Recent progress on doped ZnO nanostructures for visible-light photocatalysis

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Abstract

Global environmental pollution and energy supply demand have been regarded as important concerns in recent years. Metal oxide semiconductor photocatalysts is a promising approach to apply environmental remediation as well as fuel generation from water splitting and carbon dioxide reduction. ZnO nanostructures have been shown promising photocatalytic activities due to their non-toxic, inexpensive, and highly efficient nature. However, its wide band gap hinders photo-excitation for practical photocatalytic applications under solar light as an abundant, clean and safe energy source. To overcome this barrier, many strategies have been developed in the last decade to apply ZnO nanostructured photocatalysts under visible light. In this review, we have classified different approaches to activate ZnO as a photocatalyst in visible-light spectrum. Utilization of various nonmetals, transition metals and rare-earth metals for doping in ZnO crystal lattice to create visible-light-responsive doped ZnO photocatalysts is discussed. Generation of localized energy levels within the gap in doped ZnO nanostructures have played an important role in effective photocatalytic reaction under visible-light irradiation. The effect of dopant type, ionic size and its concentration on the crystal structure, electronic property and morphology of doped ZnO with a narrower band gap is reviewed systematically. Finally, a comparative study is performed to evaluate two classes of metals and nonmetals as useful dopants for ZnO nanostructured photocatalysts under visible light.

Keywords: Zinc Oxide; Doping; Visible light; Heterogeneous photocatalytic degradation; Metals and nonmetals; Band gap narrowing; Solar light

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1. Introduction

Development and population growth have contributed to increased global environmental pollution and energy supply demand. Industrial plants dump about 300–400 million tons of heavy metals, solvents, toxic sludge and other waste into the global waters each year, which cause severe environmental problems [1]. Also, the wide spectrum of organic pollutants, including phenols, pesticides, fertilizers, detergents, synthetic dyes, etc., which are annually produced worldwide, are lost in the wastewater stream [2]. Therefore, the removal of organic pollutants is of particular importance due to their harmful effect on the environment. Various physical, chemical and biological treatments have been widely used to convert and remove organic pollutants [3]. Advanced oxidation processes (AOPs) have gained growing attention as an alternative to traditional treatment processes for organic pollutant removal. AOPs are defined as processes which rely on in situ generation of highly oxidizing radicals involving mainly hydroxyl radicals ($\bullet\text{OH}$) for the degradation of toxic organic pollutants into non-hazardous compounds. Among AOPs, semiconductor-mediated heterogeneous photocatalysis is a promising technique, which is valuable for environmental and energy applications. Owing to its advantages such as low cost, non-toxic, complete mineralization and reusability; it has become a fast growing research area in the past decades. Some notable semiconductors applied as photocatalysts are included TiO_2 , ZnO , CdS , WO_3 , SnO_2 , ZnS , CdTe , $\alpha\text{-Fe}_2\text{O}_3$, AgNbO_3 and SrTiO_3 [4].

Among the above materials, TiO_2 in anatase form and ZnO in the wurtzite phase are the most used metal oxides as photocatalysts due to their electronic band structure. ZnO is believed to have higher efficiency in the photocatalytic performance than TiO_2 , in many cases due to its higher quantum efficiency [5-7]. ZnO nanostructures as a wide band gap (E_g) semiconductor

(3.37 eV) suffer from an intrinsic limitation to utilize only ~4% of the UV portion of solar energy as an abundant, clean and safe energy source for photo-excitation in the photocatalytic process. Therefore, considerable effort has been applied to extend the photo-response of ZnO into visible-light region (~43% of solar spectrum) [8]. Modulation of ZnO band structure to the lower band gap to tailor visible-light absorption is one of the main strategies. Various elements and methods were implemented and reported to achieve this important goal. In this review, we will describe these approaches in detail.

It is well established that doping with metals and nonmetals in ZnO structure leads to a band gap red-shift to produce visible-light-active photocatalysts [9]. In the first case, metal doping introduces the shallow- or deep-level states without changes in the band gap, but able to absorb light absorption with longer wavelengths. These intra-band states may also act as a recombination center to decrease the photocatalytic performance. In the nonmetal doping case, incorporation of dopant leads to the creation of local states inside the band gap and the absorption onset of ZnO can be extended from the UV to visible-light region through band gap narrowing [10, 11]. Till now, many studies have revealed that metal-doped ZnO using Ag, Mn, Cu, Co, Fe, Ce, Eu, and Al and nonmetal doping, including N, C, and S, lead to a red-shift in ZnO optical absorption edge to the lower energies and increase the photocatalytic activity in visible-light region. Table 1 summarizes the most abundant dopants used in ZnO structure with synthesis methods, and experimental conditions for visible-light photocatalytic applications.

