SYNTHESIS AND CHARACTERIZATION OF MESOPOROUS SnO_2 PHOTOCATALYST FOR DEGRADATION OF DYE AND VOLATILE ORGANIC COMPOUND

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Date: 8 July, 2016

Mandeep Kaur

CANDIDATE'S DECLARATION

I hereby declare that the work described in this dissertation entitled **"Synthesis and Characterization of Mesoporous SnO_2 Photocatalyst for Degradation of Dye and Volatile Organic Compound"** which is being submitted by me in the partial fulfillment for requirement of the award of the degree of M.Sc. Chemistry in the School of Chemistry and Biochemistry, Thapar University, Patiala-147004, Punjab is an authenticated record work of six months carried out by me under the guidance of Dr. Ashish Kumar, at Thapar University, Patiala from January to June 2016.

The work is original and has not been submitted for any Degree/Diploma of this or any other university.

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CERTIFICATE

This is to certify that the dissertation entitled **"Synthesis and Characterization of Mesoporous SnO_2 Photocatalyst for Degradation of Dye and Volatile Organic Compound"** that is being submitted by **Ms. Mandeep Kaur** in partial fulfillment of the requirements for the award of degree of Master of Science in Chemistry to School of Chemistry and Biochemistry, Thapar University, Patiala-147004, Punjab is a bonafide work carried out by her under my guidance and supervision. The work has reached the standard necessary for submission.

The results embodied in this dissertation have not been submitted to any other University or Institute for the award of any degree or diploma.

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ABSTRACT

The industrial and domestic waste water effluents from any sources include organic chemicals and pathogens; have maximum pollutants, which can be removed before discharging into the water bodies. One of the major water contaminated pollutant has been measured as methylene blue. Such pollutant is leading in surface water and groundwater. It will cause irreversible hazards to human and aquatic life in present era. Nanotechnology plays a main role in degrading such type of pollutant. In order to fulfill today's requirement, we have decided to handle the eco-friendly green synthesis of nanoparticles and its application by merging important fields like environmental sciences, chemical sciences, and biotechnology. Here our work emphasizes on the single step synthesis of mesoporous SnO_2 nanoparticles (SnO_2 NPs), and it was confirmed by various physico-chemical characterization techniques such as UV–visible spectroscopy, FT-IR, XRD, TEM and BET surface area. The obtained results stated that the synthesized SnO_2 NPs were in spherical shape with an average size of 2-5 nm, which resulted in a product of nanotechnology. Further, we have utilized the eco-friendly synthesized mesoporous SnO_2 NPs photocatalytic degradation of environmental concern methylene blue with first-order kinetics and volatile organic compound (chlorobenzene) showed excellent activity on 0.075 M of SnO_2 NPs due to its reduced crystallite size and high surface area.

Mesoporous SnO_2 (m-SnO_2) nanoparticles prepared by using only pure surfactant had less surface area as compared to prepared by mixture of cationic and anionic surfactants. Photodegradation of methylene blue (83%) and chlorobenzene (92.7%) was found to be efficient by using m-SnO_2 NPs. From our studies, m-SnO_2 nanoparticles showed excellent photocatalytic efficiency making it a promising photocatalyst for degradation of dyes and volatile organic compounds.

Chapter-1

Introduction

CHAPTER 1

1.0 INTRODUCTION

1.1 Nanotechnology and Nanosciences

Nanotechnology is study and application of extremely small i.e. nanosize (10^{-9} m) objects that can used in various field of science and this word brings great innovations that could be beneficial for our future [1]. Exciting thing about "nano" is it's extremely small size (nm). There is no exact definition of nanosciences and nanotechnology but US National Nanotechnology Initiative (NNI) described it as 'Research and technology development in the length scale of approximately 1-100 nanometer range at the atomic, molecular and macromolecular levels, to get a fundamental understanding of materials at the nanoscale and advantage of having small size is used to synthesis and use structures, devices and systems that show novel properties and functions .In nanotechnology much progress was not made until 1980's. After 1980's highly advanced analytical tools were developed rapidly for analysis and characterization of small object having size in nanometer and bring the ideas of human being into real atomic world.

1.2 Catalysis

Catalysis is defined as action in which catalyst takes part in a chemical reaction process and it has the ability to alter the rate of reactions, and yet itself return back to its original form without being destroyed consumed or at the end of the reactions.

Three key aspects of catalyst action

- Taking part in the reaction: react with other reactant and product molecules during the process and changes itself due to interaction between them.
- Altering the rates of reactions: it changes the rates of reaction, either rate of the reaction is increased or in some situation rate of reaction is suppressed.
- Returning to its original form: After reaction cycles are completed catalyst with exactly the same nature is 'reborn'.
- In actual practice a catalyst has its lifespan – every catalyst deactivates gradually during use.

The term catalyst is frequently used to include both the catalyst precursor and the catalytically active species. A catalyst present in chemical reaction accelerates the reaction by forming bonds with the reacting molecules, and by allowing these to react to a product, which detaches from the catalyst, and leaves it unaltered without changing it is chemical properties such that it can be reused for the next reaction.

Important factors that must be considered while using catalyst are:

- Change in the reaction conditions i.e. temperature, pressure etc.
- Concentration of catalyst.
- Catalytic turnover
- The catalyst selectivity to the desired product
- How frequently the catalyst needs renewing.

1.3 Catalysis in industry

There are numerous applications of catalysts in small-scale synthesis and in industrial production of chemicals. Catalysts containing d-block metals are of huge importance to the chemical industry: they provide cost-effective synthesis, and help to control the specificity of reactions otherwise some reaction give mixed products.

Catalysts are the workhorses of chemical transformations in the industry. Catalysts enable industrially important reactions to be carried out efficiently under practically attainable conditions by accelerating the reactions. Catalysts are used efficiently and minimize the waste production. Consequently, the chemical industry is largely based upon catalysis:

Catalysts are key in:

- Production of transportation fuels, bulk and fine chemicals all over the world
- Formation of less unwanted byproducts to prevention pollution.
- Abatement of pollution in end-of-pipe solutions (automotive and industrial exhaust)
- Providing energetically favorable mechanism to the non-catalytic reactions.

Roughly 85–90 % of all products in chemical industry are made in catalytic processes.

1.4 Homogeneous and Heterogeneous catalysts

A homogeneous catalyst is in the same phase as the components of the reaction that it is catalyzing. A wide variety of homogeneous catalysts are known ranging from bronsted and

Lewis acid widely used in organic synthesis, metal ion, organometallic complexes. With this type of catalyst, catalyst recovery is difficult and expensive, thermal stability is poor and good selectivity for single active site.

A heterogeneous catalyst is in a different phase from the components of the reaction for which it is acting. Catalyst recovery is easy and cheap, thermal stability is good and good selectivity for multiple active sites.

1.5 How the heterogeneous catalyst works

In this experiment we have use heterogeneous catalysis. In, heterogeneous catalysis both the reactant and catalyst are in different phases. At the active sites, one or more of the reactants are adsorbed on to the surface of catalyst .Interaction takes place between the surface of catalyst and the reactant molecules which makes them more reactive. Actual reaction is involved with the surface and some bond get weaken.

The reaction happens

At, this stage both the molecules of reactant might be attached to the surface or one, might be attached and is being hit by the other one moving freely in the gas or in the liquid.

The product molecules are desorbed. It means the product molecules break away. This leaves the active site available for a new set of molecules to attach to and react.

1.6 Mesoporous Metal oxides

A great effort has been made in the synthesis and application of ordered mesoporous metal oxides during the past decade. Mesoporous metal oxides have large number of applications in energy conversion and storage, catalysis, sensing, adsorption and separation. The mesoporosity has a direct impact on the properties and potential applications of such materials.

Importance of mesoporous materials

The porosity, such as pore size and specific surface area, is one of the most significant properties of porous materials. On the basis of the pore diameter, an official classification was proposed by the International Union of Pure and Applied Chemistry (IUPAC) [2-4], which is given in Table 1.1.

Table 1.1 Pores are classified according to their sizes

Classification of pores	**Pore size**
Micropores	Less than 2 nm
Mesopores	2 nm to 50 nm
Macropores	Above 50 nm

Mesoporous materials have gained a lot of attention as adsorbents for heavy dyes and harmful organic compounds, owing to their ultrahigh surface area 400-1000 $m^2 g^{-1}$, tunable pore diameter and pore surface. These are generally prepared by soft template method. They also allow molecular accessibility to large internal volumes and surface areas. Mesoporous adsorbents have good adsorption capacity and been proved to have great advantages than traditional adsorbents like activated charcoal and resins.

