## Zinc Vanadate Modified Metal Chalcogenides Nanocomposites: Synthesis, Characterization and Photocatalytic Activity



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## Dedicated to

# my loving grandmother, parents and husband

for their endless love, support and encouragement

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# List of Abbreviations

Eg	Band gap
VB	Valence band
СВ	Conduction band
FT-IR	Fourier Transform Infra-Red
XRD	X-ray Diffraction
SEM	Scanning Electron Microscopy
UV-vis	Ultraviolet-Visible
$Zn_3V_2O_8$	Zinc vanadate
ZnSe	Zinc selenide
ZnTe	Zinc telluride
nm	Nanometer
mg	milligram
mL	milliliter
COD	Chemical oxygen demand
BOD	Biological oxygen demand
mM	milli molar
SDS	Sodium dodecyl sulphate

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#### ABSTRACT

Organic contaminants from industrial or domestic effluents may be harmful to humans directly or indirectly by degrading the quality of environment. Consequently, these contaminants must be reduced to levels that are not harmful to humans and the environment before disposal. Chemical, physical and biological methods exist for the removal of these pollutants from effluents. Among the available chemical methods, heterogeneous photocatalytic oxidation has been found particularly effective in removing a large number of persistent organics in water. In this dissertation, the synthesis of Zn<sub>3</sub>V<sub>2</sub>O<sub>8</sub> and metal chalcogenides for photocatalytic organic pollutant degradation is reported. UV active photocatalyst Zn<sub>3</sub>V<sub>2</sub>O<sub>8</sub> was synthesized by co-precipitation method. However, it showed lower photocatalytic activity for dye degradation. In order to increase the light absorption spectral range and photocatalytic activity of Zn<sub>3</sub>V<sub>2</sub>O<sub>8</sub>, its heterostructures with metal chalcogenides (ZnSe and ZnTe) were synthesized. The photodegradation activity of  $Zn_3V_2O_8/ZnSe$ , for congo red dye was investigated and the activity of Zn<sub>3</sub>V<sub>2</sub>O<sub>8</sub>/ZnTe will be determined in future. UV-Vis. photodegradation of dye over Zn<sub>3</sub>V<sub>2</sub>O<sub>8</sub>-ZnSe heterostructures showed 84.3% congo red degradation, when 75% of ZnSe was present in a composite. Bare ZnSe with both cubic and hexagonal phases showed 89.4% of congo red degradation under UV-Vis. light. The as-synthesized photocatalysts were characterized by different methods. Crystal structure, morphology, purity, composition and band gaps of photocatalysts and their heterostructures were studied by XRD, IR, SEM/EDX, and UV-Vis. DRS. Results for congo red degradation clearly indicate the anomalous behavior of bare ZnSe that showed higher activity than ZnSe heterostructure with Zn<sub>3</sub>V<sub>2</sub>O<sub>8</sub>.

**Keywords:** Dye degradation; Photocatalyst; Zinc Vanadate (Zn<sub>3</sub>V<sub>2</sub>O<sub>8</sub>); Zinc Selenide (ZnSe); UV-visible light; Heterostructure; Congo red

#### **Chapter 1: Literature Survey**

#### Abstract

This chapter provides a broad account of photocatalytic degradation of organic dyes using different metal based inorganic semiconductor photocatalysts. A comprehensive literature review has been presented to clearly explicate the principle of photocatalysis and different photocatalysts used for dye degradation. I have also discussed different methods used for enhancing photocatalytic activity with main focus on heterostructure formation, which have further been employed during this work to improve photocatalytic activity of synthesized nanoparticles. The last part of this chapter includes objectives, motivation and scope of the research work.

#### **1.1 Introduction**

Our world is uninterruptedly altering. It is at the verge of a major environmental crisis. We are no more living in an environment, which is serene, but rather becoming bizarre and polluted. With an immense incursion of natural disasters, temperature fluctuations and industrial wastes, there is a great need of awareness of people about major environmental issues and their solutions. Development in industrial sector like food, glass, leather, cosmetics, plastics and paint result in large amount of organic waste, which is harmful to the life on earth. Discharge of colored effluents obstructs the access of sunlight to aquatic plants, which affects ecosystem and retards photosynthetic process [1, 2]. These issues need to be addressed in time.

#### **1.1.1 Current Environmental Problems**

**Natural Resource Depletion:** Current world population is about 7.2 billion and growing but available natural resources can only fulfill the demands of 2 billion people. Depletion of these resources due human activities will result in serious problems for mankind [3].

Fossil fuels are an imperative source of energy but burning of fossil fuels release carbon dioxide in atmosphere, which is responsible for global warming, smog, fog, acid rain and many respiratory diseases. Life cycle of fossil fuel is shown in **Fig.1.1**.



Figure 1.1: Life cycle of fossil fuel

World population is expected to increase by 33% in 2050 (UN DESA, 2015). With growing population, urbanization and industrialization the sources of energy are being consumed rapidly. About 82 % of the overall energy consumption was from fossil fuel in 2012. We are using approximately three times more than what is sustainable. According to **2016 World Energy Resources**, report [4] there was an unprecedented change in energy consumption over the past 15 years. Key trends of energy consumption during these years are illustrated in **Fig.1.2**.



**Figure 1.2:** Comparative primary energy consumption over past 15 years [4]

Therefore, there is a need to conserve these earth natural resources and make use of renewable sources of energy by exploring efficient techniques of their utilization. Renewable sources are of three different types: sustainable resources, renewable commodities and natural renewable resources. Resources which can be used for an indefinite time period are sustainable resources of energy. These resources include solar,

wind, geothermal and tidal energy. Most important sustainable resource is solar energy, which can be utilized in different ways for environment remediation. Renewable commodities are items, which are depleted, but they can be renewed by recycling, planting and harvesting. Renewable commodities include food crops, fibers, fodder, bioenergy and natural fertilizers. Natural renewable energy resources are those resources, which can replenish themselves if not polluted or degraded by anthropological activities. These resources include water, soil and hydroelectricity. Depletion of water resources is serious problem. About 70% of water on earth surface is frozen and only 2.5% is fresh. Energy resources can be replaced but nothing can replace water. About 70% of the fresh available water is consumed in agriculture, 20% in industry and only 10% is consumed by humans. Foremost cause of water depletion is pollution and is briefly discussed below.

**Pollution:** With the dawn of era of science and technology, man began losing control on ecological balance and growth of hazardous materials started. According to survey of "Pure Earth", more than 200 million people are affected by noxious waste. Industrial effluents, emerging scientific laboratories, smoke, and toxic gases are responsible for constantly polluting our environment. Improper disposal of solid waste, rapid industrialization and urbanization results in major harm to ecosystem. Major problem due to rapidly increasing pollution is acid rain due to imbalance of earth natural cycle. Acid rain results in lowering pH of water sources, which is fatal for marine life, and it affects flora and fauna equally [5].

**Water Pollution:** Water pollution is a major threat to the life on earth. All organisms need access to water. Water pollution can be due to natural phenomenon like hurricanes, tornados, volcanic eruptions but main cause of water pollution is human activities. According to United Nations, in last era rate of water use has increased twice the rate of population increase.

Development in the industrial sector is increasing toxic pollutants in all water resources, which are lethal for fauna as well as flora of our planet. Run-off to streams, rivers and oceans carries toxic elements, dyes and different microorganisms and poses risk to human health. Contaminated water contains lethal substances like heavy metals, nitrates,

nitrites, carcinogenic solids and organic waste. Plants can absorb these hazardous contaminants from water and in this way may enter in food chain.

#### 1.1.2 Textile Waste Water

Major cause of water pollution in today's world is waste from textile, pharmaceutical, cosmetics, plastic, and paper and printing ink industries. The main pollutants are different coloring agents used in these industries, which are commonly known as dyes [6]. Dyes are of different types like natural dyes, synthetic dyes and food dyes. Azo dyes are most commonly used colorants and constituent almost 70% of the organic dyes produced every year [7]. In 2014, market demand of dye increased up to 1500,000 tons. Due to toxic nature of dye, different health issues were raised and, therefore, dye degradation attained the attention of many scientists [8].

Use of synthetic dyes started in the mid of nineteenth century after the invention of mauvine in 1856 by Perkin. Due to low cost and easy production methods demand for synthetic dyes increased day by day. Discharge of these dyes as aqueous effluents during processing causes many environmental problems as these dyes are toxic and contain carcinogenic components like naphthalene, benzidine and different aromatic compounds [9, 10]. Because of inappropriate methods of dyeing almost 200,000 tons of dyes are wasted as run-offs from textile industry. Printing inks contain heavy metals, which are easily leeched to ground water and cause serious health problems in both humans and wildlife [11]. Most of the dyes persist in our environment because of their high stability to heat, light, soaps, detergents and other chemical agents. Bio degradation of dyes does not occur due to their temperature and photo stability [12].

#### **1.1.3 Methods for Treatment of Effluents from Textile Industry**

Physical, cross flow filtration, biological and chemical methods are employed for treatment of effluents from textile wastewater. Textile industry produces colorants for improving the quality of fabric. During processing toxic organic substances discharge in the industry effluents. The first step in industrial wastewater treatment is separation of different pollutants found in effluent. Oils, grease and large sized solid particles are separated by physical methods. Then chemical methods are employed for treating

effluents with same concentration of pollutants. Decrease in chemical and biological oxygen demand (COD and BOD) is attained by chemical treatment and effluents are further treated with biological methods in order to further decrease COD and BOD [13, 2].

**Physical Methods:** Physical methods involve removal of pollutants from water by using different naturally occurring forces like Vander Waals forces, electrical and gravitational forces and physical barriers. Physical methods are often used as primary source of wastewater treatment. These methods result in change of physical state of the target substance like agglomeration, vaporization etc. There occurs no change in chemical state of the pollutant [14].

Physical methods of wastewater treatment include screens, which are used for removing solid substances from water in the beginning of the treatment process, flotation, filtration, and sludge formation, adsorption, bar racks, deep bed filters and polymeric or animal membranes. Deep sand filtration is also included in physical methods of wastewater treatment. It involves filtration of water through different layers of sand, which results in removal of solid waste.

Through physical methods of waste water treatment only large sized pollutants, sediments and oils as slurry can be removed but their hazardous effect on environment cannot be handled as their occur no chemical change in the structure of toxic pollutants [15]. For degradation of toxic substances biological and chemical methods of wastewater treatment are employed [16].

**Cross Flow Filtration:** Cross filtration involves different filtration techniques used to remove particles of small size. Micro, ultra, nano and reverse osmosis are used to remove particles of size  $0.1-1.5 \mu m$ ,  $0.005-0.1 \mu m$ ,  $0.0001-0.005 \mu m$  and  $0.001 \mu m$  respectively.

**Biological Methods:** Biological methods of wastewater treatment are most commonly used methods nowadays and can be used as secondary treatment process to remove the pollutants remained after primary treatment [17]. Bacteria, nematodes and other small microorganisms are used to treat wastewater after sedimentation or flocculation processes. Biological methods are also known as green detoxification methods. Green

detoxification is a process of degradation of different toxic pollutant with environment friendly methods. This method is very cost effective and better than conventional methods of pollutants degradation. Anionic reactive were biosorped by different fungal and algal species. Direct brown MR (DBMR) azo dye was biodegraded by Acinetobacter calcoaceticus [18]. For dye degradation, mostly biological methods are used along with chemical methods. Biological methods are subdivided into aerobic and anaerobic methods.

**Aerobic Waste Water Treatment:** Presence of oxygen is necessary condition for aerobic wastewater treatment. Activated sludge, oxidation ditches, lagoon-based treatment; aerobic digestion and trickling filter are used as aerobic wastewater treatment methods [19]. First step is aeration as bacteria or other small organisms require oxygen for organic pollutant degradation. Activated sludge process is mainly employed for treatment of waste from sewage and paper and food industries [20-22].

Anaerobic Waste Water Treatment: Treatment of wastewater by anaerobic method is carried out in the absence of oxygen. Lagoon and septic tanks are used for these treatments. Anaerobic digestion is mainly used for organic pollutant degradation and for the production of biogas [19]. There is a large amount of "biological oxygen demand (BOD) and chemical oxygen demand (COD)" after anaerobic digestion so water require further treatment like aeration, filtration and disinfection [20-22].

**Chemical Methods:** Chemical treatment involves the use of chemicals to improve the water quality. Oxidants effectively kill microorganisms whereas reducing agents are mostly used to counterbalance the effect of oxidizing agents by neutralizing them. Ozonation, neutralization, chlorination are some of the examples of chemical methods.

Neutralization is mostly employed method in industries, which involve use of acid or a base to adjust the pH of water and balancing it to neutrality. Chlorination results in purifying effluents by killing bacteria and other organisms. Ozonation involve use of ozone and is very effective method in deterioration of color of dyes which are toxic [23] but duration is short about 20 minutes which make it less beneficial [24, 25]. Electrochemical and photochemical methods are also used for organic waste degradation.

Electrochemical degradation is expensive as compare to photochemical degradation as in photochemical process solar energy is used along with a catalyst. Also this method of organic pollutant degradation is environment friendly [26].

#### 1.1.4 Green Detoxification through Solar Energy

There is a great need of wastewater treatment in order to fulfill the demand of clean water with growing population and decreasing energy resources. Best method for treating polluted water would be the one, which results in complete removal of contaminants without formation of hazardous byproducts. Heterogeneous photocatalysis fulfill this requirement and results in removal of toxins from water. Sun light plays a very important role in pollutant degradation. This method is inexpensive and environment friendly [27, 28].

#### **1.2 Photocatalysis**

It is the process of adsorption of photons from sunlight in the presence of catalyst to generate electron hole pairs, which will degrade pollutants by redox reaction [29]. The catalyst used is called photocatalyst. Photocatalyst enhance the rate of reaction by adsorbing photons and by producing electron hole pairs that transform reaction precursors into product without itself being consumed [30].

Semiconductor photocatalysis have been found to be an attractive field of study because of its use for unraveling environmental pollution and energy crises. Mostly semiconducting oxides are used as a photocatalyst due to their major role in environment sanitization and solar light transformation [31, 32]. Chlorophyll is natural photocatalyst, which uses solar energy to change water and carbon dioxide into oxygen and glucose. While man-made photocatalysts like TiO<sub>2</sub>, ZnS, CdS generate electrons and holes in the presence of sunlight which convert pollutants into carbon dioxide and water. Band gap energies of different photocatalysts involved in organic pollutant degradation are schematically illustrated in **Fig. 1.3.** Photocatalysis is used for production of fuel, for heavy metals removal and for water purification. Important features of photocatalytic system are large surface area, favorable band gap, stability, appropriate morphology and reusability [33].



