

SYNTHESIS, CHARACTERIZATION AND PHOTOCATALYTIC STUDIES OF BORON DOPPED TITANIUM DIOXIDE NANOPARTICLES

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Under the Guidance Of
Asst. prof. ANU K JOHN



**DEPARTMENT OF CHEMISTRY
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CERTIFICATE

This is to certify that the project report entitled “Synthesis, Characterization and Photocatalytic Studies Of Boron Doped Titanium Dioxide Nanoparticles” is an authentic record of the project work carried out by Ms. MINNU JOHNSON (Reg.no:180011017733) in partial fulfillment of the award of the degree of Master of Science in Pharmaceutical chemistry at Bharata Mata College, Thrikkakara affiliated to Mahatma Gandhi University, Kottayam under my guidance and supervision during 2018-2020.

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Nanoparticles” is a bona-fide record of the work carried out by me under the guidance of **Anu K John**, Assistant Professor Department of Chemistry, Bharata Mata College Thrikkakara during my M.Sc. Degree in Pharmaceutical Chemistry.

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CHAPTER 1

INTRODUCTION

1.1 NANOTECHNOLOGY

Nanotechnology is a science, engineering and technology conducted at nanoscale, which is about 1 to 100 nanometers. The father of nanotechnology is Richard Feynmann. Nanotechnology has a wide range of application in the field of chemistry, biology, physics, material science and engineering. American physical society meeting at California Institute of Technology on Dec.29,1959,long before the term “nanotechnology” was used .In this talk ,feynmann described a process in which scientist would be able to manipulate and control individual atoms and molecules .With the development of Scanning Tunneling Microscope that could ‘see’ individual atoms that modern nanotechnology began. Rapid advances in material sciences and technology that enable manipulation of matter at the nanoscale will continue to allow the realization of many benefits of this technology.

Present day activity for manufacturing and use of nanomaterials is 49% in the United States, 30% in the European union, and 21% in other parts of the world. Although techniques for manufacturing nanomaterials are as varied as the materials themselves, they can be divided into two main types of approaches: “bottom-up” and “top-down” procedures. Bottom-up methods are widely used for manufacturing of metal nanoparticles, nanofilms, fullerenes, nanotubes, quantum dots etc. Top-down manufacturing can be used for obtaining computer chips, precision-engineered surfaces, metal oxides etc.

Nanotechnology is a growing global enterprise that will have large economic and social impacts as can be observed with the ever emerging products that utilize some form nanotechnological application whether it is a coating on cars to self-cleaning windows. It is often referred to as the tiny science, nanotechnology does not simply mean very small structure and products. Nano scale features are often incorporated into bulk materials and bulk surfaces. Nanotechnology is already in many of the everyday objects around us, this is only the start. It will allow limitations in many existing technologies to be overcome and thus has the potential to be part of every industry.

Nanomedicine is an application of nanotechnology to achieve breakthrough in healthcare. An important subdomain of nanomedicine is the field of in-vivo diagnosis based on imaging technologies. One of the most promising applications is molecular imaging, which refers to the characterization and measurement of biological processes at the cellular and molecular levels, and has emerged as a powerful tool to visualize molecular events of an underlying disease. Drug delivery aims to employ nanoscale carrier particles or molecules developed to improve the bioavailability and pharmacokinetics of therapeutics. Drug delivery systems can be synthesized with controlled composition, shape, size and morphology as demonstrated by examples such as programmable fusogenic vesicles. The surface properties of nanocarriers can be manipulated to increase solubility, immunocompatibility and cellular uptake. Advantages of nanotechnology include: reduction of waste products generated, and energy used, during manufacturing of conventional materials as well as nonmaterial's; research applications of nanomaterials in areas of green energy approaches, including solar energy, hydrogen, power transmission, diesel pollution control devices, and lighting; environment remediation/treatment research supporting improvement of pollutant capture or destruction by exploiting novel nanoscale structure property relations for nanomaterials used in environmental control and remediation applications; development of nanotechnology-enabled devices for measuring and monitoring contaminants and other compounds of interest, including

nanomaterials. Examples of the latter would involve development of new nanoscale sensors for the rapid detection of virulent bacteria, viruses and protozoa in aquatic environments.

