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VAN YUZUNCU YIL UNIVERSITY
INSTITUTE OF NATURAL AND APPLIED SCIENCES
MECHANICAL ENGINEERING DEPARTMENT

PHOTOCATALTIC ACTIVITY OF Zr-DOPED TiO_2 ON ORGANIC COMPOUNDS

M.Sc. THESIS

PREPARED BY: Jasım Mohammed HAWEZI
SUPERVISOR: Asst. Prof. Dr. Halil İbrahim YAVUZ

VAN-2018

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ACCEPTANCE and APPROVAL PAGE

This thesis entitled **"PHOTOCATALTIC ACTIVITY of Zr-DOPED TiO_2 on ORGANIC COMPOUNDS"** prepares by JASIM MOHAMMED HAWEZI under supervision of Asst. Prof. Dr. Halil İbrahim YAVUZ in the Department of Mechanical Engineering has been accepted as a M.Sc. Thesis. According to Legislations of Graduate Higher Education on…... /..... /..... With unanimity / majority of votes members of jury.

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Member: Asst. Prof. Dr. Hülya DURMAZ BEKMEZCİ	Signature: .....

This thesis has been approved by the committee of The Institute of Natural and Applied Science on...…../...../...…... with decision number.....

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THESIS STATEMENT

All information presented in the thesis was obtained according to the ethical behaviors and academic rules frame. And also, all kinds of statement and source of information that does not belong to me in this work prepared in accordance with the rules of these were cited to the source of information absolutely.

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Jasim Mohammed HAWEZI

ABSTRACT

PHOTOCATALTIC ACTIVITY of Zr-DOPED TiO_2 on ORGANIC COMPOUNDS

HAWEZI, Jasim Mohammed
M.Sc. Thesis: Mechanical Engineering
Supervisor : Asst. Prof. Dr. Halil İbrahim YAVUZ
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Doped-TiO_2 nanocrystalline powders (nM:TiO_2:Zr) with anatase structure .we have focused on the production of different nanostructured Zr modified TiO_2 powders as a material for photocatalytic by sol gel assist- polymerizing complexing combustion method (PCCM) and hydrothermal method and characterized by SEM Analysis, UV-VIS anylsis, XRD Analysis Of Zr Modified TiO_2 particles, XRD Analysis Of TiO_2 and 5 % ZrO_2-TiO, XPS Anlysis Of Zr Modified TiO_2 particules, XPS Anlysis Of 5%Zr-TiO_2 particules .Results revealed that the anatase structure is highly stable for all doped TiO_2 prepared compounds with enhancement in the surface area. UV-Vis diffuse reflectance spectra showed that these dopants were responsible for narrowing the band gap of TiO_2 and shifting its optical response from ultraviolet to visible-light region. The photocatalytic activities of Zr-doped TiO_2 catalysts were investigated with testingwith these materials (Methylene Blue (MB) Test, Purple Dye (PD) Test, Methly Orange (MO) Test and Malecite Green (MG) Test) . all experiments were done with the help of a xenon lantern to simulate the sun's rays., it was found that The results of the obtained tests have a longer duration than the results in the literature made with UV, they are very important in terms of cost analysis and practical use. the resulting disintegration rates are still faster than the best alternative methods. for this reason a great obstacle for the commercialization of the particle has come to an end.

Keywords: Nanotechnology, Photocatalytic, Zr-doped TiO_2.

ÖZET

Zr-KATKILI TiO_2'nin ORGANİK BİLEŞİKLER ÜZERİNDEKİ FOTOKATALİZ ETKİSİ

HAWEZI, Jasim Mohammed
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Bu çalışmanın ana hedefi Zr-katkılı TiO_2'nin organik bileşikler üzerindeki fotokataliz etkisini araştırmaktır.Bu doğrultuda önce anataz yapıdaki TiO_2 nano-kristalleri (nM: TiO_2:Zr) Zr ile katkılandırılmıştır. Bu amaçla ince asıltılı pelte (sol-gel) destekli polimerleştirici kompleks ateşleme yöntemi (PCCM) ve hidrotermal yöntemleri kullanılarak farklı nano-yapılara sahip çeşitli TiO_2 tozları (Zr-modifiye TiO_2 parçacıkları, TiO_2 ve % 5 ZrO_2-TiO) elde edilmiştir. Ardından bunlar SEM, UV-VIS, XRD ve XPS analizlerine tabi tutularak özellikleri tespit edilmiştir. Sonuçlar TiO_2 ile hazırlanmış tüm maddelerin anataz yapılarının yüksek düzeyde kararlı olduklarını ve yüzey alanlarının arttığını göstermektedir. UV-VIS dörtgen yansıma spektroskopi sonuçları TiO_2'nin bant genişliğinin daralmasından ve optik tepki alanının morötesinden görülebilir ışığa kaymasından katkı maddelerinin sorumlu olduğuna işaret etmektedir. Zr-katkılı TiO_2 katalizörlerinin fotokatilitik aktiviteleri Metilen Mavisi (MB Test), Mor Boya (Purple Dye Test), Metil Portakal (Methyl Orange Test) ve Malaşit Yeşili (Malecite Green Test) testleri ile araştırılmıştır. Gün ışığının etkilerini taklit etmek için tüm testler için bir ksenon feneri yardımıyla gerçekleştirilmiştir. Her ne kadar bu yaklaşımla testlerden sonuç almak UV yöntemine göre daha uzun sürse de, bu yöntem daha ekonomik ve pratiktir. Ayrıca ortaya çıkan çözünme de en iyi alternatif yöntemlere göre daha hızlı gerçekleşmektedir. Bu nedenle incelenen parçacıkların ticarileştirilmesinin önündeki önemli bir engel ortadan kalkmaktadır.

Anahtar kelimeler: Fotokatalitik, Nano-teknoloji, Zr-modifiye TiO_2

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Jasim Mohammed HAWEZI

/ / 2018

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SYMBOLS AND ABBREVIATIONS

Some symbols and abbreviations used in this study are presented below, along with description.

Ag	Silver
Al	Aluminum
AODs	Advanced oxidation processes
Au	Gold
B	Boron
BPA	Bis phenol A
C	Carbon
CB	Conduction band
CL^-	Chlorine
Co	Carbon monoxide
CO_2	Carbon dioxide
Cr	Chromium
CVD	Chemical vapour deposition
e^{cb}	Excited conduction band
EDC	Endocrine disrupting chemical
Fe_2O_3	Ferric oxide
GEL	Gelution
$h^{+\,vb}$	Valence band holes
H_2O	Water
H_2O_2	Hydrogen peroxide
HCLO	Hydrogen peroxide
HMEP	Hydroxy methyl ethyl phenol
MB	Methylene blue
Mn	Manganese
M-O-M	Metal oxide metal
N	Nitrogen
NO^{3-}	Nitrate
$^{\bullet}OH$	Hydroxyl radical
O_3	Ozone
S	Sulfur
SEM	Scanning electron microscopy
SiO_2	Silicon dioxide
$SO_4^{\,2-}$	Sulfate
SOL	Solution
TEM	Transmission electron microscopy
Ti	Titanium
TiO_2	Titanium dioxide
UV	Ultra-violet
V	Vanadium

VB	Valence band
VOCs	Volatile organic compounds
W	Tungsten
WO_3	Tungsten trioxide
XPS	X-ray photon spectroscopy
XRD	X-ray diffraction
ZnO	Zinc oxide
ZnS	Zinc sulfide
Zr	Zirconium
Zr-TiO_2	Zirconium doped titanium dioxide

Symbols:

Å	Angstrum
eV	Electron volt
h	Hour
L	Lıter
Min	Mınute
ng/L	Nanogram/lıter
nm	Nano metre
C^o	Celsıus degree
PH	Measure of hydrogen ion concentration
W	Watt
θ	Half the angle of diffraction
λ	X-ray wavelength

1. INTRODUCTION

1.1 Problem Statement

Nano materials have attracted senior attention in last years because of the variation in their structural, electronic, magnetic, thermal and optical properties (Zheng et al.,, 2001; Radecka et al.,, 1993). These properties of the nano particles change when their size, shape and crystal structure change. The unique properties of the nano particles locate the performance of the particles in both energy generation and environmental problems like catalysis, electronics, optics and magnetism. Semiconductors used for the photocatalytic degradation of organic molecules are usually metal oxides or metal sulfides. The most commonly studied semiconductors include TiO_2, ZnO, WO_3, Fe_2O_3, and ZnS (Fox et al., 1993). In searching for an ideal photocatalyst for treatment of organic molecules using sunlight, some factors must be taken into account; like oxidation potential and energy of the band gap. The oxidation potential is important, since the ability to form photogenerated valence band holes (h^+_{vb}) and to create hydroxyl radicals ($HO^{\bullet}_{ads}$) in water is key to its use as a photocatalyst for the oxidation of organic molecules. This is also true of the reducing power of the excited conduction band electron (e^{cb}), which must be of sufficient energy to reduce molecular oxygen to superoxide (Halmann et al., 1996). These two chemical processes are the key to the photocatalysis of organic molecules to simple gaseous products (H_2O, CO_2) and inorganic ions (NO^{3-}, SO_4^{2-}). The energy of the band gap of the semiconductor defines the energy of light needed to excite an electron to the conduction band, which leaves a positively charged hole in the valence band, h^{+vb} (Oppenländer et al., 2003). If the required wavelength for a given semiconductor to form charge carriers is outside the range of the solar spectrum, then that semiconductor is of no use for the degradation of organics using sunlight without significant electronic modification. One of the ultimate nano particles intended inorganic metal oxide is TiO_2, due to photo stability, inexpensiveness, nontoxicity, high surface area, porosity, chemical stability and relative low production cost. TiO_2 is the traditional Semiconductor photo catalysis used in the area historically. It has received much awareness during last three decades as a favorable solution for both energy generation

and environmental problems (Dumitriu et al., 2000; Takeda et al., 2001). The acceleration of a chemical processing by the existence of a catalyst with light is called photo catalytic. The catalyst accelerate the photo reaction by interaction with the substrate in its ground or excited state and/or with a major photoproduct, be based on the technique of the photo reaction and itself remaining without change at the end of each catalytic cycle.TiO_2 based photocatalysts are still the most commercialized products in the market although there are different alternatives present. They are widely used in different areas such as bactericidal and water purification applications. Some of the major applications of TiO_2 photocatalyst are shown in Figure1.1 TiO_2 photocatalyst is considered to be used for several other applications such as water disinfection, determination of dissolved organic nitrogen compounds in natural waters, photoreduction of mercuric salt solutions (Jacoby et al., 1998; Lau et al., 1998). Some of the TiO_2-based photocatalytic products that have appeared in the market in Japan are shown in Table 1.1

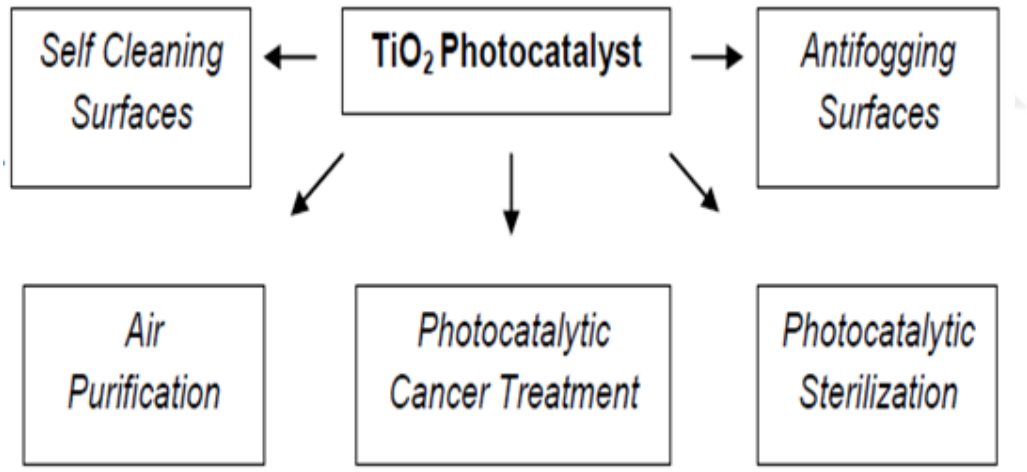

Figure 1.1 Major applications where TiO_2 photocatalyst (Fujishima et al., 2000)

Table 1.1 TiO_2-based photocatalytic products that have appeared in the market in Japan (Fujishima et al.,2008)

Categories	Products	Properties
Purification facilities	Air conditioners, air cleaners, purification system for pools	Air / water cleaning antibacterial
Household goods	Clothes, leathers, fibers, sprays, lighting	Self-cleaning antibacterial
Road construction materials	Traffic sign lamp covers, coating, road blocks, soundproof and tunnel walls	Self-cleaning, air cleaning
Interior furnishing materials	Wallpaper, tiles, window blinds	Self-cleaning antibacterial
Exterior construction materials	Glass, plastic films, tiles, tents, coating, aluminum panels	Self-cleaning
Others	Facilities for agricultural uses	Air cleaning , antibacterial

Figure 1.2 Polycarbonate plastic and epoxy resins

1. 2 Objectives

The objective of this research is to investigate photocataltic activity of Zr-doped TiO_2 on organic compounds like these materials (Methylene Blue (MB) , Purple Dye (PD) , Methly Orange (MO) and Malecite Green (MG)).

The most important objectives for the study are as followed:

(i) Characterize prepared TiO_2 and Zr-TiO_2 particles
(ii) Compare the photocatalytic activity of TiO_2 and Zr-TiO_2 in Organic Compounds degradation under irradiation by sunlight
(iii) Determine the effects of the amount of Zr - doping

1.3 Organization of the thesis

This thesis is divided into five chapters. Chapter 1 is an introduction to the motivation and objectives of the project, followed by a description of the scope of the thesis. Chapter 2 is a literature review of the photo oxidation process in wastewater treatment. In Chapter 3, the materials and analysis methods used in this study are described. The experimental results and discussions are demonstrated in Chapter 4. Finally, a summary of the findings from this thesis is presented in Chapter 5.

2. LITERATURE REVIEW

2.1 Studies on Synthesis of TiO_2 Particles

2.1.1 TiO_2 nano particles

Titanium (Ti) is a chemical element in the periodic table, atomic number 22, and atomic weight 47.90, it occurs in the fourth group of periodic table, as shown in Figure 2.1 and its chemistry shows similarities to that of zirconium and silicon, the outer electronic arrangement is $3d^2 4s^2$, and the principal valence state, correspondingly of $^{4+}$, and $^{2+}$, known as being less stable. Titanium burns in air when heated to give the oxide, TiO_2.

TiO_2 exists in three various crystal structures that are anatase (tetragonal), brookite (orthorhombic) and rutile (tetragonal), as shown in Figure 2.2 (Macwan et al., 2011). Rutile is thermodynamically stable and chemically inert phase even in strongly acidic or basic conditions but anatase and brookite are thermodynamically metastable that transform to rutile when they are heated, Table 2.1 Each crystal structure show specific chemical, physical and optical properties controlling their applications, Table 2.2 With the highest refractive index, Anatase has higher photocatalytic activity than rutile (Liu et al., 2003; Sclafani et al., 1996). rutile has found extensive use in paintings and inks as a white pigment (Cassaignon et al., 2007). But brookite is seldom interested because of its instable properties. As it is shown from the unit cells of anatase and rutile given in Figure 2.2 the basic building block consists of a titanium atom enclosed by six oxygen atoms in a more or less deformed octahedral configuration. In rutile, neighboring octahedral share one corner along [1 1 0] type directions are accumulate with their long axis. In anatase , the corner sharing octahedral form the (0 0 1) planes. They are linked with their borders with the plane of octahedral below. In all three TiO_2 structures, the accumulate of the octahedral come in three fold coordinated oxygen atoms.

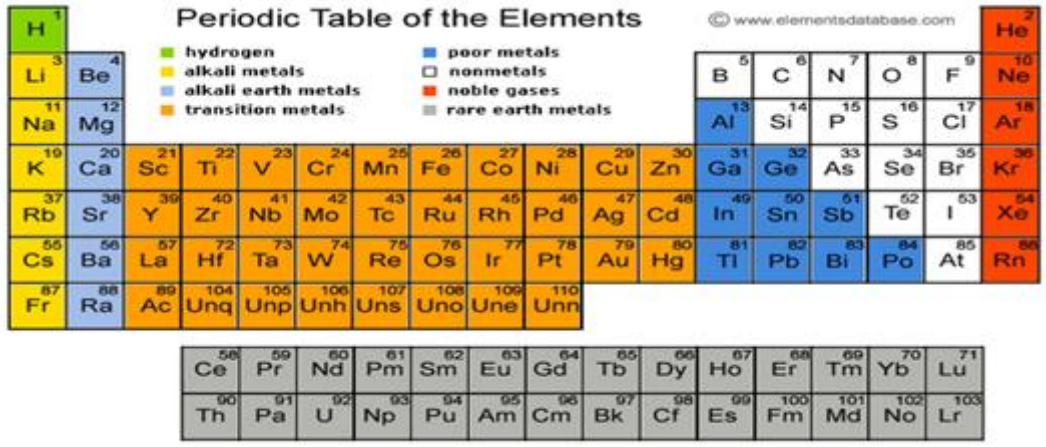

Figure 2.1 Table of elements.

