------------------------------------</td>
<td>------------</td>
</tr>
<tr>
<td>Sight specific deposition of TiO$_2$ on ZnO followed by annealing at 800 $^\circ$C</td>
<td>Size not given</td>
<td>Nanowires of Zn$_2$TiO$_4$ on ZnO Nanowires</td>
<td>158</td>
</tr>
<tr>
<td>Solid state reaction</td>
<td>Size not given</td>
<td>Shape not mentioned</td>
<td>180</td>
</tr>
<tr>
<td>Sol-Gel method</td>
<td>Size not given</td>
<td>Nano crystals</td>
<td>166</td>
</tr>
<tr>
<td>Atomic layer Deposition</td>
<td>Size not given</td>
<td>Thin film of 40 nm thickness</td>
<td>181</td>
</tr>
<tr>
<td>Electro spinning followed by thermolysis</td>
<td>Several $\mu$m (L), 110 nm(d)</td>
<td>nanofibres</td>
<td>159</td>
</tr>
<tr>
<td>Hydrothermal</td>
<td>10 $\mu$m (L), 200 nm (d)</td>
<td>nanowires</td>
<td>157</td>
</tr>
<tr>
<td>Homogeneous Hydrolysis</td>
<td>2 $\mu$m</td>
<td>nanospheres</td>
<td>182</td>
</tr>
<tr>
<td>Electrospining via MOCVD</td>
<td>Several $\mu$m (L), 20-100 nm (d)</td>
<td>nanofibres</td>
<td>183</td>
</tr>
<tr>
<td>Sol Gel</td>
<td>10 $\mu$m (L), 200 nm (d)</td>
<td>nanowires</td>
<td>157</td>
</tr>
<tr>
<td>Solid State Reaction and Atomic Layer deposition</td>
<td>Size not given</td>
<td>1-D nanowires</td>
<td>152</td>
</tr>
<tr>
<td>Thermal oxidation method</td>
<td>0.3-30 $\mu$m (L), 30-1800 $\mu$m (w)</td>
<td>Nano belt</td>
<td>184</td>
</tr>
<tr>
<td>Chemical Bath Deposition</td>
<td>Size not given</td>
<td>semispherical</td>
<td>185</td>
</tr>
<tr>
<td>Vapor phase Transport-Magnetron sputtering Deposition-Solid State Reaction</td>
<td>40-60 nm (d), 10 $\mu$m (L) (ZnO) 70-100 nm (d), 10 $\mu$m(L) Zn$_2$TiO$_4$</td>
<td>Nanowires</td>
<td>65</td>
</tr>
<tr>
<td>Solid state reaction</td>
<td>Few 100 nm</td>
<td>nanocrystals</td>
<td>186</td>
</tr>
</tbody>
</table>
Structure of zinc titanates:
Structures of TiO₂, Zn₂TiO₄, ZnTiO₃, and Zn₂Ti₃O₈ consists of TiO₆ octahedra (Figure 1.3) that are connected over common edges. Anatase and spinel like structures (Zn₂TiO₄ and Zn₂Ti₃O₈) have common 3-D frame work. In rutile and ZnTiO₃, TiO₆ octahedra connected over common edges leads to chain and/or layers. Due to these similarities of structures hypotheses regarding formation of ZnTiO₃ and Zn₂TiO₄ was postulated.

Some experimental results demonstrates that Zn₂TiO₄ and ZnTiO₃ appeared simultaneously in many cases. In anatase derived zinc titanates, the major phases were Zn₂TiO₄ and Zn₂Ti₃O₈ only trace amount of ZnTiO₃ is formed in all samples calcined in the range 700-925 °C. Trace appearance of ZnTiO₃ indicates that, little rutile TiO₂ should have existed as intermediate product. To verify this only anatase powder has been calcined at different temperatures. XRD indicates no rutile has been observed below 900 °C, while traces of ZnTiO₃ have been formed at 700 °C. This supports results of Yuan and Zhang that anatase to rutile transition could be lowered in presence of ZnO. The fact that only trace quantity of ZnTiO₃ was observed in anatase derived zinc titanate sample inferred that large numbers of grains of anatase were not transformed into rutile, otherwise large quantity of ZnTiO₃ could have been formed. Gibbs and Banfield found that grain size of nanocrystalline anatase TiO₂ can influence the rate of transformation anatase to rutile transition. It was observed that during the reaction between ZnO and TiO₂, anatase phase could be transformed into rutile phase. The extent of rutile phase was found larger than those not transformed.
anatase phase. Zhongchi Liua et. al. synthesized zinc titanates by solid state reaction route from TiO2 (anatase and rutile) and ZnO and observed that Zn2TiO4 was formed from rutile TiO2 which should not have formed as per hypothesis. It was also observed that, extent of rutile TiO2 and ZnO decrease due to formation of ZnTiO3 and Zn2TiO4 simultaneously with increase in temperature. At 800 °C about 66 % ZnTiO3 and 28 % Zn2TiO4 has been formed. However after 800 °C extent of rutile increases due to conversion of ZnTiO3 to Zn2TiO4 which indicates regeneration of rutile TiO2.

ZnTiO3 (zinc metatitanate) has pervoskite type oxide structure. Synthesis of pure phase ZnTiO3 from ZnO and TiO2 was found to be difficult since compound decomposes into Zn2TiO4 and rutile TiO2 at about 945 °C. ZnTiO3 can be synthesized by various methods like solid state reaction, Sol-Gel method evaporation induced self assembly method (EISA). This can be used as microwave resonator material, catalyst, paint and pigment, and gas sensor for CO, NO, ethanol etc.

Zn2Ti3O8 is observed to be low temperature form of ZnTiO3 which exist below 820 °C and having cubic structure. Reddy et al. showed that Zn2Ti3O8 can be synthesized by thermal decomposition of zinc titanyl oxalate at 650 °C for several hours. Cheng-Li Wang et al. synthesized Zn2Ti3O8 by hydrothermal method without using dispersing agent or mineralizer from TiCl4 and Zn(NO3)2.6H2O in aqueous medium. Yang and Swisher also pointed out that Zn2Ti3O8 is a thermodynamically stable compound up to temperatures between 700 and 800 °C. Just above this temperature, ZnTiO3 is more stable than Zn2Ti3O8. Yamaguchi et al. attempted to synthesize ZnTiO3 by simultaneous hydrolysis of zinc acetylacetonate and titanium tetraisopropoxide and also reported existence of Zn2Ti3O8 in the temperature range 600 -760 °C which decomposes in to ZnTiO3 and TiO2 above 760 °C. All these evidences confirm Zn2Ti3O8 as low temperature form of ZnTiO3.

Bartram and Selepetys pointed out that sample prepared with mole ratio ZnO:TiO2 (2:1) and calcined at 700 and 800 °C for various hours produces defect-spinel type Zn2Ti3O8 with trace amount of uncombined TiO2. This is due to missing of 4 Ti ions missing from 16 point positions of spinel type structure arrangement. Cheng-Li Wang et al. also reported that Zn2Ti3O8 as well as ZnTiO3 can be used as UV attenuating agent.
1.2 Characterization techniques

The characterization of nanoparticles is very important and essential part in the field of nanomaterials and its applications. Knowledge of structural, morphological, chemical changes in nanomaterials is required prior to their application in various filed. Various microscopic and spectroscopic techniques can be employed for the characterization of nanomaterials such as UV-Vis-DRS, PL, XRD, FSEM, TEM, XPS, BET surface area analysis etc.

In the current study, the nanostructured photocatalyst synthesized have been characterized by using techniques such as UV-Vis-DRS spectroscopy, X-Ray Diffraction technique, FTIR, FESEM, TEM, Surface Area analysis and EDAX. The techniques employed for characterization are described in brief.

Optical Characterization

Band structure in the semiconductor can be determined from UV-Vis-DRS or Photoluminescence (PL) measurement.

