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

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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 Nitrogen Doped Titanium Dioxide Nanoparticles" is an authentic record of the project work carried out by Ms. ANJITHA RAMESAN (Reg.no:180011017726) 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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DECLARATION

I Anjitha Ramesan, hereby declare that the project report entitled "Synthesis, Characterization and Photocatalytic Studies Of Nitrogen Doped Titanium Dioxide
Nanoparticles" is a bona-fide record of the work carried out by me under the guidance of **Anu K John**, Associate Professor Department of Chemistry, Bharata Mata College Thrikkakara during my

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00/07/ 2020   ANJITHA RAMESAN

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ANJITHA RAMESAN

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CHAPTER 1
INTRODUCTION

NANOTECHNOLOGY

Nanotechnology generally consider as a field of research and innovation regarding with making materials and devices on the scale of atoms and molecules . Nanoparticles are microscopic particles usually in the range of 1-100 nanometers.

A nanometer is one millionth of a millimetre. The properties of nanoparticles can be controlled by manipulating the size of the particles. Nanomaterials are significant because of their optical, magnetic, electrical and other properties. These properties are relevant in electronics medicine and other fields.

Nanomaterials have different properties because they have increased relative surface area and new quantum effects. They have much greater surface area than the conventional forms, which will give greater chemical reactivity. Quantum effects are important about materials properties and characteristics leading to the novel optical,Electrical and magnetic behaviours.

June 1999, Richard Smalley, Nobel laureate in chemistry, addressed the US House Committee on Science on the benefits of nanotechnology. "The impact of nanotechnology on the health, wealth, and lives of people," he said, "will be at least the equivalent of the combined influences of microelectronics, medical imaging, computer-aided engineering and man-made polymers developed in this century.

Nanotechnology holds the promise of new solutions to problems that hinder the development of poor countries, especially in relation to health and sanitation, food security, energy and the environment. Nanotechnology is already useful as a tool in health care research. But nanotechnology could also one day lead to cheaper, more reliable systems for drug-delivery. For

example, materials that are built on the nanoscale can provide encapsulation systems that protect and secrete the enclosed drugs in a slow and controlled manner. Filters that are structured on the nanoscale offer the promise of better water purification systems that are cheap to manufacture, long-lasting and can be cleaned. Tiny sensors offer the possibility of monitoring pathogens on crops and livestock as well as measuring crop productivity. In addition, nanoparticles could increase the efficiency of fertilisers. The application of nanotechnology in the field of renewable and sustainable energy (such as solar and fuel cells) could provide cleaner and cheaper sources of energy. These would improve both human and environmental health.

NANOMATERIALS

ISO(2015)defines a nanomaterial as a:

'material with any external dimension in the nanoscale (size range from approximately 1 – 100 nm) or having internal structure or surface structure in the nanoscale'.

Nanomaterials that are naturally occurring (e.g., volcanic ash, soot from forest fires) or are generated as incidental (unintentional) by-products of combustion processes (e.g., welding, diesel engines) are usually physically and chemically heterogeneous and often termed 'ultrafine particles'. Engineered nanomaterials, on the other hand, are intentionally produced and designed with physio-chemical properties for a specific purpose or function.

Nanomaterials are extremely small size having at least one dimension100 nm or less. They can be classified into different classes .They can be one dimensional ,two dimensional or three dimensional. Their optical properties, reactivity, toughness and other properties are depend on their size, shape and structure. So they have various industrial and domestic applications like, catalysis, imaging, energy based research ,environmental applications and medical applications. The different groups of nanoparticles include carbon nanoparticles , semiconductor nanoparticles, ceramic NPs,metal nanoparticles ,polymeric nanoparticles and lipid-based nanoparticles.

These materials have created a high interest in recent years by virtue of their unusual mechanical, electrical, optical and magnetic properties.

CARBON NANOPARTICLES

These are further referred as carbon nanotubes and fullerenes.