**Figure 1.3:** Schematic illustration of band gaps and redox potential (vs. NHE) of various semiconductors at pH=1

#### **1.2.1 Mechanism of Photocatalysis**

When photocatalysts absorb sunlight, it generates electron hole pairs. Gap exists between "valence band and conduction band" of photocatalyst named band/energy gap. Valence electrons of photocatalyst jumps to the conduction band by absorbing quanta of energy equivalent to or larger than the energy of band gap leaving holes in valence band. This state is called photo excitation state of photocatalyst. Oxygen molecules adsorbed on catalyst then trap electrons in conduction band to form superoxide radical anion ( $O_2^{-}$ ). Hydroxyl radicals are produced by the reaction of  $O^{2-}$  with protons or when water reacts with electron hole pair. These hydroxyl radicals and superoxide ions will lead to organic pollutant degradation [34, 35]. Following steps are involved in photocatalysis when UV light is absorbed by ZnO catalyst [36].

$$ZnO + hv \to e^- + h^+ \tag{1}$$

$$e^- + 0_2 \to 0_2^-$$
 (2)

#### **Oxidation Reaction**

 $h^+ + dye \to dye^+ \tag{3}$ 

$$h^+ + H_2 0 \rightarrow 0 H^{\cdot} + H^+ \tag{4}$$

#### **Reduction Reaction**

$$dye + 0H^{\cdot} \to CO_2 + H_2O \tag{5}$$

On the basis of reaction phase, photocatalysis is of different types (heterogeneous and homogeneous). Those photocatalytic reactions in which catalyst and precursors are in same phase are called homogeneous photocatalytic reactions. Heterogeneous photocatalysis is more advantageous as compare to homogeneous photocatalysis due to the possibility of reuse of catalyst, efficient utilization of sun light for catalyst excitation and complete mineralization of large number of organic compounds.

#### **1.2.2 Heterogeneous Photocatalysis**

Photocatalytic reactions in which reactants and catalysts are in different phases are known as heterogeneous photocatalytic reactions. Scheme of reaction of heterogeneous photocatalysis involve the formation of an interface between a fluid containing precursors and products of reaction and solid photocatalyst used. So, term heterogeneous photocatalysis is most commonly employed to the reactions in which solid catalyst is in contact with liquid or gas phase containing reactants and product of reaction [37].

Heterogeneous photocatalysis attained much attention due to their use in organic synthesis and environment energy related applications [38]. It is cost-effective and harmless process for organic waste removal. In heterogeneous photocatalysis light absorbing photocatalysts are in contact with gaseous or liquid phases. The ability of photocatalyst to produce OH radical by absorbing solar energy makes this process valuable. Heterogeneous photocatalysis results in gradual break down of organic waste into harmless components with no remain of original material.

#### **1.3 Synthesis of Nanomaterial**

Unique properties of nanomaterial's and their ability to enhance the properties of existing bulk material make them an important class of study. These materials have wide variety of applications in various fields such as pharmaceutical industry, life sciences, space technology and chemical industries. The properties like shape, size and crystal structure of nanoparticles can be controlled by different fabrication techniques. Two diverse approaches are being used to synthesize nanomaterial i-e top down approach and bottom up approach. **Fig. 1.4** is the schematic illustration of the difference between these two approaches of nanoparticles synthesis.



Figure 1.4: Schematic illustration of top-down and bottom-up approaches

#### **1.3.1 Top-Down Approach**

Top-down approach involves the cutting or slicing of bulk material into smaller nanosized particles. Top down approach for nanoparticles synthesis is commonly employed in semiconductor industry to make devices from electrical substrate. It is an expensive method and size control of the product is not possible with this method. Also top down methods results in products with contamination, defects and internal stress. Lithography, dry etching and ball milling are common top down methods of nanoparticles synthesis. During milling, material is fed to the container containing steel or tungsten carbide balls. Container is then rotated on its axis with high speed and material is pressed against the walls of container. In this way nano sized particles are obtained by simple top down approach. Diagrammatic representation of container used for milling is shown in **Fig. 1.5**.



Figure 1.5: Schematic illustration of internal structure of ball mill

#### **1.3.2 Bottom-Up Approach**

Bottom-up approach of nano particle synthesis involves the assembling of atoms or molecules to form nano-sized particles. Physical and chemical forces are responsible for assembling of smaller units into large material. Bottom up approach for nanoparticle synthesis is far better than top down approach as it results in nanoparticles which are homogeneous and have less defects [113]. A bottom-up method for nanomaterial synthesis consists of following strategies:

- Liquid-phase synthesis
- Gas-phase synthesis
- Vapor phase synthesis

Liquid-phase synthesis involves the processing of atoms or molecules in solutions, which results in the formation of nanoparticles. Some of the liquid phase bottom-up methods used to synthesize nanoparticles are described below. Liquid phase synthesis involves hydrothermal, sol-gel, co-precipitation and sonochemical approaches of nanomaterial synthesis [120-124]. All these methods of nanomaterial synthesis are discussed below.

**Hydrothermal Method:** Roderick Murchison coined the term hydrothermal for the first time in order to describe the changes occurring in earth crust due to change in temperature and pressure of water [119]. Hydrothermal method can be defined as "the heterogeneous process that takes place in aqueous or non-aqueous solvents above room

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temperature and at pressure higher than 1 atm". In recent years, hydrothermal method is most commonly employed for synthesis of metals and metal oxides. The product so formed is highly pure with even diameter of crystals, do not cluster together and needs no more high-temperature calcination. It is an ecofriendly and inexpensive method. Shape, crystallinity and size of nanoparticle are affected by operating temperature and pressure when synthesized by hydrothermal process [39].Large number of inorganic substances becomes soluble in aqueous medium at high temperature and pressure. Different reaction parameters like temperature, pressure and concentration of reactants can be controlled by this method during synthesis in order to maintain size and nucleation process.

The laboratory synthesis of nanomaterial is carried out in closed steel containers called autoclaves, which can endure high temperature and pressure. Precursors for synthesis of specific nanoparticles are dissolved in solvent and then precipitating agent is added drop wise. The mixtures is then poured in Teflon tube which will then be placed in autoclave and heated under desired temperature in an oven for specific time duration. As a result, highly crystalline nanoparticles with controlled dimensions are obtained.

Pei et al. synthesized highly pure zinc vanadate nanorods by hydrothermal method [76]. Cao et al. prepared wurtzite ZnSe nanostructures by adopting inexpensive and easy hydrothermal route. ZnSe nanoparticles obtained by hydrothermal method were of high purity and crystallinity [82]. Wu et al. also followed hydrothermal method for the synthesis of ZnTe with red bayberry like structure [114].

**Sol-gel Method:** Sol-gel method was first discovered in 1800s. It is a wet method for synthesizing glass material, ceramic and nanoparticles. This process involves the formation of sol and gel followed by evaporation of excessive solvent to obtain product [40]. Sol is suspension of solid solute particles in solvent whereas gel is a semi-rigid mass formed after the evaporation of solvent from sol. Mostly metal alkoxides or metal chlorides are used as precursors. Precursors undergo hydrolysis and polycondensation reactions, which results in the formation of nanopowders in colloidal solution. Sol-gel method is mainly employed for glass and ceramic material fabrication. It is inexpensive and low temperature method in which composition of product can be controlled.

**Co-precipitation Method:** Product is in the form of precipitates made from supersaturated solution. Main step of this process is nucleation. Size, morphology and properties of product are affected by Ostwald ripening and agglomeration. In this method, precursors and doping agents are separately dissolved in deionized water and then mixed under strong stirring. Then precipitating agent is added to get the precipitates of product under constant stirring for specified duration. The precipitates thus obtained are centrifuged, washed, dried and finally calcined to obtain nanocatalyst.

Ghorbani et al prepared ZnO nano particles by precipitation method. Solution of zinc nitrate in deionized water was stirred with constant addition of KOH at room temperature. As a result white precipitates obtained which were centrifuged at 5000 rpm, washed with ultrapure water and alcohol and calcined at 500<sup>o</sup>C [41]. Chang Chun Chen also prepared ZnO nanoparticle by direct precipitation method by using zinc nitrate and ammonium carbonate as precursors [42].

**Sonochemical Method:** Sonochemical method involves the use of ultrasound irradiations to synthesize nanoparticles with controllable morphologies. Irradiation of the reaction medium with ultrasonic waves will results in cavitation. Ultrasonic cavitation is related to creation, growth and implosive collapse of micro bubbles. Ultrasonic waves will reduce metal salts to generate activated metals. This process helps to

- Coat nanoparticles
- Enhance particle synthesis
- Increase rate of reaction
- Increase reaction between precursors and catalyst activity
- Utilize energy efficiently

Many chemical reactions take place as a result of high temperature (5000<sup>o</sup>C) and high pressure (approx. 1800 KPa) produced by cavitation [43, 44]. Amorphous product is obtained by sonochemical method, due to cavitation bubbles collapse, which is then heat-treated.

#### **1.4 Semiconductors as Photocatalyst**

In recent years, semiconductor photocatalysts are widely used as a high profile catalyst due to their versatile properties and diverse applications. In electronic industry and environmental remediation, semiconductors are most widely used as they result in the production of charge carriers when irradiated with light of suitable wavelength. By harvesting solar energy, semiconductor photocatalysts can degrade organic pollutants and can be used to produce fuels from renewable energy resources. Solar energy conversion efficiency of photocatalyst depends on charge recombination, charge movement, light absorption, charge separation and surface redox reaction in photoactive semiconductors [45].

**Band Structure of Semiconductors:** Band structure of the semiconductors is characterized by a number of strictly packed energy levels related with the covalently bonded atoms forming crystallites (valence band) and another sequence of diffused energy levels with comparable energy lying at high energy and related with conductivity in macromolecule crystallites (conduction band). "Energy difference between valence band and conduction band is called band gap". Different photocatalysts have different band gap and thus have different capacity for absorption of light.

As presented in **Fig. 1.6**, five main events take place when light fall on semiconductor photocatalyst: "(I) light absorption, (II) charge separation, (III) charge migration, (IV) charge recombination and (V) redox reactions [46]". Quanta of energy higher than energy of band gap are absorbed by semiconductor and results in excitation of electron to conduction band leaving behind positive charge carriers the holes. These separated charges than migrate to the interface between semiconductor surface and medium containing reactants and products or reaction where redox reaction takes place. Most of the charge carriers produced during the process recombines in bulk or on surface and release their energy as heat by creating phonons and so on. Photocatalyst should be inexpensive, abundantly available, environment friendly and can be synthesized by green methods. It should have wide light absorption spectral range and high charge mobility as recombination of charge results in low efficiency of photocatalyst for solar energy conversion. Electron-hole recombination time is approximately  $10^{-9}$  s. Whereas, the

chemical interaction with adsorbed species occurs in extended time that is within  $10^{-8}$ - $10^{-3}$  s [47].



**Figure 1.6:** Schematic illustration of photocatalyst. "Note: (I) Light absorption(II) Charge separation, (III) Charge migration, (IV) Charge recombination and (V) Redox reactions". "CB=conduction band, VB=valence band"

#### 1.5 Factors for Improving Photocatalytic Efficiency

Over the last few decades, use of semiconductor-based photocatalysts for organic pollutant degradation has attracted considerable attention but photodegradation often suffers from low efficiency. Here we will discuss different methods used so far for improving the properties of semiconductor-based photocatalytic systems.

#### **1.5.1 Nanostructuralization**

Photocatalytic applications of a wide range of nanostructures having distinctive morphologies were investigated [48]. Nanocatalyst with single crystalline nature showed better photocatalytic activity as compared to polycrystalline materials in which grain boundaries or surface defects are present which act as recombination center for photogenerated charge carriers. Recombination of charge carriers decreases the photocatalytic activity.

Boujday et al. examined the influence of crystalline nature and size of nanoparticles on photocatalytic activity. Photocatalytic activity of semiconductor photocatalysts increases with increased crystallinity and decreased size [49]. High crystal quality will result in

decreased defects in crystal structure and as a result, photocatalytic efficiency is increased. Defects act as a hub for recombination of electrons and holes generated by solar light absorption and hence decrease the photocatalytic activity. With the decrease in particle size large proportion of atoms set up on the surface as compare to interior and as a result, photocatalytic activity is enhanced. As catalytic reactions occur on the surface and decreased particle size results in an increased surface area [50]. Yao and Wang synthesized TiO<sub>2</sub> sol for UV photodegradation of methylene blue. Higher photocatalytic activity of all TiO<sub>2</sub> sol-gel nanoparticals was noticed as compared to commercial TiO<sub>2</sub>. The TiO<sub>2</sub> sol exhibited enhanced photocatalytic activity due to small particle size [51]. Dawson et al. investigated the influence of gold doping on "photocatalytic activity" of TiO<sub>2</sub>. Results showed that, composite with small sized gold particle showed better catalytic activity than that composed of large sized gold particles [52]. Swetha and Nalini studied the photocatalytic activity of Bi<sub>4</sub>NbO<sub>8</sub>Cl bulk and nanostructure under UV and solar irradiation. When irradiated with UV light nano Bi<sub>4</sub>NbO<sub>8</sub>Cl showed faster degradation of Congo red as compared to bulk [53].

Shape of crystals also affects photocatalytic activity because shape disturbs the band gap of catalyst due to dissimilar activities of main facet. Thus different morphologies of semiconductor photocatalysts results in dissimilar direct band gap, different surface area and UV-visible absorbance, which results in different photocatalytic activities. Comparative study of photocatalytic properties of Ag, ZnO, NiO and CuO showed that octahedral shape resulted in maximum photocatalytic activities while flakes shape nanoparticles showed low photocatalytic activity as compared to other shapes due to less crystallinity [54].

Doubled-shelled  $ZnV_2O_4$  hollow nanostructures,  $ZnV_2O_4$  clew like hollow spheres, Monoclinic  $ZnV_2O_4$  nanowires,  $ZnV_2O_4$  nanosheets and  $ZnV_2O_4$  nanorods were synthesized by different researchers and their photocatalytic activity showed considerable difference due to different morphologies. Among these  $ZnV_2O_4$  nanorods showed enhanced photocatalytic activity in visible light due to constrict band gap [55].

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#### **1.5.2 Doped Semiconductors**

The performance of photocatalysts can be improved by doping with noble metals or other semiconductor compounds. Kodom et al. examined the influence of doping of  $TiO_2$  with silver nanoparticles, AgNPs.  $TiO_2$  because of its broadband gap can absorb ultraviolet light only but doping with AgNPs increased the sensitivity of  $TiO_2$  to visible light. To prepare the hybrid material two distinct approaches were followed. The approach involving the generation of silver nanoparticles on the surface of  $TiO_2$  showed better photocatalytic dye degradation. Liu et al. investigated the azo dye degradation via nitrogen-doped nano-crystals of  $TiO_2$ . Doping increased the photocatalytic activity of titania as compared to commercially available  $TiO_2$  both in UV-visible region of solar spectrum [56].

Metal doped semiconductors show efficient interfacial charge transfer because Fermi level shifts to much negative potential due to doping of metals. Dawson et al. studied the influence of Au doping on TiO<sub>2</sub> performance. Doping resulted in the Fermi level transfer to much negative potential and hence increased reduction power of the composite. Laser flash photolysis examination of gold doped TiO<sub>2</sub> nanomaterial showed ~40% improvement of hole transfer ratio [52]. Zhang and J. Zhang discovered the consequence of Europium doping on the "photocatalytic activity" of BiVO<sub>4</sub>. Eu/BiVO<sub>4</sub>presented enhanced "photocatalytic activity" than pure BiVO<sub>4</sub> with low Eu content. The greater photocatalytic activity of Eu/ BiVO<sub>4</sub> composite was due to repressed recombination of electrons and holes and higher absorption in visible region of solar spectrum [57]. A. Zhang and J. Zhang also reported the "photocatalytic activity" of composite of silver with BiVO<sub>4</sub> in comparison of pure BiVO<sub>4</sub>. Ag doped BiVO<sub>4</sub> composite efficiency was much increased than pure BiVO<sub>4</sub>due to more visible light absorption [58].

