

Photocatalytic applications of transition metal and metal oxide nanoparticles

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Abstract

Transition metal and metal oxide nanoparticles have gained huge attention in the field of photocatalysis due to their ability to strongly absorb ultra violet and visible light. There are many reactions could be successfully catalyzed using nanoparticles of pure metals, metal alloys and metal oxides including semiconductor metal oxide under solar light at moderate temperatures. The increased use of these materials for treating environmental pollutants has captured the public concern has promoted the requirement to develop newer robust methods for the degradation process, which resulted in the increased demand of photocatalysis. This review would help in obtaining an overview regarding the applications of transition metals and metal oxide nanoparticles as photocatalysts. The photocatalytic applications and general background about the photocatalysis are briefly reviewed in this paper.

Keywords: Plasmonic metal nanoparticles (PNPs), Semiconductor metal oxide, Photocatalytic degradation, Metal oxide nanoparticles, Localized surface Plasmon resonance effect; Nanoparticles (NPs)

1. Introduction

1.1 Back ground on photocatalysis

The role of photocatalysts based on nanoparticles are widely spread in areas concerning organic synthesis, dye degradation, waste water treatment etc. Domestic or industrial waste water effluents are the major source of organic pollutants. These organic pollutants must be removed before they enter into the environment. In order to obtain acceptable water quality for drinking water, organic pollutants found in the ground and surface waters need treatment [1]. The exploration of natural energy sources that are environmentally clean has become crucial for the protection of environment from the increasing global scale pollution. It is

known to be a major challenge for the chemists. There are natural waste and synthetic waste but in the case of natural waste, environment has a self cleaning mechanism. While in the case of synthetic wastes, even a trace concentration of the pollutant can lead to disastrous environmental effects. Heavy metals and pesticides are a part of industrial wastes, pesticides from agricultural units and production plants must be treated before dispense to the environment in order to reduce the hazardousness. The increased concentration of these environmental pollutants attained the public concern, accelerated the requirement to develop novel methods for the degradation process [2]. Analysis on the available techniques leads to a conclusion that many of them are insufficient. This results in the development of methods that are ecologically clean with the usage of natural energy sources. This has resulted in an increased attention to the photocatalysts for application in waste water purification or pollutant degradation. Heterogeneous photocatalysis and solar light combines together in the process known as photocatalytic detoxification of waste water [3]. Recently semiconductor photocatalyst such as titanium oxide (TiO₂) has been applied in various fields with an ecological concern besides water and air purification [4].

1.2 General mechanism of photocatalysis

The natural cleansing of aqueous resources is possible using natural sensitizers which are known to be accelerators during a photo-catalytic reaction. The studies regarding this area have lead to the exploration of semiconductors that exist in nature and can help in the purification process. Later studies have confirmed the ability of these semiconductors in the solar assisted purification process of water in the environment [5]. Photocatalysis involves a catalyst which can drive a photoreaction. There are certain conditions which characterize a catalyst as a photocatalyst, which are

its cost-effectiveness, photo activity and non-toxicity. Another important advantage of photocatalysis for the removal of organic toxins is that it doesn't need any secondary disposal. The conventional methods like air stripping and adsorption using activated charcoal etc. does not remove the toxins but transfer the entities to the air or adsorbent material. The advanced oxidation processes using oxidants like hydrogen peroxide and ozone etc. are expensive and the photocatalysis needs only an ambient O_2 atmosphere. The ability of a photocatalyst depends upon the electron-hole pairs that are photogenerated. When a semiconductor atom is irradiated by photon of appropriate energy hits an electron in the filled valence band and can promote the electron to the empty conduction band leading to positive holes and excited electrons in the valence and conduction band respectively. This radiation should have energy identical or greater than that of band gap with specific energy. The bandgap is known as the energy difference between valence band and conduction band, the semiconductor owes bandgap in the range of 3 to 3.5 eV. Empty conduction band and filled valence band are characteristics of semiconductor electronic structure and because of this it can act as a sensitizer for photo reduction-oxidation processes under light irradiation. The Photogenerated electron-hole pairs (charge carriers) thus produced may choose different paths as shown in Fig.1. Primarily they can get confined in deep traps (DT) or shallow traps (ST). The input energy is dissipated as heat either by radiative or non-radiative recombination of electron-hole pair [4]. Finally, these carriers react with the electron acceptors or donors on the photocatalytic surface [6]. Redox reactions in presence of light is due to the electrons and holes that are trapped on the surface of semiconductor particle instead of the electrons in CB and holes in VB [7]. It was known that, holes from VB and electrons from CB are strong oxidising and reducing agents respectively [8].

