

**HIGH EFFICIENCY PHOTOCATALYTIC DEGRADATION OF TEXTILE
POLLUTANTS USING TUNSTEN OXIDE-TIN SULPHIDE ($\text{WO}_3\text{-SnS}$)
NANOCOMPOSITE**

Submitted in partial fulfilment of the requirements for the award of

Master of Science in CHEMISTRY

by

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DEPARTMENT OF CHEMISTRY

SCHOOL OF SCIENCE AND HUMANITIES

SATHYABAMA

INSTITUTE OF SCIENCE AND TECHNOLOGY

(DEEMED TO BE UNIVERSITY)

ACCREDITED WITH GRADE "A" BY NAAC

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MAY-2023



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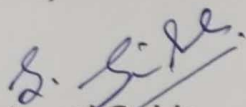
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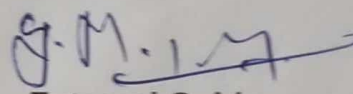
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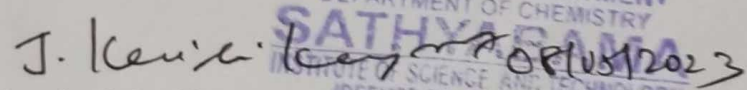
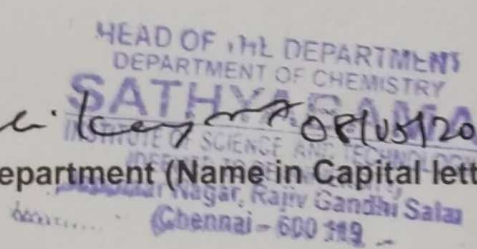
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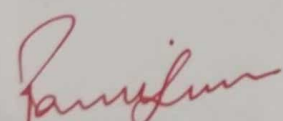
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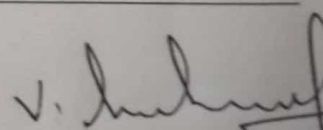

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3. DECLARATION

I Ms. G. MONISHA student of SATHYABAMA INSTITUTE OF SCIENCE AND TECHNOLOGY hereby declare that the Project Report entitled "HIGH EFFICIENCY PHOTOCATALYTIC DEGRADATION OF TEXTILE POLLUTANTS USING TUNGSTEN OXIDE-TIN SULPHIDE ($\text{WO}_3\text{-SnS}$) NANOCOMPOSITE" done by me under the guidance of Dr. S.SUNITHA, M.Sc., M.Phil., Ph.D. and Dr. G.MURUGADOSS, M.Sc., Ph.D. Scientist-E at International Research Centre, Sathyabama Institute of Science and Technology, Chennai is submitted in partial fulfilment of the requirements for the award of Master of Science degree in CHEMISTRY.

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MONISHA G

**HIGH EFFICIENCY PHOTOCATALYTIC DEGRADATION OF TEXTILE
POLLUTANTS USING TUNGSTEN OXIDE-TIN SULPHIDE (WO₃-SnS)
NANOCOMPOSITE**

VISION

**“TO EXPLORE NEW FRONTIERS IN CHEMICAL SCIENCE THROUGH
INNOVATION AND COLLABORATION”**

ABSTRACT

Tungsten oxide-Tin sulphide(WO₃-SnS) nanocomposites were synthesized by the chemical precipitation method using different ratios of Tungsten oxide and Tin sulphide. The structural, morphological, and optical properties of nanocomposites were analysed by X-ray diffraction (XRD), Fourier transform infrared spectra (FT-IR), Scanning electron microscope (SEM) and UV–Vis spectrophotometry.

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CHAPTER 1

INTRODUCTION

Metal oxides/ mixed metal oxides have numerous applications such as catalysts, superconductors, semiconductors, adsorbents and also have immense applications in medicine. Metal oxides plays a major role in many areas of physical science, chemical science and materials science.

The coordination tendency of metal ions tends to form the coordination sphere with the oxide ions around the metal ions and give rise to the close packed structure of Metal oxides. The different physical, magnetic, chemical and optical properties of metal oxides are of great interest to chemists because these are very sensitive to change in composition and structure.

The metal oxides are fascinating special consideration of scientists due to their easy mode of formation and multifunctional behavior. Transition metals make excellent catalyst as they have incompletely filled d-orbitals that allow them to both donate and accept electrons easily from other molecules.

In addition to that, these compounds can be used in formation of interstitial compounds and alloy formation. The transition metals have the special properties of formation of colored compounds and show magnetic properties.

Metal of d-block elements are used for many industrial applications. They behave as catalysts, super conducting materials, sensors, ceramics, phosphors, crystalline lasers etc. Apart from these they are excellent photoactive materials and work as photosensitizer. Mixed metal oxide (MMO) electrodes are devices with useful properties for chemical electrolysis.

Mixed metal oxide (MMO) nanoparticles (also called heterometal oxide nanoparticles) can play an appreciable role in many areas of chemistry and physics. The unique electronic and magnetic properties obtained when combining two metals in an oxide matrix have been well studied. However, the most common use for MMOs has been in the area of catalysis, and here they have found use both as the catalyst and as catalyst supports.

Developments in the field of MMO nanoparticles have produced many significant and interesting results in all areas investigated. Metal Oxide Nanoparticles are also used in the fabrication of microelectronic circuits, sensors, piezoelectric devices, fuel cells, coatings for the passivation of surfaces against corrosion, and as catalysts.

NANO PARTICLES

Nanoparticles have a special place in nanoscience and nanotechnology, not only because of their particular properties resulting from their reduced dimensions, but also because they are promising building blocks for more complex nanostructures. The normal size of particles framing a sample in the range of 1–1000 nm (1 nm = 10^{-9} m).

Nanotechnologies are now widely considered to have the potential to bring benefits in areas as diverse as drug development, water decontamination, information and communication technologies, and the production of stronger and lighter materials. Nanotechnologies involve the creation and manipulation of materials at the nanometre scale, either by scaling up from single groups of atoms or by refining or reducing bulk materials.

Ordinary materials, when reduced to the nanoscale, often exhibit novel and unpredictable characteristics such as extraordinary strength, chemical reactivity, electrical conductivity, superparamagnetic behaviour, and other characteristics that the same material does not possess at the micro- or macroscale. A huge range of nanomaterials is currently being produced at an industrial scale, while others are being produced at smaller scales as they are still under research and development.

While bulk materials have constant physical properties regardless of size, the size of a nanoparticle dictates its physical and chemical properties. Thus, the properties of a material change as its size approaches nanoscale proportions and as the percentage of atoms at the surface of a material becomes significant.

The surface can be uniform or unpredictable with surface varieties. Some nanoparticles are translucent or shapeless with single or multi gem solids either free or agglomerated. Various synthesis techniques are either being created or improved to upgrade the properties and lessen the production costs.

A few techniques are adjusted to accomplish measure explicit nanoparticles to increment their physical, chemical, optical and mechanical properties. A huge

advancement in the instrumentation has prompted an improvement in nanoparticle characterization and application.

Based on the application like imaging, diagnosis or treatment various kinds of nanoparticles have been proposed, some of them are utilized for multiple purposes.

Nanoparticles come under two main categories: organic and inorganic nanoparticles. The primary group includes micelles, dendrimers, liposomes, hybrid and minimized polymeric nanoparticles. The second group includes fullerenes, quantum dots, silica and gold nanoparticles.

1.1.1 Types of Nanoparticles

Nanoparticles are classified as 0-Dimensional (D), 1D, 2D, or 3D depending on their overall shape.

One dimensional nanomaterials

1-D nanomaterials have thin films or surface coatings and are used in the circuitry of computer chips and for anti-reflective properties and hard coatings on eyeglasses. These have been used in electronics, chemistry, and engineering. This class includes nanotubes, nanorods, and nanowires. coatings and thin films.

Two dimensional nanomaterials

2-D nanomaterials have fixed and long nanostructures with thick membranes. They are used to prepare nanopore filters used for small particle separation and filtration. Asbestos fiber is an example of 2D nanoparticles. Examples are nanotubes, biopolymers, nanowires.

Three dimensional nanomaterials

Three-dimensional nanomaterials (3D) are materials that are not confined to the nanoscale in any dimension. This class can contain bulk powders, dispersions of nanoparticles, bundles of nanowires, and nanotubes as well as multi-nanolayers.

Materials that are nanoscale in all three dimensions are 3D nanomaterials. These include quantum dots or nanocrystals, fullerenes, particles, precipitates and colloids. Some 3D systems, such as natural nanomaterials and combustion products, metallic oxides, carbon black, titanium oxide (TiO₂) and zinc oxide (ZnO) are well known, while

others such as fullerenes, dendrimers and quantum dots represent the greatest challenges in terms of production and understanding of properties.

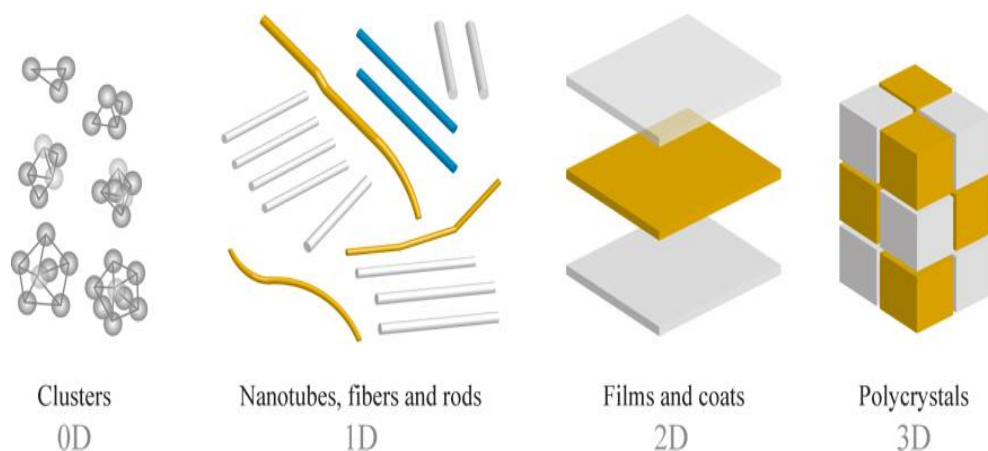


Figure 1.1: Types of nano particles

1.1CLASSIFICATION OF NANOPARTICLES

Nanoparticles can be classified into different types according to the size, morphology, physical and chemical properties. Some of them are carbon-based nanoparticles, ceramic nanoparticles, metal nanoparticles, semiconductor nanoparticles, polymeric nanoparticles, and lipid-based nanoparticles.

INORGANIC BASED NANOPARTICLES

Inorganic nanoparticles are non-toxic, hydrophilic, biocompatible and highly stable compared to organic materials. This class comprises Nanoparticles that not made of carbon or organic materials. The typical examples of this class are metal, ceramic, and semiconductor Nanoparticles. Metal Nanoparticles are purely made of metal precursors, they can be monometallic, bimetallic, or polymetallic. In addition, some metal Nanoparticles also possess unique thermal, magnetic, and biological properties. This makes them increasingly important materials for the development of nanodevices that can be used in numerous physical, chemical, biological, biomedical, and pharmaceutical application.

Semiconductor Nanoparticles are made of semiconductor materials, which possess properties between metals and non-metals. These Nanoparticles possess unique wide bandgaps and show significant alteration in their properties with bandgap tuning

compared to bulk semiconductor materials. As a result, these Nanoparticles are important materials in photocatalysis, optic, and electronic devices.

Ceramic Nanoparticles are inorganic solids made of carbonates, carbides, phosphates, and oxides of metals and metalloids, such as titanium and they can be found in amorphous, polycrystalline, dense, porous or hollow forms. They are mainly used in biomedical applications due to their high stability and high load capacity. Drug delivery systems designed for enhanced drug efficacy and reduced adverse effects have evolved accompanied by the development of novel materials.

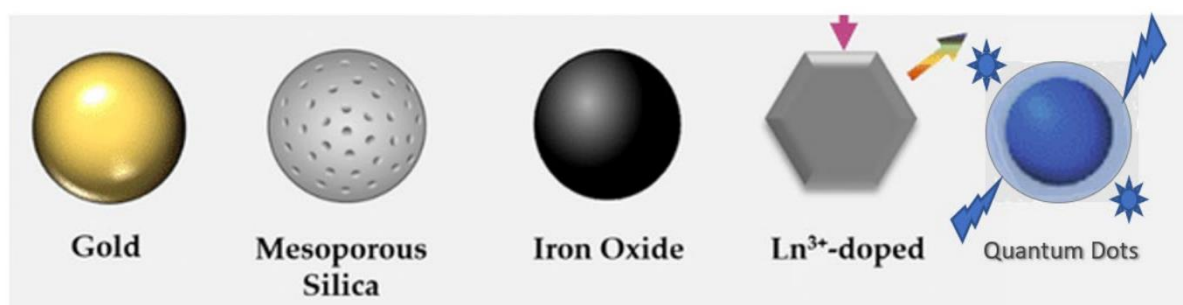


Figure 1.2: Inorganic based Nanoparticles

1.2.3 COMPOSITE BASED NANOPARTICLES

Composite nanomaterials are multiphase nanoparticles and nanostructured materials with one stage on the nanoscale measurement that can either consolidate nanoparticles with different nanoparticles or nanoparticles joined with bigger or with bulk materials or more complicated structures, for example, metal organic systems.

Nanocomposites are a class of nanomaterials wherein one or more phases at nano-sized dimension (zero dimension, one dimension, and two dimensions) are embedded in a ceramic, metal, or polymer material.

These composites might be a mixture of carbon-based, metal-based, or natural based nanomaterials with any type of metal, polymer, or ceramic based materials. Nanomaterials are synthesised in various morphologies relying upon the necessary properties for the required application.

1.3 PROPERTIES OF NANOPARTICLES

Nanoparticles can be used in a long list of applications due to their unique physical and chemical properties that do not exist in their larger-dimension counterparts of the same materials. Some of their properties are mentioned below

1.3.1. MECHANICAL PROPERTIES

Mechanical properties refer to the mechanical characteristics of a material under different conditions, environments, and various external forces. As for traditional materials, the mechanical properties of nanomaterials can be generally strength, brittleness, hardness, toughness, fatigue strength, plasticity, elasticity, ductility, rigidity, and yield stress. Magnetic nanoparticles can be superparamagnetic and responds to external magnetic fields very fast with almost zero remanence.. The mechanical properties of nanoparticles such as hardness and elastic modulus, interfacial adhesion and friction, movement law, as well as its size-dependent effect.

1.3.2 PHYSICAL PROPERTIES

The physical properties of nanoparticles are dependent on the size, shape, composition, crystal structure, surface ligand or capping agents and the medium in which they are dispersed.

1.3.3 OPTICAL PROPERTIES

Due to the quantum confinement effect, nanomaterials with small particle sizes exhibit better optical emission as well as nonlinear optical properties. The effect of size on nanoparticle optical properties is caused by two distinct phenomena: surface phenomena and an increase in energy level spacing due to the confinement of energy states, which is most notable in semiconductors.

