Thin film photocatalysis for dye degradation as an environmental remediation: using Metal oxides

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Abstract

Various thin films of metal oxides are used for the efficient dye degradation of organic dyes. In this chapter an overview on the photodegradation of dyes is given. Because of the difficulty in recycling the photocatalysts in the powder form, the thin film catalysts are gaining rapid attention photocatalytic applications. In other words semiconductor thin films are growing promisingly as photocatalyst for waste water treatment from dying industries. Thin layers of metal oxides due to their stability, charge transport and absorption properties are more suitable for this kind of applications. Thin film photocatalysts provide good efficiency and reduced equipment costs. This chapter summarizes some key factors related to improving the photocatalytic performance of thin films.

Keywords: photocatalysis; thin films; metal oxides, thin film photocatalysts

1 Introduction

Rapid increase in world population and extensive industrialization are mainly responsible for the huge environmental pollution caused by several hazardous wastes and organic contaminants. Continuous release of organic pollutants such as dyes into water sources tend to pollute water and affect not only human health but also aquatic life within them water bodies [1]. Point sources (refineries, mines, factories, power plants, etc.) are are mainly responsible for the pollution of surface and underground water than non-point sources (cars, buses, and trains etc.) [2]. According to the Lancet Commission on Pollution and Health around

1.8 million deaths worldwide are related to waterborne diseases [3]. There are different kinds pollutants include inorganic (heavy metal ions, metal oxides, metal complexes, salts, etc.), organic (dyes, pesticides, pharmaceutical additives, fertilizers, phenols, surfactants, etc.), nutrients and agricultural runoff, pathogens and so on. Among them, organic pollutants carry a in large part due to longer persistence, strong resistance and significant effect on human health. The majority of dyes are produced from industrial activity released directly into water bodies undesirable color that causes unsightly pollution, eutrophication, disturbances and limitation of biological activities of aquatic life [4,5]. Table 1. depicts the list of various organic compounds that are responsible for pollution along with their chemical structures. Several techniques have been used to remove organic compounds such as biodegradation, chemical oxidation and electrochemical conversion/combustion, ozonation, Fenton or photo-Fenton systems, ultrasound, adsorption on activated carbon, reverse osmosis, photolysis (UV), photolysis (UV/H2O2) and advanced oxidation processes (AOPs). They were found to be advanced oxidation processes effective methods of decomposition of organic pollutants. It involves the formation of highly reactive oxidizing agents for the oxidation of pollutants. Among the various AOPs, Photocatalysis has has gained increasing attention in the field of organic pollutant degradation due to its high efficiency, low cost and green method [6,7].

2 Photocatalysis

Photocatalysis is a technique that uses light and semiconductors. It shows high stability, non-toxicity, corrosion resistance and no cause of secondary pollution [8]. In 1972 Fujishima and Honda first announced the production of hydrogen by splitting water using n-type TiO2 semiconductor photocatalyst [9]. Figure 1 shows various applications of the semiconductor photocatalyst. The photocatalytic activity of a photocatalyst governs the performance of the photocatalytic process. An ideal photocatalyst should possess narrow bandgap energy, low cost, low recombination rate, safety, improved charge separation, increased efficiency at visible light, and good stability [10,11]. In addition, semiconductor photocatalysts can be used for anti-fogging, energy saving and storage, deodorization, sterilization, self-cleaning, air purification, wastewater treatment, etc. [12]. The photocatalytic mechanism involves the generation of hydroxyl radicals (OH) and superoxide anions (O_2 -). Among these two,OH has a higher oxidation potential and acts as the main oxidizing species. OH and O_2- both act as oxidants and decompose organic compounds. After mineralization, the organic pollutant produces less harmful CO_2 and H2O as reaction products, as shown in Figure 2 [13,14]. Based on the mobility of, there are two types of photocatalysts. These are mobilized photocatalyst (powder) and immobilized photocatalyst (thin film). The immobilized photoelectrodes are cheaper compared to powdered photocatalysts, difficult to recycle, and can be easily recycled after cleaning because they agglomerate due to the high loading of powdered photocatalyst. Thin-film photocatalysts have several advantages over powdered photocatalysts. For example, can be incorporated into a variety of materials by easily tuning the material properties to enable device miniaturization. Many reports on the synthesis from immobilized photoelectrodes [15-17].

