STUDY OF PHOTO-RESPONSIVE CODOPED TITANIA MESOPOROUS STRUCTURES

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INTERNATIONAL ISLAMIC UNIVERSITY ISLAMABAD

(2016)

بسم الله الرحمن الرحيم

INTERNATIONAL ISLAMIC UNIVERSITY ISLAMABAD

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A thesis submitted to

DEPARTMENT OF PHYSICS

For the award of the degree

MS Physics

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Dated: 29-01-2016

FINAL APPROVAL

CERTIFICATE

It is certified that the work presented in this thesis entitled "Study of photo responsive codoped titania mesoporous structures" by Maria Mehboob, Regtration # 243-FBAS/MSPHY/S14 is of sufficient standard in scope and quality for the award of degree of MS Physics from International Islamic University, Islamabad.

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International Islamic University Islamabad

As a partial fulfillment for the award of the degree of

MS PHYSICS

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Maria Mehboob

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SPECIAL DEDICATION

TO MY BABU G

(Malik Muhammad Afsar) & My Grand Mother

Gulzar Begum (Late)

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ACKNOWLEDGEMENT

All the Thanks and praises for ALLAH ALMIGHTY who guides us even in darkness, helps us in each and every difficult moment and is the entire source of WISDOM & KNOWLEDGE endowed to mankind and for blessing his humble creatures with mental faculty. I firmly believed that Allah never spoils any struggle and effort. Every piece of work is rewarded according to the nature and devotion put in. It is with the grace of ALLAH: the most benign and compassionate that I have been able to understand, execute and compile my research work.

All the gratitude and respects for the HOLY PROPHET (PBUH), who is forever, a torch of guidance and light of knowledge for mankind and teaches us as high ideals of life.

I feel pleasure to thank the Chairperson Physics Department, International Islamic University Islamabad to provide me the occasion for carrying out research work in this field of study.

I feel pleasure to place on record my honest thanks to my Research Supervisor Dr. Shamaila Sajjad, Physics Department, International Islamic University, Islamabad, providing technical assistance and appreciated discussion along with all the facilities to complete my research work.

I would like to record my sentiments of thankfulness to learn and well-known Research Supervisor Dr. Sajjad Ahmed Khan Leghari, Principal Scientist PAEC.

I am grateful to all my dear colleagues who helped me during the completion of my research work and thesis. Lastly but not the least, I owe my special regards to my Parents, Mamu Jan, Antes, brothers & sisters who always prayed for my improvement and victory. I would also Thanks to those people who help me directly and indirectly.

Maria Mehboob

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LIST OF ABREVATIONS

nm	Nanometer
TiO_2	Titanium Dioxide
m- TiO_2	Mesoporous Titanium Dioxide
DSSC	Dye Sensitized Solar Cell
XRD	X-Ray Diffraction
DRS	UV-Visible Diffuse Reflectance Spectroscopy
SEM	Scanning Electron Microscopy
FTIR	Fourier Transform Infrared
EDS	Energy Dispersive X-Ray Spectroscopy
PEG	Poly Ethylene Glycol
TBT	Tetra Butyl Titanate
HCL	Hydro Chloric Acid
A.G	Analytical Grade
0D	Zero Dimensional
1D	1 Dimensional
2D	Two Dimensional
3D	3 Dimensional
e V	Electron Volt
RB	Rhodamine B
MB	Methyl Blue
Θ	Diffraction Angle
P123	Pluronic123

ABSTRACT

In this work Titanium Oxide is synthesized by an altered route with improved properties. In this work silver (Ag) and nitrogen (N) codoped mesoporous-titania photo catalysts are organized by doping with 1:1% wt. ratio of silver nitrate and urea. The route reprocessed here is the Solgel method with Pluronic P123 as a soft template to sustain the spatial association and shape by changing the molecular load and composition. After production the as manufactured catalysts is characterized by using different techniques such as X-ray diffraction spectroscopy (XRD), Scanning electron microscopy (SEM), Uv-visible diffuse reflectance spectroscopy (DRS), Fourier transform infrared spectroscopy (FTIR) and Energy dispersive x-ray analysis (EDX). The Ag-N m-TiO2 codoping show optimistic behaviour towards the visible light radiation. Finally their proficiency bas been observed by the degradation of methyl blue under visible light illumination. The samples doped with Ag-N m-TiO2 shows higher photocatalytic activity as compared to pure Titania and Ag and other Nitrogen doped mesoporous titania. The photocatalyst has greater performance towards visible region due to the presence of Ag cluster on the surface of codoped catalyst because clusters entertainment as a sink for the advancement of electron for photo-.oxidation process.

CHAPTER # 1

INTRODUCTION

1.1 Introduction to Nanoscience & Nanotechnology:

1.1.2 Nanoscience:

Nanoscience is an original field of science which agreements with the study of materials that have very lesser dimensions which are in the range of nanoscale. Nanoscience is a blend of two words nano and science where nano is consequential from Greek expression "nanos" or Latin expression "nanus" which means "Dwarf" and the expression "Science" means knowledge. It is a different field that brings another advanced field nanotechnology which emphases on the nanoscale. It is an intersection between the fields such as biology, physics, chemistry, engineering, computer science and more. Nanoscience is a learning of nanometer scale. One billionth of a meter is identified as nanometer. While 10 hydrogen atoms or 5 silicon atoms combined in a row is the same as that of one nanometer. Study on essential relationships amongst physical properties and phenomena and materials dimensions in the nanometer scale is stated to as Nanoscience [1].

1.1.3 Nanotechnology:

Nanotechnology is deliberated to be the first important worldwide research earliest of the 21st century [2]. Nanotechnology is a mixture of two words "nano" and "technology" where nano is derivative from a Greek word "dwarf" which income a nanometer is one-billionth of a meter, a distance equal to two to twenty atoms or approximately 10 water molecules or equal to 6 carbon atoms breadth [3]. Nanotechnology is the fabrication and use of practical structures considered from atomic or molecular scale with at least one characteristic dimension measured in nanometers. Their size permits them to show new and noticeable improved chemical, physical and biological properties, processes and phenomena as of their size. Significant changes in behaviour are caused not only by continuous variations of characteristics with diminishing size but also by the presence of totally new phenomenon such as quantum confinement, example of which is the color of light discharging from semiconductor nanoparticles depends on their sizes.

"Nanotechnology is well-defined as the science and engineering involved in the design, synthesis, characterization and application of materials and devices whose lowest practical association in at least e dimension is going on the nanometer scale."notechnology is not purely the extension of compactness from bulk scale to nanometer scale where small structures give birth to novel and new functionality in a known interplanetary where quantum confinement happens. Materials naturally shows physical properties as that of the bulk scale even when it is in micron scale however in the nanometer collection they mostly shows physical properties particularly changed from that of bulk. Due to the transition from bulk to the atomic or molecular scale materials surprisingly show up remarkably definite properties. This technology also stresses for deep understanding of physical properties and all phenomena of nanostructured materials. It is also detected that nano sized crystals have a low melting point and compact lattice constants from their bulk counterpart due to the detail that the number of surface atoms increases at this scale and are in significant fraction to the total number of atoms or ions.

Nanotechnology covers a wide range of research field. This needs true interdisciplinary and multidisciplinary efforts for understanding and exploring this innovative class of material. Thus this technology is considered as coming technology which announces new dimensions to science and technology. This new field has wide range of applications and it touches the different domain of technology such as pharmacy, scientific tools, biotechnology, industrial manufacturing processes, advanced materials, electronics [4].

1.1.4 Nanoscale:

The term nano means "Dwarf". Nanoscale mentions to the 10^{-9}, or one billionth. In these expressions it denotes to a meter or a nanometer which is attractive the scale of atomic diameter.

Example:

Different examples of nanoscale be there:

- Sheet of paper is approximately 100,000nm abundant.
- Human hair roughly measures 50,000 to 100,000nm in thickness.
- Fingernails cultivate 1nm each second.
- A red blood cell is of 5000nm.

- **Usual size of a germ is 100nm.**
- **One inch equivalents 25.4 million nanometer.**

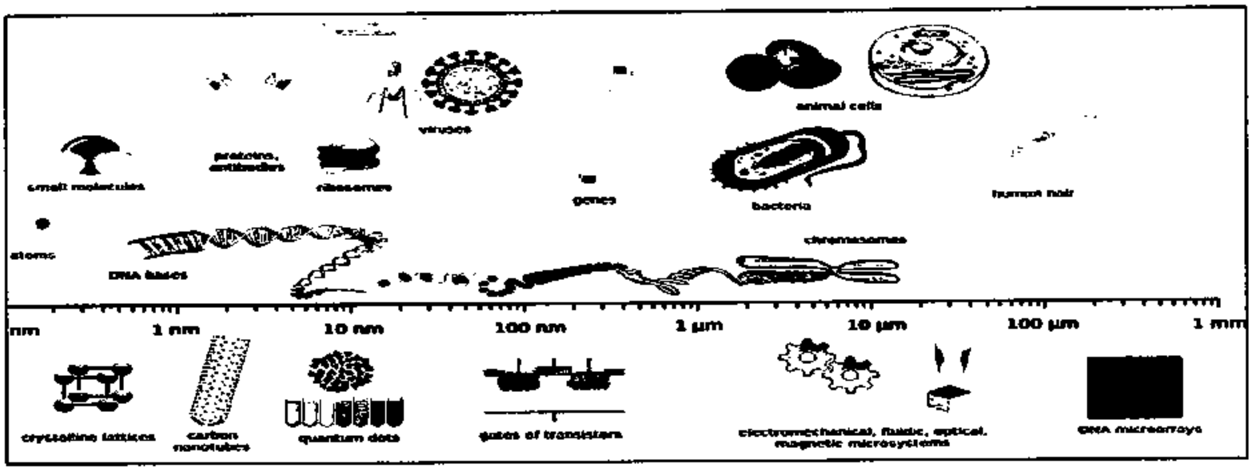


Figure # 1.1: Nanoscale equivalent belongings

1.2 Brief Past of Nanotechnology:

The term nanotechnology is really a "sunshade" that covers disciplines that have very inherent historic roots. According to R.D Booker it is quite challenging to describe the times past of nanotechnology because of two main reasons:

"Ambiguity of the word nanotechnology and improbability of the time extent analogous to the early stages of nanotechnology improvement".

But nevertheless the main idea of nanotechnology was prearranged by:

- **Richard Feynman**
- **Norio Taniguchi**
- **K. Eric Drexler**

1.2.1 Richard Feynman: *There's a sufficiently of zone at the Bottommost (1959):*

The beginning of nanotechnology was initiated with the speech of physicist Richard Feynman in December 1959. In his famed speech "There's a sufficiently of zone at the Bottommost" at an American Physical Society seminar at the California Institute of Technology he says:

"I want to construct billion tiny factories, models of individually further which stay built-up simultaneously. The principles of physics as far as I can see, do not speak against the possibility of reversing things atom by atom. It is not an effort to interrupt any laws, it is something in principle that can be done but in practice it has not been done because we are as well huge".

In his speech he proposed the power and concept of nanotechnology. He suggested that the barrier of knowledge and technology at which people should be directing could be real not only in physics but also in earlier nano sized fields.

1.2.2 Norio Taniguchi *(1974)*:

The Nanotechnology span was originally defined by *Norio Taniguchi* in Tokyo Science University in an International Symposium on Precision Engineering (ICPE) in 1974.

He used the term nanotechnology as the handling out of splitting up, merging, bending and twisting of materials by a singly atom or a molecule.

1.2.3 Eric Drexler *Molecular Manufacturing (1981)*:

In the 1980s, Eric Drexler authored the revolutionary book on nanotechnology "Engines of Creation" (Drexler 1986) in which he presented the concept of molecular manufacturing. In 1981 Drexler printed his first article on the subject in the admired scientific journal records of the National Academy of Sciences. Titled "*Molecular Engineering: An approach to the expansion of general capabilities for molecular employment*".

1.2.4 Last Scientists Donations to Nanotechnology:

In early 1980 nanotechnology and nanoscience grown so much improvement with two main enlargements:

- The confinement of cluster science.
- The discovery of the scanning tunneling microscope (STM).

Table 1.1: Key Success of nanotechnology

Year	Scientists Name	History
1981	Gerd Binning & Heinrich Rohrer	Construction of Scanning Tunneling Microscope
1982	Rosenberg	Analytically examine nanoscale structures & Improvements of nanoscale technologies
1985	Harry Kroto	Exposed fullerenes also entitled Bucky balls
1986	Calvin Quate & Christoph Gerber	Atomic Force Microscope
1990		1st Academic nanotechnology newsletter available
1991	Sumio Iijima	Exposed carbon nanotubes.
1993	Feynman	1st Feynman prize granted.
2000		President Bill Clinton broadcasted U.S National Nanotechnology Initiative (NNI)

1.3 Nanomaterials:

Nanomaterials are such materials which are moreover nano objects or nanostructured. Nano materials are made-up to be the building block of nanotechnology [5, 6].When a material dimension is lower than 100nm it can be categorized as nanomaterial. Nanomaterials can be designed according to the constraint. Nanomaterials size display new and conspicuous improved physical, chemical and biological properties, phenomenon and routes because of their size. Important changes in performance are affected not only by continuous alteration of characteristics with shrinking size, but also by the entrance of totally new sensation such as quantum confinement.

