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Doped ZnO Nanostructured and their application as photocatalytic: as Review

Abstract

There are two types of methods of synthesis of several different kinds of doped ZnO nanomaterials for photocatalytic applications, gas phase methods, include pulsed laser deposition and chemical vapor deposition and wet chemical methods such as sol-gel, electrospinning, hydrothermal, spray pyrolysis, thermo-mechanical .doping with metal ions is make local energies levels within the semiconductor energy gap, which results in prolongation of the light absorbance to the visible light region. Several studies have that metal-doped ZnO, such as N, S, and C, using Co, Fe, Cu, Eu, Ce, Ag, Mn, and Al and non-metal doping, ZnO to the reducing Energies and enhancement of photocatalytic behavior in the region of visible light.

Introduction

Nonmetals and metals were analyzed in order to transform ZnO's electronic structure to expose a shift in absorption, metals were assessed. Various properties, including Crystal design, pore size, surface area, and doped ZnO photocatalytic activity, depending on the dopant shape, concentrations, and conditions of preparation. Therefore, separate metal doping, non-metal doping becomes less likely to create recombination centers, doping generates a novel state of the valence band that leads to a reduction of the band gap by high upward valence band limit. [1-3] Amornpitoksuk et al. [4] formulated Nano-crystalline Ag-doped ZnO powders with different concentrations of Ag precursors through a minimal temperature precipitation process. They find that Ag ions add ZnO lattice by replacement on Zn^{2+} sites when Ag loading is less than 0.5 mol%

Ga and Ag doped ZnO Nano rods, supported in polyethylene by a hydrothermal microwave heating synthesis and evaluated their photocatalytic performance and antimicrobial activity towards two bacterial strains commonly found on treated-water effluents. [5] Fe-doped zinc oxide Nano star was synthesized by the process of microwave-assisted surfactant-free hydrolysis Various synthetic protocols for the synthesis of various ZnO nanostructures and literature including direct calcination of metal salt have been widely published [6], sol-gel method [7] and hydrothermal synthesis [8], simply hydrolysis followed by calcination [9-10]

Due to its equivalent physical and Chemical properties, an ideal doping for

ZnO The optical properties of the micro structure [11-12] can be modified [13-15] band-gap decreases, absorption shifts to longer wavelengths (16) and ZnO nanostructure morphology changes

Polat et al [17] prepared Cu-doped ZnO Nano rods for methylene blue degradation On glass substrates by the deposition of chemical baths (CBD). A morphological change from pyramidal geometry to hexagonal rod shapes has been observed. Zhang et al. [18] has successfully doped Cr precursor into ZnO Nano rods by hydrothermal method, and Cr-doped ZnO cluster may be the most favorable sensor for CO detection because its electrical conductivity considerably changes after the CO adsorption. Cr-doped ZnO used in the gas sensing studies of reducing and toxic gas such as ammonia; and volatile. Cd doped ZnO resulted in reduction in bandgap [19] which cause to the tuning of luminescence to visible region. Cd-doped ZnO powders synthesized by kinds methods including sono chemical method [20], hydrothermal method [21-22], sol-gel synthesis [23], and chemical synthesis method [24]. As compared to the corresponding pure oxides, the Co_3O_4/ZnO catalysts showed modified textural characteristics. The demonstrated catalytic behaviors were substantially greater than those of the pure oxides. Catalyst Co_3O_4/ZnO . The most active is formulated with zinc carbonate ($CoZnOTC$) by thermal decomposition, while the least active is the catalyst synthesized with citric acid as fuel ($CoZnOSCI$) by sol gel combustion. [25]. In order to prepare Co doped ZnO thin film including spray pyrolysis, the sol-gel method [26] has

