"Study of Photo catalytic behaviour of TiO_2 Nanopowders"

A Thesis Submitted in Partial fulfilment of the requirement for the award of the degree of

MASTER OF TECHNOLOGY
(MATERIAL SCIENCE AND ENGINEERING)

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June 2008

CERTIFICATE

This is to certify that the thesis entitled "**Study of Photo catalytic behaviour of TiO_2 Nanopowders**" submitted by Mr.Anmol Rattan Singh Roll No. 60602003 in partial fulfillment of the requirement for the award of the degree of **MASTERS OF TECHNOLGY** in **Materials Science and Engineering**, Thapar University Patiala, is a record of candidates own work carried out by him under our supervision and guidance. The matter embodied in this report is of the candidate's own record and not submitted to any other university in any part or full form for the award of such kind of a degree.

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ACKNOWLEDGEMENT

Knowledge in itself is a continuous process. I would have never succeeded in completing my task without the cooperation, encouragement and help provided to me by various personalities. With deep sense of gratitude I wish to express my sincere thanks to **Dr. O.P.Pandey**, *Professor & Head, School of Physics and Materials Science, who have been constant sources of inspiration for me throughout this project work.*

I would like to thank all the teaching staff and **Dr. Sunil Kumar,** *for their full motivation and appreciation to my work.*

I would also like to give many thanks to my friends **Manoj and Abhishek, Veerender Kumar Sharma** *for any kind of help and valuable suggestions whenever I needed out of their busy schedule.*

All my friends and my colleagues at the Materials Science & Engineering program and the School of Physics and Material Sciences and from other streams and departments are acknowledged for providing me a friendly atmosphere and encouraging me throughout this work.

I am deeply thankful to my Family, especially my younger brother Mr. Nirmol Rattan Singh for their moral support and patience has born fruit through completion of this Thesis which will result in award of the prestigious degree of M.Tech Materials science & Engineering.

Anmol Rattan Singh

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Abstract

As Titanium Dioxide nano-particles can be used for various types of industrial applications. Also the behavior of titanium dioxide nano-particles will be different at the nano-scale as surface to volume ratio is very high at this scale. For any type of photocatalytic application, surface to volume ratio is very important parameter. So, it is desirable to study the photocatalytic applications of titanium dioxide nano-particles in detail so that we can use them in industry. In this thesis we have tried to correlate the optical parameters & morphological parameters with the photocatalytic behaviour of TiO_2 nano-particles. The optical parameters studied are Photo-luminiscence and UV visible absorption. The morphological parameters studied are XRD & TEM. The photocatalytic degradation behavior is studied using Reactive Black-5 dye with TiO_2 nano-particles as the nano photocatalyst.

CHAPTER 1

INTRODUCTION

1.1 Introduction

The greek word 'nano' is referred to the length scale of one billionth of a meter. Thus nanoscience deals with the science of materials and technologies in the scale range of ~ 1-100 nm. This means, the nanoscience deals with a few hundred to a few thousand atoms or atomic clusters, whereas the microscopic word is made out of trillion of atoms or molecules. Nanoparticles are larger than individual atom and molecules, but are smaller than bulk solid; hence they obey neither absolute quantum chemistry nor laws of classical physics and have properties that differ markedly from those expected. Presently, the nanoscience and technology represents the most active discipline all around the world and is considered as the fastest growing technology revolution in the human history had ever seen. This intense interest in the science of the materials confined within the atomic scales stems the fact that these nanomaterials exhibit fundamentally unique properties with great potential of bringing plethora of next generation technologies in electronics, computing, optics, biotechnology, medical imaging, medicine, drug delivery, structural materials, aerospace, energy etc.

1.2 Nanostructured Materials

Nanostructured materials are materials with the characteristic length scale of the order of a few (typically 1 to 100) nanometers. The structure refers to the chemical

composition, the arrangement of the atoms, and the size of a solid in one, two or three dimensions effects controlling the properties of nanostructure materials which include size effects (where critical length scales of physical phenomenon become comparable with the characteristic size of the building blocks of the micro structure), changes of the dimensionality of the system, changes of the atomic structure and alloying of components, e.g. elements that are not miscible in the solid and/or the molten state. The synthesis, characterization and processing of nanostructured materials are part of an emerging and rapidly growing field. Research and development in this field emphasizes scientific discoveries in the generation of materials with controlled micro structural characteristics. Nanostructured materials may be grouped under nanoparticles, nanointermediates, and nano composites. They may be in or far away from thermodynamic equilibrium. For example nano-structured materials consisting of nanometer sized crystallites of Au or NaCl with different crystallographic orientation and chemical compositions vary greatly from their thermodynamic equilibrium.

Research in present day nanomaterials is based largely on the investigating fundamental properties of matter in nanoscale regime, however, the timely attention and efforts are essential for the transformation of these new findings into technology product so that the well assumed technology revolution will become day light reality. By now, a variety of chemical, biological as well as physical processes are established for the preparation of different kinds of nanoparticle systems and the ground breaking inventions such as scanning tunneling microcsopy (STM), atomic force microscopy (AFM), etc, made the characterization and atomic scale manipulation of nanoscale materials a practical reality.

1.3 Properties of Nanomaterials

In nanoparticles the properties (physical, chemical, biological etc.) can be selectively controlled by engineering the size, morphology, and composition of the particles. Nano materials are known to exhibit markedly different properties compared to micron sized ones. These new substances will have enhanced or entirely different properties from their bulk counterparts.

It has been shown that the various material properties such as electrical, mechanical, optical, magnetic etc are highly influenced by the fine-grained structure. Using a variety of synthesis methods, it is possible to produce nanostructured materials in the various forms like: thin films, powder, quantum wires, quantum wells, quantum dots, etc. There is also considerable interest in the generation of carbon nanostructures, which are related to the famous Bucky ball. In addition, the use of nanosized materials as fillers for composite materials are generating interest; specifically in the case of polymer nanocomposites. All materials are composed of grains, which in turn comprise many atoms. These grains are usually invisible to the naked eye, depending on the size. Conventional materials have grains varying in size any where from 100's of microns (μm) to millimeters (mm). A nanocrystalline material has grains on the order of 1-100nm. The average size of the atom is of the order of 1 to 2 Å in radius. One nanometer comprises of 10 Å, and hence in one nanometer (nm) there may be 3-5 atoms, depending on the atomic radii. Nanocrystalline materials are exceptionally strong, hard, and, ductile at high temperature, wear-resistance and chemically very active. Nanocrystalline materials are also much more formable than their conventional, commercially available micron counterparts.

1.4 Introduction to TiO_2

1.4.1 History of TiO_2

A wide range of products using TiO_2 is developed and applied in industries. One of the representative products is photo-catalyst effect of TiO_2. The need of Photo-catalyst TiO_2 in our life is increasing as the technical development and expansion of its applications and the relevant market size is growing significantly.

Since its commercial production in the early twentieth century, titanium dioxide (TiO_2) has been widely used as a pigment and in sunscreens, paints, ointments, toothpaste, etc. [1] discovered the phenomenon of photocatalytic splitting of water on a TiO_2 electrode under ultraviolet (uv) light. Since then, enormous efforts have

been devoted to the research of TiO_2 material, which has led to many promising applications in areas ranging from photovoltaics and photocatalysis to photo-electrochromics and sensors. These applications can be roughly divided into "energy" and "environmental" categories, many of which depend not only on the properties of the TiO_2 material itself but also on the modifications of the TiO_2 material host (e.g., with inorganic and organic dyes) and on the interactions of TiO_2 materials with the environment.

TiO_2 is the important inorganic compound that is widely used in our life. It is a representative white pigment used for plastics, paints, rubbers and papers. The economic development of a country is sometimes measured by usage of TiO_2 per person.
TiO_2 is very stable material in physical and chemical terms and has superior coverage and staining power because it has the highest refractive index among white pigments and accurate particle sizes and dispersibility. It is used to remove gloss from chemical textiles and improve abrasion resistance of chemical textiles as well as for pigment. Moreover, it is widely used in various areas such as electronic materials, TV braun tubes and welding rod coverings using electronic characteristics so that we always find it in our ordinary life. An exponential growth of research activities has been seen in nanoscience and nanotechnology. New physical and chemical properties emerge when the size of the material becomes smaller and smaller, and down to the nanometer scale. Properties also vary as the shapes of the shrinking nanomaterials change. Many excellent reviews and reports on the preparation and properties of nanomaterials have been published recently. Among the unique properties of nanomaterials, the movement of electrons and holes in semiconductor nanomaterials is primarily governed by the well-known quantum confinement, and the transport properties related to phonons and photons are largely affected by the size and geometry of the materials[BUR 2005]. The specific surface area and surface-to-volume ratio increase dramatically as the size of a material decreases. The high surface area brought about by small particle size is beneficial to many TiO_2-based devices, as it facilitates reaction/interaction between the devices and the interacting media, which mainly occurs on the surface or at the interface and strongly depends on the

surface area of the material. Thus, the performance of TiO_2-based devices is largely influenced by the sizes of the TiO_2 building units, apparently at the nanometer scale.