1.7 Photocatalysis

In this type of catalysis the rate of the photoreaction is modified on addition of substance (catalyst) that participate in the chemical reaction without being destroyed or consumed. Change in chemical reaction is due to absorption of light by one or more reacting species.

The photocatalytic activity in photogenerated catalysis depends on the ability of the catalyst to create electron–hole pairs, which produce free radicals (e.g. hydroxyl radicals: •OH). These further undergo secondary reactions.

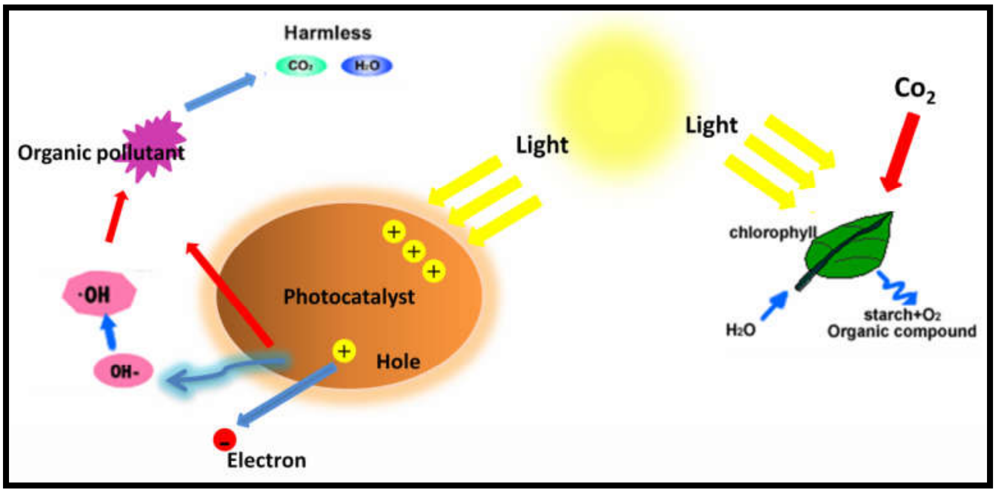

Figure 1.1 Mechanisms of Photocatalysis and Photosynthesis

1.8 Mesoporous SnO_2 Photocatalyst

Tin oxide (SnO_2) nanoparticles are diamagnetic oxide nanostructures having high surface area.

1.8.1 Physical Properties of m-SnO_2 Photocatalyst

Tin oxide appears in the form of a white powder with spherical morphology. (Density = 6.95 g/cm^3 and Molar Mass = 150.71 g/mol)

Figure 1.2 Powder SnO_2 nanoparticles

1.8.2 Thermal Properties

Melting Point = 1630°C and Boiling Point = 1800-1900°C

Mesoporous SnO_2 has attracted attention due to its optical and electronic properties and is an important n-type wide-energy-gap semiconductor ($E_g = 3.6eV$), Semiconductor nanomaterials show high catalytic efficiency, so they are marked effective for environmental and chemical application. Semiconductor photocatalysis with a primary focus on SnO_2 as a durable photocatalyst has been applied to a variety of problems of environmental interest in addition to water and air purification.

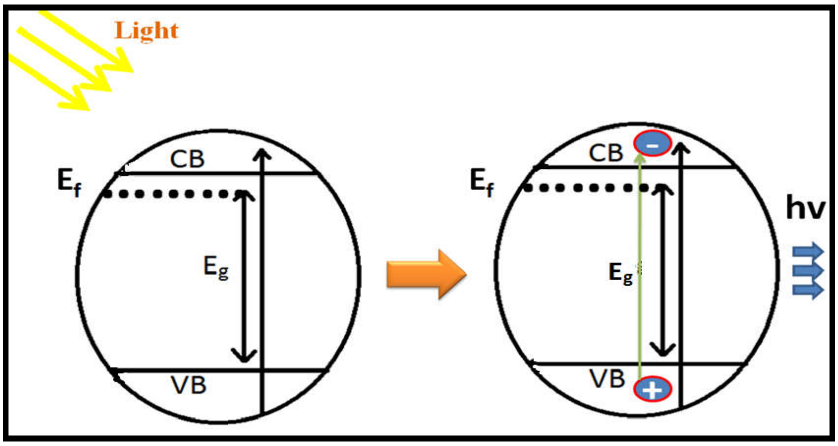

Figure 1.3 Band gap of SnO_2 photocatalyst

Semiconductors have a void region. In this region; no energy levels are available to advance recombination of an electron hole by photoactivation. The separation between filled valence bands to the bottom of the vacant conduction band is called the band gap. Semiconductor absorbs a photon which have energy equal to or greater than the materials band gap. Then photon is absorbed, excited electron move from valence band to conduction band, leaving behind hole in valence band. The excited electron and hole can recombine and release the energy gained from the excitation of the electron as heat. Generation of positive holes and electrons leads to oxidation-reduction reactions that take place at the surface of semiconductors. In the oxidative reaction, the positive holes react with the moisture present on the surface and produce a hydroxyl radical [5].

There are many semiconducting materials that are commercially available and investigated in literature as photocatalysts. But only a few of them are suitable for efficiently catalyzing the photodegradation of a wide range of organic contaminants.

Table 1.2 The semiconducting photocatalysts frequently used in literature work with their band gap energies and threshold wavelengths.

Semi Conductor	Band Gap	Threshold Wavelength
SnO_2	3.6	320
ZnO	3.2	388
TiO_2	3.2	388
WO_3	2.8	443

For a semiconductor to be photochemically active as a catalyst the redox potential of the photogenerated valence band hole must be sufficiently positive to generate -OH and the redox potential of the photogenerated conduction band electron must be sufficiently negative to be able to reduce adsorbed oxygen to superoxide radical anion. SnO_2 is photochemically active as catalyst it shows above mentioned property. Among the semiconductors, SnO_2 has become the benchmark catalyst against which the photocatalytic activity of other semiconductors is measured because of its high photocatalytic activity, large surface area, stability and non-toxicity. ZnO and TiO_2 are also good catalyst.

Other oxides like CuO and Ga_2O_3 were also used as a catalyst but they show poor performance due to lower surface area of CuO and adsorption of UV radiations by the reactor walls which decrease the activity of Ga_2O_3.

1.9 Synthesis of mesoporous metal oxides using surfactant

1.9.1 Surfactants

Surfactants have been of remarkable scientific importance because of their potential applications in fields of physical chemistry and biology [6].

Surfactants are surface active agents that lower the surface tension of a liquid, allowing easier spreading, and lower the interfacial tension between two liquids. Surfactants reduce the surface tension of water by adsorbing at the liquid–gas interface. Many surfactants assemble in the bulk solution into aggregates known as micelles. The concentration at which surfactants begin to form micelles is known as the critical micelle concentration or CMC. Their aggregation phenomena arise from various noncovalent interactions (such as ππ stacking, H-bonding, van der Waals interactions) operating at the molecular level [7].

Surfactant is classified by the existence of formally charged groups in its head.

1. N**onionic surfactant**: has no charge groups present in its head.
   Example: Polyoxyethylene glycol alkyl ether

2. Ionic surfactant: carries a net charge.
   Example: Betaines such as cocamidopropyl betaine have a carboxylate with the ammonium.

Figure 1.4 Alkyl betaine structure

3. Anionic surfactant: The charges are negative and contain anionic functional groups at their head, such as sulfate, sulfonate, phosphate and carboxylates.

Example: Sodium dodecyl sulfate (SDS) is an anionic surfactant with the formula $CH_3(CH_2)_{11}SO_4Na$.

Figure 1.5 Structure of SDS

The sodium salt is of an organ sulfate class of organics. It consists of a 12-carbon tail attached to a sulfate group is attached to 12-carbon tail i.e., it is the sodium salt of dodecyl hydrogen sulfate, the ester of dodecyl alcohol and sulfuric acid. The compound shows amphiphilic properties a hydrocarbon tail combines with a polar "headgroup".

Figure 1.6 Structure of CTAB

In pure water, the critical micelle concentration (CMC) at 25 °C is 8.2 mM , the aggregation number at this concentration is usually considered to be about 62 and the micelle ionization fraction (α) is around 0.3 (or 30%).

