



Applications of Metal/Mixed Metal Oxides as Photocatalyst: A Review

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ABSTRACT

Metal oxides/ Mixed metal oxides have wide applications as catalyst, Adsorbents, Superconductors, semiconductors, ceramics, antifungal agents and also have spacious applications in medicines. This review article is focused on their applications as photocatalyst in various organic reactions.

Keywords: Metal oxides, Mixed metal oxides, organic reaction, ceramics.

INTRODUCTION

Metal Oxides

Metal oxides play a very important role in many areas of chemistry, physical and materials science¹⁻⁶. Metal oxides are formed as a consequence of co-ordination tendency of metal ions so that oxide ions form co-ordination sphere around metal ions and give rise to close packed structure. 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 leads 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. The transition metals and

their compounds are used as catalysts in chemical industry and in battery industries. Besides, these compounds can be used in formation of interstitial compounds and alloy formation. The transition metals have the special properties of formation of coloured compounds and show magnetic properties. Metals of d-block elements are used for many industrial applications. They behave as catalysts, super conducting materials, sensors, ceramics, phosphors, crystalline lasers etc. Besides these they are excellent photoactive materials and work as photosensitizer. Mixed metal oxide (MMO) electrodes are devices with useful properties for chemical electrolysis. Metal/Mixed metal oxides have wide applications as catalyst because of their high surface area and reactive sites. Number of scientists and academicians are using metal/mixed metal oxides as catalyst in various organic reactions.

Photocatalyst

Metal / Mixed metal oxides have wide application as photocatalyst. Luminita *et al*⁷ synthesized copper sulphide powder. Thin films were developed by doctor blade deposition of Cu_xS and $\text{Cu}_x\text{S}/\text{TiO}_2$ 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 coworkers⁸ studied waste water of copper mines and copper processing plant. Simultaneous photoreductive removal of copper (II) and selenium (IV) is studied for the first time using spherical binary oxide photocatalysts under visible light from 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. Photodeposited 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*⁹ 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 multiport photocatalytic reactor under visible light illumination with methanol. 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 coworkers¹⁰ prepared the novel CuO-SnO_2

nanocomposite oxide photocatalysts. The maximum photocatalytic activity of the CuO-SnO_2 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*¹¹ showed 1-D mesoporous TiO_2 nanotube (TNT) with large BET surface area and employed for simultaneous photocatalytic H_2 production and Cu^{2+} removal from water. Cu^{2+} , across a wide concentration range of 8–800 ppm, was removed rapidly from water under irradiation. The removed Cu^{2+} then combined with TNT to produce efficient Cu incorporated TNT (Cu-TNT) photocatalyst for H_2 production. Average H_2 generation rate recorded across a 4 h reaction was between 15.7 and 40.2 $\text{mmol h}^{-1} \text{g}^{-1}$ depending on initial Cu^{2+}/Ti ratio in solution, which was optimized at 10 atmosphere. In addition, reduction process of Cu^{2+} was also a critical factor in governing H_2 evolution. In comparison with P25, its large surface area and 1-D tubular structure endowed TNT with higher photocatalytic activity in both Cu^{2+} removal and H_2 production. Neppolian *et al*¹² carried out an ultrasound – assisted method for synthesizing nationalized Pt-graphene oxide (GO) – TiO_2 photocatalyst. The Pt-GO- TiO_2 nanoparticles were characterized by diffused reflectance spectroscopy, X-Ray diffraction, N_2 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_2 is useful in developing new photocatalysts. Xu *et al*¹³ studied efficient Cu incorporated TiO_2 (Cu-TiO_2) photocatalysts for hydrogen generation 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_2 in photocatalytic hydrogen generation Magalhaes *et al*¹⁴ discovered floating photocatalysts based on composites of low density polyethylene (LDPE) containing 30, 68 and 82 wt.% of $\text{TiO}_2 \text{P}_{25}$. 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