As the most promising photocatalyst, TiO_2 materials are expected to play an mportant role in helping solve many serious environmental and pollution challenges. TiO_2 also bears tremendous hope in helping ease the energy crisis through effective utilization of solar energy based on photovoltaic and water-splitting devices. Recently, as new products utilizing the characteristics of TiO_2 are rapidly developed and applied to various areas, the competition among countries becomes fierce. The representative products are catalysts and photocatalysts using Nano type products
The structural, thermal, electronic, and optical properties of TiO_2 nanomaterials are reviewed. As the size, shape, and crystal structure of TiO_2 nanomaterials vary, not only does surface stability change but also the transitions between different phases of TiO_2 under pressure or heat become size dependent. The dependence of X-ray diffraction patterns and Raman vibrational spectra on the size of TiO_2 nanomaterials is also summarized, as they could help to determine the size to some extent, although correlation of the spectra with the size of TiO_2 nanomaterials is not straightforward.

Titanium dioxide is available in two crystal forms:

1. Rutile,
2. Anatase.

Advantages of Rutile grade to Anatase grade are the following: higher refractive index; better light-scattering; superior weather-resistance properties.

1.4.2 Current Scenario of TiO_2

The main use of titanium dioxide (TiO_2) is as a white powder pigment because of its brightness and very high refractive index. It provides good opacity to products such as paints, coatings, plastics, paper, inks, fibres, food and cosmetics. In particular, high performance grades of TiO_2 are finding a growing market in the cosmetics sector.

Titanium dioxide also has good ultraviolet (UV) light resistance properties which helps prevent the discolouration of plastics in sunlight. Sunscreens also use TiO_2 as a blocker because of its high refractive index and the ability to protect the skin from UV light.
Titanium dioxide is seeing growing demand in photocatalysts due to its oxidative and hydrolysis properties. As a photocatalyst, it can improve the efficiency of electrolytically splitting water into hydrogen and oxygen, and it can produce electricity in nanoparticle form. Applications include light-emitting diodes, liquid crystal displays and electrodes for plasma displays. Under exposure to UV light, it becomes increasingly hydrophilic and can be used for anti-fogging coatings and self-cleaning windows.
In mildly reducing atmospheres, TiO_2 tends to lose oxygen and becomes a semiconductor. The electrical resistivity of the material can be correlated to the oxygen content of the atmosphere and hence it can be used as an oxygen sensor.
However, the major consuming industries of TiO_2 are in the mature sectors in the developed world such as paints and coatings applications, paper and paperboard, and plastics. Therefore the consumption of TiO_2 tends to follow general economic trends. Producers and analysts estimate global growth for TiO_2 at around 2-3%/year.

ANP has developed a high quality of TiO_2 photocatalyst for improving the comfortable circumstances in our daily lives. The photocatalyst is a well known titania semiconductor ceramic material, which shows catalytic properties when exposed to UV light. Our photocatalyst is nano-sized semiconductor of which primary particle size is less than 5nm. Through the ANP is novel precursor technique and temperature process, ANP photocatalyst TiO_2 shows excellent self-cleaning, anti-fogging, and superhydrophilic properties which can be applied to a variety of functional coatings and environment cleaning system. ANP also enhance or deactivate the photocatalytic properties of TiO_2 by controlling doants into the TiO_2 crystal and this is truly unique feature of ANP nanotechnology

1.4.3 Crystal Structure Of TiO_2

TiO_2 unit cell comprises of two structures as shown in fig(--) i.e. rutile and anatase TiO_2. These two structures can be described in terms of chains of TiO_6 octahedra,

where each Ti^{4+} ion is surrounded by an octahedron of six O^{2-} ions. The two crystal structures differ in the distortion of each octahedron and by the assembly pattern of the octahedra chains. In rutile, the octahedron shows a slight orthorhombic distortion; in anatase, the octahedron is significantly distorted so that its symmetry is lower than orthorhombic. The Ti-Ti distances in anatase are larger, whereas the Ti-O distances are shorter than those in rutile. In the rutile structure, each octahedron is in contact with 10 neighbor octahedrons (two sharing edge oxygen pairs and eight sharing corner oxygen atoms), while, in the anatase structure, each octahedron is in contact with eight neighbors (four sharing an edge and four sharing a corner). These differences in lattice structures cause different mass densities and electronic band structures between the two forms of TiO_2

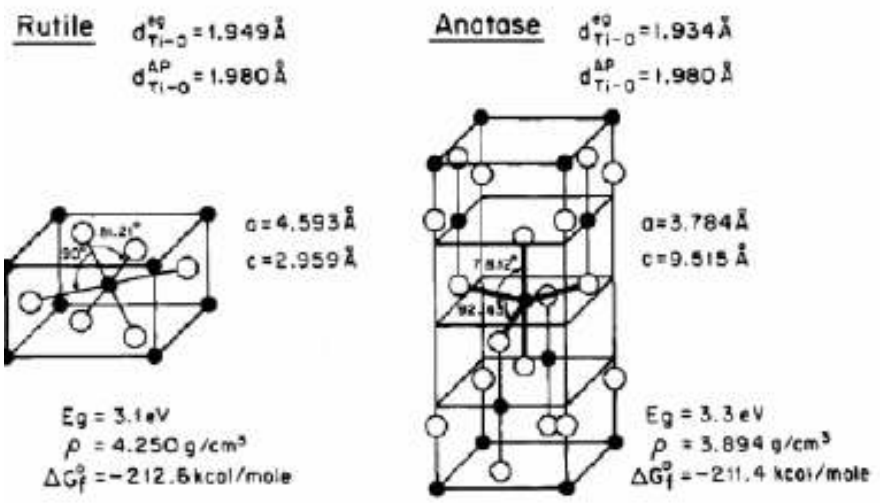


Fig-2.1 Lattice structure of rutile and anatase TiO_2.

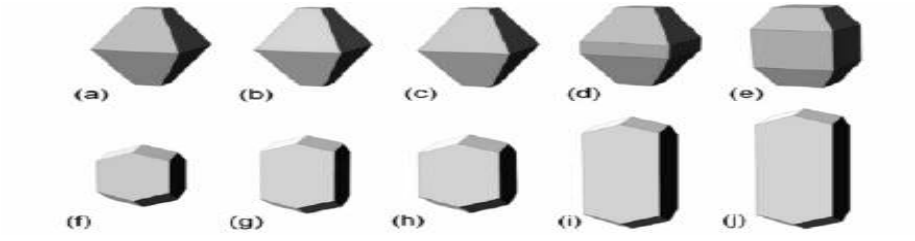


Fig-2.2 Morphology predicted for anatase (top), with (a) hydrogenated surfaces, (b) hydrogen-rich surface adsorbates, (c) hydrated surfaces, (d) hydrogen-poor adsorbates, and (e) oxygenated

surfaces, and for rutile (bottom), with (f) hydrogenated surfaces, (g) hydrogen-rich surface adsorbates, (h) hydrated surfaces, (i) hydrogen-poor adsorbates, and (j) oxygenated surfaces.

2.1 Thermodynamic Properties of TiO_2 Nanomaterials

Rutile is the stable phase at high temperatures, but anatase and brookite are common in fine grained (nanoscale) natural and synthetic samples. On heating concomitant with coarsening, the following transformations are all seen- anatase to brookite to rutile, brookite to anatase to rutile, anatase to rutile, and brookite to rutile. These transformation sequences imply very closely balanced energetics as a function of particle size. The surface enthalpies of the three polymorphs are sufficiently different that crossover in thermodynamic stability can occur under conditions that preclude coarsening, with anatase and/or brookite stable at small particle size.

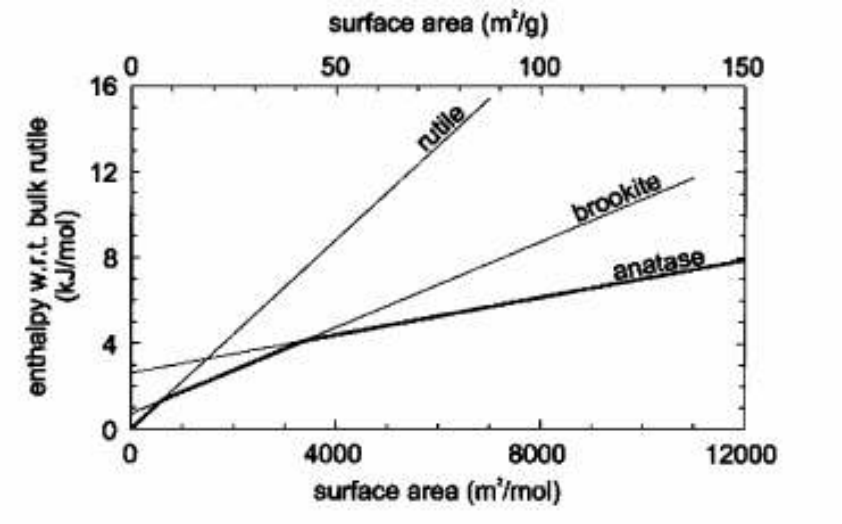


Fig-2.3 Enthalpy of nanocrystalline TiO_2.