4. Cationic surfactant: charge is positive.

Example: Cetyltrimethylammonium bromide (CTAB) a cationic surfactant.

Cationic surfactant systems are gaining much attention because of the tunability of its oppositely charged head groups. CTAB form micelles in aqueous solution. It forms micelles at 303 K (30 °C) with aggregation number 75-120 which depending on method of determination, degree of ionization, the binding constant (K°) of Br^- counterion to a CTA^+ micelle at 303 K (30 °C) is 400 M^{-1}. These micelles further formed a two dimensional hexagonal mesostructure. The template could be further removed by calcination and left a pore structure behind.

Cetyltrimethylammonium bromide is used as a soft template for synthesis of mesoporous materials. Mixtures of the anionic surfactant sodium dodecyl sulfate (SDS) and the cationic surfactant cetyltrimethylammonium bromide (CTAB) are important as they can increase the surface area and absorption ability of the synthesized mesoporous material.

The phase behavior of Incationic/anionic surfactant mixtures, the phase behavior depends on

- actual concentrations of the surfactants
- lengths of their alkyl chains, the temperature
- molar ratio.

Figure 1.7 Proposed Mechanism of nature of cationic and anionic surfactants towards metal oxides

In a pure surfactant, the two similarly charged head groups experience repulsive electrostatic interaction between them that increases the free energy to form micelles.

In catanionic mixtures, the electrostatic interaction between two oppositely charged head groups decreases the free energy to form stable catanionic vesicles, without any high-energy methods such as sonication and extrusion.

Mixtures of cationic and anionic surfactants can form several types of aggregated mesoporous structures such as precipitates, spheres, and rod-like structures etc [8].

In this work, synthesis of SnO_2 mesoporous nanoparticles is done by general method using tin precursor, anionic surfactant and cationic surfactant mixture to get high surface area and absorption efficiency of the synthesized product.

1.10 Application of m-SnO_2

Mesoporous tin oxide is one of the most exciting materials for its versatile properties such as semiconducting (large band gap, Eg = 3.6eV at 300 K) [9] piezoelectric, bio-safe and biocompatible nature. SnO_2 have wide ranging application which has a wide range of applications such as gas sensor [9], dye sensitized solar cell [10], Li –ion batteries [11], catalysis [12] and effective electrode material in electrochemical application. Semiconductor nanomaterials show high catalytic efficiency, so they are marked effective for environmental and chemical application. In recent years, the photocatalytic properties were also extensively studied. Owing to the good photoelectric conversion properties and rapid photo response, SnO_2 exhibits high photocatalytic efficiencies on decomposing organic pollutants in water. Additionally, SnO_2 is nontoxic, abundant in reserves, and easy to obtain, which make it an ideal candidate for practical applications on environmental treatments.

1.10.1 Dye degradation using m-SnO_2 as photocatalyst

Methylene blue:

Chemical formula of methylene blue is $C_{16}H_{18}N_3SCl$. It is a heterocyclic aromatic compound.

Figure 1.8 Structure of methylene blue

It has dark green colour in solid form, and gives blue colour solution when dissolved in water. Methylene Blue, a cationic dye, used in textile manufacturers is potential carcinogen and releases aromatic amines. The synthetic dyes are non-degradable by nature and create threat to aquatic life. Industries through the wastewater containing dye stuff without proper treatment in the rivers and this can create serious problem for human being. Serious side effect in human can be severe nausea, vomiting, or stomach pain, pain in your chest, trouble breathing and high fever etc. Since, one of the major pollutants is dye, under different conditions researchers across the globe attempted to degrade the dye stuff. Many conventional methods such as filtration, sedimentation and adsorption on activated carbon etc. are employed to minimize the hazardous effect of waste water containing dye [13-16]. Therefore; great attention was given on study of physicochemical properties with the activity of mineralization and photocatalytic degradation of harmful dye such as methylene blue. SnO_2 NPs act as one of the best photocatalysts, with n-type of tetragonal crystal structure and a band gap around 3.6 eV [17].

1.10.2 Degradation of volatile organic compounds

Chlorobenzene is a volatile, colorless liquid having an almond-like odor. It is not soluble in water and miscible with most organic solvents.

Figure 1.9 Structure of Chlorobenzene

Chlorobenzene is mostly used as a solvent in formulation of pesticide, in degreasing, and other industrial applications. Chlorobenzene is a central nervous system depressant, and may cause respiratory tract, eye, and skin irritation if consumed by human. Inhalation is the most possible way of human exposure to chlorobenzene. Petrol refining, plastic materials etc are primary source of emissions of chlorobenzenes. Chlorobnezene is a common environmental pollutant and is toxic compound. The degradation of chlorobenzene in presence of mesoporous SnO_2 catalyst by UV irradiation provides a possible route in developing adequate treatment methods [18].

Chapter-2

Literature Review

CHAPTER 2

2.0 LITERATURE REVIEW

2.1 Synthesis of m-SnO_2

Great efforts have been done in the past decade to synthesize SnO_2 with different mesoporous structures and morphologies, including nanorods [19], nanotubes [20] etc having high surface area and better performance. Mesoporous structures have high specific surface area, large pore volume, periodically distributed pores, and peculiar surface properties due to which they are gaining considerable research interest [21]. The mesoporous materials with particular order are regarded as excellent catalyst for photoxidation of dyes and degradation of pesticides. Nithiyanantham et al. synthesized chain-like SnO_2 nano-assemblies at room temperature by a simple wet chemical route in the presence of DNA as a scaffold [22]. Outside silica template no other morphology was seen, all the SnO_2 nanoparticles exhibit rod like morphology having diameter about 6 nm and length between 150-200 nm. Generally, metal oxides prepared using solvent based SBA -15 template leads to the formation of nano-rods and nano-wires like morphology.

Work done by Liu et al. mentioned the preparation of mesoporous SnO_2/C composite by a facile micro-emulsion method at ambient temperature followed by calcinations [23]. These composite shows good electrochemical performance because composite contains nanoparticles having crystalline size equal to 5 nm which is less than as compared to bare SnO_2 nanoparticles (15nm) [24].

Work done by Bai et al. stating “Template-free synthesis of uniform mesoporous SnO_2 nano-spheres for efficient phosphopeptide enrichment” [25] .The TEM image reported in paper reveals the mesoporous structure of a synthesized SnO_2 nano-sphere having nanoparticles having size about 5 nm.

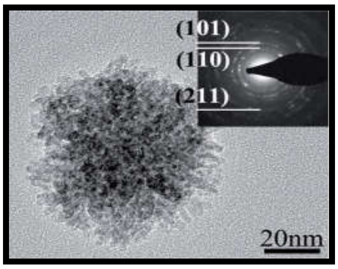

Figure 2.1 TEM image of mesoporous nano-spheres

Table 2.1 SnO_2 nanoparticles synthesis, application and physical and chemical properties.

S.No.	Applications	Methods	Physical and chemical properties	References
1.	Self-assembled SnO_2 nano-assemblies for supercapacitor	Simple wet chemical route	Particle size = 3.5 ± 0.2 nm. Chains length = 1–2 µm. Diameter = 40 ± 5 nm Surface area =163.2 m^2 g^{-1}.	22
2.	Mesoporous SnO_2 as anode materials for lithium-ion batteries	Hydrolysis depositing method	SnO_2 rod diameter =6 nm. Length range = 150–20nm. Nanoparticles agglomerated = 20nm.	23
3.	Mesoporous SnO_2/C Composites as Anode Materials for Lithium Ion Batteries	Facile microemulsion method	Particle size ~ 20 nm. Surface areas of Bare SnO_2 = 32.5 $m^2 \cdot g^{-1}$ SnO_2/C composites=88.3 $m^2 \cdot g^{-1}$	24
4.	m-SnO_2 nanospheres for efficient phosphopeptide enrichment	one-step and template-free method	Particle size = 5 nm Surfacearea =109.9 m^2 g^{-1}	25
5.	Gas sensors and electrochemical devices such as dye-sensitized solar cells	simple hydrothermal routes	Size distribution = 3.0-4.3 nm Specific surface areas as high as 110 m^2 g^{-1}.	26
6.	----	simple thermal decomposition method	Particle size = 20 nm	27
7.	nanoscaled optoelectronic devices	Rapid oxidation of elemental tin	Morphology =straight and curved ribbon. Ribbon widths = 30-160 nm Ribbons thickness= 10-30 nm.	28
8.	nanoscaled optoelectronic devices	Hydrothermal synthesis	Particle size = 8-13nm Maximum Surface area = 112 m^2 g^{-1} Morphology = flower petal, Sheets, rods and Florets of Cauliflower.	29
9.	Methylene blue degradation	Biological synthesis	Particle size = 21 nm Morphology =spherical	32

In past few year , many methods have been developed by researchers to synthesize SnO_2 including hydrothermal method [26], Thermal decomposition using [bis(2-hydroxyacetophenato)tin(II)], $[Sn(HAP)_2]$, as precursor in the presence of oleylamine ($C_{18}H_{37}N$) and triphenylphosphine (TPP) by Salavati Niasari et al. [27], rapid oxidation of elemental tin [28], Gnanam and Rajendran prepared SnO_2 powder by hydrothermal synthesis route [29], evaporating tin grains in air [30] and spray pyrolysis [31].

