STUDY OF DEGRADATION PARAMETERS BY USING CO-DOPED TUNGSTEN TRIOXIDE (WO_3) PHOTOCATALYST

By

ANAM SHAHID
(197-FBAS/MSPHY/F13)

Supervisor Name:

DR.SHAMMAILA SAJJAD

Co- Supervisor Name:

DR. SAJJAD AHMED KHAN LEGHARI

DEPARTMENT OF PHYSICS

FACULTY OF BASIC AND APPLIED SCIENCES,
INTERNATIONAL ISLAMIC UNIVERSITY,
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ANAM SHAHID

(Registration No. 197-FBAS/MSPHY/F13)

A thesis submitted to

Department of Physics

For the award of the degree of

MS Physics

Signature ____________________

Dr. Shahzad Sajjad

(Chairman, Department of Physics)

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Signature ____________________

(Dean FBAS, IIU, Islamabad)

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FACULTY OF BASIC AND APPLIED SCIENCES
DEPARTMENT OF PHYSICS

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FINAL APPROVAL

It is certified that the work presented in this thesis entitled by ''**Ms. Anam Shahid**' having **Registration No. 197-FBAS/MSPHY/F13** is of sufficient standard in scope and quality for the award of degree of MS Physics from International Islamic University, Islamabad

COMMITTEE

External Examiner

Dr Mohsin Siddique
Director TPD,
National Centre of Physics

Internal Examiner

Dr Sadaf Jamil
Assistant Professor,
Department of Physics, FBAS, IIUI

Co-Supervisor

Dr Sajjad Ahmed Khan Leghari
Principal Scientist,
PAEC

Supervisor

Dr Shammaila Sajjad
Assistant Professor,
Department of Physics, FBAS, IIUI

A thesis submitted to

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International Islamic University Islamabad

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MS in Physics

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Anam Shahid

(197-FBAS/MSPHY/F13)

DEDICATION

To

My loving Parents

In the name of Almighty Allah (S.T). The most Gracious and most Merciful.

Acknowledgement

Foremost, I am thankful to Almighty Allah (S T) whose kind divine empower me the knowledge, wisdom, talent, devotions & enabled me to complete my M S Degree In fact without Allah's blessings, this success could not be achieved I pray and hope that his merciful blessings to me will keep on showing in future as well **(INSHALLAH)**

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ANAM SHAHID
(197-FBAS/MSPHY/F13)

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Chapter No 1.

Introduction

1.1 Nanotechnology:

Nanotechnology is think through to be the first important international research introductory of the 21st century [1] Nanotechnology is formed from two words "Nano" and "Technology" where prefix "Nano" came from a Greek word "dwarf" which means a nanometer is **10^{-9}** of a meter a distance equal to two to twenty atoms or about 10 water molecules or equal to the 6 carbon atoms width [2] Nanotechnology is the invention and use of applied structures designed from atomic or molecular scale with at least one distinctive dimension measured in nanometers Their size countenances them to show new and protruding improved chemical, physical and biological properties, processes and occurrences because of their size Significant changes in performance are affected not only by constant variation of features with diminishing size, but also by the appearance of totally new phenomena such as quantum confinement A usual example of which is that the color of light emitting from semiconductor nanoparticles hinge on on their sizes

"Nanotechnology can be well-defined as the science and engineering convoluted in the design, synthesis, characterization and application of materials and devices whose smallest functional group in at least one dimension (1-D) is on the nanometer scale $10^{-9}$of a meter."

Or

"Nanotechnology can be demarcated as testifying to materials and systems with structures and components presenting different and considerably improved physical, chemical and biological properties, as well as to the phenomena and procedures enabled by the ability to control the material properties on the Nano-scale size."

Or

Nano technology is the subdivision of technology that deals with sizes and tolerances of less than 100 nanometres, particularly the operation of individual atoms and molecules.

Therefore Nano technology is reflected as a new forthcoming technology which lead new scopes to science and technology This new field has widespread collection of applications and it upsets the different fields of technology such as pharmacy, scientific tools, biotechnology, industrial manufacturing processes, advanced materials, electronics [3]

1.2 Nano Scale:

The name Nano means "Dwarf". Nanoscale refers to the 10^{-9} power, or one billionth of a meter In these terms it denotes to a meter, or a Nano meter, which is on the scale of atomic diameters

Example:

Some of the examples of nanoscale are

sheet of paper is about 100,000 nm thick
Human hair measures roughly 50,000 to 100,000 nm in diameter
Fingernails grow 1 nm every second
A red blood cell is of 5000 nm
Average size of a germ is 100 nm.
One inch equals 25 4 million nanometers

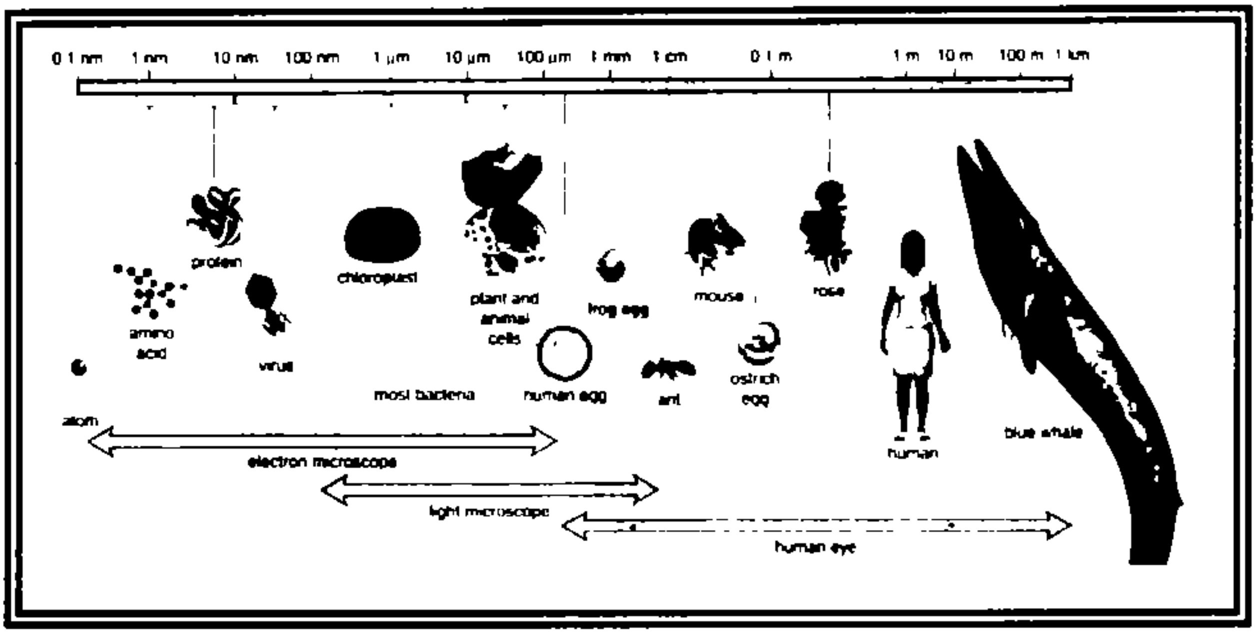


Figure 1.1: Things compared with nanoscale

1.2.1 Background of Nanotechnology: Theoretical Roots:

Conferring to R D Booker it is pretty hard to refer to the history of nanotechnology because of two main reasons **"Uncertainty of the term nanotechnology and Improbability of the time period analogous to the early stages of nanotechnology growth"**

But though, the main awareness of nanotechnology was given by

Richard Feynman
Norio Taniguchi
K Eric Drexler

1.2.1.1 Richard Feynman: There's Plenty Of Room At The Bottom (1959):

The derivation of nanotechnology was initiated with the speech of physicist Richard Feynman in December 1959 In his well-known speech "There's Plenty of Room at the Bottom" at an American Physical Society conference at the California Institute of Technology he said that,

"I need to build a billion tiny industrial unit, replicas of each other, which are manufacturing instantaneously. . . The ideologies of physics, as far as I can see, do not express in contradiction of the possibility of reversing things atom by atom. It is not an effort to encroach upon any laws; it is rather, in principle, that can be done; but in run-through, it has not been done because we are too big". — (Richard Feynman, Nobel Prize winner in physics)

In his communication he recommended the power and perception of nanotechnology He suggested that the obstruction of knowledge and technology at which people should be directing could exist not only in physics but also in other Nano-sized fields

1.2.2.2 Norio Taniguchi (1974):

The word "nanotechnology" was castoff for the first time in 1974 by Norio Taniguchi at University of Tokyo in an International Conference on Precision Engineering (ICPE) In which he used it to aspect to the excellence to engineer materials intensively at the Nano scale level The European Society for Precision Engineering and Nanotechnology presented Professor Taniguchi with its 1st Lifetime Achievement Award in Bremen, May 1999

1.2.2.3 Eric Drexler: "Molecular Manufacturing,"(1981):

In the 1980s, Eric Drexler authored the momentous book on Nano technology "Engines of Creation" (Drexler 1986), in which he presented the idea of molecular engineering In 1981, Drexler put out his first article on the subject in the significant scientific journal Proceedings of the National Academy of Sciences Titled **"Molecular engineering: An approach to the development of general capabilities for molecular manipulation."**

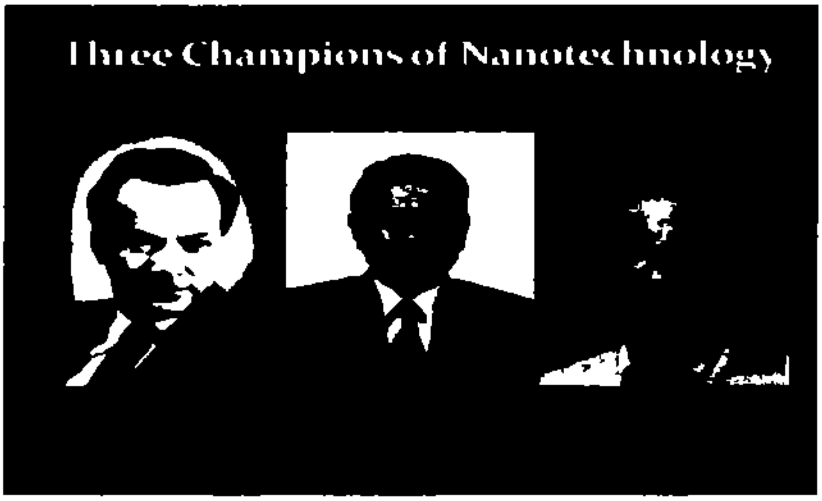


Figure 1.2: Discoverers of Nano technology

Other Scientist's Role to Nanotechnology:

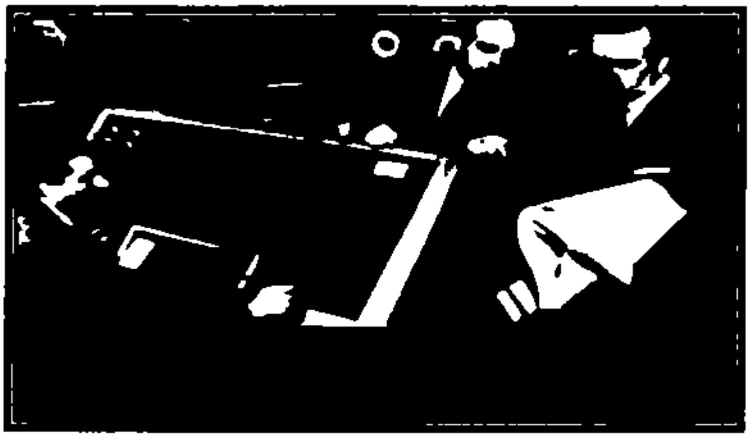


Figure1.3: Different scientist's contribution to nanotechnology

In initial 1980s Nanotechnology and Nano science became so much progressive with two key developments

The birth of cluster science

The invention of the scanning tunneling microscope (STM)

Year	**Scientist name**	**History**
1981	Gerd Binnig and Heinrich Rohrer	Invention of scanning tunneling microscope (STM).
1982	Rosenberg	Systematically examine the nanoscale structures and the developments of nanoscale technologies
1985	Harry Kroto	Discovered fullerenes which are also called Bucky balls
1986	Calvin Quat and Christoph Gerber	Atomic force microscope
1990		The first academic nanotechnology journal was published
1991	Sumio Iijima	discovered carbon nanotubes
1993	Feynman	First Feynman Prize was awarded
2000		President Bill Clinton announced the U S National Nanotechnology Initiative (NNI)

Table 1.1: Important successes in field of nanotechnology

1.3 Tungsten Trioxide (WO_3)

In the recent years mainly due to the distinctive properties of basic elements that are brought about by altering their atomic and molecular properties nanoparticle research had developed rapidly By advantage of these properties, many applications of nanoparticles have found in the field of biomedicine, cosmetics, electronics, coatings and plastics, etc Here we deals with the properties and applications of tungsten oxide nanoparticles

Tungsten trioxide or tungstic anhydride symbolized as WO_3 is a chemical compound that contain oxygen and the transition metal tungsten It is found as an intermediary in the recovery of tungsten from its raw materials [4] It occurs naturally in form of hydrates like Tungstite ($WO_3 H_2O$), Meymacite ($WO_3 2H_2O$) and Hydro Tungstite (H_2WO_4) Nano powders or nanoparticles are obtainable in the form of Nano fluids or faceted high surface area oxide particles revealing magnetism Further forms in which these particles are existing are dispersed, transparent, high purity and coated forms

1.3. 1 Chemical Properties

The chemical properties of tungsten oxide are listed below in the following table

Molecular Formula	**WO_3**
Molecular Weight	**231.8382 g/mol**
Exact Mass	**231.935675 g/mol**
Monoisotopic Mass	**231.935675 g/mol**
Complexity	**61.8**

Table 1.2: Chemical properties of tungsten trioxide.

1.3. 1 Physical Properties:

Tungsten trioxide nanoparticles appears in the yellowish color powder having approximately spherical morphology The crystal arrangement of tungsten trioxide is temperature dependent This is tetragonal at temperatures above 740 °C, orthorhombic from 330 to 740 °C, monoclinic from 17 to 330 °C, and triclinic from -50 to 17 °C The most collective assembly of WO_3 is monoclinic The table given below affords the physical properties of tungsten trioxide

Density	**7.16 g/cm^3**
Molar Mass	**231.84 g/mol**
Appearance	**Canary yellow powder**
Solubility in water	**Insoluble**
Solubility	**Slightly soluble in HF**

Table 1.3: Physical properties of tungsten trioxide.

1.3. 2 Thermal Properties:

The thermal properties of tungsten trioxide nanoparticles are given below

Properties	**Metric**
Melting Point	**1473 °C**
Boiling Point	**1700° C**

Table 1.4: Thermal properties of tungsten trioxide.