However, abnormal behaviors and inconsistent results are occasionally observed.

2.2 Electronic Properties of TiO_2 Nanomaterials

The DOS of TiO_2 is composed of Ti eg, Ti t_2g (dyz, dzx, and dxy), O pπ (in the Ti_3O cluster plane), and O pð (out of the Ti_3O cluster plane),396 The upper valence bands can be decomposed into three main regions: the σ bonding in the lower energy region

mainly due to O pσ bonding; the π bonding in the middle energy region; and O pπ states in the higher energy region due to O pπ nonbonding states at the top of the valence bands where the hybridization with d states is almost negligible. The contribution of the π bonding is much weaker than that of the σ bonding. The conduction bands are decomposed into Ti e.g.(>5 eV) and t2gbands (<5 eV). The dxystates are dominantly located at the bottom of the conduction bands. The rest of the t2g bands are antibonding with p states. The main peak of the t2g bands is identified to be mostly dyz and dzx states. In the molecular-orbital bonding diagram in Figure, a noticeable feature can be found in the nonbonding states near the band gap: the nonbonding O pp orbital at the top of the valence bands and the nonbonding dxy states at the bottom of the conduction bands. A similar feature can be seen in rutile; however, it is less significant than in anatase. In rutile, each octahedron shares corners with eight neighbors and shares edges with two other neighbors, forming a linear chain. In anatase, each octahedron shares corners with four neighbors and shares edges with four other neighbors, forming a zigzag chain with a screw axis. Thus, anatase is less dense than rutile. Also, anatase has a large metal-metal distance of 5.35 Å. As a consequence, the Ti dxy orbitals at the bottom of the conduction band are quite isolated, while the t2g orbitals at the bottom of the conduction band in rutile provide the metal-metal interaction with a smaller distance of 2.96 Å. The electronic structure of TiO_2 has been studied with various experimental techniques, i.e., with X-ray photoelectron and X-ray absorption and emission spectroscopies.

Figure shows a schematic energy level diagram of the lowest unoccupied MOs of a $[TiO_6]$ 8- cluster with Oh, D2h (rutile), and D2d (anatase) symmetry and the Ti K-edge XANES and O K-edge ELNES spectra for rutile and anatase. The anatase structure is a tetragonally distorted octahedral structure in which every titanium cation is surrounded by six oxygen atoms in an elongated octahedral geometry (D2d). The further splitting of the 3d levels of Ti^{3+} due to the asymmetric crystals is shown for rutile and anatase structures. The fine electronic structure of TiO_2 can be directly probed by Ti K-edge X-ray-absorption near-edge structure (XANES), and the right panel of Figure contains O K-edge experimental electron-energy-loss near edge structure (ELNES) spectra. 398.

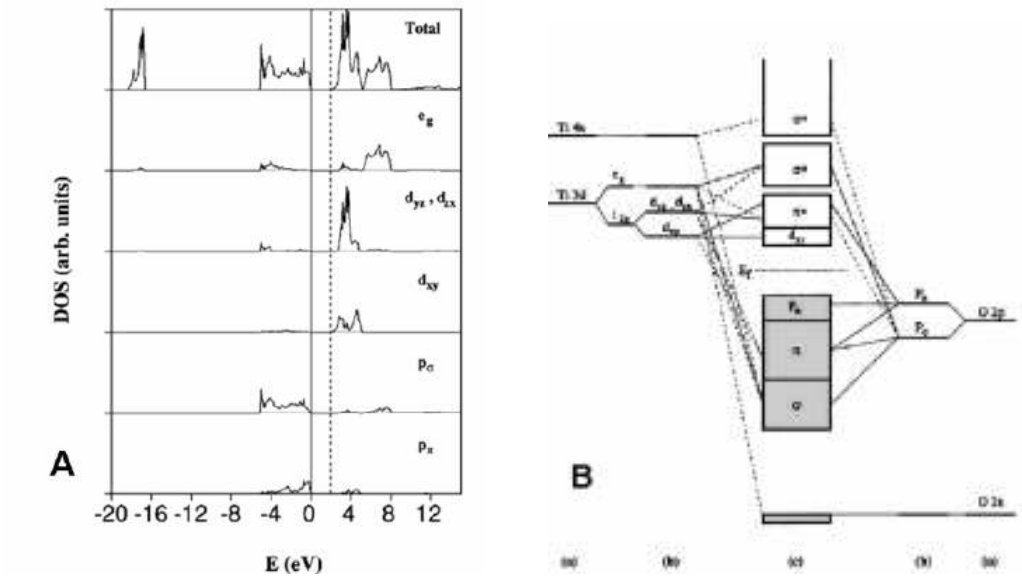


Fig-2.4 (A) Total and projected densities of states (DOSs) of the anatase TiO_2 *structure. The top of the valence band (the vertical solid line) is taken as the zero of energy. The vertical dashed line indicates the conduction-band minimum as a guide to the eye. (B) Molecular-orbital bonding structure for anatase* TiO_2*: (a) atomic levels; (b) crystal-field split levels; (c) final interaction states. The thin-solid and dashed lines represent large and small contributions, respectively.*

2.3 Optical Properties of TiO_2 Nanomaterials

The main mechanism of light absorption in pure semiconductors is direct interband electron transitions. This absorption is especially small in indirect semiconductors, e.g., TiO_2, where the direct electron transitions between the band centers are prohibited by the crystal symmetry.

2.4 Photocatalytic Properties of TiO_2

The word photocatalysis is a composite word which is composed of two parts, photo and catalysis. Catalysis is the process where a substance participates in modifying the rate of a chemical transformation of the reactants without being altered or consumed in the end. This substance is known as the catalyst which increases the rate of a reaction by reducing the activation energy. Generally speaking, photocatalysis is a reaction which uses light to activate a substance which modifies the rate of a chemical reaction without being

involved itself. And the photocatalyst is the substance which can modify the rate of chemical reaction using light irradiation. Chlorophyll of plants is a typical natural photocatalyst. The difference between chlorophyll photocatalyst to man-made nano photocatalyst (here below mentioned as photocatalyst) is, usually chlorophyll captures sunlight to turn water and carbon dioxide into oxygen and glucose, but on the contrary photocatalyst creates strong oxidation agent and electronic holes to breakdown the organic matter to carbon dioxide and water in the presence of photocatalyst, light and water.

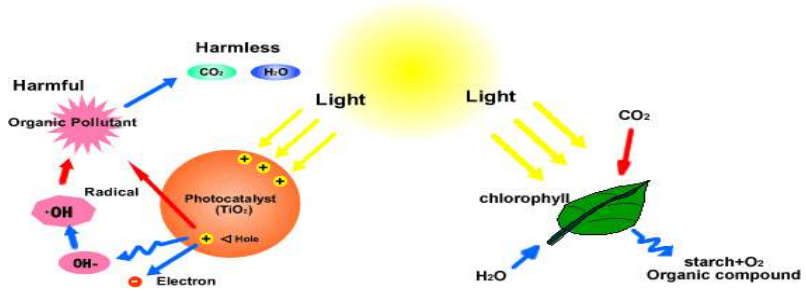


Fig-2.1

The traditional nano photo catalyst manufacture technology divides into two parts. The first step is the manufacture of the nano titanium dioxide crystal. The second is the dispersion of the sol. Since only the nano titanium dioxide with Anatase structure has the photocatalytic performance, its manufacture process must include the calcining at high temperature and crystallization. However, the high temperature will greatly affect the nano level. Therefore the particle of normal nano titanium dioxide powder is not as small as the one produced by hydrosynthesis technology. The powder produced by high - energy ball milling is even far away from that of hydrosynthesis technology in crystallization degree and particle size. During the dispersion process, the synthetic nano titanium dioxide sol should be dispersed by adjusting pH value and adding surface active agents, which may bring some impurity in the sol. Most surface active agents as dispersant have biologic toxicity, which may cause extra pollution. The solid nano titanium dioxide particle may get reunited during the process of calcining and crystallization, which will affect its quality and property. When the solid nano titanium dioxide be dispersing into sol, the reunited particle cant be recovered and this make its

secondary particle size will be much large. Hydrosynthetic photocatalyst is the nano titanium dioxide with Anatase structure synthesized directly in the sol dispersing system by means of advanced chemical hydrosynthesis technology. Generally speaking, hydrosynthetic manufacture technology can produce more stable photocatalyst of quanta level with smaller particle size. The synthesis, crystallization and dispersion of nano photocatalyst are processed in the liquid, which makes the product superior to the traditional ones. The hydrosynthetic technology is a new advanced manufacture technology of photocatalyst, which provides excellent quality and property to the product. At present, most photocatalyst sol with high quality and low reunited index is made by hydrosynthetic technology.