There are two general classes of synthesis methods for preparation of various doped ZnO nanostructures for photocatalytic applications, wet chemical approaches and gas phase methods. Wet chemical methods include hydrothermal, spray pyrolysis, electrospinning, sol-gel, thermo-mechanical, as well as sonochemical processes and gas phase methods, such as chemical vapor

deposition (CVD) and pulsed laser deposition (PLD). In the present review, we provide insight into progress of doped ZnO nanostructures by different materials and approaches for visible-light photocatalytic activity. Doping with nonmetals, transition metals, rare-earth metals and other metals will be discussed and compared in section 4.

2. Fundamentals of ZnO

ZnO is a II-VI oxide semiconductor with a direct wide band gap of 3.37 eV and a large exciton binding energy of 60 meV at room temperature [23]. Due to its excellent optoelectronic and piezoelectric properties, biocompatibility, environmentally friendly nature, and thermal stability, ZnO nanostructures are the most promising candidate for electronic and optoelectronic applications including light emitting diodes (LEDs), actuators, sensors, field-emission devices, solar cells, ultra-violet laser diodes, photocatalysts, as well as spintronic and piezoelectric devices [24-26]. Considering these advantages, several recent review articles have described progress in the growth and applications of various ZnO nanostructures with different morphologies [27-29]. We briefly report crystal structures and electronic properties of ZnO nanostructures, which undergo changes during the ZnO doping process.

2.1. Crystal structure

ZnO exists in wurtzite, rock-salt, and zinc-blende crystal structures; however, at ambient conditions, the thermodynamically stable phase is the wurtzite structure, (Figs. 1(a) and (b)) with ionicity at the borderline between covalent and ionic semiconductors. The hexagonal wurtzite crystal structure belongs to the $P6_3mc$ class in the Hermann–Mauguin notation or to the C_{6v}^4 class in the Schoenflies notation. The ZnO primitive unit cell (outlined with a thicker line in Fig. 1(a)) contains two formula units, which each zinc ion surrounded by four oxygen ions in a tetrahedral

coordination and vice versa [24]. The noncentrosymmetric tetrahedral coordination in ZnO results in the piezoelectric properties, crystallographic polarity, and is also a key factor in crystal growth and defect generation.

The wurtzite ZnO has four common crystal faces, including the polar Zn-terminated (0001) and O-terminated (000 $\bar{1}$) faces (c-axis oriented), and the non-polar (11 $\bar{2}$ 0) (a-axis) and (10 $\bar{1}$ 0) faces which both contain an equal number of Zn and O atoms. The polar and the (1010) surfaces are found to be stable; however, the (11 $\bar{2}$ 0) face is less stable [23]. The lattice parameters, commonly measured at room temperature by X-ray diffraction (XRD), are $a = 3.25$ and $c = 5.20$ Å with the ratio $c/a = 1.6$ in an ideal wurtzite structure. The a -parameter typically ranges from 3.2475 to 3.2501 Å and from 5.2042 to 5.2075 Å for the c -parameter. The variation in lattice parameters depends on the concentration of foreign atoms, defects, external strains, and temperature [24].

2.2. Electronic properties

The band structure and electronic states of wurtzite ZnO have been calculated by several theoretical approaches and determined experimentally [24]. Fig. 1(c) shows the band structure calculation using the Local Density Approximation (LDA) and incorporating atomic self-interaction corrected pseudopotentials (SIC-PP) [30, 31]. In the valence band, bands located between -10 and -5 eV correspond to the Zn 3d levels, while the upper 6 bands from -5 eV to 0 eV are mainly O 2p orbitals. The first two bands in the conduction band (CB) correspond to empty Zn 4s levels. The band gap value obtained from this calculation was reported 3.77 eV [30]. Further studies on other properties of ZnO, have been reviewed by other researchers [32-34].

2.3. Doped ZnO nanostructures

ZnO is an intrinsically n-type semiconductor due to the deviation from stoichiometry and the presence of intrinsic defects such as oxygen vacancies (V_O), zinc interstitials (Zn_i), and zinc vacancy (V_{Zn}). Doping of ZnO provides a method for controlling its structure, and consequently optical, electrical, and magnetic properties, which leads to a range of changes, including band gap value, transparency, room-temperature ferromagnetism, piezoelectricity and magneto-optical properties [24, 25, 28].