1.3. 3 Uses of Tungsten Trioxide:

Tungsten trioxide is castoff for many purposes in daily life It is commonly used in industry to manufacture tungstate for x-ray screen phosphors, for fireproofing fabrics [5], and in gas sensors [6] Due to its rich yellow color, WO_3 is also used as a pigment in ceramics and paints [1]

In recent years, tungsten trioxide has been employed in the production of electro chromic windows, or smart windows These windows are electrically switchable glass that change light transmission properties with an applied voltage [7, 8] This allows the user to tint their windows, changing the amount of heat or light passing through

1.4 Copper:

Copper is a chemical element with symbol **Cu** Its atomic number is 29 and is a flexible metal with very high thermal and electrical conductivity Copper belongs to group 11 of the periodic table, and it can share certain characteristics It has one s-orbital electron on top of a filled d-electron shell and is described by high ductility and electrical conductivity The occupied d-shells in these elements don't donate much to the interatomic interactions, which are dominated by the s-electrons through metallic bonds Unlike in metals with incomplete d-shells, metallic bonds in copper are lacking a covalent character and are relatively weak [9]

1.4. 1 Physical properties of Copper:

Uncontaminated copper is soft and flexible It has a freshly exposed surface having reddish-orange color At the macroscopic scale, presence of prolonged imperfections to the crystal lattice, such as grain boundaries, obstructs drift of the material under smeared stress, thus increasing its hardness This is the reason that copper is usually supplied in a fine-grained poly crystalline form, which has more strength than monocrystalline forms [10]

1.4. 2 Chemical Properties of Copper:

Copper does not counter with water but it does gradually retort with atmospheric oxygen to make a layer of brown-black copper oxide which, dissimilar the rust which forms when iron is visible to moist air, protects the primary copper from more widespread oxidization A green layer of corrosion (copper carbonate) can regularly be seen on deep-rooted copper constructions such as the Statue of Liberty Copper discolors itself when exposed to sulfides, which act in response with it to form numerous copper sulfides [11]

1.4. 3 Applications:

The main utilization of copper is in electrical wires i e 60%, tiling and drainage system i e 20% and industrial machinery i e 15% Copper is generally castoff as an uncontaminated metal, however when a advanced stiffness is compulsory it is pooled with further elements to make an alloy such as brass and bronze [12] A little part of copper amount is used in manufacture of compounds for nourishing appendages and fungicides in agricultural science [13, 14] Machining of copper is possible, although it is usually necessary to use an alloy for intricate parts to get good machinability characteristics

In liquids Copper compounds are castoff as a wood antibacterial, mainly in giving novel portion of structures during renewal of damage due to dry rot Textile strings use copper to create antimicrobial protective fabrics [15, 16] as do ceramic glazes, stained glass and musical instruments Electroplating commonly uses copper as a base for other metals such as nickel

Copper is used in etching, engraving as the printing plate Copper oxide and carbonate is used in glassmaking and in clay paints to divulge green and brown colors

1.5 Nitrogen:

Nitrogen is a nonmetal whose electronegativity is 3 04 [17] There are 5 electrons in its outer most shell and is, hence, trivalent in most compounds The triple bond in molecular nitrogen (N2) is one of the solidest The subsequent trouble of transformation of N2 into other compounds, and the easiness and related high energy release of changing nitrogen compounds into elemental N2, have subjugated the role of nitrogen in both environment and human cost-effective accomplishments

1.5.1 Properties of Nitrogen:

Molecular nitrogen reduces (turn to liquid) 2at 77 K (−195 79 °C) and freezes at 63 K (−210 01 °C) [18], into the beta hexagonal close-packed crystal allotropic form Lower from 35 4 K (−237 6 °C) nitrogen shows the cubic crystal allotropic form also known as the alpha phase [19] Liquid nitrogen, a liquid closer to water in look, but with 80 8% of the density The density of liquid nitrogen at its boiling point is 0 808 g/mL, is a common cryogen [20] Unbalanced allotropes of nitrogen containing more than two atoms of nitrogen have been formed in the laboratory, like N3 and N4 [21] Under very high pressures (1 1 million atm) and high temperatures (2000 K), as formed using a diamond anvil cell nitrogen polymerizes into the single-bonded cubic tasteless crystal structure The structure is similar to that of diamond, and both have tremendously strong covalent bonding N4 is called "nitrogen diamond" [22] Other as yet not produced allotropes include hexazine N6 (a benzene analog) [23] and octaazacubane N8 (a cubane analog) [24] The previous is anticipated to be extremely unstable, while the final is prophesied to be kinetically stable, for motives of orbital symmetry [25]

1.5.2 Applications of Nitrogen:

Nitrogen is castoff in high Reynolds number wind tunnels, heat treating furnaces and autoclaves to help create unbelievably resilient but lightweight materials Nitrogen is also used as a succor gas for laser cutting applications It is also utilized as a pressurizing gas It can help propel liquids over pipelines It is also castoff to shield oxygen-sensitive materials from the air and to eliminate volatile organic chemicals from process streams Assembly plants, use nitrogen in grouping with other bonding gases to weld auto parts, frames, mufflers and other mechanisms because of its capability to provide the essential atmosphere needed to produce satisfactory welds with any material It's also a significant safety constituent in airbags

Nitrogen is also used as an inert industrial gas It is used as a covering agent to separate complex products and developments from air It is also used as an eradication agent in piping and apparatus to prevent contagion

Nitrogen is an important cryogenic agent in cooling, chilling and food freezing Due to its tremendously cold temperatures, absorption freezing in liquid nitrogen is the fastest freezing method known for producing (IQF) foods It also plays a key role in tumbling spoilage, discoloration and off–flavors, giving asset to trade wrapping

A transporter and removal gas in steel manufacture, nitrogen is used to stop oxidation and is an important component in the heat-treating procedure The oil and natural gas industry utilizes nitrogen to upsurge tank reserves and breakage hydrocarbon-bearing developments to expressively increase the manufacture of oil and gas, and to recover operating effectiveness Nitrogen is recycled as a removal gas in stainless steel tube welding It is also used as a succor gas for laser cutting, and enhances plasma cutting

1.6 Photo catalysis:

Photo catalysis is the most investigated phenomena as it plays an important role for the conversion of solar energy into chemical fuel, electricity and in the decomposition of organic pollutants [26] Light is used to stimulate the catalyst to pledgee the redox reaction concerning the photo generated (electrons and holes) and the adsorbed species on the external of the catalyst In photo catalysis, light is utilized to trigger the catalyst to initiate the redox reaction between the photo produced electrons and holes and the adsorbed species on the surface of the catalyst

1.6.1 Basic mechanism of the photo catalysis:

Following are the basic steps of photo catalysis,

First of all, the incident light relates with the semiconductor material that is known as photo catalyst If the incident light energy is greater than the band gap of the photo catalyst, then this light energy will be captivated by the photo catalyst and excite the electrons from the valence band (VB) to the conduction band (CB), leaving free holes in the valence band After the creation of photo generated electron hole pair, two prospects can rise

- One of the prospects is the recombination of these species due to which heat is created
- Secondly, the movement of these species towards the surface to initiate the redox reaction

Photo produced electrons at surface start the reduction reaction with adsorbed species while holes produce strong oxidizing agents similar to hydroxyl radical by directly reacting with surface hydroxyl groups or oxidizing adsorbed species

Apart from these reduction and oxidation reactions in photo catalysis there are some subordinate reactions, which also occur These reactions develops the driving force for number of important photo catalytic applications

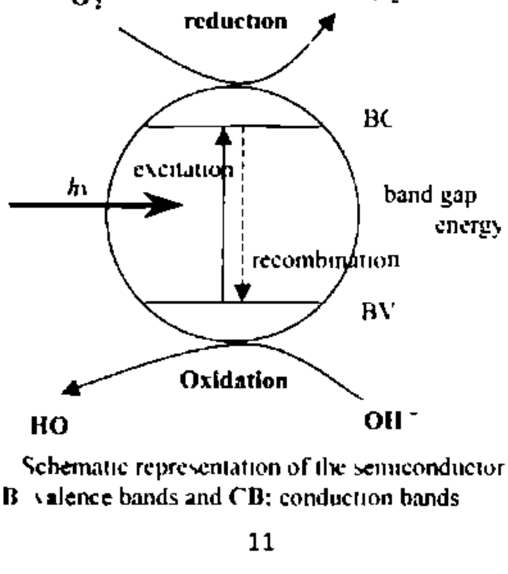


Figure 1.4: Schematic representation of the semiconductor materials
VB valence bands and CB: conduction bands

1.6.2 Properties of photo catalyst:

To show outstanding photo catalytic performance photo catalysts must have characteristic properties, corresponding small particle size, specific surface area or large space concerning the electronic levels to avoid the recombination of photo generated electron hole pair All of these properties can be accomplished by using Nano photo catalyst [27]

One main problem that is stumbled upon with photo catalyst is its separation from the reaction medium To overwhelm this problem, magnetic separation of photo catalyst has been suggested as a hopeful solution

The magnetically detachable photo catalytic systems are easy to handle as their separation from reaction medium do not require purification or centrifugation process Hence, the physical separation of a photo catalyst can easily be consummate by using the magnetically divisible photo catalysts [26] WO_3 as a photocatalyst has many advantages It needs small post-processing, which makes it inexpensive It is resistant to corrosion and inert

1.7 Catalyst:

Surrounded by many visible energetic photo catalysts, tungsten oxide (WO3), sometimes expressed as WO_{3-x} ($x = 0–1$),is auspicious photo catalyst outstanding to its small band gaps going from 2 5 to 3 0 eV, 1from 2 5 to 3 0 eV, conditionally to the stoichiometry, crystal-like assemblies and deficiencies Furthermore, the extraordinary oxidation power of valence band (VB) holes (+3 1-3 2 VNHE), nontoxicity, and own physical and chemical elasticity in the direction of punitive surroundings such as uninterrupted dealings to water and solar contamination make it very attention-grabbing photo catalyst Tungsten trioxides is discerned that to be potentially advantageous for different applications such as electrochemical [28], gas sensing [29], especially photocatalytic [30-33]

1.8 Doping:

Doping is a technique to acquaint with impurities into intrinsic semiconductor for the reason of modifying its electrical properties impurities presents in the semiconductor are according to the type of the semiconductor Lightly and reasonably doped semiconductors are mentioned as extrinsic When a semiconductor doped to such high levels so that it performs more like a conductor than a semiconductor then it treat as a degenerate Doping also growth the photocatalytic activity of the semiconductor It is seemed that between different oxide semiconductor photo catalysts WO_3 is well-thought-out to be the mostly used semiconductor because of its optical and electronic possessions and low cost, chemical stability and non-toxicity [34, 35] Due to this reason many scholars report doping of WO_3 with other elements Jiaguo Yu et al al reported Effect of calcination temperatures on microstructures and photocatalytic activity of tungsten trioxide hollow microspheres [36]

Hyeyoung Kim et al reported, Photo electrochemical and photocatalytic properties of tungsten oxide Nano rods grown by thermal evaporation [37] R Abe, K Shinmei , N Koumura, K Hara, and B,Ohtani, reported Visible-Light-Induced Water Splitting Based on Two-Step Photoexcitation between Dye-Sensitized Layered Niobate and Tungsten Oxide Photocatalysts in the Presence of a Triiodide/Iodide Shuttle Redox Mediator [38] Tungsten trioxide (WO_3) is photocatalytically stable, easy to synthesize, inexpensive, and is not dangerous to the environment.

1.9 Co doping:

The term Co doping is a grouping of two words "**co**" and "**doping**" which means countless doping of a semiconductor along with other substances Co-doping of WO_3 may be used as an real way to recover charge separation Co doping is decided to be more operative than doping with a single element [39] Co doping demonstrate improved photocatalytic activity as associated with doping

1.10 Specific Objectives of Work:

This MS work has precise aims which are termed as follows and their detail is described in the next chapters

The main determination of this work is to enhance the photocatalytic activity of co doped tungsten trioxide under the UV light irradiation The prepared catalysts were characterized thoroughly by Scanning electron microscopy (SEM), X-ray diffraction (XRD), UV–Vis diffused reflectance spectroscopy (DRS) and Fourier transform Infrared Spectroscopy (FT-IR)

Chapter No. 2

Literature Review

2.1 Tungsten Trioxide (WO_3):

A chemist Robert Oxland gave the first procedure for preparing tungsten trioxide (WO_3) Tungsten trioxide is acquired from the minerals scheelite, wolframite, and ferberite It is not soluble in H_2O and acids, but resolvable in hot alkalis It could be easily produced via simplistic processes Several scholars have set nanostructured tungsten oxides, i e nanowires [40-42], Nano rods [43-47], nanoparticles [48], nanofibers [49, 50], etc In line for smaller band gap of tungsten trioxide compare to Titania (band gap 3 0–3 2 eV) [51, 52] WO_3 exhibits well photo captivation in visible-light radiation For that reason, WO_3 can be utilized in internal chemical treatment It lesser the volatile organic gases using internal light sources where ultraviolet light is restricted WO3 has the prospective to use sun- light as energy for the handling of damaging pollutants in industrial waste-water It also has the prospective for hydrogen production as well On the other hand, pure WO3 has lesser light energy adaptation efficiency associated to TiO2 since the lessening potential is abstemiously low [53] Bearing in mind the compensations and limitations of each photo catalysts materials, investigators have engaged different strategies to modify their catalytic activity These approaches include surface and interface modifications which include control of morphology and particle size, composite materials, transition/noble metal doping, non-metal doping, Nobel metal deposition, surface sensitization have been implemented to improve the photocatalytic properties In exacting, the restriction of WO_3 as a photo catalyst can be remunerated by smearing these strategies Several efforts have been made to advance the photocatalytic activity of WO3 In the meantime the association between photocatalytic activity and physical properties has been well-known before, some scientists improved the morphology and surfaces of WO3 by concentrating on the morphology of WO_3 such as nanowire, nano rods, nanotubes, microspheres, microporous, macro porous and mesoporous structure [54-56] They enhanced the photocatalytic activity of WO3 by synthesizing of one dimensional structure to minimalize the recombination of electrons/holes and preparing of porous structure to increase the surface area [55]

2.2 Tungsten Trioxide as a Photo catalyst:

As an attention-grabbing Tungsten oxide photo catalyst acknowledged a lot of consideration among researchers The restriction of WO_3 as a photo catalyst can be remunerated by spreading on amendment strategies namely surface and interface modification in which it includes control of particle size and morphology, composite materials, transition/noble metal doping, non-metal doping, novel metal deposition, surface sensitization

2.3 Photo catalysis:

Photo catalysis is a chemical reaction which simplifies light during the reaction As it has been reported that the inorganic WO_3 is one of the most prominent photocatalytic material So it is considered to be an efficient, economical and safe for the chemical and for the organic degradation

Different ways which are used to enhance the photocatalytic activity is Co doping, Doping and composite formation But later on we will only discuss the co doing method here as it is related to our work

2.3.1 Mechanism of Photo catalysis:

An eye-catching solution to progress the photocatalytic activity of WO_3 is noble metal loading because they can be responsible for the electron pool which steered to an adequate amount of negative potentials of O_2 reduction Because due to heavy amount of O_2 Reduction, they can be responsible for an adequate amount of electron pool generation When light falls on any semiconductor catalyst, electrons are excited to their higher states The semiconductor catalyst works as the pool of electrons, thus catalyzing the reduction of O_2 through multi electron paths As a result huge amount of OH Hydroxyl radicals are attained which estimably reduce the targeted organic compound, consequently the depletion of multi electron layers results in reduction, acting as an efficient charge separator and ensuring high activity for loaded catalysts

The hydroxyl radicals are produced in both the oxidation and reduction reactions of photo catalysis These hydroxyl radicals are very oxidative in nature and non-selective with redox potential of (E_0 = +3 06 V) The utilization of different noble metals such as platinum (Pt), gold

(Au), and silver (Ag) as co catalyst showed the enhancement in the WO3 photo degradation properties [61-64]

2.3.1.1 Oxidation reactions due to photocatalytic effect:

$$UV + MO \rightarrow MO\ (h + e^-)$$ MO =metal oxide

$$h^+ + H_2O \rightarrow H^+ + \bullet OH$$

$$2h^+ + 2\ H_2O \rightarrow 2\ H^+ + H_2O_2$$

$$H_2O_2 \rightarrow HO\bullet + \bullet OH$$

2.3.1.2 Reduction reactions due to photocatalytic effect:

$$e^- + O_2 \rightarrow \bullet O_2^-$$

$$\bullet O_2 - + 2HO\bullet + H^+ \rightarrow H_2O_2 + O_2$$

$$HOOH \rightarrow HO\bullet + \bullet OH$$

2.4 Photocatalytic Activity of Tungsten Trioxide:

Xin et al [57] showed that WO_3 with a suitable structure show higher activity in the O_2 growth reaction They examined the photo catalytic activity of WO_3 at different stimulating temperatures

The WO_3 photo catalytic activity had been examined on different stimulating temperatures 3 structures of WO_3 named as Orthorhombic, Tetragonal and Monoclinic work on The Monoclinic showed superior photo catalytic activity than others and it was concluded by this examination that the WO_3 structure has convincing features in O_2 progression The studies during intervening time show that photo catalytic activity of crystallites combination resulted long time strengthening The WO_3 grain enlarged size termed as elongated strengthening, caused in reduced activity A structure of bundle of pillars having nano metric dimensions of WO_3 synthesized sample was showed by Zhao et al [58] The photo response of the catalyst was excellent Its solar to hydrogen efficiency was 3 76% in natural sunlight irradiation

The self-assembled nano porous structure of Tungsten Trioxide was reported by Guo et al having the standard orientation of hkl planes i e (002) The produced catalysts exhibit more capability than Titania nano tube arrays and WO_3 films for photo catalytic degradation [59]

2.4.1 Effect of Photo conductivity on Tungsten Trioxide (WO_3) Particles:

The exceptional effects of electrolyte pH, crystallinity and particle size of tungsten trioxide (WO_3) particles on photo conductivity was examined by Ho et al [60] After that, they formulate Cs loaded WO3 ($CsWO_3$) particles for promoting photochemical reactivity enhancement Strengthening of WO_3 particles progresses the crystallinity prominence, the particle size and shrink surface recombination loss gave rise to improvement of photocurrent Another factor that improved photocurrent was electrolyte pH due to lessening of over potentials and intensification in electrolyte conductivity To intensify the electron trapping, prevent charge recombination and growth the selectivity of a precise product so as to enhance efficiency of photocatalytic processes metal–semiconductor modifications are used predominantly [60]