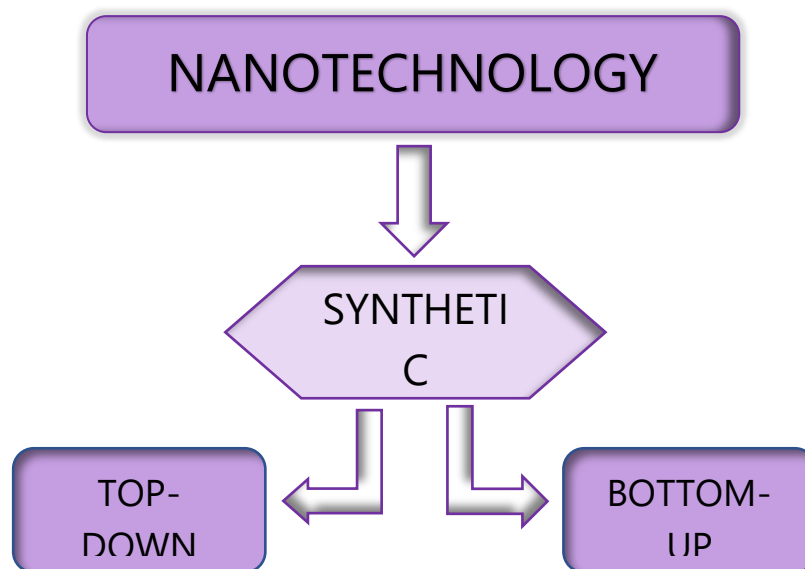
1.3.4 MAGNETIC PROPERTIES

After surface cooling, magnetic nanoparticles exhibit extraordinary new phenomena including strong field irreversibility, high saturation field, super para magnetism, extra anisotropy effects, or shifted loops. The magnetic nature of individual nanoparticles is because of narrow and finite-size effects, as well as surface effects. One of the interesting size-dependent phenomena of Nanoparticles is super-paramagnetism. As the size of the Nanoparticles decreases, the magnetic anisotropy energy per nanoparticle decreases. the Nanoparticle is defined as being superparamagnetic.

Superparamagnetic Nanoparticles display high magnetization only in the presence of a magnetic field, and once it is removed, they do not retain any magnetization.

1.4 SYNTHETIC METHODS

Approaches come under two main categories namely: top-down approach and bottom-up approach and they differ in their cost, speed and degree of quality. The Approaches have been summarised in below



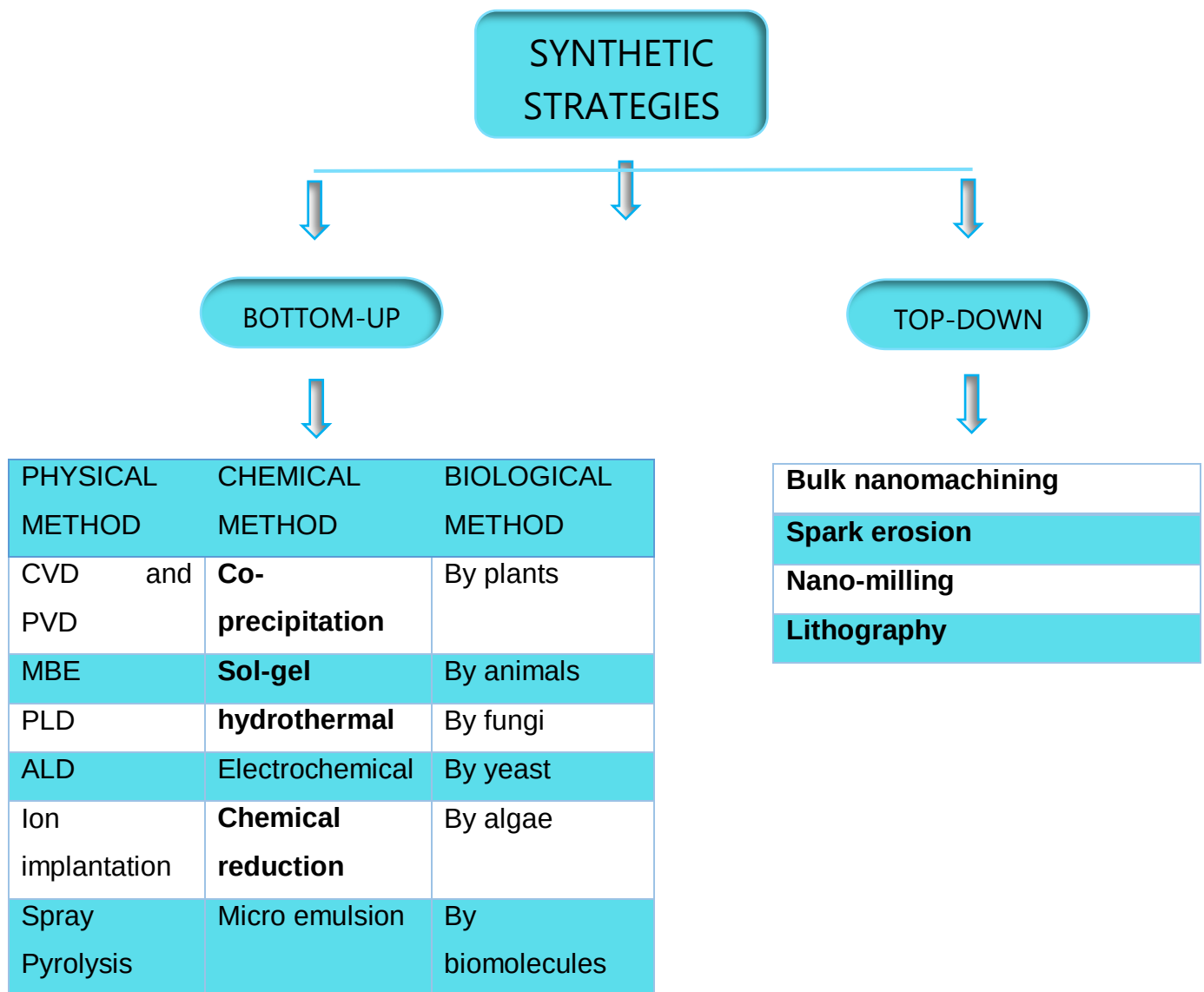


Figure 1.5.1: BOTTOM-UP and TOP-DOWN approaches

1.5. BOTTOM-UP APPROACH

This method is the reverse of top-down approach. These nanoparticles are formed from simple substances and hence it is called as building up approach. Examples are hydrothermal, chemical precipitation, pyrolysis, sol-gel, CVD, etc.

1.5.1. SOL-GEL METHOD

Two materials are involved in this method they are sol and gel. It is a low temperature process and consumes less energy. Synthesis of nanoparticles like nanotubes, nanorods can be obtained by this method. Sol-gel synthesis involves hydrolysis, condensation, gelation and drying process by various routes.

1.5.2 CHEMICAL VAPOUR DEPOSITION (CVD)

The deposition of a thin film of gaseous reactants onto a substrate is Chemical Vapour Deposition. At ambient temperature gas molecules are combined and the deposition is carried out in a reaction chamber. Chemical reaction occurs when a heated substrate comes in contact with the combined gas.

A thin film of product on the substrate surface is produced and that is recovered and used. The influencing factor in CVD is the substrate temperature. CVD produces nanoparticles that are strong, uniform and hard. CVD requires special equipment and the gaseous by products are toxic.

1.5.3 HYDROTHERMAL METHOD

Hydrothermal synthesis can be defined as a method of synthesis of single crystals that depends on the solubility of minerals in water under high pressure. The crystal growth is performed in an apparatus consisting of a steel pressure vessel called an autoclave, in which a nutrient is supplied along with water.

1.5.4 CHEMICAL PRECIPITATION METHOD

The chemical precipitation process mainly consists of three main steps such as chemical reaction, nucleation and the crystal growth. Solids obtained from the chemical precipitation have a wide particle size plus uncontrolled particle morphology, along with agglomeration. The nanoparticles obtain a narrow size distribution with certain requirements such as a high degree of supersaturation, a uniform spatial concentration distribution inside a reactor and a uniform growth time for all particles or crystals.

The chemical precipitation method has extreme advantages when compared to other synthetic methods. The chemical precipitation method is the simplest and the rapid method for the synthesis of the nanoparticles. This method offers easy control of the

particle size. It provides various possibilities to modify the particle surface and homogeneity and holds good control on the composition of nanoparticle.

Chemical precipitation method can be used from small scale to large scale and it is the most economic friendly method for the synthesis of nanoparticles.

1.6 APPLICATIONS OF NANOPARTICLES

Nanoparticles are now being used in the manufacture of scratchproof eyeglasses, crack-resistant paints, anti-graffiti coatings for walls, transparent sunscreens, stain-repellent fabrics, self-cleaning windows and ceramic coatings for solar cells.

Nanotechnology-on-a-chip is analogous to the lab-on-a-chip technology. Sensor test chips containing thousands of nanowires, able to detect proteins and other biomarkers left behind by cancer cells, could enable the detection and diagnosis of cancer in the early stages from a few drops of a patient's blood.

Owing to the large surface area to volume ratios, nanoparticles can attach multiple functional groups to it, which can locate and bind to specific tumor cells. Furthermore, the small size of nanoparticles (10- 100 nm) allows them to preferentially accumulate at tumor sites (as tumors lack an effective lymphatic drainage system). The limitations to conventional cancer chemotherapy such as drug resistance, lack of selectivity as well as solubility, can be overcome by using nanoparticles.

Nanoparticles have great potential as in vivo imaging tools and devices. Nanoparticle based contrast agents, images (e.g, ultrasound) can have favourable distribution and enhanced contrast. Nanoparticles can aid visualisation of various stages in cardiovascular problems such as blood pooling, angiogenesis, atherosclerosis, etc. Due to their small size, nanoparticles can be very useful in oncology, especially in imaging. Quantum dots when used for MRI (magnetic resonance imaging), create exceptional images of tumor sites. Cadmium selenide nanoparticles glow on exposure to UV. When injected, they enter the cancer cells, thereby highlighted them. Nanoparticles are much brighter than organic dyes and can be excited only with single light source. Thus, use of fluorescent Quantum dots can create much higher contrast images at lower costs in comparison to organic dyes. The disadvantage is that Quantum dots are made from toxic materials.

The surface of the nanoparticles should be polar to provide good aqueous solubility and prevent nanoparticle coagulation. Biomolecules can be attached to the nanoparticles to direct them to specific sites in the body, even specific organelles in a cell, or to monitor individual protein or RNA molecules. Most commonly used tags to mark the nanoparticles include monoclonal antibodies, aptamers, streptavidin or peptides. These tags must be attached with the nanoparticles covalently, and also, their quantity per nanoparticles must be controlled for efficient operation. Multivalent nanoparticles have several tags attached to them which may cause their clustering, thereby activating the cell signaling paths, giving stronger anchoring. On the other hand, monovalent nanoparticles bear single binding sites, thus prevent cluster formation. These nanoparticles are suitable to track the behaviour of individual protein molecules.

1.7 METAL OXIDES

Metal oxides are crystalline solids that contain a metal cation and an oxide anion. They typically react with water to form bases or with acids to form salts.

Metal oxides play an important role in numerous zones like chemistry, physics, and materials science. Metal oxides exhibit semiconductor, metallic or insulator properties and can adopt a number of structural geometries and it also possesses an electronic structure.

Metal oxide nanoparticles have been used in different fields due to its excellent functional properties. When metal oxides are coupled with other structures, they enhance the unique properties of the materials.

The main Metal oxides/ Mixed metal oxides have wide applications as catalyst, Adsorbents, Superconductors, semiconductors, ceramics, antifungal agents and also have spacious applications in medicines. This review article is focused on their applications as photocatalyst in various organic reactions nanoparticles are shown in the figure.

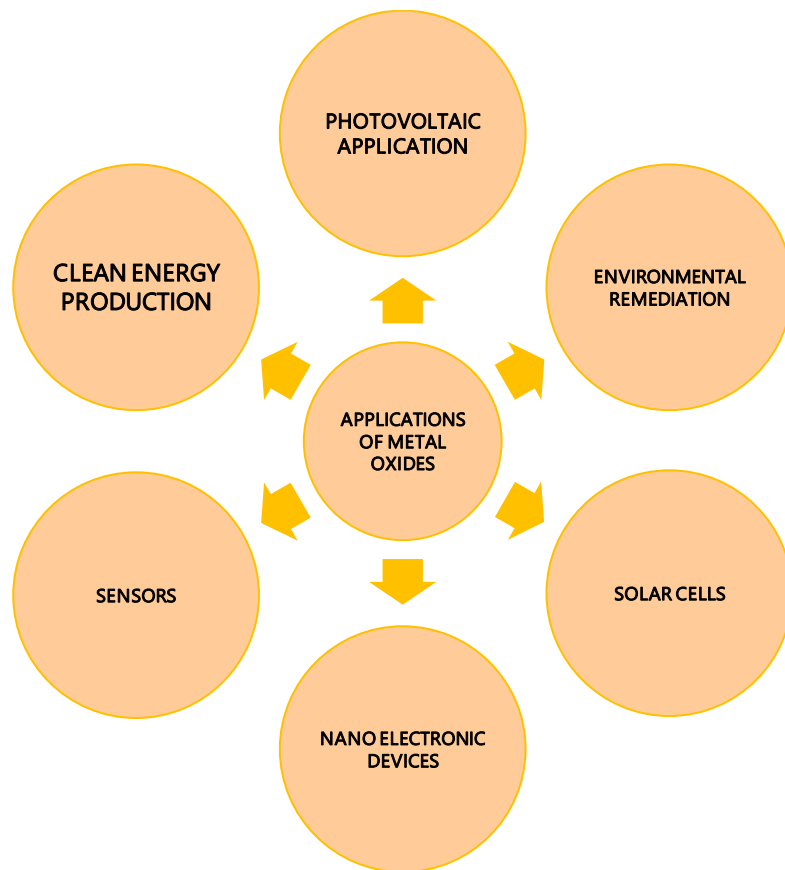


Figure 1.7(a): Applications of metal oxides

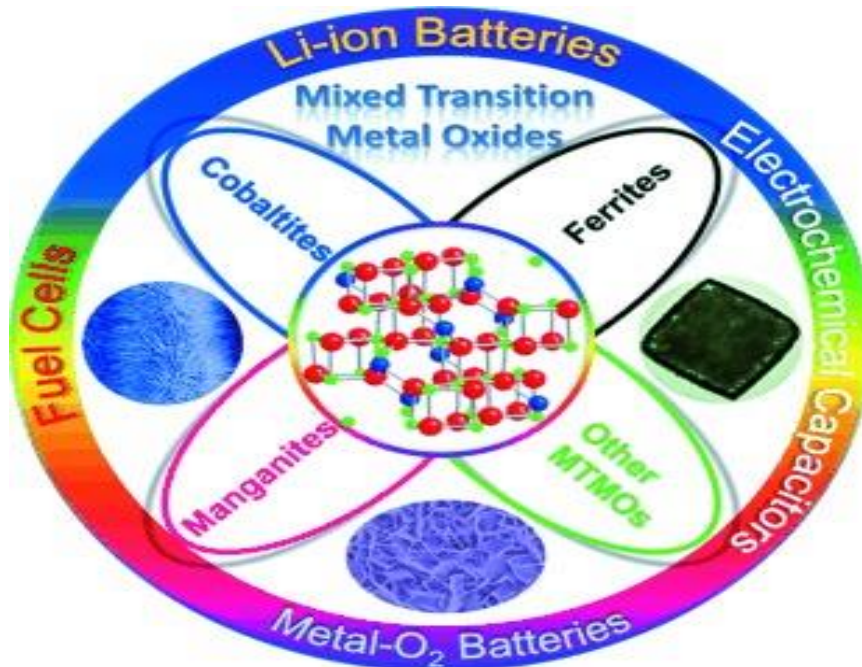


Figure1.7(b): Applications of metal oxides

1.8 TRANSITION METAL OXIDES

1.8.1 TUNGSTEN OXIDE (WO₃) NANOPARTICLE

The Transition metal oxide tungsten oxide (WO₃) is an earth-abundant metal oxide. It is an oxygen deficient n-type semiconductor having a wide electronic band gap of 2.6-3.0 eV falls under the visible region. It shows excellent electronic and morphological properties, good stability, crystallographic, electrical, optical, thermoelectrical, ferroelectric properties enhanced photoactivity with diverse crystal phases. Also, it unveils non-toxicity, high stability in drastic conditions, biocompatibility, low cost, excellent hole mobility ($10 \text{ cm}^2 \text{ V}^{-1}\text{s}^{-1}$), and tunable band gap.