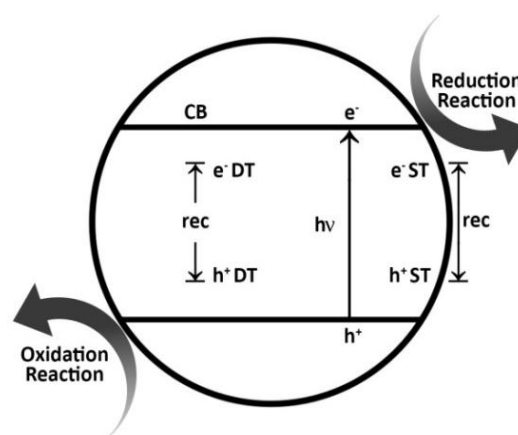


Fig.1 Mechanism of band gap excitation in semiconductor nanoparticles [4]

The photodegradation process directly or indirectly utilizes the oxidation power of holes. Both electrons and holes are present on the particle surface of small semiconducting particle suspension, because of this reductive and oxidative paths are possible in this semiconducting suspension [4]. Solar light consist of 5 % UV (200-400 nm), 43 % Visible (400-800 nm), and 52 % IR (> 400 nm) radiation. From this it is clear that the major part of the solar light includes visible and infrared light (approximately 95 %) [9], the development of catalysts with enhanced activity under solar irradiation is a challenge in photocatalysis. The role of photocatalysis based on nanoparticles, widely spread on those areas which are mainly organic synthesis, dye degradation, waste water treatment etc. Visible light driven photocatalyst is not only a part of semiconductors but also extended to the noble materials which exhibit Surface Plasmon Resonance (SPR) effect because of its interaction and then the absorption of visible light [10]. Plasmonic-metal nanoparticles (PNPs) have gained huge importance due to their strong absorption over a wide region of the solar spectrum [11]. This makes the importance of PNPs in photocatalysis. PNPs are a class of material capable of harvesting solar light energy useful for chemical synthesis. The Localized Surface Plasmon Resonance effect (LSPR) occurs in PNPs due to their strong interaction with resonant incident light. As a result of these metal nanoparticles conduction electrons gets energy from the incident solar light. This makes the PNPs important in photocatalysis. Sarina et al. have discussed that the metal nanoparticles have an

ability to function both as harvester and host of light for the catalytic sites [12]. Optical properties of these metal nanoparticles could be defined by the control over the size and geometry [13]. It was reported that gold (Au) NPs supported on a substance which is catalytically inert in presence of light, can act as a photocatalyst for organic synthesis. An example for this is the gold nanoparticles supported by ZrO_2 at 40 °C under visible light work as a photocatalyst for the direct reduction of nitroarenes to azo aromatic compounds. This work revealed the role of PNPs directed photocatalysis for the organic synthesis [14]. Another reason for the increased demand of PNPs was because of the lesser affinity exhibited by organic reactants towards the semiconducting photocatalysts due to less number of active sites on the surface for catalysing these reactions [15]. Under photocatalytic reaction conditions semiconductors with wide band gaps are chemically stable and those with narrow band gaps are unstable, which also limits their practical applications [16]. Photocatalysis based on metal nanoparticles have applications in the field of chemical synthesis due to their light harvesting nature and catalytic functions. Gold NPs were used for the oxidation of volatile organic compounds [14-15]. There are organic reactions which can possibly be driven under light irradiation and at ambient temperatures so as to reduce the unwanted byproducts that are formed at elevated temperatures. The photocatalytic degradation can also convert hazardous organic compounds to simple mineral acids, water (H_2O), and carbon dioxide (CO_2) [17]. This review mainly focuses on the photocatalysis based on the metal and metal oxide nanoparticles of transition metals for organic synthesis and degradation reaction.

2.1 Applications of Transition metal nanoparticles in photocatalysis

Photocatalysis based on metal nanoparticles have gained huge attention in the past decade due to their solar light absorption rather than its use as co-operative catalysts. Metal NPs have properties which are different from their bulk counter parts. Like semiconductors, in the case of metal nanoparticles there is no need to overcome a band gap during the irradiation under sunlight [18]. Two models have been used to explain metal-induced photocatalysis, one is LSPR and the other is inter band transition [19]. Transition between the conduction band and d-bands of the noble metals are known as inter band transition. The phenomenon such as LSPR is observed if the size