2.4.2 Photocatalytic effect of metal loaded on Tungsten Trioxide:

Abe et al [65] testified that platinum loaded tungsten oxide Pt/WO_3 demonstrates high photocatalytic activity for the decomposition of aliphatic compounds in presence of visible light From the time when this reported, many studies on the morphology modification of Pt/WO_3 such as macro porous Pt/WO_3, Pt/WO_3 nanotube and Pt/WO_3 hollow structure and the surface modification of WO_3 had been conceded out All aforementioned studies using improved WO_3 through the disintegration of organic compounds proved the visible light photocatalytic activity Yet the wide-ranging automatous examination on the dilapidation reactions and the tangled photo oxidants not done [66]

- Xu et al , with changed morphologies under hydrothermal conditions prepared WO_3 samples by hoarding different sulfates With transformed morphology Pt/ WO_3 designated extraordinarily high photocatalytic activity under visible light radiation 1 wt % Pt loaded in the cubic morphology of WO_3 sample exposed the all-out efficiency By decreasing the particle size the enhancement in photocatalytic activity can be accomplished which is prime principal to the development of the surface area

- Qamar et al study shows that the metals having both oxidation and reduction properties are not all the time promising for the progress of photocatalytic reaction of catalysts Metal deposition time and metal contents are the exceptional effects of critical parameters, on the photocatalytic activity of WO_3 The discrepancy discovered in the photocatalytic activity of nanocomposites was attributed to the size of the deposited metals [67]

- Purwanto et al research discovered the significance of scheming particle size in order to accomplish proficient photo degradation in Pt-WO_3 photo catalyst Optimum size of Pt-WO_3 indicated higher rate as compared to other sizes [68]

- Takehara et al Pt-WO_3 photo catalyst was investigated for inactivation of H_1N_1 contamination virus This photo catalyst was used for layering of wall and other exteriors to drop virus contamination accompanying with surfaces [69] The photo catalyst produced from a Hydroxyl radicals antiphons were well-thought-out to play a noteworthy role in microbial inactivation [70] Even though the Platinum is the most influential co-catalyst for high-activity WO_3 but for the reason that it is costly, it is not appropriate for a scale-up process As a substitute Platinum as a co-catalyst, metal oxide and metal ion have been intensively reconnoitered Metal oxides of $CuBi_2O_4$, $CaFe_2O_4$, TiO_2 and CuO were synthesized as a composite with WO_3 [70-75] Correspondingly, the embedding of Cu and Cu ion onto the surface of WO3 has been shepherded [76, 77] Amongst those procedures, the solicitation of CuO and $CuBi_2O_4$ as co-catalysts was furthermost encouraging CuO and $CuBi_2O_4$ mixture with WO_3 produce a proficient photo catalyst composite for volatile gas decomposition On the other hand, an aberrant performance ensues when photo degradation in an aqueous solution of organic components was convoyed The WO_3 oxide co-catalysts and composites reprobates because of well-known stirring treatment for the duration of the photo degradation test As an outcome, the co-catalyst consequence was no longer witnessed As a result, an interrelated structure for cocatalyst-WO_3 composites that was sufficiently strong to counterattack mechanical treatment is extremely required [78]

- There are three main reasons for the upgrading of photocatalytic activity of the Titania coatings when it is collective with WO_3

  1) The electron–hole recombination rate is lowered because the electrons created due to light can be conveyed to the lower conduction band of WO_3, regardless of the fact

that, positive holes moves in the direction of the valence band of Titania This clarification is schematically demonstrated in the figure 2 1[79]

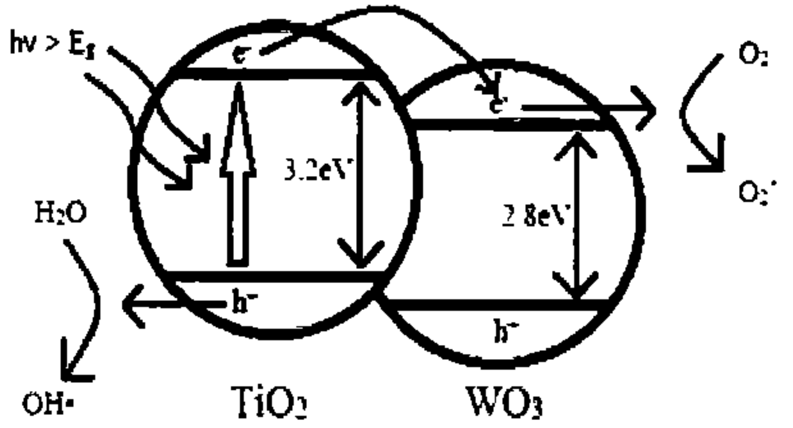


Fig 2.1. Charge transfer between TiO2and WO3bands.

2) High acidity on the outward surface of WO_3– TiO_2 as associated to pure TiO_2 can produce an advanced kinship of tungsten oxide/titania coatings for types with the electrons that are not paired for that reason, these films could fascinate more hydroxyl ions and can yield more hydroxyl radical necessary for photo oxidation antiphons

3) The light captivation volume of the tungsten oxide/titania because of the lower band gap energy, WO_3/TiO_2 classifications is complex which prime to extra production of e^- and h^+ pairs [75-78]

- Cabrera et al reported that mesoporous WO3/TiO2 films have efficaciously revealed an improved movement in the degradation of organic pollutants using the morphology controlled production for research Conforming to highly porous and polar materials the apparent of these needle-like films is super hydrophilic [79]

- Yu et al reported the preparation of WO_3/Zn O composite photo catalysts with different WO_3 concentrations It resulted in improved activity for the reason that of intensification in surface area and hydroxyl groups Crumpled photocatalytic activity was observed at the optimum calcination temperature as compared to pure catalyst [80]

- Bearing in mind the band gaps of tungsten oxide and Silver bromide, Cao et al arranged the AgBr/WO_3 photo catalyst with AgBr on the surface of WO_3 substrate The composite photocatalyst good absorption in the visible light region [81]

Chapter No. 3

Experimental Section

3.1 Materials and Reagents

3.1.1 Materials Used:

Reagents	**Formula**
Glucose	$C_6H_{12}O_6$
Ethanol	CH_3CH_2OH
Water	H_2O
Sodium Tungstate	Na_2WO_4
Copper Nitrate	$CuNO_3$
Ammonia	NH_3
Methylene Blue	MB

Table 3.1: The reagents and materials used in synthesis

3.1.2 Apparatus:

The apparatus used in this experiment are

- Hot plate
- Spatula
- Weighing Balance
- Magnetic stirrer
- Beakers
- Autoclave
- Centrifuge Machine
- Photo catalysis Assembly

3.2 Experiment Method:

The experiment method includes the following steps

3.2.1 Production of Carbon:

In a typical method Glucose was dissolved in distilled water and was autoclaved for several hours This simple method was adopted to produce carbon hollow spheres After production of carbon hollow spheres they were dissolved in the mixture of ethanol and distilled water Further five times washing was given and finally the sample was centrifuged and dried

3.2.2 Production of Tungsten Trioxide (WO_3):

Tungsten trioxide was produced by using sol-gel method In this method a specific amount of sodium tungstate Na_2WO_4 was dissolved in distilled water and a continuous stirring of several hours was given to the solution The dried carbon hollow spheres were dissolved in ethanol and a little stirring was given to the solution

After this the solution of ethanol was added drop by drop to avoid clustering, in the solution of sodium tungstate on constant heating and stirring After several hours of stirring and heating the sample was dried and five washings were given to remove the impurities

3.2.3 Co doping with metals and non-metals:

The sample produced was then again dissolved in the mixture of ethanol and distilled water and then separated into three parts This sample was then co doped with metal, non-metals and combination of metals and non-metals Co doping was done in such a way that the solution was kept on heating and constant stirring and the dopant material was dissolved in a solution of ethanol and distilled water Then it was drop wise added to the solution of Sodium tungstate and remained on continuous stirring and heating Further all the samples produced were calcined at specific temperature

For co doping with metals Copper Nitrate ($CuNo_3$) was used and for non-metals Ammonia (NH_3) was used

3.3 Characterization Techniques:

The most appreciated characteristic of materials research is the characterization of the fabricated materials that we use in demand to attain more information about them Operation and Characterization of separate nanostructures requirements not only great sensitivity and precision, but also atomic-level resolution It consequently leads to different microscopies that will play a vigorous role in characterization and measurements of nanostructured materials and nanostructures Methods used for spectroscopy magnify the sample, envisage its internal structure These techniques might be spectroscopic or can microscopic

The techniques which I used to examine materials are X-Ray Diffraction (XRD) Spectroscopy UV-vis Diffused Reflectance Spectroscopy (DRS), and Scanning Electron Microscopy (SEM) and wide angle X-Ray Diffraction (W–XRD) and small angle X-Ray Diffraction (SAS) and Microscopic analysis include scanning electron microscopy (SEM)

- ✓ X-Ray Diffraction is one of the compliant techniques that measure the complete spacing in between the rows and layers of the atoms and use to find the arrangement of a single crystal It also defines the crystal structure of unidentified material and measures the internal stress, size and shape of the small crystalline ranges It is founded in the elastic scattering that is the change of way of the electromagnetic waves motion without energy loss The experimentation of X-ray Diffraction needs an X-ray source, the sample which has to be inspected and a detector to choice the diffracted X-rays A distinctive diffraction pattern comprises of a plot that covers the reflected intensities vs the detector angle which may be 0 or 2θ For uncontaminated substance X-ray diffraction pattern is, just like an impression of the substance Insignificant sample preparation and comparatively straight forward information interpretation make it beneficial One thing should be kept in notice that sample under study must be uniform and single phase for reliable results

- ✓ To find the crystal-like structure of the polymers Wide angle X-Ray diffraction (W-XRD) is use This method is used to inspect the Bragg peaks which are scattered to wide angles The shape of diffraction help to define the phase composition of the film or chemical composition of the film, the arrangement of the films and the incidence of the film stress and the crystalline size

- ✓ Another powerful tool Small angle X-ray scattering SAXS is used for characterizing nanostructured materials where the elastic scattering of X-rays having wavelength 0 1-0 2 nm by a sample which are non-homogenous in the nm-range, is detailed at very low angles (normally at 0 1 - 10°) This array covers the info about size of macromolecules, shape, pore sizes, and distinguishing distances, and partially order of materials It has the capacity to provide the structural data about the macromolecules which range from 5 to 25 nm, of the repeat distances in some extent ordered systems of up to 150 nm

- ✓ A supreme technique for the characterization of nanostructured materials is UV-Vis Diffuse Reflectance Spectroscopy is It is a non-caustic technique and samples can be recuperated later This spectroscopic technique consists of reflection or transmission that might be internal or external of UV-Vis radiation It is highly delicate technique and it has precise limit of detection It is cast off to calculate the electronic band gap of semiconductors and is also used to measure the Reflectance Loss in Photovoltaic Cells and the Optical Properties This technique is particularly used for costly samples like proteins and enzymes

- ✓ Scanning electron microscopy is used to determine the topographic particulars of nanomaterials and the surface of films can be shown up with high tenacity and feature The SEM is considered as a greatest regularly used instruments in nanomaterials, due to SEM has amalgamation of large focus depth, great strength of resolution and liberty to observe the sample and high magnification It decides morphology particulars less than of 50nm and consist of a depth of focus 500nm times advanced as associated with optical microscope with same magnification In it the electrons bam is enhanced with a low voltage range from 1-20 kV and is scanned on the outward of the sample The electrons beam cast off for SEM characterization consists of low energy It has normally the resolution of 1nm and is used to distinguish the spatial scattering of element It gives the best results for surface morphologies and elemental analysis of the samples

3.4 Catalyst Characterization:

UV-vis diffuse reflectance spectrum (DRS), equipped with an integrated sphere assembly was used for scan

X-ray diffraction (XRD) measurements, Rigaku D/Max 2550 VB/PC apparatus (Cu $K_{\alpha 1}$ radiation, λ = 1 54056 Å) at room temperature, being operated at 40 kV and 100 mA was used to investigate the crystallographic properties

The elemental analysis, Surface morphologies and pour sizes were observed by scanning electron microscopy (JEOL JSM-6360LV)

UV-Vis absorption spectra of the samples were verified on Cary 100 UV/vis spectrophotometer

3.5 Photocatalytic Activity Measurements:

The photo catalytic performance of different photo catalysts were evaluated in the degradation of methylene blue It is representative of highly persistent pollutant We calculated their photo catalytic degradation processes on exposure to UV light The photo catalytic reactions persist for 5 h A water-cooling system chilled the water-jacketed photochemical reactor to preserve the solution at room temperature throughout the reaction In advance initialing catalysis the suspension was magnetically stirred in darkness for 30 min to begin adsorption-desorption equilibrium at room temperature Stirring was sustained to keep the mixture in suspension Samples were taken off at specific intervals and centrifuged to separate photo catalyst for investigation Then clarified through a 0 22 μ m Millipore filter paper to take out the photo catalyst The concentration of pollutant was also calculated from the height of peak using the calibration curve

Chapter No.4

Results and Discussion

4.1 Morphology of Catalyst produced through SEM:

4.1.1 Amorphous WO_3 Nano rods like structure:

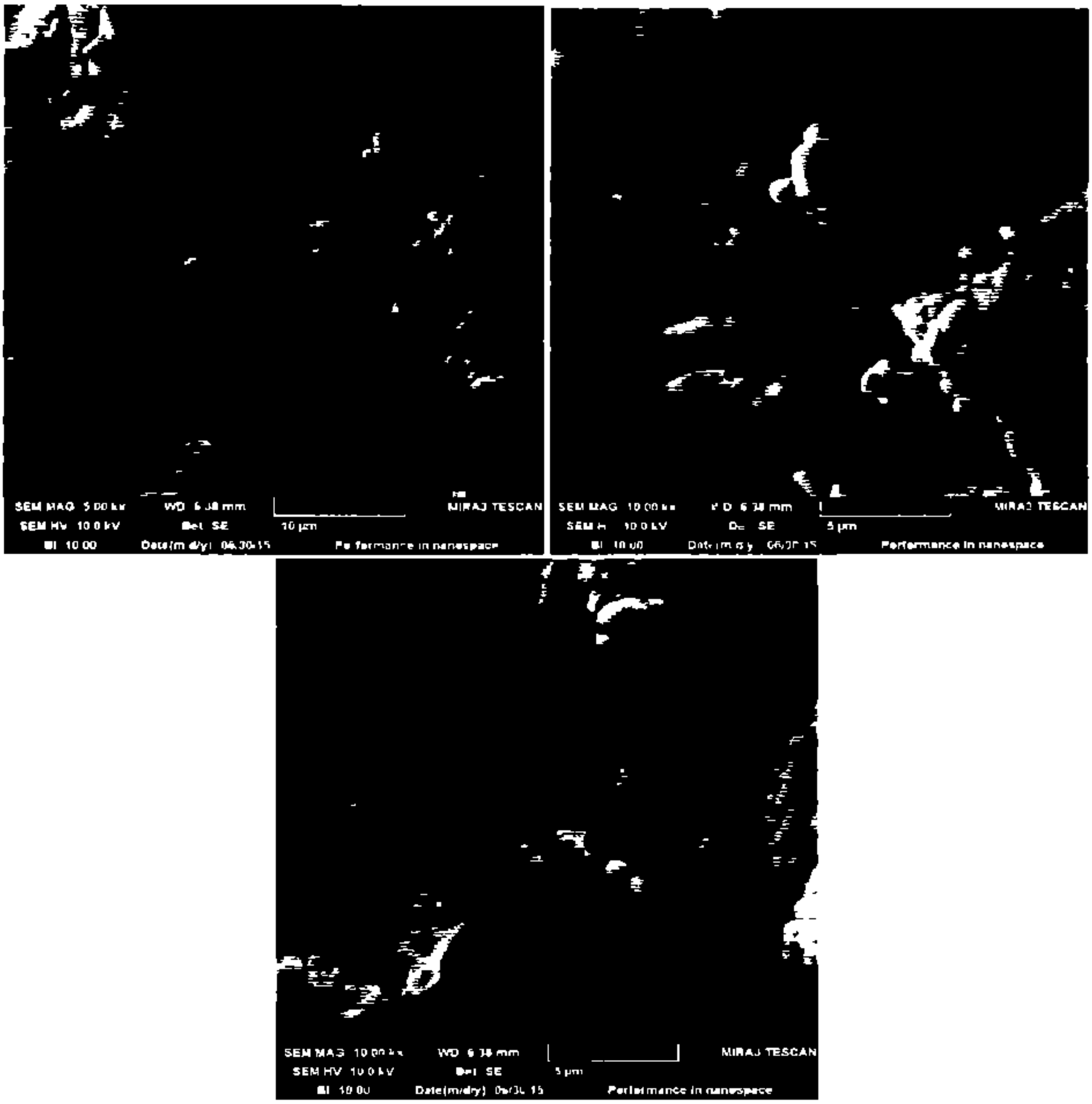


Figure 4.1.: SEM images of pure Tungsten Trioxide (WO_3) Nano rods like structure.

