SYNTHESIS, CHARACTERIZATION AND PHOTOCATALYTIC STUDIES OF BORON DOPED TITANIUM DIOXIDE NANO PARTICLES

A Project report submitted to
Mahatma Gandhi University, Kottayam
in partial fulfillment of requirement for the award of the degree of

B.Sc CHEMISTRY

BY
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Under the supervision of

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(Affiliated to Mahatma Gandhi University, Kottayam)

2017-2020

DEPARTMENT OF CHEMISTRY

BHARATA MATA COLLEGE, THRIKKAKARA
(Affiliated to Mahatma Gandhi University, Kottayam)

CERTIFICATE

This is to certify that the Project titled **"Synthesis, Characterization and Photocatalytic Studies of Boron Doped Titanium Dioxide Nano Particles"** is a bonafide work carried out by **Biyatris Salin, Reg No: 170021025606,** B.Sc Chemistry student, under my supervision and guidance and that no part of this has been presented earlier for the award of any other degree, diploma or other similar titles of recognition.

Forwarded by   Project Guide

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DECLARATION

I, Biyatris Salin, declare that the project report entitled "Synthesis, Characterization and Photocatalytic Studies of Boron Doped Titanium Dioxide Nano Particles", submitted to Mahatma Gandhi University, Kottayam, in partial fulfillment for the award of the degree of BSc.Chemistry, is an authentic record of original work done by me, under the supervision of Prof. Anu K John, Department of Chemistry, Bharata Mata College, Thrikkakara and no part of this has been previously formed on the basis for the award of any degree or assistantship of any other institution.

Place: Biyatris Salin

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ACKNOWLEDGEMENT

CONTENTS

CHAPTER 1
INTRODUCTION

Nanoscience and Nanotechnology

Nanoscience and nanotechnology is one of the most fascinating subjects and an imperative one as it finds plethora of applications in numerous fields. Nanoparticle is a microscopic particle usually in the range of 1-100 nanometers. They show properties different from that of bulk materials. The properties of these nanoparticles can be controlled by manipulating the size of these particles. Nanoparticles have a large surface area; they are highly reactive and can act as an excellent catalyst. Since they have small sizes, the electrons can be confined in them which results in many optical properties. By manipulating the dimensions of these nanoparticles we obtain quantum dots, quantum wells and quantum wires. Nanoparticles find applications in drug delivery systems, sensors, biomedicine, electrical batteries, anticancer activities etc. Nanotechnology is the fine-tuning of materials at atomic and molecular scales, where properties differ significantly from those at a larger scale. It is an interdisciplinary science including nanochemistry, nanophysics, nanoelectronics, nanobionics etc.

Classification of nanoparticles

Nanoparticles can be classified into different types based on their size, morphology, physical and chemical properties. Few of them are carbon-based nanoparticles, ceramic nanoparticles, metal nanoparticles, semiconductor nanoparticles, polymeric nanoparticles and lipid-based nanoparticles.

Carbon-Based Nanoparticles

Carbon-based nanoparticles are further classified into carbon nanotubes (CNTs) and fullerenes. CNTs are graphene sheets rolled into a tube around an axis having different helicities. These materials are mainly used for the structural reinforcement as they are 100 times stronger than steel.

CNTs are classified into single-walled carbon nanotubes (SWCNTs) and multi-walled carbon nanotubes (MWCNTs). Single-walled carbon nanotubes are made of a single layer of graphene rolled into a cylinder. Multi-walled nanotubes are composed of multiple layers of graphene forming concentric pattern around the smallest nanotube. CNTs are unique in a way as they are thermally conductive along the length and non-conductive across the tube.

Fullerenes are the allotropes of carbon having a structure of hollow cage of sixty or more carbon atoms connected by single and double bonds. The structure of C-60 is called Buckminsterfullerene. The carbon units in these structures have a pentagonal and hexagonal arrangement. These have numerous applications due to their electrical conductivity, structure, high strength, and electron affinity.

Ceramic Nanoparticles

These are inorganic solids made up of oxides, carbides, carbonates and phosphates. These nanoparticles have high heat resistance and are chemically inert. They find applications in photocatalysis, photodegradation of dyes, drug delivery, and imaging. By manipulating some of the characteristics of ceramic nanoparticles like size, surface area, porosity, surface to volume ratio, etc. They perform as a good drug delivery agent. These nanoparticles have been used effectively as a drug delivery system for a number of diseases like bacterial infections, cancer, etc.

Metal Nanoparticles

Metal nanoparticles are synthesized from metal precursors. These nanoparticles can be prepared by chemical, electrochemical, or photochemical methods. In chemical methods, the metal nanoparticles are obtained by reducing the metal-ion precursors in solution by chemical reducing agents. They have the ability to adsorb small molecules and have high surface energy. These nanoparticles find applications in research areas, detection and imaging of biomolecules and in environmental and bio analytical applications.