of metal nanoparticle is smaller when compared to the wavelength of incident light. Both Au and Ag nanoparticles can absorb intense visible light because of LSPR effect, which mainly depends on their particle geometry such as shape and size of nanoparticles [13]. Surface Plasmon Resonance is a group of oscillation produced from the conduction electrons of metal nanoparticle, when it is induced by solar radiation. Electric field of the incident light should strongly interact with the conduction electrons of metal nanoparticles. This can result in a resonance between the electric fields of an oscillating conduction electron and an incident light or otherwise it results in the formation of a plasmon with a particular frequency, which oscillates in the locality around the nanoparticle [19]. Au, Ag, and Cu are known as coinage metals, they exhibit SPR in the visible region. It was reported that LSPR absorbance maxima of Cu, Ag and Au nanoparticles with spherical structure (20 nm) was observed at 580, 400, and 530 nm, respectively [20]. Among transition metals, coinage metal NPs possess LSPR absorbance either in the visible region or near the visible region. The electron-hole pairs (charge carriers) are formed in the metal nanoparticles due to the generation of surface plasmons by the absorption of solar radiation. The absorbed energy can get exchanged from the charge carriers to the surroundings or it can result in the heating of nanoparticles. Chemical reactions can be carried out by transfer of these photo-generated energetic electrons to the adsorbate in which case it is known as plasmon assisted transfer of electrons. But the heating of NPs leads to desorption of surface adsorbed reactant molecules and it also affects the reaction rate. Excitation of metal nanoparticle conduction electrons to their higher energy levels occurs after the simultaneous absorption of light energy and heat. This phenomenon helps in catalyzing organic reactions using metal nanoparticles [21].

Zhang *et al.* synthesized benzaldehyde from benzyl alcohol by oxidation using gold NPs / zeolite (ZSM-5, Beta (β), Silicate-1, and Ts-1, A), in which zeolite act as a support for the photocatalytic gold NPs [22]. Zeolite functions as a support only without offering any photocatalytic activity by itself. The reaction was carried out under oxygen (O_2) atmosphere at 40 °C in which zeolite helps in the adsorption of reactant molecules. The reaction exhibited a product selectivity of 99 %, they argued that selectivity of this reaction should be defined by the LSPR effect of metal nanoparticles. Later research has got more interested in the exploration of alloy nanoparticles that combines the properties

of both plasmonic and non-plasmonic nanoparticles. Peiris *et al.* reported the conversion of aromatic alcohol (Ar-OH) to aldehyde (Ar-CHO) by the selective oxidation using a catalyst made up of alloy nanoparticles (Pd and Au) on ZrO_2 at 45 °C under visible light irradiation and reported 99 % yield [21]. Non-plasmonic transition metals which exhibit greater affinity towards the organic reactants can be used as catalyst for various organic reactions with the assistance of heat. Various groups have examined the photocatalytic activity of Pd/ ZrO_2 for the benzyl alcohol conversion and the results showed 94 % efficiency under visible condition and 29 % efficiency under dark conditions [23]. Alloy NPs exhibit enhanced catalytic activity due to their heterogeneity in electronic structure, which generates a strong interaction with the reactants and thereby promotes the reaction. When induced by visible light alloy nanoparticles of Au and Pd showed better performance with selectivity for the oxidation of benzyl alcohol due to the presence of palladium (Pd) sites on the surface of alloy NPs [15]. The experimental data proved that non-plasmonic transition metal NPs like Pt, Ir, Pd and Rh on ZrO_2 exhibited better photocatalytic activity for the above reaction in which Pt/ ZrO_2 showed an activity of 71 % compared to Ir/ ZrO_2 and Rh/ ZrO_2 with 34 % and 35 % respectively [23]. Chen *et al.* found that at room temperature and pressure, blue light irradiation could degrade 64 % of formaldehyde using Au NPs on ZrO_2 . Formaldehyde is a major pollutant in indoor air, highly carcinogenic, mutagenic and generally found in paints, plastics, glue and decorating items [24]. Copper NPs are generally not stable in air; this prevents its usage for the photocatalyzed epoxidations. Huang *et al.* examined the photocatalytic activity of Cu NPs on TiN without any stabilizers. When it is induced by light, it could catalyze the epoxidation of alkene in presence of air or O_2 . The charge transfer between TiN and Cu NPs helps to maintain the metallic state of copper nanoparticles. Reaction could be accelerated by the photogenerated electrons from the Cu NPs. Alkenes that are adsorbed on the surface of Cu NPs forms the copper-alkene surface complexes with the help of cyclic ether solvent generate oxygen adatoms and yielding the product epoxides under light irradiation [25]. Peiris *et al.* investigated the degradation of VOCs through photocatalysis and explained the advantages of photocatalysis compared to conventional oxidation method which requires high temperature. Photocatalysis is good for waste-water and indoor air purification at ambient temperatures. They also discussed about