Scanning Electron Microscopy (SEM) exhibits the performance in nanospace with large magnification and resolution and determine the morphology of materials at nano level **In figure 4.1.** Amorphous tungsten trioxide Nano rods are shown at 50,000 and 100,000 magnification It has rod shaped morphology with high aspect ratio i.e is given by length/ diameter In this case the aspect ratio is 3 Moreover pores can be seen on the surface of the rods which make them amorphous The average pore size is 350 nm which reveals that it has macro porous structure Preparation of tungsten trioxide Nanorods was also reported by M Gillet et al The measurement of formed nanorods differ in ranges from 1-15μm, 10-200nm and 1-50nm for the length, width and thickness, respectively [82]

4.1.2 Nitrogen Doped Tungsten Trioxide WO_3 Photocatalyst:

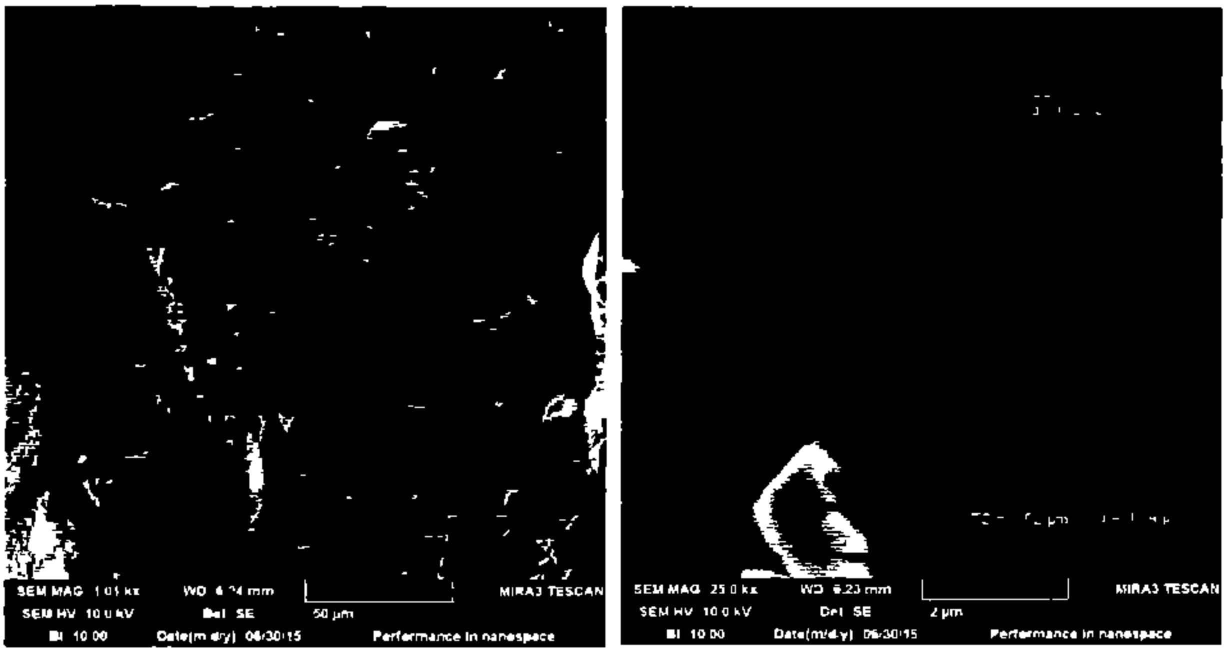


Fig 4.2: SEM image of Nitrogen Doped with Tungsten Trioxide (WO_3)

These are the SEM images of Nitrogen doped Tungsten Trioxide (WO_3) photo catalyst which reveals the morphology of the catalyst In figure 4 2 porous structures can be seen easily at very low magnifications of 1000 and 25,000 magnification which reveals that the catalyst produced is amorphous in nature Moreover the pores have different sizes that ranges from 102 nm to 259 nm, from which it is clear that this catalyst has macro porous morphology It is best for the application as a photo catalyst

4.1.3 SEM Images of copper doped Tungsten trioxide (WO_3) Photo catalyst:

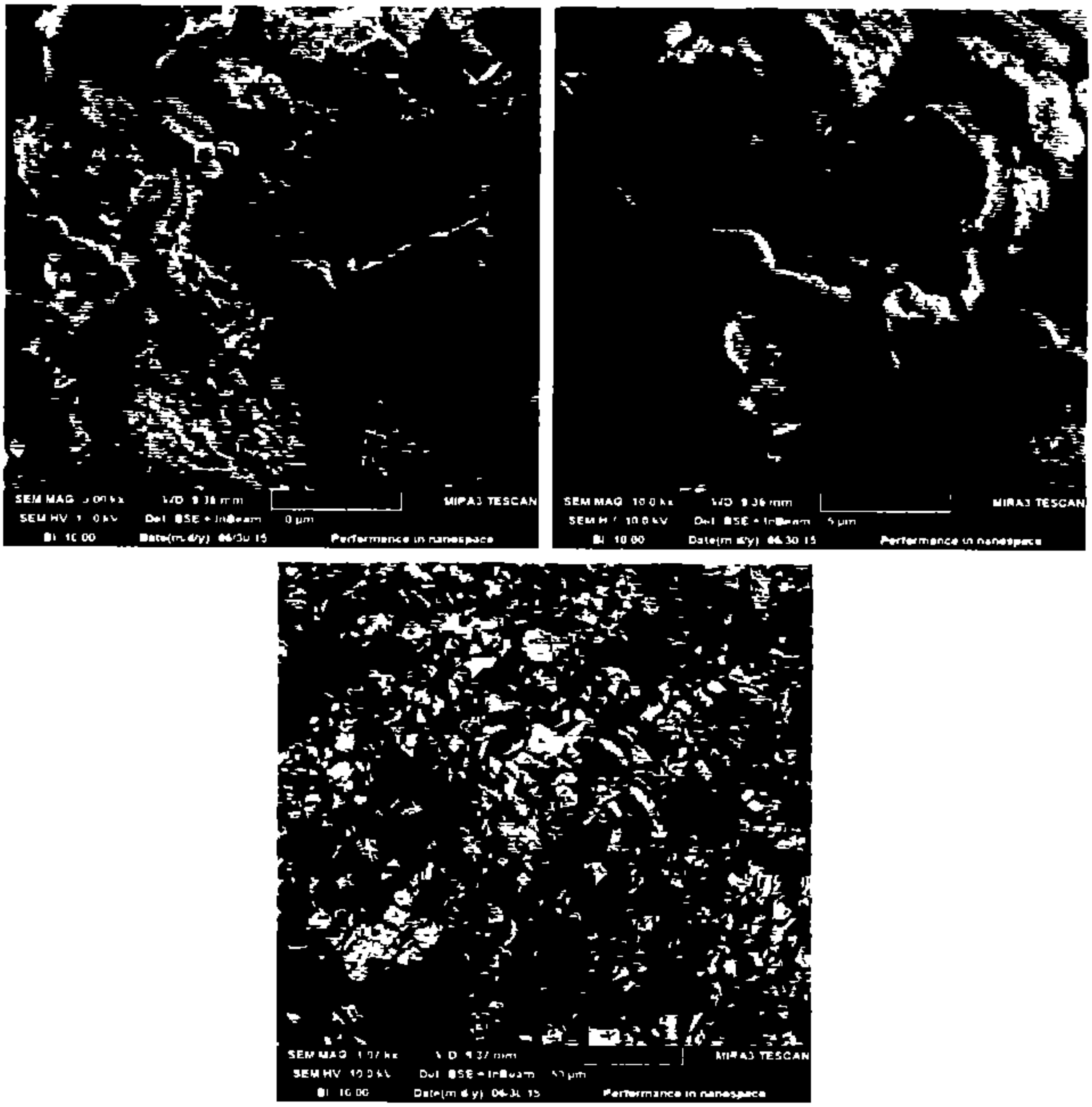


Fig 4.3. SEM images of Copper Doped with Tungsten Trioxide (WO_3)

These are the SEM images of Copper doped Tungsten Trioxide (WO_3) photo catalyst which reveals the morphology of the catalyst In figure 4.3 porous structures can be seen at 10,000 50,000 and 100,000 magnification which reveals that the catalyst produced is amorphous in nature Moreover the pores have different sizes that ranges from 100 nm to 300 nm, from which it is clear that this catalyst has macro porous morphology

4.1.4. SEM Images Of Copper & Nitrogen Doped Tungsten Trioxide (WO3):

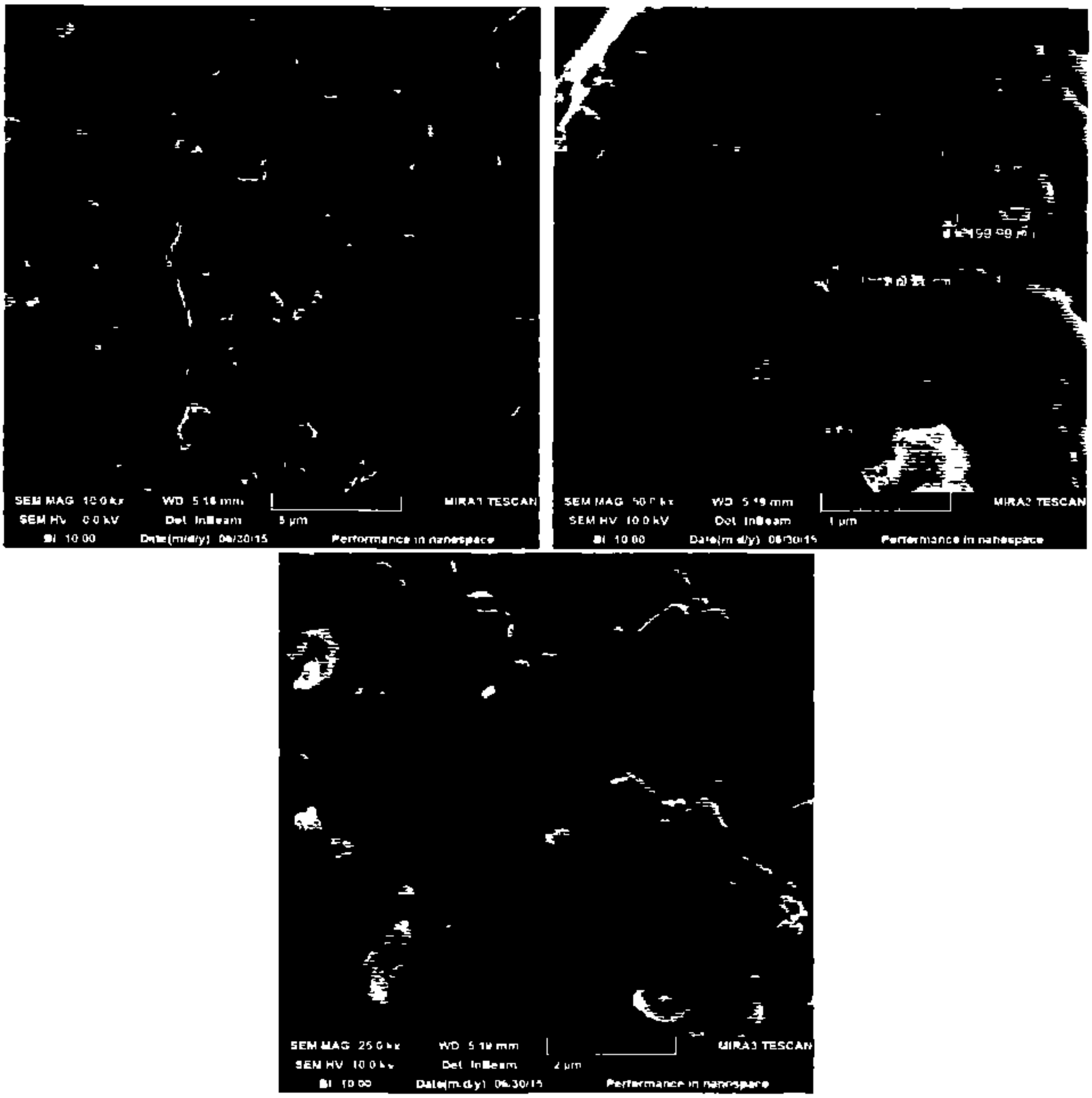
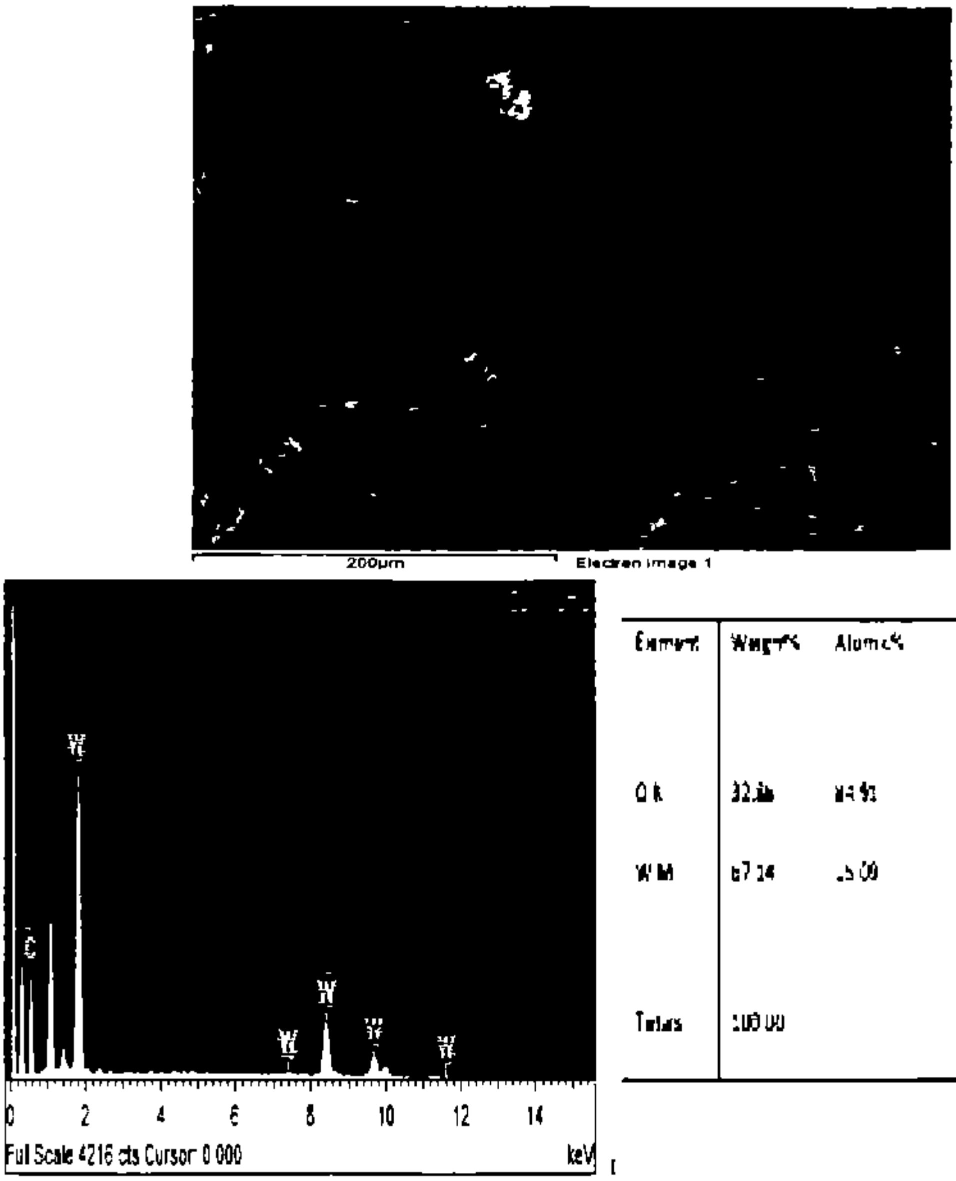