"Materials taking two of the dimensions are not limited to the nanoscale, usually display plate-like shape."

2-D Nanomaterials can be:

- Amorphous & Crystalline.
- Ready up and around of various chemical compositions.
- Recycled as a single layer & multi-layer structure.
- Put down on a substrate.
- Cohesive in a nearby matrix material.
- Metallic, Ceramic, Polymeric.

  Example: Nano-films, Nano-layers, Nano-coatings

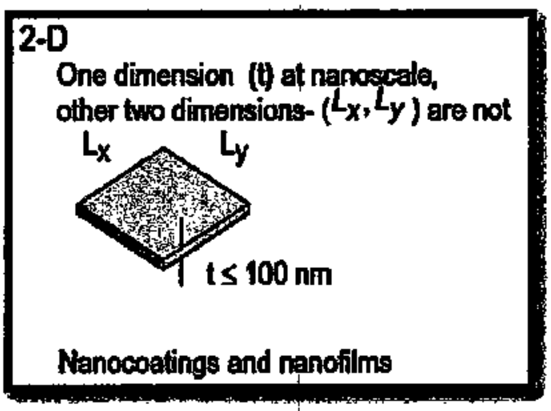


Figure # 1.5: 2- D nanomaterials

1.3.2.4 Three-Dimensional:

"Bulk nanomaterials are tools that are not limited to the nanoscale in any dimension."

These materials are categorized by having three randomly dimensions above 100nm.

3-D Nanomaterials can be:

- Materials hold a nanocrystalline structure & comprise the presence of topographies at nanoscale.
- In terms of nanocrystalline structure, Bulk nanomaterials can be collected of a multiple arrangements of nano-size crystals, most classically in different alignments.
- With deference to the feature presence at nanoscale, 3-D nanomaterials can have dispersions of nanoparticles, bundles of nanowires & nanotubes as well as per nanolayers.

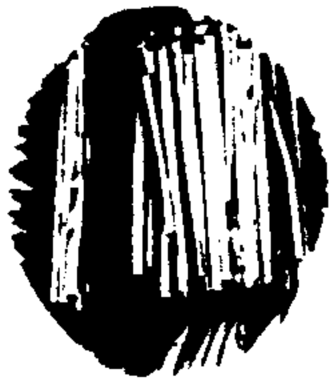


Figure # 1.6: Bundle of nanowires

1.3.3 Phase Conformations:

On the basis of this property nanomaterials are ordered as:

Table # 1. 2: Phase Conformations

Cataloging	*Resources example*	*Usage example*
Single Phase Solid	Crystalline & Amorphous Layers	Rubber & Liquid
Multi-Phase Solid	Composites	Polyimides, Nylons, Polyethylene
Multi-Phase Systems	Aerogels & Colloids	Cosmetics, Dyes, Lubricants, Colored glass, Butter

1.3.4 Process of Manufacturing:

Nanomaterials are also peculiar by the process of manufacturing which are given below:

Table 1.3: Manufacturing Process

Process Natures	*Scheme Used*
Chemical Process	CVD, Flame Synthesis

1.6 Nanocomposites:

Nanocomposites are multiphase solid materials with next to smallest one of the phase lying in the nanometer range. Nanomaterials frequently have unique properties that could enable composite materials with multiple unique properties that could simplify composite materials with multiple unique properties at the same time and they have been developed as a suitable choice to overcome the boundaries of bulk composites and uniform however it is often interesting to achieve these properties in big scale nanocomposite materials. As they hold preparation challenges related to the mechanism of elemental composition and stoichiometry that cannot be controlled by using conventional chemicals and materials. They are considered to be the materials of 21st century in the vision of displaying unique and significantly enhanced properties, functions, phenomenon and processes which are not establish in conventional composites.

Allowing to their matrix materials they are ordered into three different categories as defined below:

1.6.1 Ceramic Matrix Nanocomposite (CMNC):

In this group of composites the main volume is taken by a ceramic (an inorganic, nonmetallic solid chemical compound from the group of oxides, carbides, nitrides, borides, silicides etc). In ceramic matrix nanocomposites in most cases a metal is used as a second component. In order to attain the distinct nanoscopic properties both the metallic one and the ceramic one component are well dispersed in each other. Nanocomposites from these combinations was verified in improving their optical, electrical, magnetic and other properties.

1.6.2 Metal Matrix Nanocomposites (MMNC):

This class of nanocomposites can also be defined as reinforced metal matrix composites. These are further classified as continuous and non-continuous reinforced materials. CNT metal matrix composite is one of the most notable nanocomposite with high tensile strength and electrical conductivity.

1.6.3 Polymer Matrix Nanocomposites (PMNC):

These materials are better to expressed by the term nano filled polymer composites. Properly adding nano particulates to a polymer matrix is known as PMNC. Its performance can be enhanced often considerably by simply focusing on the nature and properties of the nanoscale filler. An example of this would be strengthening a polymer matrix by much harder nanoparticles of ceramics, clays or carbon nanotubes [8].

1.7 Photocatalysis:

The word Photocatalysis is combination of two words Photo and Catalysis where the prefix photo means "Light" and "Catalysis" is such a process in which a substance involved in changing the rate of a chemical transformation of the reactants without being changing itself in the last. Such a substance is known as the catalyst which increases the rate of a reaction by reducing the activation energy.

Photo-catalysis is defined as "Acceleration by the presence of a catalyst". Catalyst is just used to speed up a reaction. Therefore Photocatalysis has become specially an important field and heavy research topic by all fields of science including Chemistry, Physics, Surface science, Engineering and is employed today to solve a variety of environmental problems.TiO_2 is consider as the most efficient and environmental friendly photocatalyst.

1.7.1 Photocatalysis Mechanism:

TiO_2 is known as the most efficient and environmental friendly photocatalyst. The principle of TiO_2 Photocatalysis process is straightforward [9, 10]. When the absorption of light takes place with an energy larger than the band gap of TiO_2, electrons are excited from the valence band to the conduction band, creating electron-hole pairs. These electron-hole pairs migrates to the surface and react with the chemicals adsorbed here. The Photocatalysis process efficiency of mesoporous materials can be affected by two parameters:

- Surface area: A larger surface area increases the reaction rate
- Crystallinity: The presence of amorphous phases promotes recombination of electron-hole pair, thereby decreasing photocatalytic activity. The photocatalytic activity can be improved by increasing the crystallinity of the material. Crystallinity can be increased either by the doping of metals & nonmetals in pure semiconductor crystal.

Sajjad Shamaila et.al (2011) [11] reported that m-TiO_2 with high crystallinity was synthesized using the templates with the combination of P123 and PEG and the hydrolytic retardant such as acetic acid has used. The dual template shown remarkable high photocatalytic activity as compared to single one. Different characterization techniques was used to examine as prepared sample. X-ray diffraction with small and wide angle (XRD), Transmission electron microscopy (TEM), N_2 adsorption-desorption, Thermogravimetric analysis (TGA/DTA) was used for characteristics. The photo catalytic activity was observed by phenol degradation and mineralization of phenol was confirmed by high performance liquid chromatography. The observed results shown that m-TiO_2 with high crystallinity, biporous structure and thermally stable can be obtained during synthesis.

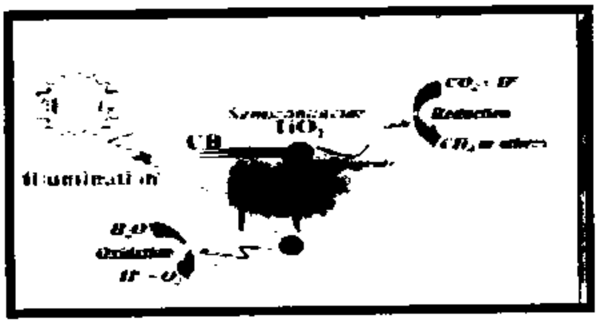


Figure # 1.8: Representation sketch of basic mechanism of photo-catalytic process

1.8 Porous Materials:

International Union of Pure and Applied Chemistry (IUPAC) classifies porous materials into three classes depending upon their pore sizes:

- Microporous materials with pore size less than 2 nm.
- Mesoporous materials with pore size in between 2 and 50 nm.
- Macro porous materials with pore size greater than 50 nm [12, 13, and 14].

1.8.1 Mesoporous Materials:

Mesoporous materials shows several geometrical mesostructured:

- Lamellar, two-dimensional (2D) hexagonal.
- Three-dimensional (3D) hexagonal, Cubic.
- Morphologies (powder, nanoparticles & film).
- Framework conformations (inorganics, organics, metals & metal oxides).

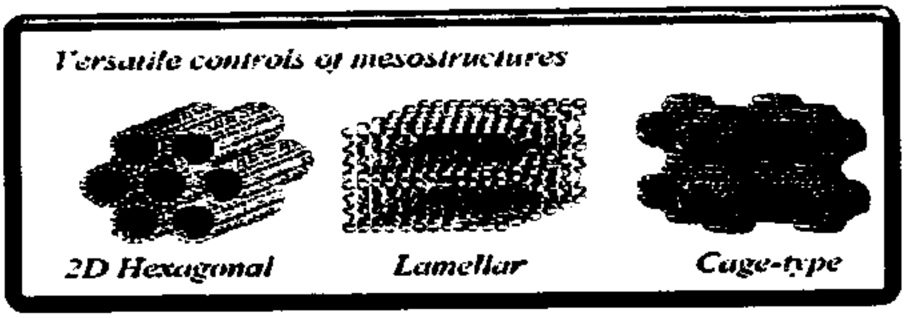


Figure # 1.9: Different geometries of mesostructured

1.9 Titanium Dioxide (TiO_2):

Titania is measured to be one of the most prominent inorganic photo catalytic material [15, 16].Titania photo catalyst is inert, photo catalytically stable, easy to synthesize, cheap and without being dangerous to the environment or humans. Titanium dioxide is also called as titanium (IV) oxide or Titania. It is one of the logically occurring oxides of titanium. Its chemical formula is TiO_2. It was discovered in 1791 in Cornwall, Great Britain by William Gregor. It was particular name by Martin Heinrich Klaproth.

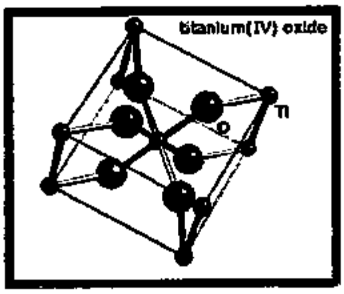


Figure 1.10: Unit cell of Titanium Oxide

1.9.1 Properties of Titanium Dioxide:

Some of the properties of Titania are listed below:

Table 1.4: Physical and Chemical properties of Titania

Physical properties	
Phase	**Solid**
Density (near r.t)	**4.506 $g.cm^{-3}$**
Liquid density atm .p	**4.11$g.cm^{-3}$**
Melting point	**1941K, 1668°C, 3034°F**
Boiling point	**3560K, 3287°C, 5949°F**
Heat of fusion	**14.15 Kj.mol-1**
Heat of vaporization	**425 Kj.mol-1**
Molar heat capacity	**25.060 J.mol-1.K-1**
Chemical properties	
Solubility in water	**Insoluble**
Electrical resistivity	**(20°C)420nΩ.m**
Magnetic ordering	**Paramagnetic**
Thermal conductivity	**21.9W.m-1.K-1**

1.9.2 Titanium Dioxide Phases:

Titania occurs in three crystalline phases:

- **Anatase**
- **Rutile**
- **Brookite**

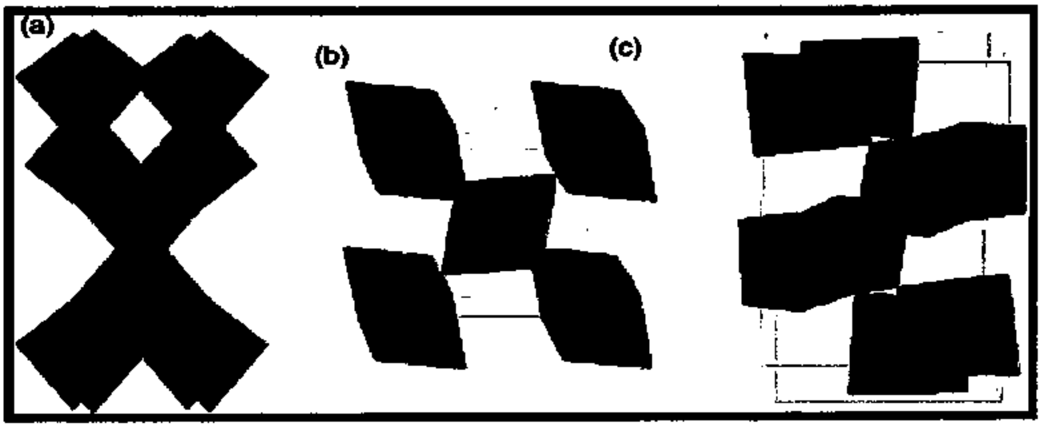


Figure # 1.11: Crystal structure of (a) Anatase (b) Rutile (c) Brookite.

