

# Versatile Applications of Metal/Mixed Metal Oxides as Photocatalyst

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## ABSTRACT:

The metal oxides / mixed metal oxides have various applications as catalyst, photocatalyst, sensors, superconductors, adsorbent, ceramics, fuels, antifungal agents and have large number of applications in medicines. These metal / mixed metal oxides play a very important role in day to day human life. Today metal oxides are attracting special attention of scientists due to their easy mode of formation and multifunctional behavior. In this article an attempt has been made to focus on their applications as Photocatalyst in various chemical reactions.

**Keywords:** Metal oxides, Mixed metal oxides, Photocatalyst, chemical reactions

## INTRODUCTION:

The different physical, magnetic, optical and chemical properties of metal oxides are of great interest to chemists because these are extremely sensitive to change in composition and structure. Extensive studies of this relationship lead to a better understanding of the chemical bond in crystal. The metal oxides are attracting special attention of scientists due to their easy mode of formation and multifunctional behavior. There are several Chemical vapor deposition (CVD) processes used for the formation of nanoparticles among which we can highlight the classical (thermally activated/pyrolytic), metalorganic, plasma-assisted, and photo CVD methodologies [1]. The advantages of this methodology consist of producing uniform, pure and reproduce nanoparticles and films although requires a careful initial setting up of the experimental parameters. Multiple pulsed laser deposition heats a target sample (4000 K) and leads to instantaneous evaporation, ionization and decomposition, with subsequent mixing of desired atoms. The gaseous entities formed absorb radiation energy from subsequent pulses and acquire kinetic energy perpendicularly to the target to be deposited in a substrate generally heated to allow crystalline growth [2]. Irrespective of the preparation method use to obtain ultrafine Nano-oxides, the studies of nanoparticle preparation yielded compelling evidence concerning the fact that crystallization does not follow a traditional nucleation and growth mechanism. Although subjected to further assessment, it appears that the simple idea that a small primary size would prime nucleation as the key step of crystallization seems essentially correct and holds certain general validity, at least in solid-solid crystallization mechanisms (e.g. heating of oxo-hydroxides to form oxides). When additional liquid/gas phase crystallization steps are involved in the final formation of the nanoparticle (e.g. as in solvothermal methods), other steps like Ostwald ripening may be also of prime importance. In any case, a lot of

novel insights have been recently uncovering in solid-solid transformations and two main theories describe crystallization to proceed either by surface (single particle) and/or interface (two or multiple particle) nucleation [3-4]. The primacy of one of them has been postulated to be a function of the oxide chemical nature and temperature, being presumably surface effects always predominant at higher temperatures. Both theories mostly received support from kinetic approaches but very recent analyzes sensitive to structural order in the amorphous precursor materials have demonstrated by key role of intraparticle local order (below 1 nm) in driving the nucleation temperature onset in a broad interval of ca. 200 K, showing that the whole crystallization mechanism of oxide nanoparticles appears only compatible with some kind of intraparticle, dimensional – restricted (“surface”) mechanisms [5]. This invokes for the crucial structural characterization of the initial, XRD- amorphous materials in order to further progress in the understanding the nanostructure influence in morphological properties of oxides.