the ability of metal NPs to generate charge carriers when it is induced by light [21]. The dyes expelled from the industrial fields are known to be highly toxic and generate hazardous effects in the environment. Azo dyes and fluorine dyes are major pollutants in environment and are known to be highly carcinogenic [26]. A group of people reported the Au on TiO_2 /bentonite for the degradation of sulforhodamine B under irradiation of both UV and visible light. The light induced SPR effect in the Au NPs causes the generation of electrons and these photogenerated electrons transferred to O_2 adsorbed on the titanium dioxide, followed by the generation of superoxide and hydroxyl radicals. These radical species are known as the initiators for the dye decomposition. These species helps in the SRB (sulforhodamine B) dye degradation explained in the above example [27]. The synthesis of metal nanoparticles through an efficient and eco-friendly manner is also important while considering it from the point of green chemistry. This concern regarding the synthesis of nanoparticles led to the development of biogenic method. Recently biogenic synthesis of metal NPs gained more attention because it is cost effective, simple and environmentally friendly. Roy *et al.* studied the photocatalytic reaction of biogenic Ag NPs synthesized from silver salts using extract of yeast. Different phases of synthesized silver NPs were examined by XRD (X-ray diffraction) analysis, morphology and particle size determination of biosynthesized NPs were done by transmission electron spectroscopy (TEM) analysis. They analyzed the degradation of methylene blue (MB) dye molecules using biogenic Ag NPs as photocatalyst under solar irradiation. The maximum absorbance of MB was observed at 660 nm and shows a gradual decrease in intensity (660 nm) during the 6 hours exposure under sunlight [28]. Sinha *et al.* synthesized copper NPs via reduction by the utilization of fish scales from *labeo rohita*. The fish scale extracts were provided stability and act as a reducing agent during the synthesis of metal nanoparticles. The synthesized copper NPs have spherical shape with surface Plasmon absorption observed in the visible region at 580 nm. They were shown to carry out photocatalytic study for the decomposition of highly carcinogenic MB dye molecules. The exposure of reaction medium under light irradiation showed absorbance with an intensity at 660 nm for MB dye, followed by a gradual decrease in intensity and the peak got disappeared after 134 min with an overall degradation of 96 % [29].

2.2 Applications of Transition metal oxide Nanoparticles in photocatalysis

Arora *et al.* pointed out that, a coordination sphere of oxide ion is formed around the metal ions because of the coordination tendency and it forms a close packed structure. Physical, magnetic and optical properties of metal oxides are dependent on the change in its composition and structure. Metal oxides have gained more attention because of their ease of preparation and multifunctional behaviour [30]. The role of metal oxides as photocatalysts is possible because of its charge transport behavior, electronic structure, and light absorption properties [31]. Solar light irradiation of a metal oxide results in the promotion of VB electrons to the CB, thus by generate electron-hole pairs/charge carriers (e^-/h^+). These photo-generated species can oxidize or reduce the reactants adsorbed on the photocatalyst surface. It is possible due to the generation of $\cdot\text{OH}$ and O_2^- radicals by the oxidation of hydroxyl anions and reduction of the O_2 respectively [6]. Both the pollutant degradation and transformation of harmful products are possible simultaneously because of the reaction using these radicals and anions [6-33]. Recent studies have shown that heterogeneous photocatalysis employing TiO_2 , ZnO and CeO_2 can be applied in degradation of pollutants to biodegradable compounds and eventually mineralizing toxic organic compounds to CO_2 and water [32]. A photocatalyst should have large surface area, desired band gap, and appropriate morphology [33]. Photocatalytic nature of metal oxides depends on their size, shape, morphology, and composition [34]. Properties of these photoactive materials can be controlled by the suitable selection of synthetic procedure in order to enhance certain properties [34-35]. It was known that cerium oxides with oxygen vacancies act as visible light photocatalysts. Ce_7O_{12} and Ce_2O_3 are oxides of cerium with band gaps in the visible region [36-37]. Muduli *et al.* synthesized mesoporous cerium oxide by a facile solvothermal method which contains cerium in different valence states. In this method ethylene glycol and isopropyl alcohol play the role of both reducing agent and solvent. Nitrogen (N_2) adsorption experiment was used to confirm the mesoporous structure and its absorption in the visible light region. The photocatalytic degradation of rhodamine B (RhB) dye molecules during the visible light irradiation was confirmed by UV-Vis spectral analysis on the colloidal mixture, involves a complete decomposition within 6 hours. Decomposed organic products were identified using GC-MS (gas