3 Thin Film Deposition Techniques

The properties and durability of the thin films can be obtained by choosing the suitable film deposition technique[18-19]. Methods of thin film deposition can be broadly categorized as either chemical or physical

methods. The disparity between chemical and physical methods of thin film deposition depends on the method by which thin film material is deposited on the substrate. The fluid precursor is used in chemical deposition technique which chemically reacts with the substrate. Since thin film material is performed through the fluid precursor, chemical deposition approaches the substrate in a conformal manner without preference to a specific direction. Chemical deposition technique includes the following methods:

3.1 Chemical Vapour Deposition (CVD):

CVD is a chemical process using the gaseous precursors. Precursor gases with substratum are transferred into a chamber. The chemical reaction between the substrate surface and the precursor continues at elevated temperatures until the target film thickness is reached.

3.2 Plasma Enhanced CVD (PECVD) Method:

In PECVD, plasma is generated in a chamber of reaction which transforms the precursors into reactive radicals, ions, neutral atoms and molecules. These atomic and molecular components interact with a substrate, and this chemical reaction causes a solid layer to form on the substratum surface. Lower temperatures (300 $\sim$ 350^{o}C) are used in PECVD for thin film deposition, while high temperatures (600 $\sim$ 900oC) are used in CVD for thin film growth.

3.3 Atomic Layer Deposition (ALD) Method:

Two or more gaseous precursors are used in Atomic layer deposition to react sequentially one at a time with the substrate surface. The thin films which this process obtains are conformal. The ALD cycle is broken down into two half reactions. Such reactions include precursor deposition and reaction chamber evacuation that run sequentially and repeatedly for each precursor. This chemical reaction takes place on the substrate and results in the formation of the desired film thickness. ALD is a step-by- step process, so it is slower, but it can also operate at lower temperatures. Sol-Gel Method: Sol-Gel is a method of chemical solution deposition, where precursor solutions are highly regulated for film deposition. The Sol-Gel approach includes alkoxides where the macromolecular oxide network is first acquired through alkoxy group hydrolysis after these polycondensation reac- tions occur. Mechanical or electromechanical processes are used in the physical deposition technique to deposit the thin films on the substrate. Depending on the temperature, pressure and other physical conditions, products to be deposited on the substrate.

In these Physical methods, the thin films formed are directional by nature, as particles pursue a specific path that guides the target to the substrate .Physical deposition technique includes the following methods:

3.3.1 Molecular Beam Epitaxy (MBE)

MBE incorporates the benefits of both chemical and physical thin-film deposition methods. Firstly, the target materials to be deposited are immediately heated until they are converted from solid to gaseous. The gaseous elements are then allowed to chemically react with the substrate surface to expand the thin film. Target material in MBE is deposited in layer form just one layer at a time. MBE is a slow method but this method has a very high degree of purity[19-23].

3.3.2 Sputtering

Sputtering is a form of physical thin film deposition in which the atoms are extracted from a target material and come to rest on a substrate[24-26]. The target material is managed at low temperatures. Plasma of a noble gas such as argon is often used as a target material in this method. Therefore, noble gas does not permit any unnecessary chemical reactions; it is a rapid and convenient method for achieving the desired film thickness level[27 -29].

3.3.3 Pulsed Laser Deposition (PLD)

It is the method of ablation. High-power laser light pulses are directed in a vacuum chamber on the surface of the target material. This results in target material being vaporized[30-31]. The ablated atoms from the target material are deposited on the substrate. Figure 1.2 demonstrates technique for pulsed laser deposition.

3.3.4 Cathodic Arc Deposition

The deposition of the cathodic arc is also known as arc- PVD. It is a kind of ion beam deposition where there is an electrical arc that blasts the ions from the target material to be deposited (known as cathode). This electric is vaporizing the material out of the target cathode. The vaporized material is condensed to form a thin film on a substrate[32].

3.3.5 Thermal Evaporation Method

The source material to be deposited in a vacuum would use an electron beam or resistive heating inside a chamber with high vacuum coating. The vacuum allows the molecules of vapor to pass directly to the substrate surface where they condense to a solid state to form a thin film[33,34].