Technology	Hydrosynthesis	Powder Redispersion	Planet Ball Milling
Manufacture Method	Chemical	Chemical	Physical Milling
Dispersion	No surface active agent	With surface active agent	With surface active agent
Primary Particle Size	1-10nm	10-100nm	80-2000nm
Crystal Structure	Fine	Fine	Bad
Reunited Index	1-10	10-100	>100
Transparency	Good	No	No
Sol Stability	Excellent	Good	Deposition
Photocatalytic Performance	Excellent	Good	Normal

2.4.1Fundamentals of Photocatalytic Water Splitting

An enormous research effort has been dedicated to the study of the properties and applications of TiO_2 under light illumination since the discovery of photocatalytic

splitting of water on a TiO_2 electrode in 1972 (Fujishima and Honda). Photocatalytic splitting of water into $H_2$and O_2using TiO_2 nanomaterials ontinues to be a dream for clean and sustainable energy sources.

Figure shows the principle of water splitting using a TiO_2 photocatalyst.

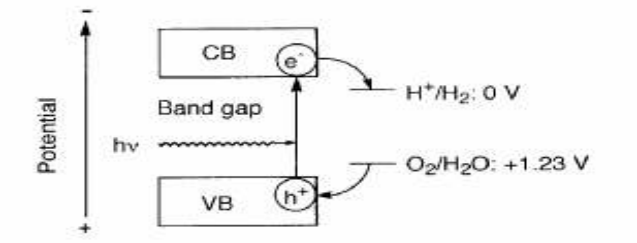


*Fig-2.2 Reaction schemes for semiconductor photocatalysts***.**

When TiO_2 absorbs light with energy larger than the band gap, electrons and holes are generated in the conduction and valence bands, respectively. The photogenerated electrons and holes cause redox reactions. Water molecules are reduced by the electrons to form $H_2$and oxidized by the holes to form O_2, leading to overall water splitting.

The width of the band gap and the potentials of the conduction and valence bands are important. The bottom level of the conduction band has to be more negative than the reduction potential of H^+ /H_2 (0 V vs NHE), while the top level of the valence band has to be more positive than the oxidation potential of O_2/H_2O (1.23 V). The potential of the band structure of TiO_2 is just the thermodynamical requirement. Other factors such as charge separation, mobility, and lifetime of photogenerated electrons and holes also affect the photocatalytic properties of TiO_2. These factors are strongly affected by the bulk properties of the material such as crystallinity. Surface properties such as surface states, surface chemical groups, surface area, and active reaction sites are also important.

The water-splitting process in return affects the local pH environment and surface structures of the TiO_2 electrode.

Salvador conducted a thermodynamic and kinetic consideration of water-splitting and competitive reactions in the photoelectrochemical cell, and they found that the over

voltage for evolution of O_2 must be minimized, which was on the order of 0.6 eV for n-TiO_2 electrodes loaded with RuO_2. Co-catalysts such as Pt and NiO are often loaded on the surface in order to introduce active sites for H_2evolution. Thus, suitable bulk and surface properties and energy structure are demanded for photocatalysts. Laser-induced photocatalytic oxidation/splitting of water over TiO_2 catalysts was studied.

REVIEW OF LITERATURE

Fujishima et al. [1] have discussed progress in the area of TiO2 photocatalysis mainly photocatalytic air purification, sterilization and cancer therapy together with some fundamental aspects and have presented a novel photoinduced superhydrophilic phenomenon involving TiO2 and its applications.

Wiszniowski et al. [2] have studied the adsorption of humic acids on TiO2 surface and described the kinetics of their photocatalytic degradation.

Ksibi et al. [3] have optimized conditions for photocatalytic degradation by UV/ TiO2 system of lignin present in mill effluents from pulp and paper industry and showed that the resulted degradation compounds could be isolated and used as valuable industrial products.

Several researchers have studied the photocatalytic degradation of various textile dyes using TiO2 under UV radiation by varying parameters like pH, catalyst loading etc.[4-7] Neppolian et al.[5] investigated the photocatalytic degradation of three commercial textile dyes with different structures using TiO2 (Degussa P25) photocatalyst in aqueous solution under solar irradiation.In addition to prompt removal of color, TiO2/ UV based photocatalysis was simultaneously able to oxidize the dye with almost complete mineralisation of carbon, sulphur and nitrogen heteroatoms into CO2, SO4 2-, NH4 +, and NO3 - respectively. The photocatalytic degradation of various dyes (Orange II, Orange G, Congo Red, Indigo Carmine, Crystal Violet, Malachite Green, Remazol Blue and Methyl Yellow) was studied, using P25 Degussa as catalyst. All dye solutions underwent a decolourization prepared TiO2 supported on alumina and glass beads and determined their photocatalytic activities by photo-oxidation of commercial leather dye, Acid brown 14 in aqueous solution illuminated with solar light[8-9]. Qaradawi and Salman (2002) used titanium dioxide (TiO2) as a photocatalyst for the detoxification of water containing methyl orange (MO), which was used as a model compound using solar radiation as an irradiation source. Khalil et al., (1999) investigated photodegradation processes of two azo dyes at TiO2/H2O interface under visible and ultraviolet light irradiation with different experimental techniques (absorption and fluorescence spectroscopy as well as total organic carbon analysis).

Titanium dioxide (TiO2), being one of the most basic materials in our daily life, has emerged as an excellent photocatalyst material for environmental purification. Linder et al., (1997) have reported that anatase TiO2 powder is highly active photocatalyst. In recent years, Degussa P25 TiO2 has set the standard for photoreactivity in environmental applications, although TiO2 produced by Sachtleben, Germany (Martin et al., 1994a & b) and Kimera, Finland show comparable reactivity. Degussa P25 TiO2 has effectively become research standard because it has (i) reasonably well defined nature (i.e. typically nonporous 70:30% anatase-to-rutile mixture with a BET surface area of 55±15 m2g-l and crystallite sizes of 30 nm in 0.1 □m diameter aggregates and (ii) a substantially higher

photocatalytic activity than most other readily available samples of TiO2. Fujishima et al., (2000) gave in his review, current progress in the area of TiO2 photocatalysis, mainly photocatalytic air purification, sterilization and cancer therapy. A novel photoinduced superhydrophilic phenomenon involving TiO2 and its applications has been presented in his review. The photocatalytic efficiency of several TiO2 (namely Degussa P25 and Millennium PC50, PC100, PC105, PC500) used as suspensions are compared for the photocatalytic degradation of 3-nitrobenzenesulfonic acid (3-NBSA) and 2,5-anilinedisulfonic acid (2,5-ADSA) by Rachel et al., (2002). With 3-NBSA, P25 is clearly the most efficient and there is no apparent relationship between photocatalytic activity and specific surface area. This result is consistent with that obtained with phenol, but a contrast was noticed with 2,5-ADSA where PC500 is more efficient than P25 in spite of a higher adsorption of the latter. In the case of TiO2 Millennium, relative photonic efficiencies □r are smaller with 3-NBSA than with 2,5- ADSA that is consistent with the electron-withdrawing effect of nitro group. For the same reason the direct photo transformation in sunlight is much more rapid with 2,5- ADSA than with 3-NBSA and 4-nitrotoluene-2-sulfonic acid.

CHAPTER 3
MATERIALS AND METHODS

In this chapter all the details about the preparation and characterization of samples has been described.

3.1 Catalysts Used In the Present Study

Degussa P25 TiO2 was procured from Degussa Company, Germany. It has a BET surface area of 50 ± 15 m2g-1 and is 70% in anatase crystal form with average particle size of 30 nm.

3.3 CHARACTERIZATION METHODS

Characterization was done with the help of PHOTOCATALYTIC STUDIES, XRD STUDIES, UV-Visible Absorption Spectroscopy and Transmission Electron Microscope.

3.2 PHOTOCATALYTIC STUDIES

1. The 100 mg/l stock solution of substrate Reactive Black 5 dye was prepared in distilled water for all the experiments, except varying initial concentration of the substrate.
2. The UV tubes were turned on and allowed to warm up for 20 minutes before the experiment was started.
3. Once the lamps were warmed up, the lab jack (with magnetic stirrer at its top) was raised or lowered until the UV radiometer measured the desired intensity at reactor plane.
4. Then 200 ml of solution was taken in the batch reactor and to it, was added the optimum amount of TiO_2, which was different for all the three compounds. The pH of the solution was noted.
5. This solution was then irradiated under UV lamp with continuous stirring using a magnetic stirrer in the UV chamber for the required period.