Nanotechnology is a platform technology that utilizes the inherently unique properties of matter that arise at the nanoscale. Applications of this technology can be found in areas of material science, energy, medicine, environment, communications and electronics among others. The enormous international S&T investments in technology research have evolving, and potentially endless possibilities. Researchers continue to find new applications for nanomaterials. Whether it is using carbon nanotubes to make vehicle composites stronger than steel, but lighter or creating medicines that can target and treat specific cells in the body, or purifying water at point of use –nanotechnology could revolutionize some of these sectors.

One of the challenges is to garner benefits without risk.

1.2 DIFFERENT TYPES OF NANOMATERIALS

Nan materials generally fall into two categories: fullerenes and inorganic nanoparticles.

1.2.1 FULLERENES

A fullerene is any molecule composed entirely of carbon, in the form of hollow sphere, ellipsoid or tube. Spherical fullerenes also called Bucky balls, and they resemble a football. Cylindrical ones are called carbon nanotubes or Bucky tubes. Fullerenes are similar in structure to graphite which is composed of stacked graphene sheets of linked hexagonal rings; but they also contain pentagonal rings. There also exist other carbon molecules similar to C_{60} with cage structure, collectively called “fullerenes” in honour of the famous American architect Buckminster Fuller.

Fullerenes were under study for potential medical use; binding specific antibiotics to the structure of resistant bacteria and even target certain types of cancer as melanoma.

1.2.2 CARBON NANOTUBES

Carbon nanotubes are often described as graphene are rolled up into the shape of cylinder. They are graphene cylinders about 1-2 nm in diameter and wrapped with endcontaining pentagonal rings. The general principle of nanotube involves producing reactive carbon atoms at very high temperatures; these atoms then accumulate in regular patterns on the surface of metal particles that stabilize the formation of the fullerenes resulting in a long chain of assembled carbon atoms.

Carbon nanotubes may be single walled (SWNT) or multiwall (MWNT'S). Depending upon the alignment of carbon atoms in the cylindrical form SWNT can be either achiral or chiral. Achiral and chiral forms can act as metals or semiconductors and yet retain the same basic nanotubes structural motif.

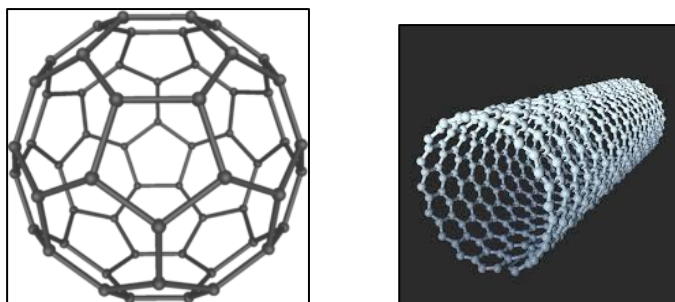


Fig.1. Fullerene and Carban Nanotubes

1.2.3. INORGANIC NANOPARTICLES

Nanoparticles made of metals, semiconductors, electrical, magnetic, optical, chemical, and other properties. Nanoparticles are characterized at the nanometre scale in one two or three dimensions leading to quantum wells, quantum wires or quantum dotes. These particles effectively act as a bridge between bulk materials and atomic or molecular structures .A bulk material should have constant physical properties, regardless of its size. Inorganic nanoparticles are mainly classified into three categories.