The n-type doping of ZnO with a donor state, achieved by replacing atoms with one or more electrons in the outer shell compared to the substituted element (Zn or O) in ZnO. Consequently, the substitution of group-III elements on Zn sites and group-VII elements on O sites, produces highly conductive n-type ZnO. The p-type doping of ZnO with an acceptor level is provided by substitution of group-I elements on Zn sites and group-V on O sites. Although, ZnO can be easily n-type doped, efforts to obtain reliable p-type doping are still a problem due to the low solubility, much higher ionization and formation energy of p-type dopants [33, 35, 36].

3. ZnO as a photocatalyst

3.1. Historical background

The increase in the world population and industrial growth have led to an increased need for pure water, clean air, and more fossil fuel usage. The combustion of fossil fuel has produced a vast amount of carbon dioxide emission in the atmosphere, and global climate change due to the “greenhouse effect”. Moreover, release of contaminants and pollutants into the air and water results in the global burden of disease. Therefore, in recent years, there has been concerned about global environmental issue and potential future energy crisis. The heterogeneous photocatalytic

process has been utilized as a promising solution for both energy generation and environmental problems [37]. Since the first discovery of the photocatalytic water splitting to hydrogen and oxygen by Fujishima and Honda [38], extensive work on heterogeneous photocatalysis has been published in an attempt to minimize the energy crisis. In addition, photocatalysis is applied in many areas for environmental applications, including air and water treatment [9], self-cleaning processes [39], disinfection reactions [40], green organic synthesis [41] and renewable energy production such as hydrogen evolution via water-splitting [42] and CO₂ reduction to hydrocarbon fuels [43]. Various applications of ZnO photocatalysts in the environment and energy fields are illustrated in Fig. 2(a).

ZnO nanostructures with different morphologies and properties have attracted much attention for photocatalytic applications, in both environment and energy fields. Up to now, more than 2500 papers have been published on the photocatalytic performance of ZnO nanostructures. All of this research investigated the influence of different factors, such as preparation method, composition, morphology, size, specific surface area, porosity, and crystalline phase. Fig. 2(b) shows the trend of publications of ZnO nanostructures as a photocatalyst in the last 15 years. It shows an evolution and an exponential growth of research for both pure and doped ZnO nanostructures.

3.2. Principles of heterogeneous photocatalysis

Catalysis plays an important role in petrochemical, refining industries, food processing and environmental remediation [44, 45]. To increase the rate of these chemical processes, UV-visible photo-irradiation can be used on a particular semiconductor photocatalyst under certain conditions. The overall process of heterogeneous photocatalysis pathways is shown in Fig. 3. Photocatalytic processes in ZnO occur with absorption of light radiation with sufficient energy

($h\nu$) to be equal to or greater than the ZnO band gap energy ($h\nu \geq E_g$). Photon absorption causes excitation and transfer of electrons (e^-) from the valence band (VB) to the conduction band (e_{CB}^-), which leads to holes (h^+) generation in the valence band (h_{VB}^+). The separation and migration of charge-carriers (e^- and h^+) to the ZnO surface are the second step. Recombination of electrons and holes may occur with release of heat or photons, leading to the reduction of quantum yield for the photocatalytic process. The recombination rate is strongly influenced by various parameters with correlation to the nature of ZnO nanostructures [46, 47]. The highly reactive electrons and holes at the surface of ZnO photocatalyst tend to perform reduction and oxidation reactions to produce hydroxyl radicals ($\bullet OH$) and superoxide anion radicals ($O_2^{\bullet -}$), respectively. In ZnO, the bottom level of the conduction band potential (-0.5 V vs. normal hydrogen electrode, NHE) is more negative than the redox potential of $O_2/O_2^{\bullet -}$ (-0.33 V vs. NHE), therefore, superoxide anion radicals can be produced by electrons. In contrast, the top of the valence band potential (+2.7 V vs. NHE) is more positive than the redox potential of $\bullet OH/H_2O$ (+2.53 V vs. NHE), so water molecules can be oxidized by holes to form hydroxyl radicals. The photocatalytic process proceeds with the participation of these reactive radical species through the following reactions [48]:

According to kinetic analyses, it has been found that the photocatalytic degradation of organic pollutants obeys a Langmuir–Hinshelwood mechanism and follows a quasi-first-order reaction with the photocatalytic decomposition rate (r) defined by [49]:

$$r = -dC(t)/dt = k_{obs}C(t) \quad (8)$$

where k_{obs} is the observed rate constant and $C(t)$ is the concentration of reactants at time t . When the concentration is very low, the apparent rate constant (k_{app}) was determined from the simplified Langmuir–Hinshelwood model as given below:

$$\ln(C_0/C) = k_{app}t \quad (9)$$

where C_0 is the initial concentration of the substance before photocatalysis. Hence, the linear fit between $\ln(C_0/C)$ and irradiation time demonstrates the photocatalytic decomposition rate. A higher k_{app} values indicates a better photocatalytic activity of an investigated sample.