In Hydrothermal methods by Fujihara et al. [26], mesopouros SnO_2 nanoparticles showed high thermal stability against particle growth owing to high surface areas as 110 m^2g^{-1} even after heating at 400 °C. In addition, particles are mesoporous and have narrow size distribution in the range between 3.0-4.3 nm. Futhermore, thermal decomposition method [27] using [bis(2-hydroxyacetophenato)tin(II)], $[Sn(HAP)_2]$, as precursor in the presence of oleylamine (C18H37N) and triphenylphosphine (TPP) by Salavati-Niasari et al. The tin dioxide nanoparticles showed tetragonal phase without any other impurities. Particles showed good morphologies with particle size in range between 14-22 nm.The XRD patterns obtained for synthesized SnO_2 nanoparticles is shown in figure.

Figure 2.2 XRD patterns of SnO_2 nanoparticles obtained in the presence of oleylamine and TPP

Hu et al. stated rapid oxidation of elemental tin [28] at 1080 °C result in synthesis of SnO_2 with a ribbonlike morphology. The as-synthesized product showed lengths of the nanoribbons up to several hundreds of micrometers, and the typical width having range of 30-150 nm and thickness having range of 10-30 nm. In the visible region, the strong photoluminescence of the nanoribbons suggested potential applications in nanoscaled optoelectronic devices. Gnanam et al. [29] prepared SnO_2 powder by hydrothermal synthesis route. The hydrothermal processing is a substitute to calcination for the crystallization of SnO_2 but it was complicated to control the size of nanoparticles. In this paper, they studied the influence of cationic, anionic and nonionic surfactants on the size, morphology as they are helpful for formation of nanoscale materials. Nanocrystalline particles size was about 8-13 nm. In their structural studies, they found that the addition of different surfactant can influence particle growth, coagulation, and flocculation. Surfactant act as a soft template and nanoparticles are fabricated by Oswald ripening mechanism. Formation of particle is very complex and surfactant assemblies are highly influenced by nucleation, growth and cogulation .Surfactants play an important role. With SDS particle size, surface area and morphology was observed to be 8 nm, 112.10 m^2g^{-1} and flower petal respectively. Further with CTAB particle size, surface area and morphology was observed to be 11 nm, 81.53 m^2g^{-1} and Florets of Cauliflower respectively. Nonionic (PEG) surfactants showed sheets and rod morphology with particle size of 13 nm and surface area of 68.98 m^2g^{-1}.

Table 2.2 Lists amount of catalyst used and reduction time taken by SnO_2 for degradation of different dyes.

S. No.	Catalysts	Dye	Amount of catalyst	Reduction time	References
1.	SnO_2	Methylene blue	0.25mg	70min	32
2.	SnO_2	Auramine O	100mg	-	33

Biological synthesis of SnO_2 nanoparticles (SnO_2 NPs) was reported by Elango et al. [32] using the methanolic extract of Cyphomandra betacea (C. betacea.). Particles are of spherical shape having average size of 21 nm. Catalytic degradation of methylene blue using SnO_2 nanoparticles was found to be effective. Dye was completed degraded in 70 min and it was stated that percentage of degradation increases with time.

In Solar-Light-Assisted photo-degradation of Azo Dyes [33], Salker et al. used SnO_2 as photocatalyst for degradation of auramine O with time under different conditions. As reported dye was completely degraded at neutral pH and resulting product was colourless. Photocatalytic degradation was found to be negligible in the absence of oxygen. Oxygen from conduction band traps photo-generated electrons and prevents the electron hole recombination .Conduction band electrons are trapped by dissolved oxygen forming superoxide ions (O^{2-}). Degradation rate increases with the amount of catalyst but after certain point saturation point occurs. In suspension, the penetration of light and number of active sites on the photo-catalyst is affected by the amount of photo-catalyst.

Volatile organic compounds including chlorobenzene are one of the harmful components present in environment and water bodies. They are harmful if consumed by humans by any mean. Recent studied have showed that these volatile organic compounds can be removed or photo catalytically decomposed by using semiconductor catalysts. Irokawa, et al [34] reported the photodegradation of volatile compound (toluene) under visible light irradiation using $TiO_{2-x}N_x$.They mentioned that 89% of toluene was photoxidized to CO_2 and H_2O under visible light.

Al-Hamdi et al. [35] prepared iodine doped tin oxide nanoparticles and used hem for photocatalytic degradation of phenol in sunlight and UV irradiations. They demonstrated that in the presence of SnO_2 nanoparticles, phenol degrades in approx 30mins and turned solution acidic due to formation of carboxylic acid. Degradation of phenol using 1% iodine doped SnO_2 nanoparticles was higher as compared to undoped SnO_2 nanoparticles under same conditions. In 50ml of aqueous phenol solution 0.065 gm of catalyst was used by them during photocatalysis under solar radiations and phenol was degraded in 3hr.Under UV irradiation, phenol was 93.4% degraded in 150 minutes.

This thesis work stress on synthesis of SnO_2 and it is characterization, further using it as a catalyst for photodegradation of dyes and volatile organic compounds. The results of degradation were obtained using UV spectrophotometer. Major advantage of using SnO_2 as catalyst is that it is non toxic, can be reused without losing it is photocatalytic activity. Furthermore, the synthesis of SnO_2 is very simple, eco-friendly and do not require conditions like high temperature and pressure.

Chapter-3

Materials and Methodology

CHAPTER 3

3.0 MATERIALS AND METHODOLOGY

In the first part of this chapter deals with materials ,instruments that are used during research work and the basic theories and principles of the main analytical methods X-ray analysis, electron microscopy, FT-IR (Fourier Transform Infrared Spectroscopy), Energy dispersive spectroscopy, UV-Visible Spectrophotometer and specific surface area measurement, are discussed. In the second part, the experimental parameters and instrumental details of all the characterization tools used in this thesis are summarized.

3.1 Apparatus Used

Beakers (50 mL and 250 mL), test tubes(10 mL), test tube stand, micro pipette, measuring cylinder, forceps, filter paper, glass rod, magnetic beads, Petri plates, flasks (50 mL), crucible and 0.22 µm nylon syringe filters, spatula, dropper.

3.2 Reagents and Chemicals

All the chemicals were purchased from Aldrich. Stannous chloride precusor was used as a tin source. Cetyltrimethylammonium bromide (cationic surfactant), sodium dodecyl sulphate (anionic surfactant) were used as surfactant template to increase surface area. Freshly prepared Sodium hydroxide (NaOH) was used as a reducing agent. Methylene blue and Chlorobenzene were used to check the photocatalytic activity of as prepared catalyst in visible light.

3.3 Instrument Used

3.3.1 Magnetic Stirrer

A magnetic stirrer of REMI 2MLH is a laboratory device, small magnetic bead has to be put inside the beaker containing all the different liquid/solid samples and this device use magnetic field to rotate magnetic bead which mixes all the samples present in it .

Figure 3.1 Magnetic stirrer used while preparing SnO_2

3.3.2 Weighing Balance

Weighing balance (SARTORINS) is used to measure accurate quantities of chemicals used. Maximum 250 gm; Denisty-0.01 mg

Figure 3.2 Weighing balance

3.3.3 Hot air oven

The hot air oven also known as digital temp indicator cum controller of PHYSILAB was used to dry the precipitates after the filtration process. Generally they are operated at the temperature of 500 C-3000 C using a thermostat to control the temperature.