1.9.3 Properties of Titanium Dioxide Phases:

Some of the properties of Anatase, Rutile and Brookite phases are listed below:

Table 1.5: Properties of Anatase, Rutile & Brookite

Property	Anatase	Rutile	Brookite	Reference
Crystal Structure	Tetragonal	Tetragonal	Orthorhombic	[17,18,19]
Lattice Parameters	4	2	8	[17,20,21,22]
Lattice Parameters	a = 0.3785nm c= 0.9514	a= 0.4594nm c= 0.29589nm	a= 0.9184nm b= 0.5448nm c= 0.5145nm	[17,20,21,22]
Density (Kgm^{-3})	3894	4250	4120	[17,20,21,22]
Experimental Band Gap	~ 3.2 eV ~ 387nm	~ 3.0 eV ~ 413nm	~ 1.9 eV ~ 650nm	[17,23,24,25,26]
Index of Refraction	2.54,2.49	2.79, 2.903	2.61- 2.63	[17,18,27,28]

1.9.4 Applications of Titanium Dioxide (TiO_2):

Mesoporous Titania is well-thought-out to be one of the promising and prominent catalyst which has widespread range of applications. It has reduced surface to volume ratio that account properties that can be applied in very useful ways. Here are some practical applications of Titania.

- Environmental Catalyst (Water & Air Purification)
- Transport Medium (Dye Sensitized Solar Cell)
- Energy Catalyst (Water Splitting)

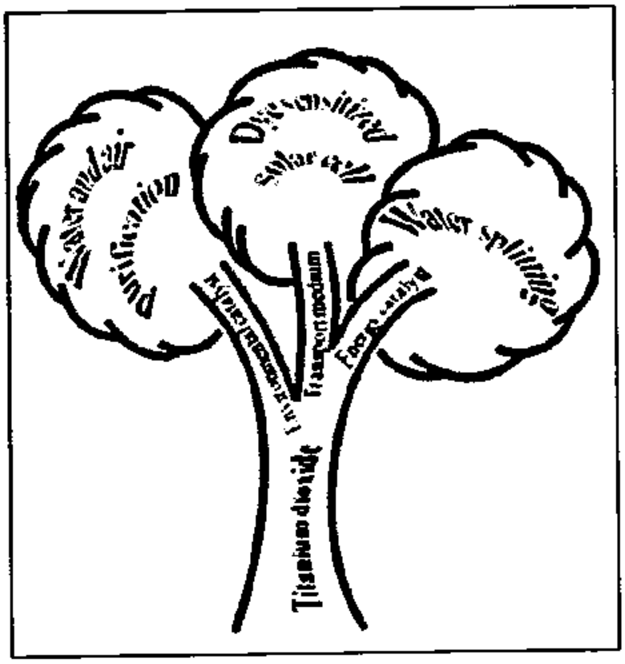


Figure # 1.12: Applications of Titania

1.10 Characteristics of Visible light driven Catalyst:

There are some approaches to synthesize visible light driven photo catalyst with following properties:

- By the replacement of Titania with transition metal.
- Non-metal atoms and other semiconductors doping into TiO_2.
- By the reduction of TiO_2 size.
- By changing the morphology and phase structure and composition of TiO2;
- By adding of holes scavengers.

1.11 Silver:

Silver is a chemical element with symbol Ag and atomic number 47. A soft, white, lustrous transition metal, it retains the highest electrical conductivity, thermal conductivity and reflectivity of any metal. Amongst the noble metals used as electron traps, silver (Ag) is enormously appropriate for industrial application due to its low price and relaxed preparation. Ag-modified TiO_2 powders have come to be current benefits due to its improvement of photocatalytic reactions and anti-microbial activity

1.11.1Applications of Silver:

Silver is used industrially in electrical contacts and conductors, in specific mirrors, window coatings and in catalysis of chemical reactions. Silver metal liquefies readily in nitric acid (HNO3) to produce silver nitrate (AgNO3), a transparent crystalline solid that is photosensitive and freely soluble in water. In count, a variety of efforts had been made to announce various metal species into the TiO_2 to enhance the photocatalytic activity or broaden the absorption of solar spectrum by the doped Titania.

Yanhui Ao et.al (2008) [29] reported that Ag doped m-TiO_2 has manufactured by Solgel surfactant assisted templating method using cetyl-trimethyle ammonium (CTAB) as structure directing agent. The prepared catalyst has been synthesized by different characterization techniques such as X-ray diffraction spectroscopy (XRD), Transmission electron microscopy (TEM), N_2 Adsorption-desorption (BET) and X-ray photoelectron spectroscopy (XPS). The aqueous solution of phenol in water is used for degradation under UV light irradiation to observe the photocatalytic activity.

The results obtained shown that changing the silver doping the crystal phase structure and photocatalytic activity has become alteration. Upon Ag doping anatase grain growth has down. When Ag doping had greater than before on m-TiO_2, the photo catalytic activity has been enhanced. But the surplus amount of Ag doping also depressed the photocatalytic activity.

1.12 Nitrogen:

Nitrogen is a chemical element with symbol N and atomic number 7. Nitrogen is a nonmetal. Molecular nitrogen ($^{14}N_2$) is largely translucent to infrared and visible radiation because it is a homonuclear molecule and, thus, has no dipole moment to couple to electromagnetic radiation at these wavelengths. Significant absorption follows at extreme ultraviolet wavelengths launch around 100 nanometers.

1.12.1 Applications of Nitrogen:

Maciej Zalas et.al (2014) [30] reported that the photo catalytic activity of m-TiO_2 had enhanced by template free Solvothermal method using N incorporation by urea. The synthesized sample was prepared under mild temperature conditions and obtained amorphous m-TiO_2. Further temperature treatment of as synthesized sample shown well defined crystalline anatase frame work of N doped m-TiO_2. The synthesized sample was characterized by using thermal analysis, Fourier Transform Infrared spectroscopy (FTIR), UV-visible diffuse reflectance spectroscopy (DRS), small and wide angle X-ray diffraction spectroscopy (XRD), high resolution transmission electron microscopy (HRTEM), and X-ray photoelectron spectroscopy (XPS), N_2 Adsorption-desorption. The photocatalytic activity has examined by using methylene blue and acetic acid decomposition and results revealed that N doped m-TiO_2 shown high photocatalytic activity as compared to undoped.

CHAPTER # 02

Literature Review:

2.1 Titanium dioxide (uncontaminated):

Titanium is deliberated to be one of the most boosting oxide which have a wide range of photo catalytic and catalytic solicitations [31].TiO_2 is one of the logically happening oxide of titanium. The learning of Titania is mostly based upon the main three crystalline phases such as rutile, anatase & Brookite and also be contingent on other forms such as nanoparticles, thin films and bulk etc. Naturally Titania is obtained in powder form which may comprise of mixture of both an amorphous and crystalline segments. The crystalline quality of Titania can be improved by using different techniques [32]. The powder form of Titania is frequently used as white pigments from ancient times. The main characteristics of Titania are that they are chemically stable, reasonable and inoffensive. Different scholars worked on both an amorphous and crystalline phases of Titania. From the last few eras titania is well-thought-out as the gifted semiconductor having large range of applications in different emergent fields such as lithium batteries, drug transport [33,34,35] , solar cells [36,37,38,39,40], gas radars and so on.

Different studies reports on the phases of the Titania.

Zdenek Dohnálek et.al in (2010) [41] reported TiO_2 (110) catalyzed rejoinders based on water, oxygen and their detachment products and also the basic points on which the catalytic and photocatalytic reactions of Titania depends. As TiO_2 (110) is the utmost stable surface form of rutile Titania. So in revisions it is deliberated as a descriptive form. In this report alcohols, water and oxygen, are to be invention latest determination related to applications in the areas of oxidation and water-splitting of carbon encompassing pollutants. The scattering of charge formed as a result and defects designed as a result of characterization to be concerted by him. They focus on the quantity of each and every site present on the surface and also on the guidance of the charges existent during adsorption methods. The information offers a model for both the pure & contaminated diffusion routes and also for the rotational dynamics.

Yalei Zhang et.al [42], in (2011) the stable form of TiO_2/rectorite (TR) was manufactured at low temperature (70°C) by inserting dispersed Titania particles into rectorite. They stated that the TR samples were categorized by using characterization techniques such as, UV-visible diffuse reflectance spectroscopy (DRS), N_2 adsorption-desorption, (HRTEM), (FT-IR) and (XRD). The surface area of TR has improved to 219 m2/g. The results gotten from TR characterization display that under the irradiations of UV light the photocatalytic activity in the disintegration of the anionic dye acid red G (ARG) was agreeable. The photo catalytic activity has fully organized by taking five photo catalytic recurrent cycles which discusses to the mesoporous structure and the large surface area of TR.

2.2 Mesoporous Titania:

Mesoporous TiO_2 has modified frame work prearrangement and fixed pore size, with distinctive surface area. The two dimensional hexagonal mesoporous Titania nanostructures rewarded much consideration because of having slight tricking effect, surface penetrability and bulky constant surface area. Mesoporous Titania has comprehensive collection of applications which involve separations, biological conversion, adsorbent materials, energy storage & catalysis [43, 44, and 45].

Some reports are inscribed below:

Shamaila Sajjad et.al in (2010) [46] stated that mesoporous TiO_2 photo catalyst can be organized by using template and hydrolytic retardant. The hydrolytic retardant and template recycled in the synthesis are acetic acid and PEG respectively. It has been testified in the paper that PEG was completely perfect template and can be used to yield the mesoporous anatase form of TiO_2 with comprehensive crystallinity. The inference of thermal treatment and molecular weights of the PEG, on the photocatalytic activity and its consequence on final structure has also studied. The phase, compositional and operational properties of the photo catalyst was characterized by consuming different characterization techniques such as XRD, Nitrogen Sorption analysis and TEM. It has been stated that when the PEG molecular weights variations, the particle size and pore size will also come to be altered. So, when the PEG molecular weights different from 600 to 20,000 as a result the size of particle of mesoporous structure diminish from 15.1 to 13.3 nm and also as a effect of it the total pore sized improved from 6.9 to 10.6 nm. This created m-TiO2 actions has been calculated and then these actions are likened with Degussa P-25 by consuming a testing compound where chloro-phenol has recycled for testing. Chromatography was used to illuminate the reaction mechanism of photo degradation.

Tae-Jung Ha, Sin-Young Jung et.al in 2011 [47] informed that the films of mesoporous oxide with extremely ordered structure has low thermal conductivities which is comparable with dense film. To use these films of mesoporous oxide which have superlative properties in different fields, it is critical to use the thermal insulation method. In this statement ordered and the disordered form of m-TiO2 films as a part of dehydrated time was synthesized. Even they has similar pores locations but still they has diverse thermal conductivities and structures of pores. In ordered to show a kith and kin between the thermal conductivities and pore structures, anticipation of the transferred heat was happened. The heat flux vector, diffusion of temperature and thermal properties of ordered mesoporous films has been estimated by fixed elemental analysis. The method of thermal insulation in the pores structure has been described by the contrast between the experimental and predicted results.

2.3 Photocatalysis:

Photocatalysis is such a chemical reaction in which light assists during the reaction. As it has been described that the inorganic Titania is one of the best noticeable photocatalytic material [48], so it was reflected to be efficient, economical and nontoxic for the chemical and organic degradation. But Titania had wide band gap unluckily, so it only shows and absorbs high photocatalytic behaviour only under the irradiation of ultraviolet rays which is 3-4% of the whole solar energy. So different attempts has made to improve the photocatalytic nature of the Titania by increasing the absorption range from UV to the visible region. In order to enhanced the photocatalytic activity of different altered nano catalyst of Titania different methods has been adopted such as introducing defects, in lattice selective metal ion doping or composite-type, noble metal supported. [49, 50, 51, 52].