3.3. Modification strategies for visible-light activity

Due to the wide band gap of ZnO, ultraviolet (UV) light must be used as the photo-initiation source. This is the major limiting factor in the application of ZnO photocatalysts because the solar spectrum constitutes of only a small fraction of UV light (~4%). Therefore, ZnO photocatalysts exhibit a poor performance under solar radiation. To harvest solar radiation, it is required to modify electronic property of ZnO nanostructures. Various strategies have been employed to improve the photocatalytic efficiency of ZnO under visible light, which contains a large fraction of the solar spectrum [8, 50, 51]. Development of visible-light-active (VLA) ZnO can be achieved by the following approaches: i) surface modification via dye sensitization, organic compound sensitization, polymer sensitization, coupling with a narrow band gap semiconductor and ii) band gap engineering with creation of defect states as well as metals and nonmetals doping. These methods have been investigated by many groups and reviewed [8, 52-

54]. Moshfegh's group has also successfully modified ZnO nanostructures toward the development of visible-light-active photocatalysts through both surface modification and band gap engineering [13, 55-61]. Doping with metals and nonmetals is being widely considered to extend the absorption wavelength range of ZnO through modifying the electronic band structure in visible-light spectrum without decreasing photocatalytic activity [10]. In the following section, we will describe various methods to modify ZnO photocatalysts for visible-light activity via doping.

4. Visible-light-responsive doped ZnO photocatalysts

Generally, photocatalytic reactions under visible light require band gap narrowing of ZnO. Band gap narrowing through ZnO doping can be achieved by three main approaches, i) the elevation of the valence band maximum, ii) lowering of the conduction band minimum and iii) introduction of localized energy levels within the band gap [37]. Fig. 4 illustrates the three different situations for achieving visible-light-driven photocatalysts such as ZnO by metal and nonmetal doping [11].

Metal doping has been proven to shift the absorption edge of the semiconductor photocatalyst to the visible range using less than 10 at% of foreign cations [37]. The interaction of the metal cation states with the valence or conduction band of ZnO leads to the creation of intra-band gap levels and induces band gap narrowing. Fig. 4(a) shows p-type doping with metal ions as electron acceptors, which introduces a level below the original conduction band in the band gap. In addition, n-type doping of metal ions as an electron donor creates a level above the valence (see Fig. 4(b)). These new states are able to absorb light with longer wavelengths. Depending on the electronegativity, ionic radius and concentration, the metal dopants occupy

substitutional or interstitial sites in the ZnO lattice or segregate to grain boundaries. Although, the mid-gap level states created by metal doping extend the light absorption to visible-light range, they may deteriorate the photocatalytic activity because the new states can act as charge recombination centers [11].

In the nonmetal doping case, as depicted in Fig. 4(c), doping creates a new valence band state that leads to band gap narrowing by elevating the valence band maximum. Therefore, unlike metal doping, nonmetal doping is less likely to form recombination centers. Thus, nonmetal doping is more effective to improve the photocatalytic activity of ZnO under visible light [10, 11, 48]. It is worthwhile to note that new band states created by doping should possess sufficient oxidation potential of hydroxyl radicals and reduction potential of superoxide radicals to produce reactive $\bullet\text{OH}$ and $\text{O}_2^{\bullet-}$ radicals (Eqs. 2 and 3) for the photocatalytic degradation reaction [37].

4.1. Nonmetal Doping

Nonmetal doping of ZnO, which is expected to substitute for oxygen atoms, has been intensively investigated. In this regard, different photocatalysts with promising results under visible light have been obtained. As discussed above, hybridization of nonmetal dopant orbitals and O 2p states of ZnO raise the upper edge of the valence band and thus narrow the band gap. Elements with lower electronegativity than oxygen and similar size to that of lattice O atoms are two main requirements for effective nonmetal dopants [37]. ZnO doping with nonmetals, such as carbon (C), nitrogen (N), and sulfur (S) can lead to the formation of intermediate energy levels and extend the valence band, which causes visible-light photocatalytic activity [62, 63]. Details of ZnO doping process by various nonmetals and consequent results are discussed.