It has many polymorphs which includes cubic, triclinic, monoclinic, orthorhombic and hexagonal. Out of these, monoclinic structure is highly stable when compared to other structures. The boiling and melting of tungsten trioxide is 1700°C and 1473°C respectively and the oxidation state of tungsten in WO₃ is +6.

Tungsten oxide is a potential candidate for various applications such as pollutant degradation, CO₂ photoreduction, and water splitting. Besides, other applications of WO₃ includes gas-sensor, bio-sensor, heavy metals ions adsorption, and antimicrobial property.

WO₃ crystallizes in the monoclinic P2₁/c space group. W⁶⁺ is bonded to six O²⁻ atoms to form distorted corner-sharing WO₆ octahedral. The corner-sharing octahedral tilt angles range from 19–26°. There are spread of W–O bond distances ranging from 1.77–2.15 Å. There are three inequivalent O²⁻ sites. In the first O²⁻ site, O²⁻ is bonded in a bent 150 degrees geometry to two equivalent W⁶⁺ atoms. In the second O²⁻ site, O²⁻ is bonded in a distorted bent 150 degrees geometry to two equivalent W⁶⁺ atoms. In the third O²⁻ site, O²⁻ is bonded in a distorted bent 150 degrees geometry to two equivalent W⁶⁺ atoms.

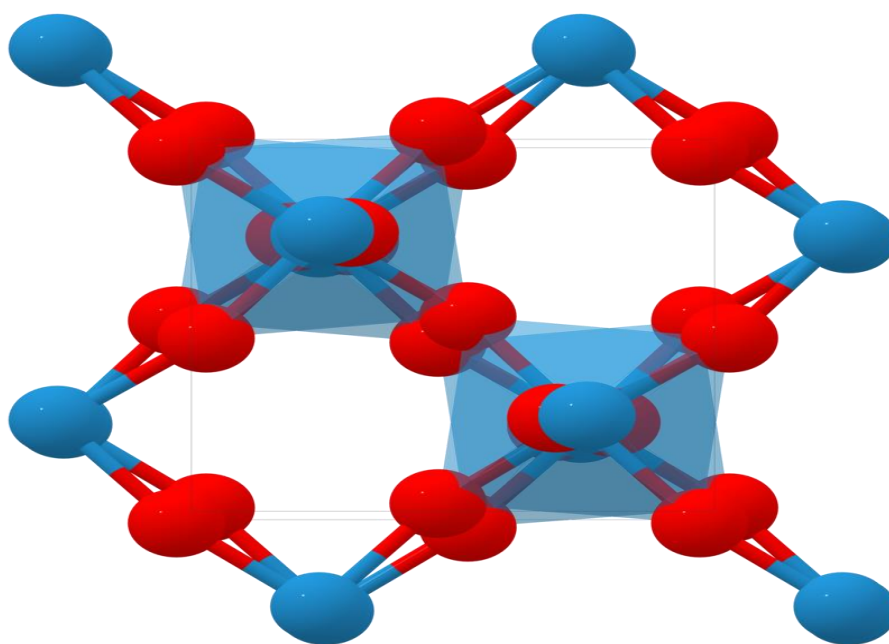


Figure 1.8.2: Crystal structure of Tungsten oxide (WO_3)

1.9 METAL SULPHIDE NANOPARTICLE

Metal sulfide nanomaterials are a novel class of metal-containing nanomaterials composed of metal ions and sulfur compounds. Metal sulfide nanoparticles have recently attracted much attention due to their unique physical and functional properties.

Metal sulfide nanoparticles used electronic, optical, optoelectronic and biomedical materials in the past decades are promising for making functional nanocomposite films due to their low toxicity and strong antibacterial activity.

Various approaches can be used to synthesize Metal sulphide nanoparticles, such as gas vulcanization approach, wet chemical approach, electrochemical deposition, mechanochemical approach, and pyrolytic approach, etc. However, Metal sulphide nanoparticles engineered by some types of approaches cannot meet the standards of biomedical applications. Generally, electrochemical deposition is widely used in

energy storage and conversion systems by synthesizing layered and reticulated metal sulfides. While the gas vulcanization approach is famous for its ability to remove heavy metals from waste water or metal scraps.

1.9.1 TIN SULPHIDE NANOPARTICLE

SnS is one of the important IV-VI type semiconductors having an orthorhombic structure, where Sn and S atoms are tightly held together with covalent bonding in a layer. These layers are attracted by weak Van der Waals forces. This material belongs to a class of isomorphic materials that exhibit strong anisotropic optical properties. This group of layered semiconducting materials display an optical band gap of 2.2–2.35 eV.

The tunable band gap makes them useful for efficient solar cell applications, mainly as a solar absorber in a thin-film solar cell, as near-infra-red detector and as photovoltaic materials.

Depending on the concentration of the tin in the SnS nanoparticles, it can exhibit both *p*- and *n*-type conduction. Their chemical stability in acidic solutions shows its applications in the visible light-sensitive photo catalysis. The versatile coordinating characteristics of tin and sulfur permit tin sulfide to adopt a variety of phases, viz. SnS, Sn₂S₃, Sn₃S₄, and SnS₂.

It has favourable properties such as high absorption coefficient in the visible region ($>10^4 \text{ cm}^{-1}$), carrier mobility of $30 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$, *p*-type electrical conductivity and photoelectric conversion efficiency. Both Sn and S are earth-abundant constituent elements, less toxic and inexpensive.

SnS possess wide potential applications. In research, because of structural, chemical, physical and luminescence properties of SnS the semiconductor nanocrystals are widely studied. SnS nanoparticles show great promise in the field of photoelectric and thermoelectric. By using solvothermal, and hydrothermal, successive ionic layer adsorption and reaction, wet chemical synthesis, pulsed laser deposition, thermal evaporation, physical vapor deposition, electrochemical methods etc., SnS nanostructures with different morphologies such as nanosheets, nanorods, nanowires and nanoflowers can be synthesized.

SnS is used in perovskite and quantum dot sensitized solar cells, photodetectors, solid-state batteries, capacitors, Sensors, holographic recording medium and an efficient visible light driven photocatalytic material due to its promising physical and chemical properties. Hence, SnS finds extensive interest in many fields of science and technology.

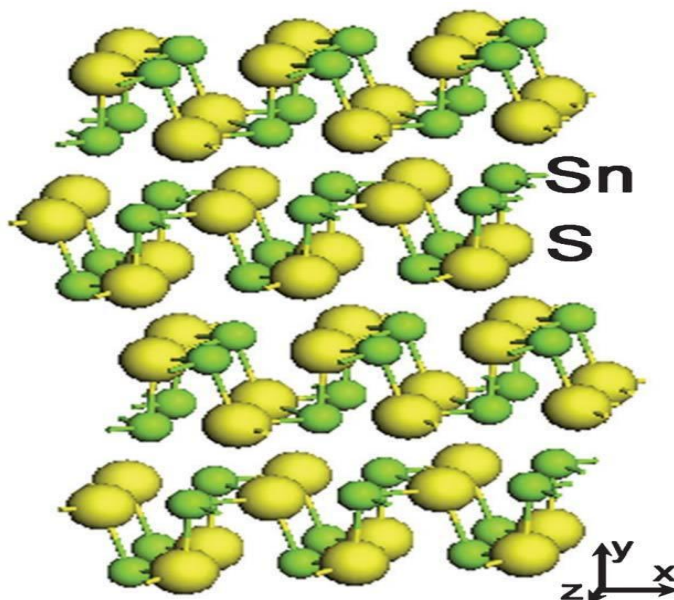


Figure 1.9.2: Crystalline structure of Tin Sulphide (SnS)

1.11 METAL OXIDE/SULPHIDE NANOCOMPOSITE

In the past few years, metal oxide/sulfide nanocomposites have played an exciting part in nanoscience and technology. The introduction of two varied vital principles for the synthesis of metal oxide/sulfide Nanocomposites including bottom-up and top-down methods has been examined with accurate size, functions, and shape.

The top-down method involves the preparation of NMs through varied synthetic approaches such as ball-milling, sputtering, lithographic techniques, and etching, whereas in the bottom-up method, chemical vapor deposition, spray pyrolysis, atomic condensation, and laser pyrolysis are some of the techniques incorporated where Nanoparticles are being grown from simpler molecules.

The investigations on the photocatalytic activity of metal oxide/sulfide-based nanocomposites show great importance in energy-related applications. A variety of

semiconducting materials, including metal oxides/nitrides/oxynitrides/sulfides, Z-scheme systems, alkali metal bases, and carbon materials including graphene, graphitic carbon nitride and carbon, have recently been employed as photocatalysts.

The most popular photocatalysts are made of nanoscale metal oxide/sulfides particles. Metal oxides, particularly transition metal oxides, alkaline earth metal, and alkali metal are widely used in air and sterilization, and water purification, virus elimination, cancer cells, bacteria, fungi, and algae. The combination of metal oxide Nanoparticles and metal sulfide Nanoparticles has shown to result in properties far superior to those of the individual properties of metal oxide Nanoparticles.

1.11.1 TUNGSTEN OXIDE-TIN SULPHIDE NANOCOMPOSITE (WO_3 -SnS)

SnS and WO_3 are semiconductors with bandgaps of about 2.2 and 2.8 eV respectively. They have been separately studied as visible-light-activated photocatalysts.

Certain chemical methods are capable of synthesizing composite photocatalysts with good mixing, intimate contact and even strong interaction between different components, which can provide the tight and firm heterointerfaces for charge transfer and reduce the separation and self-agglomeration of different components during the photocatalytic use.

The Transition metal oxide tungsten oxide (WO_3) is an earth-abundant metal oxide. It is an oxygen deficient n-type semiconductor having a wide electronic band gap of 2.6-3.0 eV falls under the visible region. It shows excellent electronic and morphological properties, good stability, crystallographic, electrical, optical, thermoelectrical, ferroelectric properties enhanced photoactivity with diverse crystal phases. Tungsten oxide is a potential candidate for various applications such as pollutant degradation, CO_2 photoreduction, and water splitting. Besides, other applications of WO_3 includes gas-sensor, bio-sensor, heavy metals ions adsorption, and antimicrobial property.

SnS is one of the important IV-VI type semiconductors having an orthorhombic structure, where Sn and S atoms are tightly held together with covalent bonding in a layer. These layers are attracted by weak Van der Waals forces. Depending on the

concentration of the tin in the SnS nanoparticles, it can exhibit both *p*- and *n*-type conduction.

It has favourable properties such as high absorption coefficient in the visible region ($>10^4 \text{ cm}^{-1}$), carrier mobility of $30 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$, *p*-type electrical conductivity and photoelectric conversion efficiency. Both Sn and S are earth-abundant constituent elements, less toxic and inexpensive.

The tungsten trioxide has monoclinic structure which is the stable structure and the tin sulphide has orthorhombic structure which is the most stable structure. This WO₃-SnS nanocomposite is an excellent photocatalyst which helps in the photodegradation process

1.12 PHOTOCATALYST

Photocatalysts are substances that, when exposed to light, trigger photocatalytic reactions. A general definition of photocatalysis is a chemical reaction brought on by photo absorption of a solid substance, or "photocatalyst," which remains unaltered during the reaction. A "photocatalyst" must therefore behave catalytically, that is, unaltered, when exposed to light.

1.12.1 PHOTOCATALYSIS

Photocatalysis is used to describe a mechanism in which light is used in the excitation of photocatalyst. Photocatalyst is not involved in accelerating the rate of chemical reaction.

It is the acceleration of a photoreaction in the presence of a catalyst. In catalyzed photolysis, light is absorbed by an adsorbed substrate. In photogenerated catalysis, the photocatalytic activity (PCA) depends on the ability of the catalyst to create electron–hole pairs, which generate free radicals (e.g. hydroxyl radicals: •OH) able to undergo secondary reactions. Its practical application was made possible by the discovery of water electrolysis by means of titanium dioxide (TiO₂).

In other words, photocatalysis is a photoinduced reaction that is stimulated in the presence of a catalyst. Photocatalysis is broadly classified into two categories: homogeneous and heterogeneous.

Homogeneous catalysis:

When both the photocatalyst and the reactant are in the same phase then the reaction is called as homogeneous catalysis. Most common examples of homogeneous catalysis are dyes, coordination compounds, natural pigments and so on.

Heterogeneous catalysis:

In this type of reaction, the photocatalyst and the reactant exist in different phase. Example of heterogeneous catalysis are transition metal chalcogenides which exhibits unique characteristics.

1.12.2 MECHANISM OF PHOTOCATALYSIS

When the photocatalyst is irradiated with light of a specific wavelength, a electron is excited to the conduction band (CB), leaving a positive hole in the valence band (VB). The hole in the VB can be utilized for oxidizing some compounds whereas the electron in the CB is used to reduce any substrate. This is shown in the figure given below

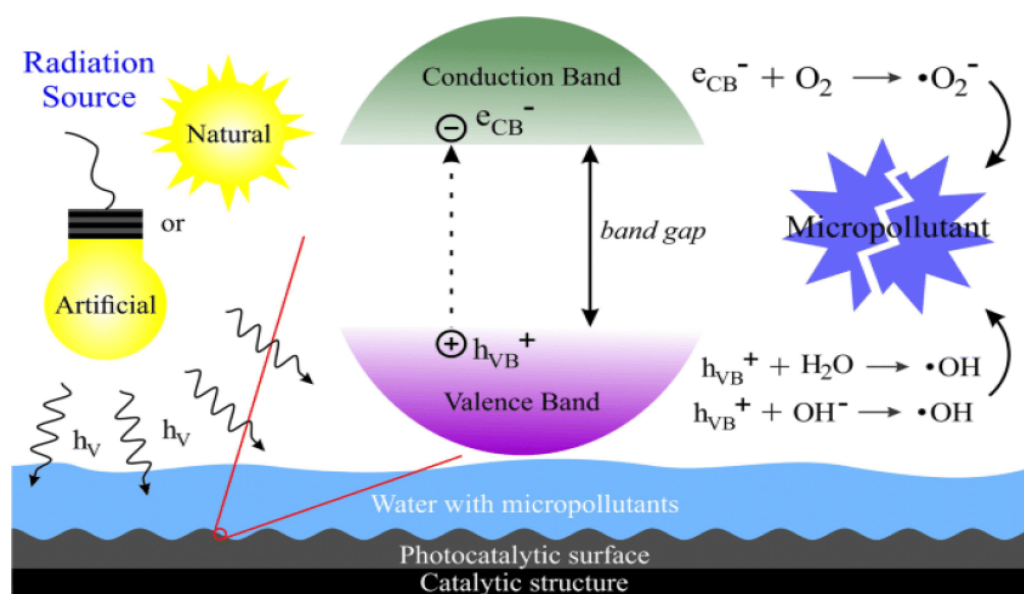


Figure 1.12.3: Mechanism of photocatalysis

APPLICATIONS OF PHOTOCATALYST

Photocatalytic technique has been proven to be one of the most “green” and successful environmental remediation techniques. Some semi-conducting materials, such as 'photocatalysts,' cause or accelerate chemical reactions when exposed to light, resulting in the decomposition of organic molecules, for example, Nanosized catalyst particles have a slightly higher reactivity than larger particles or bulk content owing to their large surface area. Charge separation happens when a photocatalyst is exposed to light with an energy greater than the photocatalyst's band gap energy.

The photocatalyst then initiates an oxidation-reduction reaction using the electrons and holes produced by charge separation. Visible absorption spectroscopy is generally used for the photocatalytic degradation of dyes.[10] The major role of the photocatalyst is shown in the figure.