#### 1.5.3 Sensitization of Semiconductor

Metal oxides semiconductors mostly have wide band gap and are UV-light receptive. As UV light covers only 4% of the solar spectrum, in order to increase the range of absorption of photocatalysts, sensitization of wide band gap photocatalyst with narrow band gap photocatalyst is promising approach. In this way semiconductor photocatalyst

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become both UV-visible light active and works by the transfer of electron from narrow to wide band gap semiconductor. The process of sensitization is schematically represented in **Fig. 1.7**.



Figure 1.7: Schematic illustration of narrow band gap sensitized wide band gap semiconductor

#### **1.5.4 Formation of Heterostructures**

Formation of heterostructure plays vital role in improving the "photocatalytic activity" of composite by controlling electron holes recombination. Researchers have developed heterostructures like Cu<sub>2</sub>O/BiVO<sub>4</sub>[59], ZnO/Ag<sub>3</sub>VO<sub>4</sub> [60], ZnO/BiOI [61], Ag<sub>2</sub>O/TiO<sub>2</sub> [62] and SrTiO<sub>3</sub>/TiO<sub>2</sub> [63], with enhanced photocatalytic activities. Fig. 1.8 showed that recombination of photogenerated electron and hole is efficiently decreased by the transfer of electron from "higher conduction band to lower conduction band" and holes from "lower valence band to higher valence band". Y. min et al. described the formation of visible light active vanadate/TiO<sub>2</sub> nanocomposites with increased "photocatalytic activities". Visible light response of titania was increased by grafted vanadate. In BiVO<sub>4</sub>/TiO<sub>2</sub> heterostructures charge transfer occurred from BiVO<sub>4</sub> to TiO<sub>2</sub> and facilitated degradation of non-sensitized dye where as in case of InVO<sub>4</sub>/TiO<sub>2</sub> heterostructure degradation of photosensitized dye was facilitated due to gradient charge transfer in order to avoid electron hole recombination. Rhodamine B degradation was conducted by vanadate/TiO<sub>2</sub> heterostructure and results showed remarkably enhanced degradation as compare to degradation in presence of TiO<sub>2</sub> (P-25). The increased photocatalytic activity of vanadate/TiO<sub>2</sub> heterostructure was because of excitation of vanadate causing charge transfer [64].

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Cao et al. [65] synthesized BiOCl/m-BiVO heterostructure and studied its "photocatalytic activity" in visible region of solar spectrum for breakdown of acid orange II, Rhodamine B and methyl orange. BiOCl/m-BiVO<sub>4</sub> showed remarkably increased photocatalytic dye degradation compared with pure BiOCl, m-BiVO<sub>4</sub>, P25 and N-TiO<sub>2</sub> due to the development of heterostructure of BiOCl and m-BiVO4 that separated charge carriers.



Figure 1.8: Schematic illustration of semiconductor heterostructure

#### 1.5.5 Co-catalyst Assisted Semiconductor-Based Photocatalyst

Co-catalysts play vital part in improving the "photocatalytic activity". Electron-hole recombination is reduced by the generation of "Schottky barrier" amongst the co-catalyst and semiconductor photocatalyst and results in enhanced "photocatalytic activity". Noble metals like platinum, gold, palladium, rhodium and silver are mostly employed as a co-catalyst with semiconductor-based photocatalytic material. **Fig. 1.9** schematically illustrates the mechanism of pollutant degradation by co-catalyst assisted semiconductor based photocatalytic activity is mainly influenced by the valence state and size of particles of co-catalyst. In case of Pd/BiVO<sub>4</sub> photocatalyst [66], the improved "photocatalytic activity" for breakdown of methyl orange was observed because of electron transfer from BiVO4 to PdO and sufficient charge separation, The electron transfer from semiconductor to co-catalyst is facilitated by the alignment of "Fermi level" of metal nanoparticles which usually lies below the conduction band minimum of the semiconductor photocatalysts. However, Pd/BiVO<sub>4</sub> photocatalysts with less or more than 1 wt% Pd showed lower activities. This might be due to the recombination of charge carriers on PdO or due to agglomeration of PdO particles on the surface of BiVO<sub>4</sub> when

present in large amount. Zhao et al. [67], examined the impact of Pt as a co-catalyst on photocatalytic activity of TiO<sub>2</sub> for sulforhodamine B breakdown. TiO<sub>2</sub>/Pt showed superior photocatalytic activity compared to pure P25 TiO<sub>2</sub>. Molecular oxygen scavenges an electron from Pt, which acts as an electron sink, and produce superoxide radical anion  $(O_2^{-})$  which transform into OH<sup>+</sup>. OH<sup>+</sup> causes the degradation of sulforhodamine-B.





#### 1.6 Typical Materials used as Photocatalysts

As early as 1972, researchers developed semiconductors for photocatalytic dye degradation like "metal chalcogenides, metal oxides, carbon nitrides, metal nitrides and III to V compounds". Important semiconductor photocatalysts are highlighted here.

#### **1.6.1** Metal oxides as a Photocatalyst

Metal oxide like zinc, titanium, cadmium, cerium, vanadium, chromium and tin are widely used for organic pollutant breakdown because of their capacity to absorb sunlight [68]. Metal oxides are activated by either visible light, ultra violet light or by combination of both. As a result of absorption of light electrons absorb energy and transfer to conduction band from valence band leaving behind holes. These photogenerated charge carriers are responsible for redox reaction and mainly produce two different radical species i-e OH radicals by oxidizing  $OH^-$  anions and  $O^{2-}$  radicals by reducing  $O_2$ . These radicals help to degrade harmful chemicals into less toxic materials or carbon dioxide and

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water. Catalyst scavenges photogenerated electrons and produce active oxygen species when photocatalytic oxidation takes place [69].

**Photocatalytic Activity of ZnO and TiO<sub>2</sub>:** Sakthivel et al. investigated the "photocatalytic activity" of ZnO and TiO<sub>2</sub> in order to degrade azo dye. In their research studies, they related the photocatalytic performance of ZnO and TiO<sub>2</sub> with each other and with other catalyst by keeping same reaction parameters. Both photocatalysts completely degrade diazo dye in sunlight and produce carbon dioxide, nitrates, water, sulphates, ammonia and chloride as byproducts. However, ZnO showed complete degradation of dye in 360 minutes while TiO<sub>2</sub> showed in 420 minutes. Comparison of photocatalytic activities of different photocatalysts showed that ZnO absorb broad spectrum of light and is most active catalyst for acid brown 14 degradation [70]. TiO2 and ZnO are used to degrade different organic contaminants because of their photosensitivity, ideal band gap and stability [71, 72].

#### **1.6.2 Ternary Metal Oxide Semiconductors as a Photocatalyst**

Ternary metal oxide semiconductors possess sharp absorption edges and hence are different from common metal oxides. In ternary metal oxides hybridization of oxygen (2p) orbital occur with the orbitals of transition metals and results in small band gap as compare to metal oxides [73].

**Photocatalytic Activity of Bismuth Vanadate BiVO4:** Guo et al. examined "photocatalytic activity" of BiVO4. Band gap of BiVO4 is 2.4 eV. BiVO4 having different morphologies as well as different crystal structures was synthesized by hydrothermal method using bismuth nitrate penta hydrate and ammonium vanadate as precursors. Different crystal structures of BiVO4 were synthesized by optimizing pH, time and molar ratios. Monoclinic scheelite BiVO4 having flower-like morphology were found to have greater photocatalytic reactivity towards RB and MB dye degradation which showed that crystal structure and morphology affects the photocatalytic reactivity [74].

Gotic et al. investigated the synthesis of  $BiVO_4$  by Hydrothermal and wet precipitation routes at room temperature. They compared the morphologies of  $BiVO_4$  synthesized by solid-state method at 700<sup>o</sup>C and at room temperature. Results showed that samples

prepared at high temperature were more crystalline with less defects than those synthesized under mild conditions through wet precipitation [75].

**Photocatalytic Activity of Zinc Vanadate:** Pei et al. synthesized zinc vanadate nanorods by hydrothermal method. Zinc vanadate showed enhanced photocatalytic activity and completely degrades methylene blue when irradiated with sunlight for 4 hours. Band gap of nanorods of Zn vanadate was found to be 2.76 eV, which shows more light absorption capacity as compared to hybrid zinc vanadate with the band gap 3.10 eV [76].

Zinc vanadate nanostructures were also prepared by Mazloom et al. by simple precipitation method by using zincnitrate tetrahydrate as a precursor, SDS as surfactant and ethylene diamine as a pH stabilizer. These nanostructures were used to photocatalytically degrade "eosin Y and methylene blue" [77]. Mondal et al. prepared cubooctahedral  $Zn_3V_2O_8$  by using zinc sulphates and ammonium vanadate as a precursor. Synthesis was carried out by first stirring and then heating precursors at  $70^{\circ}C$  on water bath. "Zn<sub>3</sub>V<sub>2</sub>O<sub>7</sub>(OH)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>" was first made. Then heating "Zn<sub>3</sub>V<sub>2</sub>O<sub>7</sub>(OH)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>"at 500<sup>o</sup>C cubooctahedral Zn<sub>3</sub>V<sub>2</sub>O<sub>8</sub> was obtained. Zn<sub>3</sub>V<sub>2</sub>O<sub>8</sub> exhibited enhanced photocatalytic activity due to its unique morphology and resulted in efficient dye degradation, leaving behind "Zn<sub>3</sub>V<sub>2</sub>O<sub>7</sub>(OH)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>" and NH<sub>4</sub>VO<sub>3</sub>[78].

#### 1.6.3 Metal Chalcogenides as a Photocatalysts

Metal chalcogenides semiconductors consists of at least one chalcogen anion i-e group VI-A elements except oxygen and electropositive element. Among all the chalcogenides ZnSe and ZnTe are extensively used for photocatalytic dye degradation and water splitting. Band gap of ZnSe is 2.7 eV and is most commonly used because of its wide spread applications in biomedical sensors, light emitting diodes, photovoltaic solar cells and as photocatalyst [79].

**ZnTe as a Photocatalyst:** Yadong Li, Yi Ding and Zhaoyu Wang described aneasy method for the synthesis of ZnTe nanorods by solvothermal method. They synthesized the product with 80-90% yield by using hydrazine hydrate as a solvent. Zn and Te were used as precursors. Effect of solvent was examined on the reaction progress, which

showed that the best crystalline nanorods could be obtained by using hydrazine hydrate, which acts as an electron donor as well as an electron transfer medium [80].

Ehsan et al. synthesized "hollow and mesoporous ZnTe microspheres" by hydrothermal process and studied the influence of various parameters like pH, temperature, NaOH on the growth mechanism of these microspheres. They also investigated the use of ZnTe microspheres for reduction of  $CO_2$  into  $CH_4$  in sunlight with solar energy conversion efficiency of 0.072% [81].

**ZnSe as a Photocatalyst:** ZnSe show enhanced photocatalytic activity for organic pollutant degradation. Feng Cao et al. demonstrated the use of ZnSe for dye degradation in 2008. They prepared wurtzite 3D flower like ZnSe nanostructures by hydrothermal method and used them successfully for photocatalytic degradation of methylene blue and ethyl violet. Feng et al. also showed that morphology play important role in controlling the efficiency of photocatalytic. Flower like nanostructures of ZnSe have wide range of applications because of their mono dispersity, large surface to volume ratio, easy recycling and high photocatalytic activity [82]. Zhang et al. synthesized hollow ZnSe microspheres by environment friendly hydrothermal method and studied its use for photocatalytic degradation of methyl orange [83]. Feng et al. prepared hexagonal wurtzite nanoparticles and nano sheets by facile solvothermal method and showed that by controlling the amount of ethylenediamine morphology can be controlled. Nanosheets of ZnSe exhibited enhanced "photocatalytic activity" in comparison of nanoparticles of ZnSe to degrade Rhodamine B in presence of ultraviolet light [84].

#### 1.7 Semiconductor Heterostructures with Enhanced Photocatalytic activity

During last three decades, semiconductor photocatalysis has made massive progress but also encounter large amount of unsettled complications. Main reasons, which decrease the photocatalytic activity of semiconductor photocatalysts, are,

- Recombination of charge carriers, which results in slow reaction rate.
- Low solar energy utilization like titania only absorb solar energy in ultraviolet wavelength range which constitute only 4-5 % of the light spectrum.
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Therefore in order to increase the capacity of photocatalysts to absorb light a great deal of efforts had been made and following methods were discovered,

- "Formation of semiconductor heterostructures" [85, 86]
- "Codeposition of noble metals"[87, 88]
- ➤ "Doping"[89, 90]
- "Surface hybridization"[91, 92]
- "Coupling with other technology"[93]

Of all these, development of semiconductor heterostructure is most efficient method for increasing the light absorption capacity and to avoid charge recombination. Semiconductor heterostructures are divided into three types on the basis of band gaps and electronic affinity of semiconductors. These include "type I, type II and type III semiconductor heterostructures" [94]. Band alignments of these three types of semiconductor heterostructure are shown in **Fig. 1.10**,



Figure 1.10: Schematic illustration of types of semiconductor heterostructures based on band gap

Generally, semiconductors with broad "band gap" absorb ultraviolet light but are photoelectrochemically stable as compare to semiconductors with constricted "band gap" which works under visible light and show photo-corrosion. In order to avoid photo corrosion usually semiconductors with narrow band gap are coated by semiconductors with wide band gap. This not only helps to increase photo stability of semiconductors but also increase their light absorption capacity. Zinc oxide (ZnO)/Zinc Selenide (ZnSe) Heterostructure with Enhanced Photocatalytic Activity: Cho et al. prepared ZnO/ZnSe nanocomposites for use in wide range of solar spectrum range. ZnO can absorb only ultraviolet light that account for ~4% of solar spectrum. In order to enhance the light absorption capacity of ZnO and to improve its photocatalytic activity Cho et al. prepared the heterostructure of ZnO with ZnSe. ZnO (band gap: 3.2 eV) was combined with ZnSe (band gap: 2.67 eV). Formation of heterostructure increased the photocatalytic activity as compared to isolated ZnO photocatalyst [95].

Bismuth Vanadate (BiVO<sub>4</sub>) and Cerium dioxide (CeO<sub>2</sub>) Nanocomposites with Enhanced Photocatalytic Activity: Wetchakun et al. prepared BiVO<sub>4</sub>/CeO<sub>2</sub> nanocomposites by combining homogeneous precipitation method with hydrothermal method. BiVO<sub>4</sub> was used as a sensitizer due to its contracted band gap (2.51 eV) as compared to pure CeO<sub>2</sub> with band gap of 2.76 eV. Loading of BiVO4 on CeO2 shifts the absorption tendency towards visible light and as a result enhanced photocatalytic activity was observed. Band gap energy of BiVO<sub>4</sub>/CeO<sub>2</sub> nanocomposites in all molar ratios was approximately 2.4 eV, which was lower than pure BiVO<sub>4</sub> and CeO<sub>2</sub>. Different molar ratios of BiVO<sub>4</sub> and CeO<sub>2</sub> showed effect on dye degradation efficiency of nanocomposites. Best photocatalytic activity was shown by 0.6:0.4 mol ratio of BiVO<sub>4</sub>/CeO<sub>2</sub> for degradation of methylene orange and methylene blue [96].