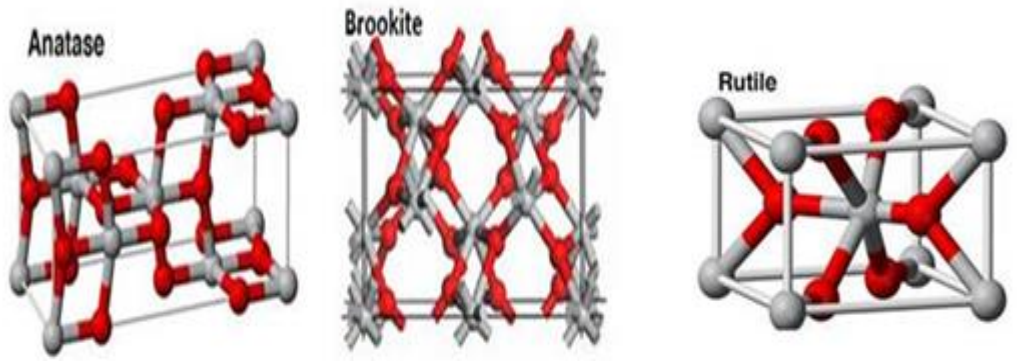

Figure 2.2 Crystallographic structures of TiO_2.

Table 2.1 Phase transition of titanium oxide.

AMORPHOUS	Temperature.	Temperature.	Temperature.
	650 °C	375 °C	510 °C
	RUTILE	ANATSE	BROOKITE

Table 2.2 Physical and chemical properties of three TiO_2 structures (Rodai et al., 2004).

Properties	Rutile	Anatase	Brookite
Molecular formula	TiO_2	TiO_2	TiO_2
Molar mass g/mol	79.866		
Crystal system	Tetragonal	Tetragonal	Orthorhombic
Energy gap Ev	3.06	3.29	
Color	White solid	White solid	White solid
Density point °C	4.27	3.90	4.13
Melting point	1855	Transformed into rutile	Transformed into rutile
Boiling point	2972		
Refractive index (nD)	2.609	2.488	2.583
Dielectric constant ε	110~117	48	78
Hardness (Mohs scale)	7.0~7.5	5.5~5.6	5.5~5.6

The phase diagram of Ti-O system is given in Figure 2.3 As seen in the Figure 2.3 Ti-O system has many stable phases, which is an indication of easy reducibility. The region Ti_2O_3+TiO_2 also includes seven phases (TinO2n-1) (Diebold and Surf. Sci.2003).

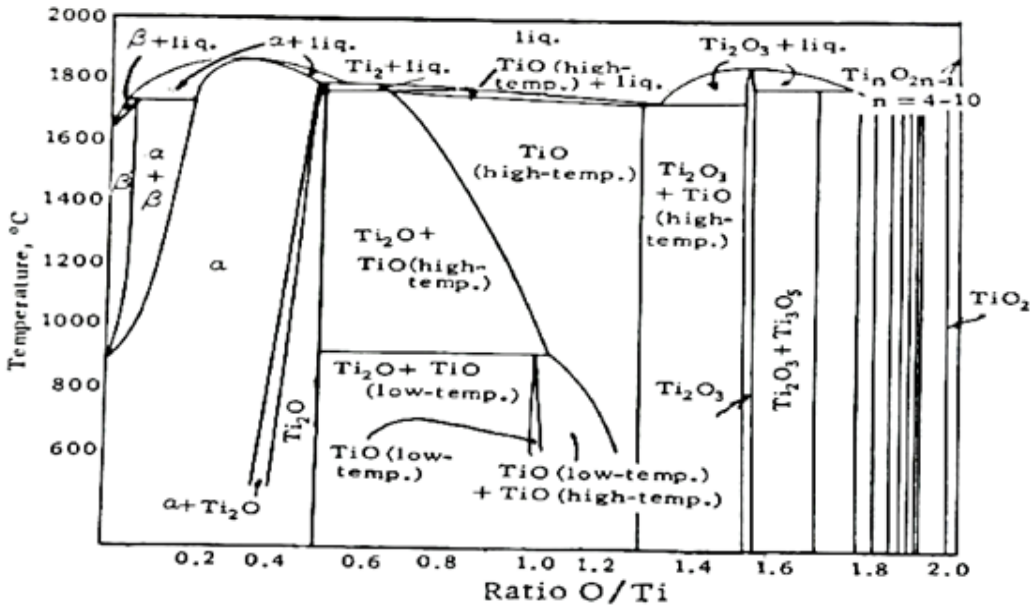

Figure 2.3 Phase diagram of Ti-O system (Samsonov et al.,1973).

In addition to the crystal structure, shape and size of the Nano particles also play a serious role in application fields. The morphology of TiO_2 particles controls the surface-to-volume ratio, thus the active sites on the particle surface. Relying on the

production methods and reaction conditions Nano sized titania particles may be spherical, tube, rod, fiber, pinecone and flower as show in Figure 2.4

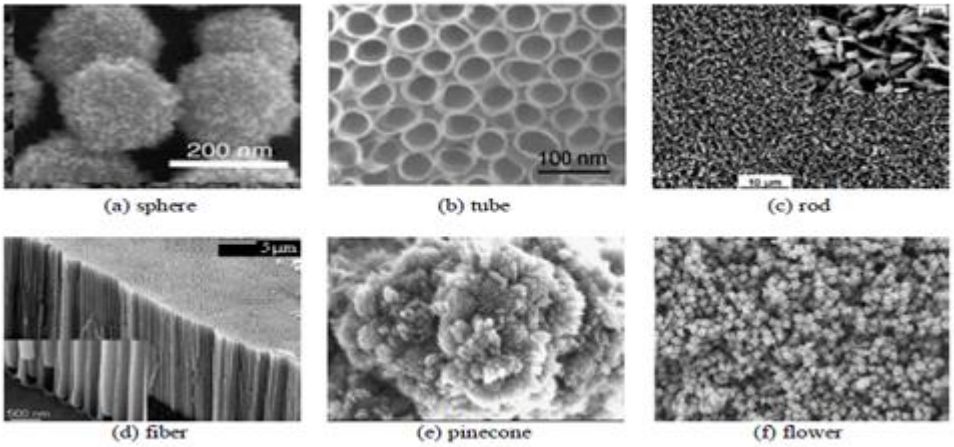

Figure 2.4 SEM images of TiO_2 nano particles.

In different morphologies (a: (Sun et al., 2010).b: (Macak et al., 2005).c, d: (Chen et al., 2007). e, f: (Li et al., 2006)).

TiO_2 is one of the ultimate studied inorganic metal oxides because of its superior optical properties of high refractive index that leads to high hiding power and whiteness, high surface area, porosity, chemical stability and relative low production cost. Thus, titania Nano crystals including optoelectronic, electronic and catalytic properties are used as sensors (Sotter et al., 2007; Diebold and U., 2003; Katayama et al., 1990).antireflection (Vicente et al., 2002). for the reduction of CO_2

(Wu et al., 2005; Liu et al., 2007). photovoltaic cells (Watanabe et al., 2006). self-cleaning (Allain et al., 2007). antibacterial-coatings (Kartsonakis et al., 2008; Evans et al., 2007). Pigment for dyeing, filler of plastics and papers (Nelson et al., 2008). and photocatalyst for environmental purifications (Sakkas et al., 2010; Xiong et al., 2010). the performance of TiO_2 Nano particles in these application fields strongly depends on their size, shape and crystal structure.

Danciu et al., (2008), Explored the preparation of TiO_2-ZrO_2 aerogels and worked at their photocatalytic activity. The best catalytic activity was obtained for 9.39 % Zr in mixed oxide.

Rehman et al., (2009), Explained the strategies of making TiO_2 and ZnO visible light active. Among the various techniques employed to produce TiO_2 sensitive to visible light, co-doping of nanometals has produced the most significant results.

Liu et al., (2009), Prepared Zr doped TiO_2 nanotube arrays by electrochemical method and studied photocatalytic activity with Rhodamine B. The results showed that, the photocatalytic efficiency of Zr doped TiO_2 nanotubes was much better than that of TiO_2 nanotubes.

Gao et al., (2010), Successfully reported the incorporation of Zr ion into bulk lattice of TiO_2 via a multi-step sol-gel process. The Zr-doped TiO_2 photocatalysts exhibited much higher photocatalytic efficiency from pure TiO_2 in the degradation of bisphenol A under UV irradiation and complete mineralization of BPA was completed. The ultimate photocatalytic activity of Zr doped TiO_2 was attributed to gradually upward shift of the conduction bands together with increasing Zr content, thus resulting in a stronger reduction power of photogenerated electrons and participate to the improved photoactivity.

Murugesan et al., (2011) . Successfully synthesized Zr^{4+}, La^{3+} and Ce^{3+} doped mesoporous TiO_2 materials by sol-gel method and evaluated their photocatalytic activity.

Mu et al., (2011), Prepared Si-doped TiO_2 nanoparticles with anatase crystalline phase by a hydrothermal method using acetic acid like a solvent. The photo electrochemical results show that doping of suitable amount of Si in TiO_2 assist in fast movement of electrons towards cathode. This can be described by the easy transfer and separation of photo produced electrons and holes.

Andronic et al., (2011),Studied the photochemical synthesis of copper sulphide/titanium oxide photocatalyst and examined its dye degradation efficiency (methyl orange and methylene blue) under UV and visible light irradiation. The enhanced activity of composite was explained by the irreversible charge separation, decrease in the kinetic bonds when interacting with the dye molecules.

Kambur et al., (2012), Reported the preparation of TiO_2-ZrO_2 binary oxide nanoparticles and estimated its performance for the photodegradation of phenol. And catalytic activity of binary oxide in 50% wt ratio was found to be high.

Kim et al., (2012), studied the preparation of visible light responsive zirconium-doped TiO_2/SiO_2 photocatalyst by sol-gel process. It was found that doping of TiO_2 with suitable amounts of SiO_2 and zirconium can enhance its photocatalytic activity. The addition of SiO_2 supress the particle size and TiO_2 phase transformation from anatase to rutile and promote thermal stability of composite. The addition of zirconium results in exact, more uniform particles and increased surface acidity of the TiO_2 catalysts due to formation of powerful surface OH groups. The absorption spectrum of Zr doped TiO_2/SiO_2 catalyst shifted significantly to visible light region as compares to TiO_2 alone.

Liu et al., (2012), Reported that cerium-doped SiO_2/TiO_2 nano structured fibers were prepared by a self-confident sol-gel method and checked its effect on the degradation of methylene blue (MB) under artificial sunlight irradiation. The 0.2% Ce-doped SiO_2/TiO_2 fibers exhibited higher photocatalytic activity towards decomposition of MB.

Mattsson et al., (2013), Synthesized Zr and Y co-doped TiO_2 nanocomposite and studied its characterization, phase stability, photocatalytic properties and surface chemical.,

Wang et al., (2013), Examined the photostability of titanium dioxide by coating it with cerium ,zirconium as well as some other transition metal oxides. It was shown these coating materials significantly get better the photo-stability of TiO_2 particles, even with a small coated amount.

Das et al., (2013), Studied the preparation of composites of new series of Ti^{4+} by co-precipitation of homogeneous solution metal salts. And derived mixed oxides show better activity towards photodegradation of methylene blue and rhodamine B and those of a physical nature of ZnO and TiO_2.

McManamon et al., (2013), Examined the effect of addition of various dopants to TiO_2 nanocomposites for the enhancement of photocatalytic activity. The different dopants used were Ag, Zr and S and were found to be efficient in doping.

Park et al., (2013), Studied semiconductor TiO_2 photocatalysts as well as the latest modifications of TiO_2 photocatalyst to get better the photocatalytic activities for an advanced oxidation process.

Kokporka et al., (2013). Synthesized the nanocomposites of mesoporous TiO_2-ZrO_2 and showed the improved photocatalytic activity by production of H_2 under visible light irradiation. Addition of ZrO_2 to TiO_2 leads to thermal stability of TiO_2 even at 800 C˚ and also retards the transformation of anatase to rutile form.

Sasikala et al., (2013), Reported that hybrid photocatalyst of ZrO_2-TiO_2-CdS nano size showed enhanced photocatalytic activity for hydrogen generation from water as compared to its constituent single phase oxides. The increased activity of many component catalyst is attributed to decreased particle size of CdS and increased age of the charge carriers resulting from the efficient interfacial transfer of photo generated electrons at the CdS/TiO_2 and CdS/ZrO_2 interface.

Matejova et al., (2013), Studied the photocatalytic reduction of carbon dioxide with the recently synthesized gold enriched TiO_2 and TiO_2-ZrO_2 catalysts which are prepared by sol-gel method. It was shown that photocatalytic activity decreases over Au/TiO_2-ZrO_2 and Au/TiO_2 compared to parent counterparts. It can be demonstrated by existence of too large Au particles which block oxide surface and either reduces the light absorption ability of catalysts.

Kapusuz et al., (2013), successfully synthesized composites by doping and co-doping B and Zr ions in anatase TiO_2 lattice by using sol-gel method to show increased photocatalytic performance to higher levels. It was consummated that photocatalytic activity of TiO_2 increased by doping with B and Zr which result in formation of oxygen vacancies in crystal and also forming Ti^{4+} defects which result in formation of more energy levels and so on increase the photocatalytic activity.

Gambhire et al., (2014), Announced the synthesis of anatase TiO_2 nanoparticles by sol-gel method which were doped with different metals and non-metals and studied their photocatalytic conduct by insulting MB. The prepared photocatalyst exhibited higher specific surface area and smaller shape particles. The high photocatalytic activity of the C-TiO_2 under visible light irradiation can be attributed to smaller particle size and high specific surface area, optical absorption and showed photocatalytic activity in the visible region.

2.2. Modifications of TiO_2 Nanomaterial's

2.2.1 Electronic processes in TiO_2 photocatalysis

Photocatalysis is excessively utilized to describe the process in which the acceleration of a reaction occurs when a material generally a semiconductor, interacts with light of appropriate energy (or of a certain wavelength) to produce reactive oxidizing species that lead to the photocatalytic transformation of a pollutant. It must be noted that during the photocatalytic reaction, at least two proceedings must occur together for the effective production of reactive oxidizing type to occur. Typically, the first include the oxidation of adsorbed H_2O by photogenerated holes, the second include reduction of an electron acceptor by photoexcited electrons, and these reactions lead to the production of a hydroxyl and superoxide radical anion, respectively (Mills et al., 1997). In photocatalysis, light of energy bigger than the band gap of the semiconductor, which excites an electron from the valence band to the conduction band, as shown in Fig.2.6 In case of anatase TiO_2, the band gap is 3.2 eV, thus UV light ($\lambda \leq 387$ nm) is desired. Fig.2.5 (Kim et al., 1998). The absorption of a photon leads to excites an electron to the conduction band (e^{-CB}) generating a positive hole in the valence band (h^{+VB})

$$TiO_2 + h_v \rightarrow h^{+\,VB} + e^{-CB} \quad \text{..... (Eq.1.1)}$$

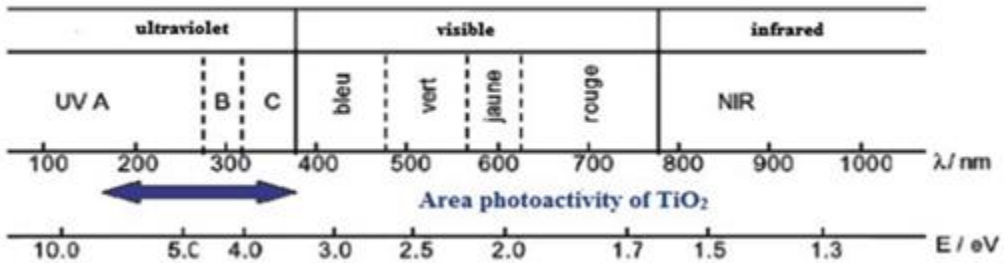

Figure 2.5 The light spectrum with the zone of action TiO_2.

by band gap illumination (Ibhadon and Fujishima et al., 2008). leading to the creation of "electrons" in the conduction band and "holes" in the valance band

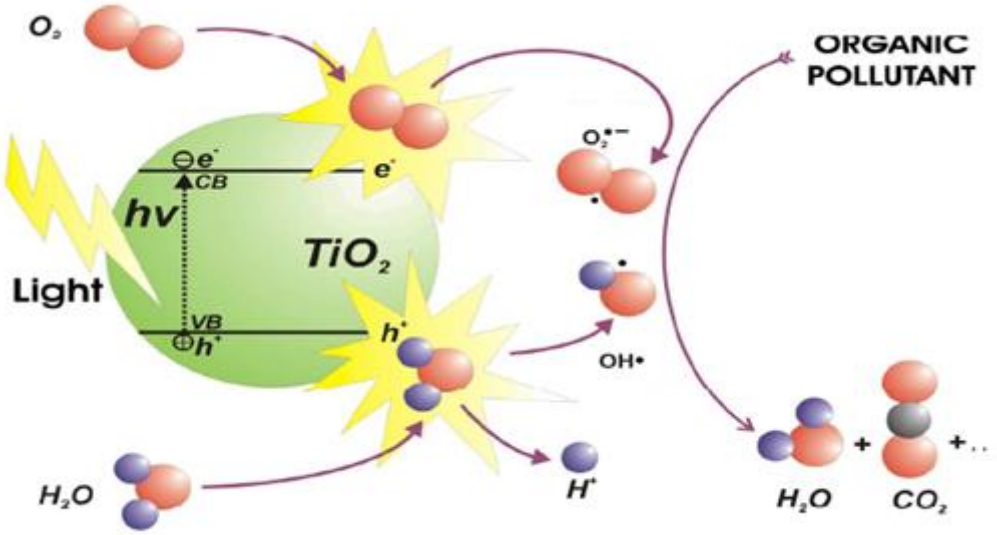

Figure 2.6 Schematic of semiconductor excitation.