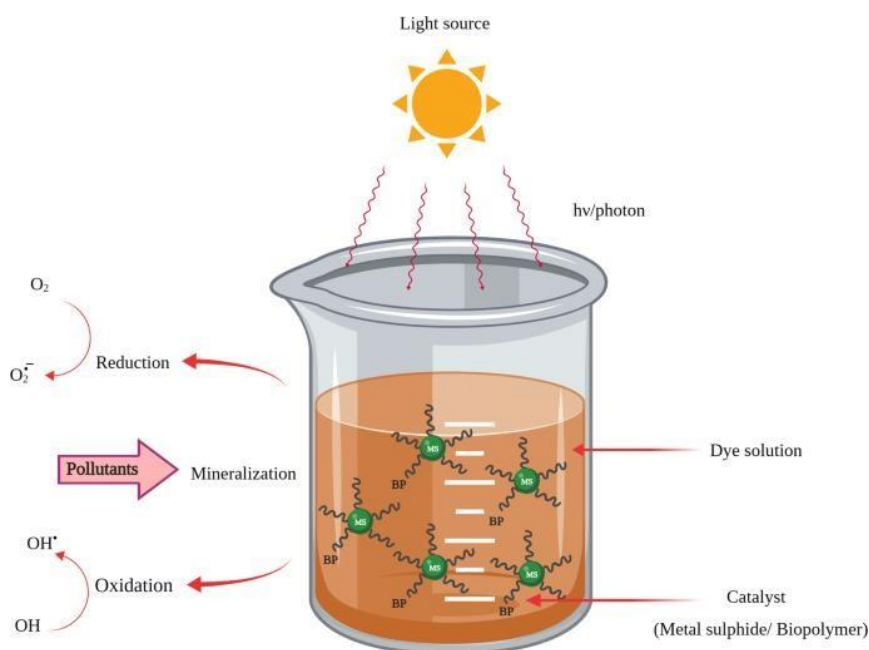


Figure 1.12.5: Role of photocatalyst

Photocatalytic degradation has gained popularity as and is used as a tool for treating dye-contaminated water among a number of treatment methods. Nanoparticles, nanowires, 2D compounds, planar films, 3D porous films, and complex hierarchical nanostructures are just some of the structures and morphologies found in photocatalysts. A variety of implementations have been developed to get the most out of these photocatalysts.

CHAPTER-2

LITERATURE SURVEY

1.Title: Synthesis of WO₃ nanoparticles for biosensing applications

Authors: Lída Santos, Célia M. Silveira, Elamurugu Elangovan, Joana P. Neto, Daniela Nunes

Journal and year : April 2022 (<https://doi.org/10.1016/j.snb.2015.09.046>)

Inference : Direct electron transfer with redox proteins, in third generation biosensors, is already proved to be favored on electrodes modified with nanoparticles. In this work, different crystallographic and morphologic structures of tungsten oxide (WO₃) nanoparticles are modified by hydrothermal synthesis at 180 °C.

2. Title: A Review on the Properties and Applications of WO₃ Nanostructure-Based Optical and Electronic Devices

Authors: Yu Yao, Dandan Sang, Liangrui Zou, Qinglin Wang, and Cailong Liu

Journal and year: 22 August 2021(DOI:[10.3390/nano11082136](https://doi.org/10.3390/nano11082136))

Inference: Tungsten oxide (WO₃) is a wide band gap semiconductor with unintentionally n-doping performance, excellent conductivity, and high electron hall mobility, which is considered as a candidate material for application in optoelectronics. Several reviews on WO₃ and its derivatives for various applications dealing with electrochemical, photoelectrochemical, hybrid photocatalysts, electrochemical energy storage, and gas sensors have appeared recently

3.Title: A novel approach for green synthesis of WO₃ nanomaterials and their highly selective chemical sensing properties

Authors : Vardan Galstyan, Nicola Poli, Annalisa D'Arco, Salvatore Macis, Stefano Lupi and Elisabetta Comini

Journal and year : 26 August 2020

Inference: Metal oxide nanomaterials are very promising candidates for the fabrication of next-generation sensing systems due to their attractive physical, chemical and electronic properties. However, the improvement of their performances to satisfy the

modern requirements in sensing technologies remains a challenging issue. Inspired by natural processes, we report a novel green synthesis approach for the preparation of WO₃ nanomaterials.

4.Title : Synthesis, thermal stability and structural transition of cubic SnS nanoparticles

Author: S.S. Hegde ^a, Prashantha Murahari ^b, BrianJeevan Fernandes ^{b 1}, R. Venkatesh ^c, K. Ramesh ^b

Journal and year : <https://doi.org/10.1016/j.jallcom.2019.153116>

Inference: Recently identified cubic polymorph of SnS (SnS-CUB) is a promising low-cost material for solar cell applications. We report on the thermal stability, structural and optical properties of SnS-CUB nanoparticles. The average crystallite size of cubic SnS nanoparticles synthesized by wet chemical method at 20 °C is about 34.9 nm and unit cell lattice parameter $a = 11.59 \text{ \AA}$. We found that cubic phase remained structurally stable up to 400 °C even though sulfur is partially re-evaporated. The sample annealed at 450 °C contains both cubic and orthorhombic phases. When the annealing temperature is increased to 500 °C, the sample completely transforms to orthorhombic structure.

5.Title: Synthesis of SnS₂/WO₃ nanocomposite with enhanced photocatalytic activity

Authors: Jing Li , Xihua Du , Long Yao , Yongcai Zhang

Journal and year: 14 February 2020(<https://doi.org/10.1016/j.matlet.2014.01.158>)

Inference : SnS₂/WO₃ nanocomposite was synthesized via hydrothermal treatment of tin(IV) chloride pentahydrate, thioacetamide and WO₃ nanoplates in deionized water at 160 °C for 6 h. The structure, composition, BET specific surface area and optical property of the as-synthesized SnS₂/WO₃ nanocomposite were characterized by powder X-ray diffraction, energy dispersive X-ray spectroscopy, transmission electron microscopy, N₂ adsorption and UV–vis diffuse reflectance spectra. The photocatalytic activity of the as-synthesized SnS₂/WO₃ nanocomposite was tested in the reduction of aqueous Cr⁶⁺ under visible-light ($\lambda > 420 \text{ nm}$) irradiation, and compared with those of SnS₂ nanoparticles and WO₃ nanoplates. It was observed that the as-synthesized SnS₂/WO₃ nanocomposite exhibited higher visible-light-activated photocatalytic

activity than SnS₂ nanoparticles and WO₃ nanoplates. The reasons accounting for the photocatalytic results were also discussed.

CHAPTER-3

AIM AND SCOPE OF PRESENT INVESTIGATION

This project work is mainly focused on the following objectives:

- To synthesis novel WO_3 -SnS nanocomposite by chemical precipitation method.
- Characterization of the nanocomposite using XRD, UV, FTIR, SEM
- Determine morphology and size of the nanocomposites
- Photocatalytic degradation of the crystal
- Summarized the obtained results

CHAPTER-4

EXPERIMENTAL AND CHARACTERIZATION TECHNIQUES

4.1 EXPERIMENTAL SYNTHESIS OF TUNGSTEN OXIDE-TIN SULPHIDE ($\text{WO}_3\text{-SnS}$)

Metal oxide – Metal sulphide-based nanocomposite have been synthesized in the chemical precipitation method is discussed below

4.2 MATERIALS

In the process of synthesizing the Tungsten oxide-Tin sulphide ($\text{WO}_3\text{-SnS}$) nanocomposite chemicals such as Sodium tungstate, polyvinyl pyrrolidone, Sodium hydroxide, Tin chloride, sodium sulphide have been used.

4.3 SYNTHESIS OF TUNGSTEN OXIDE-TIN SULPHIDE ($\text{WO}_3\text{-SnS}$)

The synthesis of Tungsten oxide-Tin sulphide nanocomposite has been prepared by the Chemical Precipitation method. It is a two-step process. The first step of the process involves synthesizing of tungsten trioxide ($\text{WO}_3\cdot\text{H}_2\text{O}$).

For this synthesis, 0.2M of Sodium tungstate (Na_2WO_4) and 2g of PVP is taken in a 100mL of deionized water and placed in a magnetic stirrer at 120⁰ C temperature.

Then take 2M sodium hydroxide in 50ml of deionized water in another beaker stir the sodium hydroxide pellets until it gets completely dissolved.

After dissolving, the 50ml of sodium hydroxide solution is added to the solution which is kept in the magnetic stirrer by using a dropper in a dropwise manner. Now the whole

solution is covered using an aluminium foil. This solution is allowed to get stirred for an hour after adding the sodium hydroxide solution.

After completing the 1 hour stirring, add few ml of deionised water to that. Allow the solution for settling. After settling, drop the water and the same process is repeated for several times. Now drop the water where it comes from the sample, finally clean the sample with acetone.

After washing with acetone remaining will be kept at hot air oven at 150 degrees for 12 hours, after drying the solution take it out from the oven and collect the sample by grinding by using mortar. The obtained product is tungsten trioxide ($\text{WO}_3 \cdot \text{H}_2\text{O}$).

The second step of the process involves the synthesis of Tungsten oxide-Tin sulphide nanocomposite ($\text{WO}_3\text{-SnS}$). The first step in this synthesis is 5g of tungsten trioxide ($\text{WO}_3 \cdot \text{H}_2\text{O}$) is taken in a 100ml of deionized water. And it is kept in the Ultrasonicator for about 10mins.

After 10mins, when the particles are thoroughly mixed in the deionized water, 0.5M of Tin chloride is added to it.

Now 2g of Sodium sulphide is taken in a 50mL of deionized water separately and the sodium sulphide flakes is allowed to get dissolved completely. After dissolving, the 50ml of sodium sulphide solution is added to the solution which is kept in the magnetic stirrer by using a dropper in a dropwise manner. Now the whole solution is covered using an aluminium foil. This solution is allowed to get stirred for two hours after adding the sodium sulphide solution.

After completing the 2 hours of stirring, add few ml of deionised water to that. The same process of washing with deionized water is done. Now drop the water where it comes from the sample, finally clean the sample with acetone.

After washing with acetone remaining will be kept at hot air oven at 150 degrees for 12 hours, after drying the solution take it out from the oven and collect the sample by grinding by using mortar. The Tungsten oxide-Tin sulphide

(WO₃-SnS) nanocomposite is synthesized.

TUNGSTEN OXIDE-TIN SULPHIDE (WO_3 -SnS) NANOCOMPOSITE

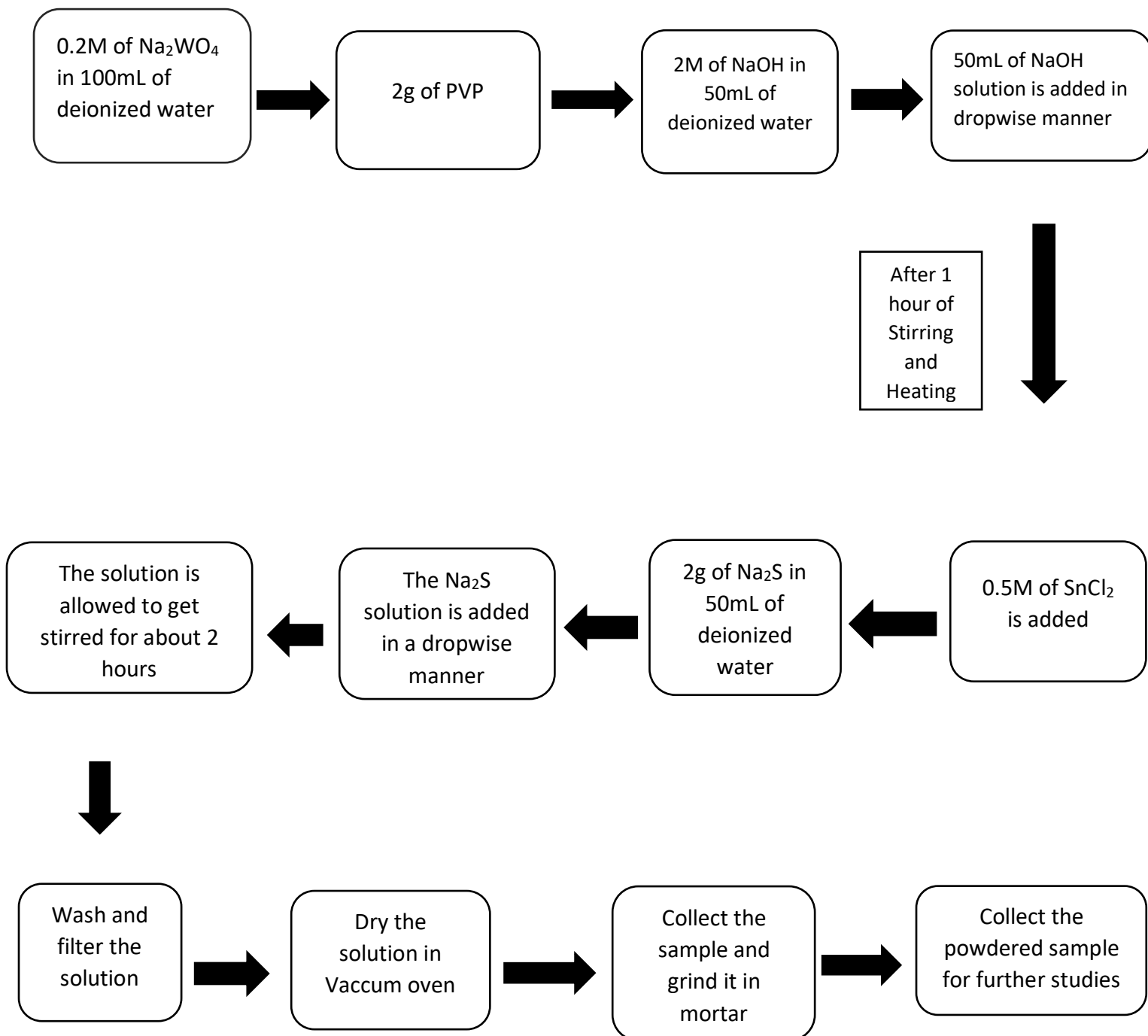


Figure 4.1: synthesis of WO_3 -SnS nanocomposite

Finally, WO₃-SnS Nanocomposite will be confirmed by characterization techniques (UV, FTIR, SEM, XRD).

4.4 CHARACTERIZATION TECHNIQUES

Crystal structure, morphology, compositional information, and photocatalytic application of the synthesized nanoparticles were characterized using the following instruments. These include X-ray Diffraction (XRD), Scanning Electron Microscope (SEM), Fourier Transform Infra-red spectroscopy (FTIR), UV-Vis spectroscopy.

