CHAPTER 1

Introduction

1.1 Introduction

With the unique properties with low resistivity and high transmittance in the visible solar region, transparent conductive oxides (TCOs) have been extensively used in optoelectronic devices such as energy efficiency windows, smart windows and electrodes for solar cells as well as flat-panel displays, etc [1-3]. In comparison with other host oxides of TCOs, Zinc oxide has attracted intensive attention because of its non-toxicity, low cost, and easy for fabrication, excluding common electro-optical properties [1-3]. Zinc oxide as a semiconductor has been used widely for its optical, electrical, optoelectronic, catalytic and photochemical properties, including optical waveguides, transparent conducting coatings and catalysis. It has a wide band gap of 3.37 eV, large exciton binding energy of 60 meV at room temperature and excellent chemical and thermal stability. In addition, it is considered to be an attractive phosphor for low voltage emissive displays [4-8]. Doping of a relevant element in zinc oxide nanostructures can tailor its intrinsic physical and chemical properties, such as luminescence, electronic and magnetic properties. Doped zinc oxide nanocrystals are expected to exhibit an efficient visible emission and be appropriate for vacuum fluorescent and field emission displays [4, 5, 8].

Trivalent lanthanide ions (Ln^{3+}) doped nanomaterials are technologically important for the potential applications in optoelectronic devices due to their unique luminescent properties. However, the parity-forbidden nature of f-f transitions of Ln^{3+} ions, and the direct excitation for most Ln^{3+} ions are usually inefficient and somewhat restrains them from applications in the mentioned practical fields. To overcome this short coming, the host sensitization, namely, the energy transfer (ET) from the excited host to Ln^{3+} ions is desirable in terms of the strong absorptions in the ultraviolet (UV) region especially for most semiconductors [9].

The degradation of the pollutants catalyzed by zinc oxide has been studied widely. When a zinc oxide surface is irradiated with a photon of energy equal to or greater than its band gap, an electron is promoted from its valence band to the conduction band leaving behind an electronic vacancy or hole in the valence band. The hole may react with surface-bound H_2O or OH^- to produce the hydroxyl radical ($OH^\bullet$) and electron is picked up by oxygen to generate a superoxide radical anions ($O_2^{\bullet-}$). Both hydroxyl radical and superoxide radical ions are excellent oxidizing agents to oxidize the organic pollutants to produce H_2O and CO_2 [10]. In order to improve the photocatalytic property of zinc oxide, an effective and practical approach is to dope some lanthanide metal elements such as Ce [11], La [12] and Nd [13] into zinc oxide photocatalyst to develop various kinds of intrinsic defects such as oxygen vacancies, zinc vacancies, zinc interstitials, and antisite defects of zinc oxide structure [14].

Various methods have been developed for the synthesis of zinc oxide and lanthanide-doped zinc oxide nanostructures, such as sonochemical [11, 15, 16], sol-gel [9, 17], hydrothermal [18], microwave irradiation [6] and pulsed laser deposition [3, 5] methods.

Sonochemical method has been known to form novel materials. Ultrasonic irradiation generates small bubbles in liquid medium with repeated formation, growth, and collapse of these bubbles in liquid medium, known as acoustic cavitation. An implosive collapse of cavitation bubbles by adiabatic compression results in very high temperature and high pressure [15].

In the present research, zinc oxide and lanthanide-doped zinc oxide nanostructure will be synthesized using sonochemical method. The phase, morphology, vibration mode and optical property of the synthesized products will be studied by X-ray diffraction (XRD), field emission scanning electron microscopy (FESEM), transmission electron microscopy (TEM), energy dispersive X-ray spectroscopy (EDX), Fourier transform infrared (FTIR) spectroscopy, UV-visible (UV-vis) spectroscopy and photoluminescence (PL) spectroscopy. In the end, photocatalytic properties of zinc oxide and lanthanide-doped zinc oxide will be investigated by studying of the degradation of methylene blue (MB) under UV light.

1.2 Properties of zinc oxide and its applications

1.2.1 Crystal structures

Zinc oxide has three crystal structures - hexagonal wurtzite, cubic zinc-blende structure and a rarely-observed cubic rock-salt (NaCl-type). Under ambient conditions, the most thermodynamically stable structure is the wurtzite form. The zinc-blende structure is metastable and can be stabilized only by epitaxial growth on cubic substrates. In both cases, each zinc ion has four oxygen neighbour ions in a tetrahedral configuration and vice versa. The cubic rock-salt structure is usually only stable under extreme pressure (~2 GPa) [19, 20].

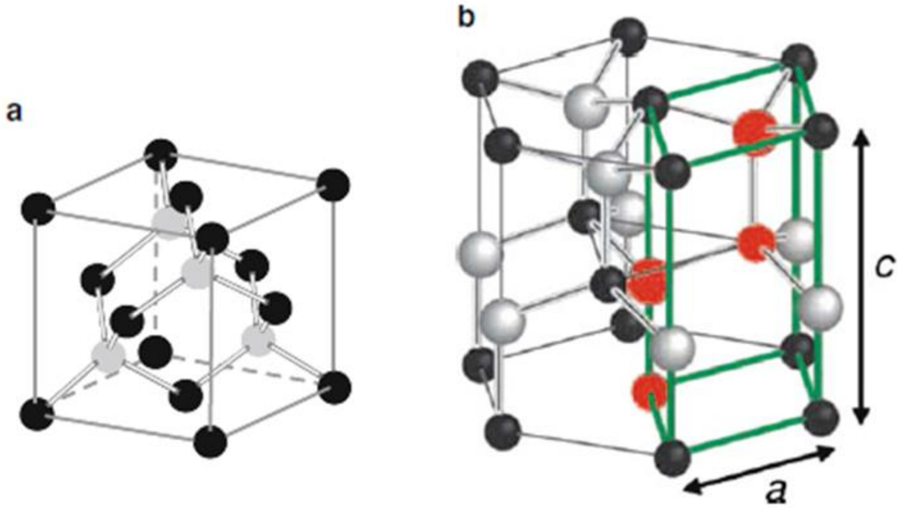


Figure 1.1 The cubic zinc-blende-type lattice (a), and hexagonal wurtzite-type lattice (b). In the wurtzite lattice, the atoms of the molecular base unit (2×ZnO) are marked by red full circles and the primitive unit cell by green lines [20].