Charge carriers able to be trapped accordingly Ti^{3+} and O^{-} defect sites in the TiO_2 lattice, or they can recombine, disperse energy (Tachikawa et al., 2007). The charge carriers can migrate to the catalyst surface and initiate redox reactions with adsorbents (Cozzoli et al., 2003). Positive holes able to oxidize OH^- or water at the surface to output $^{\bullet}OH$ radicals (Eq. 1.2) which, are quite powerful oxidants Table 2.3. The hydroxyl radicals can then oxidize organic species with mineralization producing mineral salts, CO_2 and H_2O (Eq. 1.5) (Hoffmann et al., 1994).

Table 2.3 Oxidation potential (V)

Oxidant	Oxidation potential (V)
$^{\bullet}OH$ (hydroxyl radical)	2.80
O_3 (Ozone)	2.07
H_2O_2	1.77
HCLO (hydrogen peroxide)	1.49
CL^- (chlorine)	1.36

$e^{-CB} + h^{+VB} \rightarrow$ energy (Eq. 1.2)

$H_2O + h^{+VB} \rightarrow {}^{\bullet}OH + H^{+}$ (Eq. 1.3)

$O_2 + e^{-CB} \rightarrow O_2^{\bullet-}$ (Eq. 1.4)

${}^{\bullet}OH$ + pollutant $\rightarrow\rightarrow\rightarrow H_2O+CO_2$ (Eq. 1.5)

$O_2^{\bullet-} + H^{+} \rightarrow {}^{\bullet}OOH$ (Eq. 1.6)

${}^{\bullet}OOH + {}^{\bullet}OOH \rightarrow H_2O_2+O_2$ (Eq. 1.7)

$O_2^{\bullet-}$ + pollutant $\rightarrow\rightarrow\rightarrow H_2O+CO_2$ (Eq. 1.8)

${}^{\bullet}OOH$ + pollutant $\rightarrow H_2O+CO_2$ (Eq. 1.9)

Electrons in the conduction band able to be rapidly trapped by molecular oxygen adsorbed on the titania particle, reduced to take shape superoxide radical anion ($O_2^{\bullet-}$) (Eq, 1.4) that may further react with H+ to generate hydroperoxyl radical (${}^{\bullet}OOH$) (Eq. 1.6) and moreover electrochemical reduction yields H_2O_2 (Eq. 1.7) (Emilio et al., 2006; Choi et al., 1994). These reactive oxygen species may also participate to the oxidative pathways such as the degradation of a pollutant (Eq. 1.8 and 1.9) (Tachikawa et al., 2007; Hoffmann et al., 1994; Emilio et al., 2006). The effectiveness of titania nanomaterials in the above mentioned applications mightily depend on their physical and chemical properties like of crystallinity, crystal structure, crystallite size, specific surface area, thermal stability and quantum efficiency (Ohtani et al., 1997; Aust et al., 2006). For example, in solar applications a narrower band gap energy is proper to obtain a higher photon capture efficiency. Undoped TiO_2 display a wide band gap, which allows using only a small fraction of the available solar energy (<5 %). Thus, it is very wanted to get better the TiO_2 nanomaterial in order to increase their optical activity by shifting the start of the response from the UV to the visible region. A mighty deal of research is focusing on modifying the properties of TiO_2 in order to fulfill these desirable properties. In general, the modification of TiO_2 nanomaterial can be separated into two main groups, first, bulk modification and second, Surface modification.

(i) Bulk modification

Strange-element-doping is one of the famous methods to enhance the performance of titania nanomaterial (Chen et al., 2007). Generally, two different approaches:

1) Zr, Si, or Al is added to increase the thermal stability and surface area (Durr et al., 2006; Sivakumar et al., 2004; Kitiyanan et al., 2006).

2) Fe, C, N, Cr, S, V, Mn, Co is added to shift the absorption edge over a broader range (Adan et al., 2007; Wu, J. M. and Qi, B., 2007).

In some cases, simultaneous cation and anion doping of TiO_2 also helps in improving the desirable bulk properties of TiO_2 (Wang et al., 2006).investigated the role of a potential promoter, ZrO_2, in enhancing the activity of TiO_2-xNx for the oxidation of gaseous organic compound.The nitrogen-doped photocatalysts were synthesized by reacting amorphous metal oxide xerogels via a sol-gel process with an ammonia solution, followed by calcining the products. They reported that ZrO_2 helped to prevent grain growth and preserve the surface area resulting in higher activity.

(ii) Surface modification

Sensitizing TiO_2 with inorganic or organic compounds can improve its optical absorption in the visible light region(Gratzel, 2001; Tachikawa et al., 2007). In addition, modification of the TiO_2 nanomaterials surface with other semiconductors can change the charge-transfer properties between TiO_2 and the surrounding environment(Lin et al., 2007; Robel et al., 2007).

2.2.2 Doping

Doping is occupied for the improvement of photoresponse of TiO_2. To do so, noble metals, transition metals, rare earths, and non-metals are used (Pelaez et al., 2012). Doping decreases the recombination rate of electrons and holes. Ions used for doping act as electron traps. Also, they decrease the band gap energy (Hoffmann et al., 1995).

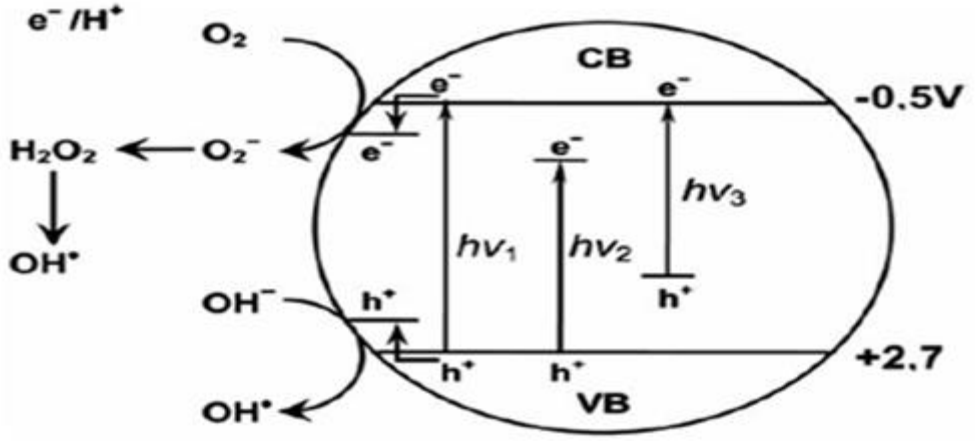

Figure 2.7 Mechanism of TiO_2 photoctalysis:
hv1: pure TiO_2: hv2: metal-doped TiO_2 and hv3: nonmetal-doped TiO_2.

2.2.2.1 Transition metal doping

Transition metal ions provide extra energy levels within the band gap of a semiconductor. The energy required from one of these levels to the conduction band is lower than photon energy required for the situation of unmodified TiO_2. In other words, doping decreases the band gap (Teh et al., 2011). Another benefit of transition metal doping is the improved trapping of electrons to prevent electron-hole recombination during illumination. Amount of dopant has a profound effect on photocatalytic activity. Very small concentrations are beneficial for the process; but large concentrations are detrimental for the photocatalytic activity of TiO_2 (Linsebigler et al., 1995). For a photocatalytic reaction to occur electrons and holes must be transferred to the surface of

the photocatalyst. Thus, dopants should be near to the surface of photocatalyst for efficient charge transfer (Gupta et al., 2011).

2.2.2.2 Zr doping

Zr acts as a stabilizing agent of anatase by shifting the anatase to rutile transformation temperature to higher values. Also, doping with cations having valance smaller than +4 accelerate the transformation due to the provision of a charge compensation mechanism by which the vacancies that enhance the atom transportation in the system are formed. On the other hand, cations with valance higher than +4 hinder ionic transformation with formation of Ti^{3+} cations that results with suppression of the transformation (Kapusuz et al., 2011; Lukac et al., 2007). Zr suppresses anatase to rutile transformation by two main mechanisms. Zr doping increases the strain energy by substituting the Ti^{4+} in anatase structure. For phase transformation to take place firstly, strain energy must be overcome to initiate the phase transformation (Kingery et al., 1976). Also, formation of Ti-Zr-O bond shifts the transformation temperature to higher values by decreasing the mobility of Ti atoms (Yang and Ferreira 1998; Reidy et al.,2006). Zr doping decreases the recombination rate of electrons-holes by trapping electrons (Kapusuz et al., 2013). Ionic radius of Zr^{4+} (0.86 Å) are bigger than that of Ti^{4+} (0.745 Å) (Shannon et al., 1969). Consequently, with a successive doping an expansion at the lattice is expected. Structure tries to compensate this energy by forming defects (Hirano et al., 2003).

2.3 Production routes of TiO_2 Nano particles

For any application field, Nano particles with the controlled crystal structure, size and shape can be synthesized by using an appropriate production method and by controlling the process parameters during the synthesis.

TiO_2 nanoparticles have been prepared by various methods such as,

1- aerosol-assisted chemical vapour deposition (Asif et al., 2012)

2- hydrolysis, micro emulsion method (Shen et al., 2011)

3- chemical precipitation method (Mashid et al., 2006)
4- chemical vapour deposition (CVD) (Jian et al., 2011)
5- sol-gel technique (Bahadur et al., 2011)
6- microwave assisted hydrothermal synthesis (Melis et al., 2012)
7- spray deposition (Uzunova et al., 2010)
8- sputtering (Song et al., 2009)
9- solvothermal method (Zhang et al., 2009)
10- thermal plasma (Tanaka et al., 2011)
11- hydrothermal method (Oh et al., 2009)
12- Flame combustion method (Zhao et al., 2007)

Among these methods hydrothermal and sol-gel method are simple method for synthesis TiO_2 nanoparticles.

2.3.1 Hydrothermal process

The hydrothermal commonly refers to any heterogeneous reaction in the existence of aqueous mineralizers or solvents under high temperature and pressure situations (Byrappaet al., 2001). This synthetic method is normally taking placed in steel pressure container called autoclaves with or without teflon liners under controlled temperature and pressure with the reaction in aqueous solutions. The temperature can be raised above the boiling point of water, arrive the pressure of vapor saturation. Temperature and the amount of solution added to the autoclave in general define the interior pressure produced (Chen et al., 2007). When selecting a suitable autoclave, the most important parameters are the experimental temperature and pressure situations and the corrosion resistance in that pressure-temperature range in a specific solvent or hydrothermal fluid. If the reaction is taking place straight in the container, the corrosion resistance is a firstly factor in the choice of autoclave material., The most successful materials which are corrosion resistant are high-strength alloys, like 300 series (austenitic) stainless steel, nickel, iron, cobalt-based super alloys, and titanium and its alloys (Byrappa et al., 2008) .To prepare nanoparticles with photocatalytic properties

many researchers have been using the hydrothermal method (Yang et al., 2009; Livraghi et al., 2013; Tang et al., 2013)

2.3.2 Sol-Gel Process

The sol-gel process has become the ultimate closely used method for the synthesis of semiconductor photocatalysts. It is a powerful method for tailoring metal oxides to suitable particular applications since a considerable number of parameters can be adjust: e.g., the nature of the precursors, catalyst nature and concentration, temperature and time of reaction, pH, addition of organic additives, reagent concentrations, the amount of water added and aging temperature and time, The main benefit of the sol-gel method is the homogeneous mixing at the molecular level of metal ion which increases the forming of polycrystalline particles with special properties. Other great benefit of the sol-gel method is that during some stage of the process, it is possible to mix different types of dopants. The combination of an active dopant in the sol during the gelation phase permits doping elements to have a direct interaction with backup in such a way that the photocatalytic properties of the material can be enhanced (Zaleska, 2008). The sol-gel method can be known as the conversion of a precursor solution into an inorganic solid by inorganic polymerization process induced by water, it utilizes as a precursor an aqueous or alcoholic mixture of metal-organic (alkoxides) or inorganic salts (chloride, acetate, nitrate, sulfate, etc.). The sol-gel process consists of the preparation of a homogeneous solution follow by the next steps: (a) transformation of the homogeneous solution into a sol by treatment with an appropriate reagent (water with or without any acid/base) (b) aging (c) shaping and (d) thermal treatment (Niederberger, 2009).The precursors are hydrolyzed and condensed to take shape inorganic polymers consist of M-O-M bonds (Brinker et al., 1990).moreover condensation results in a gel. The gels can be dried under hypercritical statuses and aerogels are produced. When the gel is dehydrated under ambient conditions, a xerogel is obtained. The gel is thereafter thermally treated to yield the desired material, and many forms such as monoliths, films, fibers, and monosized powders can be shaped. In different studies, TiO_2 has been commonly synthesized by sol-gel method using as precursor titanium (IV) n-butoxide (Su et al., 2004; Han et al., 2012; Liu et al., 2011;

Choi et al., 2011).be based on the synthesis conditions and temperature of calcination anatase or rutile phase can be gained. The influence of the nature of the oxide precursors has been showed in a research work when the preparation of TiO_2 was carried out by the sol-gel method from two various alkoxide precursors: titanium (IV) and titanium (IV) n-butoxide isopropoxide (Saragiotto et al., 2008). The catalysts were used in the photocatalytic degradation of textile dye .Reactive orange122 irradiating with a 300-W tungsten lamp. A reduction of 65.8 % in TOC was spotted with TiO_2 gained from n-butoxide precursor, while with TiO_2 from isopropoxide, the extreme mineralization accomplished was 27.7 % in 60 min. The writer's referred to the improved activity to the high dispersal of the particles gained when titanium (IV) n-butoxide was used as a precursor. Changes in the band structure can be carried out by doping TiO_2 or ZnO using various synthesis techniques. The sol-gel methods has the advantage that does not demand complicated devices and provides simple and easy means for preparing doped nanosized particles. The tungsten, silver, and tungsten/silver co-doped TiO_2 nanopowders were prepared by sol-gel method (Tobaldi et al., 2013). over the synthesis; titanium (IV) isopropoxide was hydrolyzed using a water/HNO_3 solution to prepare Ag-TiO_2, W-TiO_2, and Ag-W-TiO_2 samples, tungstic acid or silver nitrate was added to the produced TiO_2 sol. The synthesized gels were dried at 120 C°, and then, the dried gels were thermally treated at 450 and 600 C° in a static air flow. The simultaneous presence of anatase, rutile, and brookite was found out in the gels thermally treated at 450 C°. At 600 C°, the only crystalline phases were rutile and anatase. The photocatalytic activity of the samples was estimated under UVA light and visible light irradiation on the degradation of methylene blue solution. The doped and undoped titania and co-doped powders, calcined at 450 C°, display an appreciable photocatalytic activity under visible light irradiation, preferable than aeroxide TiO_2 P25 confirmed by TOC analysis. Numerous coupled semiconductor oxides have been also prepared by means of the sol-gel process including Cr_2O_3-TiO_2, TiO_2-NiO,WO_3-TiO_2, ZrO_2-TiO_2 , Fe_2O_3-TiO_2, and Fe_2O_3-ZnO, among others. precursors of together metal oxides were hydrolyzed both under stirring, The synthesis of mixed metal oxides by sol-gel method mostly affect the surface area with respect to pure metal oxide, which is a significant parameter involved in the photocatalytic activity of a semiconductor material.,

The advantages of the sol-gel process are summarized as follows (MacKenzie, 1981) :

1. Best homogeneity from raw materials.
2. Best purity from raw materials.
3. Less temperature of preparation.
4. Good mixing for multi-component systems.
5. Efficient control of particle shape, size and properties.
6. Best products from the special properties of gel.
7. The creation of special products like films.
8. Creation of new non-crystalline solids outside the range of ordinary glass formation.
9. The exact tuning of chromatographic selectivity by the possibility of creating hybrid organic-inorganic materials.
10. The chance of designing the material structure and property through the suitable selection of sol-gel precursor of other building blocks.
11. The chance of achieving enhanced constant phase stability and performance in chromatographic separations.