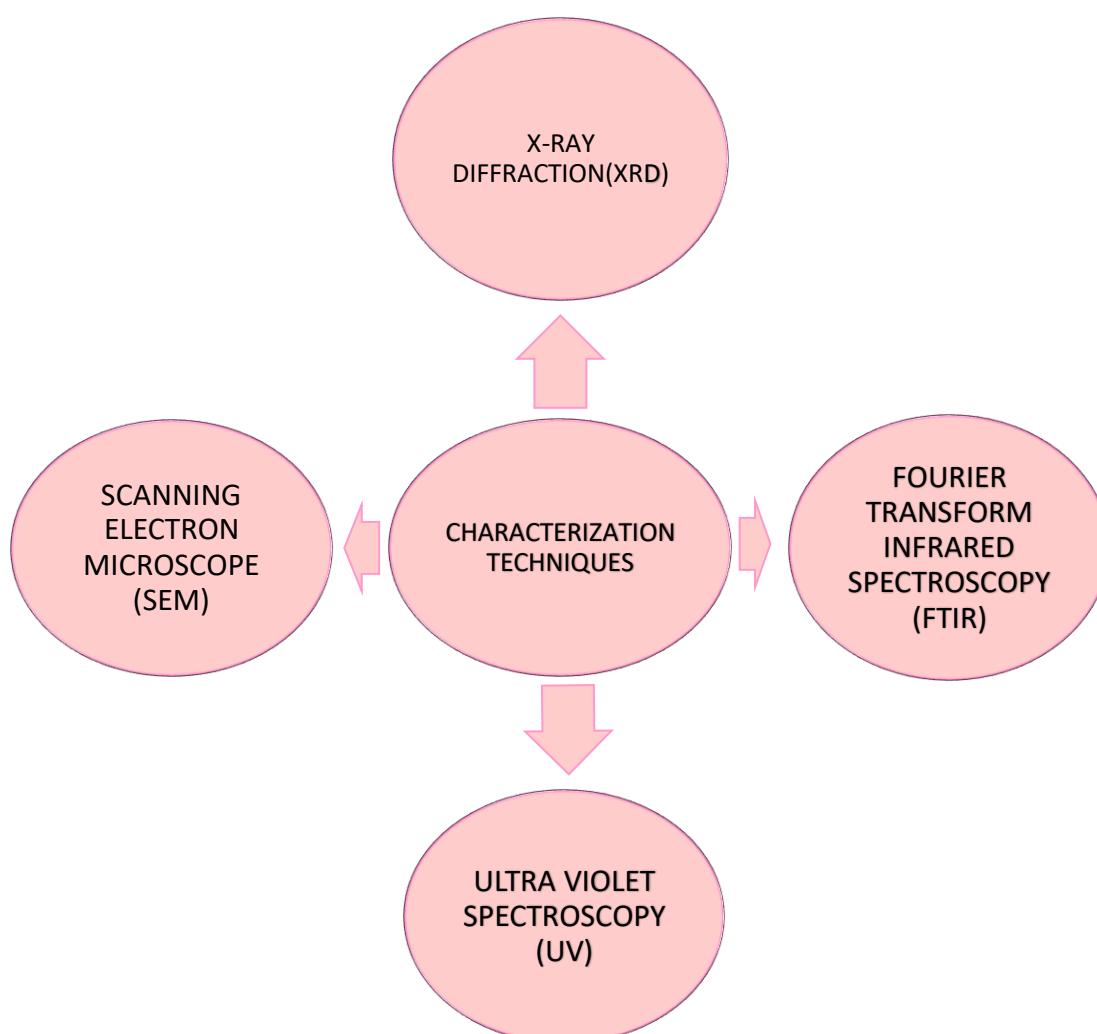


Figure 4.2: Characterisation techniques of nanocomposite

4.4.1 X-RAY DIFFRACTION (XRD)

XRD is one the characterisation technique that reveals the structural properties of nanoparticles. It provides information on the phase, chemical composition, symmetry of unit cells, crystallinity, lattice constant and properties of the nanoparticles. This technique is employed for the identification of both single and multiphase nanoparticles.

XRD is considered as one of the oldest non-destructive methods for the analysis of nanoparticles. The XRD pattern is influenced by the size and shape of the unit cell of the crystal. Consequently, properties of a material are dependent on their structure. Of about 90% solid materials are crystalline in nature and each crystalline has a significant X-ray diffraction pattern which can be used as fingerprint to detect the material.

Diffraction pattern is obtained only when the X-rays are interacted with the crystal. Information like symmetry of the unit cell, stress, strain, size of crystallite and growth orientation etc. are obtained from the diffraction patterns.

BRAGG'S LAW

When a material is irradiated with a monochromatic light of wavelength around the inter atomic distance of the material, light gets dispersed by the atoms and interfere to give rise to diffracted light with a higher intensity. The arrangement of atoms in the material is related to the intensity of the scattered light. If wavelength of light is λ and the incident angle is θ and the constructive interference is obtained at an angle 2θ from the incident beam of light if Bragg's equation is satisfied. Bragg's equation is given by,

$$n\lambda = 2d \sin \theta$$

where,

n is the diffraction order,

d is the distance between the diffracting planes and

θ is the Bragg's angle.

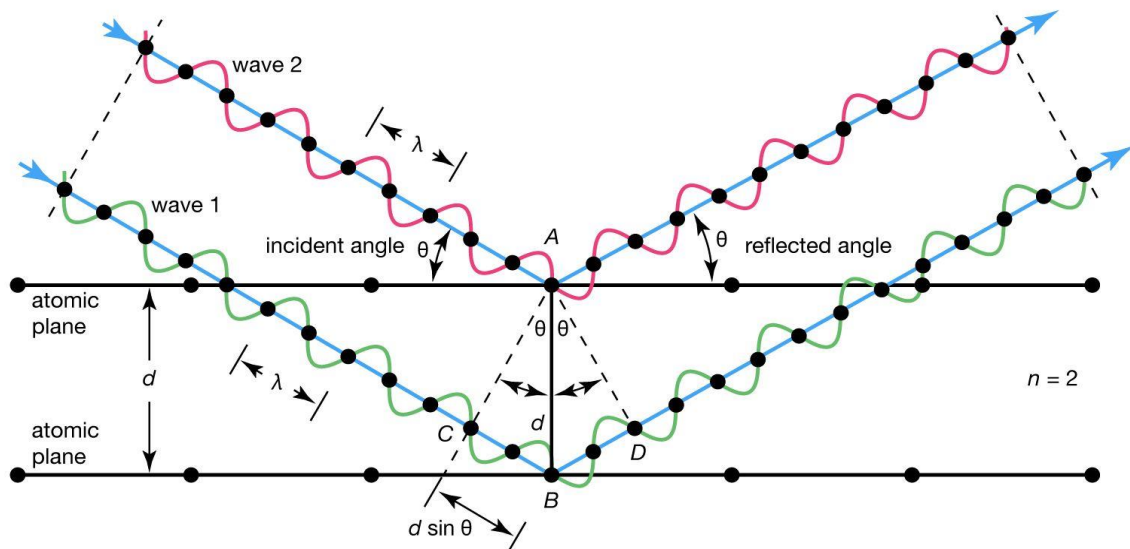


Figure 4.3: schematic representation of Bragg's law

4.4.2 SCANNING ELECTRON MICROSCOPE (SEM)

High resolution scanning electron microscope (SEM) is a very useful for the characterization of size and shape of the nanoparticle. The sample preparation and acquisition of images are relatively easy and convenient. Since the SEM image is a two-dimensional (2D) representation of three-dimensional (3D) structures from a certain viewing angle, it does provide a certain amount of 3D detail that can be used to recreate the shape of a basic structure with sub-nm precision using model-based measurement.

Secondary electrons (SEs) and/or backscatter electrons (BSE) produced when the sample is bombarded by the primary electron (PE) beam provide the signal that causes a SEM image to be created. A SEM's overall accelerating voltage is usually 30 kV. The SE has a limited escape depth in the region of a few nm owing to their low energy below 50 eV, while the BSE has a slightly higher escape depth in the range of a few nm.

The demand for SEM in laboratories to characterise nanoparticulate materials is increasing because of the application of nanoparticles in the commercial products.

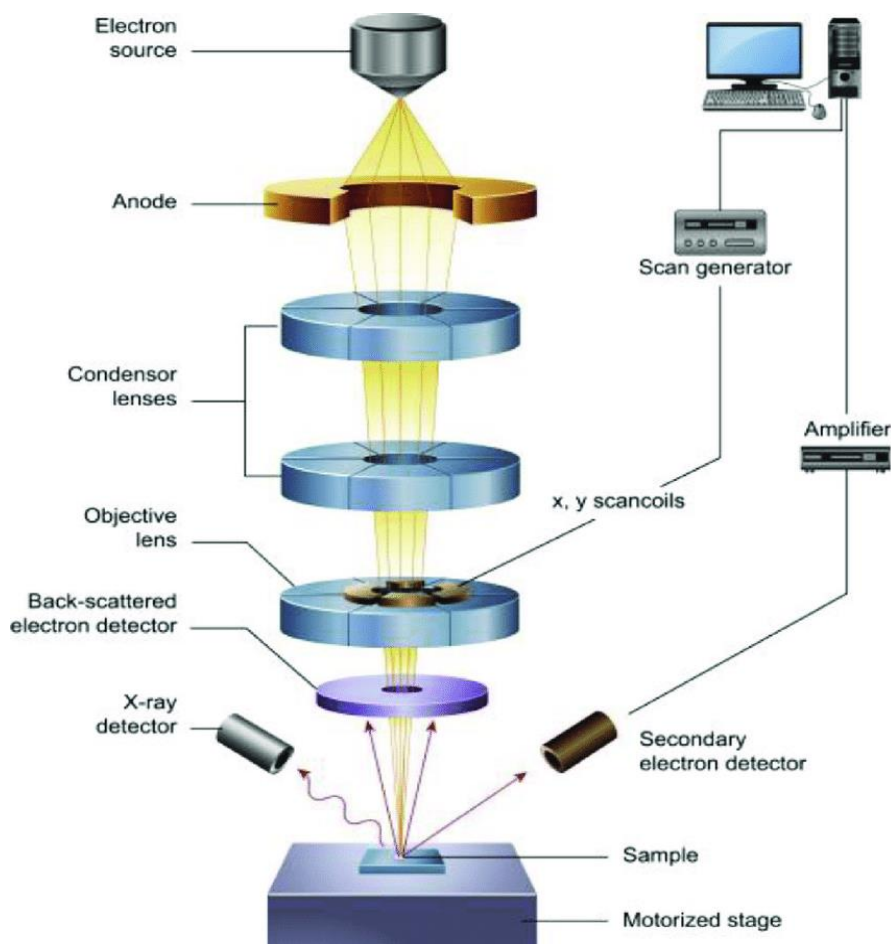


Figure 4.4.2: Schematic representation of SEM

4.4.3 FOURIER-TRANSFORM INFRARED SPECTROSCOPY

Fourier transform infrared (FTIR) spectroscopy is a very efficient non-destructive characterization technique for surface characterization of nanoparticles' surfaces, providing a specific setup is connected to the spectrometer.

it is used to determine the functional groups. The chemical structure of the nanoparticles' surface and the surface reactive sites responsible for surface reactivity can be determined under particular conditions.

The structure and bands of the synthesised nanoparticles, FTIR may be used to test a variety of components, including bulk or thin films, liquids, solids, pastes, powders, fibres, and other materials. FTIR analysis may be used for quantitative (amount)

analysis as well as qualitative (identification) analysis of materials where appropriate criteria are used. FTIR can test samples up to 11 mm in diameter and weigh in bulk or the top 1 mm of the sample.

The difficulty in FTIR characterization is mainly because of high degree of overlapping of the IR absorption bands which makes difficult for the attribution of certain functional groups, despite the fact that up to date computer-searchable databases are available.

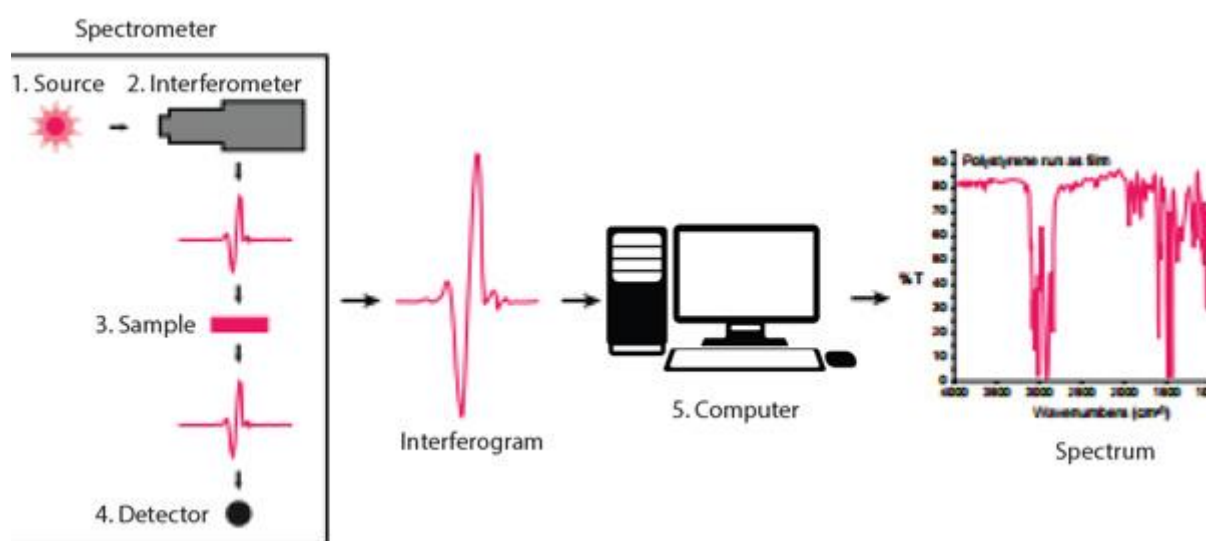


Figure 4.4: Schematic representation of FTIR

4.4.4 UV-VISIBLE SPECTROSCOPY

UV-Vis spectroscopy is an analytical technique that measures the amount of discrete wavelengths of UV or visible light that are absorbed by or transmitted through a sample in comparison to a reference or blank sample.

Absorption spectroscopy is complementary to fluorescence spectroscopy, in that fluorescence deals with transitions of electrons from the excited state to the ground state, while absorption measures transitions from the ground state to the excited state.

Molecules containing bonding and non-bonding electrons (n-electrons) can absorb energy in the form of ultraviolet or visible light to excite these electrons to higher anti-bonding molecular orbitals.

The more easily excited the electrons (i.e. lower energy gap between the HOMO and the LUMO), the longer the wavelength of light it can absorb. There are four possible types of transitions ($\pi \rightarrow \pi^*$, $n \rightarrow \pi^*$, $\sigma \rightarrow \sigma^*$, and $n \rightarrow \sigma^*$), and they can be ordered as follows: $\sigma \rightarrow \sigma^* > n \rightarrow \sigma^* > \pi \rightarrow \pi^* > n \rightarrow \pi^*$

UV/Vis spectroscopy is routinely used in analytical chemistry for the quantitative determination of different analytes or sample, such as transition metal ions, highly conjugated organic compounds, and biological macromolecules. Spectroscopic analysis is commonly carried out in solutions but solids and gases may also be studied.

All diluted inorganic solutions are uv active

Solutions of transition metal ions can be colored (i.e., absorb visible light) because d electrons within the metal atoms can be excited from one electronic state to another.

The colour of metal ion solutions is strongly affected by the presence of other species, such as certain anions or ligands. For instance, the colour of a dilute solution of copper sulfate is a very light blue; adding ammonia intensifies the colour and changes the wavelength of maximum absorption ($\lambda_{\max}$).

While charge transfer complexes also give rise to colours, the colours are often too intense to be used for quantitative measurement.

The Beer–Lambert law states that the absorbance of a solution is directly proportional to the concentration of the absorbing species in the solution and the path length. Thus, for a fixed path length, UV/Vis spectroscopy can be used to determine the concentration of the absorber in a solution. It is necessary to know how quickly the absorbance changes with concentration. This can be taken from references (tables of molar extinction coefficients), or more accurately, determined from a calibration curve.

A UV/Vis spectrophotometer may be used as a detector for HPLC. The presence of an analyte gives a response assumed to be proportional to the concentration. For

accurate results, the instrument's response to the analyte in the unknown should be compared with the response to a standard; this is very similar to the use of calibration curves. The response (e.g., peak height) for a particular concentration is known as the response factor.

The wavelengths of absorption peaks can be correlated with the types of bonds in a given molecule and are valuable in determining the functional groups within a molecule. The Woodward–Fieser rules, for instance, are a set of empirical observations used to predict $\lambda_{\max}$, the wavelength of the most intense UV/Vis absorption, for conjugated organic compounds such as dienes and ketones. The spectrum alone is not, however, a specific test for any given sample.

The method is most often used in a quantitative way to determine concentrations of an absorbing species in solution, using the Beer–Lambert law:

where A = absorbance

I = intensity of the incident is the transmitted intensity,

L = the path length

c = concentration of absorbing species

ϵ = molar absorptivity coefficient.