Semiconductor Nanoparticles

These have the properties like those of metals and non-metals. These particles have wide band gaps, which on tuning can show different properties. They are used in photocatalysis, electronic devices, and photo-optics. Few examples of semiconductor nanoparticles are GaN, GaP, ZnO, ZnS, CdS, CdSe, etc.

Polymeric Nanoparticles

These are organic based nanoparticles. Depending upon the method of synthesis, these are shaped like nanocapsular or nanospheres. A nanosphere particle has a matrix-like structure whereas the nanocapsular particle has core-shell structure. In the nanosphere structure, the active compounds and the polymer are uniformly dispersed whereas in the nanocapsular structure, the active compounds are confined and surrounded by a polymer shell. Some of the advantages of polymeric nanoparticles are controlled release, protection of drug molecules, ability to combine therapy and imaging, specific targeting, etc. They find applications in drug delivery and diagnostics. The drug deliveries with polymeric nanoparticles are highly biodegradable and biocompatible.

Lipid-Based Nanoparticles

These nanoparticles generally have a spherical shape with diameters ranging from 10 to 100nm. They consist of a solid core made of lipid and a matrix containing soluble lipophilic molecules. The external core is stabilized by surfactants and emulsifiers. These nanoparticles find numerous applications in the biomedical field as a drug carrier and delivery and RNA release in cancer therapy.

Metal Oxide Nanoparticles

Metal oxides play a vital role in various areas of chemistry, physics and material science. The elements can forms a large diversity of oxide compounds. They can adopt various

structures with an electronic structure which can exhibit metallic, semiconductor or insulator characteristics. Metal oxide nanoparticles show unique physical and chemical properties owing to their small size. Metal oxide nanoparticles find applications in optoelectronics, in fabrication of microelectronic circuits, fuel cells. Few examples of metal oxide nanoparticles are ZnO, TiO_2, CuO, MgO, ZrO_2 etc. In order to exhibit mechanical stability, nanoparticles must possess a low surface energy hence the phases that have low stability in bulk materials can be very stable nanostructures. Metal oxide nanoparticles can be synthesized from various synthetic methods. Metal oxide nanoparticles can be synthesized by co-precipitation, thermal decomposition, microemulsion, hydrothermal synthesis etc. The characterization of metal oxide nanoparticles is based on their surface analysis and characterization methods developed for bulk materials. The various spectroscopic techniques used for the characterization of metal oxide nanoparticles are SEM (Scanning electron microscope), TEM (Transmission electron microscope), Ultra Violet spectroscopy and Power X-ray diffraction (PXRD)

TiO_2 Nanoparticles

Titanium dioxide nanoparticles are one of most important metal oxide nanoparticles. TiO_2 nanoparticles are known for their numerous and diverse applications which range from common products such as sunscreens to advanced devices such as photovoltaic cells. The importance and variety of such applications have spurred enormous interest in fundamental knowledge, the fabrication and characterization of **TiO_2** based nanomaterials.

Synthesis of Nanoparticles

Synthesis of nanoparticles are generally classified into two: (1)Top-down approach and (2)Bottom-up approach. In top-down a microcrystalline material is fragmented to yield a nanocrystalline material. Eg:Vapour condensation, high energy milling etc. In bottom-up approach, individual atoms or molecules are brought together or self-assembled to form nanostructured material. Eg:Chemical precipitation, self-assembly etc.

These techniques are further classified into 3 categories namely physical methods, chemical methods and bio-assisted methods.

A) Physical Methods

1) Deposition method

In this method a solid phase material is obtained by condensing material in vapor phase. Usually a vacuum chamber is used to carry out the process. TiO_2 films with grain size less than 30nm and less than 10nm are synthesized by pyrolysis of titanium tetraisopropoxide.

2) Electrophoretic deposition

This is the most favored method of synthesis. The process involve application of DC voltage to a suspension medium which results in movement of charged particles followed by deposition on a substrate. This leads to the formation of homogeneous layer of nanoparticles.

3) Laser pyrolysis method

In this process a carrier gas introduces gaseous phase precursor into a chamber where it meets the laser beam. Elevated temperature generated by laser triggers nucleation and growth of nanoparticles. The nanoparticles are then collected by catcher equipped with a filter.

B) Chemical Methods

1) Oxidation method

In this method the titanium metal is oxidized with suitable oxidants or is anodized. Here the anodization of titanium sheets under suitable voltage in hydrogen fluoride lead to formation of TiO_2 nanotubes. Direct oxidation of titanium metal with hydrogen peroxide has also been found to lead to formation of TiO_2 nanorods.

2) Hydrothermal method

This method involves crystallizing a substance from its aqueous solution at high temperature and high vapor pressure. It is mainly carried out in an autoclave. It is an easy method to obtain nanotube morphology however it takes a longer duration to complete the process.