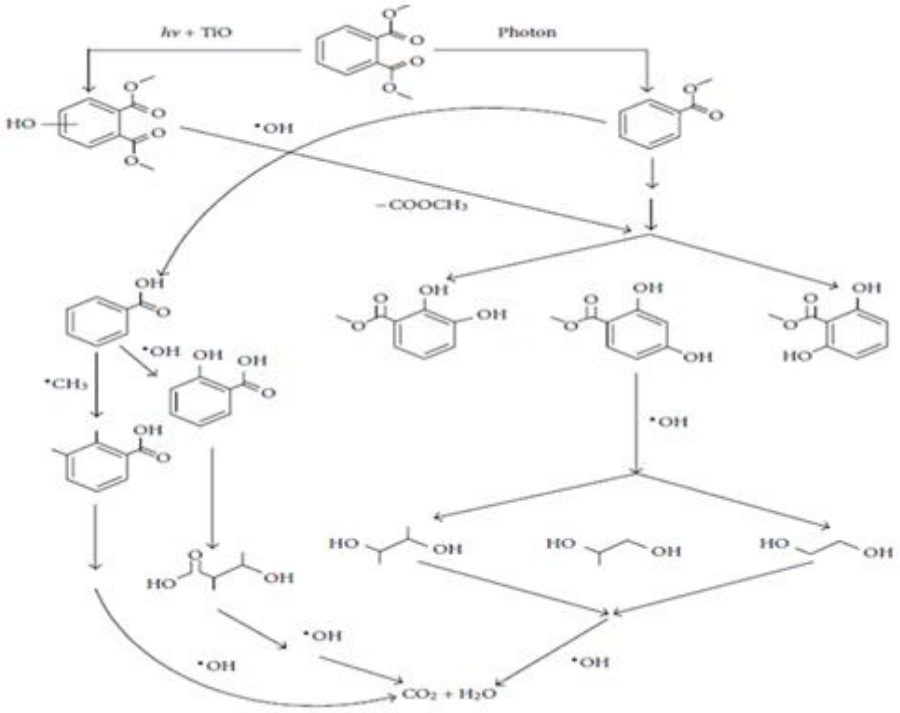

Figure 2.8 Photocatalytic Degradation Scheme X. (Ding et al., 2008)

3. MATERIALS AND METHODS

All experiments were carried out in the Mechanical Engineering Department laboratory, Faculty of Engineering University of Yüzüncü Yıl, Van, Turkey. During the period from October 2016 to November 2017.

3.1 Lab Equipment

Figure 3.1 Labrotory of nano technology.

Figure 3.2 Second-view of labrotory of nano technology.

3.2 Material Synthesis

3.2.1 Production of Zr doped TiO_2 produced by PCCM solgel technique

Zr doped TiO_2 absorber particles (Zr-T) were obtained from homogeneous solution precipitation technique 0.1 M Titanium (IV) isopropoxide and different Zirconium (IV) butoxide concentrated solution were dissolved in 2 methoxyethanol and iso-pronaol mixture (50:50 W%). The solution heated up to 80 C^o for 2h under reflux. A blue wish gel was formed when the solution cooled in room temperature. Finally, homogenous precipitates particles were annealed under open atmosphere at 500 C^o for 1 h for annealing. After annealing the particles was homogenized by ultrasonic and mechanic lab scale homogenizer. Undoped TiO_2 absorber particules were obtained with the same procedure as above except the addition Zr solution during reflux treatment.

3.2.2 Hydrothermal treatments

Autoclaves provide a physical method for disinfection and sterilization. They work with a combination of steam, pressure and time. Autoclaves operate at high temperature and pressure in order to kill microorganisms and spores.

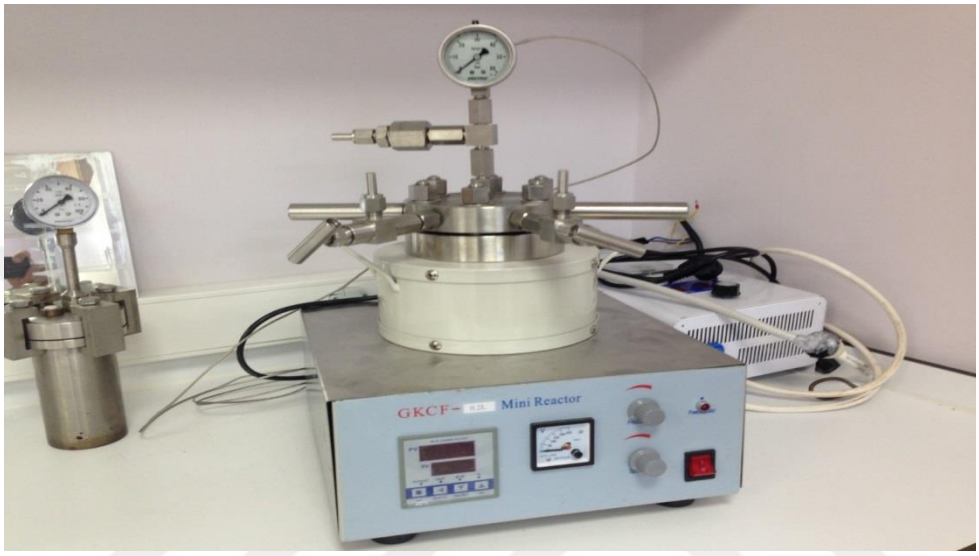

Figure 3.3 High Pressure Titanium Autoclave.

They are used to decontaminate certain biological waste and sterilize media, instruments and lab ware. Regulated medical waste that might contain bacteria, viruses and other biological material are recommended to be inactivated by autoclaving before disposal.,

Figure 3.4 Series analytical balance.

Nanoparticles are tiny, so Series Analytical Balance (Figure3.4) was used in this work, it has high capacity semi micro ranges and Anti-static glass breeze break with a thin evaporated metal coating.

Figure 3.5 Furnace for calcination.

Calcination furnace (Figure 3.5) is mainly intended for modifying ashes in various cereal products. Ash is the measurement of a mineral material remaining as non-flammable remnants of the sample. Its temperature can be set to 300 C° up to 1100 C° depending on its implementation

3.2.3 Production of Zr doped TiO_2 absorber layer produced by hydrothermal technique

Zr doped TiO_2 absorber particles (Zr-T) were obtained from homogeneous solution precipitation technique 0.1 M Titanium(IV) isopropoxide and different Zirconium (IV) butoxide concentrated solution were dissolved in 2 methoxyethanol and iso-pronaol mixture (50:50 W%). The solution heated up to 80 C^o for 2h under reflux. A blue wish gel was formed when the solution cooled in room temperature. By way of autoclave treatment that the blue wish gel was transferred into titanium autoclave where hydrothermal treatments of it was in progress at 190 C^o for 24 hours, effect of absorption of absorber layer. After autoclave treatment, the % 5 Zr particles have more

transparent than obtain by sol gel technique. Finally, homogenous precipitates particles were annealed under open atmosphere at 500 C^o for 1 h for annealing. After annealing the particles was homogenized by ultrasonic and mechanic lab scale homogenizer. Undoped TiO_2 particules were obtained with the same procedure as above except the addition Zr solution during reflux treatment.

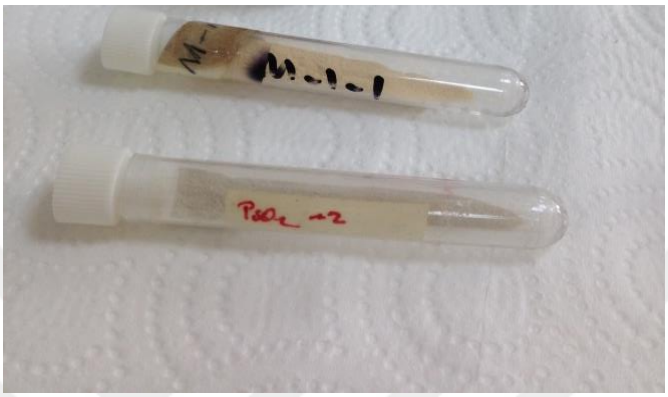

Figure 3.6 Zr doped TiO_2.

(where used in experiments) with two tubes of different concentrated % of Zr doped TiO_2.

3.3 Photocatalytic Experiment Set Up

3.3.1 Setup box

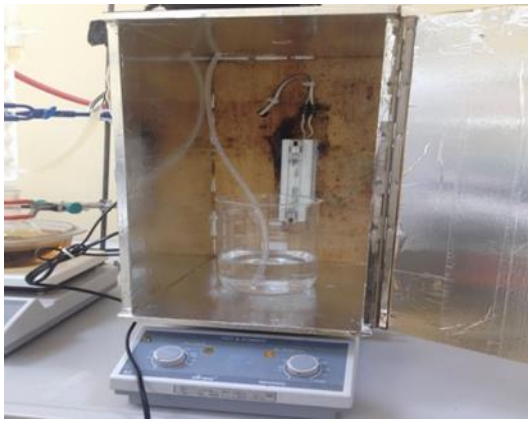

Figure 3.7 Closed wood box.

Box where used for hits light on the materials (TiO_2 , Zr doped TiO_2)

This box is made of wood and inside covered by aluminum papers in all faces to reflect all lights on the stirring solution. we put UV light bulb inside also , and during the process the box is closed we add TiO_2 and put the beaker with the solution on a stirring plate UV light bulb and a second beaker is carefully placed inside the solution to activate the TiO_2.

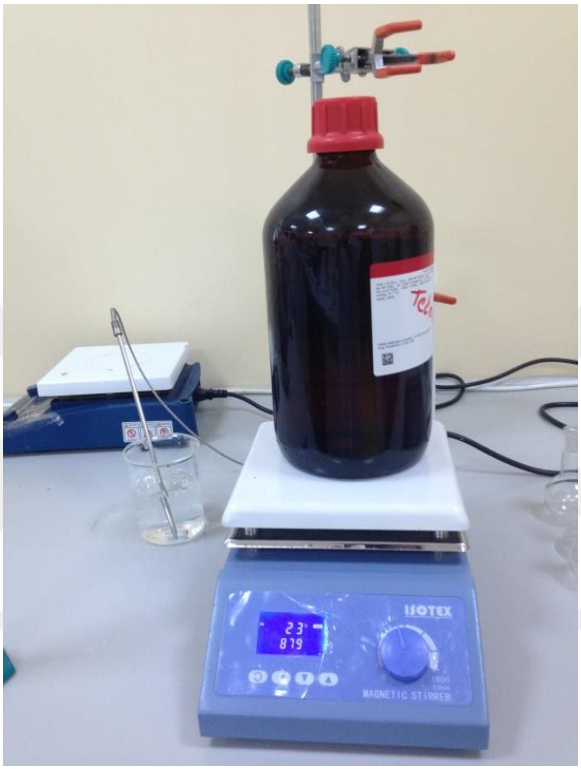

Figure 3.8 0.5 m M of Organic compounds.

We used in our experiment like precursors and then added 2.5 L of deionized water and put it on the stirring plate for one hour (this is we called solution) .

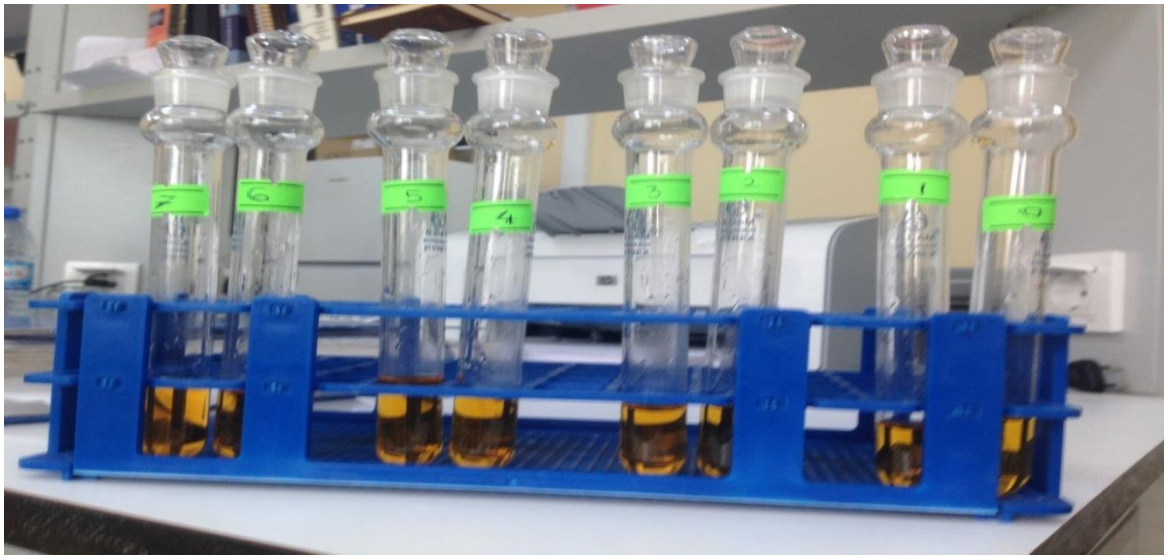

Figure 3.9 Test tubes with rack.

Every 5 minutes we take sample to test it (photocataltic activity). We measure the absorbance of specific light wavelength; and watch the concentration of the cancerogenic diminish over time.

4. RESULT AND DISCUSSION

4.1. SEM Analysis

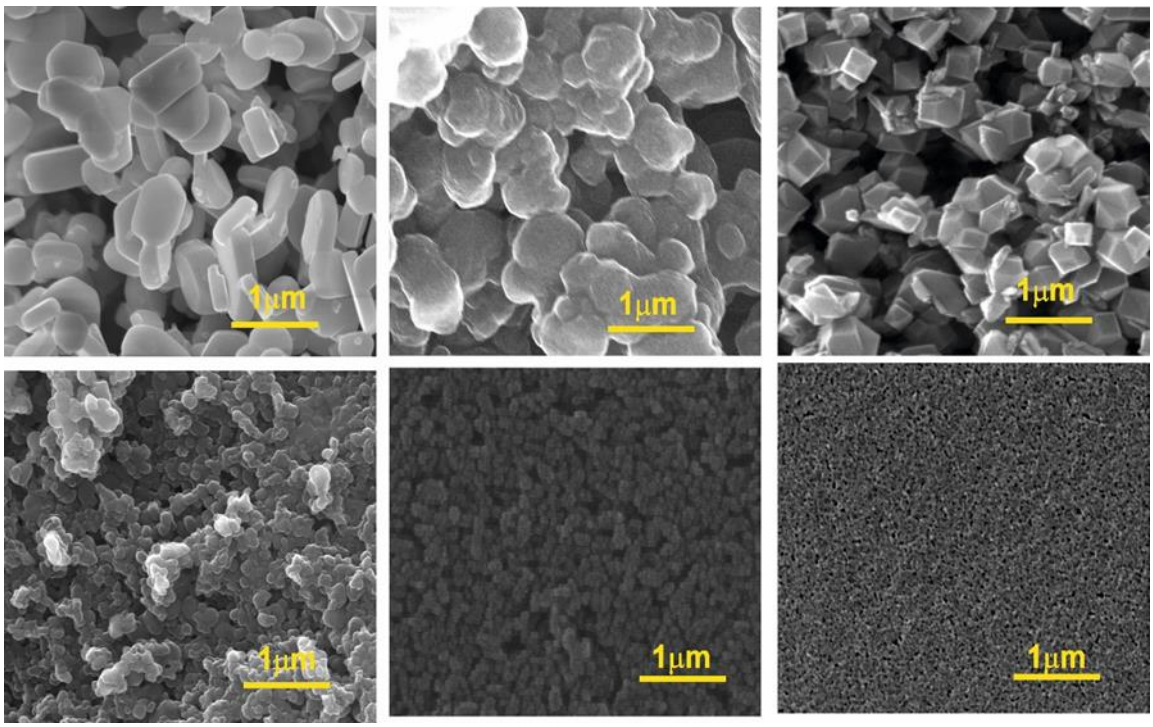

Figure 4.1 SEM images of bare TiO_2 (a), 1% Zr modified TiO_2 (b), 2%Zr modified TiO_2 (c), %5 Zr modified TiO_2 (d) % 10 Zr modified TiO_2 (e) and Bare ZrO_2 (f) obtained by autoclave hydrothermal technique.

After thermal threatment, which was described cheapter 3, homogenous precipitates particles were annealed under open atmosphere at 500 C^o for 1 h for annealing. After this step, due to needing surface caracterization, it has been conducted SEM anlysis. According to SEM results better not agglomerate particles has been obtained via hydrothermal treatment. As the zirconium concentration increases, the particle size decreases. Not only it happned, but also the surface areas of the particles being visibly increased. After autoclave treatment, the % 5 Zr particles has more transparent than obtain by sol gel technique. The best particules size has been achived by 5 % Zr addition.