Optical conductivity is fundamental properties of the metal oxides which depend upon the band gap in the metal oxides. Metal oxides are termed as conductor, semiconductor or insulator on the basis of band gap. The Band gap (Eg) is an important characteristic property of semiconductor which determines their application in optoelectronics.201

1.2.1 Ultra Violet –Visible Diffusion Reflectance Spectroscopy (UV-Vis DRS)

Band gap can be determined from optical absorbance or reflectance measurement. Reflectance is defined as ratio of reflected radiant power to the incident radiant power.202 Diffused reflectance is size dependent property since scattering of the light depends on the particles size. Diffused reflectance is the phenomenon resulting from the reflection, refraction, diffraction and absorption oriented in all direction. Due to quantum size confinement absorption of light becomes discrete like and size dependent. 203 In case of nanocrystalline semiconductors, linear (one exciton per particle) and nonlinear (multiple excitons per particles) properties arises as a result of transition between electron and electron hole to discrete or quantized electronic levels. Optical absorption of the nanosized oxides are influenced by nonstoichiometry defects
which are size dependent. The point defects in nanostructured oxides concern oxygen or cation vacancies and or presence of dopant like Ag\(^+\), Co\(^+\) etc. Vacancy defects introduce gap states in proportion to the defect number\(^{204}\). Direct and indirect band can be determined from the UV-Vis absorption or reflectance plot or tauc plot by using equation (1).

\[ \alpha \propto C_1 (h\nu - E_g)^n \]  

Where, \(\alpha\) is linear absorption coefficient, \(C_1\) proportionality constant, \(h\nu\) is photon energy, \(E_g\) is optical band gap and \(n\) is an index which takes the value \(\frac{1}{2}\) (direct), \(\frac{3}{2}\) (forbidden), 2 (indirect) depending on the nature of the electronic transition responsible for the reflection\(^{205}\). The band can be determined from tauc plot by extrapolating linear part to zero or from first derivative of the the absorbance with respect to photon energy and finding the maxima in the derivative spectra at lower energy side\(^{206}\).

### 1.2.2 Photoluminescence (PL)

Photoluminescence is the spontaneous emission of light from a material under optical excitation when light of sufficient energy is incident on material photons are absorbed followed by excitation of electron. Eventually excited electrons returns to ground state by emitting absorbed radiation. The phenomenon is known as Photoluminescence. The PL intensity is measure of the relative rates of radiative and nonradiative recombination. PL spectroscopy provides optical characterization. The PL spectroscopy is simple, versatile and non-destructive technique. This technique is one of the tool to investigate discrete electronic state. PL frequently originates near the surface hence it is used for characterization of surface\(^{207}\). The PL emission spectrum is commonly used to evaluate the extent of transfer and separation as well as trapping of the charge carriers within an activated semiconductor photocatalyst. The transfer behaviour of the photo induced electron and hole pairs can also be investigated as the recombination of the free charges contribute significantly to emission signals of the PL spectra. Weak PL signal contributes reduction of charge recombination\(^{208}\).
1.2.3 Fourier Transform Infrared Spectroscopy (FTIR)

The FTIR spectroscopy is mainly used to identify functional groups in the sample since each functional has characteristic absorption frequency. In FTIR Fourier Transformation technique with interferometer is used which gives better speed and sensitivity, atomic calibration in accuracy better than 0.01 cm\(^{-1}\) and wide variety of data processing such as Fourier Transformation, interactive spectral subtraction, baseline correction, smoothening, integration and library searching.

1.2.4 X-ray Diffraction (XRD)

X-Ray Diffraction Analysis technique is used to identify crystallographic phases. XRD analysis can be classified as single crystal XRD and Powder Diffraction Pattern analysis. XRD is non-destructive technique which is used for crystal structure analysis. Powder XRD is used to identify the crystallographic phases of material that is not in the form of single crystal. This method uses monochromatic source of X-rays and measure the pattern of diffracted radiation which is result of the constructive interference due to crystalline structure of the powder. From XRD pattern crystallite size can be determined. Crystallite size affects on the width of the peak. Broadening arises from the crystallite sizes that are small enough that not enough crystal planes are available for destructive cancellation of reflections that do not occur exactly at Bragg’s angle.\(^{209}\) Therefore, broadening of the peaks increases with decreases in the crystallite size. Hence, nanoparticle causes notable broadening of the peaks. Crystallite size \((t)\) can be calculated by Scherrer formula.\(^{210}\)

\[
t = \frac{K\lambda}{\beta \cos \theta}
\]  

Where, \(K\) is correction factor for particle shape (0.9 for sphere), \(\lambda\) is wavelength of the X-ray used, \(\beta\) is Half Width Full Maximum and \(\theta\) is angle of diffraction of respective peak.

1.2.5 Transmission Electron Microscope (TEM):

TEM is microscopic technique in which beam of electron is transmitted through sample. Transmitted electron interacts with sample and image is formed. The electrons generated are accelerated by electric potential and focused by electrostatic and
electromagnetic lenses on to the sample. The transmitted beam contains information about electron density, phase and periodicity. An image formed is magnified and focused on fluorescent screen, photographic plate or detected by CCD camera. Resolution of TEM is higher than light microscopes due to small de Broglie wavelength of electrons. One can examine ten thousand times smaller object than observed by light microscope. Electron interacts very strongly with matter giving rise to dark bright image pattern. Dark areas in the image indicate that electrons are transmitted through this dense part while bright or lighter area indicates electrons are transmitted through this region. Particle size and morphology can be determined from TEM images.

Electron Diffraction is technique in which electrons are scattered by atoms in crystal planes. The incident electron wave interacts with the atoms present in the plane and secondary electron wave generated, interfere with each other to get either constructive or destructive pattern.

Electron diffraction pattern (ED pattern) can be taken over particular area known as Selected Area Electron Diffraction (SAED) pattern. ED generates ring pattern form which crystalline pattern such as polycrystalline or single crystalline or amorphous nature and inter planer distance (d-spacing) can be determined. Particle size distribution, extent of agglomeration, dispersion of particles can also be determined from TEM images.

Elemental Analysis can also be done along with TEM images with the help of X-ray Energy Dispersive Spectrometry (EDS) or Electron Energy Loss Spectrometry (EELS) analysis.

1.2.6 Field Emission Scanning Electron Micrograph (FESEM):

In Scanning Electron Microscopic technique, High energy electron beam is scanned over the surface and the back scattering of the electron is looked at. The sample must be under vacuum and it must be conductive at the surface. If sample is nonconductive, Gold sputter coating is done on the sample. In SEM electrons are mostly generated by Tungsten filament or crystal of LaB6. In Field Emission Microscope cold source is employed to generate electrons instead of heating the technique. Field Emission is the emission of the electron from the surface of the conductor caused by strong electric
field. Electron beam produced by FE source is 1000 times smaller than that in SEM with thermal electron gun due to this image quality is distinctly improved. Therefore FESEM is very useful tool for high resolution surface imaging in the field of nanomaterials science.²¹¹

1.2.7 Surface Analysis

The texture of the nanomaterials can be characterized by surface area analysis which gives information regarding surface area, porosity, and pore volume. Pore diameter. Porous solids can have pores in the form of cavities, channels or interstices. Some pores are closed and open pairs may have different shapes like cylindrical, blind with open end, inkbottle or funnel shape. Pore size is important for the application of material. Material can be classified as microporous (d < 2nm), mesoporous, (2<d < 50 nm) and macroporous (d > 50 nm) solids. The surface properties can be studied by gas adsorption analysis. The most common method employed for surface area measurement is Braunaer- Emmett -Teller (BET) and BJH method.²¹² In BET method sample is cooled to liquid nitrogen temperature (77 K) and exposed to nitrogen gas adsorption and BET equation (3) is applied.

\[
\frac{1}{W(P/P_0) - 1} = \frac{1}{W_m C} + \frac{C-1}{W_m C} \left( \frac{P}{P_0} \right) \quad [3]
\]

Where W is weight of the gas adsorbed at relative pressure P/Po, Wm is the weight of the monolayer of adsorbate and C is the BET constant which is related to energy of adsorption of first adsorbed layer. Wm is calculated from the slope and intercept of the linear graph of \( \frac{1}{W(P/P_0)-1} \) VS \( \left( \frac{P}{P_0} \right) \). Surface area is calculated from the volume of the gas adsorbed at relative pressure 1 atm and molecular cross section area of the adsorbate (N₂) molecule.