Figure 3.3 Hot air oven

3.3.4 Laboratory Centrifuge

Centrifugation is a process that involves use of centrifugal force for the sedimentation of heterogeneous mixtures. This process is used to separate two immiscible liquids. The laboratory centrifuge (PHYSILAB) works under the principle where the centripetal acceleration will cause denser substances to move outward in the radial direction, the substances which are less dense are displaced and move to the centre.

Figure 3.4 Laboratory centrifuge

3.3.5 Muffle furnace

A muffle furnace (PREFIT INDIA) is box type oven for high temperature applications. These are used in various research labs by chemists in order to determine the proportion of sample which is non-combustible and non-volatile. It is used to calcine the samples. Calcination is a thermal treatment process for the removal of volatile fraction. Muffle furnace consists of externally heated chamber, so that material being heated has no contact with the flame. This muffle furnace can achieve a maximum temperature of 600°C.

Figure 3.5 Muffle furnace

3.3.6 Photochemical Reactor

The photochemical reactor of PERFIT is used for the degradation of dye, insecticide and Chlorobenzene. The photochemical reactor used in the experiment needs no water cooling and no dangerous high voltage is required. The normal operating temperature is approximately 35°C with the fan and without fan it is approximately 60-70°C. It has UV light approximately 1.65*10 photons/sec/cm^3 at 2537 Å.

The reactor comes complete in a "Ready to use Package" with no assembly required. The UV-Lamp is versatile, cheap with the power consumption of 400 Watts and has long life time of about 3000hours.

Caution: The UV-never looks directly at the UV-lamp or tube these radiations are harmful to eyes and skin.

Figure 3.6 Photochemical reactor

3.3.7 UV-Visible Spectrophotometer

The spectrum for the photodegradation of dye was taken with the help of UV-Visible spectrophotometer. It refers to absorption spectroscopy in the ultraviolet-visible spectral region and uses light near UV and near IR regions. Molecules which contain Non-bonding electrons can absorb the energy in the form of ultraviolet or visible light to excite the electrons to higher molecular orbital's [15]. More easily the electrons excite, longer is the wavelength of light it can absorb.

The method is based upon the beer-Lambert law:

$$A=\log10\ (I_0/I) = \varepsilon.c.l$$

This law is useful for the characterization of many compounds but doesn't hold good as a universal relationship for the concentration and absorbance of all the substances.

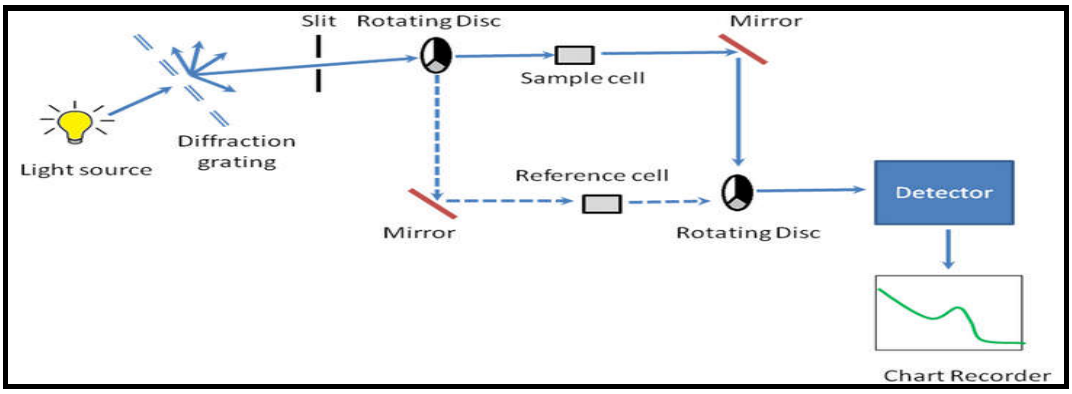

Figure 3.7 Block diagram of UV-Spectrophotometer

In this technique emission is divided into fluorescence and phosphorescence respectively, depending on being restricted or exceeding the excitation period. The energy change of quantized system is usually described in terms of

$$\Delta E = h\nu$$

ν = the frequency of the electromagnetic radiation,

3.3.8 Transmission Electron Microscopy (TEM)

In TEM, the pin-shaped cathode gets heated up by current and produces a ray of electrons. High voltage at the anode vacuum up the electron. The acceleration voltage is between 50 and 150 kV. The higher it is, the shorter are the electron waves and the higher is the power of resolution. The power of resolution is controlled by the quality of the lens-systems and especially by the technique with which the preparation has been achieved. Modern gadgets have powers of resolution that range in 2-3 Å.

The accelerated beam of electrons passes a drill-hole at the bottom of the anode.. The lens-systems consist of electronic coils generating an electromagnetic field. The beam is first focused by a condenser, and then passes through the object, where it is partially deflected. The degree of deflection depends on the electron density of the object. The greater the mass of the atoms, the greater is the degree of deflection. Biological objects have only weak contrasts since they consist mainly of atoms with low atomic numbers (C, H, N, O). Consequently it is necessary to treat the preparations with special contrast enhancing chemicals (heavy metals) to get at least some contrast. Additionally they must not be thicker than 100 nm, because the temperature is rising due to electron absorption. This again can lead to destruction of the specimen.

3.3.9 BET Surface area analyzer

There are six types of adsorption isotherms in physical adsorption and they can be classified as given in table:

Table 3.1 Types and porosity of six types of adsorption isotherm

TYPE	Porosity	TYPE	Porosity
I	Micropores	IV	Mesopore
II	Non porous	V	Mesopore
III	Non porous	VI	Nonporous

Microporous materials show type I isotherm. Type II and Type III are considered to be shown by nonporous and macroporous materials respectively. Materials having type IV and Type V exhibit mesoporosity. Type VI isotherm is rarely used. These isotherms arise due to different behaviours shown by microporous, mesoporous or macroporous materials due to different interaction between the solids, absorbate and adsorbent. From these isotherms we can get the pore size.

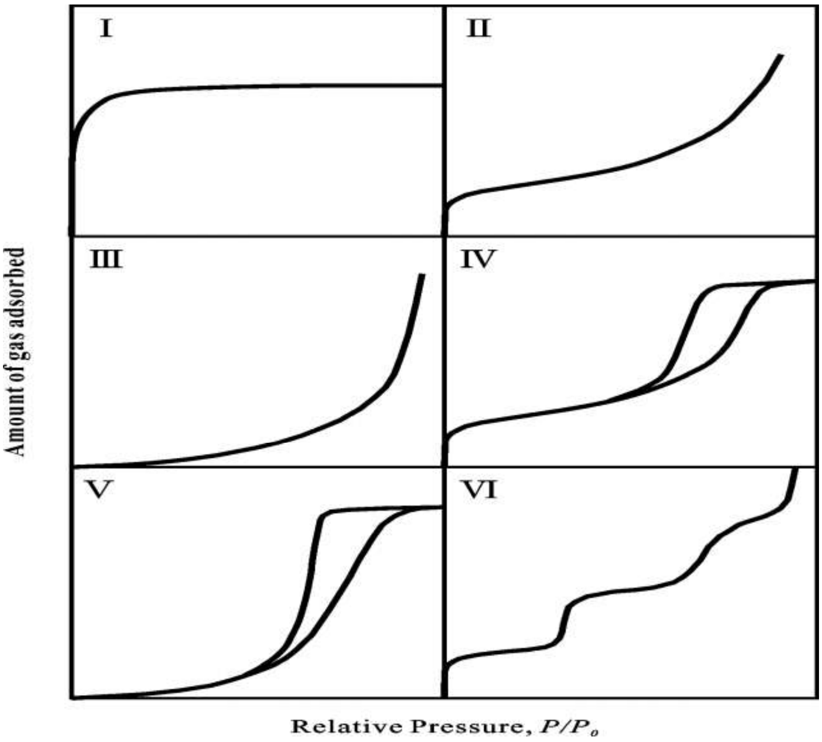

Figure 3.8 Classification of gas adsorption isotherm

3.4 Experimental Details of Samples Characterization

FT-IR (Fourier Transform Infrared Spectroscopy)

FT-IR was done to further confirm the formation of tin oxide. FT-IR of samples was carried out using Agilent Resolution Pro Carry 600 FT-IR spectrophotometer.