3.3.6 Electrohydrodynamic Deposition

Electrohydrodynamic deposition is also known as the process of deposition by elec- trospraying. In this method stress is exerted on the liquid (mixture of nanoparticles to be deposited with the required solvent such as methanol) that flows through the capillary nozzle by applying high electrical field while the substrate is held at ground potential. This stress contributes to the deposition of small liquid droplets on the substrate. The substratum is heated for solvent absolutely to evaporate. Figure 1.3 displays the electrospray method used for thin layer deposition from a suspension[35]. An significant feature of the above deposition techniques for depositing BIT films is to overcome the problem of minimizing processing temperature and time, and boost ferroelectric properties such as remnant polarization, coercive area, etc. The prerequisite for the formation of a proper bi-layered crystalline phase is that it has minimal defects, without any secondary phases being included and with optimal crystallite orientation[36].

3.3.7 Sol-gel Method

A sol is a dispersion of the solid particles in a liquid where the particles are suspended only by Brownian motions. Suspension of linear-dimensional particles between 1 nm and 1µm are called colloids produced by hydrolysis and polycondensation reactions of metal alcoxides such as Si and Ti oxides. These Si and Ti oxides are considered precursors. A precursor is a compound that takes part in a chemical reaction to create

a particular compound[37]. A gel is a state where both liquid and solid are dispersed in each other which presents a solid network containing liquid components. A gel is a porous three dimensionally interconnected semi-solid network that expands in a stable fashion throughout a liquid medium and is limited by the size of the container. A gel is said to be colloidal if the solid network is prepared using colloidal sol particles. The liquid is present between the mesh of the solid network that composes the gel that does not flow out spontaneously and is in thermodynamic equilibrium with the solid network. The sol-gel method consists of following methods:

1. The desired colloidal particles once dispersed in a liquid to form a sol.
2. The deposition of sol solution produces the coatings on the substrates by spraying or dipping or spinning. The particles in the sol are polymerized through the removal of establishing components and produce a gel in a state of a continuous network.
3. The final heat treatments pyrolyze the remaining organic or inorganic com- ponents and form amorphous substance which which can be changed into crystalline by the use of annealing method. Thin films from sol can be deposited methods are Dip coating ,Spin Coating and Spraying.

Thin films are prepared by depositing precursor solutions onto various substrates. The amorphous gel films are pyrolyzed at relatively low temperatures (300oC to 700oC) to form amorphous or crystalline oxides followed by annealing at relatively high temperature to allow crystallization.

3.3.8 Dip Coating Technique

Dip coating technique is a process where the substrate to be coated is immersed in a coating sol where a wet layer is formed and then it is withdrawn with a well- defined withdrawal speed under controlled temperature and atmospheric conditions. The dip coating technique is shown in figure 1.4. The atmosphere controls evaporation of the solvent and it leads to a gelation process which results in formation of film. The resulting film has to be densified by thermal treatment and the densification temperature depends on the composition[38].

3.3.9 Spin Coating Technique

In the spin coating process, the substrate spins around an axis which is perpendicular to the coating area[39]. The spinner is designed to coat thin films of liquids on the wafer surface. The wafer surface is then dipped with precursor solution. The wafer is then rotated with high speed. The excess precursar solution is driven off because of centrifugal force leaving a thin film of precursar on the wafer surface. The thickness of wafer is controlled by spin speed, spin time and viscosity of the solution .The spin coating process involves the four stages as shown in Figure 1.5. These stages include deposition, spin up, spin off and evaporation. In the deposition process, an excessive amount of fluid is deposited on slowly spinning substrate.

Using a nozzle the fluid is sprayed at the center of the substrate. An excessive amount of fluid is deposited to avoid coating discontinuities because the fluid may dry before it reaches the wafer edge . In the spin up process, the substrate is accelerated to its final spin speed. In liquid, rotational forces are exerted on the upward direction causing a wave front to be formed. This wave front flows to the substrate edge by centrifugal force and hence results in a uniform layer. The spin off stage is the spin coating stage where the excess solvent is removed off the substrate surface as it rotates at speeds between 2000 and 8000 rpm. The fluid is being

thinned primarily by centrifugal forces until enough solvent has been removed to increase viscosity to a level where flow ceases. In the spin coating process, evaporation is the primary method of film thinning once the fluid flow ceases. Evaporation is the complex process by which a portion of the excess solvent is absorbed into the atmosphere. If evaporation occurs before the time it may cause the formation of a solid skin on the fluid surface and results in coating defects. A variety of film thickness can be deposited by spin coating, due to film thickness being roughly inversely proportional to the square root of spin speed[40].