Different ways to expand the photocatalytic activity were: Doping, Composite formation, Co-doping

2.3.1 Doping Method:

The appetizer of defects is one of the way to improve the photocatalytic activity of Titania. Many researchers had been described on doping and details of some recent are as follows:

In 2011 Sol-gel method was used to increase the photocatalytic activity of Titania doping it with calcium ions. This idea was reported by U.G.Akpan et.al [53]. In that report photocatalyst was synthesized by using sol-gel method and then characterized the catalyst by using techniques such as N2 physisorption, X-ray photoelectron spectroscopy (XPS), XRD. To study the surface structure scanning electron microscope (SEM) was used. Fourier transform infrared (FTIR) spectroscopy and the (XPS) technique tells us about the occurrence of O, C, Ti and Ca in the sample of Titania which has doped with Ca ions. The photocatalytic degradation of acid red 1(AR1) and azo dye has been examined to find the catalyst activity under the irradiation of UV light. The results shows that the sample heated for 3.6 hrs, at 300°C in a cyclic way shows best adaptation. When the percentage of doping is less 0.3-1.0 wt. %, it increases the photocatalytic activity of Titania and 0.5 wt. % had assumed to be the best percentage of TiO2 doping with Ca ions. The pH effect on the AR1 degradation has calculated and the dye solution pH has applied a great effect on the dye degradation.

Mesoporous Titania doped with Cu2+ has enhanced with photocatalytic activity from UV to visible light and the desired catalyst has been synthesized by simple method reported by Le Yu et.al (2010) [54]. After synthesis the sample was characterized by using different techniques such as X-ray photoelectron spectra (XPS), transmission electron microscopy (TEM), and N2 adsorption-desorption, low angle and wide angle X-ray diffraction (XRD) and UV-visible absorbance spectroscopy. Then finally methylene blue degradation had examined under visible region to find the photocatalytic activity of these samples. Results show that the amount of Cu2+ doping was quite significant and it show great affect to the catalytic activity of titanium dioxide.

2.3.2 Doping with Cations and Anions:

Different modifications of TiO_2 has been implemented to increase the photocatalytic activity like:

- Doping with Cations:

For example transition metal ion dopants such as Fe, Zn, Sb, Sn doped with Titania to upturn photocatalytic activity [55, 56, 57,58, 59] and other cations like Ce, C or S when doped with anatase titania also displays high catalytic activity.

- Doping with Anions:

A number of different strategies has been working to increase the photocatalytic activity into the visible region. They include (e.g., B, C, N, F, S, Cl or Br) of Titania to attain visible light driven photocatalyst has been highest lately studied. Doping with anions for example S, N and other anions like S, C or N when doped with anatase phase of Titania also improved the photocatalytic activity under the treatment of visible light. [60, 61, 62, 63].

2.3.2 Composite Formation:

The composites development is another method to rise the photocatalytic activity of Titania.

Kexin Li et.al (2012) [64] reported that when mesoporous titania was codoped with graphene and tourmaline it shows high photocatalytic activity under the irradiation of anticipated sunlight and the catalyst has been synthesized by combination of two techniques and these techniques were Solvothermal treatment and Solgel direct condensation method, where Solvothermal treatment combines with Solgel direct condensation method. As a result of it a composite was synthesized. This synthesized composite showed an interlinked three dimensional (3D) mesostructured and also show an anatase phase structure with unchangeable size of pore and large area of surface which is from (218m2g -1). This composite has shown high photocatalytic activity under the anticipated sunlight irradiation as compare with the pure form of Titania. Then the photo degradation of organic pollutant norfloxacin and rhodamine B were examined to find the photocatalytic activity of the codoped mesoporous Titania composite. Therefore this composite had prosperously used for the eutrophic treatment of water.

Wei Zhang et.al (2009) [65] reported that nanocomposite of TiO2/adsorbent was produced by using wet chemical impregnation method and the applications of TNC was increasing day by day in waste water treatment. The morphological properties (crystal phase, surface area and particle size etc.) And the electronic properties (quantity & lifetime of charge carrier) of Titania had synthesized in samples hinge on upon the conditions occurs during the synthesis.

2.3.3 Co-Doping Methods:

Limitless doping is another way to increase the photocatalytic activity of the Titania. Some reports are as given below:

Jonghun Lim et.al (2013) [66] reported that Titania codoped with niobium and nitrogen by using a Solgel method show high photo-catalytic activity under the irradiation of visible light. Then visible light photocatalytic activities of catalyst were associated with bare Bb- and N- doped with Titania. Then the catalyst synthesized were characterized by using different characterization techniques such as diffuse reflectance UV-Visible absorption spectroscopy, powder X-ray diffraction (XRD), X-ray photoelectron spectroscopy, energy-dispersive X-ray analysis and FT-IR spectroscopy. It was detected that when Titania codoped with Nb and N, it shows significant properties different from the single doped Titania in the angle of the charge distribution of induced dopants, structural stability, defect energy levels, optical absorption and vacancy sites. The most unique thing is that the absorption of visible light by (N,NB)- Titania was prominently higher as compared with the doped sample which has band gap of 0.1 eV which is confirmed by Mott-Scottky plot, the calculations of electronic structure and Tauc plot. As the result of codoping in Titania creates mid gaps between the band gap and create. Ti3+ states that increase the photocatalytic activity under the visible light irradiation. Then degradation of 4-chlorophenol (4-CP), reduction of chromate (Cr VI) and oxidation of iodide is examined in aqueous phase under the irradiation of visible light.

Hongyuan Hao et.al (2009) [67] reported that Solgel method is used to codoped mesoporous Titania with nitrogen and iron (III) which shows high photocatalytic activity under the irradiation of visible light. In this report the surfactant (dodecyl amine) contains nitrogen was used. The catalyst were characterized by using different techniques such as (TEM), UV-visible (DRS), electron paramagnetic resonance (EPR), (XPS), low and wide angle (XRD), N2 adsorption-desorption. The results shown that codoped Titania mesostructured with Fe (III) and nitrogen is formed by mix crystal structure of Anatase and Brookite. The synthesized sample even heated at 400°C consists of large unique surface area and small size crystals and uniform distributions of pores. Under the irradiation of visible light, the photocatalytic activity is examined by 2, 4-di chlorophenol degradation. From the results it were concluded that when powder m-TiO_2 codoped it presented high photo catalytic behaviour as compared with single nitrogen doping.

2.4 Silver:

Silver is considered as soft, white, lustrous transition metal, it has the highest electrical conductivity, thermal conductivity and reflectivity of any metal. Amongst the noble metals used as electron traps. Silver (Ag) is extremely suitable for industrial application due to its low price and easy preparation.

2.4.1 Doping with Silver:

Yanhui Ao et.al (2008) [68] reported that Ag doped m-TiO2 has synthesized by Solgel surfactant assisted templating method using cetyl-trimethyle ammonium (CTAB) as structure directing agent. The prepared catalyst has been synthesized by different characterization techniques such as X-ray diffraction spectroscopy (XRD), Transmission electron microscopy (TEM), N2 Adsorption-desorption (BET) and X-ray photoelectron spectroscopy (XPS). The aqueous solution of phenol in water is used for degradation under UV light irradiation to observe the photocatalytic activity.

The results obtained shown that varying the silver doping the crystal phase structure and photocatalytic activity has become change. Upon Ag doping anatase grain growth has depressed. When Ag doping had increased on m-TiO2, the photo catalytic activity has been enhanced. But the superfluous amount of Ag doping also depressed the photocatalytic activity.

2.4.2 Codoping with Silver:

Xia Yang et.al (2009) [69] reported that one-step Solgel solvo-thermal method has been used to synthesize Titania nanocomposite by doping metallic silver and vanadium oxide in the presence of surfactant triblock copolymer P123. Different characterization techniques has been used to characterize as synthesized material. The observed results shown Ag/V TiO2 three component junction system with anatase/rutile (73.8:26.2) mixed phase structure. It was examined that extremely small size metallic particles were spread over the surface of composite. This nanocomposite as synthesized was used to examine the visible and UV-light driven photocatalyst. The photocatalytic activity was examined by the decomposition of dyes rhodamine B (RB) and coomassie brilliant blue G-250 (CBB) in an aqueous solution. It was examined that the enhanced photocatalytic activity in the visible light region is due to the vanadium oxide doping and the improvement in the quantum efficiency is due to the doping of metallic silver is key factor to determine the enhanced photocatalytic activity. It can also observed that the mixed phase structure with suitable ratio of anatase/rutile in the as synthesized sample Ag/V TiO2 enhanced the photocatalytic activity.

2.4.3 Composites of Silver:

Xingtian Yin (2012) [70] et.al reported that Titania nanotube and nanoparticle mixed composite has been synthesized by a perchlorate containing electrolyte in the presence of ultrasonic process. A rapid anodization process has been used for composite synthetization. The composite of silver-titania has been synthesized by using a stabilizing agent at low temperature in PEG 600, which also acts as a reducer to reduce Ag+ on Titania nano crystals surface. It has been observed that different characterizations techniques utilized to obtain results from the nanocomposite, (XRD), (XPS), (TEM), (EDX), UV-vis absorption spectroscopy. The photocatalytic activity of as synthesized sample was observed under UV light in the presence of methyl orange solution decomposition. The enhanced photocatalytic response has been observed in the presence of Ag nanoparticles surface plasmatic effect that is explained in the report.

2.5 Nitrogen:

Nitrogen is considered to be most abundant element on earth. It has symbol N and atomic number 7. It is nonmetal. It also uses to modify Titania to increase photocatalytic behaviour. Non-metal doping is one of the typical chemical modifications to enhance the visible light photo-catalytic activity of oxide effectively. Among various non-metallic doping elements, the nitrogen doping has been proved to be a simple and effective way to increase the visible light absorption.

2.5.1 Doping with Nitrogen:

Zhiyan Hu (2013) [71] reported that ordered arrays of 3D mesoporous Titania sphere has prepared by using two template system. It was observed in their report that both hard template (opal template) and soft template (surfactant template) can be used to synthesize N-doped mesoporous Titania spheres. Different characterization techniques has been used which include X-ray diffraction spectroscopy (XRD), Transmission electron microscopy (TEM), and scanning electron microscopy (SEM). The photocatalytic activity of RhB decomposition was observed which shown that the enhanced photocatalytic activity in the visible region which is attributable to the N doping effect. This type if Titania sphere has practical applications in the fields of water electrolysis, environmental purification and Dye-sensitized solar cell (DSSC).

2.5.2 Codoping with Nitrogen:

Ahmed Khan Leghari Sajjad (2012) [72] et.al reported that UV and visible light active photocatalyst has been prepared by using metal and nonmetal doping. It was observed that simple Solgel method can be used to synthesized the catalyst by the addition of doping with Tungsten (metal) and Nitrogen (nonmetal), and different characterizations techniques has been employed, X-ray diffraction spectroscopy (XRD), (SEM), (TEM),(FTIR) and (XPS), (UV-VDRS). The photo catalytic activity of as synthesized catalyst was observed by Rhodamine B and 2, 4-Dichloro phenol decomposition. It was observed that different new energy states developed by him and their coworkers to enhanced the photocatalytic behavior.

2.5.3 Composite of Nitrogen:

Maciej Zalas et.al (2014) [73] reported that the photo catalytic activity of m-TiO2 had enhanced by template free Solvothermal method using N incorporation by urea. The synthesized sample was prepared under mild temperature conditions and obtained amorphous m-TiO2. Further temperature treatment of as synthesized sample shown well defined crystalline anatase frame work of N doped m-TiO2. The synthesized sample was characterized by using thermal analysis, Fourier Transform Infrared spectroscopy (FTIR), UV-visible diffuse reflectance spectroscopy (DRS), small and wide angle X-ray diffraction spectroscopy (XRD), high resolution transmission electron microscopy (HRTEM), and X-ray photoelectron spectroscopy (XPS), N2 Adsorption-desorption. The photocatalytic activity has examined by using methylene blue and acetic acid decomposition and results revealed that N doped m-TiO2 shown high photocatalytic activity as compared to undoped.

Among all other dopants, silver as a metal consuming electron trapping ability and nitrogen as a nonmetal captivating band gap narrowing ability to create oxygen vacancies has been widely used to produce visible-light photocatalyst.

Ibrahim El Saliby et.al (2011) [74] reported that visible light efficient photocatalyst has been prepared by using metallic Silver and nonmetallic Nitrogen in addition to Titania. The procedure to synthesize the catalyst has been carried out simply at room temperature. As observed that for the doping of nitrogen, Degussa P25 has been treated with ammonium hydroxide and for Ag-N codoping the sample is treated with AgNO3, the as synthesized catalyst was characterized by X-ray diffraction spectroscopy (XRD), Transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS), Energy dispersive analysis (EDA) and specific area measurement. The photocatalytic behaviour of as synthesized catalysts was revealed by the solution of Methylene Blue (MB) dye. The results obtained shown that visible light reactive catalyst has been synthesized by using such dopants and it has been determined that the presence of Ag cluster on the surface of Titania shown superior performance to the codoped catalyst towards visible region because clusters behave as a sink for the promotion of electron for photo-oxidation process.

Zhifeng Jiang et.al (2014) [75] reported that green Solvothermal method has been used to synthesized nano composite for efficient visible light responsive behaviour.