CARBON NANOTUBES

Long ,thin cylinders of carbon were discovered by Sumio lijim.These are large macro molecules unique for their size, shape, remarkable physical properties. Structurally they are a sheet of graphite rolled in to a cylinder. Nanotubes have a very broad range of electronic ,thermal and structural properties that change depending on the different kind of nanotube. These properties are depend on its diameter ,length, and chirality, or twist. There also single cylindrical wall nanotubes(SWNTs) and multiple wall nanotubes (MWNTs). They have a wide range of application in material science ,electronics, chemical processing , energy management,etc. They shows extra ordinary electrical conductivity , heat conductivity ,mechanical properties .

FULLERENS

Fullerenes are discovered in 1985 by Harold. W.Kroto ,Robert.F.Curl ,Richard.E.Smalley . These are third allotropic form of carbon discovered right after graphite and diamond. These posses a cage like structure consist of 20 hexagonal and 12 pentagonal rings as the basis of an icosahedral symmetry. The C_{60} molecule is an electron deficient alkene which readily reacts with electron rich species .The C in fullerene are sp2 hybridized and it posses two bond lengths , the 6:6 bonds are considered as double bonds and are shorter than 6:5 bonds.C_{60} is seems to superaromatic as it tends to avoid double bonds in pentagonal rings, resulting in a poor electron delocalisation. That's why fullerenes act as electron deficient species.

SEMICONDUCTOR NANOPARTICLES

Semiconductor nanoparticles shows properties of metals and non-metals .They posses wide band gaps, that they can have different properties on tuning. These are widely used in photocatalysis, electronic devices and photo-optics.

QUANTUM DOTS: These are very small, only several nanometer sized semiconductor particles. Quantum dots are colloidal semiconductor nanocrystals, sized between 2-10 nanometers , made up of 10-50 atoms in diameter and grand total of
100- 100,000 atoms within the quantum dot volume. They exhibit properties between the bulk semiconductors and discrete atoms and molecules. According to the composition of QDs they

exhibit different colours of emission. Larger QDs (5-6 nm) emit larger wave length, colours such as orange or red . Smaller QDs (2-3 nm) emit shorter wave lengths, resulting in colours like blue and green. Quantum dots of same material, but with different sizes, can emit light of different colours. These are particularly significant for optical applications due to their theoretically high quantum yield. The possibility to tune the size of the quantum dots is beneficial for many applications.

METAL NANOPARTICLE

Metal nanoparticles are nanosized metals with dimensions within the size range 1-100nm. These metals have different chemical and physical properties compare to that of the bulk materials. They have properties that might considerable in various industrial applications like, lower melting points, high specific surface area ,optical properties ,magnetisation ,mechanical properties etc. In general …… free path (MFP) a metal is of the order 5-50 nm. Further increase of MFP result the scattering of electrons from the crystal surface via increasing the resistivity of the particle. The optical property is the one of the basic characteristic of a nanoparticle .For example ,20-nm gold nanoparticle has a characteristic red colour, silver is yellowish grey ,and platinum and palladium are black. They shows large surface area to volume ratio compared to bulk equivalents; large surface energies; the transition between molecular and metallic states providing specific electronic structure(local density of states(LDOS)).It has low-coordination sites which provides chemical properties and ability to store excess electrons.

POLYMERIC NANOPARTICLE

Polymeric nanoparticle are organic based nanoparticle. Based on the method of synthesis these are two types, nanocapsular and nanospheres.Nanospheres having matrix like structure and their active components and polymer are uniformly dispersed. Nanocapsular particle have core-shell structure and their active components are confined and surrounded by a polymer shell.Poilmeric nanoparticle have many applications in drug delivery and diagnosis. Polymeric nanodrug delivers are biocompatible and highly biodegradable. They are helpful in controlled release, protection of drug molecule, ability to combine therapy and imaging, specific targeting etc.