### Photocatalyst :

Metal / Mixed metal oxides have wide application as Photocatalyst some of them have been described here. Luminita *et al.* [6] synthesized copper sulphide powder. Thin films were developed by doctor blade deposition of  $Cu_xS$  and  $Cu_xS/TiO_2$  composites with photocatalytic properties. The powder and thin film properties were characterized in terms of: the Fourier transform infra-red (FTIR), the X-ray diffraction (XRD), UV–vis spectroscopy, atomic force microscopy (AFM). The semiconductors association and the films homogeneity limit the electron- hole recombination, resulting in good efficiency in dyes photo degradation even under visible light irradiation. Aman and coworkers [7] used waste water of copper mines and copper processing plant contains both copper and selenium ions with other contaminants. In this paper simultaneous photo reductive removal of copper (II) and selenium (IV) is studied for the first time using spherical binary oxide photocatalysts under visible light. For a single contaminant, EDTA is found to be the best for Cu(II) reduction whereas formic acid is the best for Se(IV) reduction. In a mixed solution both EDTA and formic acid perform very well under visible light irradiation. Photo deposited material is found to be copper selenide rather than pure copper and selenium metal. This indicates that the waste water containing copper and selenium ions can be efficiently treated under visible or solar light. Yoong *et al.* [8] followed the advantage of copper doping into  $TiO_2$  semiconductor photocatalyst for enhanced hydrogen generation under irradiation at the visible range of the electromagnetic spectrum. Two methods of preparation for the copper-doped catalyst were selected – complex precipitation and wet impregnation methods – using copper nitrate trihydrate as the starting material. The dopant loading varied from 2 to 15%. Characterization of the photocatalysts was done by thermogravimetric analysis (TGA), temperature programmed reduction (TPR), diffuse reflectance UV-Vis (DR-UV-Vis), scanning electron microscopy (SEM), Fourier transform infrared (FTIR) spectroscopy and X-ray diffraction (XRD). Photocatalytic activity towards hydrogen generation from water was investigated using a multipoint photocatalytic reactor under visible light illumination with methanol added as a hole scavenger. Three calcination temperatures were selected – 300, 400 and 500 °C. It was found that 10 wt.% Cu/ $TiO_2$  calcined at 300 °C for 30 min yielded the maximum quantity of hydrogen. Xia and coworkers [9] prepared the novel  $CuO-SnO_2$  nanocomposite

oxide photocatalysts. The maximum photocatalytic activity of the CuO-SnO<sub>2</sub> photocatalyst was observed to be calcined at 500 °C for 3 h (the molar ratio of Cu to Sn was 1:1) due to the sample with good crystallization and high surface area. Xu *et al.* [10] showed 1-D mesoporous TiO<sub>2</sub> nanotube (TNT) with large BET surface area and employed for simultaneous photocatalytic H<sub>2</sub> production and Cu<sup>2+</sup> removal from water. Cu<sup>2+</sup>, across a wide concentration range of 8–800 ppm, was removed rapidly from water under irradiation. The removed Cu<sup>2+</sup> then combined with TNT to produce efficient Cu incorporated TNT (Cu-TNT) photocatalyst for H<sub>2</sub> production. Average H<sub>2</sub> generation rate recorded across a 4 h reaction was between 15.7 and 40.2 mmol h<sup>-1</sup> g<sup>-1</sup> depending on initial Cu<sup>2+</sup>/Ti ratio in solution, which was optimized at 10 atmospheres. In addition, reduction process of Cu<sup>2+</sup> was also a critical factor in governing H<sub>2</sub> evolution. In comparison with P25, its large surface area and 1-D tubular structure endowed TNT with higher photocatalytic activity in both Cu<sup>2+</sup> removal and H<sub>2</sub> production.

Neppolian *et al.* [11] carried out an ultrasound – assisted method for synthesizing nationalized Pt-graphene oxide (GO) – TiO<sub>2</sub> photocatalyst. The Pt-GO-TiO<sub>2</sub> nanoparticles were characterized by diffused reflectance spectroscopy, X-Ray diffraction, N<sub>2</sub> BET adsorption – desorption measurements, atomic force microscopy and transmission electron microscopy. The intermediate products formed during the degradation of DBS were monitored using electrospray mass spectrometry. The ability of GO to serve as a solid support to anchor platinum particles on GO-TiO<sub>2</sub> is useful in developing new photocatalysts.