6. An aliquot of 5 ml was taken from the reactor at regular interval of time with the help of a syringe.
7. The catalyst was filtered from the sample by Millipore filter (0.45 μm). These samples were analyzed using UV-Visible spectrophotometer.
8. The pH of the final solution was noted.

Fig-3.1 shows Schematic diagram of lab scale set up for shallow pond reactor and Fig-3.2 shows the photograph of our setup.

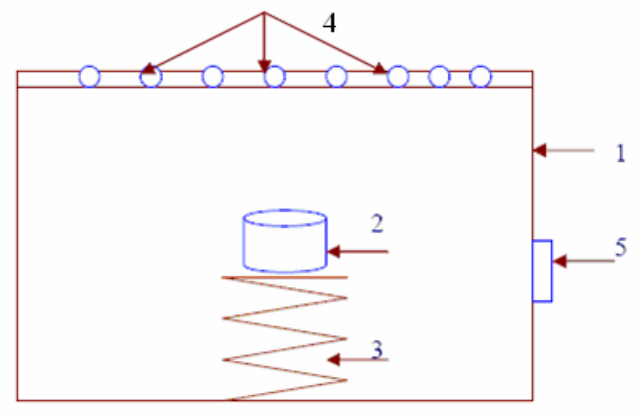


Fig-3.1 Schematic diagram of lab scale set up for shallow pond reactor:
(1) UV chamber, (2) reactor, (3) Lab jack, (4) UV lamps, (5) exhaust fan.

3.3.1 X-ray Diffraction Studies (XRD)

X-ray diffraction was used for determining the phase identification, crystal structure, lattice parameter of the crystallite solids.

For the XRD analysis, fine powder samples were mounted on the sample holder and the powder was assumed to consist of randomly oriented crystallites. When a beam of X-ray is incident on the sample, X-rays are scattered by each atom in the sample. If the scattered beams are in-phase, these interfere constructively and one gets the intensity maximum at that particular angle. The atomic planes from where the X-rays are scattered are referred to as 'reflecting planes'. The Bragg's law relates the wavelength (λ) of the X-ray reflected, the spacing between the atomic planes (d) and the angle of diffraction (θ) as follows

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

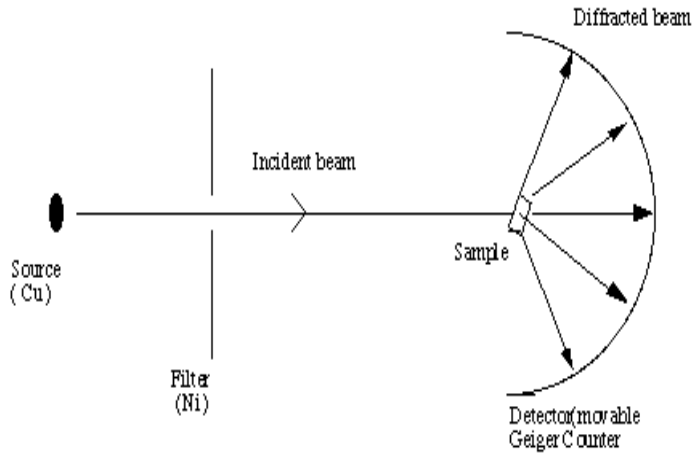


Fig 3.3- Ray diagram of XRD

for the first order diffraction, n=1, and knowing θ and λ , one can calculate the interplanar spacing d–value for a particular plane. After recording the X-ray diffraction pattern, first step involves the indexing of XRD peaks. The indexing means assigning the correct Miller indices to each peak of the diffraction pattern. The correct indexing is done only when all the peaks in the diffraction pattern are accounted for the process. There are three main methods for indexing a diffraction pattern,

(i) Comparing the measured XRD pattern with the standard data base (JCPDS-cards).
(ii) Analytical methods.
(iii) Graphical methods.

In case of fine particles, with reduction in the size of the particles, the XRD lines get broadened, which indicates clearly that particle size has been reduced. The line broadening can be a measure of the average size of the crystallites by using the Scherrer equation:

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

D_v is the average particle size

K is the Scherrer constant

λ is wave length of the radiation

β is the integral breadth of the peak located at angle θ.

3.3.2 Transmission electron microscope (TEM)

Transmission electron microscopy (TEM) is used to obtain information from samples that are thin enough to transmit electron. In TEM, the whole area of observation is illuminated using an electron source of adequate intensity. The transmitted electrons are generally used to form either an image or a diffraction pattern of the specimen .

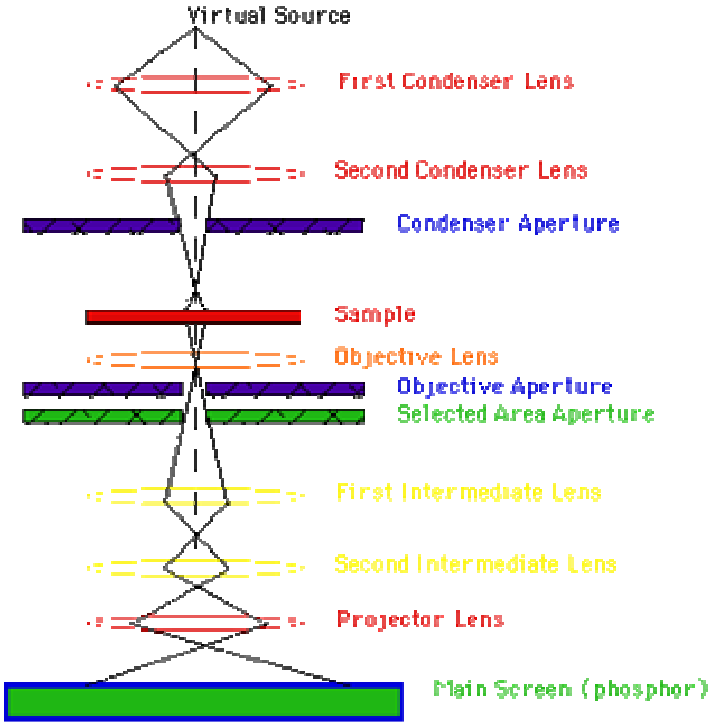


Fig-3.4

The formation of image and electron diffraction in TEM can be understood from schematic ray diagram. When a crystal of lattice spacing d is illuminated with electrons of wavelength, λ, the diffracted waves will be produced at specific angles 2θ for n =1, satisfying the Bragg's condition,

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

The diffracted waves form diffraction spots on the back focal plane. In an electron microscope, the use of electron lenses allows the regular arrangement of diffraction spots to be projected on a screen and the electron diffraction pattern can be observed. If the transmitted and the diffracted beam interfere on the image plane, a magnified image can be observed. The space where the diffraction pattern forms is called the reciprocal space, while the space at the image plane or at a specimen is called the real space.

In TEM, by adjusting the electron lenses, both the microscope images and diffraction patterns can be observed. Thus in the analysis of microstructures of materials, both observation modes can be successfully combined. In an investigation of electron diffraction pattern, the electron microscope images of the nanophosphor is first observed of the whole area and then by inserting an aperture in a specific area and adjusting the electron lenses a diffraction pattern of the area is obtained . The latter observation mode is called selected area electron diffraction (SAED). Because a selected area diffraction pattern can be obtained from each grain in polycrystal, the crystal structure and mutual crystal orientation relationship between adjacent grains can easily be clarified. The observational dimension selected from the object is usually limited to about 0.1 micrometer in diameter. However, in micro diffraction method, the diffraction pattern can be obtained from an area correspondingly to only a few nanometer in diameter. Then, by passing the transmitted beam or one of the diffracted beams through an aperture and changing to the imaging mode, the image with enhanced contrast can be observed. The observation mode using the transmitted beam is called the bright field method, and the image observed is a bright field image. When one of the diffracted beams is selected the observation mode is called as dark field method, and the image observed is a dark field image.