Inorganic Nanotubes

An inorganic nanotube is a cylindrical molecule often composed of metal oxides and morphologically similar to carbon nanotubes. Inorganic nanotubes have been observed to occur naturally in some mineral deposit. Although Linus Pauling mentioned the possibility of curved layers in minerals as early as 1930, synthetic inorganic nanotubes did not appear until Research Tenne Et.al reported the synthesis of nanotubes composed of tungsten disulfide in 1992. In the intervening years, nanotubes have been synthesized of many other inorganic materials such as vanadium oxide and manganese oxide and are being researched for such applications as redox catalyst and cathode materials for batteries.

The physical properties of inorganic nanotubes are relatively less explored. TiO_2 nanotubes may be useful as well as well purge active bioactive surface layers on titanium implant metals for orthopaedic and dental implants, as well as for photo catalyst and other sensor applications.

Nanowire

A nanowire is a nanostructure, with the diameter of the order of a nanometre (10^{-9} meters). Alternatively, nanowires can be defined as structures that have a thickness or diameter constrained to tens of nanometre or less and an unconstrained length. At these scale, quantum mechanical effects are important which coined the term “quantum wires”. Many different types of nanowires exist, including metallic (Ni, Pt, Au), semiconducting (Si, InP, etc) and insulating (SiO_2 , TiO_2). Molecular nanowires are composed of repeating molecular units either organic (DNA) or inorganic.

Nanowires have many interesting properties that are not seen in bulk or 3D materials. This is because electrons in nanowires are quantum confined laterally and thus occupy energy levels that are different from the traditional continuum of energy levels or bands found in bulk materials. The nanowires could be used, in the near future, link tiny components into extremely small circuits.

Quantum dots

Quantum dots are tiny particles, or “nanoparticles”, of a semiconductor material, traditionally chalcogenides (selenides or sulfides) of metals like cadmium or zinc (CdSe or ZnS for example), which range from 2 to 10 nanometers in diameter. Because of their small size, quantum dots display unique optical and electrical properties that are different in character to those of the corresponding bulk material. The most immediately apparent of these is the emission of photons under excitation, which are visible to the human eyes as light. Moreover, the wavelength of these photon emissions depends not on the material from which the quantum dot is made, but its size.

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 nano crystalline material eg. Vapour condensation, high energy milling etc. In bottom-up approach, individual atoms or molecules are brought together or self-assembled to form nano structured material eg. Chemical precipitation, self-assembly

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

a. Physical Methods

i) 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. TiO₂films with grain size less than 30nm and less than 10nm are synthesized by pyrolysis of titanium tetraisopropoxide.

ii) 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.

iii) 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 trigger nucleation and growth of nanoparticles. The nanoparticles are then collected by catcher equipped with a filter.

b. Chemical Methods iii)

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 TiO₂ nanotubes. Direct oxidation of titanium metal with hydrogen peroxide has also been found to lead to formation of TiO₂ nanorods.

IV) Hydro thermal 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. **v) Sol-gel method**

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 provide 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, bio molecules, 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.

TiO₂ Nanoparticles

Titanium dioxide nanoparticles are one of most important metal oxide nanoparticles. TiO₂ 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 TiO₂ based nanomaterials.

Applications of TiO₂ 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.

2) Cosmetics

TiO₂ nanoparticles act as an inorganic UV absorber. Owing to this feature TiO₂ 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

TiO₂ 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

TiO₂ is one of the most photocatalytically active materials which are 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 valence band will interact with adsorbed water molecule to form hydroxyl radical. Hydroxyl radicals and superoxide anions produced by the photocatalytic process can degrade the majority of organic compounds until the complete mineralization is achieved.

Photocatalyst 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 crystalline 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 photocatalytic 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 photo catalyst due to low cost, reasonable good efficiency, good availability, 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 favoured 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 TiO₂ nano particles

Titanium dioxide (TiO₂) 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, TiO₂ nanoparticles has been widely used as photocatalyst in many environmental and energy applications. TiO₂ 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 TiO₂ nanoparticles with optically active ions, up or down conversion luminescence can be produced. Several approaches have been introduced to increase the photocatalytic activity of TiO₂ and to extend its light absorption into the visible region such as Metal-ion implanted TiO₂, non-metal doped TiO₂, TiO₂ doped with N, C and B etc.