Zinc Selenide/Nitrogen Doped Graphene Nanocomposites with Enhanced Photocatalytic Activity: Chen et al combined ZnSe with nitrogen-doped graphene (NG). They synthesized ZnSe/nitrogen doped graphene composites by hydrothermal method using [ZnSe](DETA)<sub>0.5</sub> and graphene nanosheets as a precursor. The resulting composites showed remarkable photocatalytic activity and efficiently degraded "methyl orange dye" when irradiated with visible light. These composites can also be used in fuel cells, for storage of energy and as a sensor [97].

#### **1.8 Factors Affecting Photodegradation**

Photocatalytic degradation of "organic pollutants" is best method for treating waste water from different industries using semiconductors as catalysts like ZnO, ZnSe, TiO<sub>2</sub>,  $ZnVO_4$ , ZnS, CdS,  $Fe_2O_3$  and  $SrTiO_3$ . However, there are number of factors, which influence the activity of these semiconductor photocatalysts [98-100]. These factors include,

### **1.8.1 Effect of Photocatalyst Preparation Conditions and Size**

Nanocatalyst prepared by different methods show different photocatalytic activity. Reaction conditions play major role in controlling the activity of photocatalyst. For example, rutile  $TiO_2$  prepared under laboratory conditions showed good catalytic activities as compare to same rutile  $TiO_2$  catalyst prepared at high temperature. Size of the catalyst is also influenced by the conditions during preparation. Small sized catalysts show good photocatalytic activity but size control results in agglomeration of particles. This marks in small surface area availability for organic pollutant degradation and lowers the catalyst's efficiency. Agglomeration can be controlled by using surfactants in sol gel method.

Size of catalyst defines the distance travelled by positive and negative charge carriers towards site of reaction on catalyst surface. Large sized catalyst particles increase the chances of recombination and results in low photocatalytic activity. Addition of nanoparticles to semiconductor photocatalyst increases its photocatalytic activity [108]. With the decrease in size of nanoparticles added in semiconductor photocatalytic activity of semiconductor increases as the small sized particles act as a sink for electrons and retard charge recombination [109]. On the other hand, large sized particles trap both holes and electrons and act as recombination site. TiO<sub>2</sub> showed enhanced photocatalytic activity when sensitized with Ag nanoparticles and it highly depends on the size distribution of silver nanoparticles [110-112]. V. Subramanian found out that TiO<sub>2</sub> doping with small sized gold (Au) nanoparticles also enhanced its photocatalytic activity. It is noted that loading of 5nm Au nanoparticles showed better activity than 8nm sized Au nanoparticles [116].

## **1.8.2 Effect of Initial Organic Compound Concentration**

High concentration of organic pollutants at the start of degradation process retards the activity of photocatalyst. This results due to the adsorption of large amount of organic

compound on catalyst surface, which hinders formation of hydroxyl radical. Also escalating organic compounds initial concentration drops the performance of photocatalyst by reducing the electron transfer to conduction band.

#### **1.8.3 Effect of Dopant Concentration on Photocatalytic Activity**

Doping of photocatalyst enhances its activity by

- ✤ Electron trapping
- ✤ Narrowing band gap
- Formation of impurity energy levels
- Providing large surface area for adsorption of organic pollutants
- Oxygen vacancies

All these factors result in enhanced "photocatalytic activity" of catalyst even under visible light. However, when optimum concentration of dopant is disturbed photocatalytic activity is decreased due to decrease in surface active sites for photocatalysis and increase in electron hole recombination.

Kohtani et al. compared the photocatalytic activity of BiVO<sub>4</sub> and Ag doped BiVO<sub>4</sub>. Results showed the enhanced photocatalytic activity of Ag doped BiVO<sub>4</sub> as compared to BiVO<sub>4</sub> semiconductor [115]. L.Ge synthesized Pd doped BiVO<sub>4</sub> in order to increase photocatalytic activity and charge separation. Results showed that by loading 1.0wt% Pd on BiVO<sub>4</sub> 100% degradation of methyl orange occurs under visible light irradiation for 15 hours [66]. Also doping of TiO<sub>2</sub> with Au nanoparticles enhanced its photocatalytic activity [116].

## 1.8.4 Effect of Catalyst Loading on Photocatalytic Activity

Presence of large amount of catalyst results in high rate to degrade organic effluents because of the availability of big surface area for hydroxyl radical production [101]. However, when optimum limit of catalyst exceed, light scattering is increased also, agglomeration occur and photocatalytic activity is decreased [102]. Optimum limit depends on the intensity of light used, characteristics of catalyst and on operational parameters of reactor.

C. Mondal et al. showed the increase in methylene blue degradation with an increase in concentration of  $Zn_3V_2O_8up$  to certain optimum value after which decrease is observed due to light scattering [78]. Pardeshi and Patil examined the influence of photocatalyst amount on phenol photocatalytic degradation efficiency. Increasing the quantity of catalyst results in increase of active sites for phenol adsorption and hence photocatalytic degradation was improved. Optimum concentration of ZnO to degrade maximum amount of phenol was found to be 2.5 mg/L [103]. Lathasree et al. also investigated the consequence of photocatalyst amount to degrade phenols [104].

Venkatachalam et al. [105] investigated that optimum concentration of catalyst for maximum "photocatalytic degradation" of 4-ChloroPhenol was 2 g/L. Beyond this concentration photocatalytic degradation efficiency of catalytic material decreased due to agglomeration and light scattering effect. X. Zu et al. studied the effect of TiO<sub>2</sub> concentration on photocatalytic oxidation of aqueous ammonia and nitrite. Their experimental results showed that at low TiO<sub>2</sub> concentration (~<0.2g/L) the photocatalytic oxidation is very slow due to light absorbance and scattering by catalyst. With increase in concentration of TiO<sub>2</sub> from 0.2g/L the photocatalytic oxidation rate increases and showed maximum activity at concentration 3g/L. Increase in amount of catalyst beyond this value will decrease photocatalytic activity due to blockage of UV transmittance to the interior of reactor [117].

# 1.8.5 Effect of pH on Photocatalytic Activity

Dye solution pH balance is important in controlling the photocatalytic activity of synthesized catalysts. Adsorption and dissociation of pollutants is influenced by pH. Some researchers claimed that faster photocatalytic reactions take place in alkaline media as compare to acidic media [106]. Some are of the view that over a wide range of pH speed of reaction remains unchanged [107]. Many believed that increase in pH beyond isoelectric point of catalyst results in negatively charged surface of catalyst and adsorption of cationic molecules. Also, increase in pH results in production of hydroxyl ions and suppression of photocatalytic activity due to competition between hydroxyl ion and organic compounds for adsorption on catalyst surface. Optimum pH concentration has to be fixed for different organic effluents.

Li et al. studied the effect of change in pH on photocatalytic activity of  $TiO_2$  for Orange II degradation. They observed that complete oxidation of dye takes place at pH 2.3 and color was removed at pH 11.5 and explained the mechanism of action of electrons in dye degradation by UV/TiO<sub>2</sub> [118].

# **1.9 Scope of This Work**

In order to deal with a variety of environmental issues due to organic pollutants, there is a growing concern to establish a sustainable solution for enhancing the water quality. The scope of this research work is to save the earth from hazardous organic pollutants by synthesizing photocatalyst with enhanced photocatalytic activity for dye degradation.

Metal vanadates have been found to be an attractive class of inorganic nanomaterials that have received substantial attention as complex oxides because of their potential use for photocatalytic dye degradation. Zinc vanadate has gained considerable attention amongst all metal vanadates since zinc is of low cost, abundantly available and environment friendly metal. Also it has wide spread applications such as photocatalysis, lithium ion batteries and luminescence [77].

In present work, we have synthesized  $Zn_3V_2O_8$  and series of novel  $Zn_3V_2O_8$  modified metal chalcogenides photocatalysts. To the best of our knowledge for the first time n-type ZnSe has been combined with  $Zn_3V_2O_8$ to form a nanocomposites system. Physical composites with different weight percentage of ZnSe (0% (bare  $Zn_3V_2O_8$ ), 25%, 50%, 75% and 100% ZnSe) were prepared and their efficiency for photocatalytic dye degradation has been studied. Formation of heterostructure enhanced the photocatalytic activity of  $Zn_3V_2O_8$ -ZnSe based nanocomposites up to 40 minutes but after that decrease in activity of heterostructure as compared to bare ZnSe was observed. The reason for this decreased activity might be due to the presence of both cubic and hexagonal phases in assynthesized ZnSe. Also novel  $Zn_3V_2O_8/ZnTe$  nanocomposites were synthesized successfully and their photocatalytic activity will be checked in future.

#### **References:**

[1] L. M. S. Colpini and H. J. Alves, Dye and Pigments, 2008, 79, 525-529.

[2] T. Robinson, G. McMullan, R. Marchant and P. Nigam, Bioresource Technology, **2001**,77, 247-225.

[3] M. I. Qureshi, A. M. Rasli and K. Zaman, Journal of Cleaner Production, **2015**, 112, 3657-3666.

[4] World energy resources full report 2016

[5] A. Wellburn, Air Pollution And Acid Rain: The Biological Impact. New York: Wiley, 1988

[6] F. Rahman, Journal of Textile Science and Engineering, 2016, 6, 242.

[7] A. K. Mishra and S. Ramaprabhu, Chemical Engineering Journal, **2010**,162, 1026-1034.

[8] V. Karthik, K. Saravana, P. Bharathi, V. Dharanya and C. Meiaraj, **2014**, Journal of Chemical and Pharmaceutical Sciences, *7*, 301-307.

[9] R. Christie, Colour Chemistry. Cambridge, United Kingdom, The Royal Society of Chemistry, 2001.

[10]VS. Houk, Mutation Research, 1992, 277, 91-138.

[11] AB Dos Santos , FJ Cervantes , JB Van Lier , Bioresourse Technology, 2007, 98, 2369-2385.

[12] R. Rajamanickam and S. Nagan, Journal of Environmental Science and Engineering,2010, 52, 315-320.

[13] HD. Beyene, International Journal of Environmental Monitoring and Analysis, 2014, 2, 347-353.

[14]T. Robinson, G. McMullan and R. Marchant, Bioresource Technology, **2001**, 77, 247-255.

[15]M. Kashefiasl and F. Bahrami, Bulletin of Georgian National Academy of Sciences, **2014**, 8.

[16] E. Forgacs, T. Cserhati and G. Oros, Environment International, 2004, 30, 953-971.

[17] S. K. Sharma and R. Sanghi, Advances in Water Treatment and Pollution Prevention, **2012** 

[18] A. Mittal, Water Today, 2011

[19]K. Vijayaraghavan, Yeoung-Sang Yun, Biotechnology Advances, 2008, 26, 266-291.
[20] K. Y. Show and D. J. Lee, Biological Treatment of Industrial Effluents, 2017, 205-230.

[21] Yi Jing Chan, Mei Fong Chong, Chung Lim Law and D. G. Hassell, Chemical Engineering Journal, **2009**, 155, 1-18.

[22] Frank P. van der Zee and S. Villaverde, Water Research, 2005, 39, 1425-1440.

[23] A. R. Tehrani- Baghr, N. M. Mahmoodi and F. M. Menger, Desalination, 2010, 260, 34-38.

[24] S. Liakou, S. Pavlou and G. Lyberatos, Water Science and Technology, **1997**, 141, 279-286.

[25] O. Karahan, H. Dulkadiroglu, I. Kabdasli, S. Sozen, F. GermirliBabuna and D. Orhon, Environmental Technology, 2002, 23, 1325-1336.

[26] A. Kumar, P. Chaudhary and P. Verma, Global Journal of Environmental Research,2011, 5, 46-52.

[27] D. Bahnemann, Solar Energy, 2004, 77, 445-459.

[28] M. Schiavello (Ed.), Photocatalysis and Environment, Kluwer Academic Publishers, Dordrecht, **1988**.

[29] N. Serpone, E. Pelizzetti (Eds.), Photocatalysis, Fundamentals and Applications, Wiley, New York, **1989**.

[30] S. H. S. Chan, T. Y. Wu, J. C. Juan and C. Y. The, Journal of Chemical Technology and Biotechnology, **2011**, 86, 1130-1158.

[31] E. Pelizzetti, C. Minero, Comments on Inorganic Chemistry, 1994, 15, 297-337.

[32] A. B. Djurisic, Y. H. Leung and A. M. C. Ng, Materials Horizons, 2014, 1, 400-410.

[33] S. Malato, J. Blanco, A. Vidal and C. Richter, Applied Catalysis B: Environmental, **2002**, 37, 1-15.

[34] G. Palmisano, ab V. Augugliaro, a M. Pagliarob and L. Palmisano, Chemical Communications, **2007**, 3425-3437.

[35] Robertson, P. K. J., Bahnemann, D. W., Robertsom, J. M. C and Wood, Handbook of Environmental Chemistry, **2005**, 2.

[36] E. S. Elmolla and M. Chaudhuri, Journal of Hazardous Materials, **2010**, 173, 445-449.

[37] Jean-Marie Herrmann, Catalysis Today, 1999, 53, 115–129.

[38] A. A. Shaw, L. A. Wainschel and M. D. Shetlar, Photochemistry and Photobiology, **1992**, 55, 647-56

[39] A. Rabenau, AngewandteChemie International Edition, **1985**, 24, 1026-1040.

[40] F. Branda, Advances in Nanocomposites-Synthesis, Characterization and Industrial Applications, **2011**.

[41] H. R. Ghorbani, F. P. Mehir H. Pazoki and B. M. Rahmani, Oriental Journal of Chemistry, **2015**, 31, 1219-1221.

[42] C. C. Chena, B. Yua, P. Liub, J. F. Liua and L. Wanga, Journal of Ceramic Processing Research, **2011**, 12, 420-425.

[43] K. S. Suslick and D. J. Flannigan, Annual Review of Physical Chemistry, 2008, 59, 659.

[44] K. S. Suslick, Science, 1990, 247, 1439.

[45] J. Li and N. Wu, Catalysis Science and Technology, 2015.

[46] A. L. Linsebigler, G. Q. Lu and J. T. Yates, Chemical Reviews, 1995, 95, 735-758

[47] D. L. Greenaway and G. Harbeke, Optical Properties and Band Structure of Semiconductors: International Series of Monographs in The Science of The Solid State, **2015**, 1, Elsevier.