3.3 UV-Visible Absorption/Reflectance:

The functioning of this instrument is relatively straightforward and shown in Fig(3.5). A beam of light from a visible and/or UV light source (colored red) is separated into its component wavelengths by a prism or diffraction grating. Each monochromatic (single wavelength) beam in turn is split into two equal intensity beams by a half-mirrored

device. One beam, the sample beam (colored magenta), passes through a small transparent container (cuvette) containing a solution of the compound being studied in a transparent solvent. The other beam, the reference (colored blue), passes through an identical cuvette containing only the solvent. The intensities of these light beams are then measured by electronic detectors and compared. The intensity of the reference beam, which should have suffered little or no light absorption, is defined as I_0. The intensity of the sample beam is defined as I. Over a short period of time, the spectrometer automatically scans all the component wavelengths in the manner described. The ultraviolet (UV) region scanned is normally from 200 to 400 nm, and the visible portion is from 400 to 800 nm

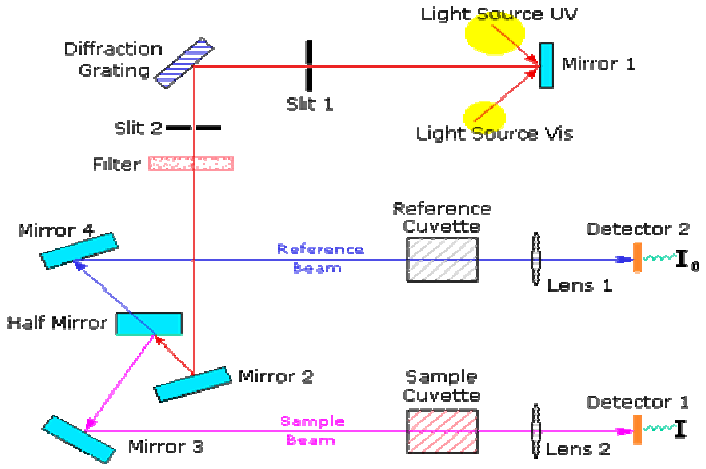


Fig-3.5 UV-Visible Absorption Set-Up

If the sample compound does not absorb light of a given wavelength, $I = I_0$. However, if the sample compound absorbs light, then I is less than I_0, and this difference may be plotted on a graph versus wavelength, as shown on the right. Absorption may be presented as transmittance ($T = I/I_0$) or absorbance ($A = \log I_0/I$). If no absorption has occurred, T = 1.0 and $A = 0$. Most spectrometers display absorbance on the vertical axis, and the commonly observed range is from 0 (100% transmittance) to 2 (1% transmittance). The wavelength of maximum absorbance is a characteristic value, designated as λ_{max}. Intensely absorbing compounds must be examined in dilute solution, so that significant light energy is received by the detector, and this requires the use of

completely transparent (non-absorbing) solvents. The most commonly used solvents are water, ethanol, hexane and cyclohexane. Solvents having double or triple bonds, or heavy atoms (e.g. S, Br & I) are generally avoided. Because the absorbance of a sample will be proportional to its molar concentration in the sample cuvette, a corrected absorption value known as the molar absorptivity is used when comparing the spectra of different compounds. This is defined as:

$$\textbf{Molar Absorptivity, } \varepsilon = A / c\, l$$

(Where A=absorbance, **c**=sample concentration in moles/liter & l = length of light path through the cuvette in cm.)

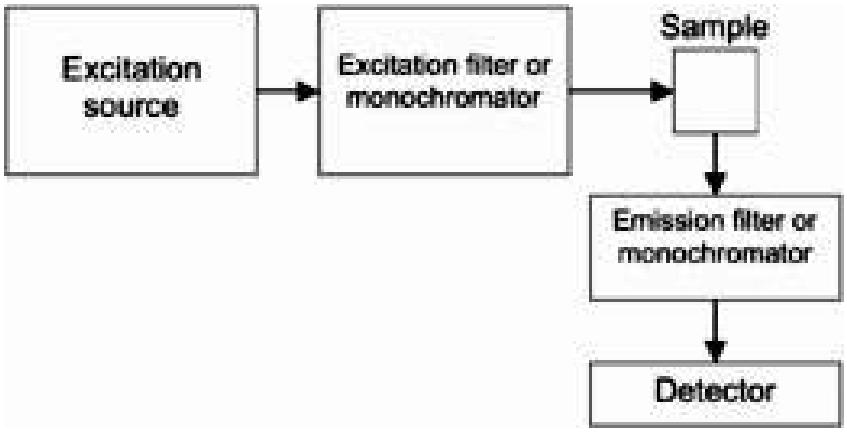
3.4 Photoluminescence

Photoluminescence spectroscopy is a contactless, nondestructive method of probing the electronic structure of materials. Light is directed onto a sample, where it is absorbed and imparts excess energy into the material in a process called photo-excitation. One way this excess energy can be dissipated by the sample is through the emission of light, or luminescence. In the case of photo-excitation, this luminescence is called photoluminescence. The intensity and spectral content of this photoluminescence is a direct measure of various important material properties. Photo-excitation causes electrons within the material to move into permissible excited states. When these electrons return to their equilibrium states, the excess energy is released and may include the emission of light (a radiative process) or may not (a non-radiative process). The energy of the emitted light (photoluminescence) relates to the difference in energy levels between the two electron states involved in the transition between the excited state and the equilibrium state. The quantity of the emitted light is related to the relative contribution of the radiative process.

The **spectrofluorometer** is an instrument which takes advantage of fluorescent properties of some compounds in order to provide information regarding their concentration and chemical environment in a sample. A certain excitation wavelength is selected, and the emission spectrum is recorded.

Generally spectrofluorometers use high intensity light sources to bombard a sample with as many photons as possible. This allows for the maximum number of molecules to be in the excited state at any one point in time. The light is either passed through a filter or Monochromator which allows you to select a wavelength of interest to use as the exciting light. The emission is collected at 90 degrees to the exciting light. The emission too is either passed through a filter or a monochromater before being detected by a PMT, photodiode, or CCD detector. The signal can either be processed as a digital or analog output. Systems vary greatly and a few things must be considered when choosing. First is signal to noise, there are many ways to look at the signal to noise of a given system but the accepted standard is by using water Raman. It has been said many times however tell me what signal to noise ratio you want and I can get it for you. This is true you can cheat on your signal to noise ratio. People do this routinely by using filters and various slit widths and never publish these settings. Make sure you compare apples with apples on this, ask for a specific band pass and no filters with 1 second integration time and use the same wavelength to compare too. Sensitivity or detection limit is another spec to look at. How little light can they measure, this is important because you may not want to waste a large amount of a specific expensive sample. Well if you can get data with very very little in the solution then great. So the standard for this would be fluorescein in NaOH, typical values for a high end instrument are in the femtomolar range. Stray light is another big issue in these instruments. Stray-light is basically how good is the monochromater of a system performing. You will get some stray light bouncing around in side the monochromator compartment and it comes through to the sample too. This matters when you have a highly scattering sample, however one can always use an excitation wavelength further away from the emission band to negate this issue or use a laser or interference filter. Stray light plays a big role in the signal to noise ratio and detection limit thus some people may have what seems to be bad stray light characteristics but they have better signal to noise ratio and detection limit, this is all in the design of the system. Thus stray light is a much less important measure than the others because if you cannot see the signal for the noise, cannot detect the sample, or have to use too much it will cost you more to buy one that you can use in the end.

Energy resolved photoluminescence (PL) emission spectra of TiO_2 nanoparticles were obtained by using spectro-flourometer as shown in fig-.



CHAPTER 4
RESULT AND DISCUSSION

4.1 PHOTOCATALYTIC RESULTS

It is clear from the photocatalytic studies that with the increase in treatment time of the dye with TiO_2 nanoparticles, degradation of the dye increases with time. Degradation is very slow in the beginning, but it is very fast after with increase in time further. Fig-4.1 to Fig-4.7 shows the Photocatalytic activity of TiO_2 nanoparticles. Fig.- 4.8 shows that without TiO_2 nanoparticles there is not much degradation of dye as is seen for dye solution with TiO_2 nanoparticles.

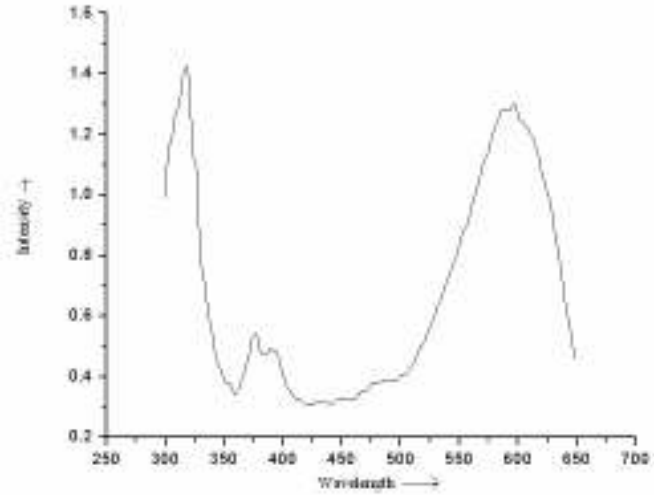


Fig-4.1 UNTREATED SAMPLE

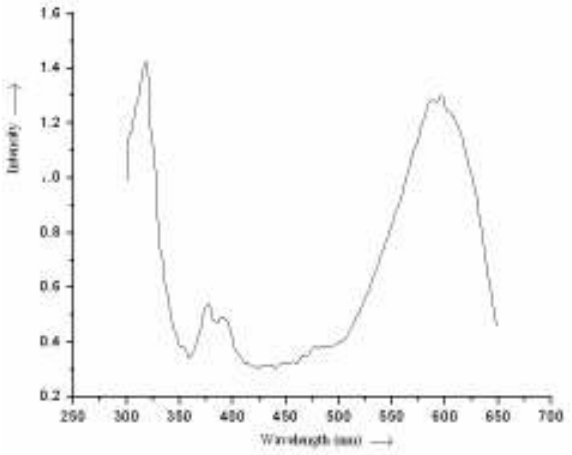
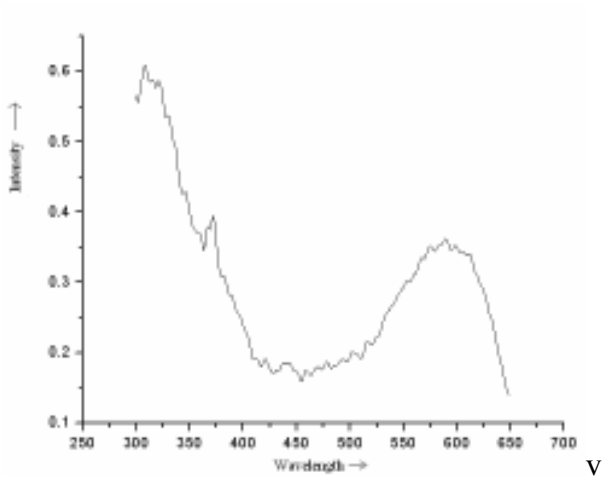


Fig-4.2 TREATED FOR 20 MIN.



v

Fig-4.3 TREATED FOR 40 MIN.