chromatography-mass spectrometry) analysis. They investigated on a series of radical scavengers and found out that hydroxyl radical ($\cdot\text{OH}$) is the active entity which helps in the degradation of RhB. They have carried out transmission electron microscopy (TEM) to confirm its mesoporous nature and nanosphere morphology. XRD analysis revealed that the as-synthesized cerium oxide material was a combination of Ce_7O_{12} (hexagonal) and CeO_2 (Cubic). X-ray photoelectron spectroscopic analysis proved that the Ce_7O_{12} contains both Ce^{4+} and Ce^{3+} valence states. Band gap determined from the Tauc plot is 2.7 eV which corresponds to the blue light absorption at 416 nm [38]. Earlier studies had reported that the band gap of ZrO_2 is in the range 3.25 to 5 eV, which depends on the preparation technique. Various groups have synthesized crystalline porous ZrO_2 NPs with tetragonal (t- ZrO_2), cubic (c- ZrO_2), and monoclinic (m- ZrO_2) phases using different methods and studied the photocatalytic degradation of methylene orange dye. They found that monoclinic zirconium oxide showed better activity compared to other phases of ZrO_2 described above. They proposed that the higher activity of m- ZrO_2 was due to the presence of oxygen deficiencies, highly crystalline nature, wide distribution of pore-size, and excess surface hydroxyl groups. UV-Vis spectroscopic results showed the photocatalytic degradation of methyl orange dye with an intense absorption at 465 nm and another less intense one at 274 nm. The absorbance of dye solution is decreased due to the destruction of homo and hetero poly-aromatic rings of dye molecules. The UV-Vis analysis showed a complete degradation of dye molecules with an efficiency of 99 % within 110 min by m- ZrO_2 compared to 90 % and 80 % degradation by t- ZrO_2 and c- ZrO_2 respectively [39]. It has already been reported that the light harvesting capability, extended life time of photogenerated electron-hole pairs and adsorption of reactants within the surface active sites of crystalline ZrO_2 with mesoporous structure leads to its enhanced photocatalytic activity. Presence of oxygen deficiency in m- ZrO_2 leads to the separation of photo-induced electron-hole pairs [40]. It was reported that efficiency of photocatalyst depends on the surface properties because light driven redox reactions mainly occurs on the surface of photocatalysts [4]. Polisetii *et al.* synthesized tetragonal ZrO_2 using the solution combustion method and later examined the photocatalytic -degradation of anionic dyes such as remazol brilliant blue R, amido black, orange G, and alizarin cyanine green (ACG), complete degradation of dyes occurred within 2 hours. They found that the synthesized ZrO_2 showed a greater

activity for the degradation of ACG when the pH is ranging from 3 to 12. The synthesis was carried out using inorganic salts in order to avoid the inhibitory effects for electron exchanges and charge transfer as the photocatalytic degradation of organic dyes also consists of electron exchanges and charge transfer [41] which makes it favourable for the industrial applications. Fakhri et al. discussed about the degradation of an anesthetic drug named Lidocaine (LDC) found in aqueous environment due to its wide spread use. BET was used to analyse the pore size and surface area of as-synthesized WO_3 NPs. XRD was used to analyse the monoclinic crystalline phases of tungsten trioxide NPs. They proposed that the tungsten trioxide NPs were excited in presence of light followed by the generation of holes and electrons pairs. Oxygen (O_2) adsorbed on the tungsten trioxide surface react with the photogenerated species to produce O_2^{2-} and H_2O_2 , which is then used to degrade the LDC. They employed the photocatalytic property of WO_3 (Tungsten trioxide) NPs for the degradation of LDC under sunlight. Tungsten trioxide NPs with a band gap of 3.21 eV showed a good absorption at a wavelength of 380 nm. They observed the maximum efficiency (pH=6) of WO_3 NPs with a degradation rate of 97.5 % and 95.48 % for LDC within an hour under sunlight and visible irradiation respectively [42]. Cheng et al. synthesized single crystalline MoO_3 nanoribbon by a hydrothermal technique without surfactant/template and investigated about the photocatalytic property of as-synthesized NPs. In this paper they deal with the \square - MoO_3 (orthorhombic MoO_3) nanoribbons with a width of 100 nm and length of several micrometers. They confirmed the nanoribbon like structure of MoO_3 using the characterization technique such as field emission scanning electron microscopy (FE-SEM) and TEM. The as-synthesized \square - MoO_3 nanoribbons have shown good activity during the photocatalytic decomposition of Rhodamine B (Rh B) dye molecules at 30 °C with the assistance of visible light irradiation. The characteristic absorption peak for Rh B appears at 552 nm, this disappeared after an hour as the irradiation time of visible light was increased. The complete degradation of Rh B was observed from the absence of absorption peaks in the visible and UV light regions of UV-Vis spectrum. The synthesized nanoribbons possess large surface area, which leads to an increased adsorption capacity and helps in collecting a large amount of organic pollutants like Rh B. After the visible light irradiation, electrons of metal oxide were promoted from their VB to the