3.3.10 Spraying/Spray Technique

In spray technique, spray solution is spread on hot substrate and other volatile by- products and excess solvent are removed in the form of vapors . Spraying technique apparatus involves spray nozzle, motor, liquid level monitors, hot plate, gas regulator valve and air tight fiber chamber and is shown in Figure 1.6.

1. Spray nozzle It consists of a tube filled with solution which is sur- rounded by the glass bulb. On applying pressure to the carrier gas, the vacuum is created at the tip of the nozzle. Hence, the solution is automatically sucked in the solution tube and the spray process starts.

2. Motor for spray nozzle To control the motion of the spray nozzle over hot a plate, the stepper motor is used.

3. Liquid level monitor The spray rate at a fixed air pressure depends upon the height of the solution measured with respect to the tip of the nozzle. The arrangement for the change in height of the solution forms the liquid level monitor.

4. Gas regulator value The gas regulator value is used to control the pressure of the carrier gas flowing through the gas tube of the spray nozzle.

5. Air tight fiber chamber The spraying system is fixed inside an airtight fiber chamber and is connected to an exhaust fan to remove the toxic gases produced during the thermal decomposition of spayed solution.Spray technique is one of the best methods used for making thin films because of its simpler construction and efficient output. In the present work for thin film preparation spray technique was employed.

4 Metal oxide thin film Photocatalysts

4.1 Zinc oxide (ZnO)

ZnO is a promising potential photocatalyst as it has a wide direct band gap (3.37eV), chemical stability, facile synthesis, low cost, large excitation binding energy (60 meV), excellent optical properties and low toxicity compared to other semiconductors [41,42]. Various methods are reported to prepare ZnO photoelectrode which includes chemical vapor deposition, pulsed laser deposition (PLD), chemical bath deposition, hydrothermal, spray pyrolysis, RF sputtering sol-gel, radio frequency plasma-enhanced chemical vapour deposition (RF-PECVD) and electrodeposition method [43-44]. Yudasari et al. have used a promising pulsed laser deposition (PLD) method for synthesis ZnO film with hexagonal wurtzite structure by optimizing laser energy and exposure time. It is one of the green approach deposition method and photocatalytic performance is examined by Rhodamine B (RhB) degradation [45]. Alfaro Cruz et al. have developed ZnO films by using

RF magnetron sputtering technique and films were annealed in air, argon and nitrogen atmosphere and observed that air annealed film show high photocatalytic activity. it may be due to the presence of large oxygen deficiencies which act as active cite to favor reaction yield. Fig.7 shows the effect of annealing environment on the surface morphology of ZnO films [46]. ZnO exhibits high recombination rate and large band

gap (3.2eV). Therefore, various strategies such as doping with cation or anion and coupled with other semiconductors are developed to minimize the recombination rate [47]. Dopants like Er, Ag, Al, Ce, Co and N are used to degrade organic dyes like RhB, azo dye and MB [48–53]. Georgiev et al. have modified ZnO film with gold nanoparticles by sol-gel method to remove malachite green from wastewater. Fig.8 shows modification in ZnO with gold nanoparticles [54]. Mimouni et al. have reported chemically sprayed Cr-In codoped ZnO thin film photocatalyst with a modified band gap (decreases from 3.3 to 3.1eV) to degrade MB dye [55]. Hussin et al. have prepared coupled ZnO/TiO2 thin films with different calcination temperatures by the sol-gel method and its photocatalytic activity was tested by photodegradation of MB dye [56].

4.2 Titanium dioxide (TiO2)

Simple metal oxide TiO2 photocatalyst is environmentally benign, abundantly available, biocompatible and able to immobilize on a variety of supports to remove several contaminants [57]. Depending on the temperature, it exists in three phases namely anatase ($<800^\circ$ C), rutile ($>800^\circ$ C) and brookite [58]. After UV irradiation, the photons of energy equal or greater than band gap energy of TiO2 ($h\nu > 3.2$ eV, i.e. $\lambda < 380$ nm) get absorb on the surface of TiO2 photocatalyst, generation of electron-hole pair takes place, holes contribute to the formation of hydroxyl radical (•HO) and electrons give superoxide anion. Both hydroxyl radical and superoxide anion interact with organic pollutants and finally get converted into harmless products [98,99]. TiO2 + UV → e- + h+ (i)

e- + O2(g) → O2- (ii)

h+ + H2O → •OH + H+ (iii)

h+ + OH(l) → •OH (iv)