Xu *et al.* [12] studied efficient Cu incorporated TiO<sub>2</sub> (Cu-TiO<sub>2</sub>) photocatalysts for hydrogen generation were fabricated by four methods: in situ sol-gel, wet impregnation, chemical reduction of Cu salt, and in situ photo-deposition. Among the four photocatalysts, the sample that was synthesized by in situ sol-gel method exhibited the highest stability. High efficiency, low cost, good stability are some of the merits that underline the promising potential of Cu-TiO<sub>2</sub> in photocatalytic hydrogen generation Magalhaes *et al.* [13] discovered floating photocatalysts based on composites of low density polyethylene (LDPE) containing 30, 68 and 82 wt.% of TiO<sub>2</sub> P25. The floating photocatalyst can be reused for at least three consecutive times without any significant decrease on the discoloration and total organic carbon removal after each reuse. Hu and coworkers [14] investigated different p-type Cu<sub>2</sub>O powders prepared from electrodeposition and subjected to analysis of their photocatalytic activity in water reduction. The electrodeposited Cu<sub>2</sub>O powders were obtained by scraping the deposited films off the substrate. The coupling was made to avoid back reactions of the photo-induced charges. Appropriate crystalline-texture tuning, as well as charge delocalization promotion, is looked to as the key issue for efficient H<sub>2</sub> generation from water reduction over p-type Cu<sub>2</sub>O photocatalysts. Xu *et al.* [15] found that highly dispersed CuO was introduced into TiO<sub>2</sub> nanotube (TNT) made by hydrothermal method via adsorption-calcination process or wet impregnation process to fabricate CuO incorporated TNT photocatalysts (CuO-TNT) for hydrogen production. This high photocatalytic activity of CuO-TNT was mainly attributed to the unique 1-D tubular structure, large BET surface area and high dispersion of copper component. Compared to wet impregnation, adsorption-calcination process was superior to produce active photocatalyst, since it was prone to produce photocatalyst with more highly dispersed CuO. Anandan *et al.* [16] reported efficient ZnO based visible-light photocatalysts, Cu(II) modified CdxZn1-xO were developed by adopting

a hybrid approach, consisting of band engineering by formation of a solid solution and surface modification of co-catalyst. Further, the visible-light activity of  $Cd_xZn_{1-x}O$  photocatalysts was greatly improved by the surface modification of  $Cu^{2+}$  ions. The strategy in the present study is a promising approach for applying ZnO – based photocatalysts for indoor applications. Mahapure and coworkers [17] demonstrated the synthesis of novel photocatalyst, zinc indium vanadate (ZIV) by solid – solid state route using respective oxides of zinc, indium and vanadium. Optical study showed the band gap around 2.8 eV, i.e. in visible region, Photocatalytic activity of phenol degradation under visible light irradiation was performed using the photocatalyst. Kansal *et al.* [18] worked on a flower like ZnO nanostructure . The phase structure and morphology of the synthesized ZnO was characterized by XRD, SEM and TEM. The comparison of photocatalyst activity of commercial and synthesized ZnO had been made. Experiments were also performed to investigate the reusability and stability of the synthesis ZnO. Liao *et al.* [19] produced a novel binary oxide photocatalyst ZnO/TiO<sub>2</sub> prepared by solgel method using citric acid as a complex reagent and its photocatalytic activity was investigated. It was showed that the addition of ZnO could enhance the activity significantly, and sulfating ZnO/TiO<sub>2</sub> with sulfuric acid resulted to dramatic enhancement, the degradation ratio of methyl orange could be up to 71.9% compared with 55% of degradation of ZnO/TiO<sub>2</sub> catalyst. Shifu Chen *et al.* [20] utilized p-type ZnO powder by decomposition of zinc nitrate at 3500 C for 1 h. p-n junction photocatalyst p-ZnO/TiO<sub>2</sub> was prepared by ball milling of TiO<sub>2</sub> in H<sub>2</sub>O solution doped with p-ZnO. The p-n junction photocatalyst p-ZnO/TiO<sub>2</sub> was characterized by UV-vis diffuse reflection spectrum, scanning electron microscopy (SEM). Namely, the p-n junction photocatalyst p-ZnO/TiO<sub>2</sub> has higher photocatalytic reduction activity. The mechanisms of influence on the photocatalytic activity were also discussed by the p-n junction principle. Yang *et al.* [21] characterize nitrogen-doped titanium oxide (TiO<sub>2</sub>- xNx) films prepared by ion-assisted electron-beam evaporation, using rutile powder as source material. The films deposited with nitrogen ion bombardment at various nitrogen partial pressures (PPN<sub>2</sub>) were investigated by X-ray diffraction patterns, Raman, UV-Vis absorption and X-ray photoelectron spectra. The series of films exhibit a consistent relationship among structures, red-shift in visible light absorption, and visible light-induced the hydrophilicity and photocatalysis. Khan and coworkers [22] evaluated well-crystalline ZnO nanoparticles (NPs) synthesized in large-quantity via simple hydrothermal process using the aqueous mixtures of zinc chloride and ammonium hydroxide. The NPs are almost spherical shape with the average diameters of  $\sim 50 \pm 10$  nm. The quality and composition of the synthesized NPs were obtained using Fourier transform infrared (FTIR) and electron dispersed spectroscopy (EDS) which confirmed that the obtained NPs are pure ZnO and made with almost 1:1 stoichiometry of zinc and oxygen, respectively. Yu *et al.* [23] checked a series of WO<sub>3</sub>/ZnO composite photocatalysts with different WO<sub>3</sub> concentrations prepared by a precipitation-grinding method followed by calcination at different temperatures The photocatalytic activity of the samples was evaluated by photocatalytic degradation of acid orange II under UV light ( $\lambda = 365$  nm) irradiation. The increase in the photocatalytic activity could be attributed to the coupling of WO<sub>3</sub>, which suppressed the growth of ZnO particles, increase of the surface

