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A Mini Review: Rare Earth Metal Doped Zinc Oxide and Photocatalysis

Yogeshwar Digambar Kaldante[1]*, Haribhau Mahipati Borate[1], Ramesh Natha Shirsat[1] & Manohar Ganpat Chaskar[2]*
[1]PDEA's Annasaheb Waghire College, Otur, Pune 412 409, India
[2]PDEA's Prof. Ramkrishna More College, Akurdi, Pune 411 044 India

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In the last two-three decades zinc oxide (ZnO) and ZnO based materials were widely explored for their photocatalytic applications. ZnO is illustrious for its diverse applications. Owing to a broad bandgap ZnO nanomaterial is very likely for photocatalysis but its activity is narrow to UV light irradiation. For improved activity of ZnO under sunlight its modification can be done by addition of another semiconductor. The doping of ZnO enhances its photodegradation performance. The properties of ZnO can be tweaked by controlling aspects such as nature of the preparation method, calcination temperature, precursors, type of dopant, dopant concentration etc. Rare earth (RE) metal proved to be graceful dopant to ZnO for the improved Photocatalytic Degradation (PCD) efficiency. Being trapping sites for photo-electrons and hence promoting separation of charge carriers RE dopants leading to high photocatalytic efficiency of ZnO. Consequently, this article presents a brief but critical review of Rare Earth (RE) metal doped zinc oxide and photocatalysis.

Keywords: Doping, Photocatalytic activity, Photocatalytic degradation, ZnO

Introduction

Recently zinc oxide (ZnO) and allied materials were widely explored for their photocatalytic applications as reflected by increasing number of publications in the same field. Huge applications for air and water purification, heavy metals reduction and hydrogen production make the semiconductor photocatalyst a material of high concern.[1] Generation of charge carriers in the semiconductor photocatalyst upon irradiation with band-gap radiation followed by redox reactions with the species present on the photocatalyst surface as shown in Fig. 1 forms the basis of photocatalysis. But rapid recombination of photogenerated charge species in photocatalysts is substantial hurdles in its associated applications. Increasing the charge separation efficiency to boost efficiency of photocatalysts is the main challenge.[2]

Many materials were reported as active photocatalysts either in UV or Visible light. Choice of semiconductor material for the photocatalytic process is one of the important tasks so that process can be achieved within minimum time and complete mineralization is also achieved. The parameters that are applied for photocatalyst choice are cost, toxicity, band gap, surface area, activity, recyclability, etc. Among the many known photocatalyst nano sized ZnO, TiO_2, SnO_2, WO_3, ZrO_2 and their modified structures satisfy above criterion hence at first sight they are most suitable materials for photocatalytic applications.[3–8] ZnO is a dependable photocatalyst having large bandgap within near ultraviolet range and also high exciton binding energy supporting emissions near to room temperature.[9]

The general reactions involved during the photocatalytic degradation (PCD) is given in Scheme-1

However, the large bandgap of ZnO restricts its photocatalytic activity under UV spectral region since it is capable of absorption of light having wavelengths below 387 nm.[10] For improved activity of ZnO under sunlight its modification can be done by addition of another semiconductor.[11] Large number of publications reporting the ZnO based development of hybrid materials for visible light mediated photocatalysis is available.

Strategies to Modify ZnO Photocatalytic Degradation Efficiency

Different approaches are present for the modification of the characteristics of ZnO for its potential applications wherein doping of ZnO with suitable metal or nonmetal elements and co-doping /coupling with other narrow band-gap semiconductors were the main themes.

The addition of a minute quantity of an impurity to an extremely pure substance is termed as 'Doping'.

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*Author for Correspondence
E-mail: ydkaldante@gmail.com; chaskarmanohar@gmail.com