3) Sol-gel method

This process is a wet chemical technique. It is a water induced reaction where an inorganic solid is formed from its precursor solution by polymerization. A dispersion of colloidal particles in a liquid is called sol which is prepared by hydrolysis and gel is formed as a result of condensation. It is a very promising method of creation for inorganic nanoparticles as it allows reaction to take place at low temperature(less than 100°) and it also provides homogeneity of composition at molecular level. Sol-gel method provides control over particle size and shape. The precursors typically used are metal alkoxide consisting of an M-O-R linkage where R is an alkyl group, O is oxygen and M is metal. The M-O bond is polarized during reaction and is susceptible to an attack from a nucleophile. The alkoxide undergo nucleophilic substitution reaction in presence of water where the alkoxy group is replaced by a hydroxyl group from water, thus hydrolysis takes place. A hydrated metal oxide network is formed by linkage of metal hydroxide and this process is called condensation.

C) Bio-assisted method

Bio-assisted methods, biosynthesis or green synthesis provides environmentally benign, cost-effective, low toxic and highly efficient method for synthesis of nanoparticles. It involves the use of bacteria, fungi, biomolecules, plant extracts etc; for synthesis of metal and metal oxide nanoparticles. Green synthesis of titanium dioxide nanoparticles using Azadirachta indica (Neem) leaf extract, leaf extract of the biodiesel plant, Jatropha curcas etc. has been reported by various researchers.

Applications of TiO$_2$ Nanoparticles

1) White pigment

Titanium dioxide nanoparticles are widely used as white pigment due to its high diffraction index and strong light scattering and incident light reflection capability. It is used to provide opacity and whiteness to products like paint, plastics, toothpastes etc.

2) In lithium batteries

Lithium ion batteries are one of most promising energy storage technology. It is widely used in mobile electronics, automobile and as a renewable energy source. Recently titanium dioxide nanoparticles are used as an anode for Li ion batteries due to its high energy storing capability.

3) Cosmetics

TiO_2 nanoparticles act as an inorganic UV absorber. Owing to this feature TiO_2 can be used in sunscreen cosmetics. It forms a transparent optical coating on skin surface. They thereby provide protection against discoloration of skin due to exposure to UV light.

4) Gas sensors

TiO_2 nanoparticles have high stability and can be easily prepared. Due to high surface to volume ratio of nanoparticles they are suitable as gas sensors. The sensing layer proved capable to detect exhaust gases from engines at suitable temperature. Its high sensitivity suggests use of this sensor for environmental purposes.

5) Photocatalytic application

TiO_2 is one of the most photocatalytically active material which is extensively used in splitting of water as well as in decomposition of organic materials.

PHOTOCATALYSIS

Photocatalysis is a process in which acceleration of a reaction occurs when a material usually a semiconductor interact with light of sufficient energy to produce reactive oxidation species or ROS. As it takes place in the presence of light, it is a light dependent reaction. Also it is a reaction in which oxidation and reduction takes place simultaneously.

When the light energy greater than the band gap energy hits semiconductor such as Titanium dioxide, electron from the valence band will be moved to the conduction band. In the case of anatase form of Titanium dioxide, the band gap is 3.2ev. Therefore ultraviolet light is required

to initiate the photocatalytic reaction. The absorption of a photon from the ultraviolet light excites an electron to the conduction band which generates a positive hole in the valence band. The electrons in the conduction band can react with molecular oxygen to form superoxide radical anion. The superoxide radical anion can be further transformed into singlet oxygen. The hole in the valance band will interact with adsorbed water molecule to form hydroxyl radical. Hydroxyl radicals and superoxide anions produced by the photo catalytic process can degrade the majority of organic compounds until the complete mineralization is achieved.

Photo catalyst is a substance which increases the rate of the reaction in the presence of sunlight consisting mainly of ultraviolet light. Most commonly used photocatalysts are Titanium dioxide, Zinc oxide, Vanadium oxide, Tungsten oxide, Molybdenum oxide, Indium oxide, Cerium oxide, Ferric oxide, Bismuth tungstate, Strontium titanate, Oxysulfides and Oxynitrides etc.

Various types of photo catalyst that we use in the photocatalysis are metals, insulators and semiconductors. Among these semiconductors is the most preferred one. The criteria for selection of semiconductor are band gap, position of top of valence band and bottom of conduction band. In the case of metals, the conduction band and the valence band are overlapping, hence there is no band gap in them. Here either oxidation or reduction takes place. In insulators there is a high band gap. Therefore it has high energy requirement for excitation of electrons from valence band to conduction band.

Factors which control the design of photo catalytic materials are band gap, carrier transport, crystallinity, surface area and chemical stability. Band gap of the material that we have to use as a photocatalyst should be in the range corresponding to that of ultraviolet light and visible light. In carrier transport, we have movement of electrons and holes (produced as a result of reduction and oxidation in the photocatalysis). Crystallinity of the solid affects both the band gap and the carrier transport. For example, an amorphous solid has a different band gap than pure cystalline solid thereby affecting the photo catalytic process. If the material has high surface area, it will have high number of activation sites. Thus the rate of the reaction will be high making it a very good catalyst. Chemical stability of the catalyst is an important factor in determining the photocatalytic activity of the catalyst because we have to reuse the catalyst several times.