CB, followed by the generation of CO_2 and HCOO radical ions from the surface adsorbed O_2 with the help of induced energy. These radicals further involved in the degradation of rhodamine B dye molecules [43]. Polycyclic Aromatic Hydrocarbons (PAHs) are a major class of persistent organic pollutants present in the environment. These compounds are released into the environment by the incomplete combustion of coal and crude oil [44]. Their ability to cross cell membranes and accumulation in lipid tissues is possible due to the hydrophobic nature of the PAHs. Guptha et al. synthesized two different forms of iron oxide, goethite (α - FeOOH) and magnetite (Fe_3O_4) without any capping agent, analysis on elemental composition was done by EDX spectroscopy. Both the forms of iron oxide were used as a photocatalyst for the degradation of anthracene [45]. At ambient temperature, the photo-degradation of anthracene by the two forms of iron oxide was carried out with the help of UV-irradiation. Analysis on the half lives for the anthracene degradation reveals that goethite is photocatalytically more efficient [46]. Choudhary et al. reported that the photocatalytic degradation of pollutants as a remediation for the removal of pollutants from contaminated surfaces [47].

Karam *et al.* reported that in comparison to the bulk powder, metal oxide nanoparticles are more efficient for the photocatalytic degradation [48]. They reported the photocatalytic activity of synthesized iron oxide nanoparticles as a remedy for the removal of polycyclic aromatic hydrocarbons, which serves as a representative study in the removal of organic pollutants [45]. Sharma *et al.* studied the degradation of methyl orange (MO) dye molecules using Fe_2O_3 nanoparticles as the photocatalyst. They have synthesized Fe_2O_3 at low temperature, characterization were done regarding its morphological, compositional, and magnetic properties using various experimental techniques like FTIR, XRD and VSM. Haematite (Fe_2O_3) is an important photocatalyst with high electronic conductivity, sensitivity, and large surface area. The degradation of methyl orange dye was monitored by plotting the absorbance at fixed time intervals using UV-Vis spectrophotometer. The change in absorbance was used to estimate the degradation rate during decomposition of methyl orange. The degradation was about 80 % in the presence of Fe_2O_3 nanoparticles under irradiation of UV-light up to 210 min [49]. Titanium oxide (TiO_2) is a prominent semiconductor photocatalyst with large band gap; because of this a high energy

UV light is needed to generate the electron-hole pairs. Titanium oxide (TiO_2) is considered to be promising in the field of photocatalysis especially in case of environmental protection and energy conversion. TiO_2 has many polymorphs and they are mainly rutile, anatase, and brookite. Anatase NPs are more efficient than rutile NPs for the hydrogen production because photogenerated electrons in anatase possess a higher reduction potential [50]. Fujishima et al used a rutile titanium oxide photoanode and Pt counter electrode for the splitting of water molecules [51].

Lan et al. pointed out that the splitting of adsorbed water molecules to gaseous oxygen and hydrogen with the help of photogenerated charge carriers on the surface of TiO_2 nanoparticle [52]. Destruction of pollutants using TiO_2 is possible because of its photo produced strongest oxidation power [53]. Photocatalytic decontamination using TiO_2 occurs in the presence of natural oxygen and sunlight under ambient conditions. Photo generated hydroxyl (OH) radicals at the valence band of titanium oxide should be able to oxidize the suspended organisms in water during the water purification process. It was reported that cyanide ions and organochlorides in soils and ground water could be removed using TiO_2 photocatalyst [54]. Various groups have reported the reduction of metal ions in water and soil using the reduction ability of photo produced electrons from the TiO_2 suspensions under UV light for the removal of toxic metal ions like Hg (II), Cd (II), Ag (I) and Pb (II) [55]. TiO_2 can act as a photocatalyst for the complete decomposition of fungi, algae, viruses, bacteria, and cancer cells to CO_2 , H_2O , and harmless inorganic ions in presence of UV irradiation. TiO_2 photocatalytic activity causes bacterial cell death due to the destruction of cell membrane followed by the loss of permeability [56]. Fujishima et al. pointed out the destruction of cancer cells in photocatalyst mediated cancer therapy, gems in operating rooms, and several organic species under direct solar light irradiation in presence of TiO_2 NPs [57]. Excitation of TiO_2 nanoparticles is possible only under UV-light, which limits its application even though it is stable and efficient. UV light occupies in a small region of the solar spectrum, which limits the applications of TiO_2 from the exploration of wide range solar spectrum. The absorption can be extended from UV to the visible region, which is important and possible using various methods. In case of electrons and holes the recombination rate can be reduced by the modification of TiO_2 surface. This surface modification can also be used to improve