area and increased amount of surface OH groups of the sample. The presence of WO<sub>3</sub> also restrained the recombination rate of e<sup>-</sup>/h<sup>+</sup> pairs. Li et al. [24] analyzed Nano-crystalline ZnO particles synthesized via an ion exchange method and used in a methyl-orange photocatalytic degradation process. An ion exchange resin mixed bed system was used in the suspension for separation of nano-ZnO and methyl-orange after photocatalysis reaction. Byproducts and other inorganic ions were transferred into resin phase. Nano-ZnO photocatalyst can be regenerated and reused. Aman et al. [25] discussed waste water of copper mines and copper processing plant contains both copper and selenium ions with other contaminants. simultaneous photo reductive removal of copper (II) and selenium (IV) is studied for the first time using spherical binary oxide photocatalysts under visible light. Highest photocatalytic reduction in a mixed solution is observed at pH 3. Their study shows that 100 ppm of mixed solution can be removed under visible light in 40 min of reaction using TiZr-10 as catalyst. Photo deposited material is found to be copper selenide rather than pure copper and selenium metal. Beydoun et al. [26] prepared magnetic iron oxide-Titania photocatalysts (Fe<sub>3</sub>O<sub>4</sub>-TiO<sub>2</sub>) using a coating technique in which the photoactive titanium dioxide was deposited onto the surface of a magnetic iron oxide core. A decrease in surface area due to sintering, along with the diffusion of Fe ions into the titanium dioxide coating are seen as contributing factors to the decline in photoactivity which accompanied an increase in the heat treatment. This is an indication of changing surface properties as heat treatment is applied. For single – phase TiO<sub>2</sub> powders, this is postulated to be due to a decrease in the surface hydroxyl (OH) groups and/or residual organics (OR) groups. The reducing duration of the heat treatment revealed that a heat treatment duration of 20 min at 4500 C was sufficient to transform amorphous titanium dioxide into a photoactive crystalline phase. Koorman and coworkers [27] synthesised and studied the photocatalytic activity of α-Fe<sub>2</sub>O<sub>3</sub> colloids. It is compared to the activities of colloids and suspensions of ZnO and TiO<sub>2</sub>. The formation of H<sub>2</sub>O<sub>2</sub> is investigated and the oxidation of organic molecules is studied with high sensitivity. While ZnO and TiO<sub>2</sub> are found to be quite active photocatalysts in the formation of hydrogen peroxide and in the degradation of chlorinated hydrocarbon molecules. Yu et al. [28] investigated in order to more easily separate TiO<sub>2</sub> photocatalyst from the treated wastewater, TiO<sub>2</sub> photocatalyst is immobilized on coal fly ash by a precipitation method. The titanium hydroxide precipitated on coal fly ash by neutralization of titanium chloride is transformed into titanium dioxide by heat treatment in the temperature range of 300–700 °C. The major iron oxide, existing in coal fly ash as an impurity, is magnetite (Fe<sub>3</sub>O<sub>4</sub>). The phase transformation into hematite (Fe<sub>2</sub>O<sub>3</sub>) by heat treatment improves the removal rate of NO gas for TiO<sub>2</sub>-coated coal fly ash. Wu et al. [29] synthesized the nanoparticles of TiO<sub>2</sub> modified with carbon and iron by sol–gel followed solvothermal method at low temperature. Its chemical composition and optical absorption were investigated by X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), photoluminescence emission spectroscopy (PL), UV–vis absorption spectroscopy, and electron paramagnetic resonance (EPR). The synergistic effects of carbon and iron in modified TiO<sub>2</sub> nanoparticles were responsible for improving visible light photocatalytic activity. Maretti et al. [30] prepared dioxo iron phthalocyanine tetrasulphonate (FeO<sub>2</sub>Pc) incorporated inside the integrality space of a layered double oxide (LDH). Evidence for the inclusion of the FeO<sub>2</sub>Pc inside the intercalary spaces of LDH was obtained from the expansion the basal layer distance of the