4.1.1. *N-doped ZnO*

Until now, among all nonmetal dopants, nitrogen has attracted the most attention. This is due to its advantages, including the similarity of nitrogen and oxygen ionic radii, N 2p and O 2p energy states, high solubility, and also low formation energy. Hybridization of N 2p and O 2p states raises the valence band upper edge and thus, band gap narrowing occurs [64-66]. Fig. 5(a) shows the two main routes of nitrogen doping in ZnO structure, including the replacement of oxygen by nitrogen (substitutional sites) or occupation of interstitial sites [67, 68]. Density functional theory (DFT) calculations have been used to provide a detailed description of the band structure and electronic property of N-doped ZnO [67, 68]. The results show only a very small structural rearrangement after substitutional doping; the corresponding new states are located only 0.30 eV above the top of ZnO valence band (see Fig. 5(a)). In addition, interstitial N occupies either octahedral or tetrahedral voids. In the more stable octahedral voids, N inserts between a lattice O and two adjacent Zn ions, resulted in N–O bond formation with a new energy state 1.4 eV above the ZnO valence band [67]. Lu et al. [69] used first-principles electronic structure calculations with a hybrid density functional and found that nitrogen substitutional doping alone was not responsible for expanding the valence band edge to longer wavelength. Instead, nitrogen dopant causes formation of oxygen vacancies and Zn interstitials during doping, which creates an appropriate electronic structure for band gap narrowing.

To verify whether N is successfully doped at O sites, X-ray photoelectron spectroscopy (XPS) characterization has been widely used. For substitutional nitrogen doping, the binding energy of the N 1s state changed from 396 to 398 eV, and 400 to 406 eV for interstitial nitrogen doping [70]. Fig. 5(b) shows high-resolution XPS spectra of N 1s for the N-doped ZnO with peaks at 396.2, 397.1, 398.7, 399.7 and 401.6 eV [71]. The two peaks located at 396.2 and 397.1

eV are related to N–Zn–N bonds and the peaks at 398.7 and 399.7 eV are assigned to O–Zn–N bonds. The peak located above 400 eV is attributed to chemisorbed species such as NO[−] or NO₂ (also see ref. [65]).

XRD is another technique to confirm the nitrogen incorporation site in ZnO lattice. The diffraction peaks shift slightly toward higher angles with a decrease in the lattice parameters, and peak broadening occurs [64, 72]. Rajbongshi et al. [72] have studied the influence of N-doping on photocatalytic activity of ZnO nanoparticles under visible-light irradiation using Raman spectroscopy. They reported two peaks at 585 and 642 cm^{−1} attributed to the local vibrational modes of the Zn–N bond due to nitrogen doping. In addition, they found that the high activity of N-doped ZnO is related to oxygen vacancies and the formation of defect states. The effect of N doping on the retardation of photo-generated electron/hole recombination was attributed to the wide photoluminescence (PL) spectrum signal with intensity quenching in the visible region.

Depending on the source of nitrogen doping and preparation methods, different properties of N-doped ZnO can be observed. Ferrari-Lima et al. [70] reported that N-doped ZnO from ammonium hydroxide possessed a higher specific surface area, which they attributed to the controlled nucleation and growth of crystallites in the presence of nitrogen. Contrary to this, Wu [73] obtained a smaller specific surface area for N-doped ZnO than for pure ZnO using NH₄NO₃ as the nitrogen source, due to the collapse of small pores in ZnO sample during calcination. Macías-Sánchez et al. [12] prepared N-doped ZnO by sol–gel with various [N]/[Zn] ratios using urea as the nitrogen source for visible-light photocatalytic degradation of 2,4-D and picloram herbicides. Different specific surface area, crystallite size and E_g were obtained for different amounts of nitrogen doping. Their results show that 30 wt% N-doped ZnO photocatalyst decreases the band gap by 0.19 eV and provides the highest photocatalytic efficiency. N-doped

ZnO nanoparticles using melamine as nitrogen source for the degradation of methyl orange dye under simulated daylight was studied by Sun et al. [74]. Their results are shown in Fig. 5(c) for the photocatalytic degradation of pure ZnO, TiO₂ and N-doped TiO₂. N-doped ZnO exhibits approximately 3.8 and 1.5 times higher photocatalytic efficiency than pure ZnO and N-doped TiO₂, respectively.