In order to broaden the effective range of light sensitivity for photocatalysis from the ultraviolet (UV) region to the visible light region, dopants modify the electronic structure of nanoTiO₂. 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 TiO₂ were prepared using modified sol-gel process. The introduction of dopant in the TiO₂ 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. The oxygen atom of TiO₂ 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, increase boron doping on TiO₂ nanoparticles result in increased oxygen vacancies and free electron formations. The phase transformation between anatase and rutile is dominated by boron into anatase TiO₂ 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 N₂ molecule to NH₃ under ambient conditions. N₂ 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 N₂ fixation, providing a cost-efficient process for sustainable NH₃ 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 densityfunctional perturbation theory are unable to reproduce the dispersion relations of the highresolution 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 result 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-TiO₂) 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-TiO₂ 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 TiO₂ nanoparticles in visible light was studied using the degradation reaction of aqueous solution of methylene blue dye. The photocatalytic property of boron doped TiO₂ was then compared with that of undoped TiO₂. TiO₂ 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 TiO₂ 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 TiO₂ nano particles

Boron doped TiO₂ nanoparticles were synthesized using Titanium isopropoxide (TIP), boric acid, methanolic leaf extract and water. Desired quantity of boric acid (corresponding to 1, 3, 5 and 7mol % of boron in TiO₂) 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. The samples were named as BT(0), BT(1), BT(3), BT(5) and BT(7) where the number in the brackets indicated the amount of dopant in mol. Percentage. Undoped TiO₂ 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-TiO₂ nanoparticles. An aqueous solution of 10 mg/L methylene blue was prepared. 0.1g of TiO₂ 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 2θ value corresponding to the peak with maximum intensity in the XRD pattern.

Figure 3.1 shows the XRD patterns of boron doped and undoped TiO₂ 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 TiO₂ does not alter by boron doping.

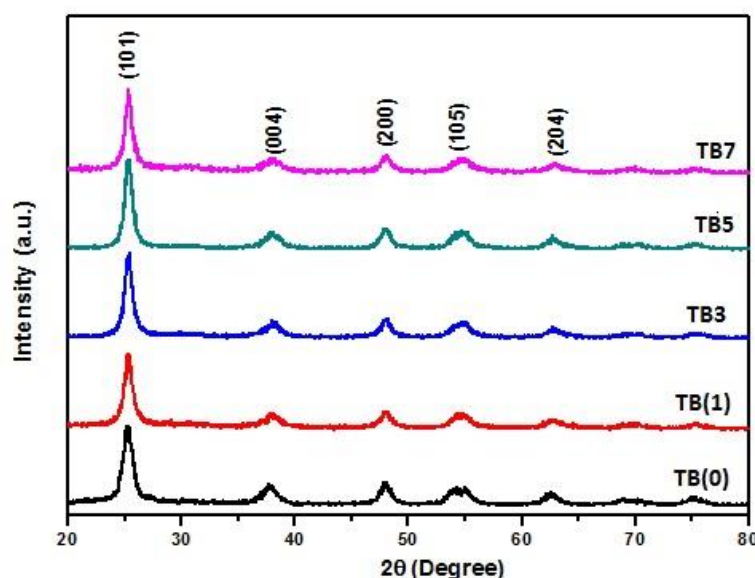


Figure 3.1. XRD patterns of boron doped and undoped TiO₂ nanoparticles

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 TiO₂ nanoparticles are shown in the table 3.1. Form these values it is clear that boron doping does not causes a significant change in the crystallite size.