Photocatalytic activity of the semiconductor depends on surface area and pore volume and pore diameter.

1.2.8 Energy Dispersive X–Ray Fluorescence

Energy Dispersive X–Ray Fluorescence (EDXRF) is analytical technique used for elemental analyses and chemical characterization of sample. It is fast, non-destructive technique and requires no sample preparation. It’s complementary method to other
methods in analytical chemistry. Each element has unique set of atomic energy levels, it emits unique set of X-rays which are characteristic of the element. In EDXRF intensities of characteristic X-rays are measured to determine the elemental composition of the sample.\textsuperscript{213}

1.2.9 Thermal Analysis (TA)

Thermal Analysis is used to determine the thermal stability of the compound as well as thermodynamic parameters such as enthalpy change, Free energy change, entropy change, phase transition. Kinetic study of the thermal decomposition can also be studied with the help of thermogravimetry analysis. Here, This technique have been used for determination of temperature at which oxide formation takes place and nature of intermediate and effect of doping on it. TG, DTG, DTA techniques have been used for the desired purpose.

1.3 Photocatalysis

Photocatalysis is the process in which change in rate of chemical reaction takes place under the action of light in presence of the substance known as photocatalyst.\textsuperscript{214}

Photocatalytic degradation is considered as favoured, promising, cleaner and greener technology for removal of toxic organic and inorganic pollutants from waste water. It is being used as weapon in combating against energy crises, global warming and environmental pollution\textsuperscript{215, 216} killing bacteria and malignant cells.\textsuperscript{217, 218}

Photocatalytic degradation is preferred over photochemical process because, in photochemical approach UV-vis radiation alone or along with oxidant such as H$_2$O$_2$, O$_3$ leads to complete destruction of pollutants,\textsuperscript{219, 220, 221} but the formation of intermediate arising from photodegradation reaction could be more harmful than pollutants itself,\textsuperscript{222, 223} while in photocatalytic degradation process dyes are decomposed into small molecules like H$_2$O, CO$_2$ etc. which are not toxic .

Visible light photocatalysis has attracted growing attention since its significant advantage is that it can be driven by visible light (43 % solar spectrum) rather than UV light (5 % of the solar spectrum). UV light is the source utilized in traditional photocatalysis.\textsuperscript{224} In recent years stress is given upon the development of highly
efficient solar light driven photocatalyst for waste water treatment as well as H₂ production via H₂S/H₂O splitting.²²⁵

In tropical countries like India, where ample amount of sunlight is available, photocatalyst using sunlight will be economical and preferable unlike other energy intensive irradiation sources. Hence there is need of an effective photocatalyst for degradation of organic pollutants under sunlight or visible light.

The intensity of solar light is not adjustable and this is an inherent limitation of solar light driven photocatalysis for contaminant degradation that cannot be fundamentally improved by developing high activity catalysts.

The photocatalytic process mainly involves i) The separation of electron–whole charge pairs, ii) transport and trapping of electrons at the surface or to the surface iii) reaction to form desired product. The photocatalytic process is always accompanied with charge pair recombination. The nanostructured metal oxides greatly influences the photocatalytic process due to high surface to volume ratio, quantum confinement and improved redox power, easier access for both the charge particles to the surface.⁸¹ The drawback of the limited size lies in higher charge pair recombination rates because of increases in number of defective sites.²²⁶ Charge pair separation can be improved by contact between two different phases which physically can separate hole and photoelectron.²²⁷ Nowadays photocatalysis has been exploited for various environmental processes such as deodorization, water purification, air purification, sterilization and soil proof.

It has been reported that semiconductor mediated photocatalysis has potential to destroy a wide range of organic and inorganic pollutants at ambient temperature and pressure with no harmful by-product.²²⁸ TiO₂ and ZnO are well known UV light photocatalyst for degradation of many pollutants owing to their high photosensitivity, stability and large band gap.²²⁹, ²³⁰, ²³¹ Amongst all polymorph of TiO₂, anatase is reported to be efficient photocatalyst. Drawback of TiO₂ photocatalyst mainly its wide band gap and limited use of sunlight spectrum can be overcome by doping with hetero cations, carbon and nitrogen.

In principle, coupling of different semiconductor oxides seems useful in order to achieve efficient electron hole pair separation under irradiation thereby increasing photocatalytic activity. An increase in life time of electron hole pair in the coupled oxides due to hole and electron transfer between the two coupling semiconductors is
crucial to photocatalytic activity enhancement in many Photocatalytic reactions.\textsuperscript{232} Photocatalytic activity also strongly depends on the bulk and surface physicochemical properties of the semiconductor catalyst such as phase composition, defects in bulk and at the surface and surface area. Many reports are available showing enhancement in photocatalytic degradation.\textsuperscript{233, 234}

1.3.1 Mechanism of Photocatalysis

![Figure 1.4: Mechanism of photocatalysis](image)

In semiconductor photocatalysis excitation of electron from valence band to conduction band is accomplished by photons having energy equal to or higher than band gap of semiconductor. This transition generates hole at valence bond thereby forming electron hole pair which is prerequisite step in all semiconductor mediated photocatalysis. There is possibility of recombination of electron and hole and dissipates energy in the form of heat. During photocatalysis electron transfer either from light activated semiconductor to substrate or from substrate to semiconductor takes place known as interfacial electron transfer. This interfacial electron transfer is the most essential and critical steps in semiconductor mediated photocatalysis. Efficiency of photocatalysis depends upon extent of the interfacial electron transfer which further depends upon position of valence band and conduction band in semiconductor with respect to redox potential of the adsorbed substrate. Potential of electron acceptor should be located below i.e. more positive than the conduction band of semiconductor while potential of the electron donor substrate should be located above the valence band i.e. more negative than of the semiconductor. Redox reaction takes place after the interfacial electron transfer to form desired product. The latter
catalytic steps are similar to the thermal catalysis. The overall semiconductor mediated photocatalytic reaction is given by equation,\(^{235}\)

\[
(\text{Ox}_1)_{\text{ad}} + (\text{Red}_2)_{\text{ad}} \rightarrow (\text{Red}_1) + (\text{Ox}_2) \tag{4}
\]

General mechanism of demineralization of organic compounds is given below.

\[
\begin{align*}
H_2O + h^+_B & \rightarrow OH^- + H^+ \tag{5} \\
o_2 + e^-_{CB} & \rightarrow O_2^- \tag{6} \\
OH^- + OC & \rightarrow H_2O + CO_2 \tag{7} \\
o_2^- + H^+ & \rightarrow OOH^- \tag{8} \\
oOH^- + OOH^- & \rightarrow H_2O_2 + O_2 \tag{9} \\
o_2^- + \text{VOC} & \rightarrow CO_2 + H_2O \tag{10} \\
oOH^- + \text{VOC} & \rightarrow CO_2 + H_2O \tag{11}
\end{align*}
\]

Hydroxyl radicals produced on surface of catalyst, oxidize most of the Volatile Organic Compounds (VOC) until complete mineralization. Recombination process competes strongly to process of mineralization thereby reducing rate of photocatalytic degradation.

The photocatalytic activity of catalyst depends not only on electronic properties but also on available active sites on surface. Photocatalyst produces large amount of oxidising species. Out of these, oxidising species which will migrates towards the surface are effective in bringing out the degradation. Therefore properties like crystal size, structure, pore size/volume density of OH groups on surface, surface charge, number and nature of trap sites, adsorption and desorption characteristics play important role in photocatalytic activity. Large surface area results in increase in number of active sites on the surface thereby increase in photocatalytic activity.