Yu et al. [66] investigated the crystallinity-dependence of ZnO for substitutional nitrogen doping via heating in ammonia gas. They found that defects in the semi-crystalline ZnO particles favored the nitrogen incorporation at 400 °C. However, higher temperature was required for N-doping of highly-crystalline ZnO, causing the undesired conversion of substitutional nitrogen to molecular nitrogen. Bhirud et al. [75] studied the effect of heat treatment at 500, 600, 700 and 800 °C for the preparation of the N-doped ZnO nanostructures by wet chemical methods using urea as a nitrogen source; conductivity type was determined by ‘hot probe’ method. The results show that N-doped ZnO converts to p-type material when heated in the temperature range 500–700 °C, and then transforms to n-type like pure ZnO at 800 °C.

Nanocomposites consisting of N-doped ZnO/g-C₃N₄ core shell nanoplates were synthesized for visible-light photocatalytic degradation of rhodamine B and the results were compared to that of pure ZnO and g-C₃N₄ [76]. The photocatalytic degradation rate of N-doped ZnO/g-C₃N₄ with 5 wt% g-C₃N₄ was 40 times higher than that of pure ZnO, more than 10 times higher than N-doped ZnO and 6 times higher than that of bulk g-C₃N₄ under visible-light irradiation. The mechanism of visible-light photocatalytic degradation and charge transfer in N-doped ZnO/g-C₃N₄ core shell structure was investigated in the presence of the charge-carrier scavengers and the results verified the Z-scheme mechanism (see Fig. 5(d)). As shown in the figure, photo-excited electrons in the CB of N-doped ZnO transfer to the VB of g-C₃N₄ via fast

recombination. Ultimately, accumulated electrons in the CB of g-C₃N₄ and holes in the VB of N-doped ZnO participate in reduction and oxidation photocatalytic reactions, respectively.

4.1.2. C-doped ZnO

Carbon doping is the second most popular approach for nonmetal doping of ZnO and has received considerable interest during recent years. Pan et al. [77] have studied the structural and magnetic properties of pure and C-doped ZnO by DFT calculations. The formation energies of carbon doping have been calculated and the results show that carbon incorporation occurs with carbon oxidation number ranging from -4, by replacing an oxygen atom (C_O), to +4 by the formation of carbonate species (C_{Zn}+2O_i). Carbon substitutional doping on Zn sites (C_{Zn}) and interstitial carbon (C_i) are also observed [78]. Tan et al. [78] calculated the formation energy of C doping by ab initio methods and showed that the formation energy of C_{Zn} and C_{Zn}+2O_i increased with decreasing of oxygen partial pressure and the formation of CO/CO₂ species occurred in an oxygen rich ambient. They also found that C_{Zn} is a donor state with the lowest formation energy and C_{Zn}+2O_i is an acceptor state with a relatively high formation energy.

Liu et al. [79] fabricated hierarchical flower-like C-doped ZnO superstructures by pyrolysis and used them for the photocatalytic degradation of rhodamine B dye and 4-Chlorophenol under visible-light irradiation. Their XPS analysis clearly show the formation of C_O with related Zn–C bonds, and of C_{Zn} with related Zn–O–C bonds, as well as adsorbed carbonate or carbon dioxide in ZnO lattice. For further elucidation of the origin of visible-light absorption, they used DFT to calculate the band structure and density of states (DOS) for pure and C-doped ZnO. They demonstrated that the localized state of C 2p energy levels appeared near the Fermi level; therefore, electrons in the VB of C-doped ZnO transferred to these new

states and then to the CB of ZnO, as a result of visible-light excitation. Cho et al. [80] synthesized C-doped ZnO nanostructures with vitamin C as a carbon dopant source and studied the photocatalytic degradation of orange-II dye under visible light. They have used energy-dispersive X-ray spectroscopy (EDS), XPS, and XRD characterization in order to elucidate the formation of C_O and Zn–C bonds (see also ref. [81, 82]). Comparing XRD lattice constants showed a lattice expansion in C-doped ZnO, which indicated that C⁴⁻ with larger ionic radius of 260 pm is substituted instead of smaller O²⁻ with 140 pm ionic radius (see also ref. [81, 83]). In contrast, in the other work, the lattice constant of C-doped ZnO became smaller, which indicated C⁴⁺ with an ionic radius of 16 pm is substituted for the larger Zn²⁺ with an ionic radius of 74 pm [13, 84].