1.2.2 Toxicology

Zinc oxide is generally categorized as a non-toxic material. Zinc oxide does not cause skin and eye irritation and there is no evidence of carcinogenicity, genotoxicity and reproduction toxicity in humans. However, the powder can be hazardous by inhalation or ingestion because it causes a condition known as zinc fever or zinc ague. The symptoms of this syndrome are chills, fever, cough, and tightness in the chest. Therefore appropriate safety precautions should be observed when preparing, packaging, transporting and handling zinc oxide [19].

1.2.3 Optical properties

Much of the recent surge in research interest in ZnO has been motivated by possible optoelectronic applications. This is because there appears to be a possibility of replacing the GaN-based compounds currently being used in optoelectronic devices operating in the blue or UV range (for example, LEDs, laser diodes and photodetectors) with a cheaper and non-toxic alternative such as ZnO. Selection of ZnO is due to the similarity of its band gap energy (3.37 eV at room temperature) with that of GaN (3.39 eV at room temperature) and, importantly, the larger exciton binding energy of ZnO (60 meV) compared to that of GaN (18–28 meV). This would be useful in light emitting devices. Band-gap engineering of ZnO is also possible. For example, alloying with CdO decreases the band gap while alloying with MgO increases the band gap. The compound $Mg/Cd_{1-x}Zn_xO$ has a band gap that is potentially tunable between 2.3 and 4.0 eV. Emission properties of ZnO nanoparticles are influenced by many factors such as synthesis method, morphology of the nanoparticles, dopants and ligands used for surface coating. Zinc-based phosphors have been known for decades, although the precise mechanism of their operation is still said to be controversial [19, 20].

1.2.4 Applications

The uses of zinc oxide have changed markedly over time. Some major uses, such as in photocopy paper as a photoconductive ingredient and in linoleum have almost disappeared. Furthermore zinc oxide is not the principal white pigment in paint anymore. Today its major uses are in the rubber industry, followed by ceramics, but it has many niche applications such as, for example, in drilling fluids for the oil and gas industry. Most recently, zinc oxide is being investigated for applications such as LEDs, transparent transistors, solar cells and memory devices and as the basis of a transparent conducting oxide for consumer devices [19, 20].

1.) Rubber

The major application of zinc oxide is currently in the rubber industry where it is used as a vulcanizing activator (a substance applied in small doses to increase the effectiveness of the vulcanization accelerator). Early un-accelerated vulcanization processes used $\sim$8 parts per hundred rubber (phr) of activator and required temperatures above the sulfur melting point for several hours. Organic accelerators allowed the amount of sulfur and vulcanization times to be significantly reduced but a significant breakthrough in the vulcanization process involved activators such as zinc oxide [19].

Zinc oxide is also used as a curing or cross-linking agent for halogen-containing elastomers such as neoprene or polysulfides. Metallic oxides not only change the rate of cure but also the ‘scorch’ (i.e. premature vulcanization caused by heat during rubber processing) in neoprene. In cable insulators such as ethylene propylene diene monomer (EPDM) rubber, the incorporation of ZnO imparts low water absorption and longer lifetime. It is also used in pressure sensitive adhesives (e.g. in epoxidized natural rubber) [19].

2.) Ceramics and concrete

The second largest application of zinc oxide is in ceramics in particular the tile industry. The relatively high heat capacity, thermal conductivity and high temperature stability of zinc oxide coupled with a comparatively low coefficient of expansion are desirable properties in the production of ceramics. In glazes, enamels or ceramic formulations, zinc oxide affects the melting point and optical properties of the glaze. Zinc oxide as a low expansion, secondary flux improves the elasticity of glazes by reducing the change in viscosity as a function of temperature and helps prevent crazing and shivering. By substituting ZnO for BaO and PbO, the heat capacity is decreased and the thermal conductivity is increased. Zinc in small amounts improves the development of glossy and brilliant surfaces. However in moderate to high amounts, it produces matte and crystalline surfaces. With regard to color, zinc has a complicated influence. It can improve or damage blues, browns, greens, pinks and is not recommended with pigments or glazes containing copper, iron, or chromium [19].

Zinc oxide acts as a metallic oxide flux in the preparation of frits and enamels for ceramic wall and floor tiles or for sanitary and tableware ceramic applications. Its fluxing action starts at around 1000 ºC (e.g. in Bristol glazes). Zinc oxide may be reduced to metallic zinc under reducing conditions in the gas-fired kiln followed by volatilization some time later. These properties are useful for low fire glazes and as a result zinc oxide is quite common in fast fire applications [19].

3.) Plastics and linoleum

Zinc oxide may provide useful benefits when added to a plastic polymer. Once again this is commonly in the form of the French or American process material. Properties such as improved heat resistance, mechanical strength and water and fire resistance are imparted to acrylic polymers, polyvinylidene fluoride (PVDF), epoxy resins and nylon-6-6. Zinc oxide may be used as a stabilizer in polyolefin resins such as high density polyethylene (HDPE), polypropylene (PP) and unsaturated polyesters, polychlorofluoro-ethylene and poly-vinyl-halides such as PVC. In these matrices it provides UV absorption properties, thermal stability and increased tensile strength. Zinc oxide-stabilized PP and HDPE are used in safety helmets, stadium seating, insulation, pallets, bags, fibers and filaments, agricultural and recreational equipment. Zinc oxide also improves the dye-ability of polyester fibers and the antistatic, fungistatic and emulsion stability of vinyl polymers [19].

In the production of linoleum, zinc oxide acts as a coloring agent which is mixed with all components such as linoleum cement, organic and inorganic fillers in a mixing unit. A typical linoleum composition may contain approximately 40% binder, 30% organic fillers, 20% inorganic mineral fillers and 10% coloring agents, including up to 5% zinc oxide [19].