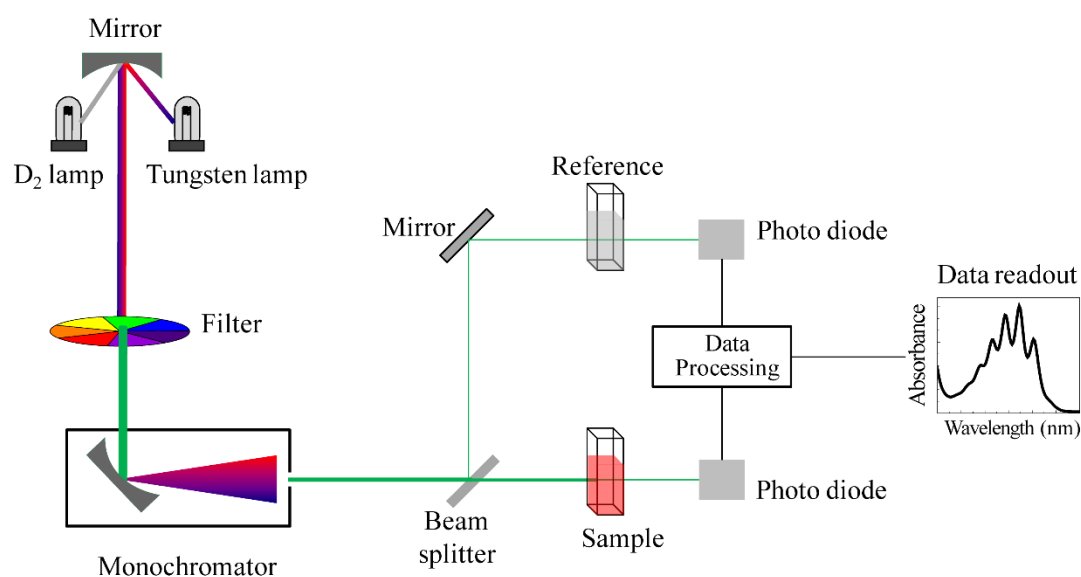


Figure 4.5: schematic representation of uv-visible spectroscopy

CHAPTER - 5

RESULTS AND DISCUSSION

Crystal structure, morphology, structural composition and functional group analysis of the given nanocomposite have been confirmed by characteristic techniques like XRD, SEM, UV-Vis spectroscopy, FTIR.

5.1 X-RAY DIFFRACTION (XRD)

Tungsten oxide nanoparticle with different ratios is taken for XRD studies.

X-ray diffraction (XRD) was used for detecting the crystalline phases represented in below figure.

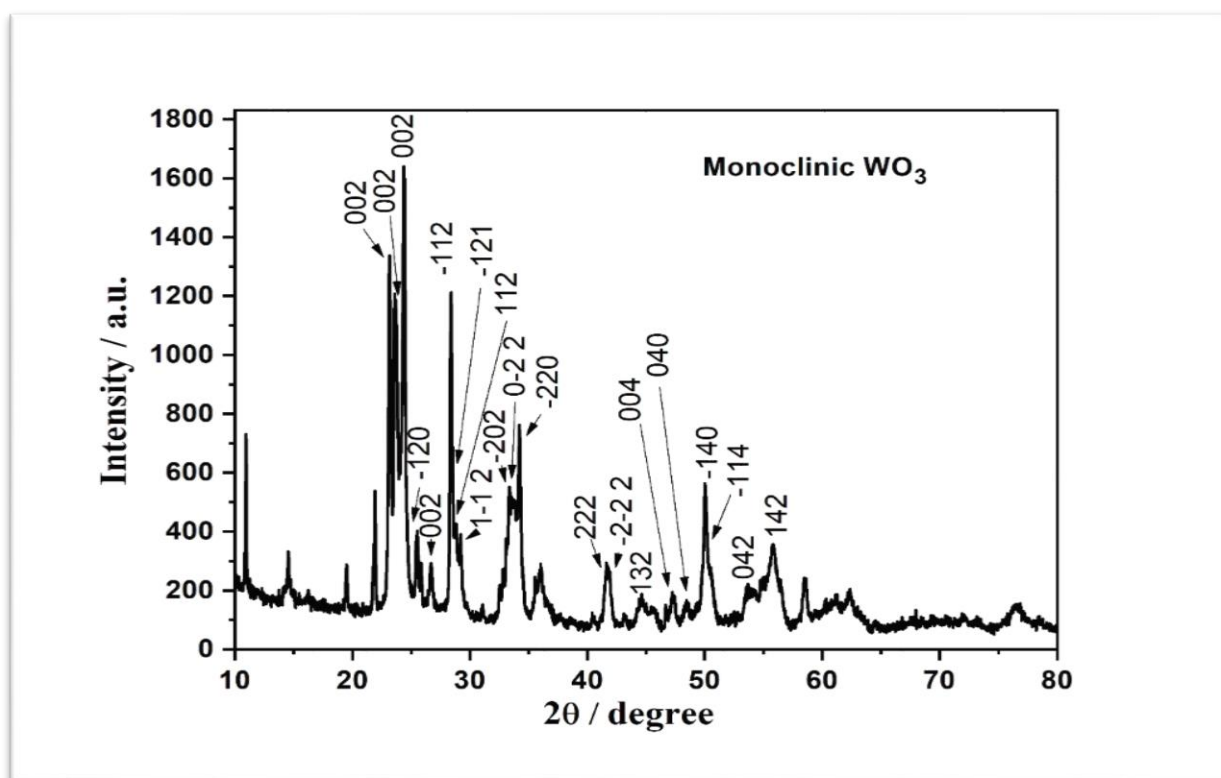


Figure 5.1.1: XRD of WO_3

S.NO	PLANE	2 THETA(DEGREE)
1	WO3 (002)	24.543
	WO3 (112)	28.53
	WO3 (140)	50.15
	WO3 (222)	41.86

Tin Sulphide nanoparticle with different ratios is taken for XRD studies.

X-ray diffraction (XRD) was used for detecting the crystalline phases represented in below figure.

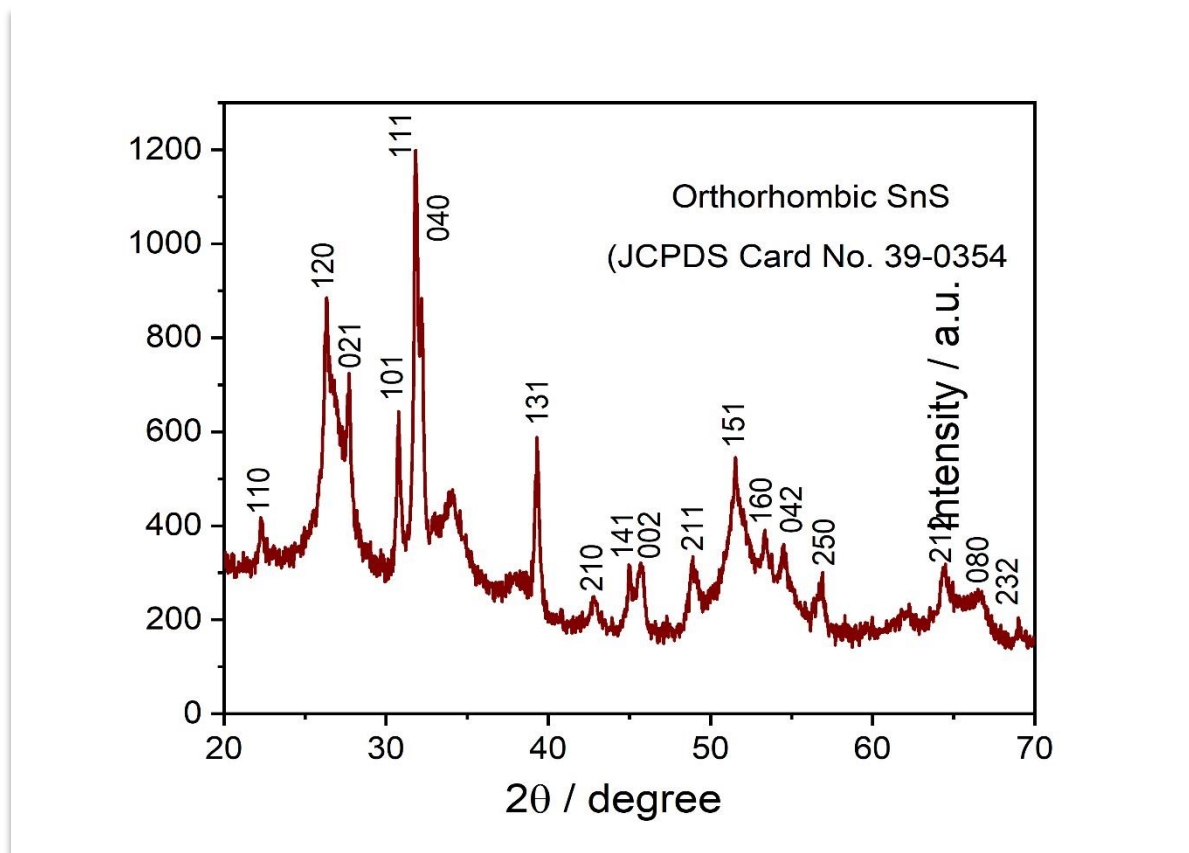


Figure 5.1.2: XRD of SnS

S.NO	PLANE	2 THETA(DEGREE)
1	SnS(111)	31.82
	SnS(131)	39.31
	SnS(151)	51.54
	SnS(212)	64.32
	SnS(250)	56.89

Tungsten oxide and Tin sulphide were elaborated with different ratios to form a homogeneous nanocomposite. X-ray diffraction (XRD) was used for detecting the crystalline phases represented in below figure.

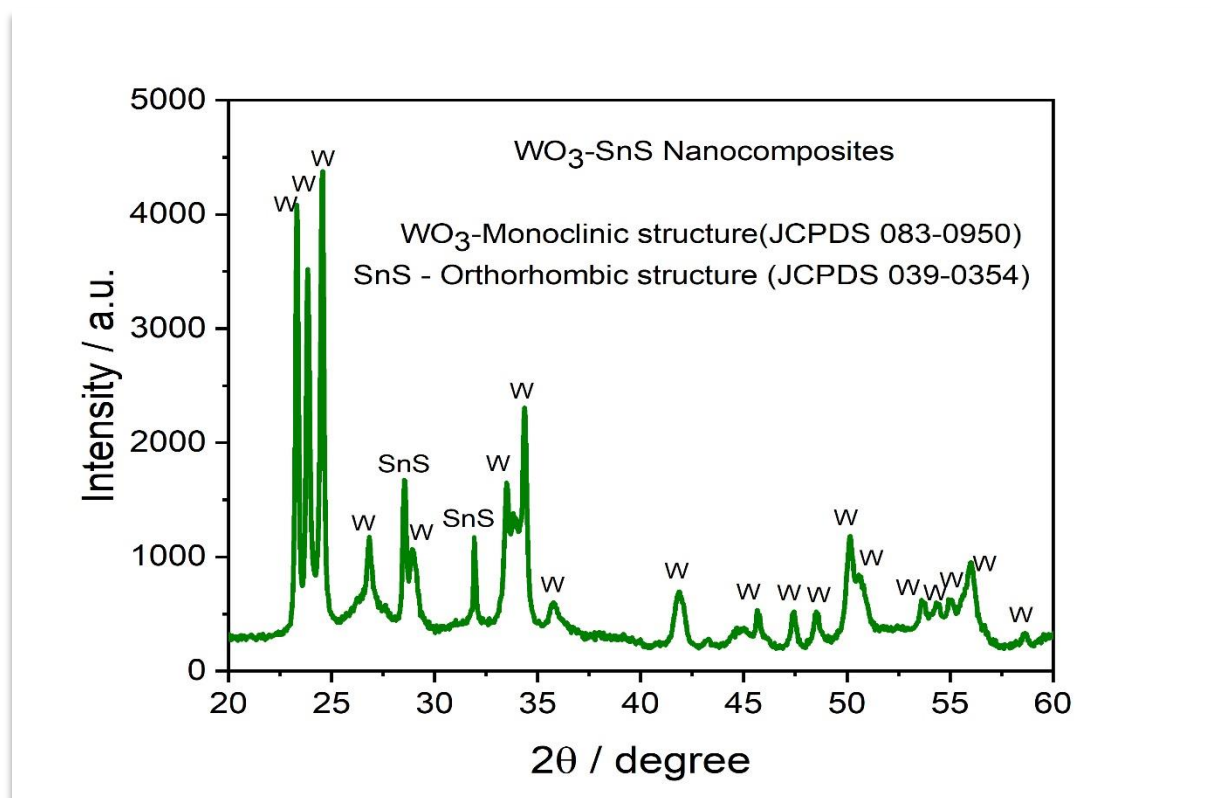


Figure 5.1.3: XRD of WO₃-SnS

S.NO	PLANE	2 THETA(DEGREE)
1	SnS (111)	31.82
	SnS (131)	39.31
	SnS (151)	51.54
	SnS (212)	64.32
	SnS (021)	56.89
2	WO3 (002)	24.543
	WO3 (112)	28.53
	WO3 (140)	50.15
	WO3 (222)	41.86

The Tungsten oxide-Tin sulphide nanocomposite have diffraction peaks where tungsten oxide having diffraction peaks at 24.54, 28.53, 50.15, 41.68 corresponding to Miller indices (002), (112), (140), (222) respectively and for Tin sulphide is well indexed to orthorhombic structure with the planes (111), (131), (151) and (212) corresponding to $2\theta = 31.82, 39.31, 51.54$ and 64.32 .

All the diffraction peaks indicate the monoclinic phase of WO_3 . No significant peaks corresponding to impurities were detected in the XRD pattern. After mixing WO_3 -SnS, peaks of both Tungsten oxide as well as tin sulphide are detected. In the nanocomposite, some intensities of the peaks changed due to peak interference.

The average crystalline sizes of the WO_3 , SnS and WO_3 -SnS nanocomposite were calculated by using Scherrer's equation.

where d is the mean crystallite size, K is the shape factor taken as 0.9, λ is the wavelength of the incident beam, β is the full width at half maximum and θ is the Bragg angle.

$$D = K\lambda / \beta \cos \theta$$

The average crystalline size was found to be 21 nm, 33.7nm and 15.5 nm for WO_3 , SnS and WO_3 -SnS nanocomposite respectively.

5.2 SCANNING ELECTRON MICROSCOPE (SEM)

Scanning electron microscope is especially used for size and shape characterization, because the required sample preparation and image analysis is relatively quick and simple. The scanning Electron Microscopy (SEM) images allowed a detailed study on the morphological structure of the nanoparticles.

The scanning electron microscope operates in the same manner as an optical microscope, but instead of detecting photon, it detects electrons scattered from the sample. The wavelength of electrons can be made shorter than that of photons

because electrons can be accelerated by an electric potential. As a result, the SEM will magnify pictures up to 200.000 times.

The morphological variations in the synthesised sample nanoparticles were detected and analysed. Tungsten oxide analysed by SEM is shown in figure.

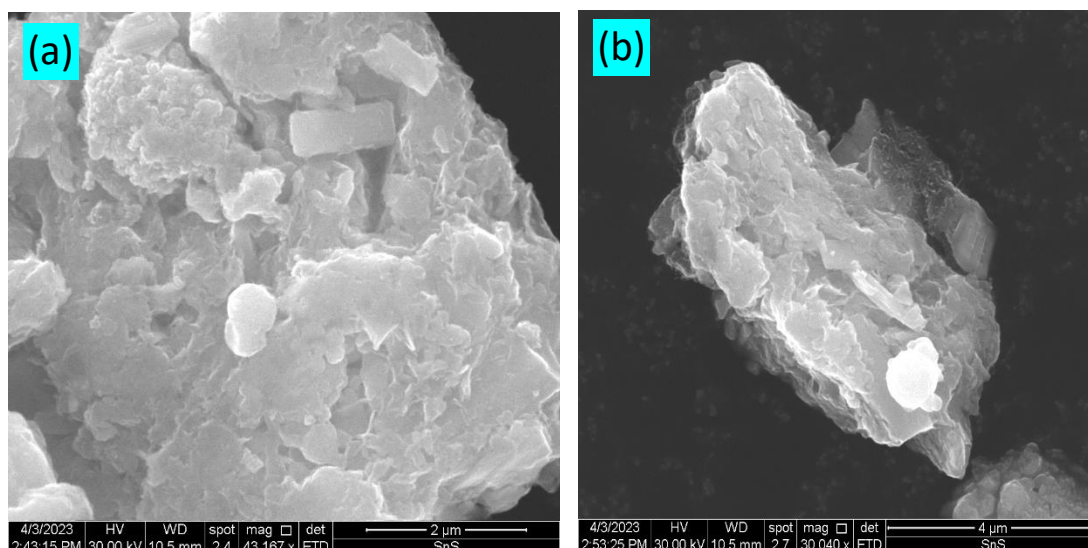


Figure 5.2.1(A-B) Different magnifications of SEM images of the WO₃ nanoparticle

Tin sulphide analysed by SEM is shown in figure.