It was reported that increase in surface area increases the recombination possibility due to increase in surface defects. These surface defects act as recombination centres for photo induced electron hole pair.

Surface hydroxyl groups participate in photocatalytic degradation process as per equation (7). Therefore increase in hydroxyl group on the surface enhances the photocatalytic degradation of organic compounds. High temperature calcination reduces the OH groups due to which photocatalytic activity decreases.

1.3.2 Reducing recombination due to Ag nanoparticles
Recombination photoelectron hole pair at the surface of the catalyst reduces the efficiency of catalyst. The recombination rate can be reduced by doping with ions or metal, hetero junction coupling, nanosized crystal. These attempts promote the separation of electron hole pair which increases the photocatalytic activity of the semiconductor. During recombination of electron hole pair energy may be released in the form of luminescence the phenomena known as photoluminescence. The intensity of luminescence increases with recombination rate of photo electron hole pair.

\[ e_{CB}^- + h\nu_B \rightarrow h\nu \ (Energy) \]  

1.3.3 Photosensitization

In photosensitization process light sensitive compounds absorb light which causes excitation of molecule. Quenching of excited state takes place either by electron transfer or energy transfer. Energy transfer to other molecules makes no chemical change while electron transfer leads to photolysis of the compound. The organic dye such as azo and xanthane dye undergo photosensitization and returns to ground state by energy transfer, therefore they can be used as sensitizer in solar cell. Direct photolysis of the organic dye has been proved to be difficult under natural environment because rate of photolysis depends on reactivity of the dye and photosensitization.236 Many researchers have attempted photodegradation of dye by using sensitizers and/or photocatalyst in aqueous medium. Photodegradation of dye using acetone, \( \text{Fe}^{3+} \) and or \( \text{H}_2\text{O}_2 \) as photosensitizers in presence and absence of \( \text{TiO}_2 \) under UV light is reported by many authors.237, 238, 235(a)

Photosensitized oxidation of the dyes in presence of semiconductor catalyst takes place by excitation of adsorbed dye by visible light to appropriate singlet or triplet state subsequently followed by electron injection form excited dye molecule to conduction band of semiconductor (e.g. \( \text{TiO}_2 \)) and forming cationic dye which undergo degradation.235(a)

\[ \text{Dye} + h\nu \rightarrow 1\text{Dye}^* \text{ or } 3\text{Dye}^* \]  

\[ 1\text{Dye}^* \text{ or } 3\text{Dye}^* + \text{TiO}_2 \rightarrow \text{Dye}^{++} + \text{TiO}_2(e\text{CB}^-) \]  

\[ \text{TiO}_2(e\text{CB}^-) + \text{O}_2 \rightarrow \text{O}_2^{**} + \text{TiO}_2 \]  

\[ \text{Dye}^{++} \rightarrow \text{degradation products.} \]
1.4 Degradation of waste water

1.4.1 Waste water threat to environment

Environmental data shows that industrial waste water consists of heavy metals, volatile organic compounds (VOC), cyanides, COD, oils, suspended solids and sulphides. Dyes are one of the major pollutant extensively used textile industry, photocatalytic industry and in photochemical applications.

Textile industry waste water is heavily charged with inconsumable dyes, surfactants, trace of metals. These effluents are biggest threat to environment. Specially, dyes and intermediates with high aromaticity and low biodegradability has been emerged as serious environmental concern. 234

The production and wide spread use of dyes inevitably results in their unplanned release into the environment where they cause potential threats to human and ecological health. Industrial dyeing process leads to annual discharge of 30000-150000 ton dyes into receiving waters. 239 The severely affected water present not only adverse aesthetic coloration but also contains significant amount of carcinogenic and mutagenic organic substances.

1.4.2 Classification of waste water

Pure and natural water is being polluted due to human activities and extent of contamination is increasing day by day. At the same time scientist and environmentalist are trying to reduce pollution and purify waste water. The technique of purification of water depends upon source of pollution, number of pollutants and their amount. Based on source of pollution waste water, it needs to be classified so that appropriate treatment can be applied for the purification. Waste water can be classified on the basis of nature of waste such as industrial, agricultural, domestic waste polluting the water. Water pollutants may be classified as inorganic, organic, biological pollutants. Inorganic pollutants are heavy metal, ions like nitrates, sulphides, chlorides, oxalates, etc. Organic pollutants are pesticides, Hydrocarbons, phenols, halogenated hydrocarbons, aldehydes, ketones, dyes, pharmaceuticals etc. Biological pollutants include bacteria, fungi, algae, amoeba, worms etc. The water pollutants are found in soluble, colloidal or suspended form.240,241,242 Considering all these factors waste water treatment method should be selected for purification.
1.4.3 Waste water treatments

All over the world researchers are looking for effective and convenient technique for the removal of the contaminants of the waste water. Various physical, chemical and biological methods are practised for waste water treatment. Physical processes includes i) Precipitation methods - coagulation, flocculation and sedimentation, ii) Adsorption methods using adsorbents like activated charcoal, silica gel and biological sludge, iii) Filtration and iv) Reverse osmosis. Chemical processes include ozonolysis, complexometric methods, ion exchange techniques, homogeneous degradation, heterogeneous degradation and Advanced Oxidation Processes (AOP). While, biological process includes aerobic and anaerobic neutralization biological treatment. The disadvantages of these techniques are- i) Physical methods are non-destructive but requires expensive post treatment ii) Chemical methods in which oxidants such as ozone, Chlorine and H₂O₂ are used successfully for dye degradation but highly expensive due to costly chemicals used . iii) Biological treatment does not degrade dye effectively because synthetic dyes resistant to aerobic degradation.

Wastewater treatment techniques can also classified as primary, secondary and tertiary treatment based on unit processes and unit operation. The primary treatment includes physical and chemical purification process. The secondary treatment deals with biological treatment and tertiary treatment includes treatment on waste water treated by primary and secondary treatment process to obtain good quality water for drinking, industrial, medicinal, agriculture etc purposes. It means in order to obtain good quality water all these processes are clubbed together.

In primary treatment process, water is treated at primary level by using screening, filtration, centrifugation, sedimentation, coagulation, gravity and floating methods. These methods are used for highly polluted water.

Secondary treatment process mainly involves use of microbe usually fungus, bacterial strains which converts organic matter into water , ammonia and carbon dioxide gases, alcohols, glucose and nitrates and inorganic matters can be detoxified. The biological treatment may also classified as aerobic (in presence of oxygen) and anaerobic process (in absence of oxygen).
Tertiary water treatment technique involves processes like distillation, evaporation, crystallization, solvent extraction, oxidation, coagulation, precipitation, electrolysis, electrodialysis, ion exchange, reverse osmosis and adsorption.

Nowadays instead of conventional oxidation processes, advanced oxidation processes like Fenton’s reagent oxidation, ultraviolet photolysis, sonolysis, UV/Fenton, photocatalysis etc. are preferred.