Cationic and anionic doping are two basic types of doping. Elements such as V, Mn, Cr, Al, Fe, Co, Ni, etc. serve as a cationic dopant(s) and the elements such as C, S, N, P etc. serve as anionic dopant(s) for ZnO and / or TiO_2 as well as other metal oxides too. Every kind of dopant has a distinctive impact on the crystal lattice of metal oxide. Localised d-states at the band gap of metal oxides (ZnO or TiO_2) due to cationic insertion are responsible for recombination photo excited electrons-holes results in declined photocatalytic activity.[12,13] Cationic doping increases passivity of photocatalyst due to unfavorable shifting of the conduction band lower than the redox potential. In contrast to the above mentioned case doping with anionic species provides p-states to proximate the valence band in the semiconductor.[14–16] Depending upon the nature of the impurity whether it is electron donor or acceptor and nature of the parent material doping also termed as n-type or p-type doping (Fig. 2). ZnO with wurtzite structure owing excess Zn and is a non-stoichiometric n-type semiconductor compound. Doping of ZnO with n-type dopants is relatively easier over p-type dopants. Group III & VII elements as substituent for Zn & O respectively may be n-type dopants for ZnO. ZnO doping with Group III elements was tried by many researchers for high-grade and excellent conductive films. AlZnO films made with MOCVD reflected high conductivity over GaZnO films made by chemical-vapor deposition (CVD).[17,18] p-type doping is a very challenging task with wide-band gap material. Substitution of Zn sites with shallow acceptors group-I elements and / or O sites with deep acceptors group-V elements may permit p-type doping in ZnO. In turns of shallowness of acceptor levels group-I elements are superior over group-V elements as p-type dopants. Because of smaller atomic radii than substitutional sites, group-I elements go to interstitial sites, so act as donors rather than acceptors. Furthermore, presence of Na and / or K as dopants forms larger bonds with O than ideal Zn–O bond length and produce lattice strain as well as some

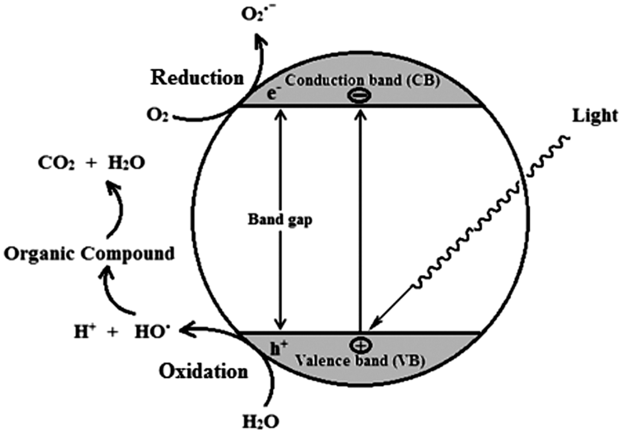
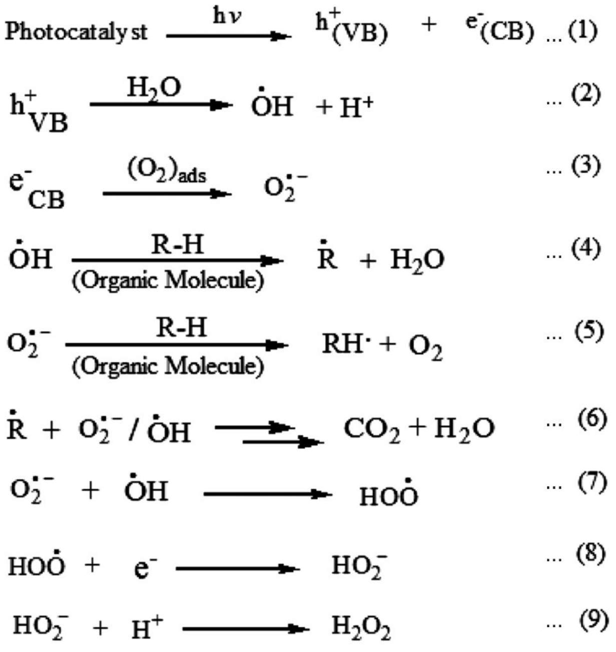
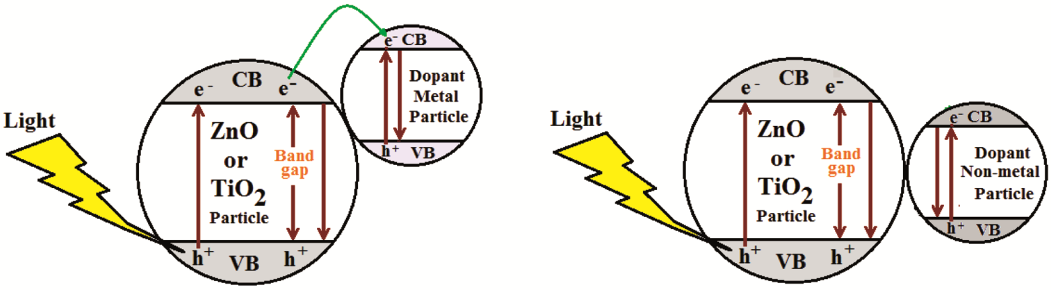