Titanium Dioxide in the nanosize has shown photocatalaytic activity and it was discovered by Akira Fujishima in 1967. Among various forms of titanium dioxide, anatase form is the most efficient photocatalyst. Titanium dioxide holds great promise in market. About 36.2% of photocatalytic work is mainly based on titanium dioxide. It is the most commonly used photocatalyst due to low cost, reasonable good efficiency, good availablity, abundance and physiochemical endurance.

Drawbacks of pure titanium dioxide as a photocatalyst

The main limitation for the industrial application of photocatalysis is its wide band gap. For example, in the case of anatase form of titanium dioxide, the band gap is 3.2eV. This means that photons of light in the ultraviolet region only can initiate the photocatalysis reaction. But we know that ultraviolet light makes up approximately 5% of the solar spectrum, whereas almost 40% of solar photons are in visible region. Therefore to enhance the efficiency of solar radiation it is necessary to modify the band gap to facilitate the visible light absorption. Also it may need extra energy which in turn increases the expenditure due to hike in power intake by UV lamp. The photocatalytic efficiency is also limited by transfer rate and transfer time of charge carriers and also by recombination rate.

Methods to overcome the limitation

(a) Doping

Titanium dioxide can be doped with non-metal ions (N, C, B, etc…) or metal ions (Au) to increase its efficiency and recombination rate. If we use anatase form of titanium dioxide, we need ultraviolet light that is only 5% of solar energy. So in order to use visible light that makes up 40% of solar energy, we can dope it with suitable dopants. By doing so we can increase the photocatalytic efficiency and avoid the usage of extra energy required due to usage of ultraviolet lamps.

Non-metal doping of titanium dioxide has shown great promise in achieving visible light active photocatalysis with nitrogen being the most promising dopant. Incorporation of nitrogen into titanium dioxide lattice is favored due to the comparable atomic size of nitrogen and oxygen, low ionisation potential and high stability of nitrogen. Other non-metal doping such as boron,

carbon, fluorine and sulphur are also found to shift the absorption band of titanium dioxide towards the visible region.

(b) Other methods

Various recent and ongoing efforts to increase the photocatalytic activity of titanium dioxide are dye sensitization, incorporation of transition metals, coupling of titanium dioxide with plasmonic nanomaterials, composition of titanium dioxide with reduced graphene oxide and carbon nanotubes

Doping in TiO_2 nanoparticles

Titanium dioxide (TiO_2) is a material having numerous applications such as bio-sensing, photocatalytic degradation of pollutants, water purification and bacterial action. It is an n-type semiconductor with high chemical stability and large refractive index. Due to its efficient photoactivity, high stability and low cost, TiO_2 nanoparticles has been widely used as photocatalyst in many environmental and energy applications. TiO_2 nanoparticles can only be activated under UV light irradiation because of its wide band gap and high recombination. Doping is an active method to extend its light absorption to the visible light region and thereby it can increase the photocatalytic activity. Doping can alter the structure, surface area and morphology. Also by doping TiO_2 nanoparticles with optically active ions, up or down conversion luminescence can be produced. Several approaches have been introduced to increase the photocatalytic activity of TiO_2 and to extend its light absorption into the visible region such as Metal-ion implanted TiO_2, non-metal doped TiO_2, TiO_2 doped with N, C and B etc.

In order to broaden the effective range of light sensitivity for photocatalysis from the ultra-violet (UV) region to the visible light region, dopants modify the electronic structure of nano-TiO_2. Doping techniques are effective and efficient despite being susceptible to thermal instability and their requirement for expensive ion-implantation facilities. Dopants have the ability to deliberate good physicochemical properties such as high crystallinity (high percentage of anatase phase), high specific surface area, and small crystallite size.

Boron doping

Doping with non-metals is one of the methods to increase the photocatalytic activity. Boron doped TiO_2 were prepared using modified sol-gel process. The introduction of dopant in the TiO_2 lattice may affect the electronic band edges or introduce impurity states in the band gap of the system. Decreasing the band gap by boron doping can extend the absorption to the visible region. When oxygen atom of TiO_2 is substituted by boron, the impurity state formed by boron lie at 2.18 eV above the valance band maximum. If the doping is interstitial, boron contributes three valence electrons to 3d states of titanium ion, and then Ti^{+4} ions are reduced to Ti^{+3} following the formation of an oxygen vacancy with excess free electrons. Thus, increased boron doping on TiO_2 nanoparticles result in increased oxygen vacancies and free electron formations. The phase transformation between anatase and rutile is dominated by boron into anatase TiO_2 causing a reduction of Ti^{+4} to Ti^{+3}, and then free electrons accumulated at conduction band and facilitated charge separation by band bending.