X-Ray Diffraction analysis

The sample was characterized by XRD PAN ANALYTICAL X'PERT PRO operated at 45KV diffractometer and Cu Kα wavelength of 1.54 Å in the range of 2θ = 1.5˚-10˚

BET surface area analysis

From the adsorption-desorption isotherms of nitrogen at 77 K, the BET specific surface areas of the tested materials was estimated using BELSORP II JAPAN GAS sorption and porosimetry apparatus.

Transmission electron microscopy (TEM)

Size and morphology of SnO_2 nanoparticles were studied from the TEM image recorded using Hitachi 7500 model with resolution upto 0.5nm operating at voltage 120kV.

Energy dispersive spectroscopy (EDS)

EDS (Energy dispersive spectroscopy) was carried on SEM-EDX, JOEL JSM-7600F, 01 operating at 30 kV.

UV-Visible Spectrophotometer

UV–Vis absorption spectra of dye, insecticide and volatile organic compound were recorded using Analytik Jena Specord 205 spectrophotometer.

Chapter-4

Methodology Details

CHAPTER 4

4.0 METHODOLOGY

4.1 Preparation of m-SnO_2

Figure 4.1 Scheme of synthesis of SnO_2

4.1.1 Chemical required

Stannous chloride precursor (1M) was used as a tin source. Cetyltrimethylammonium bromide (C_{16}TAB) was used as cationic surfactant, anionic surfactant sodium dodecyl sulphate (1M) was used to increase surface area, Sodium hydroxide (1M).

4.1.2 Procedure using only CTAB

1. The $SnCl_2.H_2O$ (1M), surfactant (C_{16}TAB) of different molar concentrations were mixed and stirred for 4hrs on magnetic stirrer.
2. Freshly prepared Sodium hydroxide (1M) was added dropwise with the help of dropper to the solution to make $Sn(OH)_2$ and after addition of NaOH, further stirring was done for 10 hrs. The product was obtained from centrifugation, washed several times with distilled water.
3. Dried in a hot Air oven at 80°C overnight.
4. Calcination was done at 600°C for 4 hrs.

4.1.3 Procedure using mixture of SDS and CTAB

1. The $SnCl_2.H_2O$ (1M), SDS (1M) and surfactant ($C_{16}TAB$) of different molar concentrations were mixed and stirred for 2hrs on magnetic stirrer.
2. Freshly prepared Sodium hydroxide (1M) was added dropwise wih the help of dropper to the solution to make $Sn(OH)_2$ and after addition of NaOH, further stirring was done for 10 hrs. The product was obtained from centrifugation, washed several times with distilled water.
3. Dried in a hot Air oven at 80°C overnight.
4. Calcination was done at 600°C for 4 hrs.

4.2 Photocatalytic Reactions

4.2.1 Monitoring UV- visible spectra of Degradation of methylene blue using mesoporous SnO_2 as photocatalyst

Chemical required: Methylene blue, deionised water, m-SnO_2 nanoparticles powder.

Procedure:

1. Stock solution was prepared by dissolving 20 mg of methylene blue dye in 1L of Deionised water in volumetric flask.
2. In a beaker 10 mL of above solution was taken and 20 mg SnO_2 powder was added as a catalyst.
3. The Lamp of photochemical reactor was switched on 20 min before the starting of reaction to stabilize, so that power of its emission spectrum gets stabilized.
4. Beaker was placed in photochemical reactor under UV-light. At regular intervals of 10minutes sample was withdrawn from the beaker for taking readings using UV spectrophotometer.
5. To remove catalyst from the liquid phase, filtration through 0.22 µm nylon syringe filters was done.

4.2.2 Monitoring UV-visible spectra of degradation of volatile organic compound (chlorobenzene) using mesoporous SnO_2 as photocatalyst

Chemicals required: Chlorobenzene, deionised water, m-SnO_2 nanoparticles powder.

Procedure:

1. In volumetric flask, 400 ppm stock solution of chlorobenzene was prepared in deionized water. In a 20 mL beaker, 10ml of above solution was taken and 4 mg SnO_2 powder was added as a catalyst.

Reaction in dark

2. Beaker was placed in dark on stirrer. At regular intervals of 2 min sample was withdrawn from the beaker for taking readings using UV spectrophotometer.
3. To remove catalyst from the liquid phase, filtration through 0.22 µm nylon syringe filters was done.

Reaction in visible light

The Lamp of photochemical reactor was switched on 20 min before the starting of reaction to stabilize, so that power of its emission spectrum gets stabilized.

4. 10 mL of stock solution was taken and 3 mg SnO_2 powder was added as a catalyst in a beaker.
5. Beaker was placed in photochemical reactor under UV light. At regular intervals of 2 min sample was withdrawn from the beaker for taking readings using UV spectrophotometer.
6. To remove catalyst from the liquid phase, filtration through 0.22 µm nylon syringe filters was done.

Chapter-5

Results and Discussion

CHAPTER 5

5.0 RESULTS AND DISCUSSION

5.1 FT-IR (Fourier Transform Infrared Spectroscopy)

The FT-IR spectra of synthesized SnO_2 nanoparticles is shown in Figure 5.1 The broad hump at 3428 cm^{-1} is observed due to the surface hydroxyls of the SnO_2 and –OH group of absorbed water molecule which produce small symmetric and asymmetric stretching vibrations. Water molecules create bending vibrations due to which peak at 1643 cm^{-1} is present.

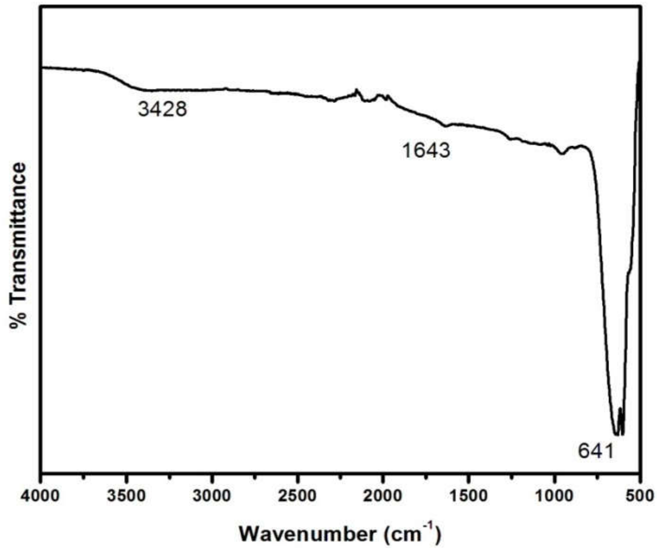

Figure 5.1 FT-IR spectra of synthesized SnO_2 nanoparticles

In spectrum of synthesized SnO_2, after calcination these peaks become weaker demonstrating that these groups have decomposed. The main sharp absorption peak observed at 641 cm ^{1} is due to the Sn–O stretching modes which confirm the formation of SnO_2 nanoparticles [36].

5.2 X-Ray Diffraction pattern

The Figure 5.2 shows XRD diffraction pattern of synthesized mesoporous nanoparticles. The peaks at 2θ degree values of 26.7 , 34.1 , 38.1 , 52.0 , 54.08 , 58.13 and 62.2 are associated with (110), (101), (200), (211), (220), (002) and (310) planes respectively. The entire peaks can be indexed as pure crystalline tetragonal phase with space group P42/nm (JCPDS: 41–1445) [27]. The Crystallite size of mesoporous SnO_2 nanoparticles was calculated from XRD data using Scherrer equation:

$$D = \frac{0.9\lambda}{\beta 1\backslash 2(Cos\theta)}$$

Where

D = Average crystallite size

β = Line Broadening in radians

θ = Bragg's angle

λ = X-Ray wavelength.