4.) Pigments and coatings

Although now largely superseded by TiO_2, ZnO remains an important white inorganic pigment in niche applications. Pigments made of ZnO are known as ‘zinc white’ or ‘Chinese white’ or ‘flowers of zinc’, with the term ‘zinc white’ now reserved for ZnO pigment produced by the French process. The pigment may be purchased in the dry form or as a paste in oil. An important property of white pigment is its low light absorbance together with high dispersion of radiation in the visible region (wavelengths of 400–800 nm). However, the scattering power depends on the particle size and also the wavelength of the incident beam. Therefore by controlling the particle size, it is possible to engineer the desired scattering power to some extent [19, 20].

Replacement of linseed-oil based exterior paints with latexbased ones during 1980s caused a significant decline in the demand for ZnO in the paint industry. However this trend was partially reversed during 1990s due to a ban in some countries on mercurycontaining latexes (mercury has been used as a fungicide and for mold control in the latex) and introduction of ZnO into the latex due to its fungistatic properties. Direct process ZnO is preferred in these applications due to its lower reactivity with resin systems [19].

5.) Cosmetics, medical and dental

A wide range of cosmetic products e.g. moisturizers, lip products, foundations, mineral make-up bases, face powders, ointments, lotions and hand creams make use of zinc oxide. One reason is that zinc oxide helps cosmetics adhere to the skin but a more important motivation is that zinc oxide is a broad-spectrum UV absorber which effectively attenuates UV radiation in both the UVA (320–400 nm) and UVB range (290–320 nm). It is photo-stable and has one of the broadest UV attenuation spectra amongst the sunblocks approved by regulatory authorities such as the USA's FDA. Performance of zinc oxide particles for UV attenuation depends on particle size with an optimal size of 20–30 nm. However it is generally used in particle size range of 30–200 nm. To facilitate its dispersion in the compositions, particles are generally surface-treated with inert coating materials, such as silicon oils, SiO_2 or Al_2O_3 [19, 20].

Clinically, ZnO promotes wound healing and keeps wounds moist and clean. High surface area ZnO (active grade) can be used in lotions or creams for the treatment of acne or of fungal infections such as athlete's foot (*Tinea pedis*). Active ZnO inhibits the growth of bacteria such as *Propionibacterium acnes* which results in less of the sebum (an oily substance secreted by the sebaceous glands in mammalian skin) being split into the free fatty acids which in turn act to inflame the follicle wall. ZnO may also be used in anti-dandruff shampoos and in the treatment of nappy rash [19].

As an ingredient in dry deodorants to reduce wetness under the arm, ZnO can be used between 0.05 and 10% by weight with average particle size in the range of 0.02–200 microns. ZnO may be used to provide a pH range desirable for deodorants designed for use on sensitive skins [19].

Zinc salts such as chloride and sulfate are useful in dental materials such as dentifrice pastes, filling material, cements and impression materials, but may cause an unpleasant lingering taste. ZnO may alleviate this problem in toothpaste, for example. In dentifrice compositions, 0.1–10% ZnO is generally added as an antiplaque, anti-gingivitis, anti-bacterial or tartar agent. Anti-plaque properties of compositions containing ZnO are improved by formation of zinc ions which slows tartar formation. Typical compositions of toothpaste, tooth gel and tooth powder containing ZnO are disclosed in the patent literature, see for example. It is recognized in the field that the useful effect of the Zn is from soluble Zn^{2+} ions rather than from ZnO itself which, as mentioned previously, is comparatively inert [19].

1.2.5 Potential and emerging applications

There are several emerging applications of zinc oxide in the area of electronics and optoelectronics, driven by specific optical or electrical characteristics of this semiconductor [19, 20].

1.) Liquid crystal displays

Transparent conductive oxides (TCOs) are currently used in a large variety of consumer goods, including liquid crystal displays. In general, they are based on indium tin oxide (ITO). However, there are concerns that indium resources will be insufficient to service future growth and there is an active quest for alternative or cheaper materials. Zinc oxide films that have been doped with n-type dopants such as Al, Ga and In are promising candidates to fill this requirement. These materials may be deposited by magnetron sputtering, and are of special interest due to their high conductivity and optical transparency, high thermal stability and relatively lower cost [19, 20].

2.) Light emitting diodes (LEDs)

A large exciton binding energy is an important factor in the design of LEDs. Zinc oxide, with the relatively high exciton binding energy of 60 meV, shows promise in blue/UV light emitters. Zinc oxide is currently being explored for applications such as in UV lasers, in blue light emitting diodes, and in organic LEDs [19, 20].

3.) Spintronics

Dilute magnetic semiconductors are potentially important materials for spintronics with proposed applications in, for example, integrated memory devices and microprocessors. Doped materials such as ZnO:Mn are of interest because of their ability to exhibit ferromagnetism above room temperature. This field is still in its earliest phases, however, and no significant commercial application of semiconductor spintronics has emerged yet [19, 20].

4.) Solar cells

Zinc oxide has a role in two disparate aspects of photovoltaic technology. First, use of transparent, conductive zinc oxide in the front electrodes of solar cells can eliminate the shadow effect related to metal-finger contacts and is also cheaper than the alternative indium oxide electrodes. Secondly, n-type zinc oxide films may also be used within the photovoltaic structure itself, for example as a tunnel junction in amorphous silicon cells or as part of the p/n junction in $Cu(In,Ga)(S,Se)_2$ cells [19].

5.) Sensors and actuators

The sensitivity of the electrical resistivity of zinc oxide to gases such as ethanol, acetylene, CO, NO and NO_2 makes it potentially useful for sensing applications. A drawback, however, is its poor selectivity. Zinc oxide nanowires may be useful in room temperature sensing applications and, for example, a glucose sensor based on zinc oxide nanorods has been reported. The piezoelectric property of ZnO makes it suitable for applications in acoustic microscopy, bulk acoustic wave (BAW), acousto-optic and surface acoustic wave (SAW) devices for use in telecommunications industries (e.g., in mobile phones and base stations), piezoelectric sensors, or torque or pressure sensors. A SAW ZnO sensor has been studied for its potential application in wine differentiation [19].