\( \text{H}_2\text{O}_2 \) is used on a large scale in photocatalytic processes for waste treatment. \( \text{H}_2\text{O}_2 \) is environmentally benign oxidant which provides \( .\text{OH} \) radical during advanced oxidation processes such as \( \text{O}_3/\text{H}_2\text{O}_2 \), \( \text{UV/}\text{H}_2\text{O}_2 \) and photo Fenton processes. Many researchers have reported that \( \text{H}_2\text{O}_2 \) enhances the photocatalytic degradation of organic contaminant under UV or visible light irradiation, especially in \( \text{TiO}_2 \) catalysed degradation.\(^{252}\)

**Advanced Oxidation Processes (AOP):** AOPs have potential to degrade organic compound into \( \text{CO}_2 \), \( \text{H}_2\text{O} \) and other inorganic compounds. Amongst AOPs photocatalytic degradation by semiconductor metal oxides /chalcogenides have been reported since last decade. Metal oxides used as semiconductor are \( \text{ZnO} \), \( \text{TiO}_2 \), \( \text{Fe}_2\text{O}_3 \), \( \text{Bi}_2\text{WO}_6 \), \( \text{H}_2\text{WO}_4 \), \( \text{Ag}_2\text{O} \), \( \text{SrTiO}_3 \), \( \text{Zn}_2\text{TiO}_4 \), \( \text{ZnTiO}_3 \), etc. while metal chalcogenides used are \( \text{CdS} \), \( \text{In}_2\text{S}_3 \), \( \text{ZnIn}_2\text{S}_4 \), \( \text{CdIn}_2\text{S}_4 \), \( \text{CdLa}_2\text{S}_4 \) etc. In case of visible light photocatalytic degradation, induction of inorganic impurities like metal oxides, a metal, metal sulphide has been attempted by many researchers to enhance the efficiency of degradation.\(^{266,267}\) The advantage of the AOP method is that, this method doesn’t generate chemical sludge and reduces toxicity of wastewater. Disadvantage is that it needs to add external agent into aqueous medium, in such case efficiency depends on solid-liquid / liquid -gas mass transfer which sometimes limits the degradation process.\(^{268}\)

Besides metal oxides and chalcogenides, polyoxometalates (POMs) have also been employed as visible light photocatalyst since they have similar photochemical properties to \( \text{TiO}_2 \).\(^{269,270}\) The photoexcited POMs have ability to degrade organic compounds completely directly or via \( .\text{OH} \) mediated oxidation.\(^{271}\) But PMOs are very difficult to separate from the homogenous system at the end of the reaction and use of support like \( \text{SiO}_2 \) is essential to increase the performance of the PMOs.\(^{272}\)
1.4.4 Classification of Dyes:

Aromatic compounds which absorb electromagnetic radiation in visible region are coloured. A dye contains chromophores and auxochromes. Dyes can be classified by several ways such as classification based on i) source ii) nature of chromophore iii) according to nuclear structure iv) Industrial classification of dye.  

Classification based on source:

i) Natural dye: These dyes are derived from natural source (animal and plant). In natural dyes colouring part of the molecule is generally negatively charged. Some of the well-known natural dye are Kermes (natural red 3), carmine (natural red 4), lac (natural red 25), hematein (natural black), saffron (natural yellow 6), etc.

ii) Synthetic dye: Dyes derived from organic or inorganic compounds are known as synthetic dyes. Synthetic dyes can be classified as direct, acidic, reactive, mordant, metal complex, vat, sulphur, disperse dye etc. However, textile can be classified into 14 group based on general dye chemistry.

Dyes according to nuclear structure:

In this mode dyes are classified on the basis of charge on colouring part of the molecule, so classified as i) anionic dye and ii) cationic dye

Industrial Classification of dyes

Dyes are classified according to the performance in the dyeing process. Worldwide around 60% dye stuff are from azo group that consumed in the textile finishing process. Major classes of the dyes are: i) Protein dyes ii) cellulose textile dye and iii) synthetic textile dyes.

Commercial dyes are known for their strong structural and color stability imparted by their high degree of aromaticity and extensively conjugated chromophores. Synthetic dyes are present in many spheres of our everyday life and their applications are continuously growing e.g. in various branches of textile industry, of the leather tanning industry, in paper production, in food technology, in agriculture research, in light harvesting arrays, in photo electrochemical cells and in hair colourings.
Chemical classification of dyes: According to system of chemical classification, dyes can be classified on the basis of nature of chromophore. These classes are Acridine dyes, anthraquinone dyes, diaryl methane dyes, triaryl methane dyes, azo dyes, cyanine dyes, diazonium dyes, nitro dyes, nitroso dyes, phthalocyanine dyes, Quinone-imine dyes, Azine dyes, Eurhodin dyes, Safranin dyes, Xanthane dyes, Indophenol dyes, oxazin dyes, Oxazine dyes, thiozole dyes, thiazin dyes, fluorene dyes, and rhodamine dyes.

Azo Dyes

Azo dye is the largest class of dyes used in textile and paper industries. Azo dyes are characterized by presence of one or more azo (-N=N-) bonds. About half the world production of dyes are from the azo group. Azo dyes can be classified as mono, diazo, triazo based on number of azo group in the compounds. These azo dyes are found in various types of dyes like acidic, basic, direct, disperse, azoic and pigments. They are very stable to UV and visible light radiation. After incorporation of Soluble azo dyes into body they split into corresponding aromatic amines by liver enzyme and intestinal flora. This can be the cause for cancer. The releasing of azo dye directly to environment can cause acute and / or chronic effect on the exposed organisms, adsorb or reflect sunlight entering into water which may result change in food chain. Thermally reversible polymerisation around the azo double bond prevail the deactivation path of their electronically excited state. Moreover, they are resistant to aerobic degradation and can be reduced to potentially carcinogenic aromatic amines under anaerobic condition or in vivo. The treatment methods on azo dye can be classified into three groups: 1) Physical methods such as adsorption, flocculation, nano filtration and ion exchange 2) Chemical methods such as oxidative process with fenton’s reagent, H$_2$O$_2$/O$_3$, H$_2$O$_2$/UV radiation, NaCl, O$_3$ photocatalytic degradation etc. 3) Biological methods such as anaerobic and anaerobic degradation. Physical methods are unable to complete decomposition of dye; Chemical methods having high cost are rarely used in actual treatment process. Biodegradation process suffers from low degradation efficiency or no degradation in some cases and requirement of large volume of reactor. The photocatalytic degradation is the promising path for complete degradation of azo dyes. The cleavage of the azo double bond, inducing their bleaching in the visible region was identified as one of the first
degradation steps in photocatalytic degradation. Thus decrease in concentration can be monitored spectrophotometrically. The cleavage of azo bond may lead to formation of intermediate which may found more dangerous than the dye. Hence, complete degradation i.e. mineralisation of organic substance into inorganic substance is very essential for the complete degradation of the dyes.

Yatmaz H. C. et al studied photocatalytic degradation of azo dye in aqueous medium using ZnO as catalyst at 480 nm irradiation. V. Mirkhani et al. studied UV light photocatalytic degradation of azo dyes using TiO2 and Ag@TiO2 with respect to parameters such as amount of catalyst, pH, flow rate of Oxygen and temperature and showed that photocatalytic efficiency has been enhanced due to Ag doping which follows pseudo first order kinetics as per Langmuir-Hinshelwood model (L-H). C. Wang et al. reported that Zn2TiO4, Zn2SnO4 and Zn2Ti0.5Sn0.5O4 synthesized by solid state reaction method are photo inactive and hence showed lower photocatalytic activity for degradation of methyl orange compare to ZnO-TiO2-SnO2 mixture.

G. Thennarasu et al. studied photocatalytic degradation of Orange G using nanocrystalline ZnO under the sunlight and observed that maximum degradation takes place at pH 6.86 following pseudo first order kinetics. The author also reported that complete mineralization takes place along with decolourization which is contradictory to the results reported by Marta Mrowetz et al.

A review of TiO2 assisted photocatalysis of azo dyes in aqueous medium was taken by I. K. Konstantinou et al. with respect to Kinetics and mechanism of photocatalytic degradation. It is observed that mechanism of degradation under UV light and solar light irradiation is not same as well order of the reaction depends upon the intensity of the radiation. Charge injection mechanism takes place under visible light irradiation while charge separation occurred under UV radiation. In experiments that are carried out using sun light or simulated sunlight (laboratory experiment) it is suggested that both photo oxidation and photosensitization mechanism occurred during the irradiation and both photocatalyst and light source are necessary for reaction to occur.