Fig. 1 — General Mechanism of Photocatalysis



Scheme 1 — Reactions involved during Photocatalysis



(a) p-type of doping in ZnO / TiO_2

(b) n-type of doping in ZnO / TiO_2

Fig. 2 — Types of doping

native defects such as vacancies. Similarly P and A's dopants from Group V also form larger bonds so they form antisites to avoid the lattice strain in ZnO. Nitrogen (N) has small ionization energy and seems to be a good contender for a shallow p-type doping in ZnO achieved by ion implantation.[17–19]

Depending upon nature of the dopant, mode of doping, semiconducting behavior of the materials, field of applications different terminologies were documented in the literature in the context of doping such as cationic and anionic doping, n and p-type doping, surface and interstitial doping, metal and non-metal doping etc. Few of them with respect to ZnO and / or TiO_2 were described in brief hereafter without going into the detailed clarification of these terminological aspects, in this review we describe the photocatalytic practices with RE doped ZnO.

Very extensive research has been presented on the various metal and non-metal doped ZnO for important applications related to diverse fields. The efficiency of PCD of the doped ZnO is found to be excellent over bare ZnO. Furthermore, diverse properties of ZnO samples may be tuned by controlling factors such as nature of the preparation method, calcination temperature, precursor materials, dopant concentration, etc. Altered bandgap and enhanced charge isolation responsible for extension of excitation range in case of doped semiconductor photocatalysts, so it will show higher PCD ability than single semiconductor photocatalysts.[20–24] Transition metal doped zinc oxide is a very deeply studied material for their photocatalytic and other applications. Large number of research papers has been available on the transition metal doped zinc oxide photocatalysts for their use in PCD of water contaminants. Few representative examples of research on transition metal doped ZnO are mentioned here. Xu *et al.*[25] reported the enhancement in PCD of Methyl Orange dye over cobalt-doped ZnO than bare ZnO due to bathochromic shift in the absorption edge. Wang *et al.*[26] reported that Ag doping to ZnO highly upgraded the PCD of MB and phenol due to the upgraded surface properties of these materials like increased specific surface area, crystal deficiencies and O vacancies. Kant and Kumar[27] studied kinetics of Methylene Blue degradation over pure and Ni doped ZnO nanoparticles under UV –Visible light and reported more activity of Ni doped ZnO over pure ZnO. Bloh *et al.*[28] have doped different transition metal ions in ZnO (Ru, Ti, Zr, Cu, Co, Fe, Mn, Ni) with variable concentrations (0.01, 0.1, and 1 atomic %) and investigated photocatalytic activity under UV-visible light illumination. According to the authors catalytic activity under UV illumination will modify with addition of nearly each mentioned dopant with an optimal modification ratio nearly 0.1 atomic %. They also observed that ZnO modified with Mn and Ru have more visible light PCD activity than any other transition metal. Krishnakumar *et al.*[29] reported Zr-codoped Ag-ZnO catalysts. Zr-Ag-ZnO hetero structure was found effective than Ag/ZnO, Zr/ZnO, Bulk ZnO (commercial), TiO_2 (P25), and TiO_2 photocatalysts at neutral pH towards solar PCD of RR 120. Milenova *et al.*[30] reported that Cu-doped ZnO is a better photocatalyst than pure ZnO in degradation of Reactive Black 5 dye under UV irradiation. Rongliang *et al.*[31] prepared Co and Mn doped ZnO nanoparticles and reported that low percentage of Mn-doping is a better photocatalyst in degradation of Rhodamine B dye. As reflected from above discussion, transition metal doped ZnO has been proven to be a highly saturated area of research, hence researchers are turning towards RE metals as keen alternative dopants for the photodegradation.