[48] H. Tong, S. X. Ouyang, Y. P. Bi, N. Umezawa, M. Oshikiri and J. H. Ye, Advanced Materials, **2012**, 24,229

[49] S. Boujday, F. Wunsch, P. Portes, J. F. Bocquet and C. C. Justin, Solar Energy Materials and Solar Cells, **2004**, 83, 421

[50] N. Lubick and K. Betts, Environmental Science and Technology, 2008, 42, 3910

[51] J. Yao and C. Wang, International Journal of Photochemistry, 2010, 2010, 6

[52] A. Dawson and P. V. Kamat, The Journal of Physical Chemistry B, 2001, 105, 960

[53] S. S. M. Bhat and N. G. Sundaram, 2015, New Journal of Chemistry, 39, 3956-3963

[54] Photocatalytic Activity of Ag, CuO, NiO and ZnO Nanoparticles

[55] L. Z. Pei, N. Lin, T. Wei, H. D. Liu and H. Y. Yu, Journal of Alloys and Compounds, **2015**, 631, 90-98

- [56] Y. Liu, X. Chen J. Li and C. Burda, Chemosphere, 2005, 61, 11
- [57] A. Zhang and J. Zhang, Journal of Hazardous Materials, 2010, 173, 265-272
- [58] A. Zhang and J. Zhang, Applied Surface Science, 2010, 256, 3224-3227
- [59] Yuan, Qing, L. Chen, M. Xiong, J. He, S. L. Luo, C. T. Au and S. F. Yin, Chemical Engineering Journal, **2014**, 255, 394-402
- [60] Kiantazh, Fariba and A. H. Yangieh, Solid State Sciences, 2015, 49, 68-77
- [61] Jiang, Jing, X. Zhang, P. Sun and L. Zhang, The Journal of Physical Chemistry C, 2011, 42, 20555-20564
- [62] Zhou, Weijia, H. Liu, J. Wang, D. Liu, G. Du and J. Cui, ACS Applied Materials and Interfaces 2, **2010**, 8, 2385-2392
- [63] Cao, Tieping, Y. Li, C. Wang, C. Shao and Y. Liu, Langmuir, 2011, 6, 2946-2952
- [64] Y. Min, K. Zhang, Y. C. Chen and Y. G. Zhang, Chemical Engineering Journal, **2011**, 175, 76-83
- [65] J. Cao, C. Zhou, H. Lin, B. Xu and S. Chen, Applied Surface Science, **2013**, 284, 263-269
- [66] Lei Ge, Materials Chemistry and Physics, 2008, 107, 465-470
- [67] W. Zhao, C. Chen, X. Li and J. Zhao, Journal of Physical Chemistry B, 2002, 106, 5022-5028
- [68] Adil and Al-Mayouf, Journal of Saudi Chemical Society, 2015.
- [69] H. Wang, L. Zhang, Z. Chen, J. Hu, S. Li, Z. Wang, J. Liu and X. Wang, Chemical Society Reviews, **2014**, 43, 5234-5244.
- [70] S. Sakthivela, B. Neppolianb, M.V. Shankarb, B. Arabindoob, M. Palanichamyb andV. Murugesanb, Solar Energy Materials and Solar Cells, 2003,77, 65-82.
- [71] S. Sakthivel, B. Neppolian, M. Palanichamy, B. Arabindoo, V. Murugesan, Indian Journal of Chemical Technology, **1999**, 6, 161.
- [72] S. Sakthivel, B. Neppolian, B. Arabindoo, M. Palanichamy, V. Murugesan, Journal of Scientific and Industrial Research, **2000**, 59, 556.
- [73] A. Kudo, H. Kato, I. Tsuji, Chemistry Letters, 2004, 33, 1534-1539.
- [74] Y. Guo, X Yang, F. Ma, K. Li, L. Xu, X. Yuan and Y Guo, Applied Surface Science, 2010, 256, 2215-2222.

[75] M. Gotic, S. Music, M. Ivanda and M. Soufek, Journal of Molecular Structure, **2005**, 744-747, 535-540.

[76] L. Z. Pei, N. Lin, T. Wei, H. D. Liu and H. Y. Yu, Journal of Alloys and Compounds, 2015, 631, 90-98.

[77] F. Mazloom, M. M-Arani, M. G-Arani and M. S-Niasari, Journal of Molecular Liquids, **2016**, 214, 46-53.

[78] C. Mondal, M. Ganguly, A. K. Sinha, J. Pal, R. Sahoo and T. Pal, Crystal Engineering Communication, **2013**, 15, 6745-6751.

[79] M. Bouroushian, ElectroChemistry of Metal Chalcogenides, 2010.

[80] Y. Li, Yi Ding and Z. Wang, Advanced Materials, 1999, 11

[81] M. F. Ehsan, M. N. Ashiq and T. He, Royal Society of Chemistry, 2015, 5, 6186.

[82] F. Cao, W. Shi, L. Zhao, S. Song, J. Yang, Y. Lei, and H. Zhang, Journal of Physical Chemistry, 2008, 112, 17095-17101.

[83] I. Zhang, H. Yang, X. Xie, F. Zhang and L. Li, Journal of Alloys and Compounds, **2009**, 473, 65-70.

[84] B. Feng, J. Yang, J. Cao, L. Yang, M. Gao, M. Wei, H. Zhai, Y. Sun and H. Song, Journal of Alloys and Compounds, **2013**, 555, 241-245.

[85] R. Wang, G. Jiang, Y. Ding, Y. Wang, X. Sun, X. Wang and W. Chen, ACS Applied Material and Interfaces, **2011**, *3*, 4154-4158.

[86] H. Ho and J. C. Yo, Journal of Molecular Catalysis A: Chemical, **2006**, 247, 268-274.

[87] B. Kraeutler and A. J. Bard, Journal of American Chemical Society, **1978**, 100, 4317-4318.

[88] V. Subramanian, E. E. Wolf and P. V. Kamat, Journal of American Chemical Society, **2004**, 126, 4943-4950.

[89] R. Asahi, T. Morikawa, T. Ohwaki, K. Aoki and Y. Taga, Science, 2001, 293, 269-271.

[90] P. V. Kamat, Pure and Applied Chemistry, 2002, 74, 1693-1706.

[91] Y. Wang, R. Shi, J. Lin and Y. Zhu, Applied Catalysis B, 2010, 100, 179-183.

[92] Y. Wang, J. Lin, R. Zong, J. He and Y. Zhu, Journal of Molecular Catalysis A: Chemical, **2011**, 349, 13-19.

[93] Y. Wang H. Zhu, Y. Xu and H. Wang, Journal of Solid State Chemistry, 2011, 184, 1433-1438.

[94] Y. Wang, Q Wang, X. Zhan, F. Wang, M. Safdar and J. He, The Royal Society Of Chemistry, **2013**.

[95] S. Cho, J. W. Jang, J. S. Lee and K. H. Lee, Nanoscale, 2012, 4, 2066.

[96] N. Wetchakun, S. Chaiwichain, B. Inceesungvorn, K. Pingmuang, S. Phanichphant, Andrew I. Minett and J. Chen, Applied Materials and Interfaces, **2012**, 4, 3718-3723.

[97] P. Chen, T-Y.Xiao, H-H. Li, J-J Yang, Z. Wang, H-B. Yao, and S-H. Yu, ACS Nano, **2012**, 6,712-719.

[98] C. M. So, M. Y. Cheng, J. C. Yu and P. K. Wong, Chemosphere, 2002, 46, 905-912.

[99] U. G. Akpan and B. H. Hameed, Journal of Hazardous Materials, **2009**, 170, 520-529.

[100] M. Sobana and M. Sawaminathan, Separation and Purification Technology, **2007**, 56, 101-107.

[101] Rauf, M.A. and S.S. Ashraf, Dyes and Pigments: New Research. Nova Science Publishers, Inc. **2009**, 70, 231-345.

[102] Sun,J., L. Qiao, S. Sun and G. Wang, Journal of Hazardous Materials, **2008**, 155, 312–319.

[103]Pardeshi, S.K. and A. B. Patil, Solar Energy, 2008, 82,700–705.

[104]Lathasree S., A. N. Rao, B. Siva Sankar, V. Sadasivam and K. Rengaraj, Catalysis, **2004**, 76, 235-246.

[105] N. Venkatachalam, M. Palanichamy and V. Murugesan, Journal of Molecular Catalysis A: Chemical, **2007**, 273, 177-185

[106] R. Terzian and N. Serpone, Journal of Photochemistry and Photobiology A: Chemical, **1995**, 89, 1633-1675

[107] N. N. Rao, A. K. Dubey, S. Mohanty, P. Khare, R. Jain and S. N. Kaul, Journal of Hazardous Materials, **2003**, 101, 301-314

[108] A.L. Linsebigler, G. Q. Lu and J. T. Yates Jr, Chemical reviews, 1995, 95, 735

[109] N. J-Renault, P. Pichat, A. Foissy and R. Mercier, Journal of Physical Chemistry, **1986**, 90, 2733

[110] F. Meng, Z. Sun, Material Chemistry and Physics, 2009, 118, 349

[111] T. Kodom, E. Rusen, I. Cslinescu, A. Mocanu, R. Fomoghi, A. Dinescu, A. Diacon and C. Boscomeal, Journal of Nanomaterials, **2014**, 8

[112] Xu, X. Xiao and F. Ren et al., Nanoscale Research Letters, 2012, 7

[113] C. Daraio and S. Jin, Synthesis and Patterning Methods for Nanostructures Useful for Biological Applications.

[114] X. –P. Wu, J. Gu, S. –M. Zhou, X. Y. Li, S, -L, Wang, L. Jin, H. Chen and J. –J. Shi, Journal of Alloys and Compounds, **2015**, 627, 166-173

[115] S. Kohtani, J. Hiro, N. Yamamoto, A. Kudo, K. Tokumur and R. Nakagaki, Catalysis Communications, **2005**, *6*, 185

[116] V. Subramanian, E. E. Wolf and P. V. Kamat, Journal of American Chemical Society, **2004**, 126, 4943-4950

[117] X. Zhu, S. R. Castleberry, M. A. Nanny and E. C. Butler, Environmental Science and Technology, **2005**, 39, 3784-3791

[118] G. T. Li, F. Z. Li, P. Y. Zhang, Y. X. Li and C. Yuan, Advanced Materials Research, **2010**, 113-116, 1878-1883

# **Chapter 2: Experimental**

#### Abstract

This chapter provides description of experimental details and chemicals used to synthesize photocatalysts for photocatalytic degradation of dye. It explains how composites of  $Zn_3V_2O_8$  and metal chalcogenides (ZnSe and ZnTe) were prepared using physical methods. At the end of this chapter, each of the techniques used to characterize the synthesized products and details of different equipment used for characterization have also been discussed.

#### 2.1 Chemicals

All the chemicals used in this project are of analytical grade and were used without further purification. Zinc acetate  $(Zn(CH_3COO)_2)$  (99.99%), Ammonium vanadate (NH<sub>4</sub>VO<sub>3</sub>) (99%), Sodium dodecyl sulfate (C<sub>12</sub>H<sub>25</sub>NaO<sub>4</sub>S) were purchased from Sigma Aldrich, Zinc powder (Zn) (>97%) from BDH, Selenium powder (Se) (>99.5%) from MERCK, Tellurium (99.8%) from Aldrich, Absolute ethanol, NaOH (99.99), KOH (85-100.5%) from Sigma Aldrich.

# 2.2 Synthesis of Bare Zinc Vanadate(Zn<sub>3</sub>V<sub>2</sub>O<sub>8</sub>) Nanostructures

 $Zn_3V_2O_8$  nanoparticles were synthesized by the reaction between  $Zn(CH_3COO)_2$ and  $NH_4VO_3$  with the molar ratio of 3:2 in the presence of SDS as a surfactant. In a typical experiment 275.22 mg of  $Zn(CH_3COO)_2$  (30 mM) was added in 50 mL of deionized water with the simultaneous addition of 0.5 g of SDS to this clear solution. An aqueous solution of  $NH_4VO_3$  was prepared in a separate beaker by adding 117 g (20 mM) of  $NH_4VO_3$  in 50 mL of deionized water. Then  $NH_4VO_3$ solution was added dropwise to the solution of  $Zn(CH_3COO)_2$  and SDS with constant stirring. Yellow suspension appeared gradually during the process. After 2 h of constant stirring NaOH solution was added drop wise to the suspension in order to adjust the pH to 8-9. The whitish precipitates of  $Zn_3V_2O_8$  were collected via centrifugation, and were washed several times with deionized water and finally with ethanol. The obtained  $Zn_3V_2O_8$  precipitates were dried at 70 <sup>o</sup>C under vacuum for 2 h, and then calcined at 600 <sup>o</sup>C for another 2 h. **Fig. 2.1** is the schematic illustration for the synthesis of  $Zn_3V_2O_8$ .



Figure 2.1: Graphical representation of Zn<sub>3</sub>V<sub>2</sub>O<sub>8</sub> synthesis

Anionic SDS surfactant plays a very important role in controlling the size and morphology of synthesized product.  $SO_4^-$  group of SDS form non-covalent linkage with the hydroxyl groups present on the  $Zn_3V_2O_8$  surface. As a result, product with controlled size is obtained as shown in **Fig. 2.2.** While in the absence of SDS agglomerated  $Zn_3V_2O_8$  particles are formed.



Figure 2.2: Schematic illustration of role of SDS surfactant on particle size distribution

# 2.3 Synthesis of Bare Zinc Selenide (ZnSe)

**Fig. 2.3** is schematic illustration of ZnSe nanoparticles synthesis. In a typical procedure 3 M KOH solution was prepared by adding 6.72 g of KOH in 40 mL of deionized water. Then 0.6 g of Zn powder and 0.39 g of Se powder were added in the clear solution of KOH and stirred until homogeneously mixed. Finally, the mixture was transferred into 100 mL of Teflon-lined stainless steel autoclave and was maintained at 200 °C for 2 h. The autoclave was allowed to cool in air at room temperature. Dirty green precipitates of ZnSe were collected via centrifugation followed by washing with deionized water and ethanol. Finally, the precipitates were dried at 80 °C under vacuum for 6 h.



Figure 2.3: Graphical representation of ZnSe nanoparticles synthesis

# 2.4 Synthesis of Bare Zinc Telluride (ZnTe)

First of all, 3 M KOH solution was prepared by adding 6.72 g of KOH in 40 mL of deionized water. Then 0.65 g of zinc powder and 0.63g of tellurium powder were added

in as-prepared KOH solution and stirred until mixture was homogenized. Finally, the mixture was transferred to 100mL Teflon-lined stainless steel autoclave and was retained at 120°C for 2 hours. The autoclave was allowed to cool in air at room temperature. Brown precipitates of ZnTe were obtained after centrifugation and washing with deionized water and ethanol. Precipitates were dried under vacuum at 70 °C for 7-8 h. Graphical representation of synthesis of ZnTe nanoparticles is shown in **Fig. 2.4**.



Figure 2.4: Graphical representation of ZnTe nanoparticles synthesis

## 2.5 Synthesis of Zn<sub>3</sub>V<sub>2</sub>O<sub>8</sub>-ZnSe and Zn<sub>3</sub>V<sub>2</sub>O<sub>8</sub>-ZnTe Nanocomposites

Physical composites of  $Zn_3V_2O_8$ -ZnSe and  $Zn_3V_2O_8$ -ZnTe were prepared by taking different amounts of obtained  $Zn_3V_2O_8$ , ZnSe and ZnTe with the respective molar ratio as shown in **Table 2.1.** Each composite was prepared by grinding precursors for half an hour using agate mortar and pestle.