coworkers¹⁵ investigated different p-type Cu₂O powders prepared from electrodeposition and subjected to analysis of their photocatalytic activity in water reduction. The electrodeposited Cu₂O 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 H₂ generation from water reduction over p-type Cu₂O photocatalysts. Xu *et al.* [16] found that highly dispersed CuO was introduced into TiO₂ 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.*¹⁷ reported efficient ZnO based visible-light photocatalysts, Cu(II) modified CdxZn_{1-x}O were developed by adopting a hybrid approach, consisting of band engineering by formation of a solid solution and surface modification of co-catalyst. The visible-light activity of CdxZn_{1-x}O photocatalysts was greatly improved by the surface modification of Cu²⁺ ions. The strategy in the present study is a promising approach for applying ZnO – based photocatalysts for indoor applications. Mahapure and coworkers¹⁸ 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.*¹⁹ worked on a flower like ZnO nanostructure. The phase structure and morphology of the synthesized ZnO was characterized by XRD, SEM and TEM. Experiments were also performed to investigate the reusability and stability of the synthesis ZnO. Liao *et al.*²⁰ produced a novel binary oxide photocatalyst ZnO/TiO₂ 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/TiO₂ 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/TiO₂ catalyst. Shifu *et al.*²¹ utilized p-type ZnO powder by decomposition of zinc nitrate at 3500 °C for 1 h. p-n junction photocatalyst p-ZnO/TiO₂ was prepared by ball milling of TiO₂ in H₂O solution doped with p-ZnO. The p-n junction photocatalyst p-ZnO/TiO₂ was characterized by UV-Vis diffuse reflection spectrum, scanning electron microscopy (SEM). Namely, the p-n junction photocatalyst p-ZnO/TiO₂ 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.*²² characterised nitrogen-doped titanium oxide (TiO₂"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 (PPN₂) 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 coworkers²³ 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 $50 \pm 10\text{ nm}$. 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.*²⁴ checked a series of WO₃/ZnO composite photocatalysts with different WO₃ 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 ($\lambda = 365\text{ nm}$) irradiation. The increase in the photocatalytic activity could be attributed to the coupling of WO₃, 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 WO₃ also restrained the recombination rate of e⁻/h⁺ pairs. Li

*et al.*⁶⁵ analysed 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.*⁶⁶ discussed waste water of copper mines and copper processing plant contains both copper and selenium ions with other contaminants. Beydoun *et al.*⁶⁷ prepared magnetic iron oxide-titania photocatalysts ($\text{Fe}_3\text{O}_4\text{-TiO}_2$) 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_2 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 coworkers²⁸ synthesised and studied the photocatalytic activity of $\alpha\text{-Fe}_2\text{O}_3$ colloids. It is compared to the activities of colloids and suspensions of ZnO and TiO_2 . The formation of H_2O_2 is investigated and the oxidation of organic molecules is studied with high sensitivity. While ZnO and TiO_2 are found to be quite active photocatalysts in the formation of hydrogen peroxide and in the degradation of chlorinated hydrocarbon molecules. Yu *et al.*⁶⁹ investigated in order to more easily separate TiO_2 photocatalyst from the treated wastewater, TiO_2 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_3O_4). The phase transformation into hematite (Fe_2O_3) by heat treatment improves the removal rate of NO gas for TiO_2 -coated coal fly ash. Wu *et al.*⁶⁰ synthesized the nanoparticles of TiO_2

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_2 nanoparticles were responsible for improving visible light photocatalytic activity. Maretti *et al.*⁶¹ prepared dioxo iron phthalocyanine tetrasulphonate (FeO_2Pc) incorporated inside the integrality space of a layered double oxide (LDH). Evidence for the inclusion of the FeO_2Pc 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.*⁶² carried out the iron incorporated mesoporous $\text{Al}_2\text{O}_3\text{-MCM-41}$ 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.*⁶³ studied waste water of copper mines and copper processing plant contains both copper and selenium ions with other contaminants. In this paper simultaneous photoreductive 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. Photodeposited 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.*⁶⁴ discovered the effect of thickness of TiO_2 coating on synergistic photocatalytic activity of TiO_2 (anatase)/ $\alpha\text{-Fe}_2\text{O}_3$ /glass thin films as photocatalysts for degradation of Escherichia coli bacteria in a low-concentration H_2O_2 solution and under visible light irradiation was investigated. The improvement in the photoinactivation of bacteria on surface of $\text{TiO}_2/\alpha\text{-Fe}_2\text{O}_3$ was assigned to formation of TiO-Fe bond at the interface. Chen-Shifu and