2. UV-VIS Anylsis

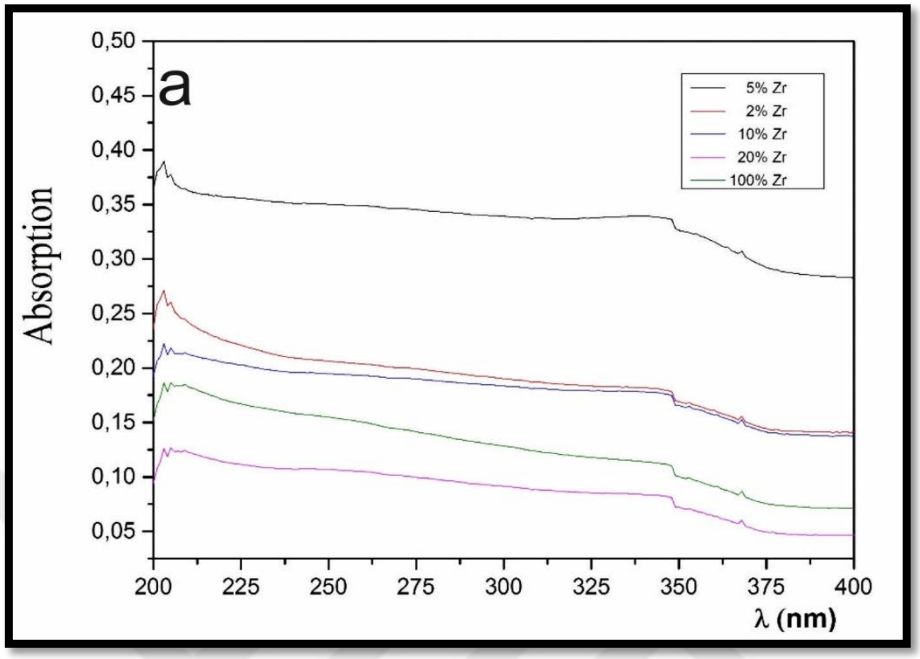

Figure 4.2 UV spectra of Zr modified TiO_2 powders obtained by Sol Gel method.

According to (Figure 4.2) 5 % Zr modified particules shows best absorption coefficient at UV region of wavelength. It has nearly 40 % transmittance, highest transmittance means that more light can be reach band gap region. In order to get higher photovoltaic exited level, the semiconductor has to be absorb part of UV region (< 400 nm).

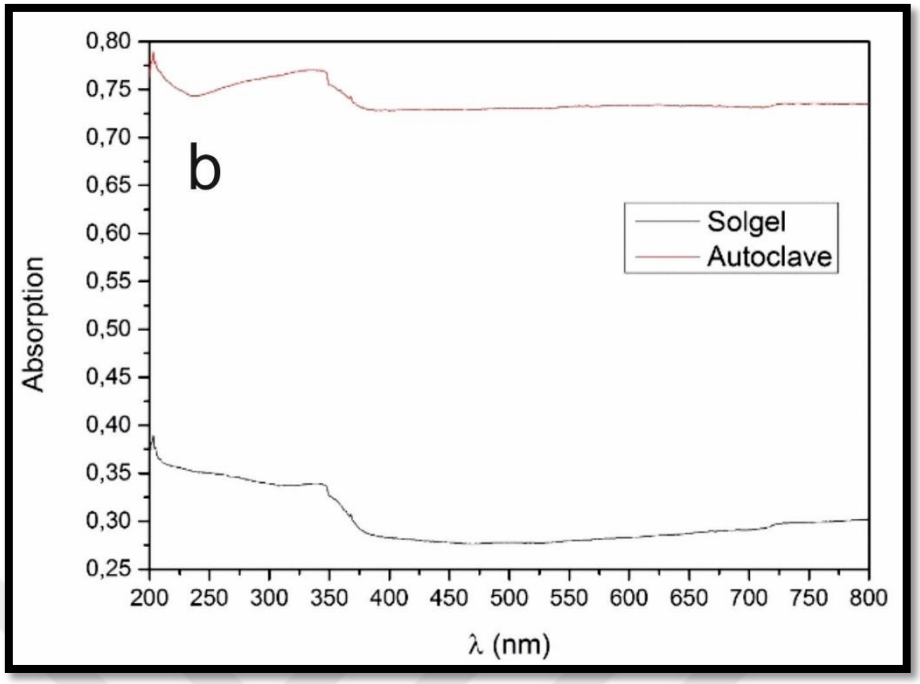

Figure 4.3 Comparison of % 5 Zr modified TiO_2 produced by sol-gel and Hydrothermal autoclave technique.

Because this part of region cannot be absorbed by TiO_2 particules easily, it has highest energy on all of the sun light spectra. Changing in transparency can be clarified by Egap shifting. Zr modified TiO_2 powders by hydrothermal method has higher absorption capability than Solgel based, it is important to band gap engineering, just change of production method, having higher band gap powders can be produced.

4.3. Egap Calculation Of Zr Modified TiO_2 Materials.

Table 4.1 Egap of Zr doped TiO2nano composite powders obtained by sol gel method

Sample	Egap (eV)	Egap
	Sol-gel	Autoclave
100 % TiO_2	3.21	2.54
2 % ZrO_2-98 % TiO_2	3.40	3.45
5 % ZrO_2-95 % TiO_2	3.80	3.95
20 % ZrO_2-80% TiO_2	4.38	4.42
100 % ZrO_2	4.90	5.7

According to Figure 4.3 and table 4.1, Zr modification effect of Egap of TiO_2. Increasing the Zr concentration in TiO_2 matrix increases the Egap of powders. The maximum Egap (4.90 eV) obtained while concentration reach the 100 % Zr. The 5 % Zr modified powder has 3.80 eV which is the higher Egap than commercial TiO_2 used photocatalytic activity. Highly Egap cause the decrease the electron recombination and decrease the electron accumulation on the semiconductor structure. It can be seen that there was a blue shift in the UV-absorption edge of the Zr modified electrodes relative to the bare TiO_2. Higher band gap means that; Zr modified absorber layer can a few absorb incident light, and allow to lighter pass TiO_2 Egap region. According to the Burstein–Moss effect, occupied donor electrons block the lowest state in the conduction band, which is responsible for the increased optical band-gap the blue shift in the optical band-gap of the Zr modified photo electrode indicating that the surface Fermi level is shifted toward the higher energy side.

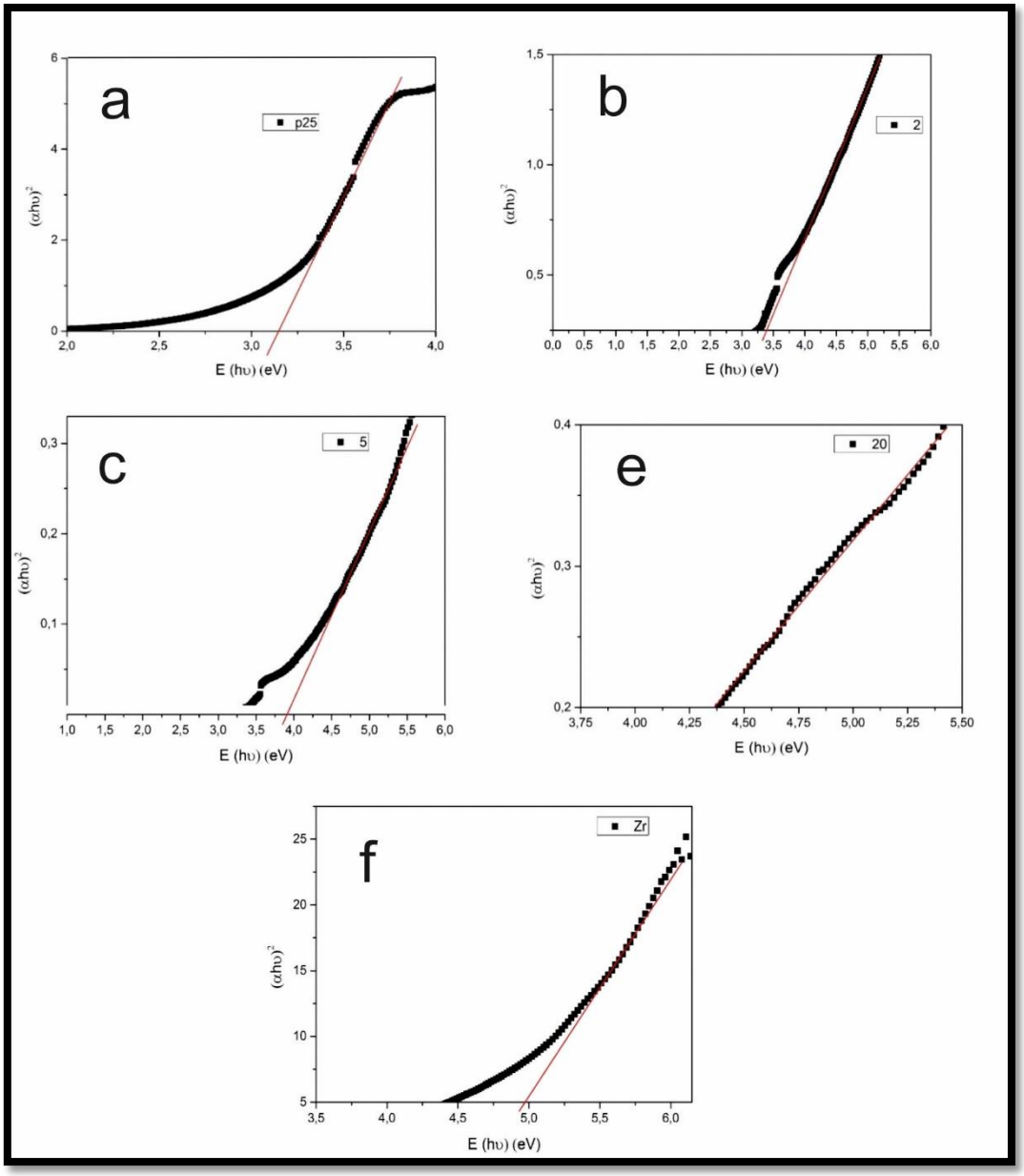

Figure 4.4 Linear portion of the (αhv) 2 vs photon energy (E (ev) graph of p25 powders (a), 2 % Zr modified TiO2 (b), 5 %Zr modified TiO_2 powders (c) 20 % Zr Modified TiO_2 powders (d), ZrO_2 powders (e) obtained by sol gel method.

4.4. XRD Analysis of Zr Modified TiO_2 Particles

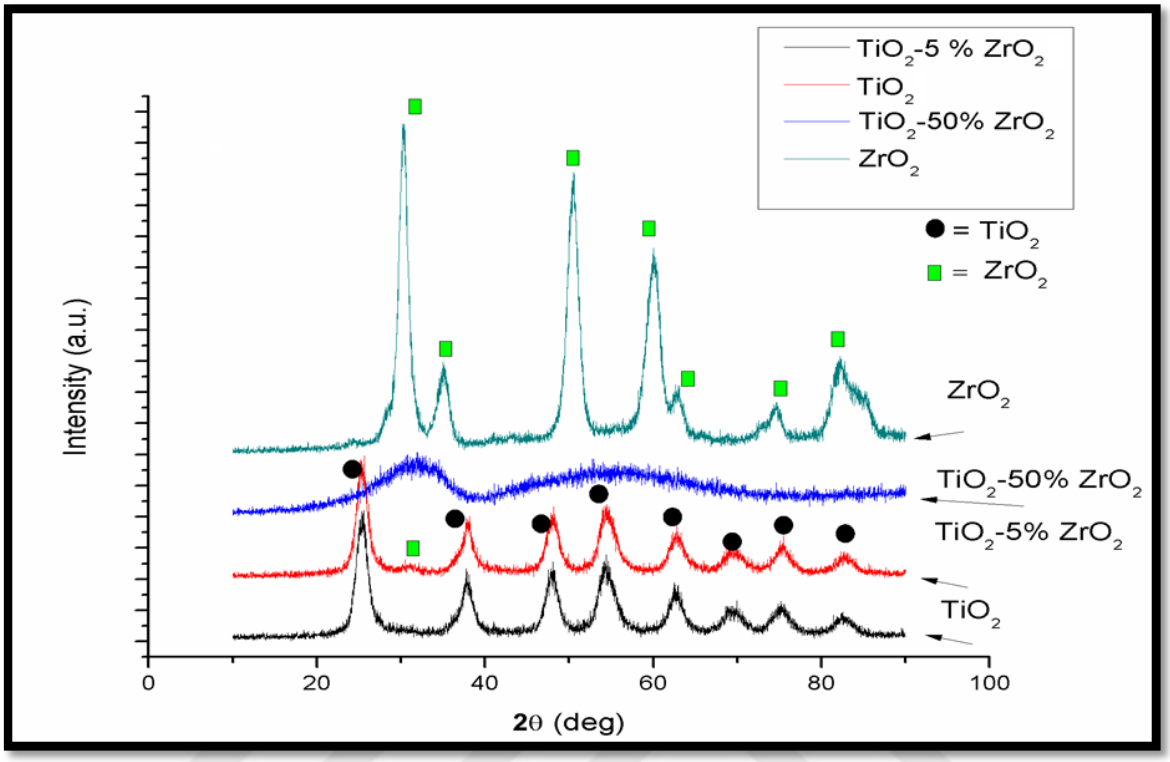

Figure 4.5 XRD patterns of ZrO2, TiO_2, 5 % ZrO_2-TiO_2 and 50 % ZrO_2– 50 % TiO_2 by obtained solgel (PCCM) method.

All samples were prepared using PCCM and and they were annealed at 500 C° for 1 hour. These results show that TiO_2 powders consist of anatase titania crystal; rutile phase could not be detected. The diffraction peaks from ZrO_2 powders can be assigned to the tetragonal structure (JCPDS 42-1164). However, ZrO_2 was dedected on % 5 Zr-TiO_2 sample. It was unwanted on photocatalytic applications.

4.5. XRD Analysis of TiO_2 and 5 % ZrO_2-TiO

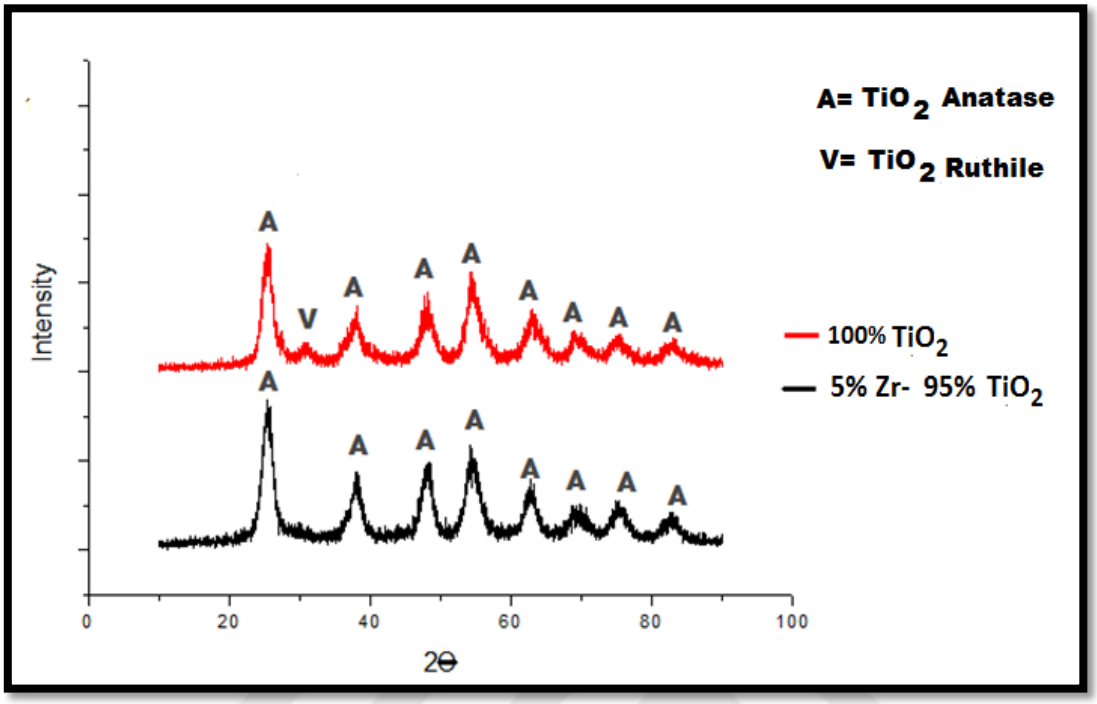

Figure 4.6 XRD patterns of TiO_2 and 5 % ZrO_2-TiO_2 by obtained hydrothermal method.

Doping of 5 % Zr did not affect the final TiO_2 powder crystalline phase. Moreover Zr is an inhibitor agent for grain growth agent for rutile, which is unwanted phases at photocatlytic application, in TiO_2 matrix. Hydrothermal treatment is more effective than solgel (PPCM) method for unwanted phase protection.