Several methods were employed to synthesize TiO2 thin film photocatalyst such as sol- gel method, atomic layer deposition, chemical vapour deposition, spray pyrolysis, etc. [59]. Hachisua et al. have reported that the synthesis of TiO2 film by electrodeposition method using newly synthesized titanium compound in N,N-dimethylformamide [60]. The utilization of semiconducting material in photocatalysis is a major issue for environmental remediation. Also due to the wide band gap, TiO2 activated under the UV region contributes to only 5% of the solar spectrum [61]. TiO2 possesses limited quantum efficiency and small electron mobility of 1 cm2/V/s. Therefore, several techniques such as sensitization, doping with transition metal ion, coupled with low band gap semiconductor and co-doping with nonmetals are employed to enhance the photocatalytic performance [62-64]. Modification with doping of metals and non- metals can effectively improve the performance due to the implantation of new energy levels in the band gap as shown in Fig.4 [65]. S doped TiO2 thin film deposited on the glass substrate by ultrasonic-assisted spray pyrolysis technique exhibits anatase crystal structure with highly visible light transparency and shows higher efficiency in photodegradation of methylene blue (MB) dye than undoped TiO2 [66]. Other non-metal dopants like B, F, I, C and N were doped to improve degradation efficiency of TiO2 thin film. Among these, doping of N is beneficial due to its high stability, small ionization energy and metastable center formation. The transparent N-doped TiO2 thin film with controllable film thickness and deposition rate prepared by the newly designed sonochemicalCVD method. Further, the photocatalytic activity of the film is verified with respect to degradation of paraoxon

pesticide [64,67–69]. There are several methods for deposition of N-doped TiO2 thin film such as ion beam assisted deposition technique, one-step low-frequency plasma-enhanced chemical vapor deposition (PECVD), inductively coupled plasma (ICP) assisted plasma sputtering method, atomic layer deposition, reactive magnetron sputtering method, sol-gel deposition method and pulsed laser deposition method [70–78]. Madhavi et al. have presented the synergetic effect of Ag nanoparticles on TiO2 and N-TiO2 thin film deposited on FTO coated glass substrate by reactive DC magnetron sputtering method and their photocatalytic properties were examined by degradation of methyl orange (MO) dye under sunlight irradiation. Fig.5 highlights the photodegradation performance of Ag/ N-TiO2

photoelectrode [79]. Several metal dopants like Gd, Co, V, Ce, Eu, Nb and Mo were doped to modify photocatalytic properties of TiO2 [80–86]. However, Cu-Doped TiO2 thin films deposited by spin coating and dip coating methods are efficient photocatalysts for H2 production, water splitting and many photo-oxidation reactions [87–89]. Furthermore, to improve decomposition time, decomposition rate and to minimize fast recombination, the composite photocatalysts were employed [90]. Covei et al. have reported that spray deposited CZTS-TiO2 thin films on a glass substrate with variable TiO2 concentration are applicable for photodegradation of methyl blue dye under visible light irradiation. Fig.6 indicates the dependence of degradation efficiency on TiO2 concentration and irradiation source [91]. Mohite et al. have prepared a bilayered structure by depositing TiO2 thin film on pre-deposited Gd doped WO3 film by using a simple chemical spray pyrolysis technique to increase degradation efficiency for salicylic acid [92]. Jia et al. uniformly deposited Pt nanoparticles in between TiO2 and WO3 film by sputter deposition technique for preparation of hybrid TiO2/Pt/WO3 film structure to remove CH3CHO (acetaldehyde) [93].

4.3 Tungsten trioxide (WO3)

Tungsten trioxide is n-type visible region active material with band gap 2.6 eV follows several exceptional characteristics such as high solar radiation absorption, excellent photostability, less indirect band gap, chemically static, non-toxic, exhibit remarkable thermal stability and higher acidic stability. Its valance band holes exhibit high oxidation potential. Various methods are available to deposit WO3 films such as template, sol-gel, anodic oxidation, thermal evaporation, chemical vapor deposition, hydrothermal, reactive magnetron sputtering and chemical spray pyrolysis. WO3 emerges as a promising material for photocatalysis, photoelectrocatalysis and electrocatalysis application [94–98]. Mohite et al. have reported photoelectrocatalytic degradation of benzoic acid using spray deposited monoclinic WO3 thin film by varying solution quantity (45 ml to 90ml) and observed that photoelectrochemical performance of WO3 films depends on crystallinity, the thickness of the films and optical absorption of the films. The schematic setup for photoelectrocatalytic degradation is as shown in Fig.9 [99]. The photocatalytic performance of WO3 is limited due to its wide band gap energy and easy recombination of generated electron-hole pairs. Therefore, doping with metals like Yb, Ga, Al, Dy and Ti is one of the way to improve its degradation efficiency. Mohite et al.have deposited Ga doped WO3 thin film by cost effective chemical spray pyrolysis technique to degrade salicylic acid and benzoic acid. The porous morphology of 2 at.% Ga:WO3 played a crucial role in the enhancement of performance due to the increase in surface area. The variation in surface morphology of the film with different doping percentage is as shown in Fig.10