Mesoporous Titania with Ag-loaded, nitrogen doped yolk shell microspheres has been synthesized by using a hollow controller as acetic acid and for the N doping source is tri-ethanol amine is used for the first time. The photo-reduction method has been used for the deposition of Ag NPs. Different characterizations techniques has been used as X-ray diffraction (XRD), Transmission electron microscopy (TEM), Energy dispersive spectroscopy (EDS), Raman spectroscopy, N2 adsorption-desorption, (BET) and (BJP) method of measurement. The photocatalytic response under visible light irradiation can be measured by the degradation of rhodamine B and ciprofloxacin. The observed results shown that Ag-N-TiO2 –YSM microsphere has enhanced photo catalytic activity as compared to others. It was also observed that a limiting amount of silver loading will increase the photocatalytic activity, more than that cannot improved in the resultant activity process. This synthesized metal hollow semiconductor has been used for many applications in Photocatalysis.

CHAPTER # 3

EXPERIMENTAL SECTION

3.1 Materials & Reagents:

3.1.1 Ingredients Used:

Table 3.1: Reagents and Materials used in synthesis are:

REAGENTS	FORMULATIONS	GRADES
Pluronic (P123)	$EO_{20}PO_{70}EO_{20}$	A.G
Tetrabutyltitanate	$Ti(OC_4H_4)$	A.G
Urea	$CO(NH_2)_2$	A.G
Silver Nitrate	$AgNO_3$	A.G
Hydrochloric Acid	HCl	A.G
Ethanol	CH_3CH_2OH	A.G

3.2 INSTRUMENT:

The apparatus used in this experiment are:

- Beakers
- Magnetic stirrer
- Hot plate
- Spatula
- Glass rod
- Glass plates
- Mechanical grinder

3.3 Catalyst Analysis:

In a typical method m-TiO2 was synthesized by simply EISA method using surfactant triblock copolymer P123 as a template. In this synthesis 1g of P123 dissolved in 60ml of ethanol and stir for one hour, then add 2ml HCl dropwise with continuously stirring. Then add 10ml

Tetrabutyltitanate (TBT) one drop after two minutes and stir it for five hours at room temperature. A transparent sol was obtained which was being transferred onto the glass plate and spread it. A uniform thin layer was dried at room at room temperature, then scratch it from glass plate and after mechanical grinding get powder calcined it to remove the template and other organic species. 1.0% wt. Ag doped m-TiO2 prepared by using AgNO3. 1.0% wt. N doped m-TiO2 prepared by using Urea. The Silver Nitrogen codoped mesoporous Titania is prepared in 1:1% wt. of Silver Nitrate and Urea.

Figure #3.1: Organized testers

3.4 Characterization Techniques:

The most appreciated aspect of materials research is the characterization of the invented materials that we use or study in order to attain more knowledge about them. Characterization when recycled in material science, means to the usage of external techniques to review into the internal structure and properties of a material. The goal or preferred results of chemical characterization is to point out and quantify the chemical constituents of a material and to evaluate its bio-compatibility.

Comprehensive and thorough knowledge of the material properties of a product under fabrication or presentation conditions is therefore serious for its success.

Analysis techniques are used purely to boost the sample, to imagine its internal structure and to gain knowledge as to the dispersal of elements within the specimen and their interactions. These analysis techniques can be spectroscopic or can be microscopic. Spectroscopic techniques includes interaction of ultraviolet, visible, and infrared radiation with matter whereas microscopic techniques mainly concern about amplification of internal structure of material by magnificent light of specific wavelength.

Spectroscopic techniques I used to analyze materials are:

- X-Ray Diffraction (XRD) Spectroscopy
- Scanning Electron Microscopy (SEM)
- Energy Dispersive X-Ray Spectroscopy (EDS)
- UV-Visible Diffuse Reflectance Spectroscopy (UV-DRS)
- Fourier Transform Infrared Spectroscopy (FTIR)

3.4.1 X-Ray Diffraction (XRD):

X-Ray Diffraction is a flexible, non-destructive technique that reveals detailed information about the chemical composition and crystallographic structure of ordinary manufactured materials. X-Ray Diffraction is founded on the elasting scattering that is the change of direction of the electromagnetic waves motion deprived of energy loss. This (XRD) experiment requires an X-Ray source, the sample to be tested and a detector to pick up the diffracted X-rays. A typical diffraction pattern comprises of a plot of reflected intensities versus the detector angle 2θ or θ. The (XRD) pattern of a clean substance is therefore like a thumbprint of the substance. Slight sample preparation and relatively straight forward data interpretation mark it advantageous. For consistent results on it should be retained in mind that sample under study must be single phase and homogeneous.

3.4.2 Scanning Electron Microscopy (SEM):

By using the Scanning Electron Microscopy, the topographic information of nanomaterials and the surface of films can be presented with great resolution. The SEM is considering as a most commonly used instruments in nanomaterials. This is because SEM has arrangement of large focus depth, great power of resolution and freedom to detect the sample and high magnification. SEM resolve morphology specifics less than of 50nm and SEM consist of a depth of focus 500nm times higher as compare with optical microscope with identical magnification. In SEM the beam of electrons accelerated with a short voltage range from 1-20 KV, is scanned on the surface of the sample. The beam of electrons use for SEM characterization consists of low energy as related with TEM. SEM usually has resolution of 1nm. It is used to identify the spatial distribution of element.

3.4.3 Energy Dispersive X-ray Spectroscopy (EDS):

Energy Dispersive X-Ray Spectroscopy (EDS) is another technique that makes use of the X-ray spectrum emitted by a solid sample bombarded with a focused beam of electrons to obtain a confined chemical analysis. All elements from atomic numbers 4 (Be) to 92 (U) can be detected in principle, though not all instruments are furnished for "light" elements (Z<10). The technique is non-destructive and has a sensitivity of 0.1% for elements heavier than C. EDS can be used to find the chemical composition of materials depressed to spot size of a few microns and to create elemental composition maps above a much broad raster area. Together these competences provide fundamental compositional information for a widespread variety of materials.

3.4.4 UV- Visible Diffuse Reflectance Spectroscopy (DRS):

UV-Visible Diffuse Reflectance Spectroscopy is a non-destructive technique that comprises of transmission or reflection (external or internal) of UV-Vis radiation. Its application in material examination measurement of the electronic band gap of semiconductors, calculation of the Optical properties and volume of the Reflectance Loss in Photovoltaic Cells.

3.4.5 Fourier Transform Infrared Spectroscopy (FTIR):

Fourier Transform Infrared Spectroscopy (FTIR) is a technique which is used to achieve a spectrum of absorption, emission and photoconductivity of a solid, liquid or gas in infrared region. The range of Infrared region is 12800~10cm^{-1}. IR radiations pass over a sample. Some of the radiations absorbed and some of it distributed from side to side (transmitted). The resulting spectrum represents the molecular absorption and transmission, creating a molecular fingerprints of the sample. FTIR spectra exposes information of unknown materials, determine the quality and consistency of a sample and also the amount of components in a mixture.

3.6 Photocatalytic Activity Measurements:

Photocatalytic efficiency of m-TiO2, Ag-m-TiO2, N-m-TiO2, N-Ag/mTiO2 Nano composites was calculated by the degradation phenomenon. Methyl Blue (MB) was used for degradation. Photocatalytic degradation of organic compounds is assembled on semiconductor photochemistry. The most effective photocatalyst for this purpose is Titanium Dioxide. The degradation of Methyl Blue (MB) an organic pollutant stayed carried out in a 100mL quartz photochemical reactor. The reaction solution contained 0.05g catalyst and 50 mL aqueous solution of 20mgL-1 of dye. Light source was a 1000 watt halogen lamp. A cut-off glass filter was used to cut-off short wavelength components (λ< 420nm) of light. During the reaction water circulates to cool the photochemical reactor to conserve the solution temperature. First the suspension was sonicated for 10 min, and then then magnetically stirred in darkness for 30 min, to established adsorption-desorption equilibrium. The samples were collected at specific intervals and centrifuged to separate photo catalyst. The concentration of (MB) was analyzed using UV-visible spectrometer at their characteristic wavelength of 464nm, respectively.

CHAPTER # 04

Results & Discussion

4.1 X-ray Diffraction Spectroscopy:

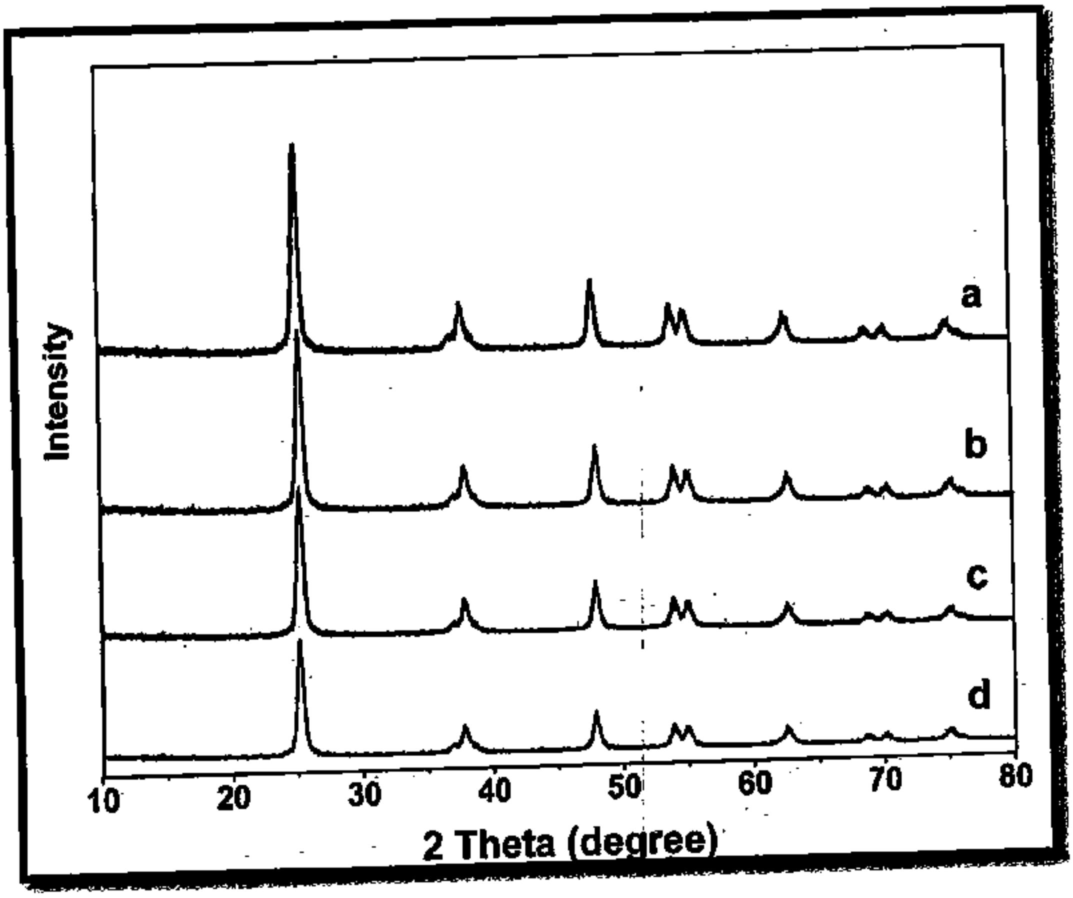


Figure 4.1. XRD patterns of pure TiO2 and different composites (a) pure m-TiO2 (b) Ag- doped m-TiO_2 (c) N doped m-TiO2 (d) Ag & N codoped m-TiO2

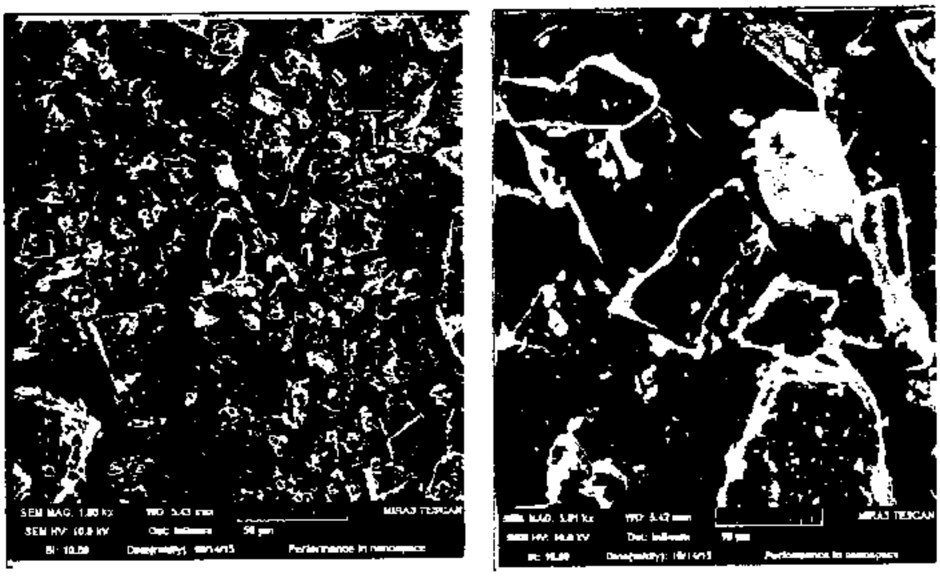
Figure 4.1 shows the XRD patterns of pure TiO_2 and different codoped photocatalyst. It can be perceived that the Ag & N doped M-TiO_2 samples show only representative peaks consistent to anatase phase TiO_2 (JCPDS 21-1272), but no obvious Silver components were detected in samples, although EDS analysis confirmed the existence of Ag (given in results and discussion). Therefore, it is believed that the silver components in Ag &N codoped m-TiO2 stayed highly distributed in the samples, with slight dimensions below XRD detection limit. The crystallite size of as prepared

TiO_2 is predictable around 9.1 nm using Scherer's equation grounded on XRD broadening of 101 peak.