4.6. XPS Anlysis of Zr Modified TiO_2 Particules

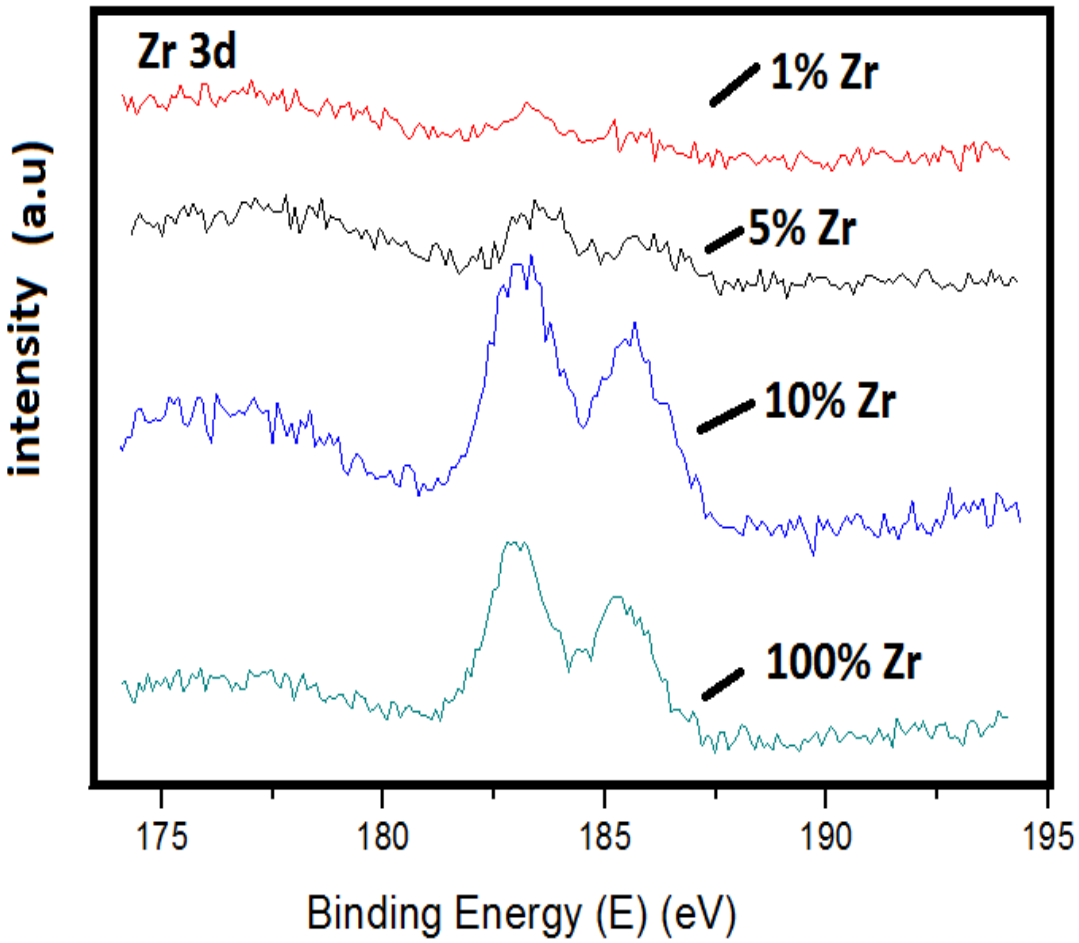

Figure 4.7 XPS analysis graph of the 3d band belonging to zirconia.

XPS analysis graph of the 3d band belonging to zirconia is shown in Figure 4.7 The zirconium pile at 100 % zirconium concentration became evident, while the concentration decreased, and at 1 % concentration, it became a rarely visible noise format. The reason for this is that zirconium ions can act as a component in the anatase matrix. This effect allows the crystal structure in low concentrations to remain intact.

4.7. XPS Anlysis of 5%Zr-TiO_2 Particules

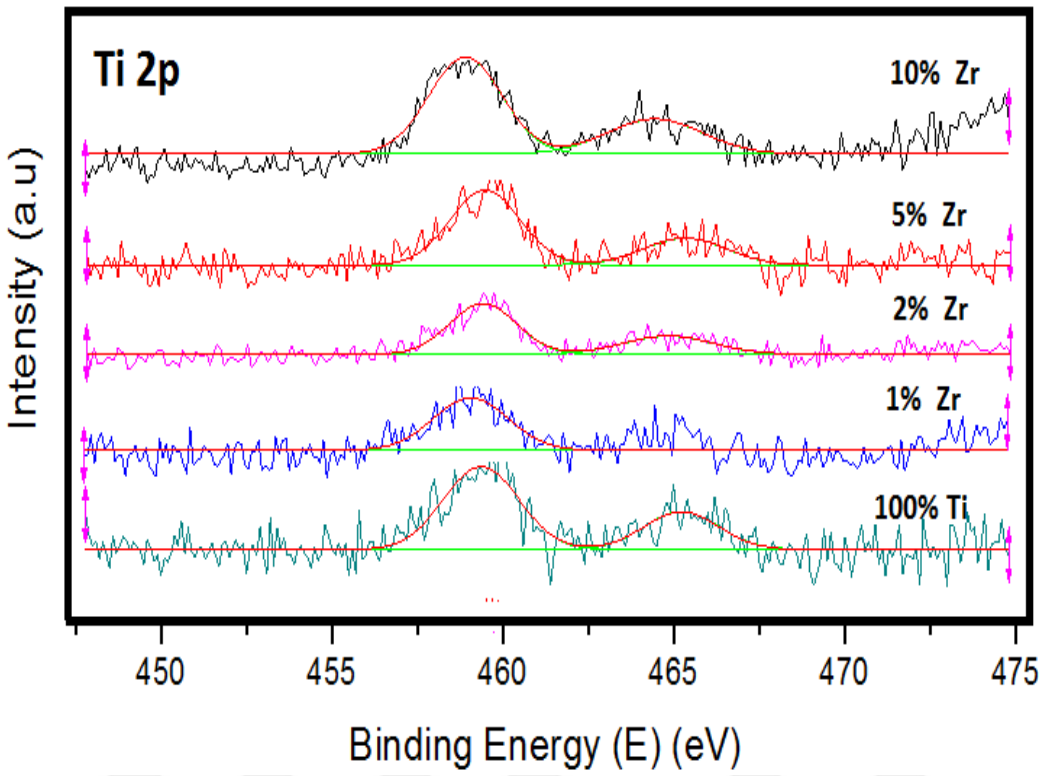

Figure 4.8 XPS analysis graph of the 2p band belonging to titanium.

XPS analysis is one of the most important methods in determining band diagrams. which is the result of XPS analysis to study the effect of zirconium on the 2P transition, which is one of the most important of the electronic passages of titanium. it is evident that the passage to the visible region, for example the UV region, in which 5 % zirconium is added as shown in this diagram. The effect of the transition at about 460 and 465 nanometers is best seen in the 5 % modified sample.

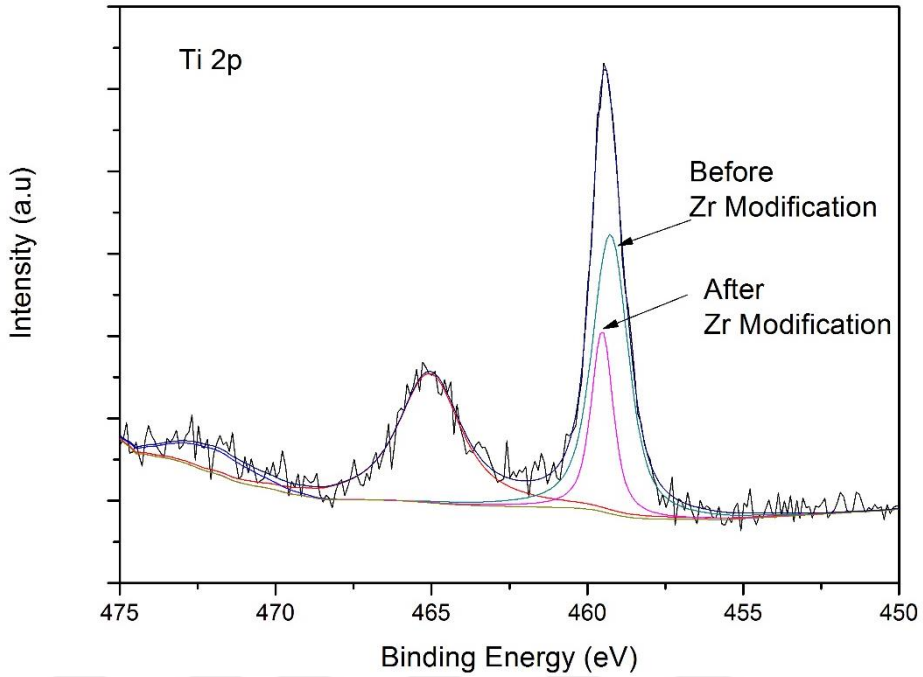

Figure 4.9 XPS analysis graph of the 2p band belonging to 5% modified titanium oxide.

It is seen that the Figure 4.9 is modified with zirconium and the two untreated samples are compared. the Zr modification has caused the 2p peak to shift to the visible region from the long wavelength (low energy level), i.e. the UV absorbing band. the photocatalytic assays were continued with only 5 % Zr-modified particles as this effect was not seen in other particles.

4.8. Photocatalytic Analysis

4.8.1. Methylene Blue (MB) Test

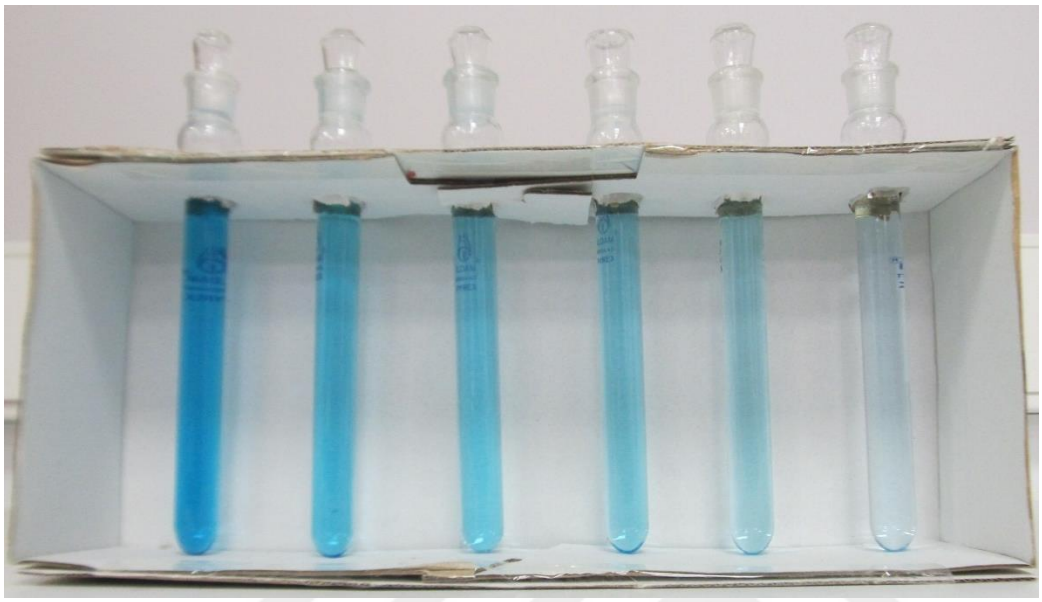

Figure 4.10 0.1 mmol of methylene blue, photocatalytic reaction, 15 min.

A graph containing time values versus photocatalytic concen-tration of 0.1 mmol methylene blue was immediately given under the test photograph. all the experiments were done with the help of a xenon lantern to simulate the sun's rays. Although the results of the obtained tests have a longer duration than the results in the literature made with uv, they are very important in terms of cost analysis and practical use. the resulting disintegration rates are still faster than the best alternative methods. for this reason a great obstacle for the commercialization of the particle has come to an end.

4.8.2. Purple dye (PD) test

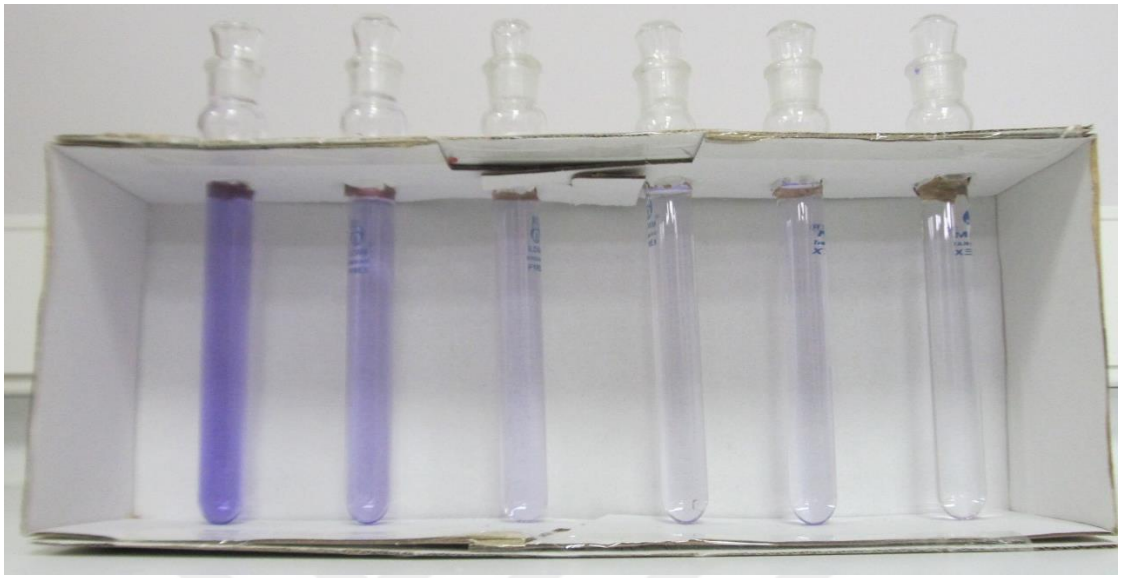

Figure 4.11 0.1 mmol of methylene blue, photocatalytic reaction, 15 min.

A graph containing time values versus photocatalytic concentration of 0.1 mmol purpele dye was immediately given under the test photograph. all the experiments were done with the help of a xenon lantern to simulate the sun's rays. Although the results of the obtained tests have a longer duration than the results in the literature made with uv, they are very important in terms of cost analysis and practical use. the resulting disintegration rates are still faster than the best alternative methods. for this reason a great obstacle for the commercialization of the particle has come to an end.

4.8.3. Methly orange (MO) test

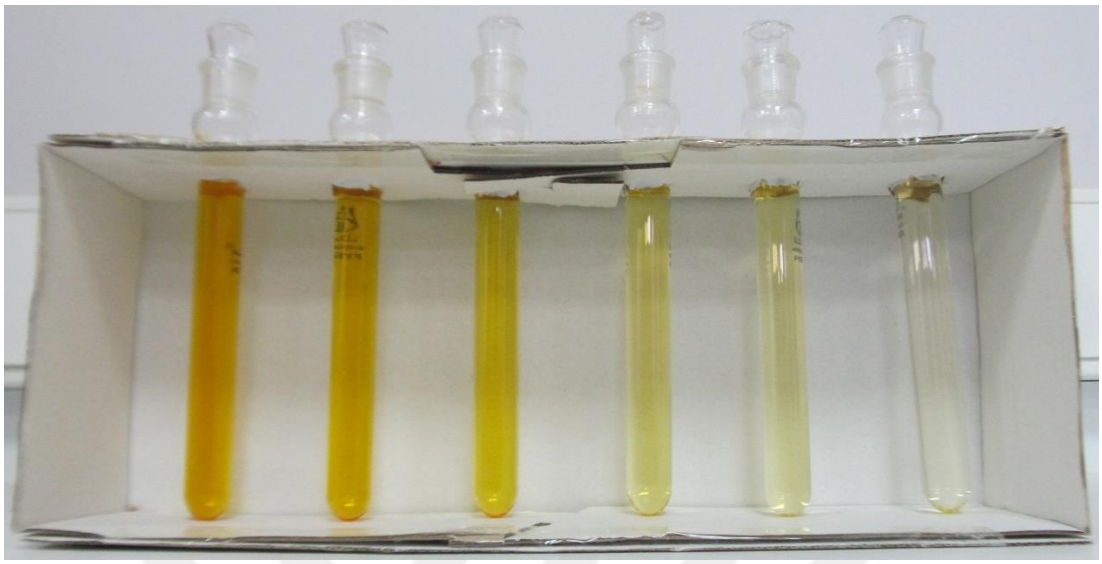

Figure 4.12 0.1 mmol of methylene blue, photocatalytic reaction, 15 min.

A graph containing time values versus photocatalytic concentration of 0.1 mmol methy orange was immediately given under the test photograph. all the experiments were done with the help of a xenon lantern to simulate the sun's rays. Although the results of the obtained tests have a longer duration than the results in the literature made with uv, they are very important in terms of cost analysis and practical use. the resulting disintegration rates are still faster than the best alternative methods. for this reason a great obstacle for the commercialization of the particle has come to an end.