Rare Earth (RE) Metal Doped ZnO Photocatalysts

In recent times, RE/ZnO photocatalysts have greatly attracted researchers. In photocatalysts, the promotion of the surface properties as well as the capability of electron transfer is deeply related to the unique photo-catalytic and redox properties of RE dopants. The RE/ZnO has been known to have better PCD activity over pristine ZnO.[32] Doping of rare earth metals (e.g., La, Pr, Nd, Tb, Er, Eu, Dy and Sm) in ZnO shows red shift in band gap hence favors not only visible light absorption and surface defects for separation of electrons but also, creates substantial lattice defects in to the ZnO lattice due to the charge compensation and the ionic radius disparity between RE ion and Zn^{2+}, which may put enormous suspicions to the origin of photo activities. Many research groups have been involved in the studies of rare earth metal doped ZnO for their use in photocatalytic degradation of water contaminants. Few representative examples of research are summarized here. Khatamian *et al.*[33] informed lanthanide doped ZnO photo catalyst. They have been doped with ZnO with La(III), Nd(III) and Sm(III). They reported the highest rate of degradation of 4-nitrophenol is highest with La (III), Nd(III) and Sm(III) loading of wt % respectively up to 4, 4 and 8. Among the various catalysts, the four weight percent Nd/ZnO showed highest PCD activity towards 4-nitrophenol. The Nd-ZnO was proven to be a prevalent photocatalyst independently by the research groups involving Kumar and Sahare[34] for the photodegradation Rhodamine B, Yayapao *et al.*[35] for the PCD of Methylene Blue and Zhao *et al.*[36] for the PCD of Methyl Orange. Highest PCD efficiency of 1 mol% Nd doped ZnO over other mentioned catalysts was revealed from this study. Among the independent studies on the PCD of Methylene Blue with RE/ZnO, Yayapao *et al.*[37] (with 3 & 1 mol% Dy and Nd doping in ZnO), Yu *et al.*[38] (with 4.8 mol% Er-ZnO), Phuruangrat *et al.*[39] (with 3 mol% Eu), Phuruangrat *et al.*[40] (with 3 mol% Ho) reported the highest PCD efficiency of 3 mol% Dy-ZnO using UV light for 5 h. Zong *et al.*[41] reported the most activity of 1 mol% Eu-loaded ZnO over 3 mol% Nd-loaded ZnO for the degradation of Methyl Orange. Khataee *et al.*[42] synthesized Dy-doped ZnO and reported the enhanced activity of Dy-doped ZnO than pure ZnO in the degradation of textile dye under visible light. Oprea *et al.*[43] reported Gd(III) doped ZnO photocatalysts and reported Gd(III) doped ZnO was a better catalyst than pure ZnO. Also Ghouri *et al.*[44] reported enhanced photocatalytic activity of Gd-doped ZnO than pure ZnO. Dipa Rani *et al.*[45] were doped ZnO with Nd(III) and reported that 1% Nd doped ZnO has better photocatalytic activity than pure ZnO. Kai-Sheng *et al.*[46] reported that Er-doped ZnO photocatalysts are better than pure ZnO for degradation of organic compounds. Sin *et al.*[47] synthesized Sm (III) doped ZnO and found it was more active in visible light for the degradation of 2, 4 –dichlorophenol and recyclable without appreciable loss in photocatalytic activity. Sin *et al.*[48] synthesized Ce-doped ZnO and found that 2 atom% Ce-doped ZnO absorbs at longer wavelength than pure ZnO and therefore it displayed better photocatalytic activity in visible light than pure ZnO in the degradation of phenolic compounds. Kumar and Sahare[49] reported the boosted PCD of Rhodamine B dye with 0.05 mol% Gd doped ZnO. Anandan *et al.*[50] have studied degradation of 2,4,6- trichlorophenol over La-doped ZnO nanoparticles obtained via co-precipitation method. Likely other researchers[51–53] also have studied La-doped ZnO for various applications. Pascariu *et al.*[54] obtained ceramic nanostructured La-doped ZnO by electrospinning route and studied its properties. Pascariu *et al.*[55] also have reported La, Er and Sm-doped ZnO synthesis for the degradation of congo red dye. John and Rajakumari[56] have reported solid state synthesis of Er/ZnO and studied its electrical and magnetic properties. Vaiano *et al.*[57] reported Pr, Ce and Eu doped ZnO for the removal of Eriochrome Black T Dye, highest activity was credited to Pr-ZnO. Divya and Pradyumnan[58] prepared Pr doped ZnO and studied degradation of methylene blue dye, Pr-ZnO is found three-fold times more active than ZnO. Chouchene *et al.*[59] have reported solvo thermal synthesis of Ce-doped ZnO and studied degradation of the Orange II dye. Fenwick *et al.*[60] have synthesized Gd, Eu, and Tb doped ZnO, and studied their structural, optical and magnetic properties. Aisah *et al.*[61] have studied degradation of methylene blue over hydrothermally synthesized Ce-doped ZnO. Arulanantham *et al.*[62] have synthesized Er-doped ZnO and studied their structural, morphological and photocatalytic properties. Djaja and Saleh[63] have studied degradation of methyl orange over Ce-ZnO. Logamani *et al.*[64] have synthesized Nd and Gd-doped ZnO and studied photocatalytic properties towards degradation of methylene blue. Nguyen *et al.*[65] have reported gel combustion synthesis of La-doped ZnO and studied degradation of methyl orange. Jagtap *et al.*[66] have studied selective N-acetylation with simultaneous S-oxidation of o-amino thiol over Ce-doped ZnO nanocomposite at ambient conditions. Hastir *et al.*[67] have studied sensing application of Tb-doped ZnO toward ethanol and acetone and found a maximum sensing ability of 4% Tb-doped ZnO. Zeng *et al.*[68] have reported doping of ZnO with trivalent rare earth metals Pr, Sm, Tb, Ho, Tm and Eu and studied the photoluminescent properties of synthesized materials.