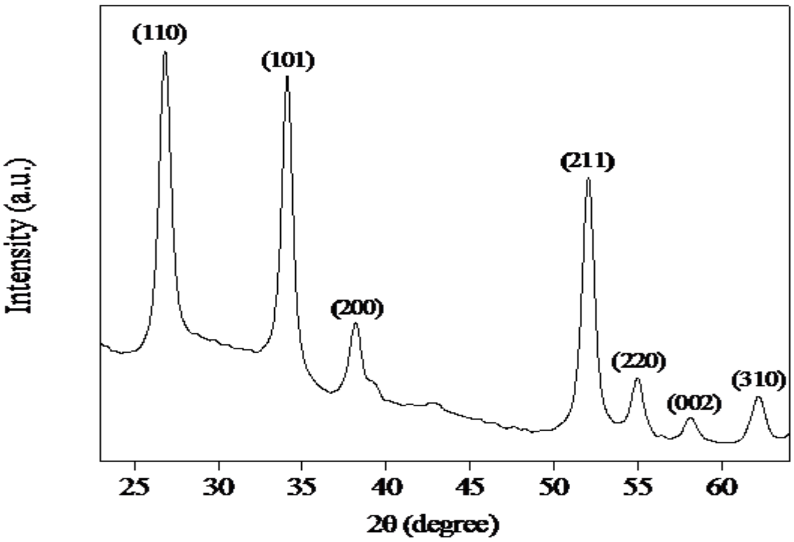

Figure 5.2 XRD Pattern of mesoporous SnO_2 nanoparticles

Crystallite size of mesoporous SnO_2 nanoparticles calculated was found to be 4.49 nm and lattice strain was equal to 0.0349 nm.

5.3 Transmission electron microscopy (TEM) Analysis

The morphological information is revealed by TEM images. The surface of SnO_2 nanoparticles is seen smooth with spherical pores having particle size ranging from 2-5 nm which is clearly shown in Figure 5.3. These images were recorded using a copper grid dipped in a solution containing SnO_2 nanoparticles dispersed in ethanol by ultrasonication for 10 min. This micrograph depicts the micelle formation due to addition of surfactants. The pore diameter estimated from the micrographs is around 6 nm which is in accordance with nitrogen adsorption-desorption measurements [29].

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Figure 5.3 TEM images of SnO_2 nanoparticles

5.4 Energy dispersive analysis (EDS)

The elemental information of the catalyst is confirmed by Energy dispersive analysis (EDS) which confirms the existence of SnO_2 on the mixture of surfactants. The spectra revealed the deposition of SnO_2 onto the surface of surfactant and weight percentage ratio of prepared catalyst.

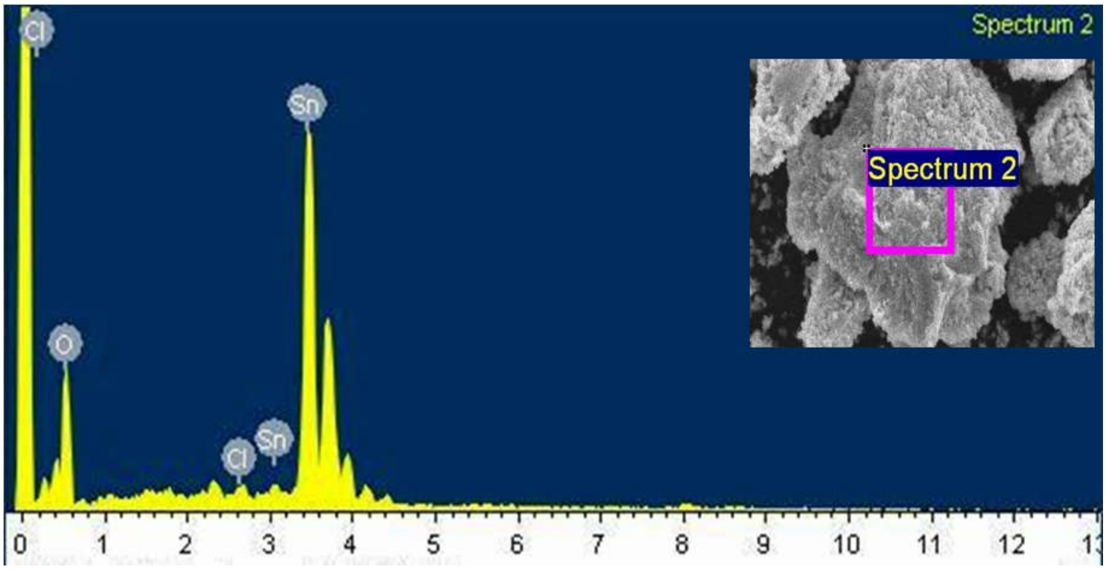

Figure 5.4 EDS spectrum of SnO_2 nanoparticles

5.5 BET surface area analyzer

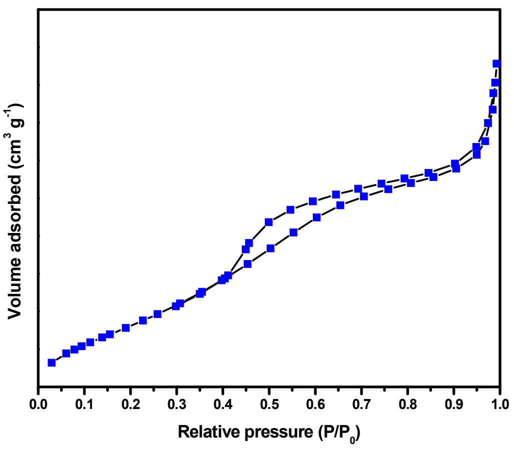

Figure 5.5 (a) N_2 adsorption-desorption isotherm of SnO_2 nanoparticles

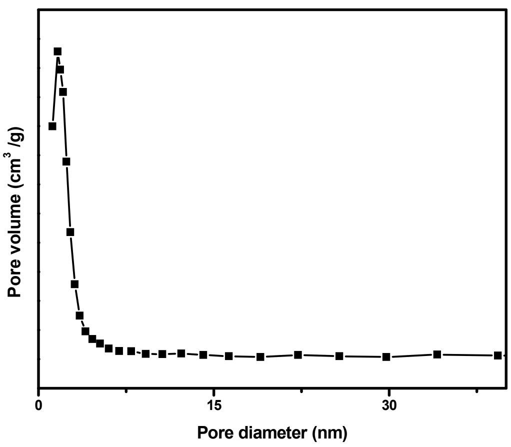

Figure 5.5 (b) BJH plot of synthesized SnO_2 nanoparticles

Figure 5.5 (a) displays the nitrogen adsorption-desorption isotherms of SnO_2 nanoparticles. It is clearly observed that the catalyst represents the type IV isotherm according to IUPAC classification with H1 type hysteresis loop approximately at relative pressure from 0.3-0.9. These all features indicate the uniform mesoporous nature of the catalyst. The BET specific surface area of the synthesized sample is 104 m^2g^{-1}. Pore distribution curves are obtained from desorption branch of nitrogen isotherm via BJH (Barrett-Joyner- Halenda) method are shown in Figure 5.5 (b). It was analyzed that the pore volume is around 0.1408 cm^3g^{-1} and mean pore diameter is 5.37 nm.

Table 5.1 Textural parameters of synthesized SnO_2 using cationic and anionic surfactants

Concentration used	**Surfactant**	**Surface Area (m^2g^{-1})**	**Mean pore Diameter(nm)**	**Total Pore Volume(cm^3g^{-1})**
0.0125 M	CTAB	8.45	36.72	0.077
0.25M	CTAB	7.23	46.76	0.084
0.25M	CTAB+SDS	104	5.37	0.140

Firstly, SnO_2 was prepared by using only CTAB with different concentrations as 0.0125 M and 0.25 M. From BET it was observed that with 0.0125 M and 0.25 M of CTAB, the surface area of synthesized SnO_2 was very less 8.45 m^2g^{-1} and 7.23 m^2g^{-1} respectively.

Then to increase the surface area, mixture of anionic and cationic surfactant was tried. With 0.25M of CTAB (Cationic surfactant) and SDS (anionic surfactant), the surface area of SnO_2 nanoparticles was very much higher. The specific surface area using mixture of surfactants was 104 m^2g^{-1}.The mixture of cationic and anionic surfactant yields greater surface area as compared to pure surfactant. The reason for this fact is due to greater synergetic effect and less critical aggregation concentration of the mixture. This is due to electrostatic attraction between metal ions (positive charge) and SDS (negative charge) which result in huge micelle formation.