4.8.4. Malecite green (MG) test

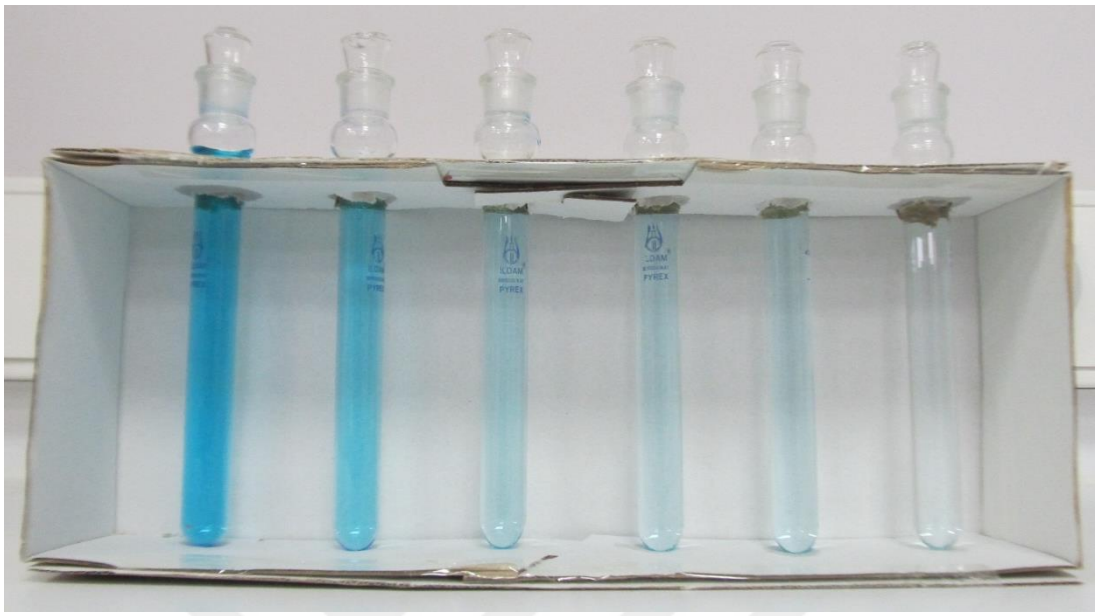

Figure 4.13 0.1 mmol of methylene blue, photocatalytic reaction, 15 min.

A graph containing time values versus photocatalytic concen-tration of 0.1 mmol Malecite Green was immediately given under the test photograph. all the experiments were done with the help of a xenon lantern to simulate the sun's rays. Although the results of the obtained tests have a longer duration than the results in the literature made with UV, they are very important in terms of cost analysis and practical use. the resulting disintegration rates are still faster than the best alternative methods. for this reason a great obstacle for the commercialization of the particle has come to an end.

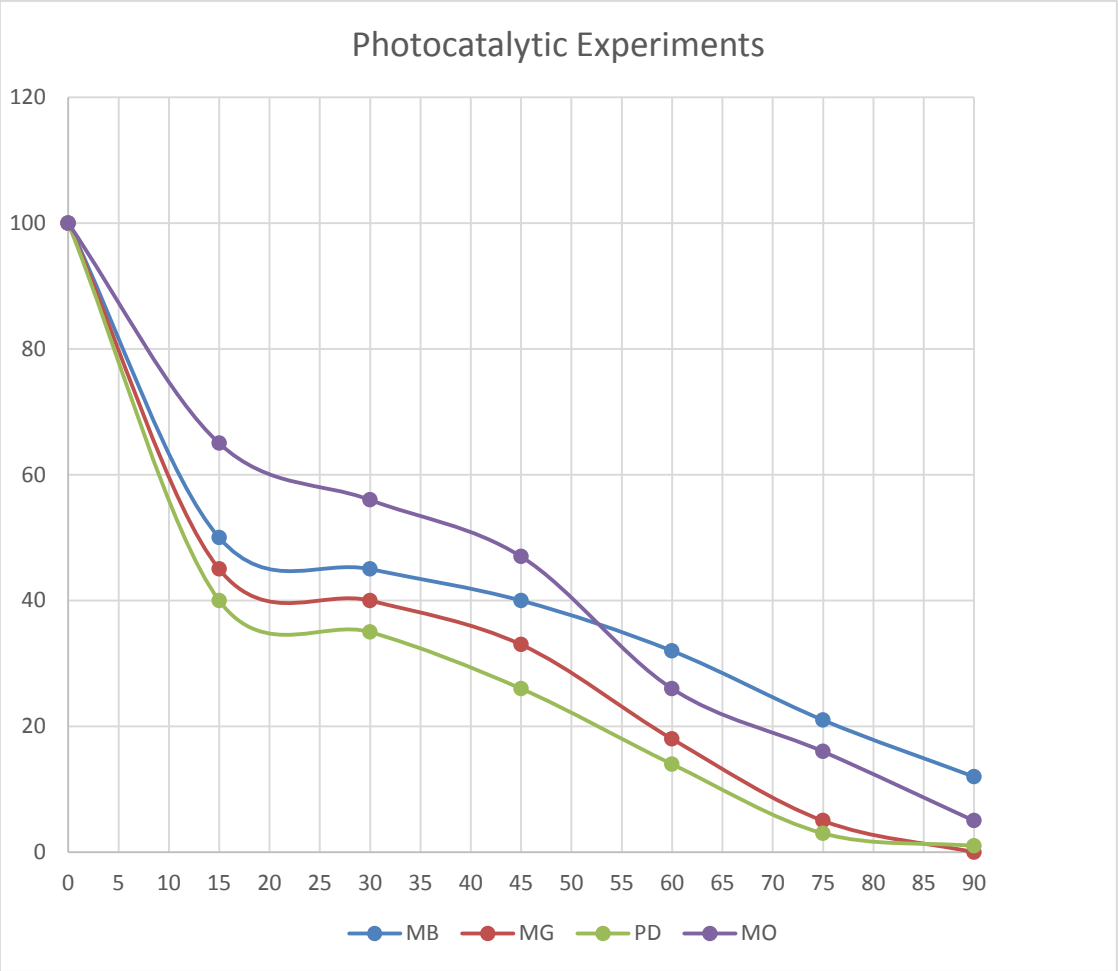

Figure 4.14 0.1 mmol of starter chemicals vs time graph.

When the time graph is examined, the malachite that is breaking down fastest under the sunlight is green. the slowest breaking was methylene blue.

5. CONCLUSION

In the literature many photocatalytic materials modification have been reported such as using different metal oxide semiconductors ZnO, Nb_2O_5 and ion doped TiO_2 (N, Au , Zn, W or Zr). Zr is an inhibitor agent for grain growth agent for rutile, which is unwanted phases at photocatalytic application, in TiO_2 matrix. In addition, Zr-doped TiO_2 exhibited significantly higher photocatalytic efficiency than TiO_2. In this thesis, Zr doped concentration effect on optical properties on photocatalytic applications were studied. we have focused on the production of different nanostructured Zr modified TiO_2 powders as a material for photocatalytic by sol gel assist- polymerizing complexing combustion method (PCCM) and hydrothermal method. The photocatalytic characteristics of Zr doped TiO_2 with various Zr doping contents and bare TiO_2 were examined. Zr modification is positively effect on photocatalytic application to enhance highly efficient reactions.

1) Zr modification (ZM) decrease the particules size of TiO_2 particules.
2) ZM increase the optical properties of TiO_2
3) ZM increase the Egap of TiO_2 which is directly effect on absorbtion
4) ZM increase the dye loading capacity
5) ZM increase the photocatalytic efficiency of TiO_2, these improvements is maximazied in 5% Zr modification.

In conclude, ZM is increase the phovoltaic performance of DSSC. This improvements were found maximum at 5 % Zr modified TiO_2. 5 % Zr modified TiO2 is an alternative material for absorber layer on photocatalytic apllications. When the time of decolorization is examined, the malachite that is breaking down fastest under the sunlight is green. the slowest breaking was methylene blue. Although the results of the obtained tests have a longer duration than the results in the literature made with UV, they are very important in terms of cost analysis and practical use. the resulting disintegration rates are still faster than the best alternative methods. for this reason a great obstacle for the commercialization of the particle has come to an end.

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APPANDIX-EXPANDED TURKISH SUMMARY (TÜRKÇE)

ÖZET

Zr-KATKILI TiO_2'nin ORGANİK BİLEŞİKLER ÜZERİNDEKİ FOTOKATALİZ ETKİSİ

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Bu çalışmanın ana hedefi Zr-katkılı TiO_2'nin organik bileşikler üzerindeki fotokataliz etkisini araştırmaktır. Bu doğrultuda önce anataz yapıdaki TiO_2 nano-kristalleri (nM: TiO_2:Zr) Zr ile katkılandırılmıştır. Bu amaçla ince asıltılı pelte (sol-gel) destekli polimerleştirici kompleks ateşleme yöntemi (PCCM) ve hidrotermal yöntemleri kullanılarak farklı nano-yapılara sahip çeşitli TiO_2 tozları (Zr-modifiye TiO_2 parçacıkları, TiO_2 ve % 5 ZrO_2-TiO) elde edilmiştir. Ardından bunlar SEM, UV-VIS, XRD ve XPS analizlerine tabi tutularak özellikleri tespit edilmiştir. Sonuçlar TiO_2 ile hazırlanmış tüm maddelerin anataz yapılarının yüksek düzeyde kararlı olduklarını ve yüzey alanlarının arttığını göstermektedir. UV-VIS dörtgen yansıma spektroskopi sonuçları TiO_2'nin bant genişliğinin daralmasından ve optik tepki alanının morötesinden görülebilir ışığa kaymasından katkı maddelerinin sorumlu olduğuna işaret etmektedir. Zr-katkılı TiO_2 katalizörlerinin fotokatilitik aktiviteleri Metilen Mavisi (MB Test), Mor Boya (Purple Dye Test), Metil Portakal (Methyl Orange Test) ve Malaşit Yeşili (Malecite Green Test) testleri ile araştırılmıştır. Gün ışığının etkilerini taklit etmek için tüm testler için bir ksenon feneri yardımıyla gerçekleştirilmiştir. Her ne kadar bu yaklaşımla testlerden sonuç almak UV yöntemine göre daha uzun sürse de, bu yöntem daha ekonomik ve pratiktir. Ayrıca ortaya çıkan çözünme de en iyi alternatif yöntemlere göre daha hızlı gerçekleşmektedir. Bu nedenle incelenen parçacıkların ticarileştirilmesinin önündeki önemli bir engel ortadan kalkmaktadır.

Anahtar kelimeler: Fotokatalitik, Nano-teknoloji, Zr-modifiye TiO_2

1. GİRİŞ

Problem Tanımı

Yapısal, elektronik, manyetik, termal ve optik özelliklerindeki çeşitlilikler nedeniyle nano-malzemelere gösterilen ilgi son yıllarda ciddi şekilde artmıştır. (Zheng et al.,2001; Radecka et al.,1993). Nano-parçacıkların bu özellikleri ebatları, şekilleri ve kristal yapıları ile birlikte değişiklik göstermektedir. Nano-parçacıkların eşsiz özellikleri onları hem enerji üretimi hem de kataliz, elektronik, optik ve manyetizma gibi konularda önemli hale getirmektedir. Organik moleküllerin fotokatalitik bozunuma uğratılmaları amacıyla kullanılan yarı-iletkenler genellikle metal oksitleri ve metal sülfitlerinden elde edilmektedir. En yaygın kullanılan yarı-iletkenler TiO_2, ZnO, WO_3, Fe_2O_3 ve ZnS'dir (Fox and M. A. 1993). Organik moleküllerin güneş ışığı kullanılarak işleme tabi tutulmalarında kullanılacak en ideal fotokatalizör belirlenirken, oksitlenme potansiyeli ve bant genişliği gibi mutlaka göz önüne alınması gereken bazı etmenler vardır. Oksitlenme potansiyeli önemlidir zira değerlik kuşağında (valence band) fotojenere boşluklar elde etme ve suda hidroksil radikalleri oluşturma kabiliyeti organik moleküllerin fotokatalizi için kilit öneme sahiptir. Bu durum aynı zamanda iletim kuşağında (conduction band) uyarılmış elektronun (e^{cb}) gücünün indirgenmesi için de geçerli olup potansiyel moleküler oksijeni süperoksit'e indirgeyecek kadar kuvvetli olmalıdır (Halmann ve M.M.1996). Bu iki kimyasal işlem organik moleküllerin basit gaz çıktılarına (H_2O, CO_2) ve inorganik iyonlara (NO_3^-, SO_4^{2-}) dönüştürülmelerinde kilit öneme sahiptir. Bir yarı-iletkenin şerit boşluğu enerjisi, o yarı iletkenin iletim şeridinde bir elektronun uyarılması için gereken ışıksal enerji miktarını belirtmektedir; bu elektron uyarımı değerlik kuşağında pozitif yüklü bir delik bırakır, v^{+hb} (Oppenländer ve T., 2003). Eğer herhangi bir yarı-iletkenin yük taşıyıcılar üretmek için ihtiyaç duyduğu dalga boyu güneş spektrumu dışında ise, o yarı-iletken hatırı sayılır bir elektronik değişime maruz bırakılmadıkça gün ışığı kullanarak organiklerin indirgenmesinde kullanılamaz. TiO_2, foto-kararlı yapısı, ucuzluğu, zehirli olmayışı, yüksek yüzey alanına ve gözenekli yapıya sahip olması ve kimyasal kararlılığı nedeniyle bu amaçla değerlendirilen en iyi metal oksitlerden biridir. Bu özellikleri nedeniyle TiO_2 foto-kataliz alanında kullanılagelen bir yarı-iletken olmuştur. TiO_2 son otuz yılda hem enerji üretimi hem de çevresel problemlerin giderilmesi alanlarında

giderek artan bir ilgi kazanmıştır (Dumitriu et al.,2000; Takeda et al.,2001). Kimyasal bir işlemin bir katalizör varlığı altında ışık kullanılarak hızlandırılması işine fotokatalizasyon denmektedir. Katalizör, nötr veya uyarılmış haldeki substrat ile ve/veya önemli bir foto-mamul ile etkileşime girerek foto-reaksiyonu hızlandırmakta ve her bir kataliz döngüsü sonunda kendisi değişime uğramadan kalmaktadır. Her ne kadar bazı alternatifleri olsa da, pazarda en yaygın olarak bulunabilen ve ticarileştirilmiş fotokatalizörler TiO_2 temelli olanlardır. Bunlar bakterisit ve su arındırma uygulamaları gibi çeşitli alanlarda yaygın şekilde kullanılmaktadır. TiO_2 fotokatalizörlerinin başlıca kullanım alanlar şekil 1.1'de gösterilmektedir. Su dezenfeksiyonu, doğal sulardaki çözünmüş halde bulunan organik azot bileşiklerinin tespiti, cıvalı tuz çözeltilerinin foto-indirgenmesi gibi farklı alanlarda kullanılmaları da değerlendirilmektedir (Jacoby et al., 1998; Lau et al.,, 1998). Japonya'da pazarda görülen bazı TiO_2 bazlı fotokatalizör ürünler Tablo 1.1'de gösterilmektedir.

1.2 Amaçlar

Bu çalışmanın amacı Zr-katkılı TiO_2'nin kanserojen maddeler gibi organik bileşikler üzerindeki fotokataliz etkisini araştırmaktır .

Bu doğrultuda bu çalışmanın ana hedefleri aşağıdaki şekilde belirlenmiştir:

(i) Hazırlanmış TiO_2 ve Zr-TiO_2 parçacıklarının özelliklerinin tespiti

(ii) TiO_2 ve Zr-TiO_2'nin gün ışığı altında BPA indirgeme performanslarının kıyaslanması

(iii) Zr-katkılama işleminin etkilerinin tespiti

1.3 Tezin Yapısı

Bu tez çalışması beş ana bölüme ayrılmıştır. Birinci bölüm projenin gerekçelerini ve amaçlarını açıklayıp, tezin kapsamı hakkında bilgi vermektedir. İkinci Bölüm foto-oksitlenme süreçlerinin atık su işlenmesinde kullanımına dair literatür taramasından oluşmaktadır. Üçüncü bölümde bu çalışmada kullanılan yöntem ve malzemeler açıklanmıştır. Dördüncü bölümde deneysel sonuçlar ve bunlar üzerinden tartışmalar sunulmuştur. Son olarak beşinci bölümde tez bulguları özetlenmiştir.

3. YÖNTEM VE GEREÇLER

Tüm deneyler Yüzüncü Yıl Üniversitesi Makine Mühendisliği Bölümü Van, Türkiye laboratuvarlarında, Ekim 2016 ile Kasım 2017 tarihleri arasında gerçekleştirilmiştir.

3.2 Malzemelerin Sentezi

3.2.1 PCCM İnce Asıltılı Pelte (SolGel) Yöntemi ile Zr Katkılı TiO_2 Hazırlanması

Zr katkılı TiO_2 tutucu parçacıklar (Zr-T) homojen çözelti çökeltme yöntemi ile hazırlanmıştır. Bu amaçla 0.1 M Titanyum (IV) izopropoksit ve farklı Zirkonyum (IV) bütoksit konsantre çözeltisi 2 metoksietanol ve izo-pronaol çözeltisinde (50:50 ağırlık) içinde çözdürülmüştür. Çözelti geri akış altında 2 saat 80 C^o'de ısıtılmıştır. Çözelti oda sıcaklığına kadar soğutulduğunda mavimsi bir jel oluşmuştur. Sonunda homojen çökelti parçacıkları açık atmosfer altında 500 C^o'de 1 saat tav edilmiştir. Tavlamadan sonra parçacıklar laboratuvar ölçekli ultrasonik ve mekanik türdeşleştiriciler ile homojenize edilmiştir. Katıksız TiO_2 parçacıkları yukarıdaki işlemlerin geri akım altında Zr eklenmesi adımı çıkarılarak tekrarlanması ile elde edilmiştir.