It is difficult to conclude whether photocatalytic oxidation is superior to the photosensitized oxidation. But the photosensitizing mechanism will help to improve the overall efficiency and make the photo bleaching of dyes using solar light more
feasible.\(^{284}\) It is also not possible to find out whether the process takes place on the surface of the catalyst, in the solution or at interface.\(^{285}\)

_**Ollis et al.**\(^ {286}\) reviewed the studies reported for the effect of light intensity on the kinetics of the photocatalytic process and stated that i) at low intensity (0-20 mW/cm\(^2\)) rate would increases linearly with increase in light intensity (first order), ii) at intermediate intensity beyond certain value (\(\sim 25\) mW/cm\(^2\)) the rate would depend upon the square root of the light intensity (1/2 order) and iii) at high light intensity the rate is independent of light intensity. This is likely because at low light intensity reactions involving electron hole formation are predominant and electron-hole recombination is negligible. However at increased light intensity electron hole pair separation competes with recombination thereby causing lower effect on rate of the reaction.

Acid Orange 7 (AO-7) is the most studied dye amongst the azo dyes with respect photocatalytic degradation under various experimental conditions. Hence degradation of AO-7 could be considered as model compound for oxidative degradation studies of azo compounds \(^{235(a)}\). The photocatalytic degradation of model Azo dye (AO-7) in aqueous TiO\(_2\) dispersion has been studied by _M. Stylidi et al._ under visible light (\(\lambda > 400\) nm) irradiation. The Author showed that visible light photons contribute to the decolorization, but having order of the reaction greater than second order.\(^{287}\) _Pengfei Ji et al._\(^{288}\) examined adsorption and photocatalytic degradation of Acid Orange 7 (AO7) by CeO\(_2\) under visible light irradiation and observed strong adsorption of AO7 on surface of CeO\(_2\) as compared to TiO\(_2\) (P25) followed by degradation into smaller molecules. The author concluded that superoxide anion radical (O\(_2^-\)) oxidative species is responsible for photodegradation. Adsorption of water molecules on surface of catalyst and formation of oxidative species like OH\(^-\), OH\(_2^-\) has also been reported. The author also concluded that h\(_{VB}\)^+ is not active species.

The photocatalytic degradation of various dyes like Orange –II, Orange –G, Congo Red, Indigo Carmine, Crystal Violet, Malachite Green, Ramazole Blue and methyl Yellow has been studied by _C. Hachem et al._\(^ {289}\) and compared with P-25. Kinetic study reveals that degradation process follows zero order or first order kinetics with respect to dyes.

_J. Fernández et al._\(^ {290}\) carried out photocatalytic degradation of Acid Orange II in a concentric cylindrical photo reactor with mercury lamp using TiO\(_2\) at various pH
under oxygen flow throughout the experiment and observed maximum rate of degradation at pH \( \sim 6.0 \). N. Daneshvar et al.\textsuperscript{291} studied effect of pH, Concentration of ZnO, presence of UV light, presence of H\(_2\)O\(_2\) and ethanol on degradation of Acid orange 7 (AO7) and found that photocatalytic degradation of AO7 is maximum at pH 7.

**Acid Orange 8**

Acid Orange 8 (Figure 1.5) is azo dye contains one azo group having dark orange color and soluble in water.

![Structure of Acid Orange 8](image)

**Figure 1.5: Structure of Acid Orange 8**

[Molecular formula: C\(_{17}\)H\(_{13}\)N\(_2\)NaO\(_4\)S, Mol. Wt.: 364.36]

Acid Orange 8 (AO8) is toxic and carcinogenic in nature. It is observed that azo compounds can split off cancer causing arylamines. Azo double bond has been considered to be most unstable part of the azo compounds. The azo bond can be easily broken by heat, light and enzymes which results into formation arylamines.

Marta Mrowetz et al.\textsuperscript{281} investigated kinetics of degradation of two azo dyes namely Orange 8 and Acid red 1 and chlorophenol in aqueous medium in presence of TiO\(_2\) by UV photocatalysis and sonolysis as well as combined photocatalysis and sonolysis. Kinetic study indicates that all three modes studied follows pseudo first order kinetics as per Langmuir–Hinselwood model and also reported evolution of H\(_2\)O\(_2\) during degradation. Mechanism of degradation was found to be different for UV photocatalysis and sonolysis. In the case of UV photocatalysis, OH- ions adsorbed on
surface of catalyst undergoes oxidation by holes generated in the semiconductor valence band through photo induced promotion of electrons into the conduction band. At the same time conduction band electron interacts with adsorbed $O_2$, leading to superoxide anions $O_2^-$ and hydroperoxide radicals $OH_2$. All these species formed plays important role in photocatalytic degradation of organic compounds under air saturated conditions.

In sonolysis, $OH^-$ and other radicals are generated from water scission under extreme pressure and temperature conditions created by implosion of cavitation bubbles.

In the case of photocatalytic degradation of azo dyes, another possible reaction is that, electronically excited azo dyes gets adsorbed on surface of the catalyst and electrons can be injected into conduction band of photocatalyst. Radical cations formed are oxidised by oxygen containing species adsorbed on surface of catalyst.

P. Mehata et al. also reported visible light photocatalytic degradation of Acid Orange 8 (AO8) by TiO$_2$ using tungsten source at various pH and concentration of AO8 and amount of catalyst. The author observed maximum efficiency for 100 ml ($3 \times 10^{-5}$ M) AO 8 using 300 mg TiO$_2$ at pH=9. The degradation follows first order kinetics at the rate $7.35 \times 10^{-5}$ s$^{-1}$. The author suggested mechanism in which AO8 as well as H$_2$O and oxygen is adsorbed on surface of catalyst followed by reaction between excited AO8 and reactive species $O_2^-$, $OH^-$ and $OH_2$. The process leads to produce end product CO$_2$ and H$_2$O through intermediates obtained substituted nitrotoluene, 1-nitro-2naphthol, toluene and naphthalene. Effect of nature of catalyst studied under optimum condition shows highest activity of TiO$_2$ amongst ZnO and ZnS. The author has not reported additional time for mineralization of intermediate product formed during degradation as reported by Marta Mrowetz et al. R. Mehata et al. investigated that homogeneous photocatalysis of AO8 using Fenton reagent and heterogeneous photocatalytic degradation using TiO$_2$ under 2 x 200 W tungsten lamps. The results indicate that, degradation depends upon concentration of dye, concentration of TiO$_2$ and fenton reagent, concentration of H$_2$O$_2$ and pH of the solution. The degradation reaction follows pseudo first order kinetics. The result also indicated that photocatalytic degradation using fenton reagent is more effective compared to degradation using TiO$_2$. Chi Ming Ma et al. carried out decomposition of azo dyes namely: Acid orange 8, acid blue 29 and acid blue 113 in aqueous solutions by
Vacuum UV (VUV) based Advanced Oxidation process (AOP). The author observed that VUV based AOPs are more efficient for degradation of azo dyes than VUV based direct photolysis.

**Xanthene Dye**

Xanthene dyes are one of the important class of family of dyes. Amongst xanthenes dye Rhodamine dyes are having uttermost importance because of their photochemical and photophysical properties. Rhodamine dyes are well known for their high fluorescence quantum yield, hence they are used in various applications like single molecule detection, fluorescence labelling, dye laser, conversion and storage of solar energy. They are also used in medical field for various purposes such as, for staining of damaged cells as antitumor agent.

**Rhodamine B (Mol. Formula: C_{28}H_{31}ClN_{2}O_{3}, Mol. Wt.: 479.02)**

Rhodamine B (Rh-B) is a xanthene dye widely used as colorant in textile and food stuff. It is also used as tracer dye in water to determine the rate and direction of flow and transport. Biotechnological application of Rhodamine dyes such as fluorescence microscopy, flow cytometry, Fluorescence correlation spectroscopy are well known. Rh-B is harmful if swallowed by human being and animals and causes irritation to skin, eyes and respiratory track. The carcinogenicity, reproductive and developmental toxicity, neurotoxicity and chronic toxicity towards human and animals have been experimentally proven.