6.) Zinc oxide in textiles

The application of zinc oxide (produced by the wet chemical process) to fabrics such as cotton and polyester may impart beneficial antimicrobial characteristics, enhanced whiteness, resistance to UV radiation and anti-static properties. However, large-scale application of zinc oxide in the textile industry has not yet occurred to our knowledge. In any case, in our opinion the commercial penetration of such a product into the Organisation for Economic Co-operation and Development (OECD) markets will very likely run into consumer concerns regarding the safety of nano-particles. While a clear medical case can be readily made for use of zinc oxide or other nanoparticles in a product such as sunscreen, their use in consumer clothing might be harder to sell [19].

1.3 Photocatalytic activities and mechanism

According to the mechanism of semiconductor photocatalysis, when a photon of energy equal to or greater than its band gap width irradiates ZnO nanoparticle, it leads to the formation of electron/hole (e^-/h^+) pairs with free electrons produced in the empty conduction band (e^-_{CB}) leaving behind an electron vacancy or "hole" in the valence band (h^+_{VB}). Once the charge separation is maintained the electron and hole may migrate to the surface of photocatalyst where they participate in redox reactions with organic substrate dissolved in water in the presence of oxygen. Specially, h^+_{VB} may react with surface-bound H_2O or OH^- to produce the hydroxyl radical and e^-_{CB} is picked up by oxygen to generate superoxide radical anion as indicated in Eqs. (1.1)–(1.3) mentioned below:

$$\mathrm{ZnO} + h\nu \rightarrow e^-_{CB} + h^+_{VB} \tag{1.1}$$

$$O_2 + e^-_{CB} \rightarrow O_2^{\bullet -} \tag{1.2}$$

$$H_2O + h^+_{VB} \rightarrow OH^{\bullet} + H^+ \tag{1.3}$$

Alternatively, direct absorption of light by the dye, can lead to the transfer of photogenerated electron from the excited state of the dye to the conduction band of the semiconductor which results in the generation of hydroxyl radicals and superoxide radical anions. The various steps involved in dye degradation are summarized in the following equations:

$$\mathrm{Dye}_{ads} + h\nu \rightarrow \mathrm{Dye}_{ads}* \tag{1.4}$$

$$\mathrm{Dye}_{ads}* + \mathrm{ZnO} \rightarrow \mathrm{Dye}_{ads}^{+} + \mathrm{ZnO}\,(e^-) \tag{1.5}$$

$$\mathrm{ZnO}\,(e^-) + O_2 \rightarrow O_2^{\bullet -} + \mathrm{ZnO} \tag{1.6}$$

$$O_2^{\bullet -} + 2H_2O + e^- \rightarrow 2H_2O_2 \tag{1.7}$$

$$H_2O_2 + e^- \rightarrow OH^{\bullet} + OH^- \tag{1.8}$$

It has been suggested that the generated hydroxyl radicals ($OH^{\bullet}$) and superoxide radical anions ($O_2^{\bullet-}$) are the active oxidizers and drive the photodegradation or mineralization of the dye molecule.

Dye or Pollutant + $O_2^{\bullet-}$/$OH^{\bullet}$ → intermediates
↓
degraded or mineralized products.

Generally, the proper amount of oxygen vacancies can entrap electrons from semiconductor, resulting in the holes to diffuse to the surface of the semiconductor and causes oxidation of the organic substrate. In addition, the hydroxyl group acidity increases with decrease in electron density within the semiconductors and thus enhances the photocatalytic activity of ZnO. Due to this role, increase in the number of oxygen vacancies improves the photocatalytic performance of photocatalysts [21, 22].

The whole mechanism of photocatalytic degradation has been depicted in Figure 1.2.

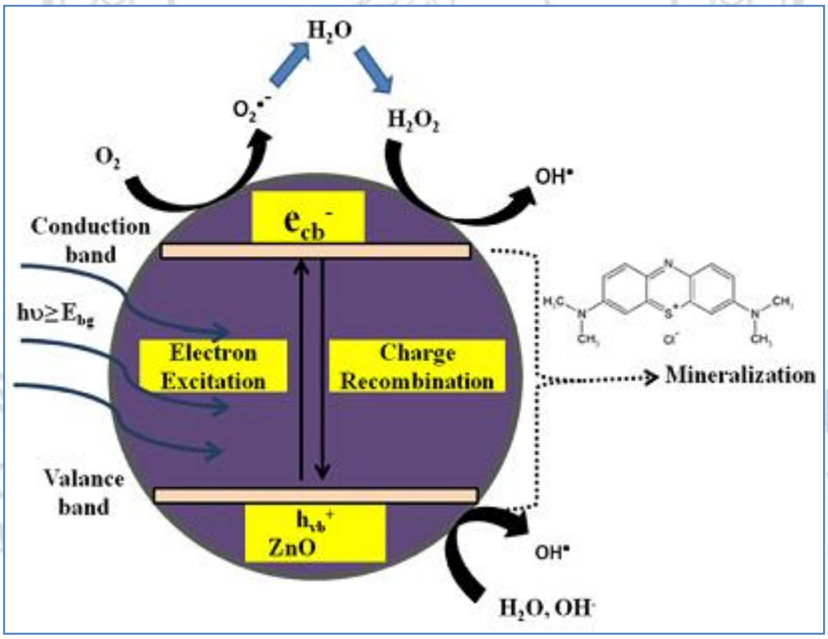


Figure 1.2 Mechanism of photocatalytic degradation of methylene blue [21].