Table 3.1. Average grain sizes of B-doped samples

Sample name	Particle size (nm)
TB(0)	11.1
TB(1)	11.1
TB(3)	11.2
TB(5)	11.6
TB(7)	10.2

Optical absorption studies

Optical absorption properties of boron doped TiO₂ 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 TiO₂ material. Form the figure, it is observed that the absorption peak of boron doped samples showed a tailing towards the visible region (red shift) which proves the incorporation of boron in the TiO₂ crystal lattice. As the percentage of dopant increases, the shift becomes more prominent. This bathochromic shift is due to the increased absorption from the visible region which is due to the decrease in the band gap.

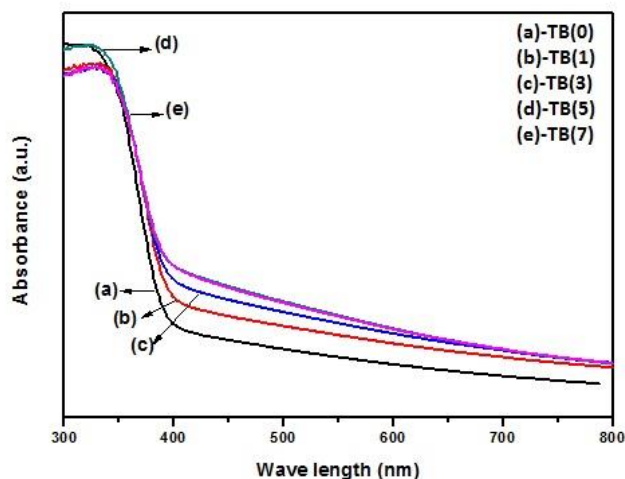


Figure 3.2. UV-DRS Spectra of boron doped and undoped TiO₂ nanoparticles

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 $R_{\text{sample}}/R_{\text{standard}}$ (R_{standard} is the reflectance of the reference BaSO₄ and R_{sample} is the reflectance of the sample analysed). Band gaps were obtained by plotting $[f(R)hv]^2$ v/s hv and extrapolating the straight portion of the graph to the X axis. The obtained band gaps for boron doped and undoped TiO₂ are shown in the table 3.2. From the table it can be observed that boron doping leads to a decrease in the band gap of TiO₂. This reduction in the band gap of boron doped TiO₂ is due to the introduction of impurity levels within the band gap of TiO₂ by the presence of boron. As the percentage of dopant increases, the extent of reduction in the band gap became more prominent.

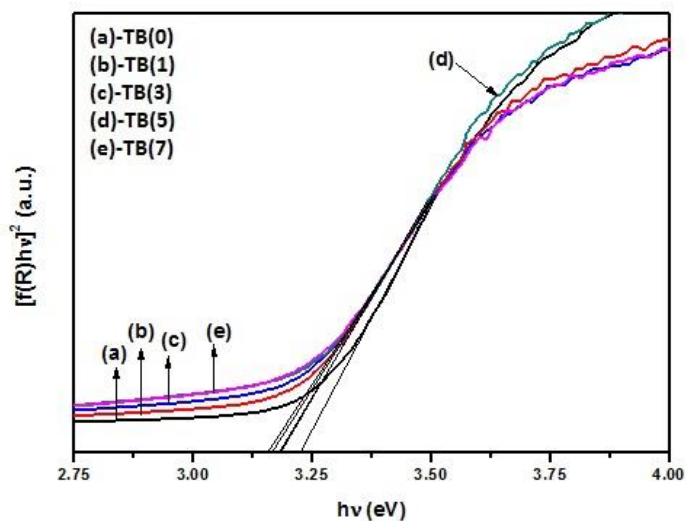


Figure 3.3. Kubelka- Munk plots of boron doped and undoped TiO₂ nanoparticles

Table 3.2 Band gaps of undoped and B-doped samples

Sample name	Band gap(eV)
TB(0)	3.23
TB(1)	3.22
TB(3)	3.20
TB(5)	3.19
TB(7)	3.17

b) Photocatalytic studies

The visible light photocatalytic activity of B-doped and undoped TiO₂ 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 3.7. It is an ISO standard testing method for determining the photocatalytic activity of surfaces.