coworkers³⁵ developed p-n junction photocatalyst p-CaFe₂O₄/n-ZnO prepared by ball milling of ZnO in H₂O doped with p-type CaFe₂O₄. The Structural and optical properties of the p-n junction photocatalyst p-CaFe₂O₄/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 spectra³⁶. The mechanism of influence on the photocatalyst activity were also discussed by the p-n junction principle. Smith *et al.*³⁷ developed sulfated Fe₂O₃-TiO₂ (SFT) synthesized by treatment of immanite ore with sulfuric acid. The presence of sulfated Fe₂O₃-TiO₂ and mixed phase of Fe₂O₃-TiO₂ was confirmed by DRIFT spectra and XRD. The dispersion of sulfate displayed thermal stability up to 5000°C. The photocatalytic activity was evaluated by the oxidation of 4-chlorophenol (4-CP) in aqueous medium under UV-vis and visible light irradiation. Zhang *et al.*³⁸ induced Bi₂WO₆ 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 Bi₂WO₆ powder (SSR) in the degradation of phenol. Seup *et al.*³⁹ 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 tinania 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 coworkers⁴⁰ worked on the commonly used photocatalyst, TiO₂ (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. Zhang *et al.*⁴¹ utilized titanium isopropoxide, ammonium carbonate and nickelous nitrate 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 method⁴². The effects of annealing temperature and component on the phase composition and photocatalytic activity were investigated. Nickel atoms existed in the form of Ni₂O₃, dispersed on the surface of TiO₂, suppressed the recombination of photo-induced electron-hole pairs, raised the photo quantum efficiency, and led to the enhancement of photocatalytic performance. Shifu and coworkers⁴³ characterized p-n Junction photocatalyst NiO/TiO₂ was prepared by sol-gel method using Ni(NO₃)₂·6H₂O and tetrabutyl titanate [Ti(OC₄H₉)₄] as the raw materials. The results show that, for photocatalytic reduction of Cr₂O₇, the optimum percentage of doped-NiO is 0.5% (mole ratio of Ni/Ti). The photocatalytic activity of the p-n junction NiO/TiO₂ is much higher than that of TiO₂ on the photocatalytic reduction of Cr₂O₇. The mechanisms of influence on the photocatalytic activity were also discussed by the p-n junction principle. Sreethwaong *et al.*⁴⁴ 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. Xu *et al.*⁴⁵ checked a magnetically separable photo catalyst TiO₂/SiO₂/NiFe₂O₄ (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 SiO₂ layer between NiFe₂O₄ and TiO₂ shell prevented effectively the leakage of charges from TiO₂ particles to NiFe₂O₄, which gave

rise to the increase in photocatalytic activity. Kudo *et al.*⁴⁶ analyzed the structure of nickel-loaded $K_4Nb_6O_{17}$ photocatalyst in an overall water splitting reaction by means of XPS, EXAFS, TEM, and XRD. $K_4Nb_6O_{17}$ has an ion-exchangeable layered structure which possesses two different kinds of alternating interlayer spaces, i.e. interlayers I and II, where K^+ ions are located. Therefore, each niobate macroanion sheet is regarded as a “two-dimensional” photocatalyst where H_2 and O_2 evolve at different sides of the layer. Neppolian *et al.*⁴⁷ discussed an ultrasound-assisted method for synthesizing nanosized Pt-graphene oxide (GO)- TiO_2 photocatalyst. The Pt-GO- TiO_2 nanoparticles were characterized by diffused reflectance spectroscopy, X-ray diffraction, N_2 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_2 compared to the P-25 (TiO_2). 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.*⁴⁸ 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. Yoong and coworkers⁴⁹ discussed the advantage of copper doping onto TiO_2 semiconductor photocatalyst for enhanced hydrogen generation under irradiation at the visible range of the electromagnetic spectrum. 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. The reduction of band gap as a result of doping was estimated and the influence of the process parameters on catalytic activity was explained. Biswal *et al.*⁵⁰ synthesized a novel composite CdS-ZnS/ Zirconium – titanium phosphate

(ZTP) photocatalyst working under visible light. N_2 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.*⁵¹ used an environmental friendly nanocrystalline $NixTiO_2$ ($x=5$ and 7%) synthesized by hydrothermal method. The requisite quantity of commercial TiO_2 and $Ni(NO_3)_2 \cdot 6H_2O$ 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_2 and nanofibred particle to hydrothermally treated TiO_2 samples. Reza and coworkers⁵² followed Zn 1-X Cu XS and Zn 1-xNiXS 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 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 catalysts. Lee *et al.*⁵³ prepared colloidal solutions containing nano-sized TiO_2 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. Wang *et al.*⁵⁴ showed homogeneous mixed Cr-doped $Ba_4In_2O_7/In_2O_3$ 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.*⁵⁵ 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 700°C 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 TiO₂ (20 wt %). Catalyst using tetraisopropoxide as precursor. This new photocatalyst was totally stable under UV irradiation. Nukajima et al.⁶ synthesized thermally stable mesoporous Ta₂O₅ by a sol-gel technique using a material having a BET surface area of 145 m² g⁻¹, mesopore diameter of 3.5nm, and mesopore volume of 0.20 ml g⁻¹. The formation of thicker walls results in higher thermal stability than tantalum oxides prepared by a ligand – assisted templating method.