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	A mount of	Amount of	Amount of
Molor Datio	Amount of	Amount of	Amount of
	Zn3V2O8(g)	ZnSe (g)	ZnTe (g)
Zn <sub>3</sub> V <sub>2</sub> O <sub>8</sub> /ZnSe 3:1	187.5	62.5	-
Zn <sub>3</sub> V <sub>2</sub> O <sub>8</sub> /ZnSe 1:1	125	125	-
Zn <sub>3</sub> V <sub>2</sub> O <sub>8</sub> /ZnSe 1:3	62.5	187.5	-
Zn <sub>3</sub> V <sub>2</sub> O <sub>8</sub> /ZnTe 3:1	187.5	-	62.5
Zn <sub>3</sub> V <sub>2</sub> O <sub>8</sub> /ZnTe 1:1	125	-	125
Zn <sub>3</sub> V <sub>2</sub> O <sub>8</sub> /ZnTe 1:3	62.5	-	187.5

 $\label{eq:constraint} \begin{array}{l} \textbf{Table 2.1:} \ \text{Molar ratio and amount of } Zn_3V_2O_8, \ \text{ZnSe and } Zn_3V_2O_8/\text{ZnSe and } \\ Zn_3V_2O_8/\text{ZnTe nanocomposites.} \end{array}$ 

# 2.6 Characterization Techniques

The as-synthesized semiconductor photocatalysts have been characterized by different techniques to investigate their crystal structure, surface functional groups, morphology, size, composition and band gap. A Rigaku diffractometer with Cu-K $\alpha$  radiation equipped with graphite monochromator was used to analyze the crystal structure of as-synthesized products. XRD patterns were entered in the 2 $\theta$  range of 10<sup>0</sup>-80<sup>0</sup> with a step size of 0.05<sup>0</sup> and time count of 1 second. Morphology and composition of as-synthesized product was analyzed by Hitachi S4800 field emission scanning electron microscopy (FESEM) with energy dispersive X-ray spectrometer (EDX). A lambda 750 UV/Visible spectrophotometer with 200-800 wavelength range and BaSO<sub>4</sub> as a reference was used for collecting UV-visible diffuse reflectance spectra.

**Photocatalytic Activity:** Photocatalytic activities of ZnSe, Zn<sub>3</sub>V<sub>2</sub>O<sub>8</sub> and ZnSe/ Zn<sub>3</sub>V<sub>2</sub>O<sub>8</sub> nanocomposites (with varying amount of ZnSe i.e. 25%, 50% and 75%), were investigated by irradiating aliquot with ultraviolet as well as visible light for congo red degradation at room temperature. 3000 W Xe arc lamp (PLS-SXE300, Beijing Trusttech Co. Ltd.) was used as a source of light for carrying out congo red degradation. Lamp was placed 15 cm above the conical flask of 250 mL having 75 ppm of congo red in dark. Two blank experiments, one with congo red solution and light and another with congo red solution and each catalyst, were performed. Results showed no loss of spectral intensity after 1 h continuous irradiation of congo red solution without catalyst. Similarly, no change in intensity was observed when dye solutions with ZnSe, Zn<sub>3</sub>V<sub>2</sub>O<sub>8</sub> and their composites were placed one by one in dark without any light source. Then in order to

establish adsorption-desorption equilibrium between dye solution and photocatalysts, experiments were performed taking one photocatalyst at a time and stirring 100 mg of photocatalyst (ZnSe,  $Zn_3V_2O_8$  and their nanocomposites respectively) in 100 mL of congo red solution for 10 minutes in dark. The solutions were then exposed to light irradiations. 5 mL of the solution was taken from each conical flask, centrifuged and then was analyzed. Changes in congo red concentration as a function of time were analyzed by UV-Vis spectroscopy [Shimadzu UV 2550].

The detail of characterization techniques is as follow:

#### 2.6.1 X-Ray Diffraction (XRD)

X-ray diffraction is a unique nondestructive method for the determination of crystallinity of synthesized materials. XRD analysis can only be used for crystalline samples. According to A. W. Hull (1919) "all the crystalline substances provide patterns, same substances always give same pattern and in a mixture each substance give its own pattern independent of the other". So it is used as a finger-printing tool for identification of crystal structure, various polymorphic forms, preferred crystal orientation, percent crystallinity and other parameters like average grain size, crystal defects and strain. XRD helps to identify constituents of sample and area under peak gives relative amount of each component present.

Bragg investigated the diffraction of x-ray from crystal planes. When x-rays fall on two adjacent layers of solid crystal, they are scattered. The beam reflected by lower plane of crystal travels more distance than beam reflected by upper plane of crystal. Constructive interference of these monochromatic x-rays diffracted from lattice planes at specific angles produce peaks and constructive interference is only possible when Bragg's law ( $n\lambda$ =2*dsin*  $\Theta$ ) is satisfied [1, 2]. Bragg's diffraction is schematically illustrated in Fig. 2.5. It explains the interference pattern of x-rays scattered by crystal and gives relation between wavelength of electromagnetic radiations, diffraction angle and lattice spacing. The results from XRD analysis are obtained in the form of diffractogram, which is a plot of diffraction angle verses intensity.



Figure 2.5: Schematic illustration of Bragg's diffraction

X-ray diffractometers contain three main components: x-ray tube, sample holder and x-ray detector as shown in **Fig. 2.6**.



Figure 2.6: Schematic illustration of main components of X- ray powder diffractometer

X-ray tube also known as cathode ray tube consists of negatively charged metal cathode and positively charged target material (anode) of Cu, Fe, Cr, Mo or Rh. In a cathode ray tube heating of filament, produce electrons, which are bombarded on anode to generate xrays. Only electrons with sufficient energy to dislocate inner shell electrons can produce x-rays. These x-rays are filtered through monochromator, collimated and directed on sample. **Fig. 2.7** is schematic representation of path followed by x-ray beam after passing through sample. The X-ray diffractometers is constructed in such a way that rotation of specimen at an angle  $\theta$  is carried out in x-rays path. The device used for rotation of sample and detector is called "goniometer". X-ray detector swaps at an angle of 2 $\theta$  and is fixed on a support for collection of diffracted x-rays. Constructive interference of incident beam of x-rays with crystalline sample gives XRD pattern after passing through detector [3, 7].



**Figure 2.7:** Schematic illustration of path followed by X-ray beam after striking sample X-ray diffraction is mainly used to

- Identify unknown crystalline material, phases and orientation
- Identify fine minerals like kaolinite
- Determine sample purity
- Identify unit cell dimensions

Experimental

- Analyzing thin films thickness
- Determine structural properties like grain size, strain, epitaxy, phase composition and thermal expansion.

#### 2.6.2 Fourier Transform Infrared Spectroscopy (FT-IR)

Fourier transform infrared spectroscopy (FTIR) is promising analytical technique used to determine bonds in compounds and functional groups present in molecules or on the surface of synthesized materials. The wavelength range of infrared region is 4000 cm<sup>-1</sup> to 400 cm<sup>-1</sup>. Vibrations of atoms can be measured by using IR spectroscopy, which helps in determining functional groups [6].

Basic principle of FT-IR involves the excitation of molecules from lower vibrational energy state to higher vibrational energy state i-e from ground state to excited state, when infrared radiations pass through them. In FT-IR, spectroscopy only those frequencies are absorbed which match with the vibrational frequency of bond therefore it is also known as vibrational spectroscopy. The distance between nuclei of atoms in molecules, increases as a result of absorption of IR radiation while the frequency of vibration does not change so each molecule require quantized energy to promote it to higher vibrational energy level [5]. IR spectrum is mostly represented as a plot of absorbance versus wavenumber.

FT-IR spectrophotometer consists of source of radiation, sample compartment, optical chopper, monochromator, detector, amplifier and recorder as shown in **Fig. 2.8.** Sources of radiation are Nernst filament and Globar filament. Nernst filament is composed of oxides of zirconium, thorium and yttrium and is in the form of hollow cylinder of 2 mm in diameter and 20 mm in length whereas Globar is a bonded silicon carbide rod of 5-7 mm diameter and 50 mm length. When these rods are electrically heated from 1500-2200 K, they emit infrared radiations. The radiation produced by source is divided into two beams of equal intensity. One beam passes through the sample while the other acts as a reference beam. The absorption by sample is directly measured from the difference in intensity between two beams.

The two beams are reflected by mirrors to a light chopping device called optical chopper, which rotates at a definite speed, and reflect the sample beam and reference beam to monochromator. Monochromator consists of grating mirror, which convert the polychromatic light into monochromatic light. Monochromator rotates slowly, focus monochromatic reference beam, and sample beam into detector. The detector works on the principle of thermocouple. This thermocouple detector converts the thermal energy (infrared radiation) into electrical energy (alternating current). When the sample absorbed radiation of a particular frequency, the detector will receive an intense reference beam and a weak sample beam, which leads to an alternating current. The signal is amplified by an amplifier. The recorder records the absorption bands. IR spectrum is thus obtained in the form of plot of absorption against wavenumber [4, 5].



Figure 2.8: Schematic illustration of FT-IR spectrophotometer

# **Applications:**

- IR spectroscopy helps to determine the number and nature of bonds in a compound.
- It is used to detect functional groups present in compound under investigation.
- It helps in the determination of structure of organic compounds by correlation and interpretation of spectra.
- Impurities present in compounds can also be detected with IR spectroscopy.
- IR spectroscopy is also used to find the percentage composition of a mixture of compounds.

• IR spectroscopy is also used to determine the progress of reaction.

# 2.6.3 Scanning Electron Microscopy (SEM)

Scanning electron microscopy (SEM) is an excellent analytical technique used for analyzing the surfaces of different materials under investigation by utilizing focused electron beams. It is a powerful tool for identifying and studying contamination in samples, defects, unknown particulates and interactions of matrix- reinforcement. Topography, composition and morphology of material become clear by the highly resolved three-dimensional images with the magnification of ~X50, 000.

**Scanning Electron Microscopes:** Dr. Charles Oatlev and his students developed Scanning Electron Microscope in 1950, which is type of an electron microscope. It works on the basic principle of light microscope but for magnification of an object electron beam is used instead of photons. Beam of energetic electrons is ejected by an electron gun, which is positioned at the top of instrument [11, 12]. Main components of scanning electron microscope are schematically illustrated in **Fig. 2.9**.

Two types of guns are used for generating electrons viz "Thermionic gun and Field emission gun". Heating of filament for ejecting electrons is carried out by thermionic guns while utilization of electrical field for electron emission is carried out by Field emission guns. Number of electrons used directly affects the magnification.

Scanning electron microscopes consists of number of electromagnetic lenses for directing electrons down the column towards the sample. These lenses are placed in vacuum chamber and are in the form of tube enveloped in coil commonly known as "solenoids". Solenoids are aligned for focusing electron beam. These alignments result in voltage fluctuation and thus increase and decrease in the speed with which electrons hit the surface of sample. Sample compartment contains sample stage for stable support of samples. Sample stage of SEM shows horizontal and vertical movement (X, Y), rotation (R) and tilting (T). Field of view is selected by X and Y movements while Z and T movements help to adjust resolution and depth of focus.



Figure 2.9: Schematic illustration of components of scanning electron microscope

Now a days, computer controlled sample stage is in use which can be adjusted simply by mouse Incident beam of electron when strikes the sample surface, x-rays and three different types of electrons (primary backscattered electrons, secondary electrons and Auger electrons) are ejected from the surface of sample [13]. **Fig 2.10** is schematic illustration of different electron beams produced when incident beam interacts with sample. Secondary electron detector, backscatter detector, diffracted backscatter detector and x-ray detector are different types of detectors used to detect different scattered electrons. The sensitivity of particular secondary electron microscope depends on the type of detectors it holds. Backscattered electrons help to determine distinctions in multiphase specimen while secondary electrons give information about topography and morphology of sample [14]. Incident beam of electron interacts with surface of specimen and results in ejection of electrons from the surface. The images obtained by interaction give information about specimen size, shape and composition.



Figure 2. 10: Schematic illustration of interaction of incident electron beam with sample surface

# 2.6.4 Scanning Electron Microscopy (SEM)/Energy Dispersive X-Ray Analysis (EDX)

SEM in conjunction with an Energy Dispersive X-Ray Analyzer is used to provide highresolution images to check elements in or on specimen surface and investigation of semiquantitative elemental composition of sample. It also helps to detect metal coatings and foreign particles. From "10 mm  $\times$  10 mm to ~ 1  $\mu$ m  $\times$  1  $\mu$ m", area can be analyzed by SEM/EDX and image resolution is from mm to ~50 nm.

EDX detector filters the specific x-rays of various elements into an energy spectrum and this spectrum is analyzed in order to find the quantity of particular element. Energy spectrum is in the form of graph between X-ray counts and energy.

# **Applications:**

SEM/EDX is used to get information about morphology, topography and composition of the sample under investigation. Surface defects, impurities, interphase studies, differences in chemical compositions and identification of crystal structure can also be carried out via SEM. SEM/EDX is used in industries like automotive, material, ceramic, aerospace, minerals, semiconductors, health devices, automotive and medicine for quality control and compositional analysis of their products [12, 14].

#### 2.6.5 UV-Visible and UV-Vis Diffuse Reflectance Spectroscopy(DRS)

UV-Vis diffuse reflectance spectroscopy is used to study optical properties of powdered samples and work on the same basic principle of UV-Vis spectroscopy. UV-Vis spectroscopy is also known as electronic spectroscopy as it involves the promotion of electrons from ground state to higher energy state. The wavelength range of electromagnetic radiation for ultraviolet region is from 10 nm-400 nm while wavelength range of electromagnetic radiation for visible region is from 400 nm-800 nm. Absorption of electromagnetic radiation by a molecule in both regions depends on same principle; therefore they are collectively called ultraviolet-visible spectroscopy.

When molecule absorb electromagnetic radiations of required wavelength electronic transition occur from the highest occupied molecular orbital (bonding or non-bonding) which has low energy to the lowest unoccupied molecular orbital (anti-bonding) which has high energy. The wavelength of radiation absorbed depends on the energy difference between already occupied orbital and the orbitals to which electrons are promoted. In most cases, several transitions occur resulting in the formation of several bands in absorption spectrum, which is known as UV/Vis spectrum. This spectrum provides information of the concern molecule [8]. UV-Vis diffuse reflectance spectrum is a plot of percentage reflectance versus wavelength.

The instrument used to measure the absorption bands in UV/Vis spectrum is called spectrophotometer or spectrometer. **Fig 2.11** is schematic illustration of components of UV/Vis spectrophotometer. The source of radiation is tungsten filament lamp and hydrogen-deuterium discharge lamp. The tungsten filament lamp provides radiation of wavelength greater than 375 nm, which covers visible region while hydrogen-deuterium discharge lamp gives a radiation of wavelength below 375 nm, which covers ultraviolet region. Better spectrometers can measure up to a short wavelength of about 185 nm. However, ordinary spectrometer cannot measure accurately below 200 nm in UV region.

To study below 200 nm the whole path is evacuated. This region below 200 nm is called vacuum ultraviolet region. The ultraviolet radiations are reflected by a solenoid mirror to the monochromator. A monochromator consists of entrance slit, exit slit, prism and mirrors to deflect the radiations. Monochromator convert polychromatic light to monochromatic light by prism. The monochromatic light beam exits the monochromator and is used in the remainder of the instrument.