1.4 Degradation mechanism of methylene blue

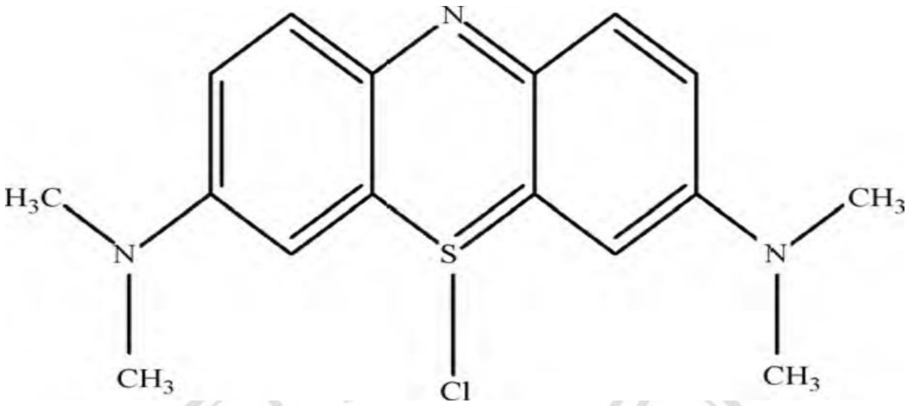
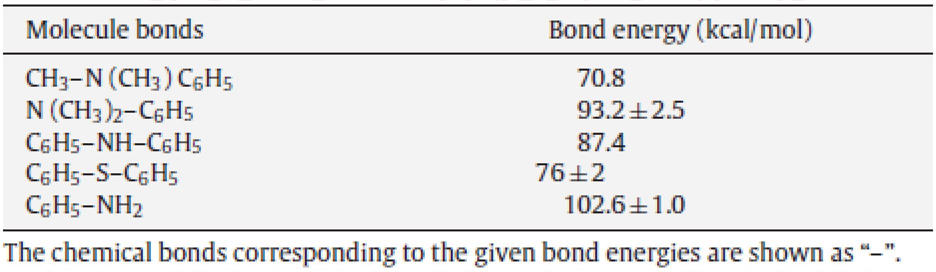


Figure 1.3 Chemical structure of a methylene blue molecule [23].

Chemical reactions consist of the breaking of old bonds and the formation of new ones. According to the bond dissociation energy (BDE) theory, the lower the BDE is, the more active the chemical bond is and the easier it is for old bonds to break and new bonds to form. The main bond energy data of methylene blue molecules are shown in Table 1.1[23].

Table 1.1 Chemical bonds energies in a methylene blue molecule [23].



Molecule bonds	Bond energy (kcal/mol)
CH_3–N (CH_3) C_6H_5	70.8
N $(CH_3)_2$–C_6H_5	93.2 ± 2.5
C_6H_5–NH–C_6H_5	87.4
C_6H_5–S–C_6H_5	76 ± 2
C_6H_5–NH_2	102.6 ± 1.0

The chemical bonds corresponding to the given bond energies are shown as "–".

Based on the intermediate and final products detected, the degradation mechanism for methylene blue is analyzed and described, as shown in Figure 1.4. During the dissolution of the methylene blue molecule, Cl^- is first ionized and exists in the detached state. N–CH_3, which is connected to 7C or 12C, has the lowest BDE value in the methylene blue molecular structure. During the bombardment of the radical species, the N–CH_3 bond is first broken and the –CH_3 is oxidized into HCHO or HCOOH. C–S and C–N are the most active parts of the remaining structure of the methylene blue molecule. During the bombardment of •OH, the two bonds are broken more easily. In the latter period of the DBD process, an abundance of radical species in the methylene blue solution is generated. These oxidize organic molecular structures until they are finally transformed into inorganic ions, such as CO_2, H_2O, Cl^-, SO_4^{2-} and NO_3^- [23].