Many works have been carried out in Boron doping. Xin Mao and his coworkers, by using density functional theory, predicted that a single B-atom decorated BN edge (B@BN) can act as a metal-free catalyst for the conversion of an N_2 molecule to NH_3 under ambient conditions. N_2 fixation on the B@BN edge exhibits an extremely low overpotential of only 0.13V through a distal mechanism. Their findings highlight a novel single atom metal-free catalyst for N_2 fixation, providing a cost-efficient process for sustainable NH_3 production.

Zhaohe Dai and his co-workers reported that graphene can maintain a large fraction of its pristine strength and stiffness after substituting boron for carbon atoms. Counter-intuitively, boron doping can ameliorate the brittle nature of the original lattice by deflecting the cracks and enabling damage-tolerant behaviours. They further offer a direct mapping between the Raman spectra and the measured mechanical performances that can show the relationship between doping structure and mechanical properties of graphene. This work offers important implications for the rational design of graphene-based systems that require chemical modifications and also utilize that the mechanics of graphene.

Hualin Lin and his co-workers developed a two-step method for preparation of boron, nitrogen and phosphorus ternary doped hierarchically porous graphene aerogels by using boron phosphate as both B and P precursor and ammonia as N dopant. As prepared B/N/P ternary doped hierarchically porous graphene aerogels can serve as the next generation of metal-

free catalysts and alternatives to precious metal catalysts for oxygen reduction reaction and fuel cells.

Fabio Caruso and his co-workers reported evidence of a non-adiabatic kohn anomaly in boron-doped diamond, using a joint theoretical and experimental analysis of the phonon dispersion relations. They demonstrate that standard calculations of phonons using density-functional perturbation theory are unable to reproduce the dispersion relations of the high-resolution inelastic x-ray scattering. On the contrary, by taking into account non-adiabatic effects within a many-body field-theoretic framework, they obtain excellent agreement with their experimental data. This results indicates a breakdown of the Boron-oppenheimer approximation in the phonon dispersion relations of boron-doped diamond.

OBJECTIVE AND SCOPE OF THE WORK

Objective of the current work is to synthesize boron doped titanium dioxide (B-TiO_2) nanoparticles by phytochemical assisted green method and to study the photocatalytic properties of the synthesized nanoparticles. The plant used in the current study was Chromolaena Odorata. The phytochemicals present in the methanolic leaf extract of the plant acted as both reducing agent and capping agent in the synthesis of B-TiO_2 nanoparticles. Titanium isopropoxide was used as the titanium precursor and boric acid was used as the source of boron. The nanoparticles obtained by this method were characterized by X-ray diffraction studies and UV- Visible spectroscopy

The photocatalytic activity of boron doped TiO_2 nanoparticles in visible light was studied using the degradation reaction of aqueous solution of methylene blue dye. The photocatalytic property of boron doped TiO_2 was then compared with that of undoped TiO_2. TiO_2 nanoparticles are one of the most studied metal oxide nanomaterial due to its outstanding photocatalytic property. Due to the wide band gap of this material, the visible light photocatalytic activity is limited. Doping is a solution for this problem. Boron is proved to be an appropriate candidate for doping in TiO_2 to improve the visible light photocatalytic performance.

CHAPTER 2
MATERIALS AND METHODS

SYNTHESIS OF BORON DOPED TITANIUM DIOXIDE NANOPARTICLES

a) Preparation of Chromolaena odorata leaf extract

Chromolaena Odorata plant leaves were collected from Bharata Mata College campus, Thrikkakara, and cleaned well with distilled water. The leaves were then shade dried for several days and ground to powder. Methanolic leaf extract was prepared by taking 10 g of the leaf powder in 100 ml methanol in a round bottom flask and refluxed at 50 °C for 4 hours. The extract was filtered twice through Whatman No.1 filter paper and used for further experiments.

b) Synthesis of boron doped TiO$_2$ nano particles

Boron doped TiO$_2$ nanoparticles were synthesized using Titanium isopropoxide (TIP), boric acid, methanolic leaf extract and water. Desired quantity of boric acid (corresponding to 5mol % of boron in TiO$_2$) was weighed out into a 100 ml beaker. To this, 20 ml leaf extract containing 0.5 ml of water was added. A solution of 2.5 ml TIP in 5 ml methanol was added to the above solution. pH of the solution was ~6. The solution was magnetically stirred at room temperature. After one hour, temperature was increased to 40°C. Stirring continued for 2 hours and then it was kept unstirred for 3 hours at the same temperature. The semisolid (gel) obtained was heated at 100°C for three hours and the resultant solid precipitate was powdered and calcined at 400°C for 2 hours. Undoped TiO$_2$ nanoparticles were prepared in the same method without adding boric acid for the comparison of photocatalytic activity.

c) Photocatalytic activity experiment

Methylene blue was used as the model pollutant for the determination of photocatalytic activity of B-TiO$_2$ nanoparticles. An aqueous solution of 10 mg/L methylene blue was prepared. 0.1g of TiO$_2$ nanoparticles were added to 100 ml of the dye solution in a beaker. It was stirred for 1 hour to attain adsorption-desorption equilibrium. pH of the solution was 6. It was then kept

under a 125 watt high pressure mercury vapour lamp at a distance of 15 cm from the lamp. The dye solution was kept on a magnetic stirrer to get continuous stirring throughout the experiment. A UV cut off filter was placed on the top of the beaker to block the passage of UV rays. 5 ml of sample was taken in every 30 minutes, centrifuged for 10 minutes, filtered using 0.22µm nylon 6 syringe filter and absorbance was measured using visible spectrophotometer (spectrophotometer 104-systronics) at a wavelength of 663 nm corresponding to the maximum absorption wavelength of methylene blue.