CONCLUSION

Above literature mentioned shows wide application of metal/mixed metal oxides as photocatalyst in various reactions like Cu_xS/TiO₂ composites is used in combustion of gases, photoreductive removal of metal ions, for enhanced hydrogen generation, photocatalytic H₂ production and Cu²⁺ removal from water, different p-type Cu₂O powders prepared from electrodeposition and subjected to analysis of their photocatalytic activity in water reduction, photocatalyst support was obtained by chemical vapor decomposition at 700°C of an ethane – hydrogen mixture over a woven glass microfiber supported nickel catalyst. So metal/mixed metal oxides have broad applications as photocatalyst in various conversions.

REFERENCES

- Noguera. C., *Physics and Chemistry at Oxide Surfaces; Cambridge University Press: Cambridge, U.K*, 1996
- Kung. H.H., *Transition Metal, Oxides: Surfaces Chemistry and Catalysis; Elsevier; Amsterdam*, 1989
- Henrich V.E., Cox P.A., *The Surface Chemistry of Metal Oxides, Cambridge University Press; Cambridge UK*, 1994
- Wells A.F., *Structural Inorganic Chemistry 6th ed; Oxford University Press; New York*, 1987
- Rodriguez J.A., Fernandez M.G., *Synthesis, Properties and Applications of Oxide Nanoparticles Wiley : New Jersey* 2007
- Fernandez M.G., Martinzes A.A., Hanson J.C., Rodriguez J.A., *Chem. Rev.* 2004 *104* ,4063.
- Andronic L., Isac L. and Duta A. ,*J. of Photochem. And Photobiology A: Chem*, 2011., *221* 30-37.
- .Aman N, Mishra T., Hait J. and. Jana R.K, *J. of Hazardous Mat.*, 2011 *186* ,360-366.
- Yoong L.S., Chong and. Dutta B.K, *Energy*, 2009.,*34* 1652-1661.
- Xia H.I, Zhuang H.S., Zhang T. and Xiao D.C., *J. of Environmental Science*, 2007 *19* 1141-1145.
- S. Xu, J. Ng, A. J. Du, J. Liu and D.D. Sun., *International J. of Hydrogen Energy*, 2011.,*36* 6538-6545.
- B. Neppolian, A. Bruno, C.L. Biachi and M.A. Kumar, *Ultrasonic's Sonochemistry*, 2012.,*19* 9-15.
- S. Xu, J. Ng, X. Zhang, H. Bai and D.D. Sun, *International J. of Hydrogen Energy* 2010,*35* 524-56.
- F.Magalhaes, Flavia, M. Logo, *Desalination*, 2011., *276* ,266-271.
- C.C. Hu, J.N. Nian and H. Teng, *Solar Energy Mat. and Solar Cells*, 2008., *92* 1071-1076.
- S. Xu, A.J. Du J. Liu, J. Ng and D. Sun, *International J. of Hydrogen Energy*, 2011., *36* 6560-6568.
- S. Anandan, N. Oshashi and M. Miyuchi *Appl. Catalysis B: Environment* , 2010., *100* ,502-509.
- S.A. Mahapure, V.H. Rane, J.D. Ambedkar, L.K. Nikan, R. Mari Muthu, M.V. Kulkarni and B.B. Kale, *Mat. Research Bulletin* , 2011 *46* ,635-638.
- S.K. Kansal A.H. Ali, S. Kapoor and D.W. Bohnemann, *Separation and Purification Technology*, 2011., *80* ,125-130.
- S. Liao, H. Donggen, D. Yu, Y. Su. And G. Yuan, *J. of Photochemistry and Photobiology A :*