Fig 4.4. SEM Images Of Copper & Nitrogen Doped Tungsten Trioxide (WO3):

These are the SEM images of Copper and Nitrogen doped Tungsten Trioxide (WO_3) photo catalyst which reveals the morphology of the catalyst In figure 4.4 porous structures can be seen at 10,000 50,000 and 100,000 magnification which reveals that the catalyst produced is amorphous in nature Moreover the pores of different sizes can be seen easily i e 128 nm, 138 nm, 199 nm and 203 nm, from which it is clear that this catalyst has macro porous morphology

4.2 Elemental Analysis of Photo catalysts:

4.2.1. EDX of Tungsten Trioxide (WO_3):

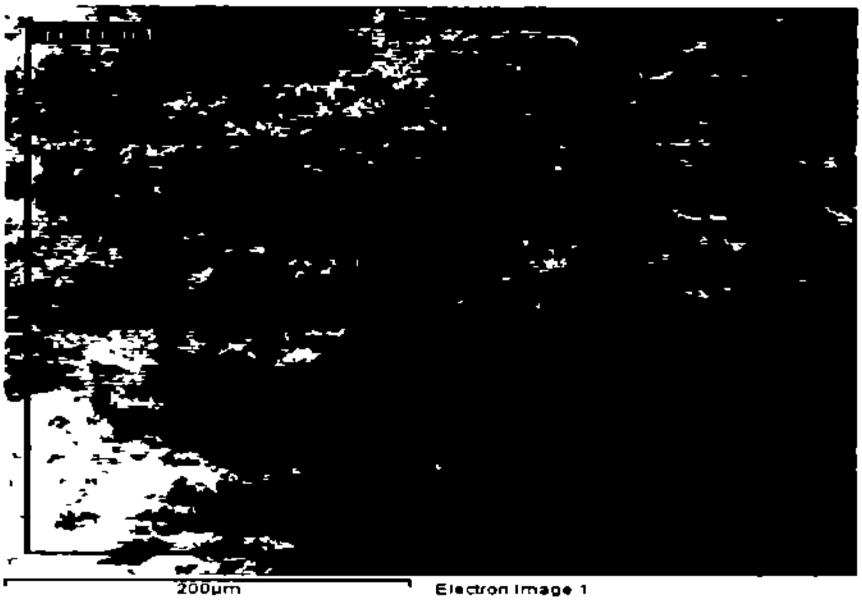


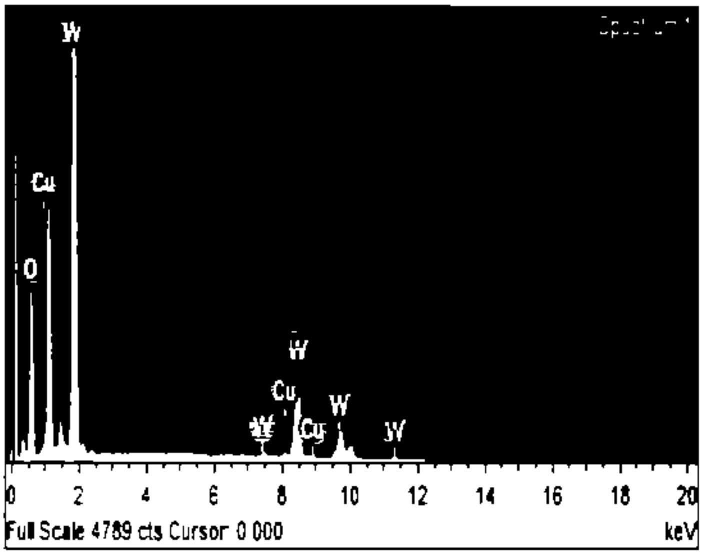
Element	Weight%	Atomic%
O K	32.66	84.93
W M	67.34	15.00
Totals	100.00	

Fig 4.5. EDX analysis Of Tungsten Trioxide (WO_3)

EDX analysis is carried out to get the elemental analysis of WO3 EDAX spectra gives different elemental gives observed peaks are of O, W respectively and table shows there weight percentage and atomic percentage W, O supports the elements in sample, which can be used in photo catalysis

4.2.3. EDX analysis of Copper doped Tungsten Trioxide (WO_3):



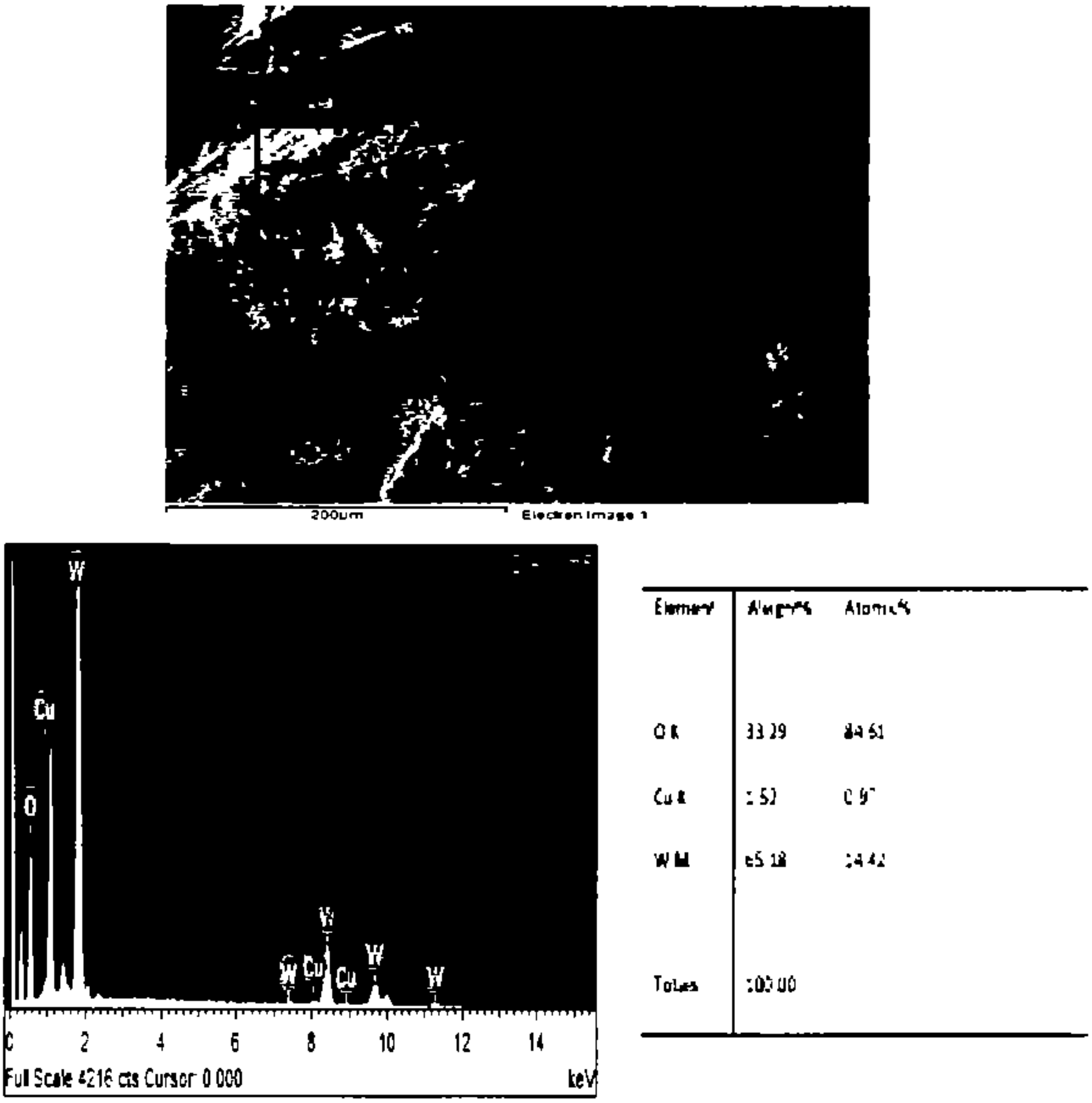


Element	Weight%	Atomic%
O K	33 59	84 79
Cu K	1 49	0 95
W M	64 92	14 26
Totals	100 00	

Fig 4.7. EDX analysis of Copper Doped Tungsten Trioxide (WO_3)

EDX analysis is carried out to get the elemental analysis of copper doped WO3 EDAX spectra gives different elemental gives observed peaks are of O, W, Cu respectively and table shows there weight percentage and atomic percentage W, Cu, O supports the elements in sample, which can be used in photo catalysis

4.2.4. EDX of Copper and Nitrogen doped WO_3:



Element	Weight%	Atomic%
O K	33.29	84.61
Cu K	1.53	0.97
W M	65.18	14.42
Totals	100.00	

Fig 4.8 EDX analysis of Copper and Nitrogen doped Tungsten Trioxide (WO_3)

EDX analysis is carried out to get the elemental analysis of copper and nitrogen doped WO3 EDX spectra gives different elemental gives observed peaks are of O W, Cu respectively and table shows there weight percentage and atomic percentage Cu, W, O supports the elements in sample, which can be used in photo catalysis

4.3. FT-IR Analysis of Photo Catalysts:

4.3.1. FT-IR analysis of Tungsten Trioxide (WO_3):

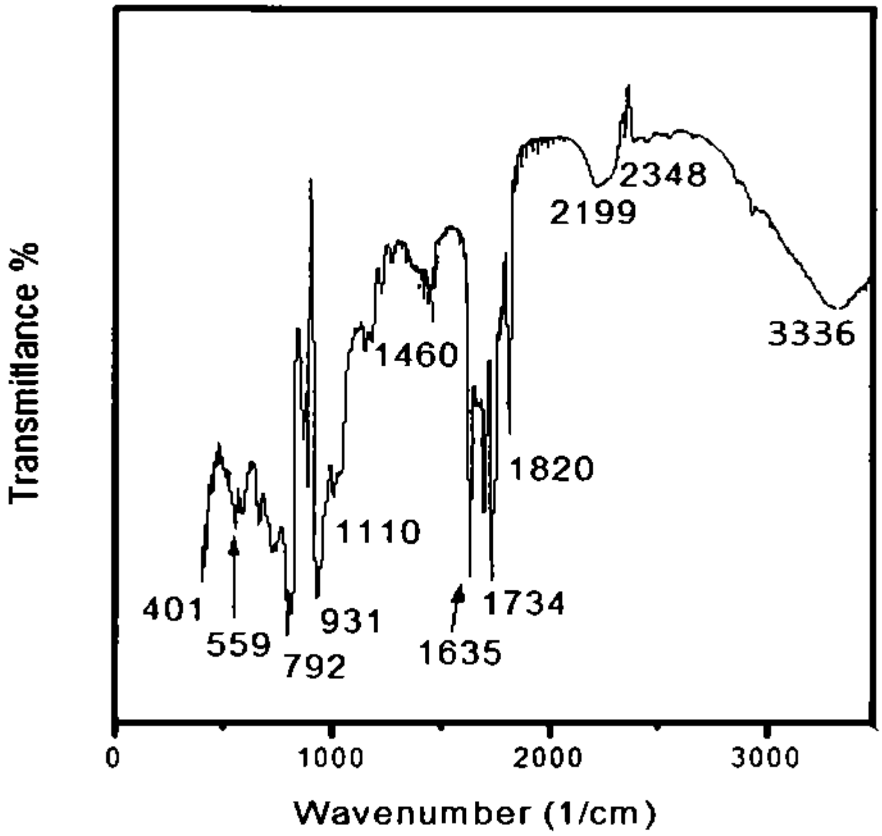


Fig 4.9. FT-IR Results of Tungsten Trioxide (WO_3)

Sr No	Wavenumber(cm^{-1})	Transmittance %
1	792 86	4 79
2	935	5 55
3	1635	6 06
4	1734	5 97
5	3336	11 72

Table 4.1. Calculation of Transmittance for the mentioned peaks in the graph.

In fig 4.9 FT-IR results of Tungsten Trioxide are shown Here the absorbance is calculated in table 4.1 For the aforementioned peaks on the graphs In the graph of WO_3, the broad peaks are of water, while the peaks near to origin (0, 0) replicates the confirmation of bonding between W and O The occurrence of these peaks are taken into consideration irrespective of the absorbance characteristics Because of the transpose of absorbance which is Trans conductance in our main concern for photo based applications The FT-IR spectra of WO_3 was found from 400 – 900 cm^{-1} the characteristics absorption was at 3336 cm^{-1} was attributed at aromatic and -OH stretching and that at 1635 cm^{-1} revealed the aromatic and –OH bending vibrations There was no characteristics peak shown at 2370 cm^{-1} which confirms the removal of Carbon [82]

4.3.2. FT-IR analysis of Nitrogen doped Tungsten Trioxide (WO_3)

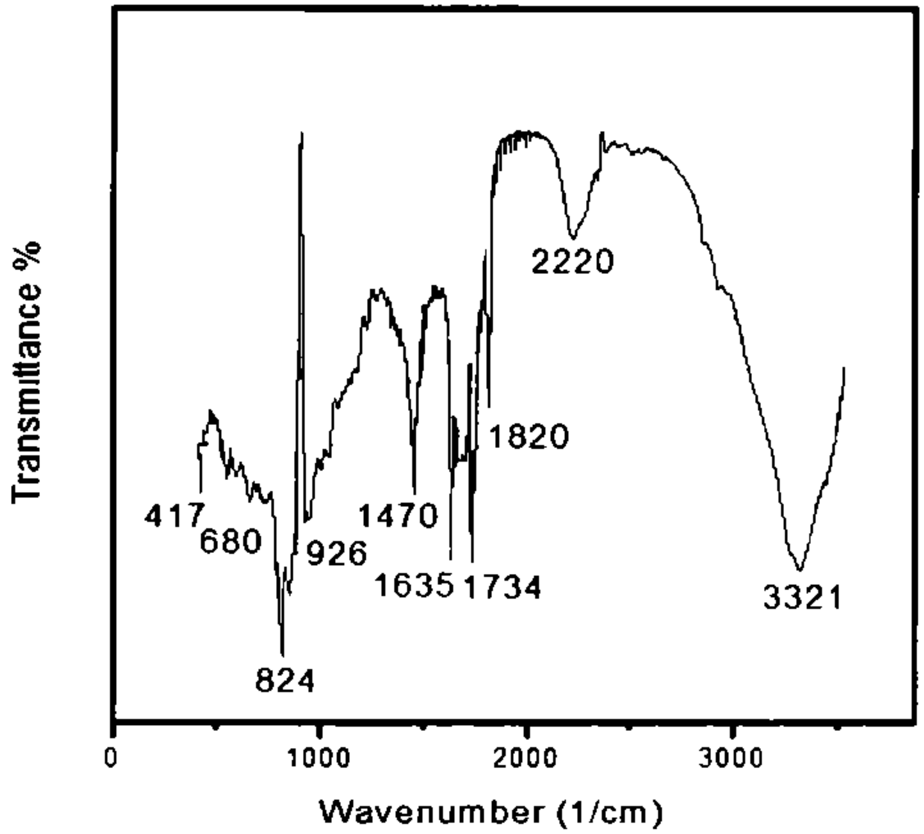


Fig 4.10. FT-IR Analysis of Nitrogen doped Tungsten Trioxide (WO_3)

Sr No	Wavenumber(cm^{-1})	Transmittance %
1	417	7.32
2	1470	10.46
3	1635	9.2
4	1734	9.11
5	3321	8.92

Table 4.2. Calculation of absorbance for the mentioned peaks in the graph.