the absorption from UV to the visible region of solar light [58]. Doping of TiO_2 results in reduction of band-gap, generation of mid-gap states, and increases the charge carrier separation [59]. The reduction of titania band-gap using dopants such as carbon, nitrogen or sulfur results in improved photocatalytic activity due to its prolongation of absorbance from UV to the visible light region. Various groups have reviewed the photocatalytic efficiency of black titanium oxide nanomaterials and they discussed about the relation between the structure and property in terms of preparation methods. They have given a new direction into the future development of black TiO_2 nanomaterials for the photocatalytic applications [52]. Black titanium oxide exhibits a broad range of visible light absorption and build up a separation in charge. Structural engineers offered the strategy for TiO_2 surface structural change includes colour change from whiteness to blackness. Amorphous surface layer is an important feature of black titanium oxide nanomaterials. Most of the black titanium oxide nanomaterials possess oxygen vacancy and this has a crucial influence on the activity and reaction kinetics occurring on the surface of metal oxides [60]. Surface disorder could create an effect on optical and electrical properties of black titanium oxide including the band gap narrowing. Studies revealed that Ti^{3+} defect in black TiO_2 nanoparticles is able to promote the hole-trapping and thereby generate a separation between the electron-hole pairs. Various groups have studied the photocatalytic behaviour of black TiO_2 nanocrystals for the degradation of methylene orange dye. When induced by solar light irradiation the photocatalytic hydrogen production rate of black TiO_2 was reached about $10 \text{ mmol h}^{-1} \text{ g}^{-1}$ [61]. Katwal and coworkers synthesized copper oxide (CuO) NPs by an electrochemical method and analyzed the photocatalytic activity during organic dye degradation using irradiation of sunlight. They investigated on the photocatalytic activity of copper oxide NPs using the degradation of methyl red (MR), methylene blue (MB), and congo red (CR) dyes under illumination of sunlight up to 120 min. The absorbance maxima observed in the UV-Visible analysis for MR, CR, and MB dyes were at 410, 497, and 664 nm respectively. The degradation rate was found to be 85 %, 93 %, and 90 % for CR, MB, and MR dyes respectively within 2 hours irradiation of solar light. They pointed out that MR and MB are more prone to oxidation in comparison to CR because of its chemical structure. Reaction between the photogenerated holes and adsorbed water molecules on the surface of CuO NPs leads to the formation

of highly active hydroxyl radicals. The degradation of dyes was carried out using the photo generated superoxide and hydroxyl radicals [62]. Yusoff et al. synthesized zinc oxide (ZnO) NPs through precipitation (ZnO-p) and hydrothermal method (ZnO-h), studied the photocatalytic degradation of phenol molecules. The rate of phenol degradation was about 20 mg/L of initial phenol concentration for ZnO-h and 30 mg/L for ZnO-p at pH 3, 1st order kinetics was observed based on the Langmuir Hinshelwood mechanism. They calculated the efficiency of photocatalysts using Langmuir-Hinshelwood model and found out the rate constants as 0.8548 h⁻¹, 1.1305 h⁻¹ for ZnO-h and ZnO-p respectively [63]. It was known that efficiency of photocatalyst is directly proportional to apparent rate constant. It was also reported that higher amount of hydroxyl (OH) groups and surface adsorbed H₂O molecules thus facilitate the photodegradation of phenol [64]. They also monitored chemical oxygen demand (COD) value of phenol solution, when the reaction extended up to an hour, there is a notable reduction in the COD value. This is because of the rapid degradation of phenol molecules due to its contact with ZnO NPs. It was known that the main advantage of ZnO (bandgap -3.02 eV) in comparison to TiO₂ is the wide range of absorption in UV region. Kruefu et al. used flame spray pyrolysis to synthesize vanadium pentoxide (V₂O₅-bandgap-2.6 eV), which known for its ease of availability, low price, improved optical and electrical properties. They preferred this method to obtain NPs with high surface area. The investigation regarding its crystalline nature, morphology, and size of the NPs were done via XRD, FE-SEM, and HR-TEM respectively. UV-Vis spectrophotometer was used to calculate the residual concentration of methylene blue in the solution, obtained from the withdrawn 5 mL solution at 10 min intervals. They observed degradation rate was about 81 % and 1 % for methylene blue in presence and absence of V₂O₅ nanoparticles respectively. Degradation follows the pseudo 1st order kinetics with a rate constant of 0.0135 min⁻¹ [65]. Kanoi et al. synthesized CoO NPs by thermal dehydration method using glycerol as the stabilizing agent. The resultant CoO NPs shows distinct absorption in the visible region. They collected different waste water samples and treated the mixture of water and CoO NPs under light irradiation for measuring the catalytic activity for oxidation of pollutants. They observed a decrease in the values of COD and total dissolved salt (TDS), confirmed the ability of cobalt oxide NPs to oxidize the pollutants in waste water under light irradiation. They made a further confirmation