Moshfegh's group [13] recently utilized multi-walled carbon nanotubes (MWCNTs) as a source of carbon doping in C-doped ZnO nanofibers applied as a photocatalyst for degradation of methylene blue dye under visible light. As shown in Fig. 6(a), comparing Raman spectra of MWCNT with C-doped ZnO indicated a downward shift in peak positions due to the formation of new Zn–O–C bonds between MWCNT and ZnO as a result of C_{Zn} formation. As evidence for visible-light activity and band gap narrowing of C-doped ZnO, band gap energy was also calculated using Tauc's formula. Based on data analysis, band gaps of 3.13 and 3.01 eV are obtained for pure and MWCNT-doped ZnO, respectively (Fig. 6(b)). Fig. 6(c) illustrates the mechanism for photocatalytic activity of MWCNT-doped ZnO under visible-light irradiation. MWCNTs as a photo-sensitizer absorb visible-light irradiation and transfer the photo-generated electrons into the CB of ZnO for dye degradation on the ZnO surface; the positive-charged CNTs remove electrons from the VB of ZnO and left holes behind. Zhu et al. [81] prepared C-doped ZnO/g-C₃N₄ nanocomposites which showed enhanced visible-light photocatalytic activity for the

degradation of methylene blue dye in comparison to pure ZnO, g-C₃N₄ and mechanical-blended ZnO/g-C₃N₄. Recently, Moshfegh's group [57] investigated the effect of oxygen vacancy (V_O) and interstitial carbon doping (C_i) on the photocatalytic performance of C-doped ZnO electrospun nanofibers. Fig. 7(a) shows enhanced photo-degradation of methylene blue dye on C-doped ZnO vs. pure ZnO under visible-light irradiation. It was found that the synergistic effect of V_O and C_i played an important role in obtaining better photocatalytic activity. They studied the recombination rate of electrons and holes during the reaction using PL. Fig. 7(b) shows PL signal quenching and retardation of e/h recombination in C-doped ZnO in comparison to pure ZnO.

Photoelectrochemical (PEC) water-splitting reaction on C-doped ZnO was also investigated to produce H₂ as a solar energy fuel [85, 86]. Kochuveedu et al. [86] described the incorporation of C into the ZnO lattice causing formation of carbonate species. Their results show the creation of a new energy level above the VB of ZnO by the hybridization of O 2p and C 2p orbitals leads to band gap narrowing. They found that the PEC activity rate for C-doped ZnO was ten times more efficient than for pure ZnO photo-anodes under similar conditions.

4.1.3. S-doped ZnO

Due to the larger Bohr radius of the S atom than O and the difference in their electronegativity, it is suggested that sulfur doping of ZnO can modify its optical, electrical and photocatalytic properties. Photocatalytic properties of S-doped ZnO under visible light have not been investigated widely and are somewhat controversial. Particularly, there are some reports about the band gap broadening due to the S doping because of the Burstein–Moss effect [87, 88]. In contrast, other reports have indicated band gap narrowing [14, 89]. These contradictory results

on S-doped ZnO must be clarified using a specific concentration and doping methods from both theoretical and experimental viewpoints.

Theoretical and experimental studies of S-doped ZnO can provide useful information on the role of S atom doping and material properties. Zhang et al. [90] used DFT calculations to investigate the relation between sulfur doping and photocatalytic activity. They reported that the physical properties of S-doped ZnO are influenced by the different substitutional sites of S in ZnO lattice. For S_O-doped ZnO, the S 3p states are located above the valence band and mix with O 2p states which result in band gap narrowing. They described the crucial factors in the photocatalytic activity of S-doped ZnO which correlate with introduction of V_O and V_{Zn} in ZnO crystal lattice and retardation in electron/hole recombination.

4.2. Metal doping

4.2.1. Transition metal doping

Transition metal (TMs) doping in ZnO crystal lattice is one of the well-known strategies for tuning the band gap of ZnO to make it a visible-light-active photocatalyst [50, 91]. TM doping can modify the morphology, particle and crystallite size of ZnO host. It is well established that TM doping inhibits ZnO growth, which leads to the production of smaller nanostructures with higher surface area [92]. Substitution of TM cations modify the environment of Zn in ZnO lattice and change its electronic band structure and introduce many crystal defects such as oxygen vacancies. Oxygen vacancies may act as efficient electron traps and lead to an enhancement in photo-generated electron/hole separation efficiency [93]. Transition-metal dopants have often been used because of their non-full d or f orbitals [94]. The ZnO optical absorption edge extends into visible-light region after TM doping. Actually, as depicted in Fig.