LIPID-BASED NANOPARTICLES

Lipid based nanoparticles are spherical in shape. They are under diameter 10 nm to 100 nm. The structure of lipid base nanomaterial consist of a solid core made of lipid and a matrix made of soluble lipophilic molecules. External core of the nanoparticles are stabilised by surfactants and emusifiers.These nanoparticle play an important role in biomedical field. Applications include drug carrier, delivery and RNA release in cancer therapy.

METAL OXIDE NANOPARTICLES

Metal oxides have a wide rang of applications in chemistry, physics and material science. The elements can form a large variety of oxide compounds. They can exhibit either metalic,semiconductor or insulator characterristics.Because of their small size they shows different and unique physical and chemical properties. They found application in optoelectronics fabrication of microelectronic circuits, fuel cells. These can be synthesised via co-precipitation, thermal decomposition ,microemulsion ,hydrothermel synthesis 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, Power X-ray diffraction (PXRD)

SYNTHESIS OF NANOMATERIALS

Synthesis of nanomaterials is of great importance ,as particles build up from a few hundred atoms posses properties different from bulk. The main possible routes for the synthesis of nanomaterials are (a)Bottom up and (b) Top down .In bottom up it means small to big, like the structures are build up from individual atoms or molecules. This method is based on molecular recognition and self assembly eg.vapour condensation, mechanical grinding. But in top down

approach nanostructures are build up from big to small ,by breaking up bulk materials e.g. chemical precipitation, self assembly.

They also classified in to chemical, physical and bio-assisted methods.

a. Physical Methods

i) Deposition method

In this method a solid phase material is obtained by condensing material in vapour 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.

ii) Electrophoretic deposition

This is the most favoured 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 lead to 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 TiO_2 nanotubes. Direct oxidation of titanium metal with hydrogen peroxide has also been found to lead to formation of TiO_2 nanorods.

iv) Hydrothermal method

This method involves crystallizing a substance from its aqueous solution at high temperature and high vapour 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

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.

BIO-ASSISTED METHOD

Generally this is biosynthesis or green synthesis of nanoparticles. The method is eco friendly ,cost effective, low toxic and highly efficient method. IN this method the synthesis is carried out by means of bacteria,fungi,bio molecules, plant extracts etc. This is a widely using method for the synthesis of metal and metal oxide nanoparticles. The recent report of researches include bio synthesis of titanium dioxide nanoparticles using leaf extract of Azardirachta indica(neem),biodiesel plant,jatropha cureas etc.

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 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 photocatalyst 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 TiO$_2$ nano particles

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.

NITROGEN DOPING

The doping process of nitrogen gives a positive improvement in photo activity of TiO$_2$ i.e. The photocatalysis TiO$_2$ can be applied under UV and visible light ; it is an impact of the overlapping of the p and 2p orbital of nitrogen and oxygen, and this process resulted in a reduction of band gap of the modified TiO$_2$

Cristina Pablos and co-workers proposed an electrochemical enhancement of photocalalytic disinfection on aligned TiO_2 and nitrogen doped TiO_2 nanotubes, in 2017. the aim of their word was to study electrochemically assisted photocatalysis with nitrogen titania photoanodes under visible and UV-visible irradiation for the inaction of E-coli. Aligned TiO_2 nanotubes were synthesized by anodizing Ti fail. N doped titania nanotubes and N, F co doped titania films were also prepared with the aim of extending the active spectrum into the visible. Electrochemically assisted photocatalysis gave higher disinfection efficiency in comparison to photocatalysis for all material tested. The N-doped TiO_2 nanotube electrode gave the most efficient electrochemically assisted photocatalytic inactivation of bacteria under UV-VIS irradiation but no inactivation of bacteria was observed under only irradiation

Vy Anh Tran and co-workers introduce the use of N doped TiO2 in dye sensitized solar cells, in 2017. They aimed to improve the efficiency of DSC3 photo anodes. The effects of N doping on the structure, morphology, and crystallography of N-TNT were analysed by transmission electron microscopy (TEM), infrared spectroscopy (R)Raman spectroscopy, and x-ray photoelectron spectra (XPS). Results & indicate that doping enhanced the efficiency of N-TNT cells, by giving the optimum value ($\eta=7.36\%$) with 2M Nitrogen dopant compared to $\eta=4.75\%$ of TNT cells.