from the pH values that are not changed before and after the treatment of waste water samples with CoO NPs. Therefore the reduction in COD values from 36441 mg/L to 27524 mg/L thus indicates that the oxidation is because of the photocatalytic activity of CoO NPs and not because of the chemical neutralization [66]. Jayakumar et al. synthesized NiO NPS via chemical precipitation method and studied the photocatalytic degradation of methylene blue dye molecules under light irradiation. They have done phase identification using XRD and found that the formed NiO have an fcc structure. The analysis on elemental composition was done by using EDX spectra and found out the presence of Ni and O in the formed NiO nanoparticles. FE-SEM was used to analyze the morphology of synthesized nanoparticles and the formed NiO nanoparticles have an oval shape. They prepared a suspension of NiO and methylene blue and kept it under solar irradiation for measuring the absorbance of sample at regular intervals of 30 min using UV-Vis spectrophotometer. As the reaction time increases there was an increase in the degradation rate of methylene blue from the aqueous medium under irradiation of sunlight [67].

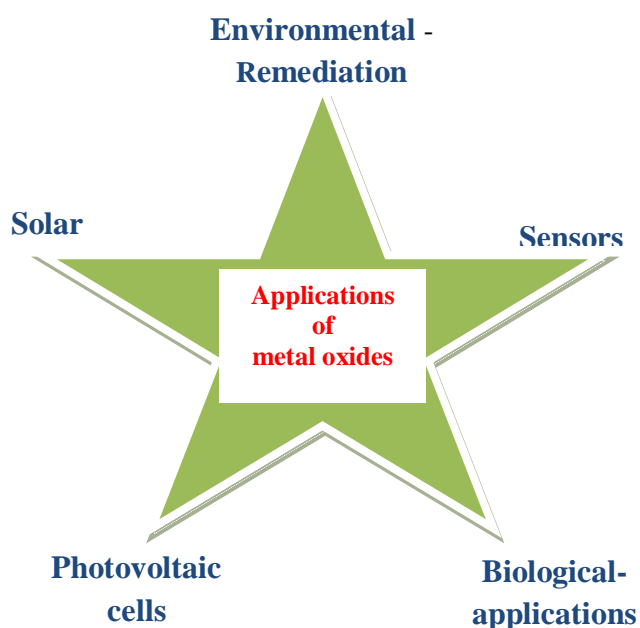


Fig. 2 Applications of metal oxides [32]

Metal oxides gained technological importance due to its applications in electronics and remediation of environmental pollutants. These are possible because of their ability to produce electron-hole pairs when it is induced by required amount of

energy. The introduction of dopants can decrease the band-gap of metal oxides, generate mid-gap states, extend the separation of photogenerated species, and increase the levels of surface adsorbed species. All the examples explained above are a short description regarding the applications of metal oxides as photocatalysts. This application is possible due to their stability, biocompatibility, and the ability to generate charge carriers under irradiation of sunlight. Metal oxides can be used for the decomposition of organic toxins, photovoltaics and splitting of water. This extended the technological applications of metal oxides in the field of energy storage, hydrogen production and discarding of environmental pollutants [6].

3. Conclusion

Direct metal nanoparticle photocatalysis attained an increasing attention, due to its nature on light harvesting and ability to catalyze the reaction. Because of these metal nanoparticles are known as efficient energy systems able to generate hot electrons under irradiation of solar light. These energetic photogenerated hot electrons could be able to react with reactant molecules located on the surface of metal NPs. It was already known that metal NPs have a greater affinity towards the organic reactants and owns high amount of conduction electrons by the combined effect of light and heat from the induced irradiation. All these makes metal nanoparticles as a prominent class of material for the synthesis and degradation of organic compounds under irradiation of sunlight. It is possible to tune the LSPR wavelength by variation in the metal nanoparticle geometry such as size, shape and composition [13]. By the suitable selection of synthetic method, it is possible to design nanostructures that are able to explore the complete solar spectrum. We can use a method in order to extend the absorption of metal oxide NPs from UV to the visible region, which involves surface modification of metal oxide photocatalysts. It will reduce the recombination rate of photogenerated charge carriers on the metal oxide surface. This surface modification can be employed to extend the absorption from UV to visible region. Another method is the coupling of metal oxides with narrow band-gap semiconductors which makes the ability to absorb visible light. The introduction of dopants can decrease the band-gap of metal oxides, generate mid-gap states, extend the separation of photogenerated species, and increase the levels of surface adsorbed species. Now research is concentrated on the development of photocatalysts with enhanced activity by the proper

tuning of visible light sensitive photocatalyst. Photocatalytic activity of metal oxides depends on the size, shape, morphology, and composition [35]. Properties of metal oxide NPs can be controlled by the suitable selection of synthetic procedure in order to enhance certain properties of these photoactive materials [35-36]. We hope this review can inspire more research to promote the understanding and development of the transition metal and metal oxide NP applications in photocatalysis.

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