host. The solid is able to act as an effective photocatalyst for the degradation of aqueous phenol. Pradhan et al. [31] carried out the iron incorporated mesoporous Al<sub>2</sub>O<sub>3</sub>-MCM-41 nanocomposites, synthesized by sol-gel and followed by wetness impregnation method. They were found to be active photocatalysts for evolution of hydrogen energy from water in the presence of sacrificial agent under visible light illumination. The textual properties (high surface area, narrow pore size, large pore volume and mesoporosity), visible light active band gap energy 1.90 eV and small practical size (47.95nm) collectively contribute for high hydrogen production ability. Aman et al. [32] studied waste water of copper mines and copper processing plant contains both copper and selenium ions with other contaminants. In this paper simultaneous photo reductive removal of copper (II) and selenium (IV) is studied for the first time using spherical binary oxide photocatalyst under visible light. Their study shows that 100 ppm of mixed solution can be removed under visible light in 40 min of reaction using TiZr-10 as catalyst. Photo deposited material is found to be copper selenide rather than pure copper and selenium metal. This indicates that the waste water containing copper and selenium ions can be efficiently treated under visible or solar light. Akhavan et al. [33] discovered the effect of thickness of TiO<sub>2</sub> coating on synergistic photocatalytic activity of TiO<sub>2</sub> (anatase)/ $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>/glass thin films as photocatalysts for degradation of Escherichia coli bacteria in a low-concentration H<sub>2</sub>O<sub>2</sub> solution and under visible light irradiation was investigated. The improvement in the photoinactivation of bacteria on surface of TiO<sub>2</sub>/ $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> was assigned to formation of TiO-Fe bond at the interface. Hen -Shifu and coworkers [34] developed p-n junction photocatalyst p-CaFe<sub>2</sub>O<sub>4</sub>/n-ZnO was prepared by ball milling of ZnO in H<sub>2</sub>O doped with p-type CaFe<sub>2</sub>O<sub>4</sub>. The Structural and optical properties of the p-n junction photocatalyst p-CaFe<sub>2</sub>O<sub>4</sub>/n-ZnO were characterized by X-ray powder diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), UV-vis diffuse reflection spectrum (DRS) and fluorescence emission spectra [35]. The mechanism of influence on the photocatalyst activity were also discussed by the p-n junction principle. Smith et al. [36] developed sulfated Fe<sub>2</sub>O<sub>3</sub>-TiO<sub>2</sub> (SFT) synthesized by treatment of ilmenite ore with sulfuric acid. The presence of sulfated Fe<sub>2</sub>O<sub>3</sub>-TiO<sub>2</sub> and mixed phase of Fe<sub>2</sub>O<sub>3</sub>-TiO<sub>2</sub> was confirmed by DRIFT spectra and XRD. The dispersion of sulfate displayed thermal stability up to 5000C. The photocatalytic activity was evaluated by the oxidation of 4- chlorophenol (4-CP) in aqueous medium under UV-vis and visible light irritation. Zhang et al. [37] induced Bi<sub>2</sub>WO<sub>6</sub> photocatalyst synthesized via a facile low-temperature combustion synthesis method, using glycine as the fuel. The photocatalytic activities of the as-synthesized samples were evaluated by the photo degradation of rhodamine B (RhB) and phenol under visible - light irradiation. The photocatalyst showed much enhanced visible photocatalytic efficiency, up to 94.2% in 4 h, than the bulk Bi<sub>2</sub>WO<sub>6</sub> powder (SSR) in the degradation of phenol. Seup et al. [38] examined a magnetically separable photocatalyst prepared by a continuous multi step spray pyrolysis process. In the first step, nickel ferrite core particles were prepared by an ultrasonic spray pyrolysis. In the second step, tetraethyl orthosilicate (TEOS) and titanium isopropoxide (TTIP) were sequentially injected and coated on the surface of the core particles coated layers were decomposed to form silica and Titania layers in a final furnace reactor. The Titania- silica layered particles displayed higher photo activity. The strong adhesion between the coated layer and the nickel ferrite core is