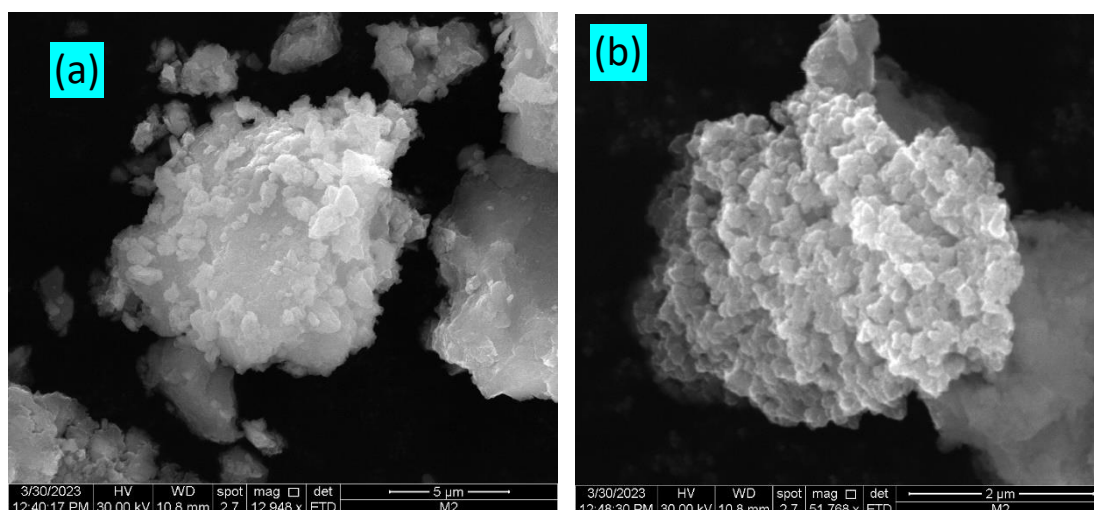


Figure 5.2.2(A-B) Different magnifications of SEM images of the SnS nanoparticle

The morphological variations in the synthesised sample nanoparticles were detected and analysed. WO₃-SnS nanocomposite thus synthesised at low temperature was analysed and the images are displayed in the below figure

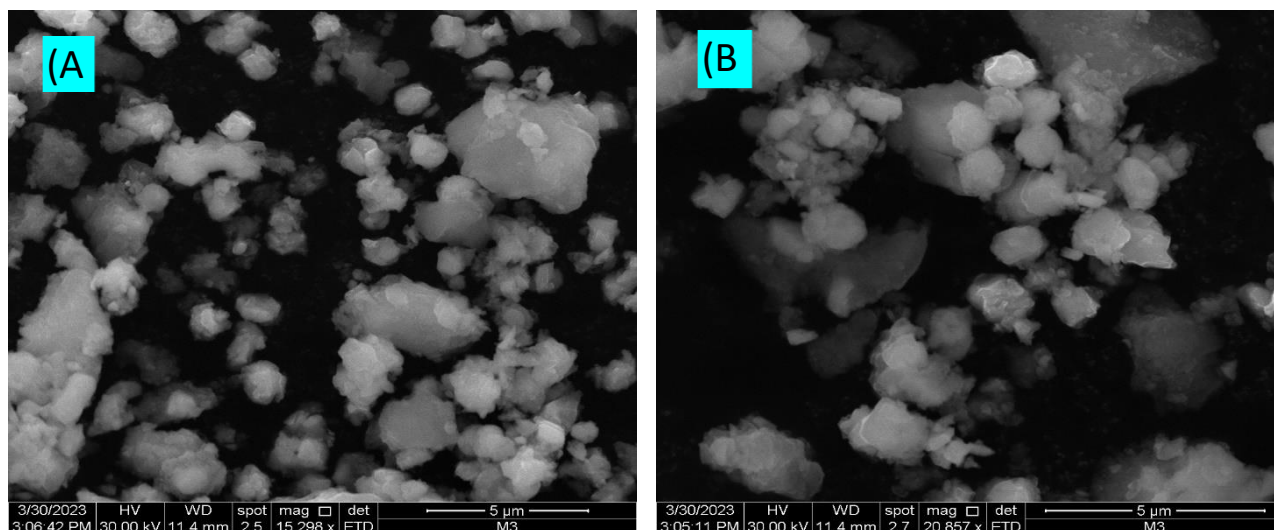


Figure 5.2.3(A-B) Different magnifications of SEM images of the WO₃-SnS nanocomposite.

WO₃-SnS nanocomposites show the cubic and spherical morphology

5.3 FOURIER-TRANSFORM INFRARED SPECTROSCOPY

This technique is used to determine the functional groups present in the given nanocomposite. FTIR spectra exhibit characteristic vibrations of WO₃ particles in the range 400–4000 cm⁻¹

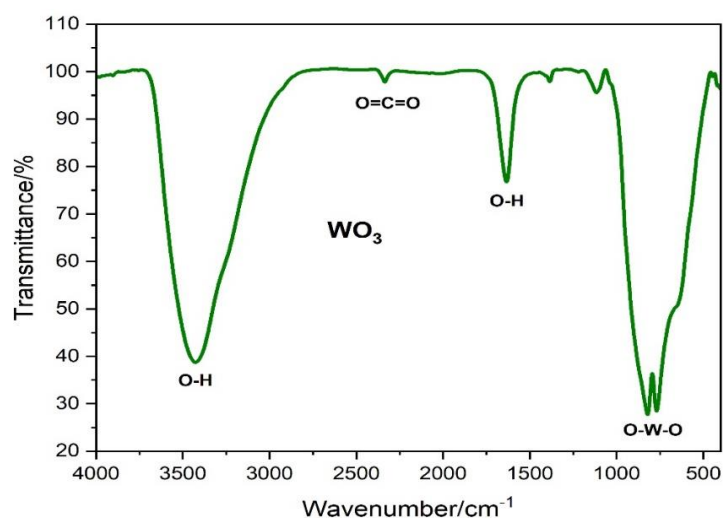


Figure 5.3.1: FTIR OF WO₃ NANOPARTICLE

S.NO	FUNCTIONAL GROUP	WAVENUMBER (CM ⁻¹)
1	O-H	3433
2	O=C=O	2337
3	O-H	1643
4	O-W-O	826
5	O-W-O	774

The above table shows that the various functional groups present at different wavenumbers, in this O-H group observed at 3433 cm⁻¹ then O=C=O group was observed at 2337 cm⁻¹ then after this other O-H group was observed at 1643 cm⁻¹ and then the bands at 826 cm⁻¹ and 774 cm⁻¹ are attributed to the O–W–O stretching mode in WO₃.

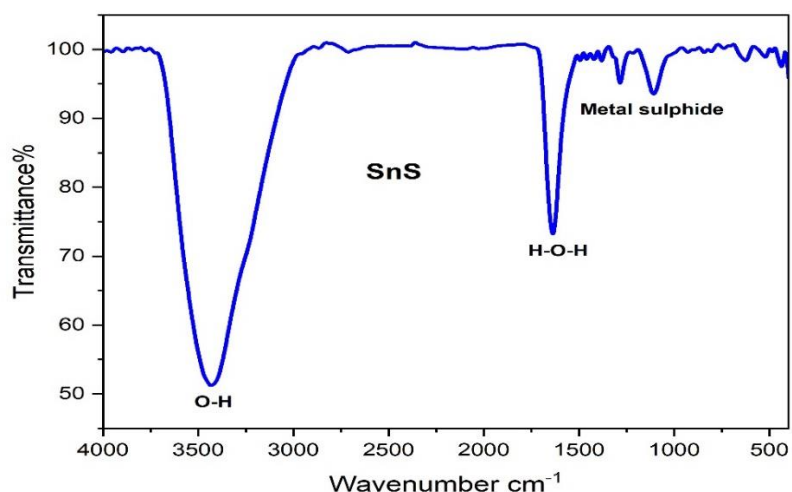


FIGURE5.3.2: FTIR OF SnS NANOPARTICLE

S.NO	FUNCTIONAL GROUP	WAVENUMBER (CM ⁻¹)
1	O-H	3436
2	H-O-H	1644
3	Metal sulphide	1290
4	Metal sulphide	1106

The above table shows that the various functional groups present at different wavenumbers, in this O-H group observed at 3436 cm⁻¹ then H-O-H group was observed at 1644 cm⁻¹ then after this the metal sulphide peak is observed at 1290¹ and at 1106 cm⁻¹

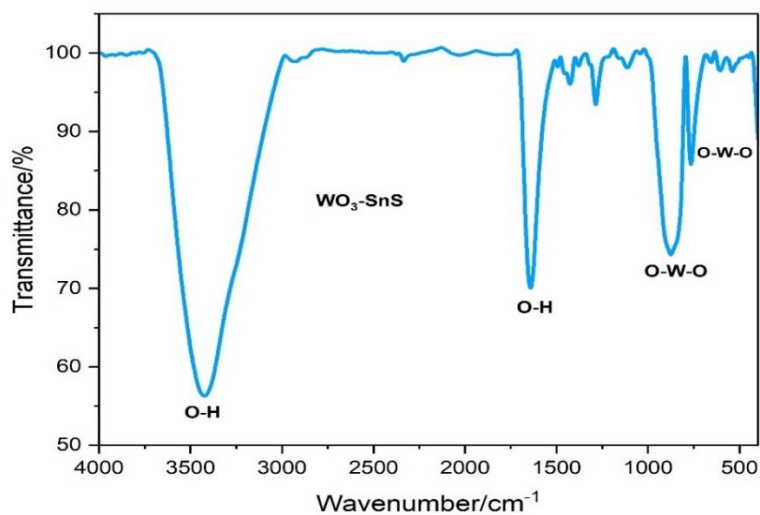


Figure5.3.3: FTIR OF WO₃-SnS NANOPARTICLE

S.NO	FUNCTIONAL GROUP	WAVENUMBER (CM ⁻¹)
1	O-H	3429
2	O-H	1645
3	Metal sulphide	1289
4	Metal sulphide	1128
5	O-W-O	883
6	O-W-O	770

The FTIR spectra of Tungsten oxide-Tin sulphide nanocomposite is taken. The band appeared at 3429 cm⁻¹ is related to stretching vibration of a surface hydroxyl group, which is probably due to the fact that re-adsorption of water from the ambient atmosphere has occurred. The band appeared at 1645 cm⁻¹ is related to stretching vibration of tungsten hydroxyl (W–OH) bond. The spectrum shows a strong

band at 800–600 cm⁻¹ range for O-W-O stretching mode which is observed at 883 cm⁻¹ and 770 cm⁻¹ then after this the metal sulphide peak is observed at 1289cm⁻¹ and at 1128 cm⁻¹.

5.4 UV-Visible SPECTROSCOPY

Ultraviolet-visible (UV-Vis) spectroscopy is a widely used technique in many areas of science ranging from bacterial culturing, drug identification and nucleic acid purity checks and quantitation, to quality control in the beverage industry and chemical research.

It is a quantitative technique used to measure how much a chemical substance absorbs light. This is done by measuring the intensity of light that passes through a sample with respect to the intensity of light through a reference sample or blank.

This spectroscopy technique is also used to determine the absorption of the given nanocomposite under suitable conditions.

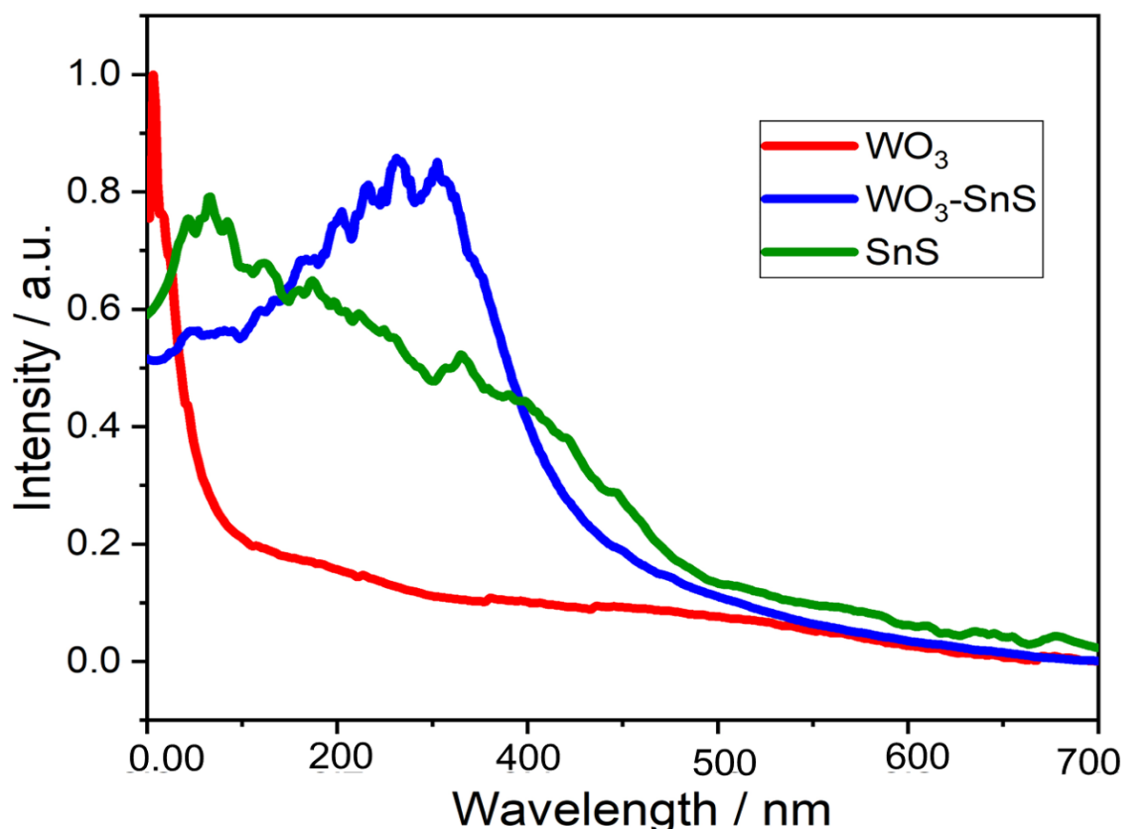


Figure 5.4.1: UV-VISIBLE SPECTRA OF WO₃, SnS AND WO₃-SnS

From the graph, we come to know that the absorption peak of WO₃, SnS and WO₃-SnS nanocomposites which are 360nm, 500nm and 470nm respectively.

5.5 PHOTODEGRADATION STUDY

5.5.1 Photocatalytic activity test

Rose Bengal (RB) was chosen as the model organic pollutants to test the photocatalytic dye degradation analysis for the catalyst. Typically, a catalyst (20 mg) was added into the 50 ml of aqueous dye solution (20 mg L⁻¹) then, the dye solution was kept in dark room to attain the adsorption and desorption equilibrium of dyes on surface of catalyst. Then, the dye solution was irradiated on sunlight for overall time period of 120 minutes. 2 ml of solution was taken at appropriate interval of time. The collected solution was centrifuged and filtered using a 0.2 μm syringe filter. The

degradation efficiency is determined by the degradation of organic dyes on UV-Vis spectrophotometer. The degradation efficiency is calculated by the formula,

$$\text{Degradation efficiency (\%)} = \frac{C_0 - C}{C_0} \times 100 \quad (1)$$

Where C and C₀ are initial and final concentration of dye molecules. After 1st completed the photocatalytic reaction, the catalyst was collected by centrifuge and washed with water and dried at 70°C. The regenerated catalyst was used to evaluate the stability and reusability of catalyst by degradation the dye solution.