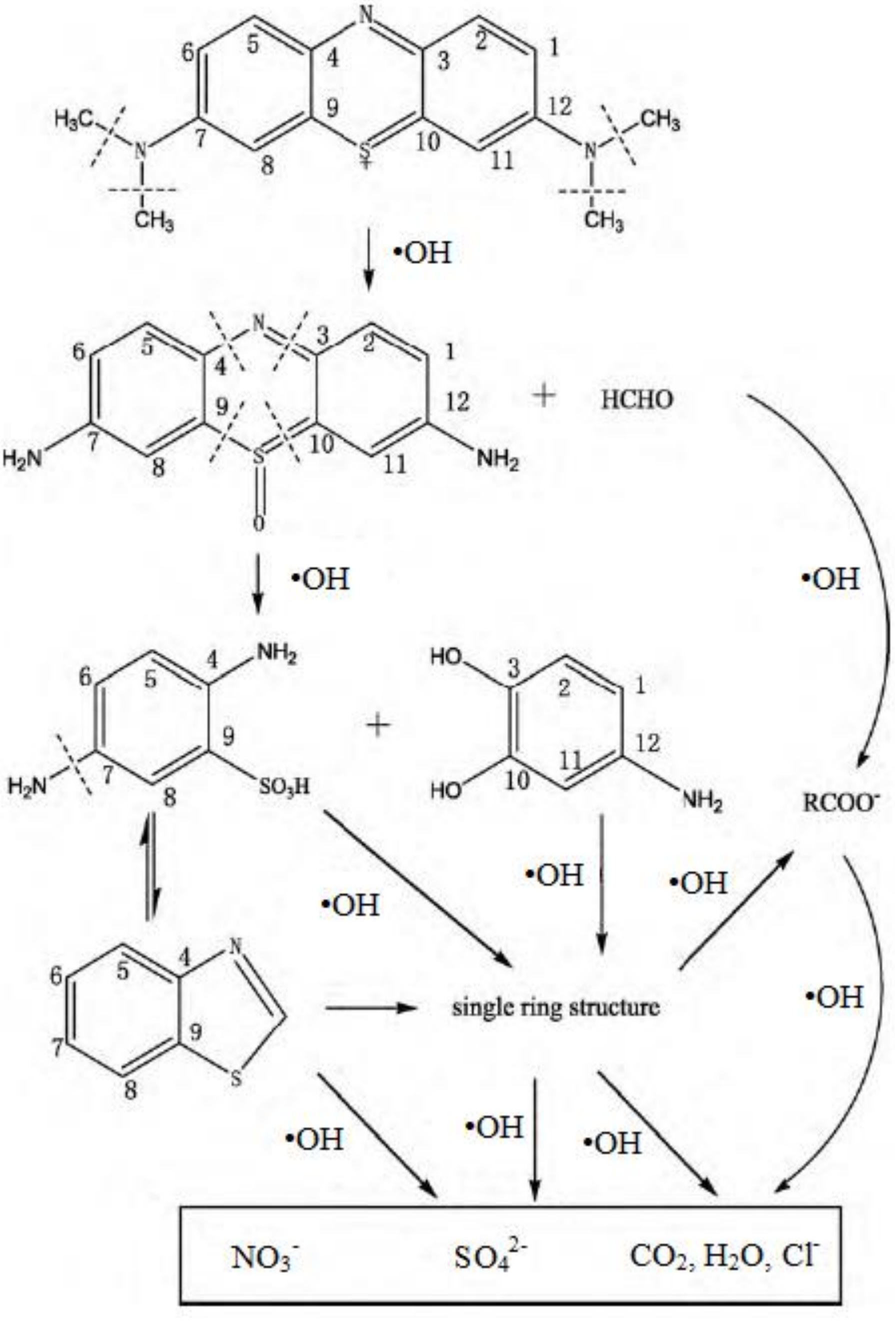


Figure 1.4 The degradation path of the methylene blue molecule [23].

1.5 Sonochemical method

Sonochemistry is a very attractive process used for synthesizing this nanosized material. It can lead to more uniform distribution of nanoparticles, smaller sizes, slightly higher surface area and better thermal stability and phase purity than that achieved by the conventional method. Ultrasonic radiation (20 kHz–10 MHz) is supplied to molecules, which undergo chemical reaction by the acoustic cavitation-formation (nucleation) of bubbles, growth by the diffusion of solute atoms into the bubbles and mechanical collapse of bubbles in a liquid solution when their sizes are excessive. Upon the collapse of a bubble, chemical bonds are broken. This theory claims that very high temperatures (5000–25,000 K) are obtained upon the collapse of the bubble. Since this collapse occurs in less than a nanosecond, very high cooling rates, in excess of 10^{11} K/s, are also obtained. This high cooling rate hinders the organization and crystallization of the products. For this reason, in all cases dealing with volatile precursors where gas phase reactions are predominant, amorphous nanoparticles are obtained. While the explanation for the creation of amorphous products is well understood, the reason for the nanostructured products is not clear. One explanation is that the fast kinetics does not permit the growth of the nuclei, and in each collapsing bubble a few nucleation centers are formed whose growth is limited by the short collapse. If, on the other hand, the precursor is a non-volatile compound, the reaction occurs in a 200 nm ring surrounding the collapsing bubble. In this case, the sonochemical reaction occurs in the liquid phase. The products are sometimes nanoamorphous particles, and in other cases, nanocrystalline. This depends on the temperature in the ring region where the reaction takes place. The temperature in this ring is lower than inside the collapsing bubble, but higher than the temperature of the bulk. Suslick has estimated the temperature in the ring region as 1900 ºC. Generally, these products are nanomaterials (amorphous or crystalline) with different shapes, sizes and structures. When ultrasonic radiation is supplied to chemical solutions, their molecules vibrate and the concentration and temperature are homogenized. The radiation has the influence on the reaction to proceed with efficiency within very short time. Subsequently, pure products are synthesized [24-26].

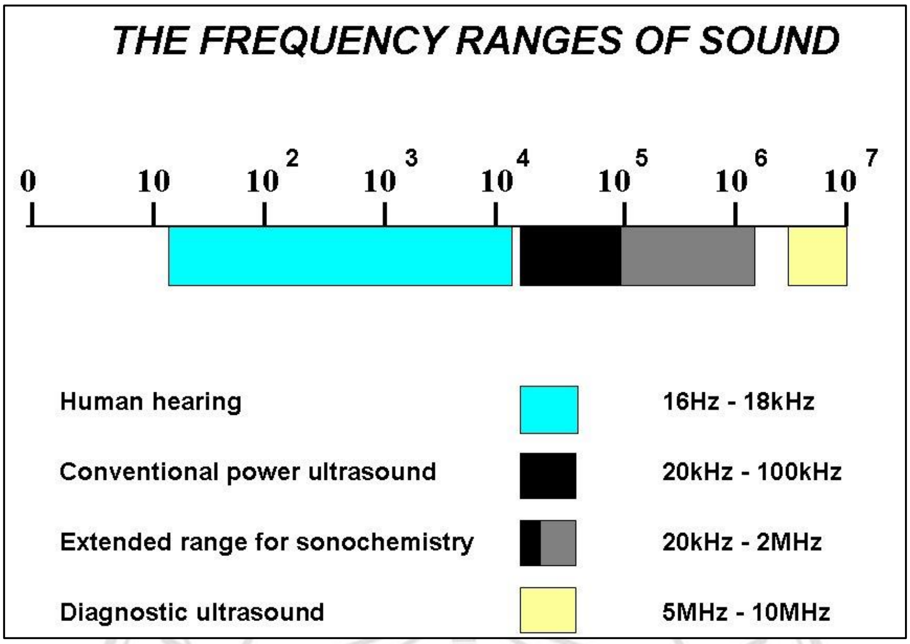


Figure 1.5 Frequency ranges of sound [27].