The beam splitter splits this monochromatic beam into two beams of equal intensity. One beam passes through reference cell while the other beam passes through the sample cell. Sample cells/Cuvets are mostly rectangular with a path length of 1 cm. The longer path length cells are used for low concentration samples. Cuvet are usually made of quartz because quartz is transparent in both UV/Vis regions. Glass is not used because it show strong absorption in UV region. Two cells i-e reference cell and sample cell, which are used in double beam spectrometer, have identical path length and transmit radiation of same extent.

Usually samples are scanned in very dilute solutions. One milligram of a compound, which is under investigation, is accurately weighed and dissolves in suitable solvent to make a solution up to 100 ml. A little of this solution is taken in a sample cell to expose for radiation. The absorption by sample is determined from difference between the intensities of reference cell beam and sample cell beam at each wavelength. This difference is either measured by ratio recording method or optical null method.

The two beams are then reflected to optical chopper. It consists of rotating semicircular mirror, which rotates at a frequency of approximately 10 cycles per second. As the chopper rotates, it causes the reference beam and the sample beam to be reflected alternately to the detector. The detectors most commonly used in spectrometers are phototubes and photomultiplier tubes. In double beam instrument, photomultiplier tube is used because it can detect lower intensity radiation than phototube. At the given moment, the beam impinging on the detector is either reference beam or samples beam. When the sample absorbs light then the intensity of sample beam become lowered. Thus, the detector receives an intense beam from the reference cell and a weak beam from a sample

cell. As the detector, work as thermopile so the combination of intense and weak beam in detector results in generation of electric current which flows from detector to amplifier.

The amplifier is used to amplify only the alternating current in detector. The ratio of the intensities of the reference beam and sample beam is amplified and fed to a self-balancing potentiometric pen recorder. The recorder receives the amplified ratio from the amplifier. The recorder records the absorbance against wavelength. The graph thus obtained is called UV/Vis spectrum [8, 10]



Figure 2. 11: Schematic illustration of components of UV/Vis spectrophotometer

# **Applications:**

Most important applications of UV/Vis spectroscopy involve [9]

- The determination of structure and functional group of a compound.
- It can also be used to determine ionization constant.
- Rate of reactions that involve a change in absorbing group can be determined by UV/Vis spectroscopy.
- Stereo-chemical details in certain molecules can also be determined by UV/Vis spectroscopy.
- It helps to distinguish between conjugated and non-conjugated system and gives information about extent of conjugation.
- UV/Vis spectroscopy is also used for the detection of impurities.

References

#### References

[1] W. H. Bragg, W.L. Bragg, R. W. James and H. Lipson. The Crystalline State: Volume 1, New York: The Macmillan Company, **1934** 

[2] B. D. Cullity. Elements of X-ray Diffraction. Addison-Wesley Publishing company, **1978**.

[3] C. Suryanarayana and M. G. Norton. X-Ray Diffraction: A Practical Approach. Springer Science & Business Media, **1998** 

[4] H. W. Siesler, Y. Ozaki, S. Kawata and H. M. Heise, eds. Near-Infrared Spectroscopy: Principles, Instruments, Applications. John Wiley & Sons, **2008** 

[5] Stuart, Barbara. Infrared Spectroscopy. John Wiley & Sons, Inc., 2005

[6] F. M. Mirabella., ed. Modern Techniques in Applied Molecular Spectroscopy. Vol.14. John Wiley & Sons, **1998** 

[7] K. R. Hebbar. Basics of X-Ray Diffraction and its Applications. I. K. International Publishing House Pvt. Limited, **2007** 

[8] H. -H. Perkampus. Encyclopedia of Spectroscopy. Weinheim; New York: VCH, © 1995

[9] H. -H. Perkampus. UV/VIS Spectroscopy and its Applications. Springer, Berlin, Heidelberg

[10] B. J. Clark, T. Frost, M. A. Russell. UV Spectroscopy: techniques, instrumentation, data handling. London; New York: Chapman & Hall, **1993** 

[11] J. Goldstein. Scanning electron microscopy and x-ray microanalysis. Kluwer Academia/Plenum Publishers, **2003** 

[12] L. Reimer. Scanning electron microscopy: physics of image formation and microanalysis. Springer, **1998** 

[13] R. F. Egerton. Physical principles of electron microscopy: an introduction to TEM, SEM, and AEM. Springer, **2005**.

[14] A. R. Clarke. Microscopy techniques for materials science. CRC Press (electronic resource), **2002** 

[15] F. Mazloom, M. M-Arani, M. G-Arani and M. S-Niasari, Journal of Molecular Liquids, **2016**, 214, 46-53

# Chapter 3: ZnSe/ Zn<sub>3</sub>V<sub>2</sub>O<sub>8</sub> Nanocomposites

#### Abstract

Due to rapidly increasing pollution and stringent requirement for environmental fortification from toxic industrial waste, a lot of work is being done for synthesizing environment friendly materials. In this chapter, photocatalytic degradation of congo red by using ZnSe,  $Zn_3V_2O_8$  and nanocomposites of  $ZnSe/Zn_3V_2O_8$  is discussed in detail. Also the details of characterization results are discussed which confirm the crystallinity, morphology, composition, band gap and the photocatalytic activity of synthesized material.

# **3.1 Phase Analysis**

XRD pattern helped to determine the structural phase and purity of as-synthesized material. The characteristic XRD pattern of novel  $Zn_3V_2O_8/ZnSe$  nanocomposites with different component weight percentages in comparison with bare  $Zn_3V_2O_8$  and ZnSe are shown in **Fig. 3.1. Fig. 3.1(a)** shows the XRD pattern of bare  $Zn_3V_2O_8$  which is in good agreement with the available standard pattern (JCPDS no.00-034-0378). No other peaks were observed, which indicates the purity of products. Diffraction peaks of bare ZnSe, **Fig. 3.1(a)** shows a good match with the cubic ZnSe according to "Joint Committee on Powder Diffraction Standards ((JCPDS) file no. 00-037-1463). The XRD patterns of Zn\_3V\_2O\_8/ZnSe nanocomposites (**Fig. 3.1 (b-d**)) showed distinctive diffraction peaks of both Zn\_3V\_2O\_8 and ZnSe crystalline phases. It is clear from **Fig.3.1(b-d**) that when Zn\_3V\_2O\_8 is present in low concentration the diffraction pattern of Zn\_3V\_2O\_8/ZnSe nanocomposites material was similar to pure ZnSe pattern. However, with an increase in amount of Zn\_3V\_2O\_8, diffraction pattern show much resemblance with that of pure Zn\_3V\_2O\_8 XRD pattern. The high crystallinity of pure Zn\_3V\_2O\_8 and ZnSe is indicated by the sharp and narrow peaks in their XRD patterns (**Fig. 3.1 a and e**)

Crystallite size (D), lattice constant and cell volume for  $Zn_3V_2O_8$  and ZnSe were calculated by using XRD data. Results are in good agreement with the reported data.

Sample	Crystallite size (D) (nm)	Lattice constant (a) (Å)	Cell volume (V) (Å <sup>3</sup> )
Zn <sub>3</sub> V <sub>2</sub> O <sub>8</sub>	117	8.2990	584.7
ZnSe	95	5.6688	182.17

Table 3. 1:Crystalline parameters derived from XRD patterns for Zn<sub>3</sub>V<sub>2</sub>O<sub>8</sub> and ZnSe



Figure 3. 1: (a) bare Zn<sub>3</sub>V<sub>2</sub>O<sub>8</sub>, (b) 25% ZnSe, (c) 50% ZnSe, (d) 75% ZnSe and (e)100% ZnSe

Fourier transform infrared spectrum of as-synthesized  $Zn_3V_2O_8$  helped to determine the surface chemistry of semiconductor photocatalyst. **Fig. 3.2** illustrates the FTIR spectrum of  $Zn_3V_2O_8$ , recorded to detect the residual organic compound on its surface. Bands at 3509cm<sup>-1</sup> and 1585cm<sup>-1</sup> are attributed to the stretching and bending vibrations of OH group of water molecules adsorbed on the  $Zn_3V_2O_8$  surface. Band at 789 cm<sup>-1</sup> and 664 cm<sup>-1</sup> substantiates with VO<sub>4</sub> vibrational modes in coral like  $Zn_3V_2O_8$ . Stretching vibration of Zn-O gives absorption band positioned at 418 cm<sup>-1</sup> which corresponds to ZnO<sub>6</sub> vibration modes [1, 2]. Bands at 1100-1250 cm<sup>-1</sup> indicates the presence of S-O and CO<sub>2</sub> adsorbed from atmosphere [3, 4]. Weak bands at 2930cm<sup>-1</sup> and 2840cm<sup>-1</sup> can be assigned

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to the asymmetric and symmetric stretching vibrations of aliphatic -CH<sub>2</sub>- groups [5]. Thus, FTIR spectrum of  $Zn_3V_2O_8$  indicates the presence of small amount of SDS attached on catalyst surface, which plays role in prevention of nanoparticles agglomeration.



Figure 3. 2: FT-IR spectrum of Zn<sub>3</sub>V<sub>2</sub>O<sub>8</sub>

# **3.2 Morphological and EDX Analysis**

Morphological investigation for all the prepared photocatalysts utilizing SEM has been shown in **Fig. 3.3**. Bare  $Zn_3V_2O_8$  particles possess agglomerated spherical morphology with size distribution in the range of 55-60nm as shown in **Fig. 3.3(a)**. Bare ZnSe particles are cubic in shape with uniform size distribution in the range of 85-95nm **Fig. 3.3(b)**. Nanocomposites with 25% ZnSe show well dispersed spherical and cubic geometries. Cubic ZnSe forms layers over spherical  $Zn_3V_2O_8$  as the amount of ZnSe is increased to 50% in nanocomposite. Upon further increase in the amount of ZnSe to 75% ZnSe particles agglomerates on  $Zn_3V_2O_8$  surface.



**Figure 3.3:** SEM images of  $ZnSe/Zn_3V_2O_8$  nanocomposites with different amount of ZnSe: (a) 0% ZnSe (bare  $Zn_3V_2O_8$ ), (b) 25%, (c) 50%, (d) 75% and 100% (bare ZnSe)

EDX analysis also confirmed the purity of product. In **Fig. 3.4(a-e)** EDX spectra of bare ZnSe, bare Zn<sub>3</sub>V<sub>2</sub>O<sub>8</sub> and their nanocomposites with different content ratios are shown. **Fig. 3.4(a)** confirms the purity of Zn<sub>3</sub>V<sub>2</sub>O<sub>8</sub> as all the peaks in spectrum corresponds to Zn and Se. Also **Fig. 3.4(b)** indicates the purity of as-synthesized ZnSe with no impurity peak in the spectrum. In addition, the EDX compositional investigation for Zn<sub>3</sub>V<sub>2</sub>O<sub>8</sub>/ZnSe nanocomposites, with 25%, 50% and 75% ZnSe, has been recorded as well and the results are presented in **Fig. 3.4(c-e)**. These outcomes uncover that every one of the components in the composites are in concurrence with the desired stoichiometric proportions. At the point when 50% ZnSe is present than the ratio of V and Se is 1:1 (**Fig. 3.4(d)**) and when 25% ZnSe is present the ratio of V to Se is 2.2:1 (**Fig. 3.4(c)**). The proportion of V to Se is 1:2 in a composite where 75% ZnSe is present (**Fig. 3.3(e)**).

Energy Dispersive X-ray (EDX) elemental mapping also helped to determine the composition and elemental distribution of as-synthesized material. The elemental map for bare  $Zn_3V_2O_8$ , ZnSe and their nanocomposites with different component ratios is shown in **Fig. 3.5(a-e).** The micrograph (**Fig. 3.5(c)**) clearly shows that when 25% ZnSe is combined with 75%  $Zn_3V_2O_8$ , nanocomposite is formed with the uniform distribution of Zn, V and O all over the surface, which acts as a base. ZnSe nanoparticles have been well dispersed with the base  $Zn_3V_2O_8$ . Elemental mapping for the nanocomposites with 50%

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and 75% of ZnSe likewise concur well with the previously mentioned discussions and conclusions (Fig. 3.5(d and e)).



**Figure 3. 4:** EDX analysis for (a) Zn<sub>3</sub>V<sub>2</sub>O<sub>8</sub>(b) ZnSe and ZnSe/Zn<sub>3</sub>V<sub>2</sub>O<sub>8</sub> nanocomposites with different amount of ZnSe: (c) 25%, (d) 50% and (e) 75%





**Figure 3.5:** EDX elemental mapping of (a) bare  $Zn_3V_2O_8$ , a) bare ZnSe and ZnSe/ Zn<sub>3</sub>V<sub>2</sub>O<sub>8</sub> nanocomposites with varying amount of ZnSe (c) 25%, (d) 50%, (e) 75%

# 3.3 Ultraviolet-Visible Diffuse Reflectance Spectroscopy

The photocatalytic properties of a catalyst are firmly identified with the arrangement of its band energy levels. UV-Vis diffuse reflectance spectroscopy, (DRS) was used to determine the optical properties and band gaps of  $Zn_3V_2O_8$  and ZnSe. UV/Vis. diffuse reflectance spectrum of  $Zn_3V_2O_8$  is shown in **Fig. 3.6(a)**.  $Zn_3V_2O_8$  band gap was calculated via Tauc plot as shown in inset of **Fig.3.6(a)**. Reflectance factor, F(R) was utilized rather than absorption factor in UV DRS and calculated via Kubelka-Munk expression as shown in equation (1).
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$$F(R) = \frac{(1-R)^2}{2R} = K/S$$
(1)

Where R is absolute reflectance, K is Molar absorption co-efficient and S is scattering coefficient. Optical Band gap of  $Zn_3V_2O_8$  was determined to be 3.2eV by means of Tauc plot as shown in inset of **Fig.3.6** (a)

A UV/Vis DRS spectrum of ZnSe is shown in **Fig. 3.6(b)**, which clearly indicates that ZnSe show strong absorption in blue region of the solar spectrum ~at 480nm. Kubelka-Munk function was utilized to change the diffuse reflectance spectrum to equivalent absorption coefficient. Optical band gap of ZnSe was found to be 2.6eV by means of Tauc plot [6] as appeared in inset of **Fig.3.6 (b)**.





Figure 3.6: UV/Vis spectrum, with the Tauc plot of as synthesized (a)  $Zn_3V_2O_8$  and (b) ZnSe in the inset

#### 3.4 Photocatalytic Activity Mechanism

The percentage degradation of congo red as a function of time by using ZnSe,  $Zn_3V_2O_8$  and their composites is shown in **Fig. 3.7.** Percentage degradation of dye was calculated by using equation (2).

$$\eta = \frac{C_{\circ} - C_t}{C_{\circ}} \times 100 \,(\%) \tag{2}$$

Where  $C_{\circ}$  is initial concentration and  $C_t$  is concentration of dye with time t. The results obtained are shown in **Table 3.2**.