attributed to the features of the multi-step process, where in the core particles are exposed to high temperature in the second reactor for only a few seconds and transformation of the core particles into non-magnetic particles is prohibited. Liu and coworkers [39] worked on the commonly used photocatalyst, TiO<sub>2</sub> (anatase) immobilized on porous nickel using 3 wt% polyvinyl alcohol (PVA) as the binder. The observance of photocatalytic degradation of Sal under pH values and initial concentrations was explained by the adsorption behavior of Sal. The parameters of the Langmuir Hinshelwood expression have been determined by different experimental ways. Hang et al. [40] utilized titanium isopropoxide, ammonium carbonate and nickel nitrate were used as the sources of titanium, nitrogen, and nickel to prepare titania photocatalyst co-doped with nitrogen and nickel by means of the modified sol-gel method [41]. The effects of annealing temperature and component on the phase composition and photocatalytic activity were investigated. Nickel atoms existed in the form of Ni<sub>2</sub>O<sub>3</sub>, dispersed on the surface of TiO<sub>2</sub>, suppressed the recombination of photo-induced electron-hole pairs, raised the photo quantum efficiency, and led to the enhancement of photocatalytic performance. Chen-Shifu and coworkers [42] characterized p-n Junction photocatalyst NiO/TiO<sub>2</sub> was prepared by sol-gel method using Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O and tetrabutyl titanate [Ti(OC<sub>4</sub>H<sub>9</sub>)<sub>4</sub>] as the raw materials. The results show that, for photocatalytic reduction of Cr<sub>2</sub>O<sub>7</sub>, the optimum percentage of doped-NiO is 0.5% (mole ratio of Ni/Ti). The photocatalytic activity of the p-n junction NiO/TiO<sub>2</sub> is much higher than that of TiO<sub>2</sub> on the photocatalytic reduction of Cr<sub>2</sub>O<sub>7</sub>. The mechanisms of influence on the photocatalytic activity were also discussed by the p-n junction principle. Sreethwaong *et al.* [43] evaluated photocatalytic activity of mesoporous titania supported nickel oxide photocatalyst synthesized by single – step sol-gel (SSSG) process combined with surfactant assisted template method investigated for hydrogen evolution from an aqueous methanol solution, in comparison with one prepared by conventional incipient wetness impregnation (IWI) method. Characterization results demonstrated the significant modification of physical characteristics of the single-step sol-gel photocatalyst, anticipated to relating to the observation of higher photo catalytic hydrogen evolution activity. Shihong Xu *et al.* [44] checked a magnetically separable photo catalyst TiO<sub>2</sub>/SiO<sub>2</sub>/NiFe<sub>2</sub>O<sub>4</sub> (TSN) with a typical ferromagnetic hysteresis prepared by a liquid catalytic phase transfer method. When the intensity of applied magnetic field weakened to zero, the remnant magnetism of the prepared photocatalyst faded to zero. The magnetic composite showed high photocatalytic activity for the degradation of methyl orange in water. A thin SiO<sub>2</sub> layer between NiFe<sub>2</sub>O<sub>4</sub> and TiO<sub>2</sub> shell prevented effectively the leakage of charges from TiO<sub>2</sub> particles to NiFe<sub>2</sub>O<sub>4</sub>, which gave rise to the increase in photocatalytic activity. Kudo *et al.* [45] analyzed the structure of nickel-loaded K<sub>4</sub>Nb<sub>6</sub>O<sub>17</sub> photocatalyst in an overall water splitting reaction by means of XPS, EXAFS, TEM, and XRD. K<sub>4</sub>Nb<sub>6</sub>O<sub>17</sub> has an ion-exchangeable layered structure which possesses two different kinds of alternating interlayer spaces, i.e. interlayers I and II, where K<sup>+</sup> ions are located. Therefore, each niobate macroanion sheet is regarded as a “two-dimensional” photocatalyst where H<sub>2</sub> and O<sub>2</sub> evolve at different sides of the layer. Neppolian *et al.* [46] discussed an ultrasound-assisted method for synthesizing nanosized Pt-graphene oxide (GO)-TiO<sub>2</sub> photocatalyst. The Pt-GO-TiO<sub>2</sub> nanoparticles were characterized by diffused reflectance spectroscopy, X-ray diffraction, N<sub>2</sub> BET adsorption-desorption measurements, atomic force microscopy and transmission electron microscopy. The mineralization of