The first order kinetic reaction value was used to determine the correct degradation rate of RB as follows;

$$-\ln(C/C_0) = kt \quad (2)$$

Where, k = rate of reaction constant and t is time. The Photocatalytic dye degradation activity were performed during the well sun shining between 11:00 AM to 2:00 PM in clear sky. The average solar light intensity was measured about 1.00 x 10⁵ lux.

Result and discussion

5.5.2 Photocatalytic activity

The photocatalytic degradation efficiency of as prepared catalysts of WO₃, SnS, and WO₃-SnS nanocomposites were resolute by the degradation of RB dye under irradiation of Sun light. When irradiating the RB dye solution, the concentration of the dye was noticeably reduced, and it was confirmed by the significant colour variation. For WO₃ and SnS catalyst, the catalyst influences the organic molecule to achieve the efficiency of about 58.3% and 71.8% within 120 minutes, respectively. The photocatalyst experiment was further extended to WO₃-SnS nanocomposite sample. The degradation reaction of WO₃-SnS sample was performed by the same experimental condition. The rate of electron-hole pair delayed recombination and higher light absorption were achieved by incorporation of WO₃ and SnS structure results increased the degradation efficiency. Compared to pure WO₃ and SnS catalyst, WO₃-SnS catalysts reached high efficiency of degradation of 94.5% and UV spectra shown in Fig.1(a-c)[1,2].

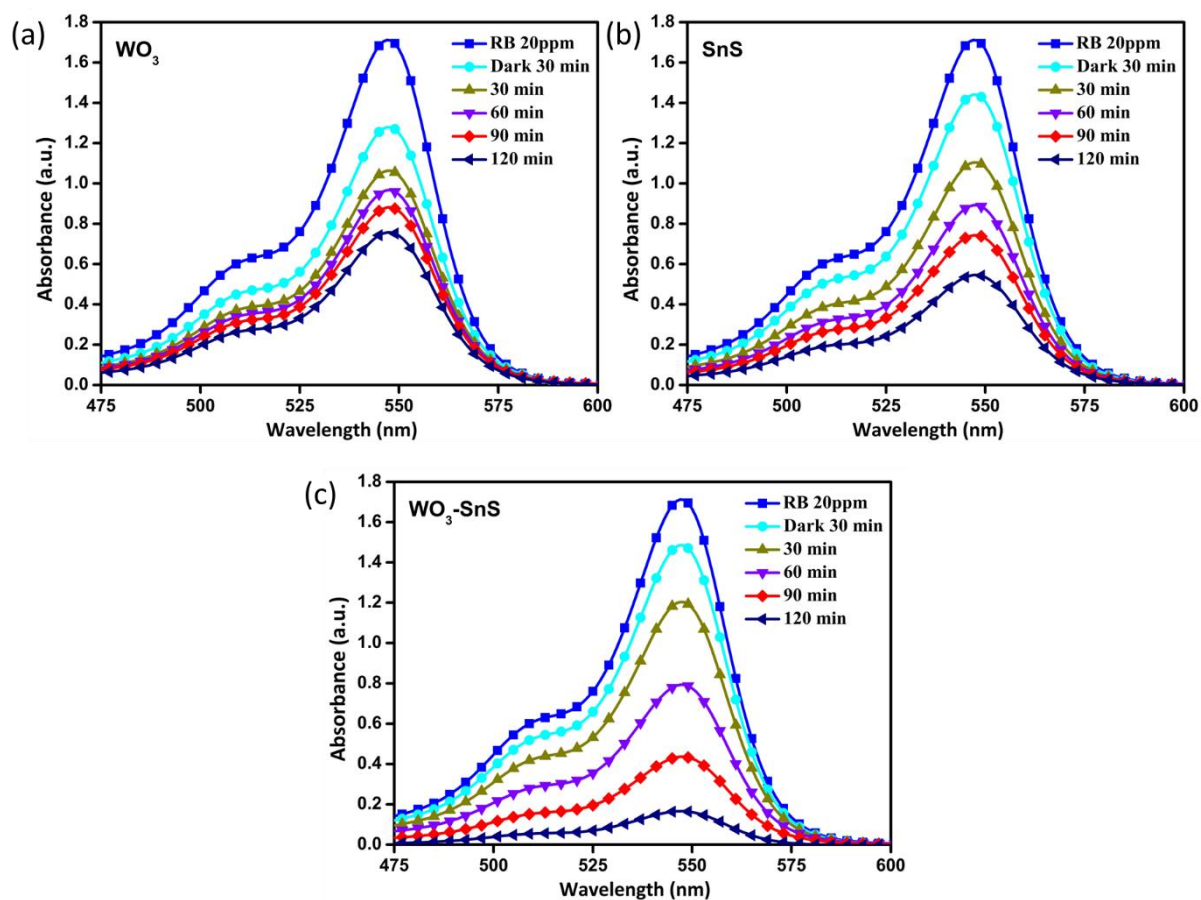


Figure.1 (a-c) represents the UV-visible spectra for the RB with occurrence of catalysts WO_3 , SnS , and $\text{WO}_3\text{-SnS}$ were irradiated by sun light for 120 minutes.

The significant improvement of the degradation efficiency is due to the composite effect of different nanoparticle of $\text{WO}_3\text{-SnS}$ lattice sites, it reduces recombination of excited charge carriers (electron-hole pair). Fig.2(a) depicts the changes in initial and final concentration of dye in the presence and absence of photocatalyst against the light irradiation with respect to time (t) for the RB dye solution. The $\text{WO}_3\text{-SnS}$ catalyst shows highest degradation ability due the fact that sub energy-level act as traps for recombination. Based on the sub energy level of the conduction band helps to produce the large number of reactive oxygen species (ROS).

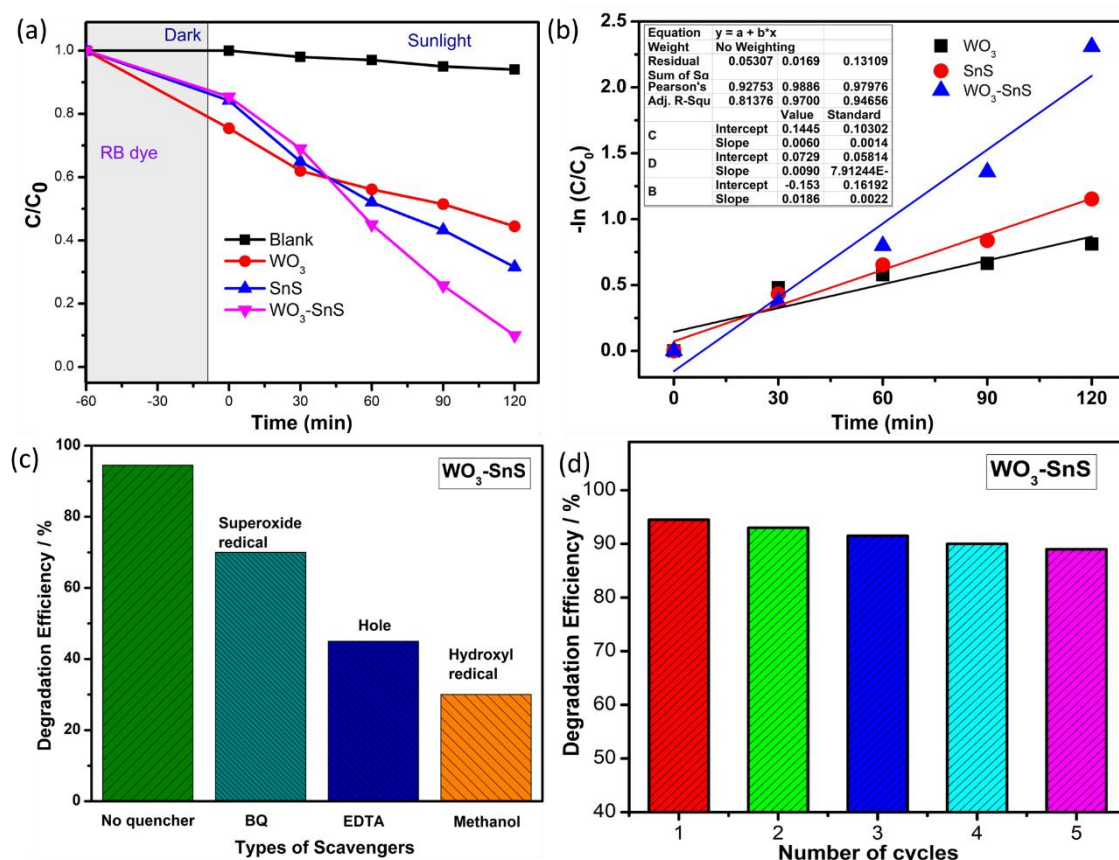
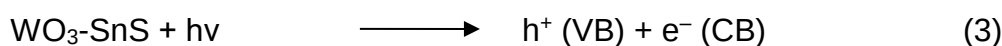


Figure.2 (a) C/C_0 versus time interval plot of RB dye (b) $-\ln(C/C_0)$ versus time interval plot of RB dye (c) Scavengers study (d) reusability test graph of photocatalytic activity.

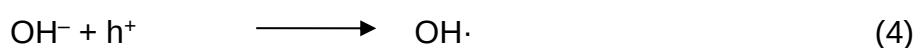
Addition investigation of pseudo-first order kinetics studies shown in Fig.2(b) the degradation rates were 0.013 min^{-1} , 0.020 min^{-1} and 0.042 min^{-1} for WO_3 , SnS, and $\text{WO}_3\text{-SnS}$ nanocomposites against RB dye, respectively. From the studies rate constant value and R^2 values are listed in the Table.1.

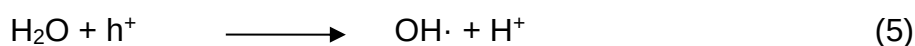
The mechanism of RB dye degradation for the $\text{WO}_3\text{-SnS}$ catalyst is described as follows,

(i) Formation of electron hole pair

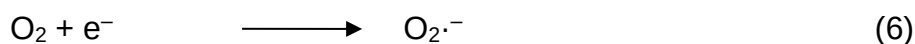


(ii) Formation of hydroxyl radicals





(iii) Formation of superoxide radicals



(iv) Photo degradation of Rose Bengal dye



Basically, a heterogeneous photocatalytic dye degradation reaction is composed of two consecutive steps, i) Dye molecules interact with the catalyst (adsorption occurs on the surface) ii) Photodegradation of the dye begins. So, the photocatalytic system is majorly depending on adsorption and photodegradation capability of the catalyst. Subsequently, as the highest degradation efficiency achieved for the $\text{WO}_3\text{-SnS}$ nanocomposites amongst all catalyst, it was only select for the scavenger study for further understanding the degradation mechanism. In general, the photo active catalyst produces the reactive oxygen species (h^+ , $\text{OH}\cdot$, and $\text{O}_2^{\cdot-}$) and it is important to categorise which reactive species impacts a major role during photo degradation. Hence, the h^+ , $\text{OH}\cdot$, and $\text{O}_2^{\cdot-}$ are eliminated by accumulation of related scavengers such as EDTA (h^+ scavenger), Methanol ($\text{OH}\cdot$ scavenger), and p-BQ ($\text{O}_2^{\cdot-}$ scavenger) into reaction solution, respectively. Fig. 2(c) illustrates the efficiency of with and without scavengers. Since scavenger studies, the Methanol only shows the prominent deviations in efficiency of dyes. Therefore, the hydroxyl radicals play significant role the overall photodegradation efficiency [3].

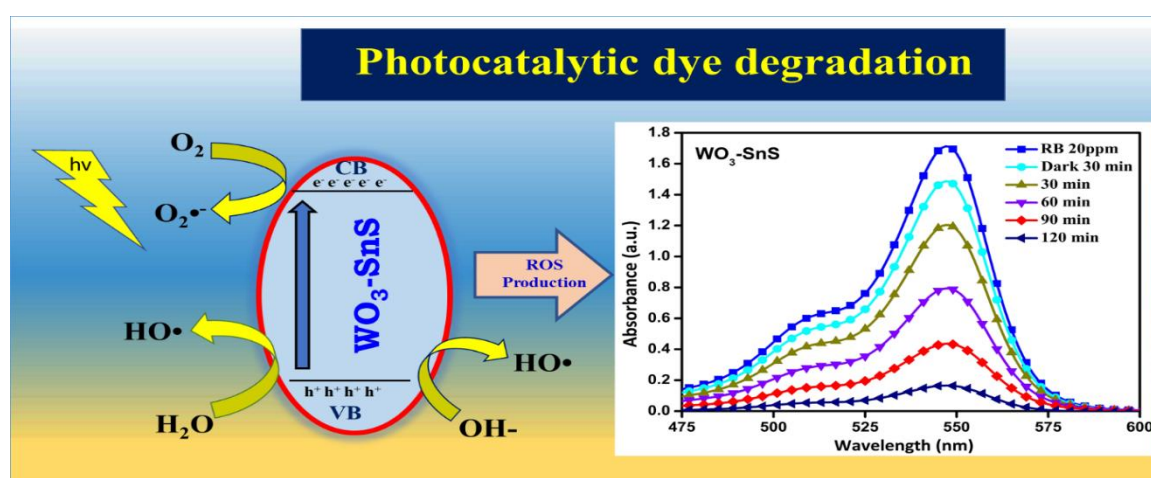


Figure. 3. Schematic diagram illustrating the mechanism of charge separation and photocatalytic activity of photocatalyst under the sunlight irradiation

Table 1 photocatalytic activity result of WO₃, SnS and WO₃-SnS nanocomposites.

S.No	Catalyst	Band gap (eV)	Degradation efficiency (%) (120 minutes)	K (min ⁻¹)	R ²
Rose Bengal (20 ppm)					
1	WO ₃		58.3	0.013	0.81
2	SnS		71.8	0.020	0.97
3	WO ₃ -SnS		94.5	0.042	0.95

Additionally, a very essential study is stability and reusability of photocatalysts (WO₃-SnS nanocomposites). For reusability test, the results reveal the stability of the catalyst and there is no significant loss in degradation efficiency even after five cycles of the photocatalytic process shown in Fig. 2(d). After 5 cycles, the efficiency of catalyst is decreased due to the loss of sample while washing process.

Reference:

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SUMMARY AND CONCLUSION

Mixed Metal Oxide nanocomposite have attracted much attention due to its application in catalysis, dye degradation, electrode materials in battery and optoelectronic devices.

Polyvinylpyrrolidone was used as a surfactant to reduce the particle size.

The low temperature based WO_3 -SnS nanocomposite was synthesized by the two-step chemical precipitation method.

Equal concentration of precursors was used.

Crystallite structure and size was confirmed by XRD. The size of the crystallite was calculated using the Debye Scherrer formula, the size was found to be 15.5nm for the nanocomposite.

The SEM microscopy demonstrated the synthesized nanoparticles were in nanoscale region with asymmetric surface morphology structure.

Organic functional groups presence on the surface of the nanoparticles were identified using FT-IR spectroscopy.

The investigated photocatalytic result demonstrated that WO_3 -SnS nanocomposite showed excellent dye degradation of ROSE BENGAL which is due to its effective charge carriers creation and by the free radical formation during the light irradiation.

Therefore, the synthesized cost effective and low temperature WO_3 -SnS nanocomposite could be the most suitable candidate for the removal of toxic compounds from the textile pollutants, through the photocatalysis.

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