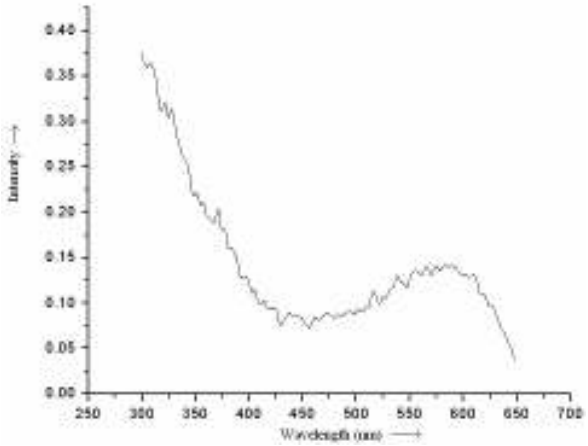


Fig-4.4 TREATED FOR 60 MINS

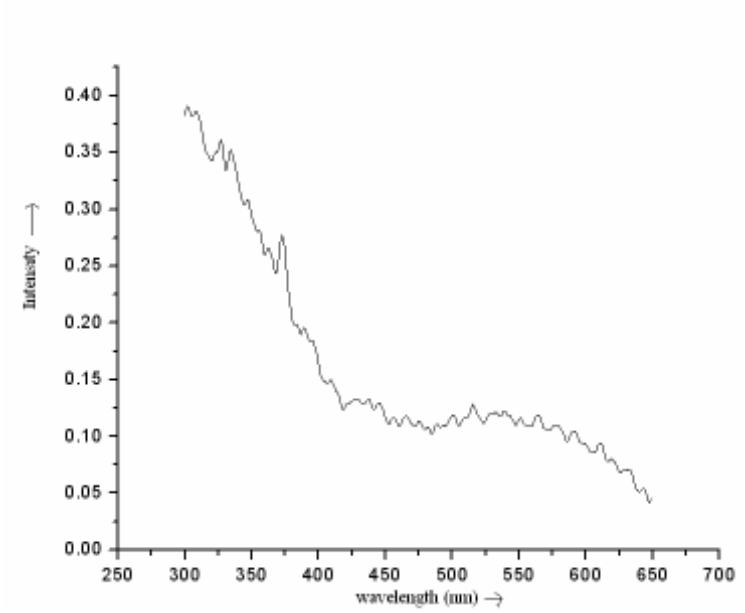


Fig-4.5 TREATED FOR 80 MINS

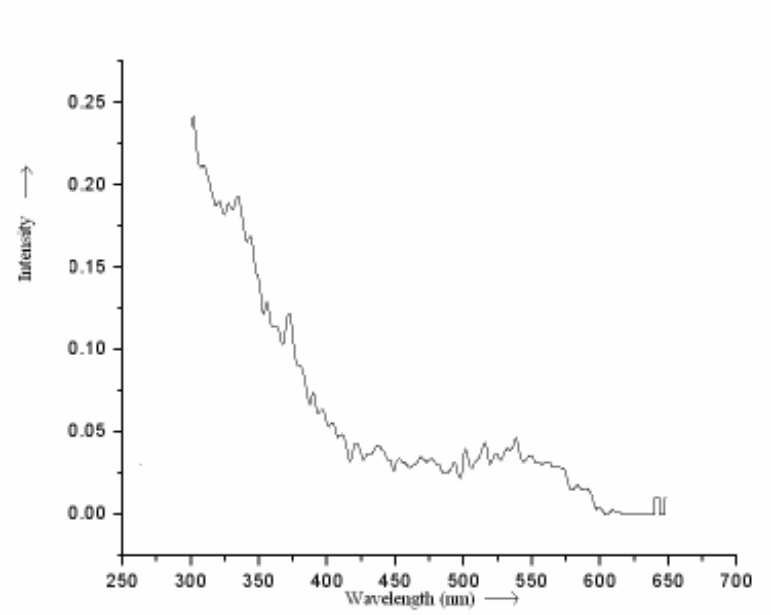


FIG-4.6 TREATED FOR 100 MIN.

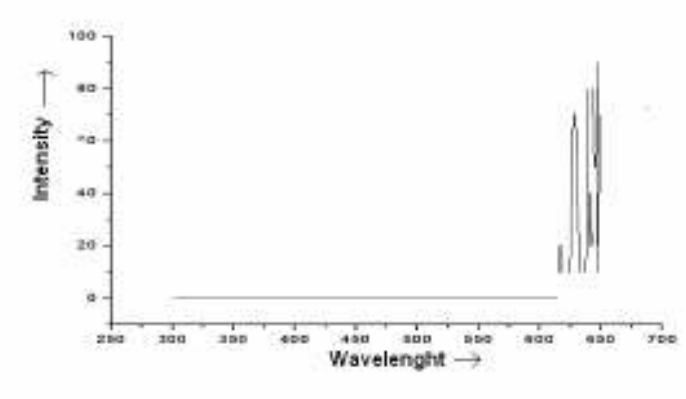


FIG-4.7 TREATED FOR 120 MIN.

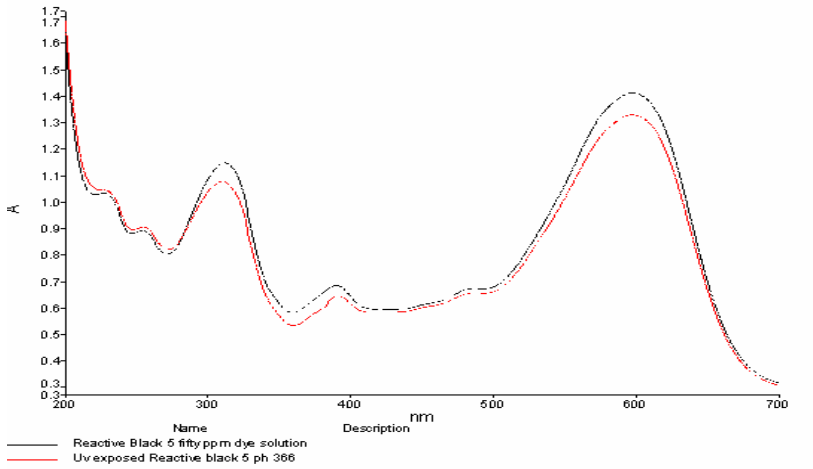


FIG-4.8- Treated for 60 min. (unexposed dye solution (black line), exposed dye solution without TiO_2 nanoparticles(red line).

4.2 PHOTOLUMINESCENCE RESULTS

Energy resolved photoluminescence studies have been conducted to see the internal mechanism occurring in titanium dioxide when illuminated by UV light. Excitation and emission spectra has been studied using spectroflourometer. Fig-4.8 and Fig-4.9 shows the various emissions at 300 nm excitation. Fig-4.8 shows the emissions at 250 nm excitation. Fig-4.9 shows the excitation spectra at 420 nm emission. From the graph it is clear that the absorption is occurring at 3.35 eV which corresponds to the absorption of UV photons. The second absorption is occurring at 3.22 eV which shows the occurrence of second phase in the TiO2

nanoparticles as reported by Degussa Germany. It is clear from these results that electron hole pairs are generated with the UV light. It means they are very much suitable for Photocatalytic activity.