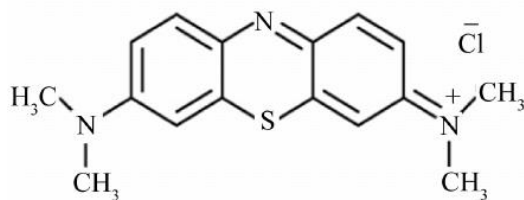


Fig.3.4.Chemical structure of Methylene blue

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

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

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 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.3.4. For both undoped and boron doped samples, the dye solution was degraded as time proceeds. But the extent of degradation was different. For undoped TiO_2 nanoparticles, 84 % of dye was degraded after 3 hours of irradiation. In the case of boron doped samples, the percentage of degradation increases as the amount of dopant increases up to 5 mol. % of dopant. Further increase in the percentage of dopant leads to a decrease in the photodegradation of dye solution. Maximum degradation of 94% was shown by the sample BT(5) in which the percentage of dopant is 5 mol. %.

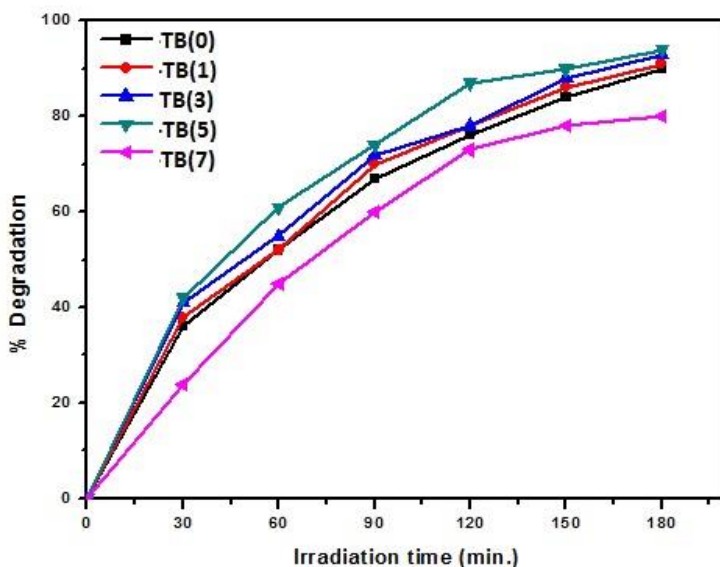


Figure 3.5. Photodegradation of TiO₂ and B-TiO₂

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 carbondioxide.

In boron doped samples, 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 Ti⁴⁺ ions to Ti³⁺. These Ti³⁺ ions produce defect states just below the conduction band. Both of these types of impurity levels within the band gap of TiO₂ cause a decrease in the band gap and thus boron doped TiO₂ has an improved ability to tap visible light. In addition to that the tendency of recombination of the exited electron and hole reduces significantly by the introduction of impurity states within the band gap. As a result, boron doped TiO₂ showed an excellent improvement in the photocatalytic activity. But after an optimum concentration (5mol.%), further increase in the amount of dopant causes a decrease in the photocatalytic activity. This is due to the fact that the impurity levels generated by the dopant now act as the recombination

centers and facilitate the recombination of charge carriers which results in the decrease in the photocatalytic activity.

CHAPTER 4

CONCLUSION

Boron doped and undoped TiO₂ 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 indicated that there is no significant change in the particle size on doping. Also there is no appreciable change in the peak positions which indicate that boron doping does not affect the crystal structure of TiO₂. 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 TiO₂ 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 TiO₂ by the formation of impurity levels within the band gap of TiO₂. This trends continued up to an optimum concentration of the dopant (5 mol. %).

From the results, it can be concluded that the synthesis method we adopted here is an easy and economical way of synthesizing boron doped TiO₂. 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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