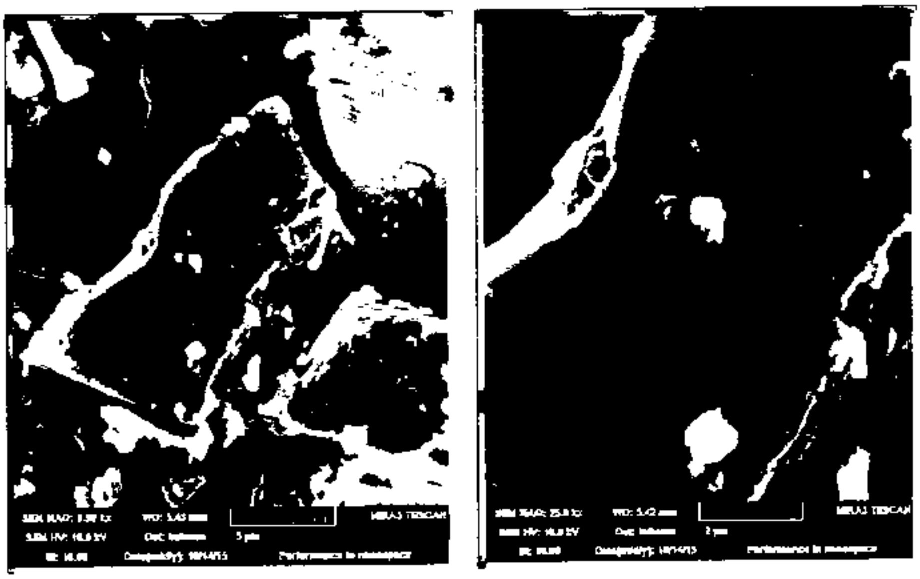
4.2 Scanning Electron Microscopy (SEM):

The surface morphology and microstructure of pure m-TiO2 and Ag-N-co doped m-TiO2 sample are observed by the SEM images. Sol–gel preparation results in amorphous titanium dioxide, which is calcined at elevated temperatures in order to convert it into a crystalline form. To prevent agglomeration during thermal-induced crystallization, surfactants or amphiphilic block copolymer is commonly added into the sol–gel solution, which is very efficient in templating nanostructures. The pure ordered mesoporous TiO2 was synthesized by the Sol-gel method using P123 surfactant as a template. The figures below reveals that the effect of P123 addition on surface microstructure of mesoporous-TiO2 was investigated by scanning electron microscopy which consists of irregular shaped primary particles. It has been concluded that the sample prepared by addition of P123 is porous in nature. These figures depicts that only irregular and agglomerated structures are obvious which show loose agglomerates with significant quantity of inter particle voids and pure mesoporous structure.

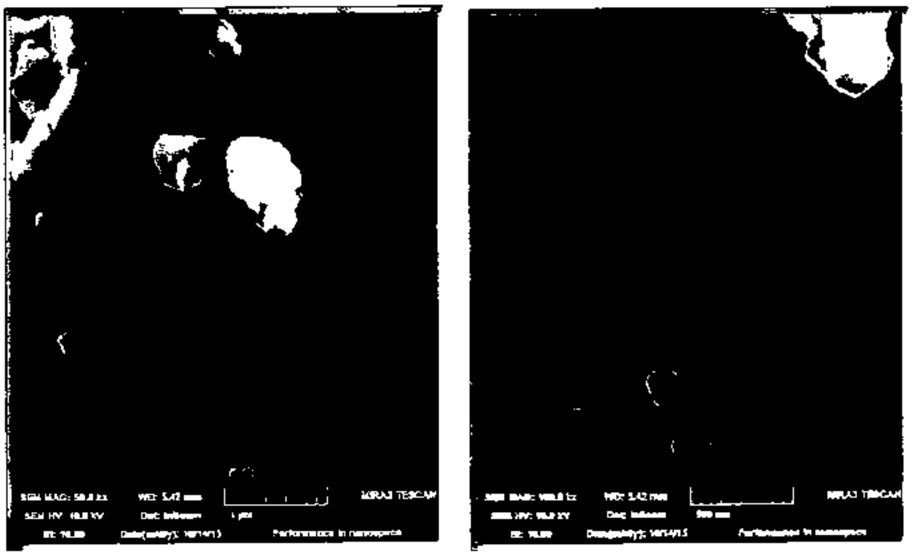
4.2.1 Composite m-Titanium Dioxide:



(a) (b)



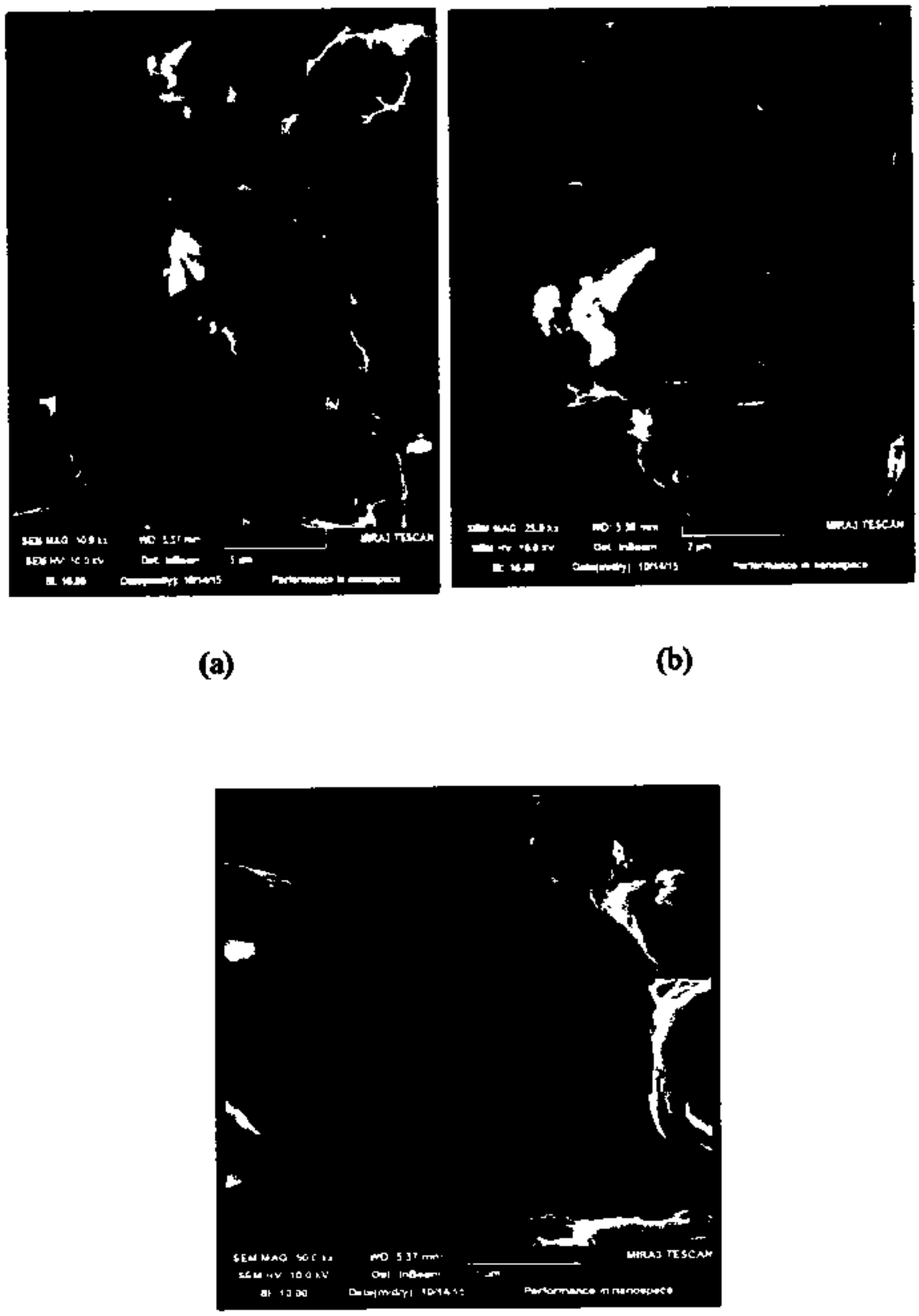
(c) (b)



(e) (f)

Figure # 4.2.1: SEM Images (a), (b), (c), (d), (e), (f) of Composite Codoped m-TiO_2 with Ag-N at different magnifications

4.2.2 Pure m-Titanium Dioxide:



(a) (b)

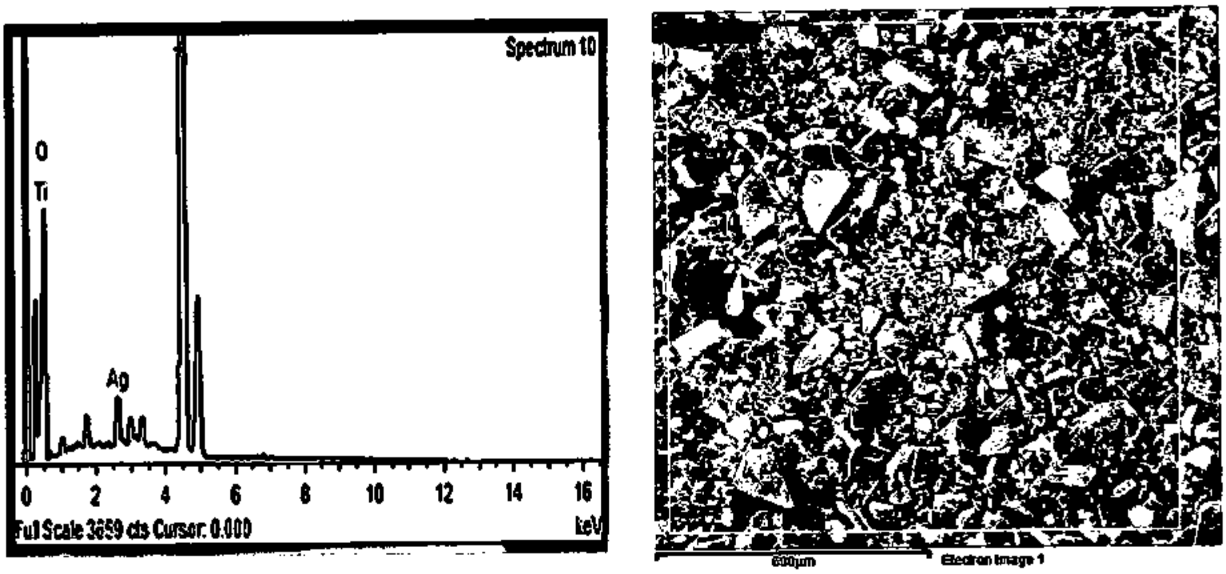
(c)

Figure # 4.2.2: SEM image of m-porous Titania (a), (b), (c) at different magnifications discloses mesoporousity.

4.3 Energy Dispersive X-ray Spectroscopy (EDS):

Quality analysis of the Nanocomposite and Pure m-TiO_2 was obtained by EDS and used to identify the composition of different element in the sample.