[100,101]. Dong et al. have studied the synergistic effect of Pt and Ag alloy nanoparticles on WO3 thin film for photodegradation of MB solution under visible light irradiation [102]. Duta et al. have found that the use of polymer additive and doping with Cd effectively enhanced photocatalytic properties of monoclinic spray

deposited FTO/WO3 thin film to remove MO and MB dye from wastewater [103]. Graphene/WO3 thin film prepared by nano-particle deposition system for various wt% of graphite showed remarkable photocatalytic efficiency for degradation of MB dye [104].

4.4 Bismuth oxide (Bi2O3)

Bismuth oxide is another promising p-type direct band gap semiconducting metal oxide photocatalyst having a band gap of about 2.8eV and able to undergo facial water oxidation. Various shapes of Bi2O3 utilized for degradation of several dyes or organic compounds like MB, RhB, MO, malachite green, CBBG-250, acetaldehyde, 4-chlorophenol, gases and drugs. Bismuth oxide exhibits several polymorphs such as alpha (monoclinic), beta (tetragonal), gamma (body centered cubic), delta (face-centered cubic) and omega (triclinic) phases [106,106]. Weidong et al. have proposed that the degradation efficiency of sol-gel deposited Bi2O3 thin film for RhB dye varies with increase in annealing temperature and shows 100% efficiency at 550 $^{\circ}$ C due to the high portion of tetragonal phase [107,108]. Bi2O3 nanoparticles as prepared by the chemical bath reaction method immobilized as a thin film on the ITO substrate by using a drop-casting route show considerably good performance in decoloration of RhB dye within 40 minutes [109]. -Bi2O3 film deposited on glass by magnetron sputtering confirms high decoloration rate for MO solution compared with TiO2 films and TiO2-P25 Degussa particles under UV irradiation [110]. Hajra et al. have reported that hydrothermally synthesized nitrogen modified Bi2O3 film follows higher decoloration performance for RhB dye than pure Bi2O3 film due to the insertion of oxygen vacancies and decrease in band gap energy from 3.01eV to 2.75eV [111]. The detail investigation for phoelectrocatalytic performance of CBD grown Bi2O3 and novel Ag decorated Bi2O3 films reveals Ag@ Bi2O3 film showed 97% efficiency in removal chlorinated phenol under UV-visible radiation. As compare to Bi2O3, Ag has a lower work function which means it would able to induce energy levels to separate photogenerated electron-hole pairs. Furthermore, the importance of hydroxyl radicals for photodegradation is confirmed by employing tert-butyl alcohol as OH● scavenger [112].

The Bi2O3 film prepared by reactive magnetron sputtering used as a template for the deposition of TiO2 film to eliminate MB dye under UV illumination. Grape shaped Bi2O3 coated titania photoelectrode have prepared by electrodeposition method for photoelectrocatalytic oxidative degradation of Acid Orange 7 under visible light irradiation [113,114].

4.5 Tin oxide (SnO2)

SnO2 is an n-type semiconducting material with band gap 3.6 eV possess unique electrical and opical properties, non-toxicity, high electron mobility, low cost, harmless, high chemical stability and show photocatalytic activity under UV region. Furthermore, it follows great flexibility in structure and morphology [115,116]. The SnO2 thin film synthesized by cost- effective galvanic technique exhibit orthorhombic structure and high surface area. Due to porosity, it shows high photocatalytic performance to degrade MO dye into small molecules like CO2, H2O, $NO3^{-}$, etc. within 120 minutes [117]. Ameur et al. have deposited polycrystalline tetragonal structured SnO2 film on the glass as well as on Polyetherimide (PEI) flexible substrate by facile spray pyrolysis method to degrade Crystal Violet (CV) dye with 80% efficiency under UV irradiation [118]. The comparative study between homemade spray deposited undoped SnO2 and fluorine-doped SnO2 (FTO) thin film revealed that FTO exhibited higher 95% efficiency to degrade MB dye than that of undoped SnO2 film with 78% efficiency due to generation of a large number of electrons [119]. Hydrophilicity and photocat-