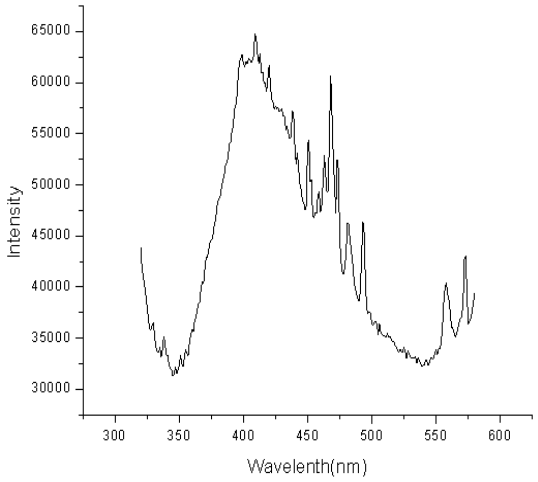


Fig-4.9 Emission at 300 nm excitation

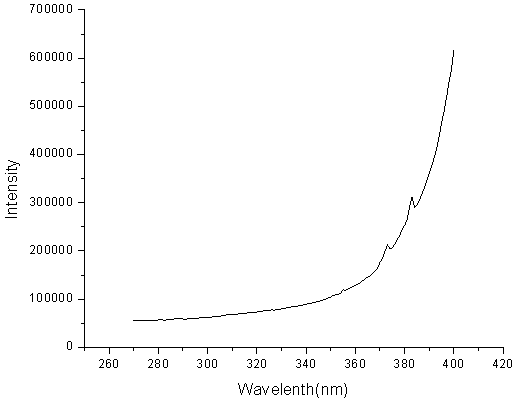


Fig-4.10 Excitation spectra at 420nm emission

4.3 UV-VISIBLE REFLECTANCE RESULTS

Fig-4.10 shows the diffuse reflectance spectra of titanium dioxide nanoparticles. The absorption edge comes to be 370 nm. The band gap comes out to be 3.35 eV in comparison to bulk particles which has a band gap of 3.4 eV.

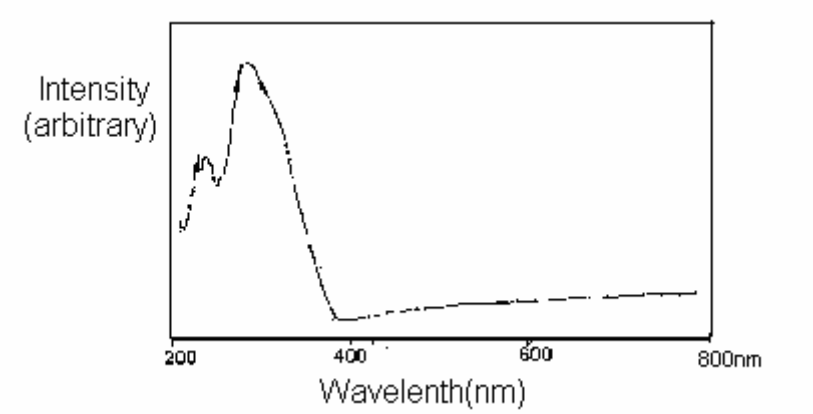


Fig-4.11

4.5 XRD RESULTS

Fig-4.11 shows the XRD of titanium dioxide nanoparticles showing both the rutile and Anatase phases. The average grain size of the highest intensity peak comes out to be 14.7 nm using Scherer formula. The highest intensity peak corresponding to angle 25.220° correspond to (211) plane corresponding to anatase phase. The XRD studies also confirms the occurrence of two phases in the degussa germany TiO2 samples. In Fig. 4.11 we have represented peaks showing anatase phase by ‘a’ and rutile phase by ‘r’.

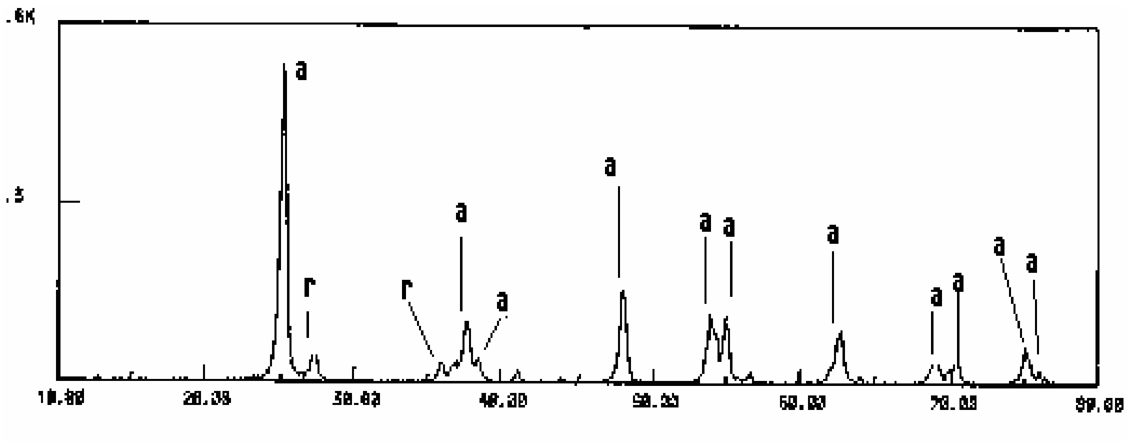


Fig-4.12 XRD spectra of TiO_2 nanoparticles

4.6 TEM RESULTS

Fig-4.12 shows the TEM of titanium dioxide nanoparticles. TEM results show that these particles are uniformily distributed. The color contrast of the particles is showing the existence of two type of phases.

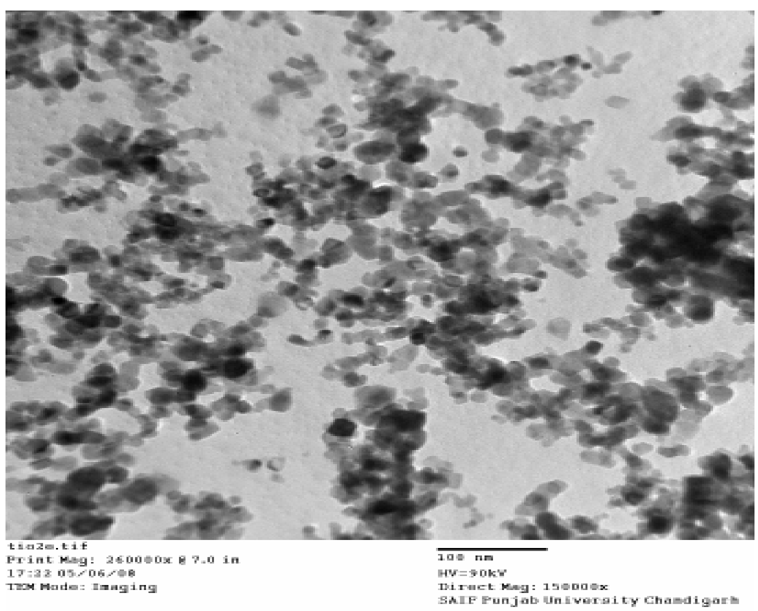


Fig-4.13

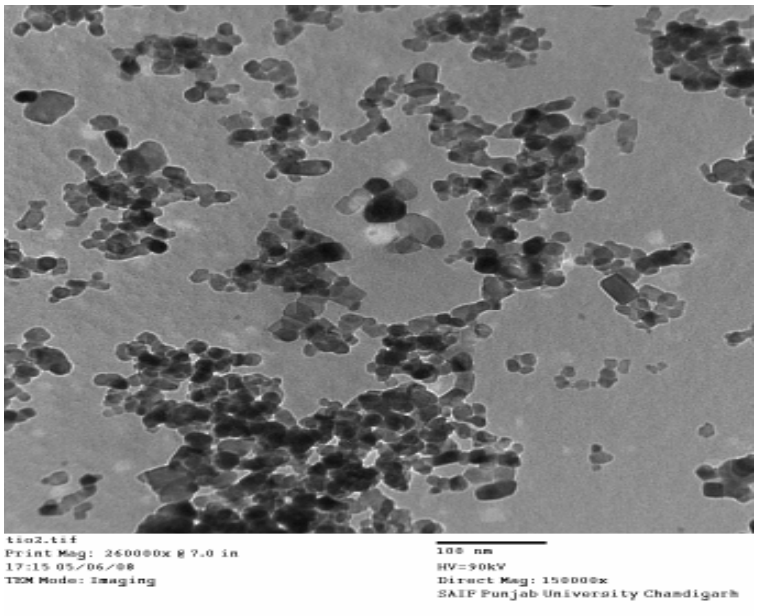


Fig-4.14

This degradation of dye under UV light is mainly due to the generation of electron-hole pair when the TiO_2 particle absorbs photon of light more than its band gap energy (3.2 eV for TiO_2). This electron – hole pair leads to the formation of hydroxyl radical and superoxide radical anion and these radicals are the primary oxidizing species in the photocatalytic oxidation processes. But when degradation is done under sunlight, the degradation of dye uses both UV and visible part. A sensitized photocatalytic process may also be operable, according to which the adsorbed dye molecule is excited by visible light and thus acts as photosensitizer. Due to this, the degradation rate is more under similar conditions under sunlight than only UV in the lab scale.

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