Thirupathi Boningari and co-workers proposed novel one-step synthesis of nitrogen-doped TiO_2 by flame aerosol technique for visible-light photocatalysis, in 2018.It was the first time, N doped TiO_2 was successfully synthesized by a novel-single-step flame spray pyrolysis (FSP) method. Their x-ray photoelectron spectroscopy shows that, as-synthesized N-TiO_2 catalyst predominantly is the form of interstitial nitrogen (Ti-O-N). The increase in the primary nitrogen content does not impact the band gap energies whereas increase the secondary source monotonically decreased the bandgap energies.

This observed lowering of the band gap energy for the flame made N-dope TiO_2 materials implies-that the N doping in TiO_2 by aerosol method is highly effective in extending the optical response of TiO_2 in the visible region

Yueying Li and companions were report the first demonstration of non-metal TiN as plasmonic boosted to significantly enhancing the photo electro Chemical Water Splitting performance of TiO_2, in 2019 The conductive TiO_2 not only affords Plasmon resonance on the N-TiO_2 enable high photoactivity in a broadband UV-vis light region, but also assist in the charge generation-separation-transportation-infection efficiency of TiO_2 for enhanced water oxidation kinetics. The

TiN/N-TiO$_2$ heterostructure manifests a high and durable photo current density and substantiates an outstanding visible-light-diven photocurrent density without the use of any hole scavenger and co catalysts. This study will enrich the fundamental understanding of nonmetal plasmonic effect in and beyond the field of photoelectrochemical water splitting.

In 2020 Pourya Mehdizadeh and co-workers experiment the visible light activity of nitrogen Doped TiO$_2$ by Sol-Gel method using various Nitrogen sources such as triethylamine, N, N, N', N1-tetramethylethane-1,2, -diamine, ethyldiamine, 1,2-phenyleenediamine, propanolamine and propylenediamine. Then the effect on properties by the source of product was investigated. The prepared products get characterised successfully Results indicate that the effective separation of photo-induced electron and hole pair, and improvement of pollutant decomposition under UV and visible light irradiations are due to doping of N in titania. The photo catalytic activities of N-doped TiO$_2$ nanoparticles were evaluated using the photodegradation of methyl orange under the irradiation of U

V & visible light. It confirm that the photocatalytic activity of N-TiO$_2$ is better than the pure TiO$_2$. According to their studies the photocatalytic activities of the N-TiO$_2$ with different nitrogen sources, trimethylamine with 2 molar ration was chosen as the optimum.

OBJECTIVE AND SCOPE OF THE WORK

Objective of the current work is to synthesize nitrogen doped titanium dioxide (N-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 N -TiO$_2$ nanoparticles. Titanium isopropoxide was used as the titanium precursor and urea was used as the source of nitrogen. The nanoparticles obtained by this method were characterized by X-ray diffraction studies and UV- Visible spectroscopy

The photocatalytic activity of nitrogen doped TiO$_2$ nanoparticles in visible light was studied using the degradation reaction of aqueous solution of methylene blue dye. The photocatalytic property of nitrogen 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. Nitrogen 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 NITROGEN 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 nitrogen doped TiO_2 nano particles

Nitrogen doped TiO_2 nanoparticles were synthesized using Titanium isopropoxide (TIP), urea, methanolic leaf extract and water. Desired quantity of urea (corresponding to 1, 2, 3 and 4 mol % 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. The samples were named as NT(0), NT(1), NT(2), NT(3) and NT(4) where the number in the brackets indicated the amount of dopant in mol. percentage. Undoped TiO_2 nanoparticles were prepared in the same method without adding urea 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 N-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 2θ value corresponding to the peak with maximum intensity in the XRD pattern.