Characterization Techniques

a) X-Ray Diffraction (XRD)

The X-Ray diffraction patterns of the samples were taken by powder XRD method using Bruker AXS D8 Advanced X-Ray Powder Diffractometer with Cu K alpha radiation. Crystal structure and phase purity of the samples were determined from the XRD pattern by comparing the obtained results with standard reference data (JCPDS). By the substitution of θ values in Debye-Scherrer equation, the average size of the nano particles were calculated.

b) UV-Visible Spectroscopy

UV spectrum of metal oxide nano particles was taken using Varian, Cary 5000 UV-Vis-NIR Spectrophotometer. For taking the UV spectrum, water was used as the solvent. The λ_{max} values of the samples were obtained from the spectrum.

CHAPTER 3
RESULT AND DISCUSSION

a) Material characterization

X-Ray Diffraction Studies

X-Rays are electromagnetic waves having very short wavelength of the order of a fraction of Å. Powder X-Ray diffraction is a very important experimental technique that has been used to determine the crystal structure including lattice constants and geometry, identification of unknown phases, defects, grain size, etc. Grain size is determined by broadening of X-Ray diffraction peaks. This peak broadening is normally caused by finite size effect of crystallites. The grain size can be calculated from the broadening of the diffracted beam using the Debye-Scherrer formula,

$$t = \frac{K\lambda}{\beta cos\theta}$$

Where t is the crystallite size or grain size, *K* is a dimensionless constant that may range from 0.89 to 1.39, depending on the specific geometry of the scattering objects. λ is the wavelength of X ray (1.5406 Å for Cu K alpha radiation), β is full width at half maximum of X ray peak, and θ is the Bragg angle and it is obtained from the 2 θ value corresponding to the peak with maximum intensity in the XRD pattern.
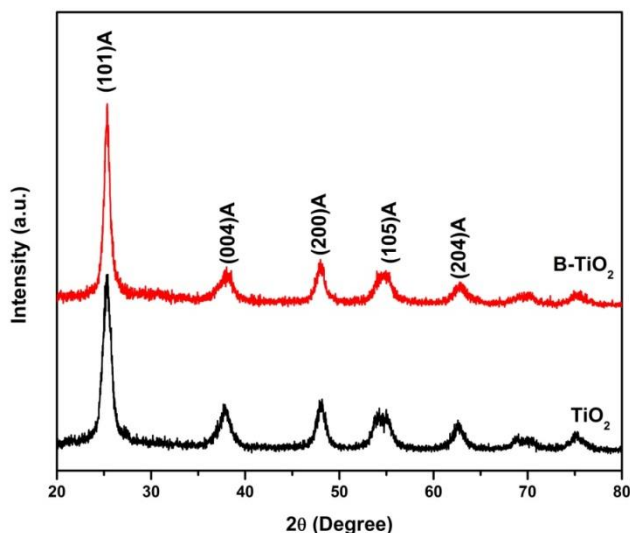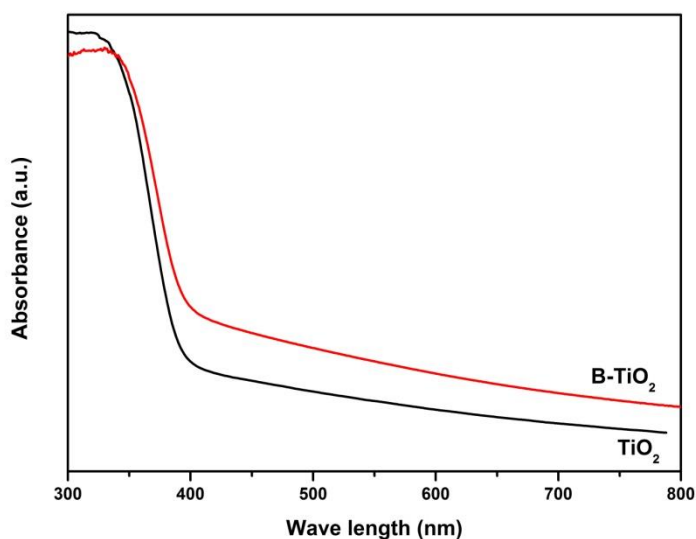
Figure 3.1. XRD patterns of boron doped and undoped TiO_2 nanoparticles