In **fig 4.10.** FT-IR analysis of Nitrogen doped-WO_3 is given which shows that sharp peaks denotes the confirmation of bonding between N-W and W-O at 1470 cm^{-1}, 1635 cm^{-1} and broad peak for water was found at 3321 cm^{-1} and no characteristics peak is shown peak at 2370 cm^{-1} which reveals that carbon spheres are removed. The main peak of nitrogen was observed at 1470 cm^{-1}. The material is identified as nitrogen-doped WO_3 [82]

4.3.3. FT-IR analysis of Copper doped Tungsten Trioxide (WO_3):

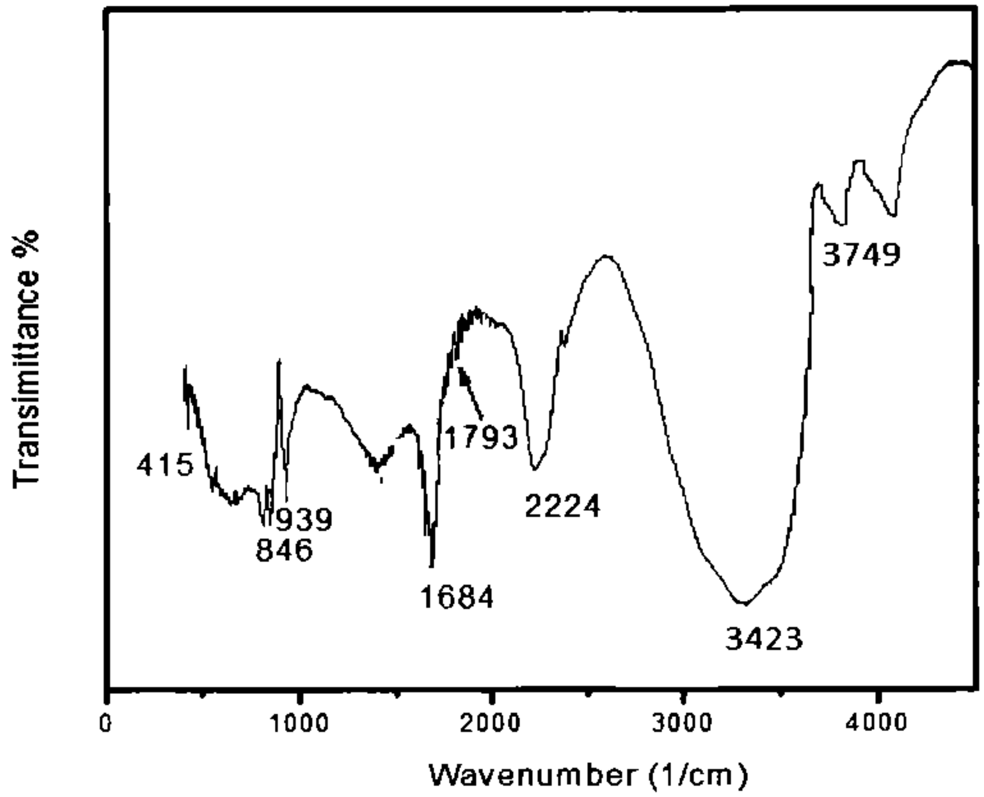


Fig 4.11. FT-IR analysis of Copper doped Tungsten Trioxide (WO_3)

Sr No	Wavenumber(cm^{-1})	Transmittance %
1	846	4 17
2	939	4 63
3	1684	3 36
4	2224	5 26
5	3423	2 61

Table 4.3. Calculation of absorbance for the mentioned peaks in the graph.

In fig 4 11.The graph of Copper doped WO_3 shows, the broad peaks for water again, while the peaks near to origin replicates the confirmation of bonding between Cu-WO_3 and W-O The main peaks observed from range 400 - 900 cm^{-1} was for tungsten trioxide and 1684 – 2224 cm^{-1} was for copper The occurrence of these peaks are taken into consideration irrespective of the absorbance characteristics

4.3.4. FT-IR analysis of Nitrogen and Copper doped Tungsten Trioxide (WO_3)

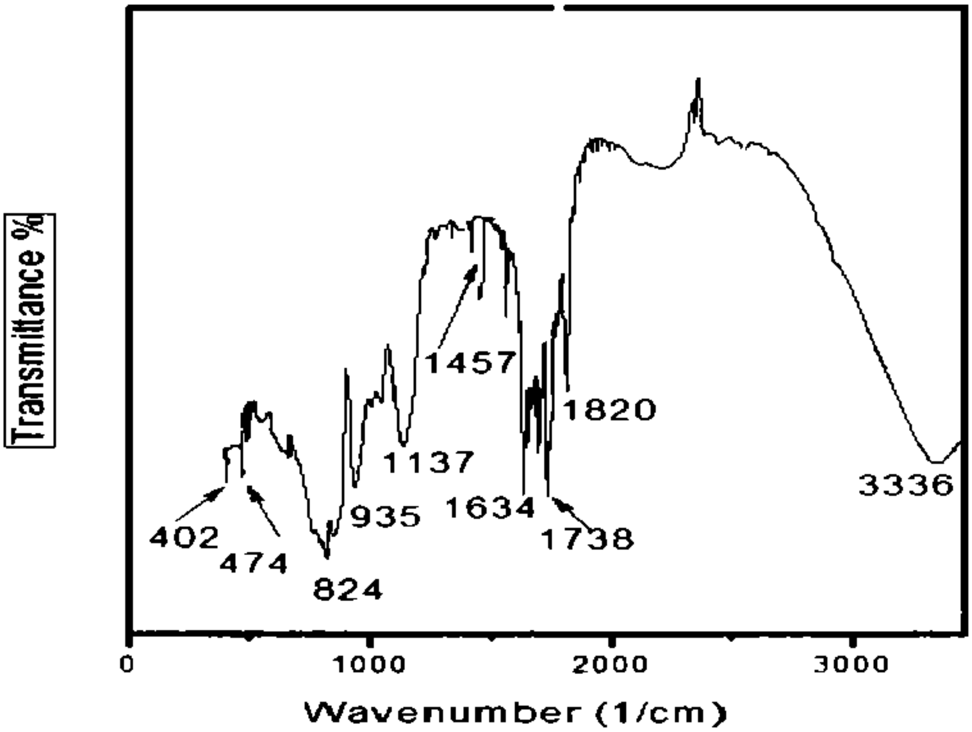


Fig 4.12. FT-IR analysis of Nitrogen and Copper doped Tungsten Trioxide (WO_3)

Sr No	Wavenumber(cm^{-1})	Transmittance %
1	824	5 96
2	1137	8 83
3	1634	7 59
4	1738	7 52
5	3336	8 35

Table 4.4. Calculation of absorbance for the mentioned peaks in the graph.

In fig 4.12. FT-IR analysis of Copper and Nitrogen doped-WO_3 is given in which graph of Cu-N-WO_3 reveals the broad peaks for water, while the sharp peaks mimics the confirmation of bonding between Cu-W, Cu-O, Cu-N and W-O at 1634 cm^{-1} and 3336 cm^{-1} and no characteristics peak is shown peak at 2370 cm^{-1} which reveals that carbon spheres are removed The material is identified as copper, nitrogen-doped WO_3

4.4. UV Diffuse Reflectance Spectroscopy Analysis:

4.4.1. UV-DRS analysis of Tungsten Trioxide (WO_3):

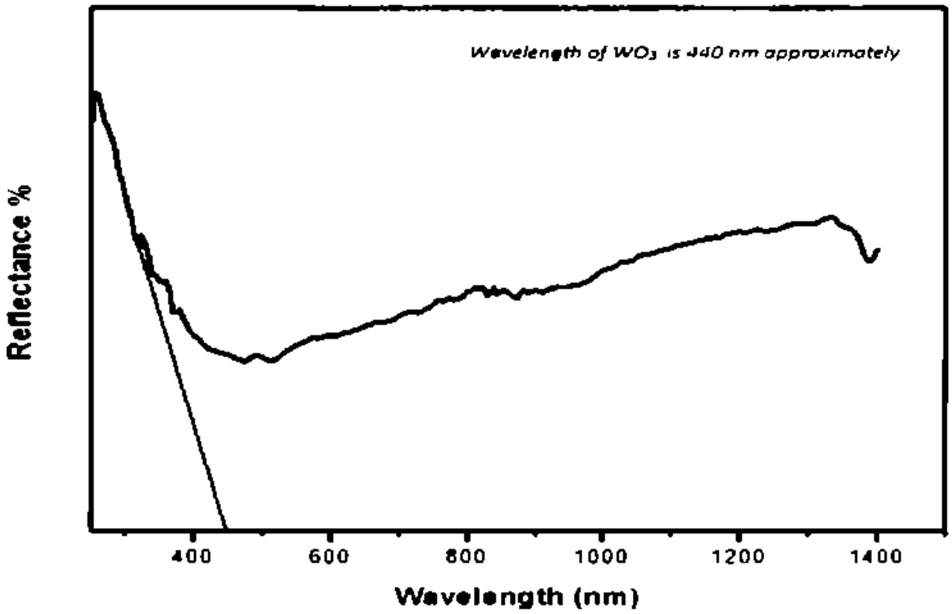


Fig 4.13(a).UV-drs analysis of Tungsten Trioxide (WO_3)

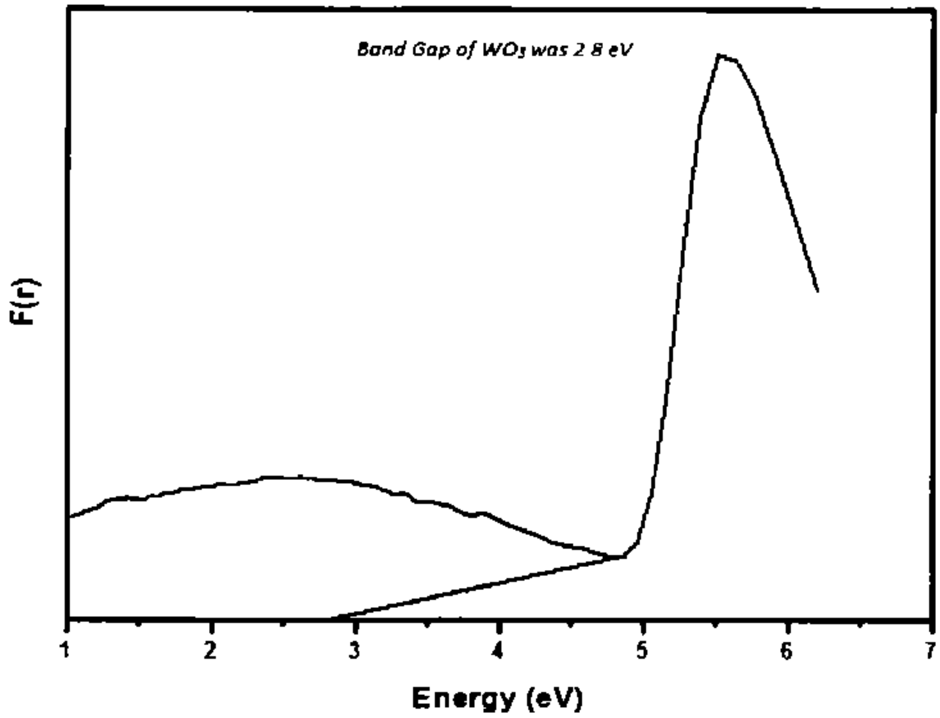


Fig 4.13 (b). Calculation of band gap of Tungsten Trioxide (WO_3)

In **Fig 4.13(a)**. UV-drs analysis of Tungsten Trioxide (WO_3) has been given which shows the peak of Tungsten Trioxide (WO_3) at 440 nm approximately which discloses that its photocatalytic activity lies in Visible region

In **Fig 4 13(b)**. The indirect optical band gap of Tungsten Trioxide (WO_3) is calculated using the wavelength of the peak by putting it in the formula

$$E = h\nu$$

Or

$$\nu = c/\lambda$$

Where h is Planck's constant and ''v'' is the frequency, ''c'' is speed of light and '' λ'' is the given wavelength

By putting values we find the optical band gap of WO$_3$ 2 8 eV which exhibits the amorphous nature of Tungsten Trioxide (WO$_3$) [84] In the visible region the average transmittance was about 75% for Tungsten Trioxide (WO$_3$)

4.4.2. UV-DRS analysis of Nitrogen doped Tungsten Trioxide (WO$_3$):

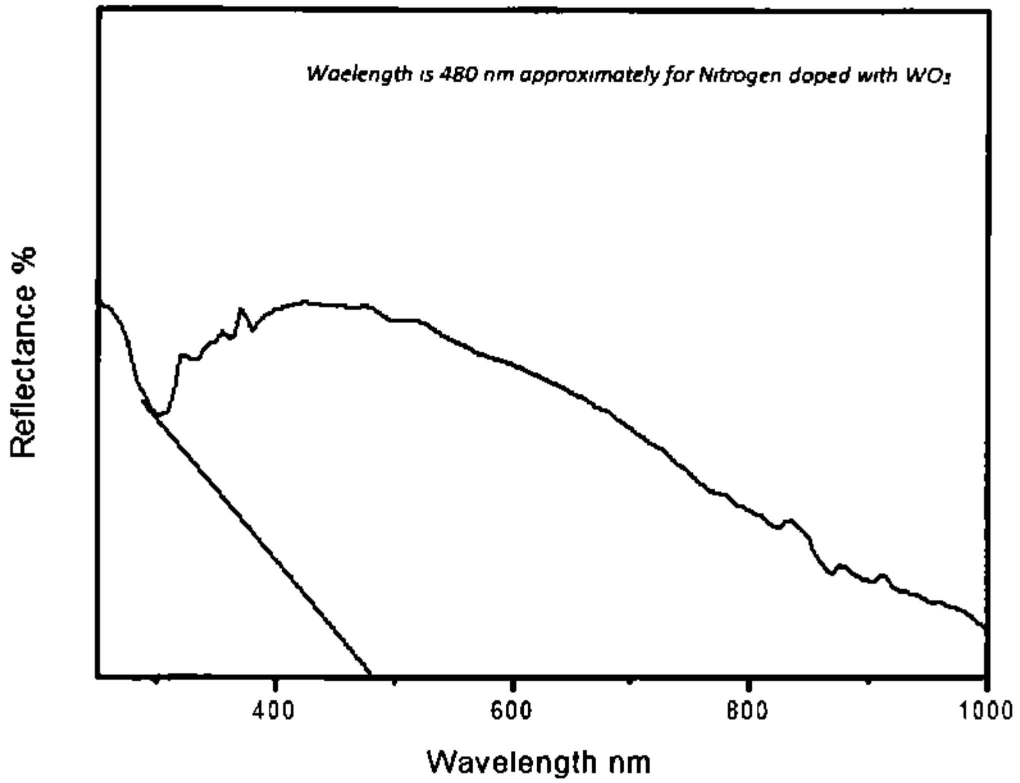


Fig 4.14 (a). UV-DRS analysis of Nitrogen doped Tungsten Trioxide (WO$_3$)

In **Fig 4.14(a).** UV-drs analysis of Nitrogen doped Tungsten Trioxide (WO$_3$) has been given which shows the peak of Nitrogen doped Tungsten Trioxide (WO$_3$ photo catalyst at 480 nm approximately which discloses that its photocatalytic activity lies in Visible region

In **Fig 4.14(b).** The indirect optical band gap of Nitrogen doped Tungsten Trioxide (WO$_3$) is calculated using the wavelength of the peak i e 480 nm We find the optical band gap of WO$_3$ 2 58 eV approximately which exhibits the amorphous nature [84]

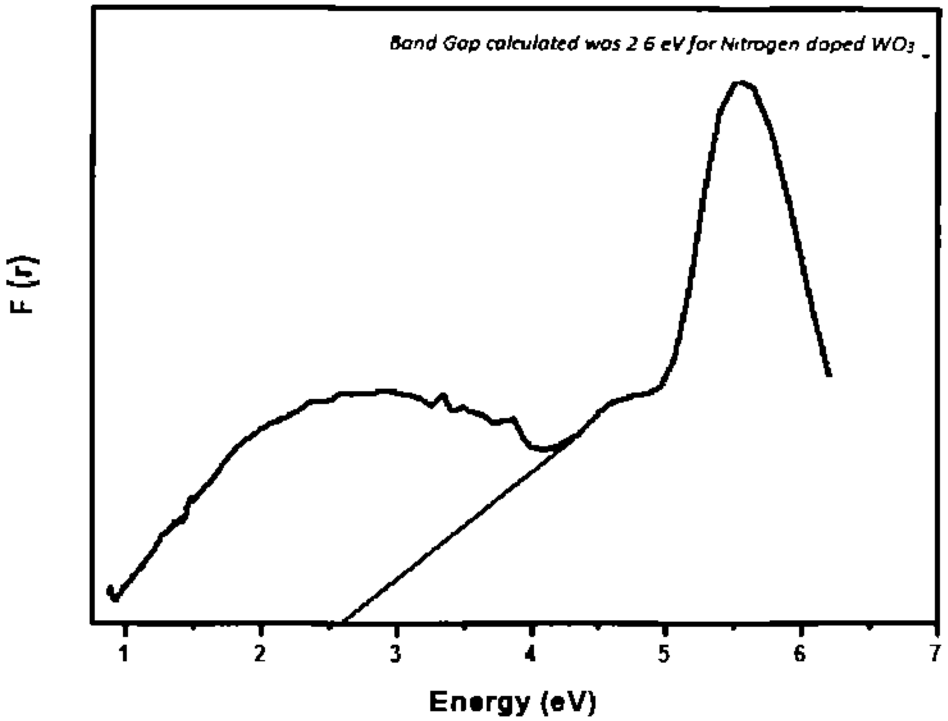


Fig 4.14 (b). Band gap calculation of Nitrogen doped Tungsten Trioxide (WO_3).