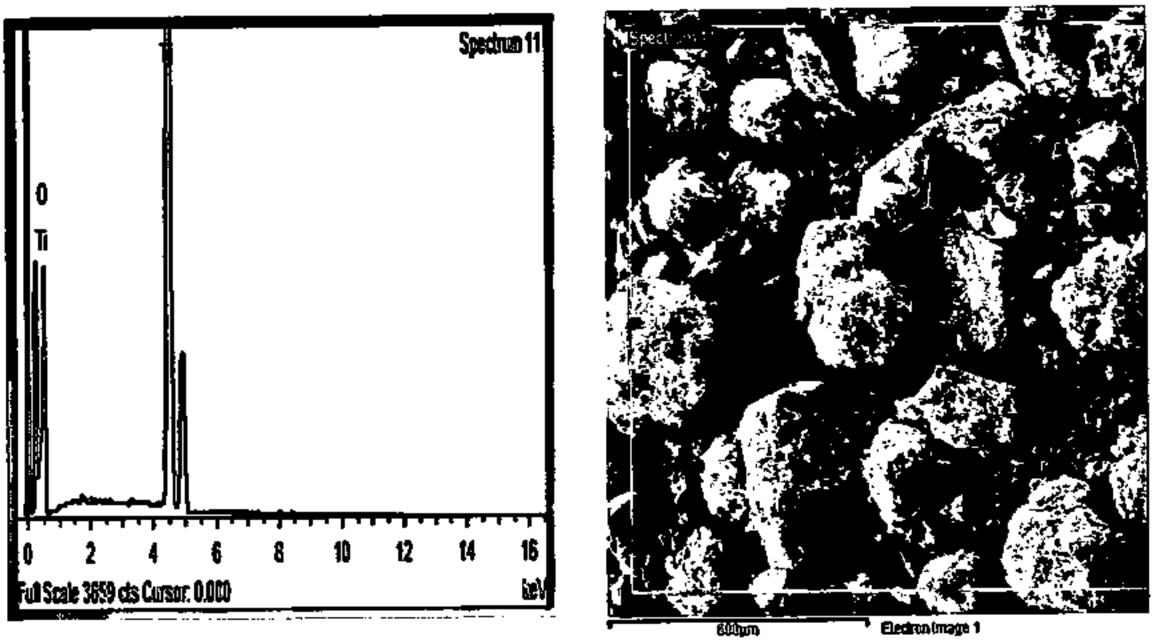
Figure 4.3 (a), (b) shows the 1% ratio of the element in the sample.



(a)

Figure # 4.3: EDS Image (a) of mesoporous Titania with 1% codoped with Ag & N

Element	Weight%	Atomic%
O K	45.05	71.41
Ti K	53.25	28.19
Ag L	1.70	0.40
Totals	100.00	



(b)

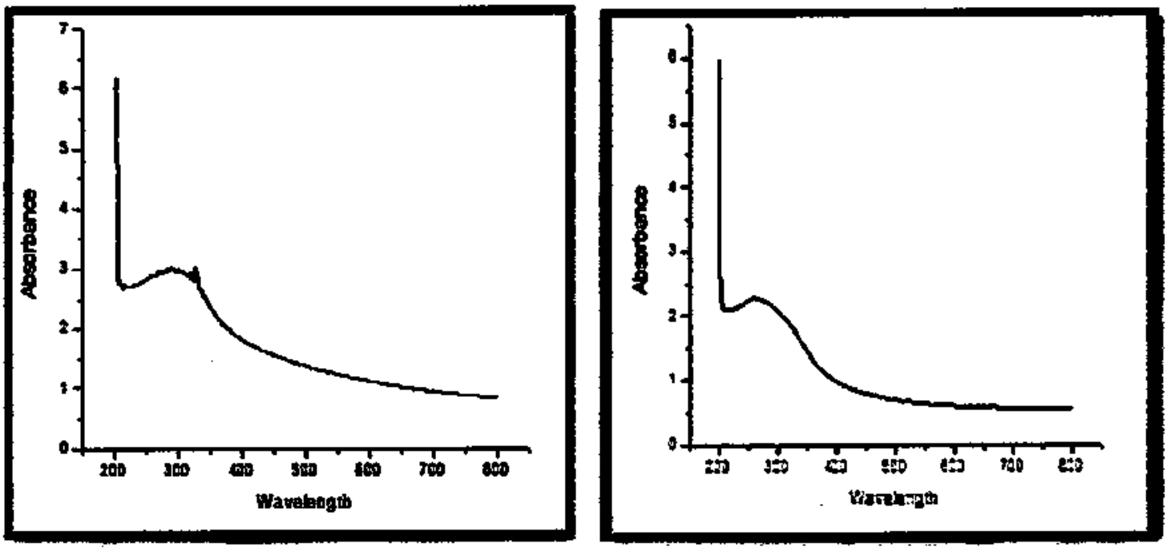
Figure # 4.3: EDS Image of (b) of pure mesoporous Titania with percentage.

Element	Weight%	Atomic%
O K	46.89	72.55
Ti K	53.11	27.45
Totals	100.00	

4.4 UV-vis Diffuse Reflectance Spectroscopy (DRS):

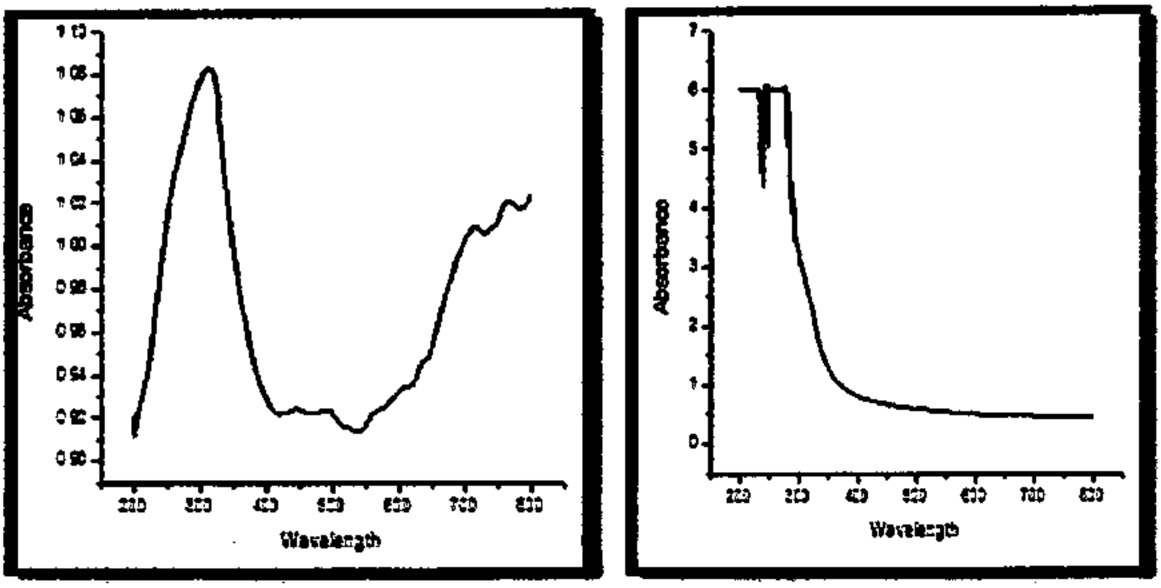
The Titania a UV light approachable semiconductor by funds of a band gap of 3.2 eV at wavelength of 387nm for Anatase and 3.0 eV at wavelength of 413 nm for Rutile. At this wavelength range Titania can absorb simply visible light. The mesoporous Titania, Ag doped mesoporous Titania, N doped mesoporous Titania and Ag & N codoped m-TiO_2 samples show substantial absorption about 400-600nm. This red-shifted absorption could be due to the oxygen vacancies generated during the co-doping process. The age band of these vacancies is due to the bulk and surface defects prompted by the codoping effect. The codoping with two elements can increase the number of oxygen vacancies in TiO_2 and thus sort the absorption further red shifted.

UV-visible diffuse absorption spectra of pure m-Titania and Ag-N codoped mesoporous Titania was explained below:



(a) (b)

Figure 4.4 (a) (b): UV-vis spectra of Ag doped $mTiO_2$ and codoped Titania



(c) (d)

Figure 4.4 (c) (d): UV-vis spectra of N doped mesoporous Titania and m-TiO_2

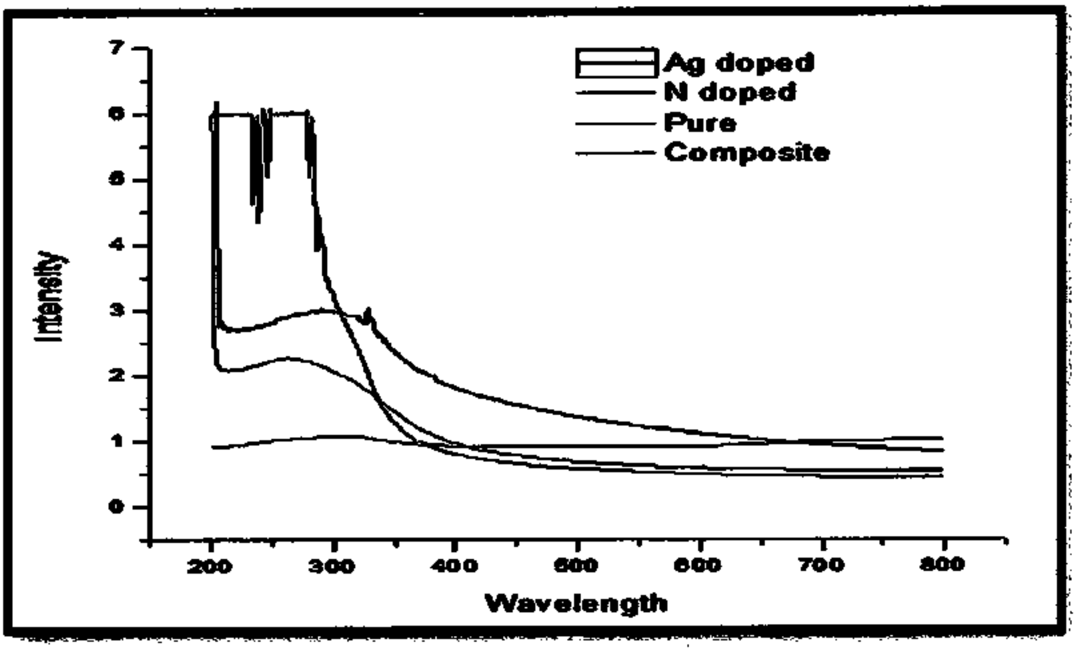


Figure 4.4 (e): UV-vis spectra of codoped (Ag & N) m-Titania

4.5 Fourier Transform Infrared Spectroscopy (FTIR):

The FTIR Spectra of pure Titania, co-doped/ composite and doped with N and Ag reveals that the intensities and broad band is ascribed to the stretching vibrations of Ti-O molecules and the deformation vibrations of (H-O-H) are indication of large amount of water molecules on the surface of catalyst. The presence of large extent of hydroxyl group are the favorable for photocatalytic process.

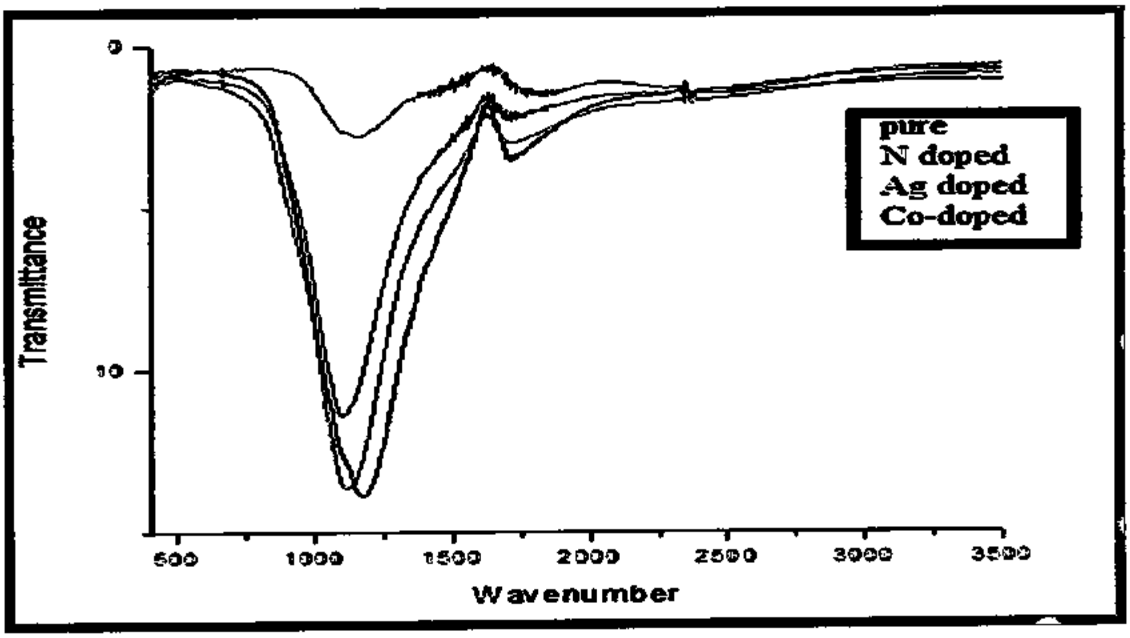


Figure 4.5: FTIR spectra of pure, composite and doped with N& Ag

4.6 Photocatalytic Degradation of Organics:

The photocatalytic degradation of the sample can be observed in the presence of Methylene blue. Pure mesoporous Titania displayed no significance absorbance for visible lights due to the large band gap of Titania (3.2 eV). The codoped Titania shows better photocatalytic activity than pure Titania and single element doped mesoporous Titania. In case of Ag doped Titania, the anatase titania act as an electron acceptor which is beneficial to the effective separation of electron hole pairs generated in TiO_2 and inhibits their recombination.