ZnSe with narrow band gap is effectively excited by visible light, which incited the generation of photoelectrons and holes. Electron in the conduction band of ZnSe can be transferred to  $Zn_3V_2O_8$  conduction band leaving behind holes in the valence band of ZnSe. In this way photocatalytic, activity can be improved by successful separation of charge carriers. The results for  $Zn_3V_2O_8$  showed better activity of composite up to 40 minutes after that activity of composites started decreasing as compared to bare ZnSe. Meanwhile, holes in the valence band can react with water to generate H<sup>+</sup> and OH<sup>-</sup> and electrons in conduction band of Zn<sub>3</sub>V<sub>2</sub>O<sub>8</sub> can result in formation of O<sup>2.-</sup> (superoxide)

anionic radical. This superoxide radical anion can react with water to form OH<sup>•</sup> radical, which results in organic dye degradation due to its strong oxidizing ability.

Time (min)	5	10	15	20	25	30	35	40	45	50	55	60
Catalyst		Percentage Degradation of Congo Red Dye										
$Zn_3V_2O_8$	0.25	1.75	9.85	15.87	18.46	28.15	28.32	28.82	28.91	29.10	29.45	29.84
ZnSe	14.61	17.04	20.80	27.15	29.74	40.26	50.87	59.64	72.76	82.45	84.05	89.46
(a) 25% ZnSe	2.84	8.60	19.29	23.89	29.90	38.68	47.20	49.20	51.46	54.88	60.36	65.85
(b) 50% ZnSe	14.53	13.53	17.96	22.97	29.57	43.44	51.29	51.87	53.63	58.14	63.95	69.76
(c) 75% ZnSe	14.53	18.46	21.97	31.74	36.09	48.70	55.05	62.74	66.49	70.25	77.27	84.30

**Table 3. 2:** Percentage degradation of Congo red by  $Zn_3V_2O_8$ , ZnSe and their nanocomposites with different amount of ZnSe: (a) 25% (b) 50% and (c) 75%

The following possible mechanism is proposed for congo red degradation via  $Zn_3V_2O_8/ZnSe$  photocatalysts.

$$ZnSe + hv \to ZnSe(e^{-} + h^{+})$$
(3)

$$ZnSe(e^{-}) + Zn_3V_2O_8 \to ZnSe + Zn_3V_2O_8(e^{-})$$
 (4)

$$Zn_{3}V_{2}O_{8}(e^{-}) + O_{2} \rightarrow Zn_{3}V_{2}O_{8} + O_{2}^{-}$$
(5)

$$O_2^- + H_2 O \to H_2 O_2 + OH^- + OH^-$$
 (6)

$$H_2O_2 + Zn_3V_2O_8(e^-) \to Zn_3V_2O_8 + OH^- + OH^-$$
 (7)

$$ZnSe(h^+) + H_2O \rightarrow ZnSe + OH^- + H^+$$
(8)

$$O_2^{-} + H^+ \to HO_2 \tag{9}$$

$$2HO_2 \to H_2O_2 + O_2 \tag{10}$$

$$H_2 O_2 \to 2HO^{-} \tag{11}$$

$$HO_{2}^{-}/O_{2}^{-}/HO^{-} + dye \to CO_{2} + H_{2}O$$
 (12)



 $O_2^{-}/HO^{-} + dye \rightarrow CO_2 + H_2O$ 

Figure 3.7: Schematic illustration of dye degradation on Zn<sub>3</sub>V<sub>2</sub>O<sub>8</sub> /ZnSe nanocomposites Table 3.1. Shows when Zn<sub>3</sub>V<sub>2</sub>O<sub>8</sub> with a band gap of 3.2eV was used, only 29.84% of dye molecules were degraded after 60 minutes under UV/Vis. light irradiation, therefore showing much lower activity of  $Zn_3V_2O_8$ . This lower quantum efficiency of  $Zn_3V_2O_8$ could be ascribed to its reduced light absorption spectral range and  $e^{-}/h^{+}$  recombination. Composites of  $Zn_3V_2O_8$  with different amount of ZnSe ((a) 25%, (b) 50% and (c) 75%)) were than employed as a catalyst, in order to increase the quantum efficiency of  $Zn_3V_2O_8$ under UV/Vis. light irradiation. Formation of heterostructure of Zn<sub>3</sub>V<sub>2</sub>O<sub>8</sub> with ZnSe resulted in an increase of  $Zn_3V_2O_8$  photocatalytic activity as shown in Fig. 3.8. When composite with 25% ZnSe was used, 65.8% of the congo red molecules were degraded after 60 minutes. With an increase in the amount of ZnSe to 50% and 75% in a composite, the percentage degradation of congo red was increased to 69.7% and 84.3% after 60 minutes as shown in Fig.3.8. These results indicate an increase in the activity of  $ZnSe/Zn_3V_2O_8$  composites with an increasing content of ZnSe. The possible reason of increased activity is reduced charge recombination and increased solar light absorption range of composites as compare to bare Zn<sub>3</sub>V<sub>2</sub>O<sub>8</sub>.



**Figure 3.8:** % degradation of Congo red as a function of time using Zn<sub>3</sub>V<sub>2</sub>O<sub>8</sub>, ZnSe and their composites with varying amount of ZnSe: 25%, 50% and 75%

ZnSe showed 89.46% of Congo red degradation after 60 minutes. ZnSe is showing very high activity itself but when heterostructure was formed, it showed decrease in its activity with increasing content of  $Zn_3V_2O_8$ . This can be due to blockage of active sites of ZnSe by  $Zn_3V_2O_8$  addition. Also the comparison of XRD pattern of as-synthesized ZnSe with cubic ZnSe XRD pattern showed that the as-synthesized ZnSe has both cubic and hexagonal phases **Fig. 3.9**.



Figure 3.9: XRD pattern of (a) single phase ZnSe and (b) multiple phase ZnSe

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It might be possible that ZnSe with both phases itself has formed heterostructure which resulted in its high activity. As single phase ZnSe i.e. cubic ZnSe showed only 60% Congo red degradation after 60 minutes while multiple phase ZnSe showed 89.4% congo red degradation as shown in **Fig. 3.10**. But valid reason behind anomalous behavior of ZnSe/Zn<sub>3</sub>V<sub>2</sub>O<sub>8</sub> composites photocatalytic activity for dye degradation is still unknown.



**Figure 3.10:** % degradation of Congo red as a function of time using single phase and multiple phase ZnSe

## References

[1] S. Ni, X. Wang, G. Zhou, F. Yang, J. Wang and D. He, Journal of Alloys and Compounds, **2010**, 491, 378-381

[2] M. Wang, Y. Shi and G. Jiang, Materials Letters, 2014, 122, 66-69

[3] M. S-Niasari, L. saleh, F. Mohandes and A. Ghaemi, Ultrasonics Sonochemistry, **2014**, 21, 653-662

- [4] Dong, Z. Du, Y. Zhao and D. Zhou, Powder Technology, 2010, 198, 325
- [5] J. Liu, Y. Wang and D. Sun, Journal of Renewable Energy, 2012, 38, 214-218
- [6] J. Tauc, R. Grigorovici and A. Vancu, Physica Status Solidi B, 1966, 15, 627-637

# Chapter 4: ZnTe/ Zn<sub>3</sub>V<sub>2</sub>O<sub>8</sub> Nanocomposites

## Abstract

 $Zn_3V_2O_8$  has been combined with different amount (25%, 50% and 75%) of ZnTe to form heterostructures for various photocatalytic applications focusing on environmental remediation. This chapter includes the details of all the techniques used to characterize the synthesized ZnTe, Zn<sub>3</sub>V<sub>2</sub>O<sub>8</sub> and ZnTe/Zn<sub>3</sub>V<sub>2</sub>O<sub>8</sub> composites.

## 4.1 Structural Analysis

XRD analysis helped to determine the crystal structure of synthesized materials. XRD pattern of as-synthesized  $Zn_3V_2O_8$  (Fig. 4.1(a)) showed its phase purity and orthorhombic geometry in accordance with available standard pattern (PDF file no. 00-034-0378). The diffraction pattern of ZnTe (Fig.4.1 (e)) shows a good match with standard diffraction pattern (JCPDS file no. 15-0746). Sharp peaks show the crystalline nature of ZnTe. XRD patterns of Zn<sub>3</sub>V<sub>2</sub>O<sub>8</sub>/ZnTe nanocomposites with different content of ZnTe (25%, 50% and 75%) are shown in Fig. 4.1 (b-d). Diffraction patterns clearly indicate the successful preparation of Zn<sub>3</sub>V<sub>2</sub>O<sub>8</sub>/ZnTe nanocomposites, as peaks for both ZnTe and Zn<sub>3</sub>V<sub>2</sub>O<sub>8</sub> are present in the diffraction patterns of composites.

Crystallite size (*D*), lattice constant (*a*) and cell volume (*V*) for  $Zn_3V_2O_8$  and ZnTe have been calculated by using XRD data as shown in **Table 4.1.** Crystallite size was calculated with the help of Scherrer formula (**eqn 1**) while lattice constant and cell volume were calculated by using **eqn 2 and 3**. All the calculated parameters are in good agreement with the reported data.

$$D = K\lambda/\beta \cos\theta \tag{1}$$

$$1/d^2 = (h^2 + k^2 + l^2) / a^2$$
 (2)

$$V = a^3 \tag{3}$$

Sample	Crystallite size (D) (nm)	Lattice constant (a) (Å)	Cell volume (V) (Å <sup>3</sup> )
$Zn_3V_2O_8$	117	8.2990	584.7
ZnTe	70	6.0958	226.513

Table 4. 1:Crystalline parameters derived from XRD patterns for Zn<sub>3</sub>V<sub>2</sub>O<sub>8</sub> and ZnTe



**Figure 4. 1:** XRD pattern of (a) Bare Zn<sub>3</sub>V<sub>2</sub>O<sub>8</sub>, (b-d) Zn<sub>3</sub>V<sub>2</sub>O<sub>8</sub>/ZnTe nanocomposites with 25%, 50% and 75% ZnTe respectively, and (e) 0% Zn<sub>3</sub>V<sub>2</sub>O<sub>8</sub> (Bare ZnTe)

#### 4.2 Morphological and EDX Analysis

SEM images of all the synthesized catalysts are shown in **Fig. 4.2**, which help to study the morphology of the product and its size distribution. It is clear from **Fig. 4.2(e)** that ZnTe particles have prism like shape with uniform distribution having a size in a range of 35-45nm. Bare  $Zn_3V_2O_8$  exhibits agglomerated spherical shape **Fig. 4.2(a)**, with uniform size distribution in the range of 50-60nm. The SEM images of nanocomposites with

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different amount of ZnTe (b: 25%, c: 50% and e: 75%) show well dispersed spherical  $Zn_3V_2O_8$  and prism like ZnTe particles. It is evident from **Fig. 4.2(c)** that when 25% ZnTe is present in nanocomposite, well-dispersed spherical and prism like nanoparticles are observed in close contact with each other. Upon further increase in the amount of ZnTe to 50% **Fig. 4.2(c)** prism like ZnTe particles started decorating on the surface of spherical Zn<sub>3</sub>V<sub>2</sub>O<sub>8</sub>. When amount of ZnTe reach to 75% it formed agglomerates on spherical Zn<sub>3</sub>V<sub>2</sub>O<sub>8</sub> particles as shown in **Fig. 4.2(d)**.



Figure 4. 2: SEM images of  $Zn_3V_2O_8/ZnTe$  nanocomposites with different amount of ZnTe: (a) 0% (i-e., bare  $Zn_3V_2O_8$ ), (b) 25%, (c) 50%, (d) 75% and (e) 100% (i-e., bare ZnTe)

EDX spectroscopy has been used to determine the elemental composition and stoichiometry of product. EDX spectroscopic results for  $ZnTe/Zn_3V_2O_8$  nanocomposites **Fig. 4.3 (b-d)** clearly show that all the elements in composites are present in good agreement with the stoichiometric ratios. Pure ZnTe, EDX analysis confirms that all the elements are present in accordance with stoichiometric ratios as shown in **Fig. 4.3(a)**. EDX compositional analysis of bare  $Zn_3V_2O_8$  is shown in Fig. 3.3(b), which indicates that all the elements are in desired stoichiometric ratio.



Figure 4. 3: EDX analysis for (a) ZnTe, nanocomposites of  $ZnTe/Zn_3V_2O_8$  with different amount of ZnTe: (b) 25%, (c) 50% and (d) 75%

## 4.3 Ultraviolet-Visible Diffuse Reflectance Spectroscopy

A UV/Vis DRS spectrum of ZnTe is shown in **Fig. 4.4**, which clearly indicates that ZnTe show strong absorption ~at 556 nm. Kubelka-Munk function was utilized to change the diffuse reflectance spectrum to equivalent absorption coefficient. Optical band gap of ZnTe was found to be 2.2 eV by means of Tauc plot as appeared in inset of **Fig.4.4**.



Figure 4.4: UV/Vis spectrum, with the Tauc plot of as synthesized ZnTe

# **Chapter 5: Summary and Outlook**

During this work, ZnSe,  $Zn_3V_2O_8$  and ZnTe were successfully synthesized as an active photocatalysts for dye degradation. In order to enhance the activity of  $Zn_3V_2O_8$ , nanocomposites were formed with different amount of ZnSe and ZnTe. ZnSe based  $Zn_3V_2O_8$  nanocomposites have successfully been utilized as an efficient material for dye degradation. Highlights of research work for this thesis are summed up as follow:

## **5.1 Highlights**

- Coral like Zn<sub>3</sub>V<sub>2</sub>O<sub>8</sub> photocatalyst is successfully synthesized by precipitation method.
- ZnSe is synthesized by using zinc powder and selenium powder as a precursor by simple hydrothermal route.
- Zn<sub>3</sub>V<sub>2</sub>O<sub>8</sub> is successfully combined with different amount (25%, 50% and 75%) of ZnSe in order to decrease the charge recombination by the formation of close interface.
- Formation of composites is confirmed by XRD, SEM, EDX and UV/Vis. spectroscopy.
- Zn<sub>3</sub>V<sub>2</sub>O<sub>8</sub>-ZnSe nanocomposites are then used as an efficient photocatalytic system for dye degradation.
- 75% ZnSe brings about the enhancement of photocatalytic activity of Zn<sub>3</sub>V<sub>2</sub>O<sub>8</sub> by suppressing the charge recombination.
- Zn<sub>3</sub>V<sub>2</sub>O<sub>8</sub>-ZnTe nanocomposites are also synthesized successfully using a physical method.
- Formation of heterostructures is confirmed by XRD, SEM, EDX and UV/Vis spectroscopy.

## **5.2 Future Perspectives**

Degradation of organic pollutants by using photocatalysts is cost effective and easy method. The extent of study could be much developed if additional time and .

characterization facilities are available. Future plan is to check the photocatalytic activity of synthesized  $Zn_3V_2O_8$ -ZnTe nanocomposites for dye degradation and to synthesize a material which can absorb large spectrum of solar energy and can effectively degrade pollutants into less toxic substances. For enhancement of activity following strategies may be adopted in future.

- Computational techniques would be combined with experimental techniques so as to provide the better work strategy in future for enhancing the photocatalytic activity.
- Efficient methods for charge separation may be developed in order to get desired results.

Future work may also explore the visible light photocatalytic reduction of  $CO_2$  by using  $Zn_3V_2O_8$ -ZnSe and  $Zn_3V_2O_8$ -ZnTe nanocomposites.