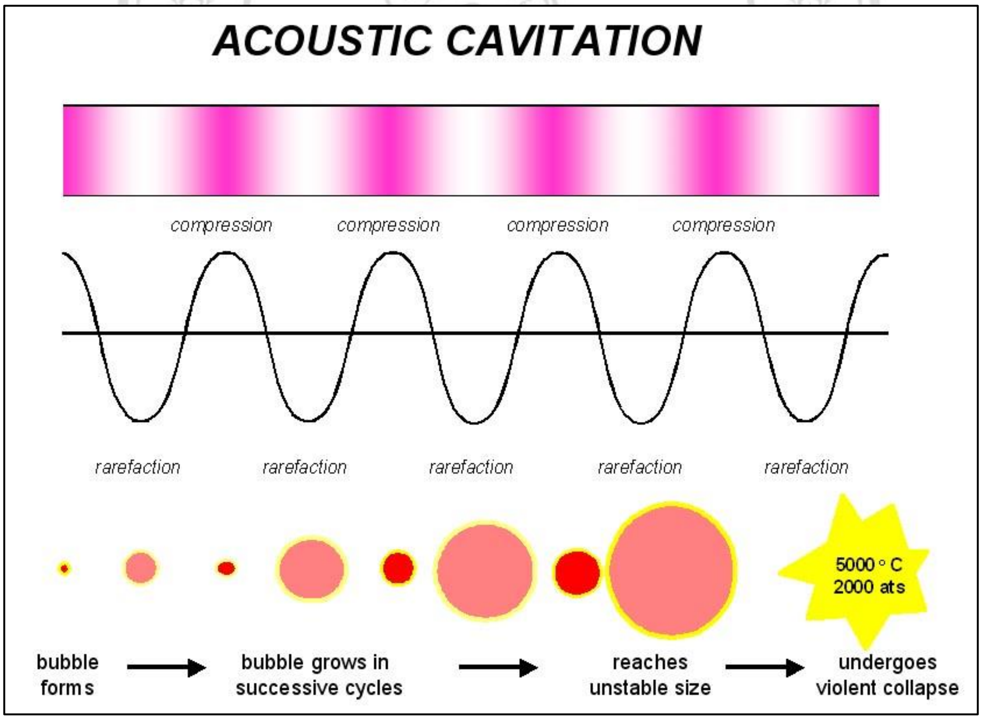


Figure 1.6 Generation of an acoustic bubble [27].

1.6 Literature Review

Anandan *et al.* have synthesized and characterized La-doped ZnO nanoparticles with different La contents by various sophisticated techniques such as XRD, UV–vis, AFM, XPS, and EM. The XRD results revealed that La^{3+} is uniformly dispersed on ZnO nanoparticles in the form of small La_2O_3 cluster. According to the research, particle size of La-doped ZnO was much smaller as compared to that of pure ZnO and decreases with increasing La concentration loading. Rough and high porous surface of La-doped ZnO was observed by AFM, which was critical for enhancing the photocatalytic activity. The photocatalytic activity of La-doped ZnO in the degradation of monocrotophos (MCP) was studied. The effects of the adsorption of MCP, wavelength, and the solution pH on the photocatalytic activity of La-doped ZnO with different La loading were studied and the results were compared with pure ZnO and pure TiO_2. It was observed that the rate of degradation of MCP over La-doped ZnO increased with the increasing of La loading up to 0.8 wt% and then decreased afterwards. It was found that the doping of La in ZnO promoted to achieve complete mineralization of MCP within a short irradiation time. Among the catalyst studied, the 0.8 wt% La-doped ZnO was the most active, showing high relative photonic efficiencies and high photocatalytic activity for the degradation of MCP [12].

Iqbal *et al.* have grown LaCe-co-doped ZnO nanoparticles with an average size of 20 nm using a soft chemistry route. Structural investigations demonstrated that the LaCe-co-doped ZnO nanoparticles have a wurtzite structure. Oxidation and vibration state studies revealed that La and Ce ions were successfully doped into ZnO and provided evidence for the presence of a large number of defects in the crystal structure. Photoluminescence properties of these nanoparticles exhibited an interesting prominent large red-shift in the ultraviolet region with the co-doping of two rare-earth metals, which resulted to the good prospects for use in visible high-efficiency luminescent flat displays and excellent solar light activated photocatalysts [28].

Zhou *et al.* have synthesized and characterized Nd-doped ZnO nanoparticles with different Nd contents by X-ray powder diffraction, UV–vis, X-ray photoelectron spectroscopy, infrared spectra, and high-resolution transmission electron microscopy. The results revealed that the particle size of Nd-doped ZnO was much smaller than that of pure ZnO, which was critical for enhancing the photocatalytic activity. The photocatalytic activity of Nd-doped ZnO with different Nd loading was compared with pure ZnO, and the effects of the solution pH in the degradation of C.I. Reactive Blue 4 were studied. It was observed that the rate of degradation of C.I. Reactive Blue 4 over Nd-doped ZnO increased with the increase in Nd loading up to 2.5 mol % and then decreased. The rate of degradation reached the maximum value approximately at pH 11 and then decreases. Among the catalyst studied, the 2.5 mol % Nd-doped ZnO was the most active, relating to the degradation rate of C.I. Reactive Blue 4 could reach 91.25% in 90 min when the concentration of the catalyst was 0.1 g/L [13].

Karunakaran *et al.* have prepared 2% Ce-doped ZnO by sonochemical wet impregnation method and followed by calcination at 500 ^{o}C. The products were characterized by XRD, EDS, XPS, SEM, FTIR, UV–vis, and PL, including N_2-adsorption and desorption isotherms. The research showed that doping reduced the intragranular resistance and recombination of the photogenerated electron–hole pairs, with the shifts of the optical absorption edge to visible region. Under UV-A light or natural sunlight (950±25 W.m^{-2}), the doped oxide effectively catalyzed the oxidation of cyanide and subsequently the cyanate as well. The catalysis followed Langmuir–Hinshelwood kinetics. The solar photocatalysis was controlled by the area of catalyst and the UV photocatalysis enhances with the photon intensity. The doped oxide also showed an antibacterial agent and its bactericidal efficiency. Test with Escherichia coli in the absence of any illumination was larger than those of the un-doped oxides [11].

Mishra *et al.* have synthesized flower-like ZnO nanostructures by starch-assisted sonochemical method and the effect of starch and ultrasound on the formation of ZnO nanostructure has been investigated. It is observed that starch and ultrasonic wave both plays a vital role on the growth of ZnO nanostructure. X-ray diffraction (XRD) pattern indicated that the synthesized flower-like ZnO nanostructures were hexagonal. FTIR spectrum confirms the presence of starch on the surface of flower-like ZnO nanostructure. The photoluminescence spectrum of flower-like ZnO nanostructure consists of band-edge emission at 393 nm as well as emission peaks due to defects. On the basis of structural information provided by X-ray diffraction (XRD) and morphological information by Scanning Electron Microscopy (SEM), a growth mechanism is proposed for formation of flower-like ZnO nanostructures. Differential Scanning Calorimetry (DSC) of starch in liquid medium confirms that gelatinization is a two step process involving two phases [15].