3.2.2 Hidrotermal İşlemler

Otoklavlar dezenfeksiyon ve sterilizasyon için fiziksel bir yöntem sunmaktadır. Bu cihazlar buhar, basınç ve zamanı bir arada kullanarak çalışırlar. Otoklavlar yüksek sıcaklık ve basınçta çalışarak mikroorganizmaları öldürür.

Bunlar bazı biyolojik atıkları dekontamine etmek ve laboratuvar cihaz, donanım ve ortamlarını sterilize etmek için kullanılabilirler. Bakteri, virüs ve başka biyolojik maddeler içerebilecek ve denetime tabi tıbbi atıkların atılmadan önce otoklav kullanılarak arındırılması önerilmektedir.

Nano-parçacıklar çok küçük olduklarından, bu çalışmada Series Hassas Terazisi (Şekil 3.4) kullanılmıştır; bu aletin yüksek mikro-genişlik kapasitesi vardır ve ince metal kaplamalı anti-statik özellikli camdan imal bir beheri bulunmaktadır.

Kalsinasyon fırını (Şekil 3.5) genelde tahıllı ürünlerin çeşitli amaçlarla kül edilmesinde ve içeriklerinin incelenmesinde kullanılmaktadır. Küller, bir numunenin fırınlanmasından geriye kalan yanmaz özellikte mineral maddelerdir. Bu cihazın sıcaklığı uygulama amacına bağlı olarak 300 C° ile 1100 C° arasında ayarlanabilmektedir.

3.2.3 Zr Katkılı TiO_2 Tutucu Katmanın Hidrotermal Yöntem ile Üretilmesi

Zr katkılı TiO_2 tutucu parçacıklar (Zr-T) homojen çözelti çökeltme yöntemi ile hazırlanmıştır. Bu amaçla 0.1 M Titanyum (IV) izopropoksit ve farklı Zirkonyum (IV) bütoksit konsantre çözeltisi 2 metoksietanol ve izo-pronaol çözeltisinde (50:50 ağırlık) içinde çözdürülmüştür. Çözelti geri akış altında 2 saat 80 C^o'de ısıtılmıştır. Çözelti oda sıcaklığına kadar soğutulduğunda mavimsi bir jel oluşmuştur. Bu mavi jel titanyum otoklavına alınarak 190 C°'de 24 saat işlenmiş ve bu şekilde tutucu tabakanın absorbe olması sağlanmıştır. Otoklavdan sonra elde edilen % 5 Zr'li parçacıklar asıltılı pelte (sol-gel) yönteminden elde edilenlere oranla daha transparan yapıda olmuştur. Sonunda homojen çökelti parçacıkları açık atmosfer altında 500 C^o'de 1 saat tav edilmiştir. Tavlamadan sonra parçacıklar laboratuvar ölçekli ultrasonik ve mekanik türdeşleştiriciler ile homojenize edilmiştir. Katıksız TiO_2 parçacıkları yukarıdaki işlemlerin geri akım altında Zr eklenmesi adımı çıkarılarak tekrarlanması ile elde edilmiştir.

3.3 Fotokalatiz deney düzeneğinin kurulması

3.3.1 Düzenek kutusu

Bu kutu ahşaptan yapılmış olup karıştırma çözeltisine tüm ışığı yansıtması için iç kısmının tüm yüzeyleri alüminyum kağıtlar ile kaplanmıştır. Kutunun içinde ayrıca bir de UV ışık ampulü bulunmaktadır. İşlem sırasında kutu kapalı konumdadır. Kutunun

içine beher kabı ile bir karıştırma plakası ile birlikte çözelti konmakta, ardından ikinci beher dikkatlice çözeltiye yerleştirilerek TiO_2 aktive edilmektedir.

4. SONUÇLAR ve TARTIŞMA

4.1. SEM Analizi

Bölüm 3'te detayları belirtilen termal muameleden sonra homojen çökelti parçacıkları açık atmosferde 500 C^{o}'de 1 saat tav edilmiştir. Bu adımdan sonra ise yüzey özelliklerinin tespiti için parçacıklar SEM (Scanning Electron Microscopy: Taramalı Elektron Mikroskobisi) analizine tabi tutulmuştur. SEM analizleri hidrotermal yöntem ile elde edilen parçacıkların kümeleşmediğini ve dolayısıyla daha uygun olduklarını göstermektedir. Zirkonyum konsantrasyonu arttıkça parçacık büyüklüğü azalmaktadır. Bunun yanı sıra, parçacıkların yüzey alanları da belirgin şekilde artmaktadır. Otoklav muamelesinden sonra elde edilen % 5 Zr parçacıklar asıltılı pelte (sol-gel) yöntemiyle elde edilen parçacıklardan daha transparan olmaktadır. En uygun parçacıklar % 5 Zr ilavesi ile elde edilmiştir.

4.2.UV-VIS analizi

Şekil 4.2 a'da da görülebileceği üzere % 5 Zr ile modifiye edilmiş parçacıklar en iyi emilim katsayısını dalga boyunun UV bölgesinde göstermektedir. Parçacıklar bu bölgede neredeyse % 40 aktarganlık (transmittance) değerine sahiptir; yüksek aktarganlık bant boşluklarında daha fazla ışık ulaşabileceği anlamına gelmektedir. Daha yüksek fotovoltaik uyarım seviyelerine ulaşmak için bir yarı-iletkenin UV bölgesindeki (<400 nm) ışığı emmesi gerekmektedir.

Tayfın bu bölümü TiO_2 parçacıkları tarafından kolayca emilemediğinden, en yüksek enerjiyi güneş ışınları tayfı bölgesinde göstermektedir. Transparanlığın değişmesi ise bant boşluğunda bir kayma olarak tezahür eder. Hidrotermal yöntem kullanılarak Zr ile modifiye edilmiş TiO tozlarının asıltılı pelte (sol-gel) yöntemiyle elde edilenlere göre daha yüksek emilim kabiliyeti vardır. Bu durum bant boşluğu tasarımı açısından önem arz etmektedir; bu yaklaşım ile yalnızca üretim yöntemini değiştirerek daha geniş bant boşluğuna sahip tozlar üretilebilecektir.

4.3. Zr ile Modifiye Edilmiş TiO_2 Malzemelerinin Bant Boşluklarının Hesaplanması

Şekil 4.3 ve Tablo 4.1, TiO_2'nin Zr ile modifiye edilmesinin bant boşluğu üzerindeki etkilerini göstermektedir. Bunlardan anlaşılabileceği üzere TiO_2'deki Zr konsantrasyonu artırıldıkça tozların bant boşluğu da artmaktadır. % 100 Zr yoğunluğuna ulaşıldığında elde edilecek azami bant boşluğu 4.90 eV iken, % 5 Zr modifiyesi ile elde edilen bant boşluğu değeri 3.80 eV olup, bu değer fotokatalitik amaçla kullanılan ticari TiO_2'nin değerinden yüksektir. Yüksek bant boşluğu elektron rekombinsasyonunu azaltarak yarı-iletken üzerindeki elektron birikimini düşürmektedir. Zr ile modifiye edilmiş elektrotların UV-emilim sınırlarında saf TiO_2'ye oranla bir maviye kayma gözlenmektedir. Daha yüksek bir bant genişliği Zr ile modifiye edilmiş tutucu katmanın belirli bir düzeydeki ışığı emdiği ve bunun dışında kalanların TiO_2 bant boşluğu bölgesine geçmesine izin verdiği anlamına gelmektedir. Burstein-Moss etkisi prensibine göre, bağlanmış verici elektronlar iletim bandındaki en düşük seviyeyi bloke etmektedir; bu durum da bant boşluğunun artmasında rol oynamaktadır. Zr modifiyeli foto elektrotların bant boşluğunda görülen maviye kayma Fermi seviyesinin yüksek enerji yönüne doğru kaydığını da göstermektedir.

4.4. Zr ile Modifiye Edilmiş TiO_2 parçacıklarının XRD Analizi

Tüm numuneler PCCM ile hazırlanmış ve 500 C°'de 1 saat tav edilmiştir. Numunelerin XRD analiz sonuçları TiO_2 tozlarının anataz yapıdaki titanyum kristallerinden oluştuğunu göstermektedir ve numunelerde rutil faza rastlanmamaktadır. ZrO_2 tozlarının difraksiyon tepeleri beşgen bir yapıda toplanabilmektedir (JCPDS 42-1164). Bununla beraber % 5 Zr-TiO_2 numunelerinde ZrO_2 de tespit edilmiştir. Bu durum fotokatalizör işlevi için arzu edilmeyen bir durumdur.

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4.5. TiO_2 ve %5 ZrO_2-TiO'nun XRD Analizleri

% 5 Zr katkılandırması TiO_2 tozlarının kristal fazlarında değişikliğe neden olmamıştır. Dahası Zr, TiO_2 fotokatalitik uygulamalarda arzu edilmeyen rutil fazdaki yapılanmaların oluşmasını da baskılamaktadır. İstenmeyen bu fazın oluşmasını engellemede hidrotermal işlem asıltılı pelte (PCCM) yönteminden daha etkilidir.

4.6. Zr ile Modifiye Edilmiş TiO_2 parçacıklarının XPS Analizi

Zirkonyum' ait 3 boyutlu bant'ın XPS analizini gösteren grafik şekil 4.7'de verilmiştir. %100 Zirkonyum seviyesinde tepe oldukça belirginken %1 konsantrasyonda zor görülebilen bir dalgalanma şeklindedir. Bunun nedeni zirkonyum iyonlarının anataz yapıda bir bileşen görevi görebilmesidir. Bu etki kristal yapının düşük konsantrasyonlarda bile sağlam yapıda kalmasını sağlamaktadır.

4.7. % 5 Zr-TiO_2 parçacıklarının XPS analizi

XPS analizi bant diyagramlarının tespitinde kullanılan en önemli yöntemlerden birisidir. Zirkonyumun 2P geçişindeki etkisinin incelenmesi için bu diyagramlardan yararlanılmıştır; bu geçiş titanyumun elektronik geçişleri arasında en önemli olanıdır. % 5 zirkonyum ilavesi halinde UV bölgesinden görüşebilir ışık bölgesine bir geçiş olduğu diyagramda açıkça görülebilmektedir. 460 ve 465 nanometreye olan geçişler en iyi % 5 modifiye edilmiş numunelerde görülmektedir.

Şekil 4.9'da zirkonyum ile modifiye edilmiş bir numune ile hiç işlem görmemiş iki numune karşılaştırılmaktadır. Zr modifikasyonu 2p tepesinin UV emici bant olarak da bilinen uzun dalga boyundan (düşük enerji seviyesi) kaymasına neden olmuştur. Diğer numuneler üzerinde böyle bir değişiklik gözlenmediğinden, fotokatalitik değerlendirmeler yalnızca % 5 Zr ile modifiye edilmiş parçacıklar üzerinde yürütülmüştür.

4.8. Fotokalatitik Analiz

4.8.1. Metilen mavisi testi (MB)

Zaman değerlerine karşı 0.1 mmol metilen mavisinin fotokatalitik konsantrasyonlarını gösteren bir grafik test fotoğrafının hemen altında verilmiştir. Güneş ışınlarının etkilerini oluşturabilmek adına tüm deneyler bir ksenon farı yardımıyla yapılmıştır. Her ne kadar bu yaklaşımla testlerden sonuç almak UV yöntemine göre daha uzun sürse de, bu yöntem daha ekonomik ve pratiktir. Ayrıca ortaya çıkan çözünme de en iyi alternatif yöntemlere göre daha hızlı gerçekleşmektedir. Bu nedenle incelenen parçacıkların ticarileştirilmesinin önündeki önemli bir engel ortadan kalkmaktadır.

4.8.2. Mor boya testi (PD)

Zaman değerlerine karşı 0.1 mmol mor boyanın fotokatalitik konsantrasyonlarını gösteren bir grafik test fotoğrafının hemen altında verilmiştir. Güneş ışınlarının etkilerini oluşturabilmek adına tüm deneyler bir ksenon farı yardımıyla yapılmıştır. Her ne kadar bu yaklaşımla testlerden sonuç almak UV yöntemine göre daha uzun sürse de, bu yöntem daha ekonomik ve pratiktir. Ayrıca ortaya çıkan çözünme de en iyi alternatif yöntemlere göre daha hızlı gerçekleşmektedir. Bu nedenle incelenen parçacıkların ticarileştirilmesinin önündeki önemli bir engel ortadan kalkmaktadır.

4.8.3. Metil portakalı testi (MO)

Zaman değerlerine karşı 0.1 mmol metil portakalının fotokatalitik konsantrasyonlarını gösteren bir grafik test fotoğrafının hemen altında verilmiştir. Güneş ışınlarının etkilerini oluşturabilmek adına tüm deneyler bir ksenon farı yardımıyla yapılmıştır. Her ne kadar bu yaklaşımla testlerden sonuç almak UV yöntemine göre daha uzun sürse de, bu yöntem daha ekonomik ve pratiktir. Ayrıca ortaya çıkan çözünme de en iyi alternatif yöntemlere göre daha hızlı gerçekleşmektedir.

Bu nedenle incelenen parçacıkların ticarileştirilmesinin önündeki önemli bir engel ortadan kalkmaktadır.

4.8.4. Malaşit yeşili testi (MG)

Zaman değerlerine karşı 0.1 mmol malaşit yeşilinin fotokatalitik konsantrasyonlarını gösteren bir grafik test fotoğrafının hemen altında verilmiştir. Güneş ışınlarının etkilerini oluşturabilmek adına tüm deneyler bir ksenon farı yardımıyla yapılmıştır. Her ne kadar bu yaklaşımla testlerden sonuç almak UV yöntemine göre daha uzun sürse de, bu yöntem daha ekonomik ve pratiktir. Ayrıca ortaya çıkan çözünme de en iyi alternatif yöntemlere göre daha hızlı gerçekleşmektedir. Bu nedenle incelenen parçacıkların ticarileştirilmesinin önündeki önemli bir engel ortadan kalkmaktadır.
Zaman grafiği incelendiğinde en hızlı parçalanmanın malaşit yeşilinde, en yavaş dağılmanın ise metilen mavisinde gerçekleştiği görülmektedir.

5. SONUÇ

Literatürde, ZnO, Nb_2O_5 ve iyon katkılı TiO_2 (N, Au, Zn, W, ya da Zr) gibi farklı metal oksit yarı-iletkenlerin kullanılması gibi çok çeşitli fotokatalitik malzeme modifikasyonları incelenmiştir. Zr, TiO_2 yapısında fotokatalitik uygulamalar için istenmeyen bir faz olan rutil fazın oluşmasını baskılayan bir maddedir. Ayrıca Zr ile katkılandırılmış TiO_2, normal TiO_2'den çok daha yüksek fotokatalitik verimlilik göstermektedir. Bu tezde Zr katkısının konsantrasyon seviyesinin fotokatalitik uygulamalar üzerindeki etkileri de incelenmiştir. Bu nedenle hidrotermal ve asıltılı pelte (sol-gel) destekli polimerleştirici kompleks ateşleme yöntemi (PCCM) yöntemler ile elde edilmiş farklı nano-yapıya sahip TiO_2 tozları üretilmiştir. Farklı oranlarda Zr katkısı içeren ve hiç içermeyen TiO_2 numunelerinin fotokatalitik özellikleri değerlendirilmiştir. Zr modifikasyonunun fotokatalitik uygulamalar üzerinde olumlu etkileri tespit edilmiştir.

1) Zr modifikasyonu (ZM) TiO_2 parçacıklarının boylarını küçültmüştür.
2) ZM TiO_2 'nin optik özelliklerini geliştirmiştir.
3) ZM TiO_2 'nin bant boşluğunu artırmıştır, bunun emilim üzerinde doğrudan etkisi vardır.
4) ZM boya yükleme kapasitesini artırmaktadır.
5) ZM TiO_2'nin fotokatalitik etkisini artırmaktadır. En yüksek verim artışı % 5 Zr modifikasyonunda gerçekleşmiştir.

Sonuç olarak, ZM DSSC'nin fotovoltaik performansını artırmaktadır. En yüksek gelişimin % 5 Zr ile modifiye edilmiş TiO_2'de gerçekleştiği görülmüştür. % 5 Zr ile modifiye edilmiş TiO_2 fotokatalitik uygulamalarda iyi bir alternatif emici tabaka olarak öne çıkmaktadır. Renk kaybı süresi incelendiğinde gün ışığı altında en hızlı dağılan boyanın malaşit yeşili olduğu, en yavaş dağılımın ise metilen mavisinde gerçekleştiği görülmektedir. Her ne kadar bu yaklaşımla testlerden sonuç almak UV yöntemine göre daha uzun sürse de, bu yöntem daha ekonomik ve pratiktir. Ayrıca ortaya çıkan çözünme de en iyi alternatif yöntemlere göre daha hızlı gerçekleşmektedir. Bu nedenle incelenen parçacıkların ticarileştirilmesinin önündeki önemli bir engel ortadan kalkmaktadır.

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