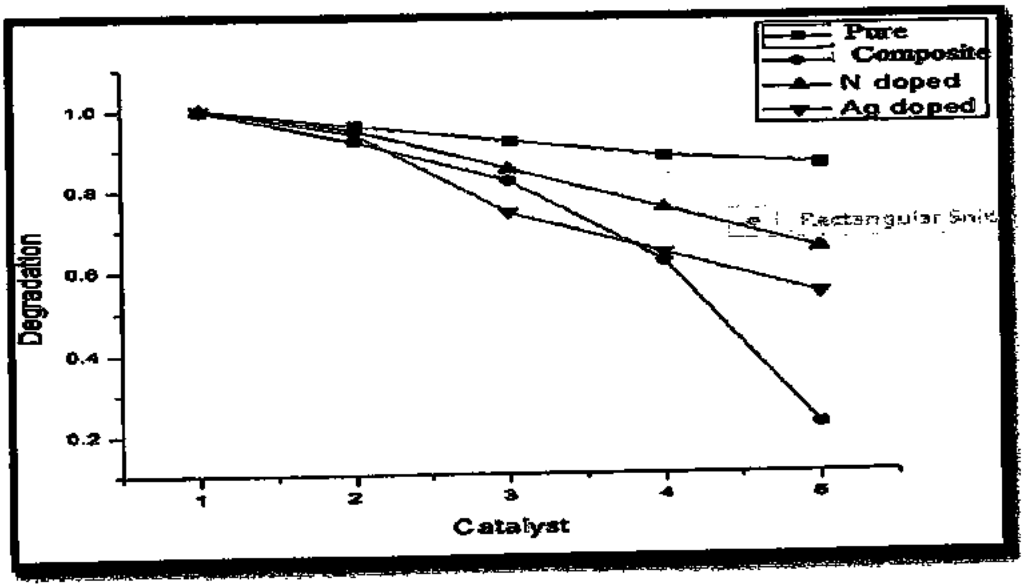


Figure 4.5: Photocatalytic degradation of Methylene blue by using m-TiO_2, Ag & N doped mesoporous, Ag doped m-TiO_2, and N doped m-TiO_2

CONCLUSION

- Titania was successfully synthesized by using novel combination of Ag and N.
- Ag & N codoped mesoporous Titania Photocatalyst was prepared by using P123 surfactant as a template in the Solgel method.
- As a result of codoping of TiO_2 with Ag & N, photocatalytic activity shifts to visible region. Therefore, this is a suitable combination for enhancement in photocatalytic activity is assumed to be promising visible-light-driven photocatalyst.
- So Ag & N codoped m-TiO_2 catalyst shows prominent absorption in 400-600nm range. Thus this combination shows a great progress for the application in photo catalytic process.

References

[1] Guozhong Cao. (2003), Nanostructure & Nanomaterials.

[2] Walsh, S., Mangematin, V. (2012), Technovation 32,157–160.

[3] S. K. Sahoo, PhD, S. Parveen, Ms, J.J.Panda. (2007), Nanotechnology, Biology and Medicine 3, 20–31.

[4] Kumiko Miyazaki, Nazrul Islam. (2007), Technovation 27, 661–675.

[5] Kelly A. (1985), Compos Sci Technol, 23 (3): 171–99.

[6] Kelly A, Zweben C. (2000), Editors, Vols. 1-6 Elsevier.

[7] T.T Eric, Li Chunyu, Chou Tsu-Wei. (2005), Journal Composite Science & Technology, Vol.65, Pp.491–516.

[8] Pedro Henrique Cury Camargo, Kestur Gundappa Satyanarayana, Fernando Wypych. (2009), Journal Materials Research, Vol. 12, Pp. 1–39.

[9] Fujishima A, Rao T N and Tryk D A 2000 J. Photochemical. Photobiol. C 1- 1

[10] Mills A and Le Hunte S 1997 J. Photochem. Photobiol. A 108 -1

[11] Sajjad Shamaila, Ahmed Khan Leghari Sajjad, Feng Chen, Jinlong Zhang Catalysis Today 175 (2011) 568–575

[12] Yamauchi Y, Suzuki N, Radhakrishnan L and Wang L 2009 Chem. Rec. 9- 321

[13] Kimura T and Kuroda K 2009 Adv. Funct. Mater. 19- 511

[14] Ariga K 2004 Chem. Rec. 3- 297

[15] Tianhao Ji, Fang Yang, Yuanyuan Levy, Jiayue Sun. (2009), Materials Letters 63, 2044-2046

[16] Subramanian V, Wolf E, Kamat Pv. (2001), J Phy Chem, B.105: 11439-46

[17] Mohamed Abdelmoula. (2011), Northeastern University.

[18] V. W.H.Baur. (1961), Acta Crystalloger. 14,214.

[19] Peters G, Vill V (1989) Verlag Berlin.

[20] Burdett Jk, Hughbanks T, Miller Gj, Richardson Jw Jr, Smith Jv (1987) J Am Chem Soc 109: 3639.

[21] Ceram. (2002), Titanium Dioxide—Titania, Azom Version 2.0, Azom Pty. Ltd258.

[22] Enc. Of Minerals, 2nd Ed. (1990).

[23] Beltran A, Gracia L, Andres J. (2006), J Phys Chem B 110: 23417

[24] Daude N, Gout C, Jouanin C. (1977), Phys Rev B 15:3229

[25] Mardare D, Tasca M, Delibas M, Rusu Gi. (2000), Appl Surf Sci 156:200

[26] R. Zallen and M.P. Moret. (2006), Solid State Communications, V 137, Issue 3, Pages 154-157.

[27] Azom Version 2.0, Azom Pty. Ltd

[28] (1990), Enc. Of Minerals, 2nd Ed.

[29] Y.Ao etal. /Journal of Physics and Chemistry of Solids69 (2008)2660–2664

[30] M. Zalas / Catalysis Today 230 (2014) 91–96

[31] Zdenek Dohnálek, Igor Lyubinetsky, Roger Rousseau. (2010), Progress In Surface Science 161-205.

[32] Yin H, Wada Y, Kitamura T, Kambe S, Murasawa S, Mori H, Sakata T, Yanagida S (2001), J Matter Chem 11(6):1694

[33] L.T. Lu, L.D. Tung, J. Long, D.G. Fernig, N.T.K. Thanh. (2009), J. Mater. Chem. 19, 6023.

[34] T. Beuvier, B. Calvignac, G.J.R. Delcroix, M.K. Tran, S.Kodjikian, N. Delorme,(2011), J.Mater.Chem. 21, 9757.

[35] W. Wei, G.H.Ma, G.Hu, D.Yu, T.Mcleish, Z.Su, Z.Shen. (2008), J.Am.Chem.Soc. 130, 15808.

[36] J.J.Wu, X.J.Lue, L.L.Zhang, F. Q.Huang, F.F.Xu. (2009), Eur.J.Inorg.Chem.40, 2789.

[37] S.C.Yang, S.C.Yang, J.Kim, J.M.Hong, H.G.Kim, I.D.Kim. (2008), Adv. Funct, Mater.20, 1059.

[38]X.J.Lu,X.L.Mou,J.J.Wu,D.W.Zhang,L.L.Zhang,F.Q.Huang,F.F.Xu.(2010),Adv.Funct.Mater.20,509.

[39] M.Luo, K.Cheng, W.J.Weng, C.L.Song, P.Y.Du, G.Shen, G.Xu, G.R.Han. (2009), Nanoscale Res.Lett.4, 809.

[40] P.Z.Araujo, V.Luca, P.B.Bozzano, H.L.Bianchi,G.J, G.J, G.J, G.J, G.J .D.A.Arturosoler-Illia, M.A.Bleasa.(2010), Acsappl.Matter.Interfaces 2,1663.

[41] Binary Prasai, Bin Cai, M. Kylee Underwood, James P. Lewis, D.A. Drabold, J Mater Sci Doi 10, 1007/S10853-012-6439-6

[42] Yalei Zhang, Yadan Guo, Gaoke Zhang, Yuanyuan Gao. (2011), Applied Clay Science 51, 335-340

[43] M.E.Davis. (2002), Nature. 417, 813-821

[44] S.Yuan, Q.Sheng, J.Zhang, F.Chen, M.Anpo, W.Dai. (2006), Catal.Lett. 107, 19-24.

[45] A.M.Lui, K.Hidajat, S.Kawi, D.Y.Zhao. (2000), Chem. Commun. 1145-1146

[46] Sajjad Shamaila, Ahmed Khan Leghari Sajjad, Feng Chen, Jinlong Zhang. (2010), Materials Research Bulletin 45, 1375-1382.

[47] Tae-Jung Ha, Sin-Young Jung, Jun-Hyun Bae, Hong-Lim Lee, Ho Won Jang, Seok-Jin Yoon, Sangwoo Shin, Hyung Hee Cho, Hyung-Ho Park. (2011), Microporous and Mesoporous Materials 144, 191-194.

[48] Dvoranová D, Brezová V, Mazur M, Malati Ma. (2002), B: Environ. 37: 91-105

[50] Martin St, Morrison Cl, Hoffmann Mr. (1994), J Phys Chem. 98: 13695-704.

[51] Jiang Hb, Gao L, Zhang Qh. (2002), J Inorg Mater. 17: 787-91.

[52] U.G. Akpan, B.H. Hameed. (2011), Journal of Colloid and Interface Science 357, 168-178.

[53] Xu Xh, Wang M, Hou Y, Yao Wf, Wang D, Wang H. (2002), J Mater Sci Lett.21 : 1655-60.

[54] Le Yu, Shuai Yuan, Liyi Shi, Yin Zhao, Jianhui Fang. (2010), Microporous and Mesoporous Materials 134, 108-114.

[55] Shuai Yuan, Qiaorong Sheng, Jinlong Zhang, Feng Chen, Masakazu Anpo, Qinghong Zhang. (2005), Microporous and Mesoporous Materials 79, 93-99.

[56] J.J. Yang, D.X. Li, Z.J. Zhang, Q.L. Li, H.Q. Wang. (2000), J. Photochem. Photobiol. A: Chem., 137, 197.

[57] Z.H. Yuan, J.H. Jia, L.D. Zhang. (2002), Mater Chem. Phy., 73.323.

[58] H. Takagi, Y. Fujishiro, M. Awano. (2001), J.Mater. Sci., 36, 949.

[59] L.Y.Shi, H.C.Gu, C.Z.Li. (1999), Chin.J.Catal. 20,338.

[60] R. Asahi, T. Morikawa, T. Ohwaki, A. Aoki, Y. Taga. (2001), Science 293-269.

[61] Y. Sakatani, K. Okusato, H.Kioke, H. Ando. (2001), Photocatalysis 4, 51.

[62] T. Ihara, M. Ando, S. Sugihara. (2001), Photocatalysis 5, 19.

[63] T. Umebayash, T. Yamaki, H. Ito, K. Asai. (2002), Appl. Phys. Lett. 81, 454.

[64] H. Irie, Y. Watanabe, K. Hashimoto, (2003), Chem. Lett. 32, 772.

[65] Wei Zhang A, Linda Zou, Lianzhou Wang. (2009), Applied Catalysis A: General 371, 1-9.

[66] Kexin Li, Tong Chen, Liushui Yan, Yuhua Dai, Zhimin Huang, Huiqin Guo, Lingxiao Jiang, Xuehui Gao, Jingjing Xiong, Dongyang Song. (2012), Catalysis Communications 28, 196-201.

[67] Jonghun Lim, Palanichamy Murugan, Narayanan Lakshminarasimhan, Jae Young Kim, Jae Sung Lee, Sang-Hyup Lee, Wonyong Choi. (2013), Journal of Catalysis.

[68] Yanhui Ao, Jingjing Xu, Degang Fu, Journal of Physics and Chemistry of Solids 69(2008) 2660–2664.

[69] Xingtian Yin, Colloids and Surfaces A: Physicochemical. Eng. Aspects 410 (2012) 153– 158

[70] Zhiyan Hu, Materials Letters106 (2013)421–424

[71] Ahmed Khan Leghari Sajjad, Sajjad Shamaila, Jinlong Zhang, Materials Research Bulletin 47 (2012) 3083–3089

[72] Maciej Zalas, Catalysis Today 230 (2014) 91–96.

[73] Ibrahim El Saliby, Journal of Industrial and Engineering Chemistry 17 (2011) 358–363

[74] Zhifeng Jiang, Nanoscale, 2015, 00, 1–14

[75] Xia Yang, Journal of Physics and Chemistry of Solids69 (2008)2660–2664.