alytic activity of sol-gel deposited tetragonal SnO2 thin film was improved by the incorporation of Ni and Fe dopants [120]. To improve the visible light harvesting efficiency and recombination rate of SnO2-ZnO thin film, the films were doped with Fe and B. These co-doped films were used to remove formaldehyde in aqueous solution under UV irradiation [121]. Covei et al. have prepared heterostructure (SnO2)- Cu2ZnSnS4-TiO2 thin film by spray pyrolysis techniques to photodegrade MB dye, imidacloprid and phenol under simulated solar irradiation[178]. SnO2(TiO2) elongated octahedral nanoparticles film deposited on FTO by the hydrothermal method were sensitized by CdS nanoparticles to increase the removal rate for MO [122].

4.6 Cuprous oxide (Cu2O)

Cuprous oxide is metal oxide photocatalyst having a narrow direct band gap of 2.17 eV and it is beneficial for the removal of dye molecules, the evolution of H2 and O2 and solar cell application under visible light radiation [123]. It exhibits p-type semiconductivity due to Cu vacancies. Cu2O is one of the potential candidate for photocatalytic application as it is cost- effective, less toxic, good environmental acceptability and reduces electron-hole recombination due to effective adsorption of molecular oxygen [124]. the Hydrothermal coating of Cu2O film on FTO supported TiO2 is reported as promising photocatalyst in MB degradation using a homemade thin-layer micro-reactor due to effective separation of electrons and holes. Moreover, photoelectrode prepared by electrodeposition of Cu2O film on TiO2 loaded ITO substrate was utilized for electron storage [125]. Further, to improve the stability of Cu2O/TiO2film, Dongliang et al. have allowed the growth of Cu- Cu2O mixture on sputter-deposited TiO2 film [126]. The Cu2O/α-Fe2O3 p-n heterojunction thin film was synthesized by electrodeposition of Cu2O layer on α-Fe2O3 and its photoelectrocatalytic activity is studied through the removal of oxytetracycline under visible light at 0.5V [127]. WO3/n-Cu2O and WO3/p-Cu2O composite thin film photocatalysts were prepared on the Ti substrate by cathodic electrodeposition method with different cathodic density and WO3/p-Cu2O film show higher degradation efficiency for Orange II degradation within 60 minute [128].

4.7 Cerium oxide (CeO2)

CeO2 is another rare-earth metal oxide that exhibits efficient photocatalytic activity due to its high oxygen storage capacity and offers resistance to photocorrosion. Furthermore, it has high activity, high thermal stability, remarkable redox and environmentally friendly properties. Fig.11 shows photocatalytic mechanism of CeO2 after irradiation [129–130]. Heavily N-doped CeO2 film synthesized by ion beam assisted deposition method with continuous nitrogen bombardment showed a red shift and smooth surface morphology with the increase in nitrogen loading [131]. Verma et al. have deposited CeO2–CeTi2O6 thin film by cost-effective and low temperature sol-gel method on the glass substrate. The prepared film possesses higher photocatalytic efficiency to decompose eosin (yellow) under UV–visible light irradiation as compared to TiO2 film [190]. Ismail et al. have reported a comparative study of multilayer and thick layer growth of CeO2 on 3D mesoporous TiO2 film deposited by a spin coating method on a soda-lime glass substrate. The multilayer CeO2-TiO2 film showed higher efficiency towards MB dye degradation than thick CeO2-TiO2 film under UV radiation [132]. The TiO2–CeO2 composite film prepared by magnetron sputtering exhibits higher performance as compared to TiO2 and CeO2 film in consequences of a decrease in band gap energy and separation of electron-hole due to drifting of an electron from TiO2 to CeO2 . Recently, the coupled CeO2 -[poly(methyl methacrylate)] (PMMA) film with no agglomeration synthesized by Latha et al. have found

to be effective for photodegradation of congo red and MO under visible light irradiation due to production of defect levels in CeO2 [133].