unique advantages such as low cost, easy deposition process, fast adjustment of composition as well as the manufacture of wide area films and dopants [27], magnetron sputtering [28] pulsed laser deposition [PLD] [29]. Several studies have centered on magnetic Co/ ZnO and electrical properties. [30-31], Without any major distortion in the lattice structure, Co(II) can be substituted for Zn(II) sites since the Co(II) ionic radius is smaller than the Zn(II) [32-34]. Moshfegh's group have successfully modified ZnO nanoparticles through band gap engineering to visible-light-active photo catalysts [35-42]. In oxidation discolorations of contaminant fabric coloring dye reactive black in slurry reactor, that metal (Mn, Ni, Co, Ag, and Cu)-doped activated ZnO powders have higher photocatalytic activities compared to that of pure ZnO outstanding in its photocatalytic efficiency. The state of being discolored of the dye results to afflicted charge carrier separation and the rise specific surface area. Unmodified ZnO has been shown a four times lower degradation rate than silver modified ZnO and a three times less rate than the commercial TiO₂ photocatalyst (Georgekutty et al. 2008) [43]. Pure zinc oxide displayed in reaction for methyl red degradation in solutions, a similar behavior compared to Ag-N-co-doped ZnO nanoparticles under UV irradiation (Welderfael. 2013). (Kant 2012) [44] indicates that the Ni dopant has an important impact under the UV-visible region on photocatalytic activity. Ag/Fe₂O₃-doped ZnO nanostructures were fabricated for photo oxidation of methyl blue (MB) dye under visible light irradiation. The photocatalytic activity of ZnO and Ag-ZnO nanostructure which studied in presence visible light, using Cibacron Brilliant Yellow 3G-P CB dye

The photocatalytic activity of the Ag doped ZnO nanofibers were determined the degradation of methylene blue (MB) under UV light irradiation. It was found that higher (MB) degradation rate resulted ability of fibers was improved with Ag addition and higher Ag incorporation. For pure ZnO fibers, the degradation of its initial amount was 52% of methylene blue after 270 min of UV irradiation time. Fe has oxidation states to increase the activity of ZnO photo catalysts applied to Fe. ZnO doping with Fe and Cr will lead to the production of a ferromagnetic character photo catalyst that promotes environmental congregation after photo oxidation. Property important of Fe dopant is a number of states of oxidation, namely Fe⁴⁺, Fe³⁺, and Fe²⁺ [45-48]

$$\text{ZnO} + h\nu \rightarrow e^- + h^+ \quad (1)$$

$$\text{Fe}^{3+} + e_{\text{CB}^-} \rightarrow \text{Fe}^{2+} \text{ (electron trap)} \quad (2)$$

$$\text{Fe}^{2+} + \text{O}_{2(\text{ads})} \rightarrow \text{Fe}^{3+} + \text{O}_2^- \quad (3)$$

$$\text{Fe}^{3+} + h\nu_{\text{VB}^+} \rightarrow \text{Fe}^{4+} \text{ (hole trap)} \quad (4)$$

$$\text{Fe}^{4+} + \text{OH}^- \rightarrow \text{Fe}^{3+} + \cdot\text{OH} \text{ (hole release)} \quad (5)$$

To degrade the contaminants, the active oxidant species are OH· and O₂⁻ radicals. The supply of Fe-induced traps increases if Fe is doped in concentrations greater than the optimum concentration. The production of Fe³⁺ and Fe²⁺, Fe sites work as recombination centers because Fe⁴⁺ interacts with electrons and Fe²⁺ interacts with a hole to provide Fe³⁺. Therefore the photo-induced electron/hole will not, photocatalytic activity reduces and produce active oxidant species. The nanostructures of Mn doped ZnO have higher rate constant and photo degradation efficiency as it has higher surface defects, crystallinities and length, than others. Some researchers have reported that the opposite results while the Mn doped ZnO increases the photocatalytic activity under UV irradiation [49-50]. Tsuzuki et al.

evaluated the Mn-doped ZnO nanoparticles and undoped that doping with Mn reduced the photocatalytic activity of ZnO for the degradation of RhB dye. Compared to undoped ZnO, Cu/ ZnO doping has been found to result in increased photocatalytic activity (Fu et al. 2011) [51]. Liu et al. (2008) [52] and Xu et al. (2010) [53] stated that the photocatalytic efficiency was enhanced by the implementation of Cu₂O and CuO.