4.4.3. UV-DRS analysis of Copper doped Tungsten Trioxide (WO_3):

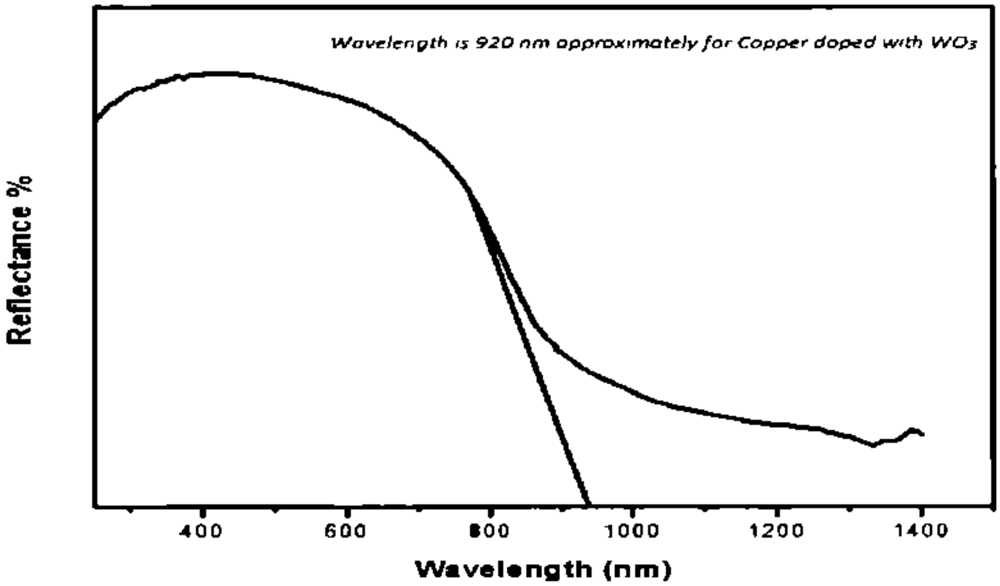


Fig 4.15 (a). UV-DRS analysis of Copper doped Tungsten Trioxide (WO_3)

In **Fig 4.15 (a)**. UV-DRS analysis of Copper doped Tungsten Trioxide (WO_3) has been given which shows the peak of Copper doped Tungsten Trioxide (WO_3) photo catalyst at 920 nm approximately which discloses that its photocatalytic activity lies in Visible region.

In **Fig 4.15 (b)**. The indirect optical band gap of Copper doped Tungsten Trioxide (WO_3) is calculated using the wavelength of the peak i.e. 920 nm. We find the optical band gap of WO_3 1.3 eV approximately.

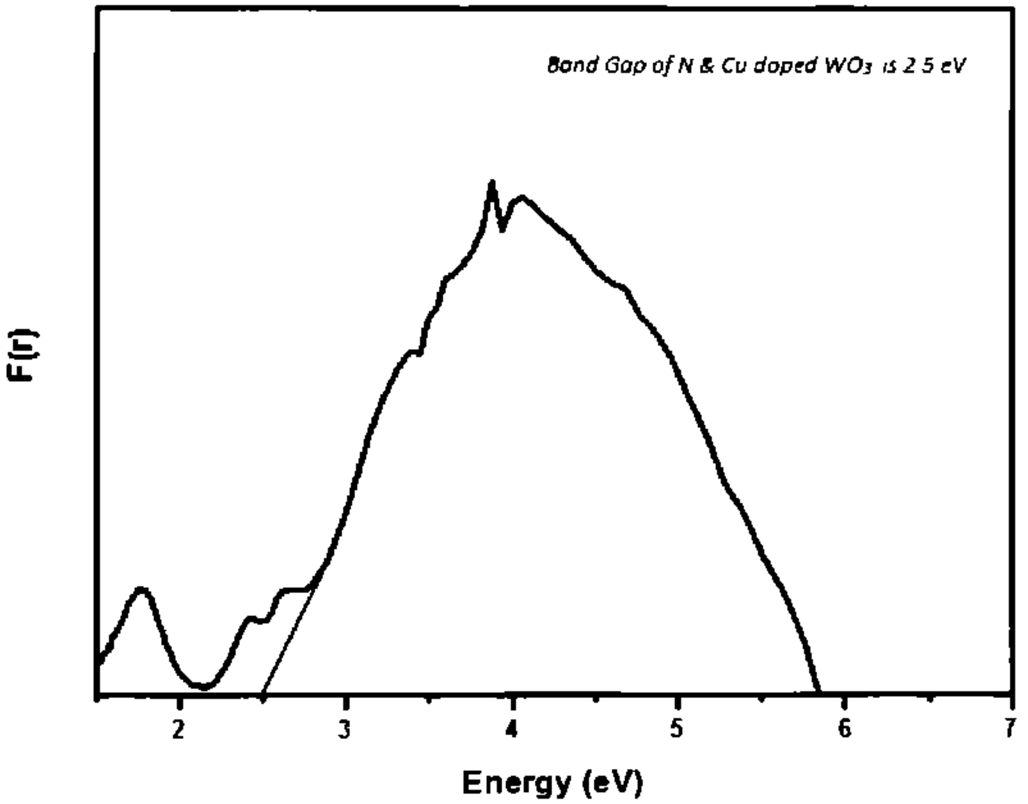


Fig 4.15 (b). Band Gap Calculation of Copper doped Tungsten Trioxide (WO_3)

4.4.4. UV-DRS analysis of Nitrogen & Copper doped Tungsten Trioxide:

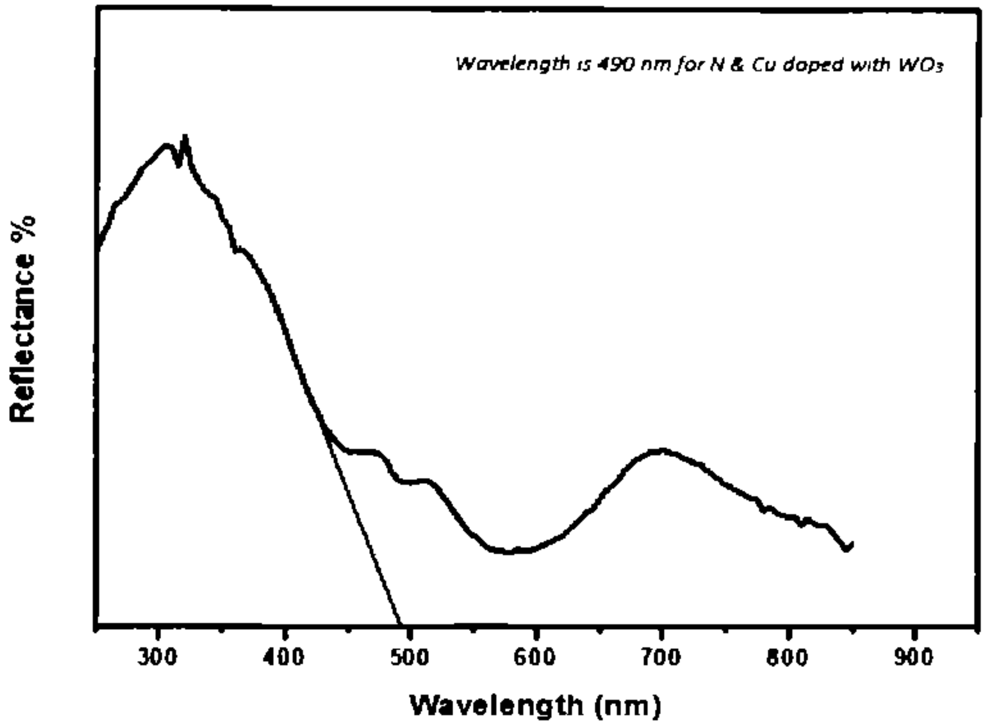


Fig 4.16 (a). UV-DRS analysis of Nitrogen and Copper doped Tungsten Trioxide (WO_3)

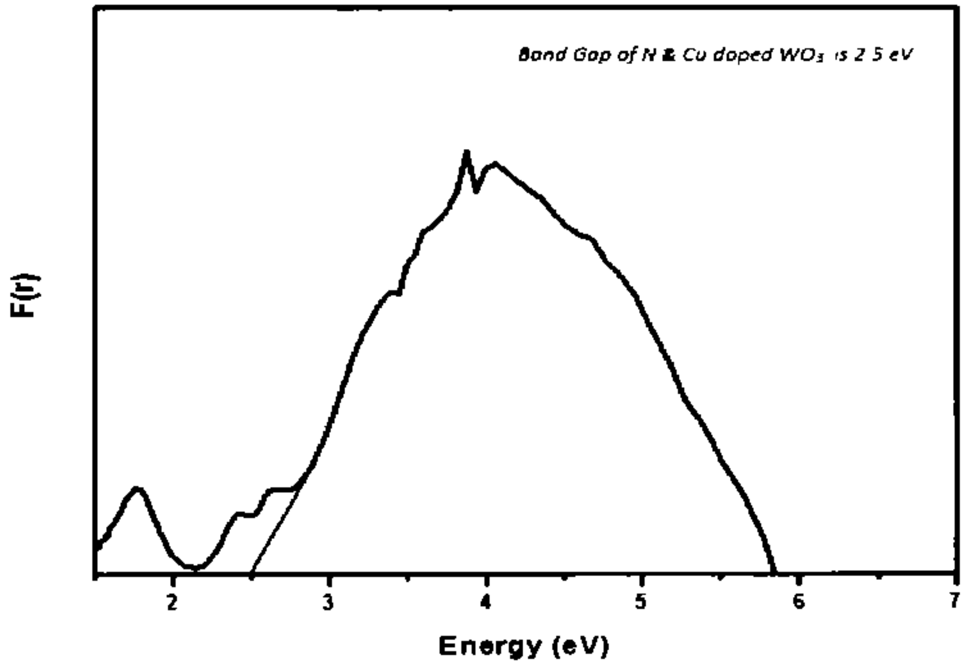


Fig 4.16 (b). Band Gap Calculation of Nitrogen and Copper doped Tungsten Trioxide.

In **Fig 4.16 (a)**. UV-DRS analysis of Copper doped Tungsten Trioxide (WO_3) has been given which shows the peak of Copper and nitrogen doped Tungsten Trioxide (WO_3) photo catalyst at 480 nm approximately which discloses that its photocatalytic activity lies in Visible region

In **Fig 4.16 (b)**. The indirect optical band gap of Copper and Nitrogen doped Tungsten Trioxide (WO_3) is calculated using the wavelength of the peak i e 480 nm We find the optical band gap of Copper and Nitrogen doped Tungsten Trioxide (WO_3) is 2 6 eV approximately

4.5 X-Ray Diffraction Results (XRD):

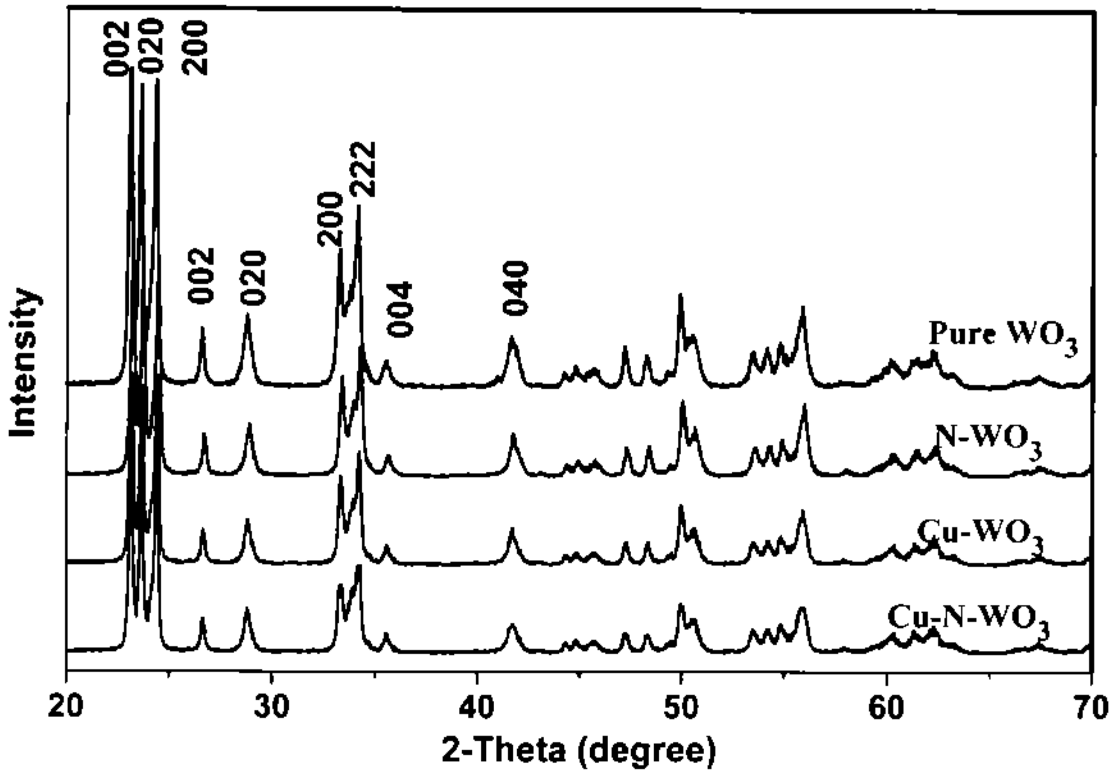


Fig 4.17. XRD analysis of WO_3, N-WO_3, Cu-WO_3, N-Cu-WO_3.

In Fig 4.17 XRD analysis of WO_3, N-WO_3 Cu-WO_3 and N-Cu-WO_3 is shown. The exact crystalline structures for WO_3 are shown by XRD studies of samples. The sharp peaks were observed at 2Θ - 24.2, 34.2 and 49.8 were indicative of monoclinic structure of Tungsten Trioxide.

The XRD pattern of other composites produced by doping with nitrogen and copper showed the change in intensity for the observed peaks. There was a minor change in intensities N-WO_3 Cu-WO_3 N-Cu-WO_3 samples, respectively. No other information was supplied by the composites of WO_3 because of 1% by weight addition of the dopants. No other changes were observed for the composites other than change in intensities.

4.6 Photo catalysis Results of Catalyst:

4.6.1 Photo catalysis of Tungsten Trioxide:

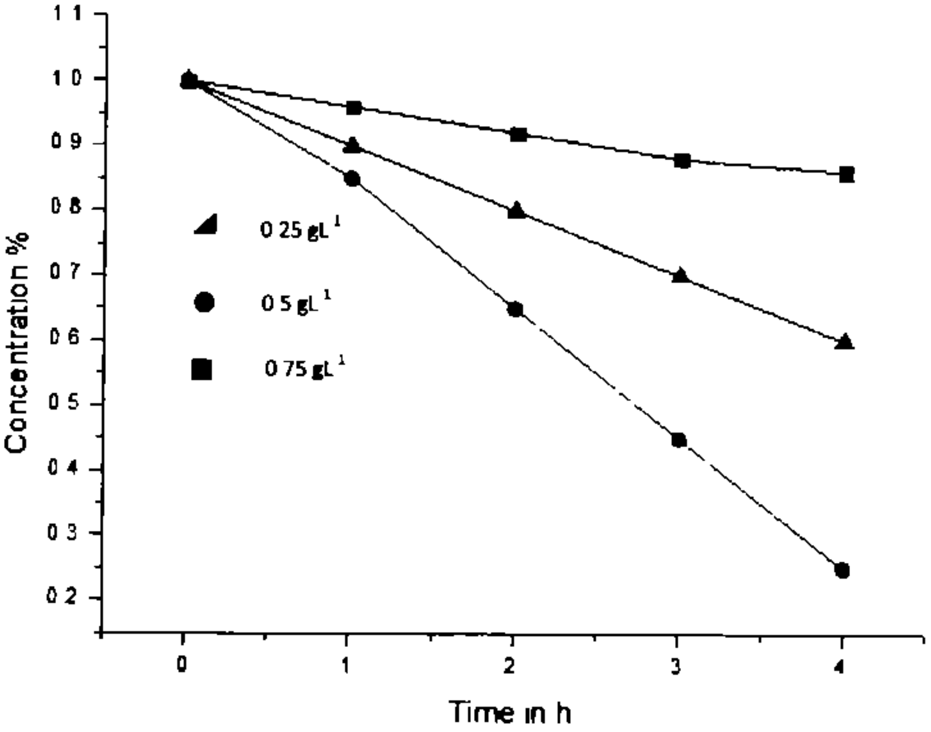


Fig 4.18. Photocatalytic activity of WO_3 under UV light.