![Structure of Rhodamine –B](image)

[9-(2-carboxyphenyl)-6-diethylamino-3-xanthenylidene]-diethylammonium chloride]

**Figure 1.6: Structure of Rhodamine –B**
Ming Ge et al. \(^{252}\) performed photocatalytic degradation of Rh-B under sunlight using peanut shaped BiVO\(_4\) in presence of H\(_2\)O\(_2\) and reported that peanut shaped BiVO\(_4\) /H\(_2\)O\(_2\) system. Almost complete degradation of RH-B was observed in 60 min under sunlight irradiation. Shuijin Yang et al. \(^{307}\) carried out photocatalytic degradation of RH-B at various pH with H\(_3\)PW\(_{12}\)O\(_{40}\)/SiO\(_2\) sensitized by H\(_2\)O\(_2\) under simulated sunlight and observed that degradation reaction follows first order kinetics as well as rate increases with concentration of catalyst and decreases with initial concentration of Rh-B. Swee-Yong Pung et al. \(^{308}\) studied effect of different morphologies of ZnO on photocatalytic degradation of Rh-B in aqueous medium under UV light, where rod like ZnO found to be most effective. The degradation process follows first order kinetics. LI Jing-yi et. al. \(^{309}\) investigated photocatalytic degradation of Rh-B using TiO\(_2\) nano strips and P25 under visible light irradiation. The research demonstrated that the intermediates ethanediotic acid, 1,2-benzenedicarboxylic acid, 4-hydroxy benzoic acid, and benzoic acid were almost same in presence of TiO\(_2\) and P25 systems but benzoic acid is not formed in case of P25 catalyst system. It was also demonstrated that intermediate products formed under UV and visible light may be same, but there is further decomposition of intermediate into CO\(_2\), H\(_2\)O under visible light irradiation.

The photocatalytic degradation performed by Dongfang Zhang \(^{310}\) reveals that the efficiency of photocatalytic bleaching of Rh-B aqueous solution using Au/TiO\(_2\) is more efficient than that of bare TiO\(_2\) sample upon UV-vis light activation. Degradation kinetics of Rh-B dye in aqueous suspension can be well simulated by the Langmuir-Hinshwood model and obeys pseudo first order law with rate constant 0.0252 min\(^{-1}\). B. Pan et al. \(^{261}\) employed polymer based CdS nano composite for visible light photocatalytic degradation of Rh-B and observed that regardless of visible light photodegradation, host functional group on polymer, accelerate the degradation rate. The author also reported degradation of Rh-B even in dark which may be due to physicochemical adsorption because of non porous structure and polystyrene nature of the host materials. The polystyrene nature facilitates the absorption process of dyes of aromatic structure through specific π-π interaction and micro filling. \(^{311}\)

**Dye Degradation**

Conventional waste water treatment technologies are ineffective for removing dyes because many dye compounds are highly resistant to biological, physical and chemical
treatments. Physical process includes coagulation, electro-coagulation and adsorption of dyes on charcoal.

Therefore considerable effort had been made to develop advanced methods for remediating dye contaminated waters. Among the treatments employed photocatalytic degradation methods are widely applied due to their potential capability of complete degradation of organic dye molecule to mineralized end product such as CO₂, NH₃. The capacity originates from OH• (Oxidation potential 2.8V) generated during photocatalytic process which render many complex organic compounds susceptible to decomposition.

Many researchers proposed that the mechanism of photocatalytic degradation under visible light and UV light irradiation is not same. The process of photosensitization involves initial excitation of dye molecule rather than catalyst molecule (TiO₂). Charge is then injected from singlet or triplet excited state of the dye into the conduction band of the semiconductor particles whereas dye is converted to its cationic radicals. The injected electron can reduce the surface chemisorbed oxidants usually O₂, to yield oxidizing species O₂•-, HO₂• and OH• radicals which can cause photodegradation.

1.4.5 H₂S splitting

H₂S gas is colorless gas with characteristic foul odour of rotten eggs. It occurs in petroleum gas, crude oil refineries and volcanic eruption. H₂S gas also results from bacterial breakdown of organic matter in absence of oxygen such as in swamps and swears by the process anaerobic digestion. It is heavier than air, very poisonous, corrosive, flammable and explosive. Trace amount of H₂S has poisonous effect on nobel metal catalyst used in industrial process such as hydrogenation, synthesis of ammonia by Heber’s process, and fuel cells. Various techniques are being employed for H₂S decomposition like thermal, thermochemical, electrochemical, plasmochemical and photochemical process. Removal of H₂S in industries on large scale has been done by absorption or stripping of H₂S in aqueous solution of ethanolamine followed by Claus process to decompose H₂S into H₂O and S.

\[ \text{H}_2\text{S} + \frac{1}{2} \text{O}_2 \rightarrow \text{H}_2\text{O} + \text{S} \]

This process is not economically feasible due to high cost of chemical process and further creates environmental crises too. Thermal decomposition of H₂S at high
temperature is well known but equilibrium conversion is very low even at high temperature due to high free energy ($\Delta G = 33$ kJ/mol).

Green Power Corporation in association with Indian Institution of Science developed gas cleaning process based on the redox reaction of chelated polyvalent metal ion. In this process aqueous solution of Fe$^{2+}$ and Fe$^{3+}$ is used for scrubbing H$_2$S from biogas.

The photocatalytic splitting of H$_2$S to generate H$_2$ is environmental friendly approach which has been employed by many researchers in UV region and attempts are accelerated to develop visible light photocatalyst for utilization of naturally available solar energy.

Research group led by B B Kale is extensively working on development of visible light active photocatalyst and wide applicable technique for industries. Kale et al$^{323}$ reported synthesis of nanostructured CdLaS$_4$ and its use as solar light driven photocatalyst for H$_2$ generation via H$_2$S splitting. Chaudhari et. al$^{324}$ and Bhirud et. al$^{325}$ have developed nanostructured visible light active photocatalyst ZnIn$_2$S$_4$ and CdIn$_2$S$_4$ and reported that photocatalytic efficiency is higher than single component sulphides like CdS, In$_2$S$_3$. It is well known that photo corrosion of CdS restricts its use as a photocatalyst. Apte et al$^{326}$ developed glass embedded CdS photocatalyst to overcome the photo corrosion problem and reported improved efficiency as well. Mahapure et al.$^{327}$ attempted visible light induced H$_2$S splitting using ZnIn$_2$V$_2$O$_9$ and observed to be highest efficiency amongst the metal oxides reported earlier.

Sincere efforts are undertaken by many researchers worldwide to develop the photocatalyst and compatible technique. Naman S A. et al attempted gas solid phase photocatalytic production of H$_2$ via H$_2$S splitting. MA Guijun et al. also reported gas-solid phase photocatalysis using TiO$_2$ (P25), ZnS, Cu-ZnS and ZnIn$_2$S$_4$.$^{328}$ The photocatalytic activity of CdS can be enhanced by adding ZnS the wide gap semiconductor. Promoters like Ag$_2$S can also enhance the activity of the catalyst.$^{329}$ The synthetic dyes are also used as photosensitizers to sensitize the wide gap semiconductor.$^{330}$ R. Priya and S Kanmani reported effect of photosensitizers such as Rhodamine B, Eosin Y, Methylene Blue ,Methyl Violet on H$_2$ generation from H$_2$S splitting using photocatalyst [(CdS/ZnS)/Ag$_2$S,+RuO$_2$/TiO$_2$].$^{331}$
1.5 Thesis Objectives and Motivations

Research is going on worldwide related to synthesis of nanoparticles, characterization and their potential application in various fields. Researchers are working hard and trying to tackle the issues like energy, fuels, environmental pollution etc. Nanoscience and technology have capacity to solve these issues. Waste water is one of the biggest threat to environment. Visible light photocatalytic treatment to waste water may be effective and efficient technique. Efficiency of the process depends upon the activity of the photocatalyst in visible region, stability, wide range applicability for degradation of waste and treatment plant. Fulfilment of ever increasing demand of energy is challenging task since natural resources are decaying day by day. Hydrogen generation via H\textsubscript{2}S splitting could be amicable solution for fuel generation since; H\textsubscript{2}S is amply available from various sources. H\textsubscript{2}S is harmful to human health as well as environment and one of the pollutants in waste water as well as in air. H\textsubscript{2}S splitting will reduce environmental pollution as well as it will generate H\textsubscript{2} a clean fuel.