DBS was enhanced by a factor of 3 using Pt-GO-TiO<sub>2</sub> compared to the P-25 (TiO<sub>2</sub>). In the presence of GO, an enhanced rate of DBS oxidation was observed and when doped with platinum, mineralization of DBS was further enhanced. The initial solution pH had an effect on the rate of photocatalytic oxidation of DBS, whereas no such effect of initial pH was observed in the sonochemical or sonophotocatalytic oxidation of DBS. Hayat et al. [47] find out photocatalytic oxidation of phenol using nickel oxide (NiO) nanoparticles synthesized by sol-gel method. The morphology of synthesized catalyst was studied by using field emission scanning electron microscopy (FESEM), energy dispersive X-ray spectroscopy (EDX) and high resolution transmission electron microscopy (HRTEM) and X-ray diffraction (XRD). The photocatalytic activity of NiO was evaluated by degradation of phenol under irradiation of unique source like UV laser. The degradation of the phenol followed a pseudo first-order rate kinetics. L.S. Yoong and coworkers [48] discussed the advantage of copper doping onto TiO<sub>2</sub> semiconductor photocatalyst for enhanced hydrogen generation under irradiation at the visible range of the electromagnetic spectrum. Three calcination temperatures were selected – 300, 400 and 5000 C. It was found that 10 wt% Cu/TiO<sub>2</sub> calcined at 300 °C for 30 min yielded the maximum quantity of hydrogen. The reduction of band gap as a result of doping was estimated and the influence of the process parameters on catalytic activity is explained. Biswal et al. [49] synthesized a novel composite CdS-Zns/ Zirconium – titanium phosphate (ZTP) photocatalyst working under visible light. N<sub>2</sub> adsorption – desorption, diffuse reflectance UV-vis spectroscopy (DRUV-vis), photoluminescence. Results towards hydrogen production with an apparent quantum efficiency of 9.6% under visible light illumination. Nakhate et al. [50] used an environmental friendly nanocrystalline Ni<sub>x</sub>TiO<sub>2</sub> (x=5 and 7%) synthesized by hydrothermal method. The requisite quantity of commercial TiO<sub>2</sub> and Ni(NO<sub>3</sub>)<sub>2</sub> 6H<sub>2</sub>O was leached in alkaline medium using hydrothermal reactor at 120°C. The reported method is effective for the synthesis of visible light driven photocatalyst and easy to scale up. XRD results showed that nickel was doped in the form of NiO. SEM picture shows spherical morphology to Ni-Doped TiO<sub>2</sub> and nanofibred particle to hydrothermally treated TiO<sub>2</sub> samples. Reza and coworkers [51] followed Zn<sub>1-x</sub>Cu<sub>x</sub>S and Zn<sub>1-x</sub>Ni<sub>x</sub>S nanocomposites were synthesized by using a controlled co-precipitation. The nanocomposite materials were characterized by the use of UV – Vis spectra, atomic absorption spectroscopy, X-ray, diffraction patterns, transmission electron microscopy image and Brunauer- Emmet Teller method. The maximum degradation of dye was obtained at pH 5-7. The Zn<sub>0.94</sub>Ni<sub>0.06</sub>S and Zn<sub>0.90</sub>Cu<sub>0.10</sub>S nanocomposites show the highest photoactivity. The influence of hydrogen peroxide and several anions were studied on the photoactivity of proposed catalysts. Lee et al. [52] prepared colloidal solutions containing nano-sized TiO<sub>2</sub> particles successfully obtained by adding a small amount of water and employing solvothermal method. A thin film obtained from this colloidal solution exhibited much better properties than another film obtained via a sol – gel method. X.L.Wang et al. [53] showed homogeneous mixed Cr-doped Ba<sub>4</sub>In<sub>2</sub>O<sub>7</sub>/In<sub>2</sub>O<sub>3</sub> nanocomposite (Cr-BIO) synthesized by a simple sol-gel method. The Cr-BIO powder was characterized by thermogravimetric (TG), X-ray diffractions (XRD) scanning electron microscopy (SEM) and UV-vis diffuse reflectance spectrometry. The electrode exhibited obvious photo-assisted chargeable properties in KOH aqueous solution as the discharge time increased remarkably under the xenon light irradiation. The photo-assisted chargeability of HSA/Cr-BIO electrode was then discussed. Nicolas