Figure 3.1 shows the XRD patterns of nitrogen 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, 54.7 and 62.9 corresponding to the reflections at lattice planes (101), (004), (200), (105), (211) 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 nitrogen doping.
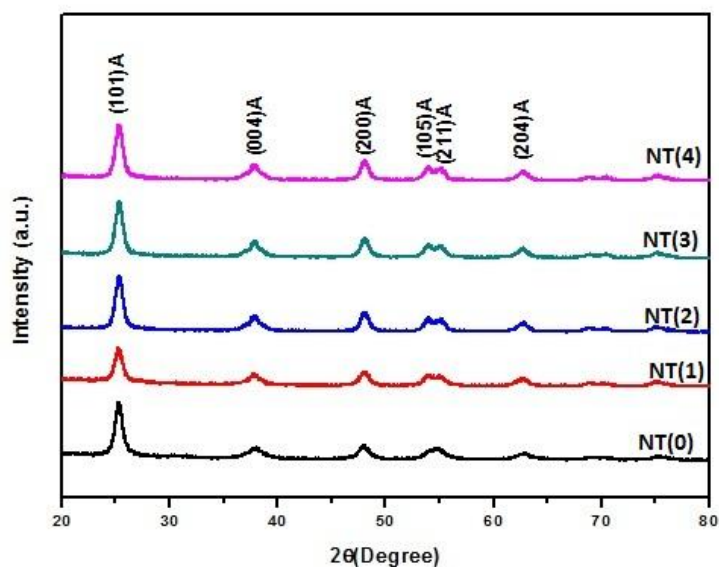
Figure 3.1. XRD patterns of nitrogen doped and undoped TiO$_2$ nanoparticles

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 TiO$_2$ nanoparticles are shown in the table 3.1. Form these values it is clear that nirogen doping causes a slight decrease in the average size of the particles.

Table 3.1. Average grain sizes of N-doped samples

Sample name	Particle size (nm)
NT(0)	11.1
NT(1)	10.8
NT(2)	10.3
NT(3)	10.9
NT(4)	10.5

Optical absorption studies

Optical absorption properties of nitrogen 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 nitrogen doped samples showed a tailing towards the visible region (red shift) which proves the incorporation of nitrogen in the TiO_2 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.
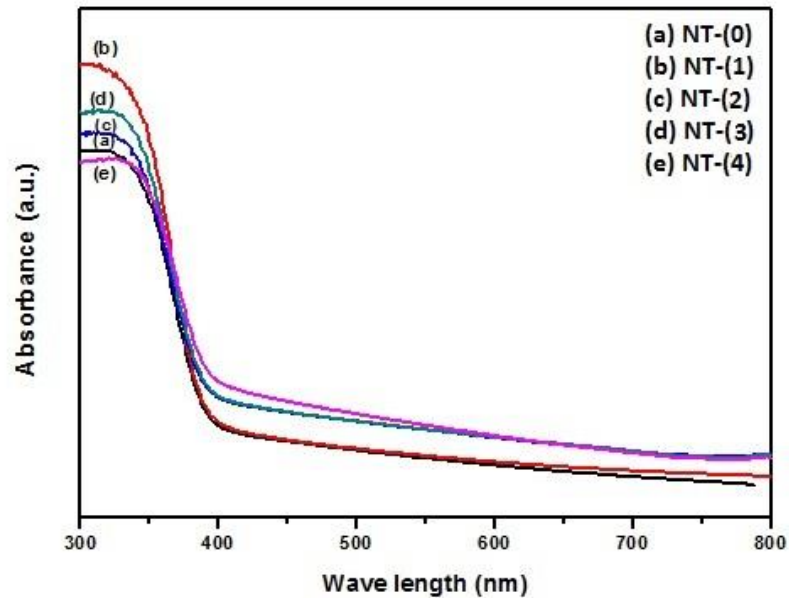