Figure 3.1 shows the XRD patterns of boron doped and undoped TiO_2 nanoparticles. From the graphs it is clear that all the samples are crystalline in nature. All the undoped and doped samples are purely in anatase phase (PDF no. 21-1272) with major diffraction peaks at 25.3, 37.9, 48.0, 53.8 and 62.9 corresponding to the reflections at lattice planes (101), (004, (200), (105) and (204) respectively. There is no significant change in the positions of peaks during doping. This is explained as the lattice structure of TiO_2 does not alter by boron doping. The XRD patterns show a significant peak broadening and this is due to the reduction in particle size. The crystallite size was estimated from the peak broadening using Debye-Scherrer formula. The calculated crystallite sizes for undoped and boron doped TiO_2 nanoparticles are as 11.1nm and 10.5nm respectively. From these values, it is clear that boron doping causes a slight decrease in the particle size of TiO_2 nanoparticles.

Optical absorption studies

Optical absorption properties of boron doped TiO_2 were studied using UV-Diffuse reflectance spectra (UV-DRS). Figure 3.2 shows the UV-DRS spectra of the doped and undoped samples. Both undoped and doped samples exhibited absorption maximum in the range of 320-350 nm which is an indication of the formation of TiO_2 material. Form the figure, it is observed

that the absorption peak of boron doped sample showed a tailing towards the visible region (red shift) which proves the incorporation of boron in the TiO_2 crystal lattice. This bathochromic shift is due to the increased absorption from the visible region which is due to the decrease in the band gap.


Figure 3.2. UV-DRS Spectra of boron doped and undoped TiO_2 nanoparticles

Band gaps of undoped and B-doped samples were determined with the help of Kubelka-Munk equation:

$$\frac{K}{S} = f(R) = \frac{(1-R)^2}{2R}$$

Where K is the absorbance coefficient, S is the scattering coefficient and R is the reflectance which is equal to $R_{sample}/R_{standard}$ ($R_{standard}$ is the reflectance of the reference $BaSO_4$ and R_{sample} is the reflectance of the sample analysed). Band gaps were obtained by plotting $[f(R)h\nu]^2$ v/s $h\nu$ and extrapolating the straight portion of the graph to the X axis. The obtained band gaps for boron doped and undoped TiO2 are 3.24eV and 3.19 eV respectively. This reduction in the band gap of boron doped TiO_2 is due to the introduction of impurity levels within the band gap of TiO_2 by the presence of boron.
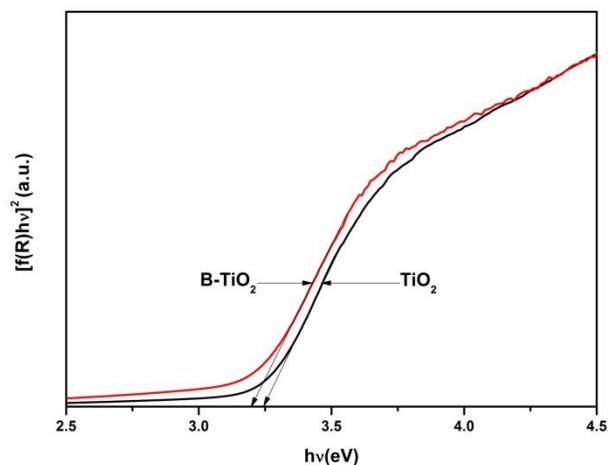
Figure 3.3. Kubelka- Munk plots of boron doped and undoped TiO$_2$ nanoparticles

b) Photocatalytic studies

The visible light photocatalytic activity of B-doped and undoped TiO$_2$ was determined by analyzing the photo degradation reaction of methylene blue(MB) aqueous solution. It is also known as methylthioninium chloride and it is a synthetic basic dye. It is an organic chloride salt having 3,7-bis(dimethylamino)phenothiazin-5-ium as the counter ion. Structure of methylene blue is given in Figure 3.4. It is an ISO standard testing method for determining the photocatalytic activity of surfaces.
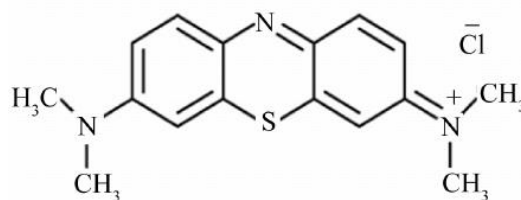

Fig.3.4. Chemical structure of Methylene blue

Photocatalytic degradation rate of MB aqueous solution can be calculated by the formula,

$$D = \frac{(A_0 - A)}{A_0} \times 100 \%$$ (3.3)