Ekambaram et al. (2007) [54] stated that Mn/ZnO, Co/ZnO, and ZnO less active than Ni-doped ZnO. Influence of Co-/Mn-/ Cu-doping on the photocatalytic performance of the ZnO nanostructures. Lead to effects of types in morphology, surface defects, that porosity and high specific surface areas played a significant role in modulating the photocatalytic activity of ZnO nanostructures. For the photocatalytic degradation of methyl orange by Cu-doped ZnO nanoparticles under UV light. Results indicate that higher Cu concentrations decrease the recombination rate of photo-generated electrons and holes. Fu et al. [55] Mohan et al. [56] by prepared Nano rods For the photo-degradation of resazurin dye, using the vapor transport process. Cu/ Zince Oxide Nano rods with narrower band gap. The band differences in ZnO and CuO are 3.4 eV and 1.2 eV [57-60]. They may be used in the photo decomposition of various materials under UV irradiation in aqueous media [61-63].by preparing CZO-rGO nanocomposite by reduced graphene oxide (r GO) Nano sheets to extend the light adsorption and to improve the efficiency of the separation of photo generated electron-hole pair and the light harvesting [64-72].

using a facile hydrothermal method synthesized Cd doped ZnO nanostructures. The sunlight induced

photocatalytic activity was evaluated towards the degradation of methylene blue (MB)dye.an increase in Cd dopant concentration in ZnO showed a redshift in The UV-Visible absorption spectra. The spectra show defect-related visible emission band and near band edge emission. Cd/ZnO exhibits photo degradation of (MB)dye compared to undoped ZnO, because Cd²⁺ ion capture photogenerated electrons and restrain recombination of electron and hole [73-75].During the preparation process, the addition of Co ion into ZnO nanoparticles results in small particle size with a large surface area preferred for photocatalytic. [76-78]. And also connected to the combined effects of higher defect concentration and vacancies in oxygen [79-80].Several studies shown that Co doped ZnO increases the activity nanomaterials of ZnO; in some reports, it significantly decreases [81-86].The higher rate of increase porosity in the glassy process after silica consumption. Because the presence of (ZrO₂) results to the formation of (ZrSiO₄). The addition of ZrO₂ to DD3 clay in a previous work gives the highest amount of porosity on the ceramic surface [87]. Transition metal oxides are some of the catalysts used in current photo degradation. ZnO is among the oxides that Changes in the morphology of Nanoparticale zinc oxide [88-89] photocatalytic activity for Al-doped ZnO was investigated [90]. More studies show that the process variables synthesis technique affects the properties of Al-doped zinc oxide and the formation of a broader [91-92] or smaller Al-doped ZnO band gap [93-94].Due to the collapse of small pores in the ZnO sample during calcination, N-doped ZnO has a smaller specific surface area than pure ZnO using NH₄NO₃ as the nitrogen source obtained by Wu [95], When preparing N/ZnO for

visible-light photo degradation by sol-gel process and the source of nitrogen using urea of picloram herbicides and 2,4-D by Macias. [96]. different amounts of nitrogen doping were obtained band gap and crystallite size for various different surface areas. Their results show provides the highest photocatalytic efficiency, The band gap is decreased by 0.19 eV. Nanocomposites were Synthesized of N/ ZnO/g-C3N4 core shell Nano plates for rhodamine B by visible-light oxidation process and the comparison to g-C3N4 and pure ZnO [97]. Cho et al. [98] formulated vitamin C with a carbon dopant source for C-doped ZnO Nanomaterials and studied the effect of visible light on orange-II dye by photo degradation. In order to elucidate the formulation of Co and Zn C bonds, they have used (EDS), XRD, and XPS representation. [99-100]. photocatalytic activity and stability are increasing using Cerium/ ZnO nanomaterials [101-102]. Ionic radii of Zn^{2+} ion is much smaller than both Ce^{4+} and Ce^{3+} . Ce doping causes surface area increase, crystallite and particle size decrease, Favored for the reactions of photo-catalysis [103]. Zinc oxide Valence band with different energy levels, induced by new electronic transition states and visible-light absorption obtains [104]. In addition, The red shift and blue shift occur through doping at the optical absorption edge of ZnO. Showing a rise in dopant concentrations of Eu. Furthermore, the highest photo degradation occurs in 0.2 % Eu-doped ZnO. [105] of methyl orange. Zeng et al. [106] prepared Eu-doped ZnO nanoparticles with a wider band gap compared to pure ZnO, which contributes to enhanced photocatalytic activity under UV light. Their PL emission spectra indicate a slower e/h recombination rate