4.8 Ferric oxide (Fe2O3)

Fe2O3 is a popular post-transition metal oxide photocatalyst which exists in four different crystal structures as hematite (α-Fe2O3), maghemite (ν-Fe2O3), magnetite (Fe3O4) and wüstite (FeO). Among these candidates, hexagonal hematite (α-Fe2O3) exhibits good photocatalytic properties than conventional photocatalysts like TiO2, ZnO, etc. Due to its narrow band gap (2.1eV), it covers a larger portion of the solar spectrum [134]. α-Fe2O3 provides widespread availability, high absorbance and chemical stability which affects its photocatalytic application. The spray deposited rhombohedral α-Fe2O3 photoelectrode prepared by Mahadik et al. found to exhibit n-type direct band gap semiconductivity with variation in band gap energy (2.14 to 2.21 eV) due to different substrate temperatures and enhance degradation of RhB due to change in electronic structure [135]. Kawahara et al. have reported electrochemically assisted α-Fe2O3 film on a silica glass substrate by using a metal organic deposition (MOD) method to remove 2- naphthol and film show high performance compared to conventional TiO2 film [136]. Zhang et al. synthesized α-Fe2O3 thin films by liquid-phase deposition method (LPD) on the Ti substrate to study the phoelectrocatalytic degradation of MO dye. The films annealed at 600 ° C showed higher efficiency, it might be due to the higher porosity and photocurrent density [137]. Iervolino et al. have presented the comparative study of electrodeposited pure Fe2O3, Ti- Fe2O3 and Ni- Fe2O3 photoanodes. Among these, Ti- Fe2O3 films with 1 g/L glucose as organic additive showed high efficiency for photoelectrocatalytic H2 production at 0.5V within 12 hours and photocurrent density of films increases with applied potential [138]. Fe2O3- TiO2 film deposited by the sol gel method with four different precursor solutions showed photoactivity towards photo-oxidation of MB dye [139]. Akhavan and Azimirad have synthesized TiO2/Fe2O3/glass thin film by sol-gel and thermal evaporation technique to remove Escherichia coli bacteria. The formation of heterostructure enhances the charge transfer between TiO2 and Fe2O3 [140]. According to Akhavan, an increase or decrease in thickness of TiO2 or Fe2O3 layers respectively in TiO2/Fe2O3/glass photoelectrode is attributed to improved degradation of Escherichia coli bacteria [141]. Mahadik et al. have further compared Fe2O3, TiO2 and TiO2/Fe2O3 composite films prepared by chemical spray pyrolysis technique on glass and FTO substrate to study photocatalytic performance by using RhB as a model pollutant. The TiO2/Fe2O3 composite film exhibited high degradation efficiency (98.86%), narrower band gap, higher Raman peak intensity and higher activity due to the presence of Fe3+ which enhances the life time of electron and holes as compared to Fe2O3 and TiO2. Moreover, 2% Au doped Fe2O3 film deposited on a large area (64cm2) FTO showed higher photoelectrocatalytic degradation of salicylic acid under visible light than pure Fe2O3 film which was attributed to scavenging of surface electrons by Au(III). The Fig.12 represents Chemical Oxygen Demand (COD) as function of time and extinction spectra of Au doped Fe2O3 photocatalyst [142,143].

4.9 Conclusions

Several metal oxide semiconductors have been identified to be potential photocatalysts for dye waste-water treatment. Among the photocatalysts studied, titanium dioxide and zinc oxide are the most widely used metal oxides in AOP. However, other metal oxides could also be used as photocatalysts in this context. This review paper reports and summarizes recent modifications applied to metal oxides used for dye waste-

water treatment. Most of these were conducted on titanium dioxide because it is the conventionally preferred photocatalyst in AOP. Through appropriate catalyst modifications, not only can the degradation efficiency of certain dyes and reusability of metal oxides be enhanced, but the band gap can also be lowered to modify the treatment activity under visible light irradiation. Different modifications of titanium dioxide using metals (e.g. noble metals, transition metals and lanthanides) and non-metal compounds (e.g. nitrogen, sulfur, carbon and phosphorus) have been tested, and the results showed that such modifications enhanced the photocatalytic activity of titanium dioxide, either under UV or visible light irradiation. Metal oxides such as zinc oxide, vanadium oxide, tungsten oxide, molybdenum oxide, indium oxide and cerium oxide could also be used as photocatalysts in dye waste-water treatment, but they are often considered inferior to titanium dioxide. Additional studies are being conducted on other metal oxide semiconductors to determine whether their roles as photocatalysts can be expanded in the future.

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