All above discussed experimental findings highlighted that the RE doped semiconducting ZnO photocatalysts not only shows good optical and enhanced luminescence properties, but also it is effective for the deletion of organo-contaminants by means of photocatalysis. This could be attributed to the amplified particle surface area, reduction of band gap energy, developed adsorption ability of the particle surfaces and dopant-ZnO interfaces. Selection of a particular element for its specific applications is totally based on its optical properties as a photocatalyst. The band gap energy basically influences the nature and photocatalytic properties of semiconductor material. The bandgap lowering of

ZnO via suitable dopant insertion than bare ZnO is a well-studied subject. Irradiation of ZnO with solar or artificial light gives rise to a large number of electrons in the conduction band which in reaction with oxygen molecules leads to the formation of superoxide anions. Presence of the RE metal at the ZnO surfaces enhances the adsorption of oxygen thereby promoting generation of potent oxidizing species. Hence increase the rate of photocatalytic degradation. Addition of the RE dopant into ZnO also enhanced the luminescence intensity of material. The additional RE metal dopants being as a luminescent center greatly alter the related property of the doped ZnO. Functioning as a trapping centre / site for electrons the RE dopants assists the isolation of photogenerated charge carriers hence contributes to great photocatalytic efficiency.[32]

Impact of Co-Dopants on Photocatalytic Degradation Efficiency

The quick electron-hole pair recombination can also be prevented to some extent by the presence of co-dopants. It is reported that the TM and / or REM co-doped ZnO shows better PCD efficiency than undoped ZnO and single dopant ZnO systems. Some representative examples of related research are mentioned here as boosted PCD of Methylene Blue over Ag-Au-ZnO reported by Senthilraja *et al.*[69], and over Ni-Th-ZnO reported by Vignesh *et al.*[70] In the same respect the enhanced PCD of Naphthol Blue Black over Ce-Ag-ZnO reported by Subash *et al.*,[71] PCD of Methyl Orange over Er-Al-ZnO reported by Zhang *et al.*,[72] PCD of Reactive Red 120 over Zr-Ag-ZnO reported by Subash *et al.*,[73] and PCD of Acid Black 1 over Zr-Ag-ZnO reported by Subash *et al.*[74] The co-dopants reduce the recombination of electron-hole in ZnO by trapping electrons from the conduction band and hence supports the production of more and more electron-hole pairs hence contributes to enhanced rate of PCD of the dyes.[32]

Conclusions

Doping of ZnO permits the tuning of physical, chemical, optical, electrical, structural and morphological characteristics of the ZnO so that its uses and applications can be increased. P-type doping is a challenging task with ZnO but n-type doping is relatively easier. Improved ZnO systems found to be the highly promising photocatalyst with enhanced PCD efficiency under solar/natural and artificial light (UV/visible) irradiation. As per the conclusions of many literatures on modified ZnO systems, reduced probability of rate of recombination of charge carriers is one the most significant factors contributing to their altered PCD efficiency. Diverse amendment methodologies or routes with chemical additives have been established therein doping (metal / non-metal / rare earth) and co-doping with ZnO gave a positive outcome in terms of reducing recombination of charge carriers and shifting the absorption spectrum of ZnO towards visible region. Rare earth (RE) metal proved to be promising dopant to ZnO for the improved PCD organic pollutants. The additional RE metal dopant functions as luminescent centers thereby greatly altering the luminescence property of RE/ZnO materials. RE dopants functions as electron trapping sites as well as endorse the isolation of photogenerated charge carriers hence contributes to more PCD efficiency than bare ZnO. High catalytic activity, photostability, and nontoxicity of modified ZnO systems make them valuable for industrial applications in future. The modified ZnO nanostructures can be useful for the applications such as gas sensing, solar cell, optoelectronic devices, hydrogen generation, degradation of contaminants etc. Still there is a wide scope for research in the field of modified ZnO systems. So one can thoroughly understand the lattice and electronic structure of ZnO and hence be able to know the effect of different cationic, anionic, small bandgap of semiconductor, and elements doping/loading on ZnO photocatalyst.

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Conflict of interest

The authors declare that they have no conflict of interests.

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