Considering all these issues, work is focused on development of visible light versatile photocatalyst and effective technique for the degradation and H\textsubscript{2} generation via H\textsubscript{2}S splitting.

The work presented in the thesis address the synthesis characterization of solar light driven nanostructured undoped and doped zinc orthotitanates (Zn\textsubscript{2}TiO\textsubscript{4}) and their application as visible light photocatalyst for dye degradation (Acid orange -8 and Rhodamine –B) under sun light and H\textsubscript{2} generation via H\textsubscript{2}S splitting under visible light source. The work has been divided into six chapters. First chapter covers introduction and literature survey, Second, third and fourth chapter includes synthesis of zinc orthotitanates and their characterization. Fifth chapter includes application of synthesized zinc orthotitanates as visible light photocatalyst for waste degradation (Dye degradation and H\textsubscript{2}S splitting). Sixth chapter consists of summary of the work done, scope and future planning. Brief chapter-wise outline is given below.

**Chapter 1: Introduction**

This chapter includes literature survey on i) nanostructured metal oxides with respect to synthesis, properties and their application in various fields. Emphasis is given on binary metal oxides of zinc and titanium ii) Photocatalytic dye degradation iii) Photocatalytic H\textsubscript{2}S splitting to generate Hydrogen.
Many researchers employed Zn_2TiO_4 for removal of H_2S at high temperature from coal mines. Zn_2TiO_4 is not reducible due to H_2S unlike ZnO. So we thought that Zn_2TiO_4 can be the good candidate compared to ZnO and TiO_2 for H_2S splitting for the generation of H_2. Band gap of Zn_2TiO_4 (3.1 eV) lies at boundary of UV and visible region which can be easily tuned to visible region by metal doping. We have attempted doping Ag, and Co metal in lieu of Zn sites in Zn_2TiO_4, considering the ionic size of dopant metal ion and Zn^{2+} ion.

Chapter 2: Synthesis of zinc orthotitanates by combustion method

Literature survey indicates that synthesis Zn_2TiO_4 is attempted by methods like solid state synthesis, Polymeric precursor method, Chemical bath deposition method, Co precipitation method etc. Combustion method has been used for synthesis of metal oxides but no reports found for Zn_2TiO_4.

In this chapter zinc orthotitanates were synthesized by combustion method using multiple fuel system. The synthesized compounds were characterized by techniques such as XRD, FTIR, EDXRF, FESEM, TEM, BET surface area, UV-vis DRS and PL spectroscopy.

Chapter 3: Synthesis of zinc orthotitanates by solvothermal method

This chapter includes synthesis of zinc orthotitanates by glycothermal method (Solvent –Ethylene glycol) followed by thermal decomposition of intermediate. It also includes optimization of solvothermal methods. The optimization process includes use of solvents like H_2O, methanol and ethylene glycol as well as optimum temperature and period for solvothermal process and thermal decomposition of the intermediate to get the desired product. The synthesized compounds were characterized by techniques such as XRD, FTIR, EDXRF, FESEM, TEM, BET surface area, UV-vis DRS and PL spectroscopy. The intermediate obtained was characterized by Thermal analysis.

Chapter 4: Synthesis of zinc orthotitanates by template base combustion method

Novel approach has been employed for the synthesis of Zn_2TiO_4. In this approach Whatman filter paper has been used as template for synthesis of nanomaterial. Whatman filter paper is made up of cellulose which gets completely burned at 450 °C i.e. papers are ash less as per literature. Solution of precursors is used for this purpose.
The synthesis method has been optimized with respect to solvent and temperature of the combustion process.

The as synthesized zinc orthotitanates were characterized by XRD, FTIR, FESEM, TEM, BET surface area, UV-vis DRS and PL spectroscopy.

**Chapter 5: Application of zinc orthotitanates as photocatalyst**

The as synthesized photocatalyst were employed for the degradation of organic waste like dyes and H$_2$S splitting to generate Hydrogen the clean fuel. Degradation of dyes which comes out as industrial effluent is the concern issue. Photocatalytic degradation of waste will be the comprehensive solution in the future. As a part of the development of Photocatalytic degradation of waste, we have selected Acid Orange-8 and Rhodamine B industrial dyes. Undoped Zn$_2$TiO$_4$ and metal doped Zn$_2$TiO$_4$ have been employed as solar light driven photocatalyst. Photocatalytic dye degradation has been performed under sun light and H$_2$S splitting under visible light source. Kinetic studies of the photocatalytic degradation of dyes have been performed.

The chapter also includes development of equipments like reactor for dye degradation under sun light, microscale H$_2$S gas generator, Gas measuring cylinder.

**Chapter 6: Summary**

This Chapter includes comprehensive summary of the work included in the thesis. It also includes scope of the work and future plan.
References

37 Mahmoud Goodarz Naseri and Elias B. Saion, *Advances in crystallization process*, www.intechopen.com


52 Mimani T.. *Resonance* 2000;5:50–7,


65 Yi Yang, Xiao Wei Sun, Beng Kang Tay, Jian Xiong Wang, Zhi Li Dong, and Hai Ming Fan, Adv. Mater. 2007, 19, 1839–1844
99 Luth, H.; Surface and interface of solid materials; Springer, Berlin, 1997
110 Elbio Dagotto, Takashi Hotta, Adriana Moreo, Physics Reports 344 (2001) 1-153
111 Clive D. Chandler, Christophe Roger, and Mark J. Hampden-Smith, Chem. Rev. 1993, 93, 1205-1241
114 http://download.ebooks6.com/Chapter-3-Perovskite-Perfect-Lattice-download-w18481.pdf
115 Vladan Stevanovic, Mayeul d’Avezac, and Alex Zunger, J. Am. Chem. Soc. 2011, 133, 11649–11654
123 Atsuto Seko, Fumiyasu Oba and Isao Tanaka, *PHYSICAL REVIEW B* 81, 054114 (2010)
133 Fan, H. J.; Yang, Y.; Zacharias, M. *J. Mater. Chem.* 2009, 19, 885
149 H. Birnbauamnd, R. K. Scot, *Notes*, 72, 1398 (1950)
157 Liyuan Wan, Xinyong Li, Zhenping Qu, Yong Shi, Hong Li, Qidong Zhao, Guohua Chen, *Journal of Hazardous Materials* 184 (2010) 864–868
159 Dongfei Sun, Xingbin Yan, Jiangtao Chen, Shengxue Yu, Litian Hu and Qunji Xue, *Cryst Eng Comm*, 2011, 13, 3905–3909


172 ObraDovic N, Pavlovic V. *Ceram Inter* 2009;35:35–7


207 Timothy H. Gfroerer, John Wiley & Sons Ltd, Chichester, 2000, 9209-9231.


252 Ming Ge, Lu Liu,Wei Chen and Zhen Zhou, *CrystEngComm*, 2012, 14, 1038
253 J. Fenoll, P. Hell’m, C. M. Martínez et al., *Applied Catalysis B*, vol. 115-116, pp. 31–37, 2012.


277 ZHAO ZongShan, LIU JingFu, TAI Chao, ZHOU QunFang, HU JingTian2 & JIANG GuiBin, Sci China Ser B-Chem. 2008 , 51 ( 2) , 186-192
288 Pengfei Ji, Jinlong Zhang, Feng Chen, Masakazu Anpo, Applied Catalysis B: Environmental, 85, 2009, 148–154
296 Rachita Mehta and Menka Surana, Der Pharma Chemica, 4 (1), 2012, 311-319


316 P.V. Kamat, *Chem. Rev.* 93, **1993**, 267


328 MA Guijun, YAN Hongjian, ZONG Xu, MA Baojun, JIANG Hongfu, WEN Fuyu, LI Can, Chinese Journal of Catalysis, 29(4), 2008, 313–315