In the formula, D represents the photocatalytic degradation rate of methylene blue aqueous solution, A_0 is the absorbance of MB aqueous solution before the photocatalytic reaction, and A is the absorbance of MB aqueous solution after being catalyzed by the TiO_2 nanoparticles.
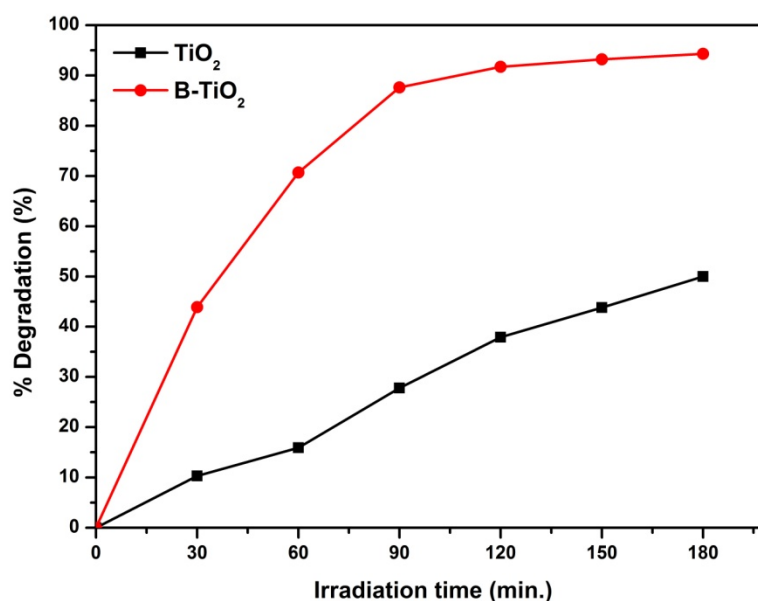
Figure 3.5. Photodegradation of TiO_2 and B-TiO_2

Figure 3.5 shows the photo catalytic decomposition of MB in the presence of undoped and boron doped TiO_2 under visible light radiation. The plot of percentage degradation versus time of irradiation is shown in Figure 3.5. For both undoped and boron doped samples, the dye solution was degraded as time proceeds. But the extent of degradation was different. For undoped TiO2 nanooparticles, only 50 % of dye was degraded after 3 hours of irradiation. But boron doped sample showed a degradation of 94.3 % after 3 hours of irradiation.

The mechanism of the photocatalytic degradation of dye using undoped and boron doped TiO2 nanoparticles are explained as follows. When light of suitable wave length falls on the photocatalyst, electrons are excited from the valence band to conduction band. The excited

electrons in the conduction band will interact with the oxygen molecule to form superoxide radicals and the holes in the valence band will interact with the adsorbed water molecules to form hydroxyl radicals. These high energy species will react with the dye molecules adsorbed on the surface of the catalyst and decompose it to harmless end products like water and carbon dioxide.

In boron doped sample, boron introduces impurity levels within the band gap approximately at 2.18eV above the valance band. In addition to that, boron is able to donate all the three valance electrons to lattice Ti ions which results the reduction of Ti^{4+} ions to Ti^{3+}. These Ti^{3+} ions produce defect states just below the conduction band. Both of these types of impurity levels within the band gap of TiO_2 cause a decrease in the band gap and thus boron doped TiO_2 has an improved ability to tap visible light. In addition to that the tendency of recombination of the excited electron and hole reduces significantly by the introduction of impurity states within the band gap. As a result, boron doped TiO_2 showed an excellent improvement in the photocatalytic activity.

CHAPTER 4
CONCLUSION

Boron doped and undoped TiO$_2$ nano materials were synthesized by phytochemical assisted sol gel method using methanolic leaf extract of Chromolaena odorata. Titanium isopropoxide was used as the precursor for titanium and boric acid was used as the boron source. The characterization of the synthesized materials was done using X-Ray Diffraction and UV-Visible Spectroscopy. The XRD patterns revealed that both boron doped and undoped nano particles were crystalline in nature. It also gave information about the crystalline purity of the synthesized materials. Particle size was roughly estimated from XRD patterns with the help of Debye-Scherrer formula. The results showed a slight decrease in particle size on doping. But there is no appreciable change in the peak positions which indicate that boron doping does not affect the crystal structure of TiO$_2$. UV-Visible absorption spectra of the samples showed a tailing in the absorption peak towards the longer wavelength region by doping with boron which proves the incorporation of boron in the TiO$_2$ crystal lattice. The reason of this red shift is the increased absorption from visible region. This is due to the decrease in band gap by the introduction of boron which is further proved from the band gaps obtained from the Kubelka Munk plots.

The photocatalytic property of boron doped and undoped samples were investigated by analyzing the photodegradation of methylene blue aqueous solution. From the results, it is obvious that the boron doping considerably increase the visible light photocatalytic property of TiO$_2$ by the formation of impurity levels within the band gap of TiO$_2$.

From the results, it can be concluded that the synthesis method we adopted here is an easy and economical way of synthesizing boron doped TiO$_2$. The method avoids the usage of chemicals as reducing agents and capping agents hence can be considered as green. The green synthesized boron doped samples showed superior photocatalytic properties compared to the undoped one. Boron doping can further be confirmed by EDX and XPS techniques. This photocatalyst can be used for various applications due to its excellent visible light photocatalytic property.

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