Anandan et al. [107] synthesized La-doped ZnO nanomaterials for degradation of 2,4,6-trichlorophenol by precipitation method. by increasing in La dopant concentration results to band gap broadening and crystal size decrease Because of the formation of the La O Zn bond on the surface that hinders crystal grain growth. Therefore, smaller particle size and appropriate active sites for pollutant adsorption are given by greater surface area. Khataee et al [108] by the Sono Chemical Method prepared Dy-doped ZnO nanoparticles for acid red 17 degradation. Under visible-light irradiation, Dy/ ZnO shows the strongest photocatalytic decolorization. The stronger photocatalytic operation for the association between two Dy^{3+} and Dy^{4+} oxidation states is Dy-doped ZnO. using for visible-light-active photo catalysts with other elements by co-doping of Al-doped ZnO (AZO) nanocrystals [109], for photocatalytic hydrogen production by Huo et al. [110] synthesized Y doped AZO by the sol-gel process. Their results show that pure ZnO smaller optical absorption in the whole light region than the Y-AZO nanoparticles. The major effects of the co-doping process on the catalytic efficiency of doped ZnO within the visible range are shown in the figure. 1.

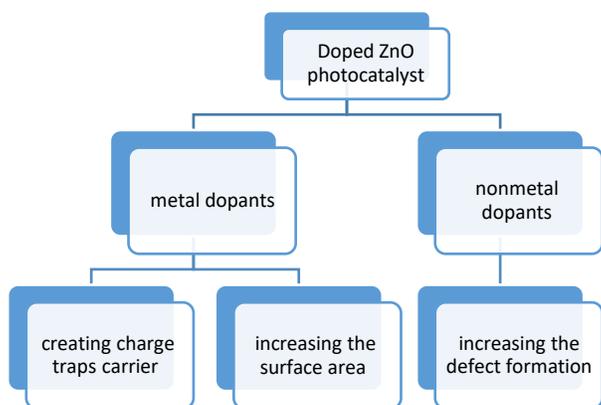


Fig. (1). General features of nonmetal and metal doping of ZnO photo catalyst under the visible-light.

An appealing configuration is also explored to change the electronic structure and extend the absorption of visible light by integrating rare-earth (RE) atoms in the ZnO structure. The energy gap shifts are due to i) formulation of local defect level band by RE metals ii) the ionized impurities using potential variation introduced, iii) ZnO conduction or valence band variance and 4f,5d states of RE metals by charge transport [111]. In addition, doping results in the efficient suppression of the recombination of the photo-generated (hole/electron). This results in the RE metal's ability to trick the electrons, For several applications, photo catalysis is applied in more fields, like water and air control [112], disinfection processes [113], self-cleaning methods [114], renewable energy sources, such as the production of hydrogen by water splitting [115], green chemical synthesis [116] and CO₂ reduction for hydrocarbons [116] [117]. ZnO photo catalysts' industrial uses in electric fields are showing in figure 2 .

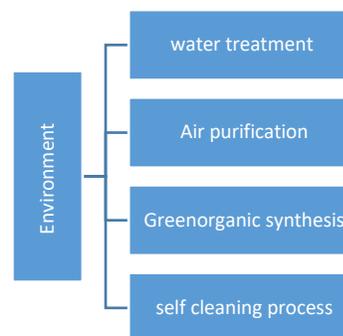


Fig. (2) Photocatalytic environment applications of Zinc oxide

A donor state, obtained by replacing atoms with one or more electrons in the outer shell with n-type ZnO doping compared to the substitution atom (Zn or O) in ZnO. As a result, Replacement of group-VII elements at O sites and group-III elements at Zn sites by highly conductive n-type ZnO-type elements. Substitution of group-V on O sites and group-I elements on Zn sites, of p-type ZnO doping, provides an acceptor stage. While ZnO can easily be doped with the n-type, efforts to produce reliable p-type doping are yet a problem due to higher ionization, p-type dopant low solubility. [118-120].

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