The loading of Catalyst in photo catalytic procedures has a significant influence that can strongly influence the degradation of dye. With different concentration of Tungsten Trioxide (WO_3) the experiment was performed and it was observed that by increasing the concentration up to 0 5 g L^{-1} the catalyst exhibits the increased photo degradation proficiency and then decreased as observed in Fig 4.17. This response of the catalyst was due to accessibility of active sites on the catalyst surface and the diffusion of UV light into the suspension made up of methyl blue (MB) and the catalyst used i.e. Tungsten Trioxide (WO_3). The total active sites surface area increased by means of increasing the quantity of catalyst [85]. In the meantime, there was a decrease in UV light penetration because of enlarged smattering effect as a result of an intensification in the turbidity of the suspension. So the photo triggered volume of suspension reduced. Furthermore, to keep the handling expenditures low for industrial use, it is important to use intermediate concentration that is in our case was 0.5 g L^{-1} referred as the optimum catalyst concentration

4.6.2 Photocatalytic Activity of Nitrogen doped Tungsten Trioxide:

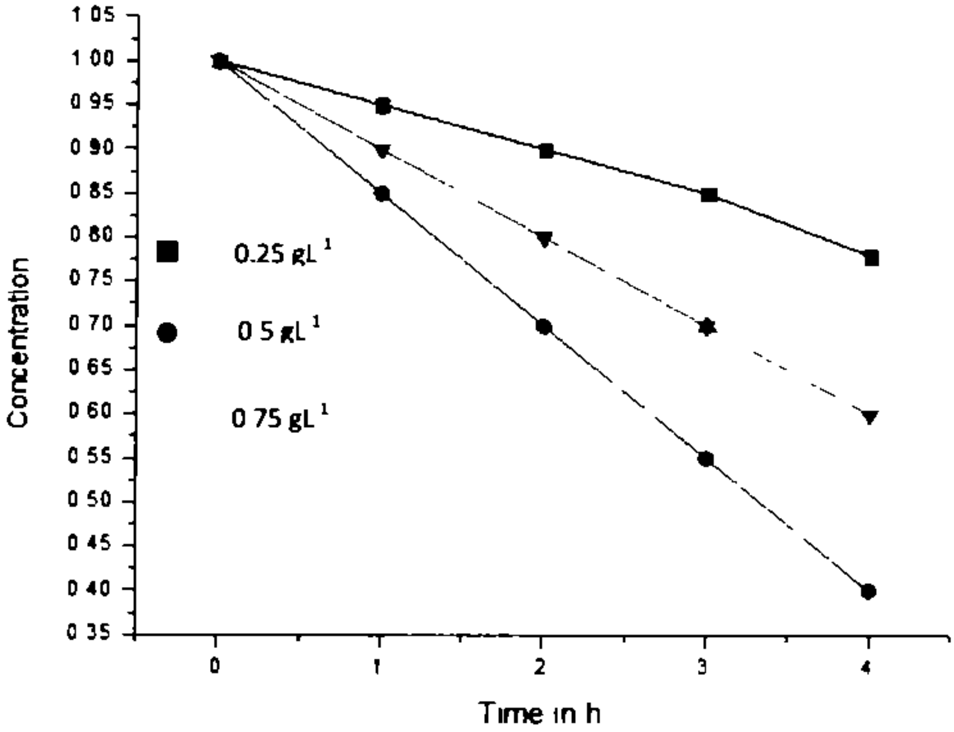


Fig 4.19. Photocatalytic activity measurement of Nitrogen doped Tungsten Trioxide

With different concentration of Nitrogen doped Tungsten Trioxide (WO_3) catalyst the experiment was performed and it was observed that by increasing the concentration up to 0 5 g L^{-1} the catalyst exhibits the increased photo degradation proficiency and then decreased as observed in Fig 4 18 for the increased concentration of the catalyst. At 0 25 gL^{-1} the catalyst showed a very little degradation similarly for the 0.75 gL^{-1} this was due to the response of the catalyst to accessibility of active sites on the catalyst surface and the diffusion of UV light into the suspension made up of methyl blue (MB) and the catalyst used i e Nitrogen doped Tungsten Trioxide (WO_3) The total active sites surface area increased by means of increasing the quantity of catalyst. In the meantime, there was a decrease in UV light penetration because of enlarged smattering effect as a result of an intensification in the turbidity of the suspension So the photo triggered volume of suspension reduced Intermediate concentration that is in our case was 0.5 g L^{-1} referred as the optimum catalyst concentration exhibits the best result for degradation

4.6.3 Photocatalytic Activity of Copper doped Tungsten Trioxide:

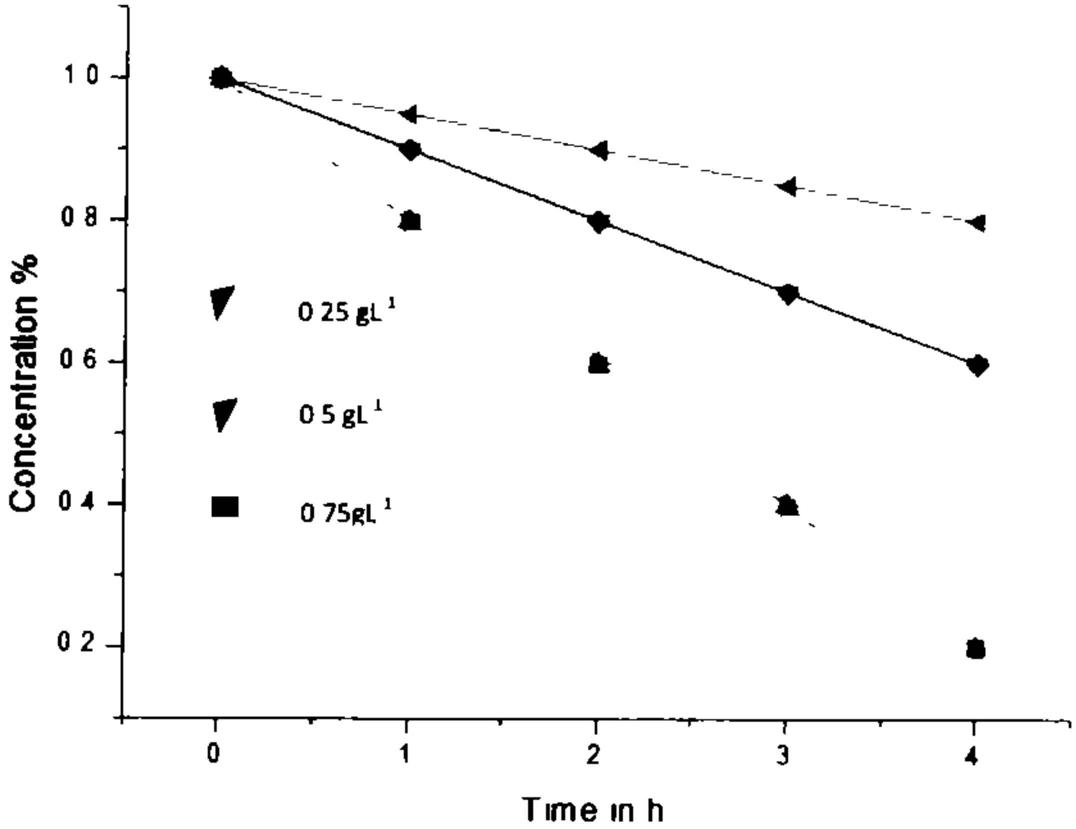


Fig 4.20. Photocatalytic Activity of Copper doped Tungsten Trioxide.

With different concentration of Copper doped Tungsten Trioxide (WO_3) catalyst the experiment was performed and it was observed that by increasing the concentration up to 0 5 g L^{-1} the catalyst exhibits the increased photo degradation proficiency and then decreased as observed in Fig 4 19 for the increased concentration of the catalyst At 0.25 gL^{-1} the catalyst showed a very little degradation similarly for the 0 75 gL^{-1} this was due to the response of the catalyst to accessibility of active sites on the catalyst surface and the diffusion of UV light into the suspension made up of methyl blue (MB) and the catalyst used i.e Copper doped Tungsten

Trioxide (WO_3) The total active sites surface area increased by means of increasing the quantity of catalyst. In the meantime, there was a decrease in UV light penetration because of enlarged smattering effect as a result of an intensification in the turbidity of the suspension. So the photo triggered volume of suspension reduced. Intermediate concentration that is in our case was 0 5 g L^{-1} referred as the optimum catalyst concentration exhibits the best result for degradation

4.6.4 Photocatalytic Activity of Copper & Nitrogen doped Tungsten Trioxide:

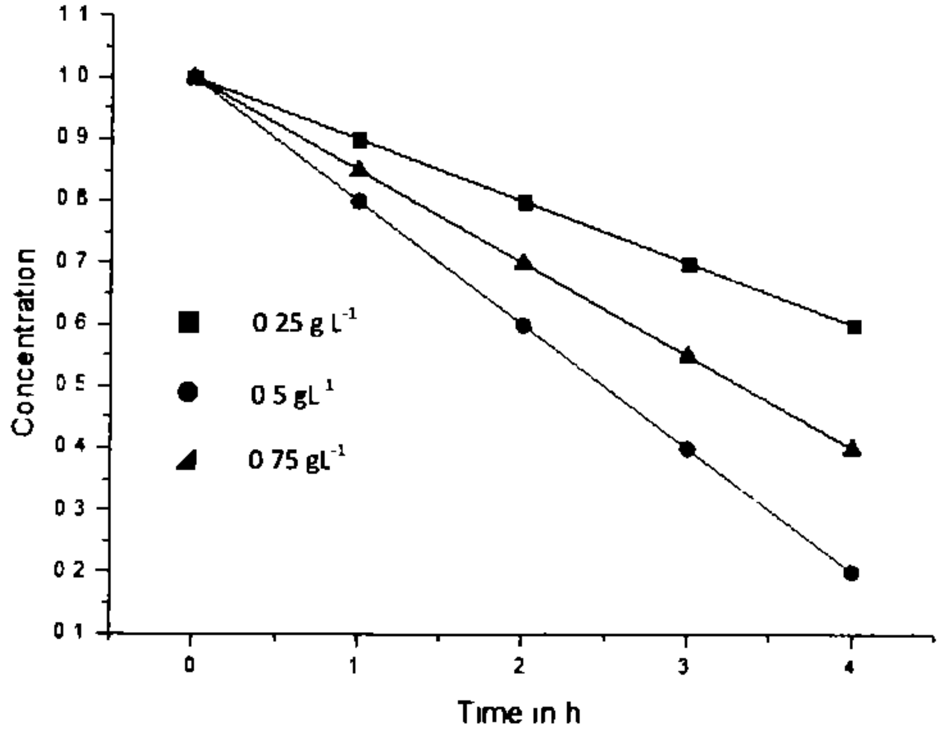


Fig 4.21. Photocatalytic Activity of Copper & Nitrogen doped Tungsten Trioxide

With different concentration of Copper & Nitrogen doped Tungsten Trioxide (WO_3) catalyst the experiment was performed and it was observed that by increasing the concentration up to 0 5 g L^{-1} the catalyst exhibits the increased photo degradation proficiency and then decreased as observed in Fig 4.19 for the increased concentration of the catalyst At 0 25 gL^{-1} the catalyst showed a very little degradation similarly for the 0 75 gL^{-1} this was due to the response of the catalyst to accessibility of active sites on the catalyst surface and the diffusion of UV light into the suspension made up of methyl blue (MB) and the catalyst used i e Copper & Nitrogen doped Tungsten Trioxide (WO_3). The total active sites surface area increased by means of increasing the quantity of catalyst. In the meantime, there was a decrease in UV light penetration because of enlarged smattering effect as a result of an intensification in the turbidity of the suspension So the photo triggered volume of suspension reduced. Intermediate concentration that is in our case was 0.5 g L^{-1} referred as the optimum catalyst concentration exhibits the best result for degradation

4.6.5 Photocatalytic Activity measurements of all the catalysts with different Concentrations:

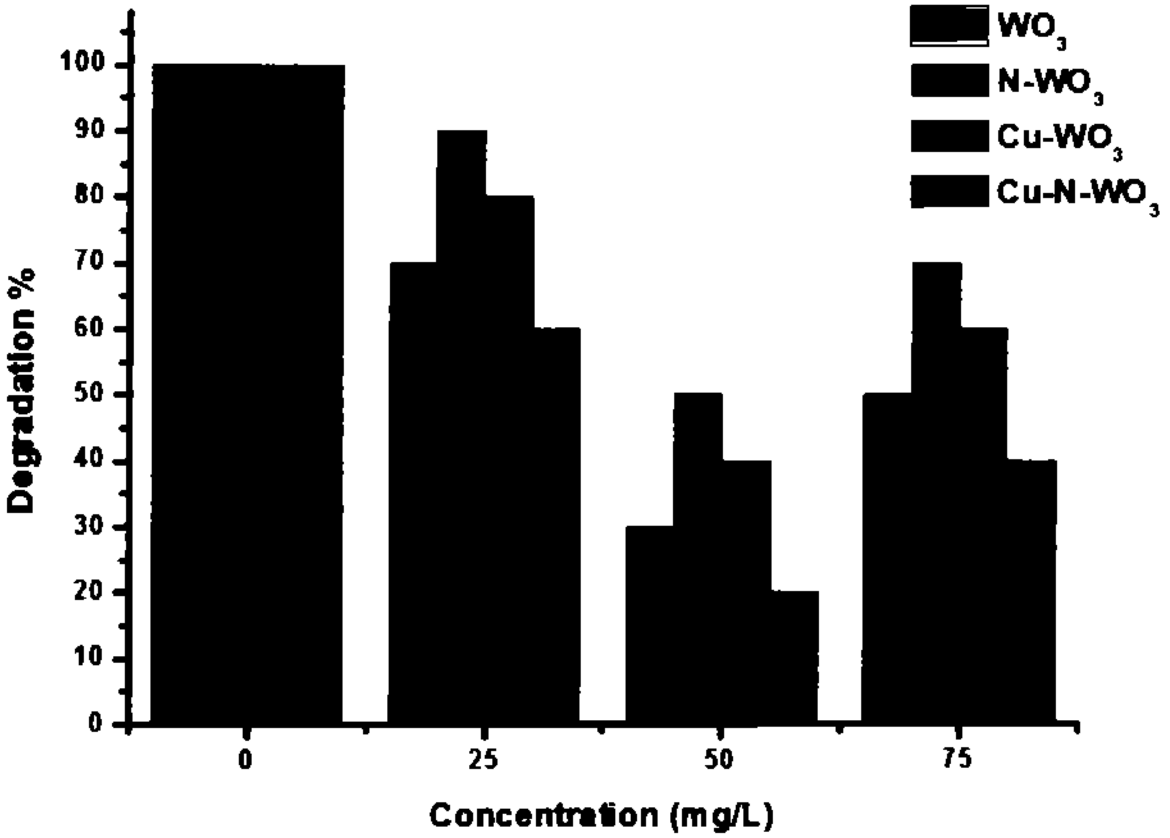


Fig 4.22. Photocatalytic Activity measurements of all the catalysts with different concentrations.

This graph interprets the maximum degradation of all the catalysts at concentration of 50 % which reveals that 0 5 gL^{-1} is the optimum catalyst concentration for all the catalysts If we decrease or increase the concentration the degradation % decreases due to the captivity of UV light at activity surfaces

CONCLUSIONS

- The cost effective catalysts using Tungsten Trioxide were produced by co-doping, using simple wet chemical methods

- The produced catalyst were characterized by the following techniques

  1) SEM (Scanning Electron Microscopy)

  2) FT-IR (Fourier Transform Infrared Spectroscopy)

  3) UV-DRS (Diffused Reflectance Spectroscopy)

  4) EDX Analysis

Using all these techniques the production of WO_3, N- WO_3 Cu- WO_3 N-Cu- WO_3 photo catalysts were confirmed SEM reveals that all the photocatalysts produced were having porous structure which was very useful for photocatalysis As pores absorb more light and provide more active sites for the process of Photocatalysis

- The produced Catalysts were also Photo Catalyzed to measure the concentration

FUTURE PRESPECTIVES

- The produced Photo Catalysts can be used as a Source of Energy
- It can also tackle with the energy crisis of Pakistan
- It can be used in all possible energy applications
- It can be used in Gas sensing
- The main application of these catalysts are in Photo catalysis

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