Figure 3.2. UV-DRS Spectra of nitrogen doped and undoped TiO_2 nanoparticles

Band gaps of undoped and N-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 nitrogen doped and undoped TiO2 are shown in the table 3.2. From the table it can be observed that nirogen doping leads to a decrease in the band gap of TiO_2. This reduction in the band gap of nitrogen doped TiO_2 is due to the introduction of impurity levels within the band gap of TiO_2 by the presence of nitrogen. As the percentage of dopant increases, the extent of reduction in the band gap became more prominent.
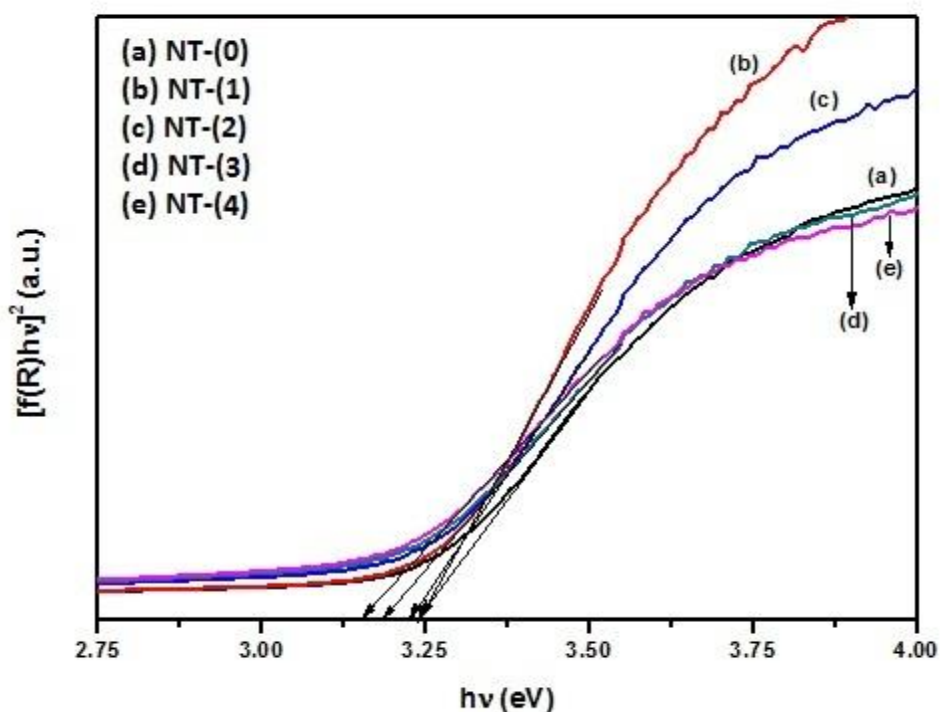

Figure 3.3. Kubelka- Munk plots of nitrogen doped and undoped TiO_2 nanoparticles

Table 3.2 Band gaps of undoped and N-doped samples

Sample name	Band gap(eV)
NT (0)	3.23
NT(1)	3.23
NT (2)	3.22
NT (3)	3.18
NT (4)	3.16

b) Photocatalytic studies

The visible light photocatalytic activity of N-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 Figure3.7.It is an ISO standard testing method for determining the photocatalytic activity of surfaces.
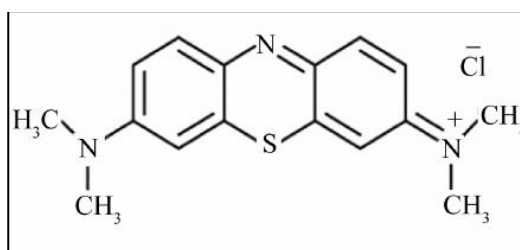