Figure 5.5.3 Mechanism of formation of spherical SnO_2 nanoparticles

5.6 Evaluation Photocatalytic degradation of dyes and volatile organic compound

UV–visible absorption spectrum

Absorption edge at 400 nm of tin oxide nanoparticles was observed in UV–visible absorption spectrum owing to the direct electronic transition of tin oxide. Methylene blue present in solution containing SnO_2 nanoparticle catalyst does not degrade in dark. In the absence of catalyst photolysis of methylene blue is only 7%, which can be neglected. Therefore we found that both catalyst and UV light are major requirement for the photocatalytic oxidative degradation of methylene blue. The photodegradation of MB is carried out under Visible light irradiation for different time intervals. MB dye solution was irradiated for different time intervals. The degradation was monitored prior to decrease in the intensity of adsorption peak corresponding to 665 nm in the UV-Visible spectra of the MB aqueous solution treated with SnO_2 catalyst [37].

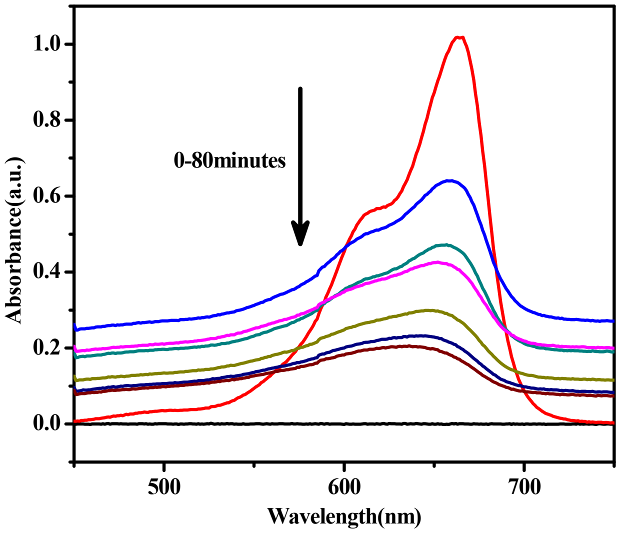

Figure 5.6.1 UV spectrum of methylene blue in visible light

From figure 5.6.1 it was conformed that methylene blue was degraded 83 % in 80mins when SnO_2 was used as catalyst in the presence of UV irradiation.

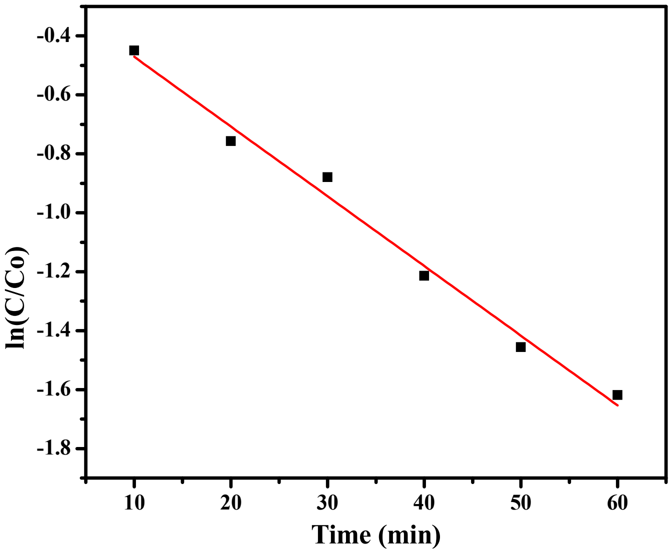

Figure 5.6.2 Kinetic analysis of degradation of methylene blue in presence of SnO_2 catalyst

The graph of $\ln(C/C_o)$ versus time gives a linear relationship. Figure 5.6.2 confirmed that degradation of methylene blue follows a pseudo first–order reaction kinetics following equation:

$\ln(C/C_o) = -kt$

Where C_o is initial concentration of methylene blue solution, C is measured concentration of methylene blue solution and K is rate constant of photodegradation.

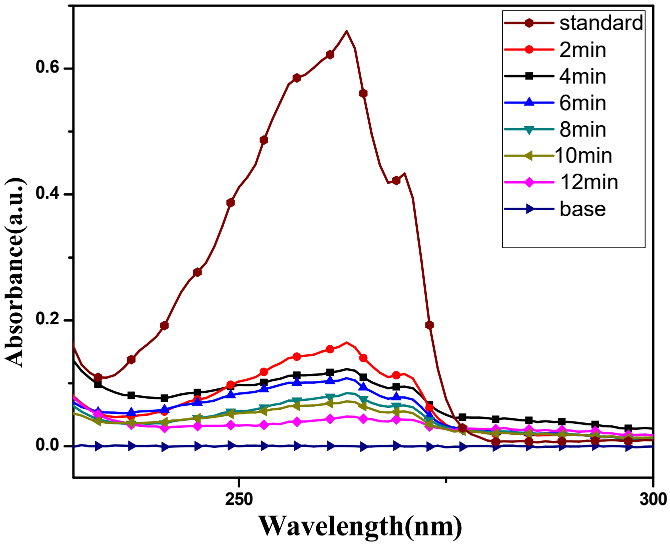

Figure 5.6.3 UV spectrum of chlorobenzene in visible light

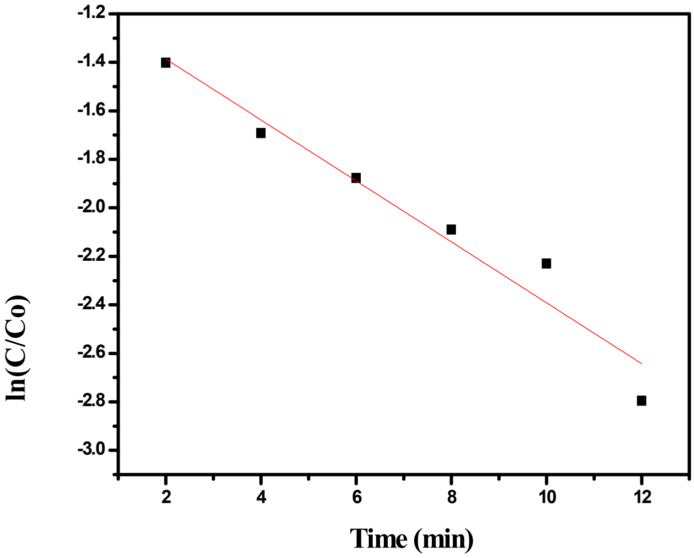

Figure 5.6.4 Kinetic analysis of degradation of methylene blue in presence of SnO_2 catalyst

From 400 ppm solution of chlorobenzene, 10 mL was taken in beaker and 3 mg m-SnO_2 nanoparticles powder was added as catalyst. Peak of chlorobenzene in UV spectrum was observed at 260 nm. In absence of catalyst extent of photolysis was very less. On irradiation with visible light, chlorobenzene was degraded 92.7% in just 12 min. As depicted in graph, in starting two minutes, there is sharp decrease in height of the peak at 260 nm, this is due to absorption on the surface of catalyst .After absorption, degradation starts. Therefore, SnO_2 is an excellent catalyst for degradation of chlorobenzene. Therefore, present catalyst is proved to be better for degradation of various harmful organic pollutants present in water.

Chapter-6

Conclusions and References

CHAPTER 6

6. CONCLUSIONS

The mesoporous SnO_2 nanoparticles were synthesized using a general method that is easy and does not require high temperature and pressure conditions. Mesoporous SnO_2 nanoparticles were synthesized by using cationic (CTAB) and anionic surfactants (SDS). Characterization of prepared SnO_2 was investigated using different characterization techniques such as TEM, EDS, FTIR, BET and UV spectrophotometer. The TEM images of the composite confirmed that particles had spherical shape with size range between 2-5 nm. Further, from BET surface area analyzer the surface area of synthesized SnO_2 observed was 104 m^2g^{-1}. SnO_2 nanoparticles prepared using only pure surfactant had less surface area as compared to prepared by mixture of cationic and anionic surfactants .Therefore, Surfactant addition was very important aspect as it influences particle growth, coagulation, surface area, pore diameter and other factors. Furthermore, m-SnO_2 nanoparticles were used as photocatalyst for degradation of dyes (methylene blue) and volatile organic compound (chlorobenzene) under UV-Visible light. Methylene blue was degraded to 83% and Chlorobenzene was degraded upto 92.7 % in just 12 minutes using SnO_2 as catalyst showing good catalytic efficiency in degradation of harmful dyes. From our studies, SnO_2 showed excellent photocatalytic efficiency making it a potential catalyst for degradation of dyes and volatile organic compounds.

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