Keller et al. [54] was carried out to reduce the drawbacks related to the use of provides or immobilized catalysis in gas – and liquid – phase applications, a new material for the use as photocatalyst support was obtained by chemical vapor decomposition at 7000C of an ethane – hydrogen mixture over a woven glass microfiber supported nickel catalyst. The presence of hydrophilic oxygenated groups located at the outer surface of the carbon nanofibres allowed the sol-gel preparation of a woven glass microfiber – carbon nanofiber supported TiO<sub>2</sub> (20 wt %). Catalyst using tetraisopropoxide as precursor. This new photocatalyst was totally stable under UV irradiation. K. Nukajima et al. [55] synthesized thermally stable mesoporous Ta<sub>2</sub>O<sub>5</sub> by a sol-gel technique using a material having a BET surface area of 145 m<sup>2</sup> g<sup>-1</sup>, mesopore diameter of 3.5nm, and mesopore volume of 0.20 mLg<sup>-1</sup>. The formation of thicker walls results in higher thermal stability than tantalum oxides prepared by a ligand – assisted templating method.

### CONCLUSION:

Above mentioned literature shows wide applications of metal /mixed metal oxides as Photocatalyst in various reactions like the maximum degradation of dye was obtained at pH 5-7. The Zn 0.94 Ni 0.06S and Zn 0.90Cu 0.10 S nanocomposites show the highest photoactivity. The influence of hydrogen peroxide and several anions were studied on the photoactivity of proposed catalyst. colloidal solutions containing Nano-sized TiO<sub>2</sub> particles successfully obtained by adding a small amount of water and employing solvothermal method. A thin film obtained from this colloidal solution exhibited much better properties than another film obtained via a sol – gel method. Homogeneous mixed Cr-doped Ba<sub>4</sub>In<sub>2</sub>O<sub>7</sub>/In<sub>2</sub>O<sub>3</sub> nanocomposite (Cr-BIO) synthesized by a simple sol-gel method. So, metal/mixed metal oxides have broad applications as Photocatalyst in various chemical reactions.

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