Fig.3.4. Chemical structure of Methylene blue

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

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

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 nitrogen 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 nitrogen doped samples, the dye solution was degraded as time proceeds. But the extent of degradation was different. For undoped TiO2 nanooparticles, 84 % of dye was degraded after 3 hours of irradiation. In the case of nitrogen doped samples, the percentage of degradation increases as the amount o dopant increases up to 2 mol. % of dopant. Further increase in the percentage of dopant leads to a decrease in the photodegradation of dye solution. Maximum degradation of was shown by the sample NT(2) in which the percentage of degradation is 98%.
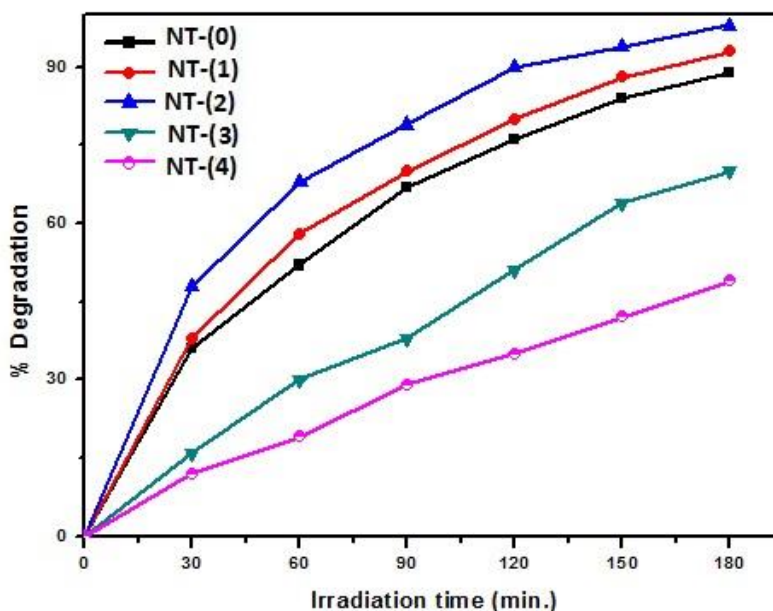
Figure 3.5. Photodegradation of TiO_2 and B-TiO_2

The mechanism of the photocatalytic degradation of dye using undoped and nitrogen 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.

From the XPS analysis, it is obvious that the nitrogen is introduced in TiO_2 lattice and form impurity levels. Also, Pl spectra and XPS confirm the existence of oxygen vacancies. Also, from the HRTEM images it is clear that the high energy {001} facet is exposed in the samples. The coexistence of both {101} and {001} facets can effectively contributes towards the phtotcatalytic activity. But always a competition is there between the photoreaction and recombination of charge carriers. As the percentage of dopant exceeds certain limit, the process of recombination predominates over photo oxidation or photo reduction[31]. This is the reason of the decrease in photo catalytic activity beyond certain optimum value of dopant concentration. This optimum concentration depends on the nature of nitrogen source.

Nitrogen as a dopant can alter the band structure by narrowing the band gap by introducing impurity levels within the band gap. Also nitrogen doping leads to the formation of oxygen vacancies in the crystal. Both of these factors facilitates the increased absorption of visible light and retard the tendency of recombination of photogenerated charge carriers. This synergic effect results an increase in the phtotcatalytic activity. But after an optimum concentration (2mol.%), 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

Nitrogen 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 urea was used as the nitrogen source. The characterization of the synthesized materials was done using X-Ray Diffraction and UV-Visible Spectroscopy. The XRD patterns revealed that both nitrogen 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 a slight decrease in the particle size by doping. Also there is no appreciable change in the peak positions which indicate that nitrogen 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 nitrogen which proves the incorporation of nitrogen 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 nitrogen which is further proved from the band gaps obtained from the Kubelka Munk plots.

The photocatalytic property of nitrogen 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. This trends continued up to an optimum concentration of the dopant (2 mol. %).

From the results, it can be concluded that the synthesis method we adopted here is an easy and economical way of synthesizing nitrogen 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 nitrogen doped samples showed superior photocatalytic properties compared to the undoped one. Nitrogen 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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