Deng *et al.* have synthesized ZnO hollow spherical structures by a facile template-free sonochemical process. The structures and morphologies of products have been characterized by XRD, SEM and TEM. The results revealed that hollow spherical structures possess a hexagonal wurtzite structure with the inside and outside diameters of about 400 and 500 nm, respectively. The walls of the hollow structures were self-assembled by nanoparticles, partly composed of hexagonal nanoflakes with 40 nm in side lengths. Room temperature photoluminescence (PL) spectrum showed a UV emission at ∼384 nm and a broad green emission centered at 535 nm. A possible formation mechanism was also proposed, according to experimental results [29].

Chiu *et al.* reported several significant photodecomposition rates of methylene blue (MB) obtained before and after the refluxing process of the as-synthesized two-dimensional (2D) zinc oxide (ZnO) nanopellets. Each photodecomposition rate of MB was found to be highly dependent of the weight of photocatalyst. The existing photodecomposition rate has been successfully improved to a factor of 22 times through the refluxing process in excessive pyridine where the surface capping ligand (oleic acid) was removed from the 2D ZnO nanopellets. On the other hand, the refluxed photocatalyst (0.04g) in this study was found to exhibit excellent recyclability up to three cycles. Furthermore, X-ray powder diffraction spectrums for the refluxed photocatatalyst, respectively, before and after three cycles of photocatalytic reactions, have generated the same patterns showing that the photocatalyst was stable and able to be used as an efficient photocatalytic material. Hence, these 2D ZnO nanopellets would provide a new alternative route as a highly efficient photocatalyst for wastewater treatment [30].

Venkatesha *et al.* have synthesized flower shaped zinc oxide (ZnO) microstructures via electrochemical method by electrolyzing of an aqueous solution of sodium nitrate using sacrificial zinc anode and steel cathode. Investigation on the effect of current density showed that flower shaped structures formed at lower current density, while irregular ZnO clusters formed in addition to flowers at higher current densities. Well defined microflowers formed in neutral and basic electrolyte solutions better than in acidic solution. The SEM results revealed that the flower shaped microstructures have a diameter of 2–3 μm and possess several petals of 1–2 μm in length. Photocatalytic behavior of the synthesized product was investigated through Levafix Blue CA (LB) dye degradation under UV light. The effect of operating parameters like the catalyst load and the initial dye concentration on the rate of dye degradation was studied. Almost 100% decolorization and 95% Chemical Oxygen Demand (COD) removal were achieved under optimum experimental conditions, which suggested due to the potential photocatalytic behavior of the synthesized ZnO [10].

Roy *et al.* reported the effect of Nd doping on structure, electrical and optical properties of nanocrystalline ZnO prepared through a modified ceramic route. The X-ray diffraction and transmission electron microscopy studies revealed that annealed samples were single phase of pure nanocrystalline ZnO. The optical band gap for different compositions, estimated from ultraviolet–visible spectroscopy study, showed a little increasing tendency. By doping with Nd, the samples were able to anneal at lower temperature. The dc electrical conductivity of the samples decreased with the increase in the Nd concentration. The ac electrical measurements showed the hopping conduction as the dominant mechanism. The results were being explained on the basis of band structural change due to the Nd doping in the host lattice and by the Correlated Barrier Hopping model [31].

Khatamian *et al.* have synthesized lanthanide doped ZnO nanoparticles with different Ln (Ln = La, Nd and Sm) contents by polymer pyrolysis method and characterized by various techniques such as XRD, UV–vis, SEM, TGA, and TEM. The XRD results revealed that Ln^{3+} is uniformly dispersed on ZnO nanoparticles in the form of small Ln_2O_3 cluster. From SEM and TEM images it was found that the particle size of La-doped ZnO is much smaller as compared to that of pure ZnO. The photocatalytic activity of La-doped ZnO in the degradation of 4-nitrophenol (4-NP) was studied. The effects of the type and amount of loadings on the photocatalytic activity of Ln-doped ZnO were studied and the results were compared with pure ZnO. It was observed that the rate of degradation of 4-NP over Ln-doped ZnO increases with increasing La, Nd and Sm loading up to 4, 4 and 8 wt% and then decreases. It was found that the doping of

Ln in ZnO helps to achieve complete mineralization of 4-NP within a short irradiation time. Among the catalysts, the 4 wt% Nd-doped ZnO was the most active and showing high photocatalytic activity for the degradation of 4-NP [32].

Faisal *et al.* successfully report the synthesis of highly efficient Ce-doped ZnO nanorods photocatalysts under mild hydrothermal conditions utilizing polyamines triethylenetetraamine (TETA) as the cross-linking agents for the first time. The XRD patterns demonstrate that the ZnO nanorods are highly crystalline and Ce ions were successfully incorporated into the lattice position of ZnO. Presence of Ce^{3+}, Ce^{4+} and Zn^{2+} ions cerium doped ZnO nanorods has been confirmed by XPS analysis. SEM images show that with increasing Ce doping, very thin fluffy or porous like structures on smooth ZnO nanorods were appeared. The lattice spacing between the adjacent lattice planes in the HRTEM images is measured to be approximately 0.52 nm, confirming the ZnO nanorod grows along [0001] direction. Optical characterizations indicate that the Ce doping can shift the absorption edge of ZnO to the visible range and reduce the band gap. The prepared photocatalysts have been compared with commercial photocatalysts Hombikat UV-100 by the determination of their photonic efficiencies for degradation methylene blue. All Ce doped samples exhibited superior photocatalytic performance than either pure ZnO nanorods or Hombikat UV-100. 0.5% Ce doped ZnO exhibits highest photocatalytic activity among the prepared samples [33].

1.7 Research Objectives

1.7.1 To synthesize the zinc oxide and lanthanide-doped zinc oxide nanostructures by sonochemical method.

1.7.2 To characterize the synthesized materials by variety of techniques such as XRD, FTIR, FESEM, TEM, HRTEM, SAED and EDX. Energy band gap and emission wavelength by UV-visible absorption and photoluminescence (PL) are also included for the characterization.

1.7.3 To study the photocatalytic activity of the synthesized materials in the solution containing methylene blue.