- Chem.*, 2004 *168* .,7-13.
21. S. Chen, W. Zhao, W. Liu and S. Zhang ,*Appl. Surface science*, 2008 *255* .,2478-2484.
 22. M.C. Yang, T.S. Yang, M.S. Wong, *Thin Solid Films*, 2004., *5* 469-470.
 23. S.B. Khan, M. Kaisal, M.M. Rahman and A. Jamal, *Talanta* ., 2011,*85* 943-949.
 24. C. Yu, K. Yang, Q. Shu, J. Cyu, F. Cao and X. Li, *Chenise J. of Catalysis*, 2011.,*32* 555-565.
 25. Y.Li, Z. Jiao, N. Yang, H. Gao, *J. of Environmental Sciences*, 2009 *22*., 569-572.
 26. N. Aman, T. Mishra, J. Hail and R.K. Jana, *J. of Hazardous Materials*, 2011.,*186* 360-366.
 27. P. Beydoun and R. Amal, *Mat. Science and Engineering :B*, 2002.,*94* 71-81.
 28. C. Kormann, D.W. Bahnemann and M.R. Hoffman, *J. of Photochemistry and Photobiology A: Chem.*, 1989., *48* 161-169.
 29. Y.T.Yu, *Power Technology*, 2004 ., *146*., 154-159.
 30. Y. Wu., J. Zhang, L. Xiao and F. Chen, *Appl. Surface Science*, 2010.,*256* .,4260-4268..
 31. L. Maretti, E. Carbonell, M. Alvaro, J.C. Scaiano and H. Garcia, *J. of Photochemistry and Photobiology A: Chemistry*, 2009., *205* .,19-22.
 32. A.C. Pradhan, S. Martha, S.K. Mahanta and K.M. Parida, *Int. J. of Hydrogen Energy*, 2011.,*36* 12753-12760 .
 33. N. Aman, T. Mishra, J. Hait and R.K. Jana, *J. of Hazardous Materials*,2011., *186* .,360-366.
 34. O. Akhavan, *Appl. Surface Science*, 2010., *257* .,1724-1728.
 35. C. Shifu, Z. Wei, L. ei, Z. Huaye and Y. Xiaoling, *Chemical Engineering J.*, 2009., *155* 466-473.
 36. C. Shifu, Z. Wei, L. Wei, Z. Huaye, X. Xiabing and C. Yinghao, *J. of Hazardous Materials*, 2009., *172* .,1415-1423.
 37. Y.R. Smith, J.J. Antony Raj., V. Subramanian and B. Viswanthan, *Colloid and Surfaces A: Physico Chemical and Engineering Aspects*, 2010., *367* .,140-147.
 38. Z.Zhang, W.Wang and M.S.W.Yin, *Journal of Hazardious Materials*, 2010.,*177*.,1013-1018.
 39. S. Chung, S.B. Park and D.W. Kang, *Materials Chem. and Physics* , 2004., *86* .,375-381.
 40. H. Liu, S. Cheng, J. Zhang, C. Cao and S. Zhang, *Chemosphere*, 1999., *38* .,283-292.
 41. X. Zhang and Q. Liv. *Appl. Surface Science*, 2008., *254*., 4780-4785.
 42. X. Zhang and Q. Liv. *Appl. Surface Science*, 2008., *254*., 4785-4790.
 43. C. Shifu, Z. Sujuan, L., Wei and Z. Wei, *J. of Hazardous Materials*, 2008., *155* .,320-326.
 44. T.Sreethawong, Y. Suzuki and S. Yoshikawo, *Int. J. of Hydrogen Energy*, 2005., *301* 1053-1062.
 45. S. Xu, W.S. Guan, J. Yuan, M. Chen and J. Shi, *Chinese J. of Chemical Engineering* 2007, *15* 190-195.
 46. A. Kudo, K. Sayama, A. Thanaka, K. Asakura, K. Domen, K. Maruya and T. Onishi, *J. of Catalysis*, 1989., *120* ., 337-352.
 47. B.Neppolian, A. Bruno ,C.L.Bianchi and M.Ashok Kumar, *Ultrasonics Sonochemistry*, 2012., *19*.,9-15
 48. K.Hayat, M.A.Gondal, M.M.Khaled and S.Ahmed , *Journal of molrcular catalysis A:Chemical* , 2011.,*336*.,64-71
 49. L.S.Yoong, F.K.Chong and B.K.Dutta ,*Energy*, 2009.,*34*.,1652-1661
 50. N.Biswal, D.P.Das ,S.Maratha and K.M.Parida ,*International journal of hydrogen energy*, 2011.,*36*.,13452-13460
 51. G.G.Nakhate, V.S.Nikam ,K.G.Kanade , S.Arbut ,B.B.Kal and J.O.Baeg ,*Material chemistry and physics* ,2010.,*124*.,976-981
 52. R.Pouretedal and M.H.Keshavarz ,*Journal of alloys and aompounds*.2010,*50*.,130-135
 53. S.H.Lee ,M.Kang ,S.M.Cho, G.Y.Han ,B.W.Kim ,K.J.Yoon and C.H.Chung , *Journal of photochemistry and photobiology A:Chemistry*, 2007., *146* , 121-128
 54. X.L.Wang ,J.P.Tu, S.F.Wang, Y.F.Yuan, K.F.Li and J.Zhang ,*Journal of alloys and compounds*, 2008.,*462*.,220-224
 55. N.Keller, G.Rebmann, E.Barraud ,O.Zahraa and V.Keller, *Catalysis Today*, 2005.,*101* .,323-329
 56. K.Nakajma, D.Lu, M.Hara ,K.Dome and J.N.Kondo, *Stusies in surface science and catalysis* , 2005., *158*.,1477-1484.