4(a) and (b), the energy band gap value of ZnO is not changed by TM doping, but incorporation of the dopants induces mid-gap energy states which can be excited by visible light [94]. It is well accepted that this is related to the sp-d spin exchange interaction between ZnO band-edge electrons with localized d-electrons of the TM ion [95]. The electronic transitions associated with TM-doped ZnO nanostructures could be assigned to three types of transitions, which are described as follows: i) electron excitation from the VB to CB of ZnO host, ii) dopant-induced d–d internal transitions and iii) charge transfer transitions between the host CB and the dopant d-state and also between the host VB and the dopant d-state [96]. Type (ii) and (iii) transitions can occur under visible light. Photo-generated holes remain in the VB of ZnO and then migrate to the surface to produce active •OH radicals. The excited electrons are trapped in the TM dopant sites, and then react with the adsorbed O₂ to produce O₂^{•-}. These active species participate in photocatalytic degradation reactions.

Some transition metals such as Fe and Cu have oxidation states which can be useful to increase the activity of ZnO photocatalysts. ZnO doping with appropriate concentrations of Fe and Cr can result in the formation of photocatalyst with ferromagnetic properties which is beneficial for photocatalyst gathering from the environment after the degradation reaction. There have also been some reports showing that ZnO photocatalytic activity was significantly decreased after doping with TM ions such as Fe, Co, Ni and Mn. In the following sections, the role of TM dopants including Ag, Mn, Cu, Fe, and Co will be reviewed.

4.2.1.1. Ag-doped ZnO

Introduction of Ag in ZnO nanostructures has received great attention to make ZnO a visible-light-active photocatalyst [97-101]. Many discussions have been presented to explain the

function of Ag, when it is doped in ZnO crystal lattice. Li et al. [102] investigated the structural, electronic, and optical properties of Ag-doped ZnO using first-principles calculations. Their results reveal that Ag ions act as an electron acceptor in ZnO material. Therefore, it can be used to generate p-type conductivity in pristine ZnO. Moreover, introducing Ag creates acceptor levels inside the ZnO energy band gap and, as a result, decreases the E_g value. But, according to their results, in some cases Ag-doped ZnO shows n-type conductivity behavior. In addition, they considered 2.08 at% Ag dopant concentration, which contained one Ag substitution at an interstitial sites (Ag_i), one Ag substitution at an O site (Ag_O) and one Ag substitution at a Zn site (Ag_{Zn}). They calculated the formation energies (E_f) for a single Ag dopant in these different positions under Zn-rich and O-rich conditions. Their results show that E_f values are the lowest for the Ag_{Zn} substitution, which indicates that the Ag dopant prefers to substitute on the Zn site under both O-rich and Zn-rich environments. In addition, the results of partial density of states (PDOS) calculations have shown that for Ag_{Zn} -doped ZnO, a new acceptor state is created above the VB. Therefore, electrons can be excited from the VB to this gap state, which leads to a visible-light absorption edge. As the Ag doping concentration increases, more impurity mid-gap states are introduced, causing a significant red-shift of absorption edge. Ag_O substitution creates Ag 5s gap states and shifts the Fermi level upward into the CB. Thus, Ag_O -doped ZnO exhibits n-type semiconducting character. The authors concluded high concentrations of the Ag_{Zn} and Ag_O would be effective methods to make ZnO a visible-light-active photocatalysts.

Incorporation of the Ag ion in ZnO crystal lattice has been confirmed by XRD, XPS and Raman spectroscopy. Since the Ag^+ radius is larger than the Zn^{2+} radius, so the unit cell volume increases [15]. As a result, substitution of Ag in ZnO lattice leads to a measurable peak shift toward lower XRD 2θ values (see Fig. 8) [103]. XPS spectrum of the core level region of Ag

$3d_{5/2}$ in the Ag-doped ZnO shows a peak shift toward lower value compared to the bulk Ag (368.0 eV) due to the formation of Ag-O-Zn bond [104]. Raman spectra peak shifts toward the higher wave number, indicates the lattice expansion of doped ZnO due to the Ag substitution [98].

Due to the larger radius of Ag^+ than Zn^{2+} , Zn ions may be hardly substituted by Ag ions. Therefore, more incorporation of Ag in ZnO than a critical value leads to the aggregation of Ag atoms at the grain boundaries and formation of separated particles and clusters [15, 97, 105]. Amornpitoksuk et al. [15] synthesized nanocrystalline Ag-doped ZnO powders via a precipitation method at low temperature with various concentrations of Ag precursors. They found that when the Ag loading is less than or equal to 0.5 mol%, Ag ions introduce in ZnO lattice by substitution on Zn^{2+} sites. But, if Ag doping increases more than this critical value, from 0.6 to 1.0 mol%, Ag atoms bond together and form Ag clusters at the ZnO grain boundaries. Shinde et al. [98] approved that when Ag doping exceeds the optimum value, electron mobility of ZnO thin films decreases due to enhancement in the film disorder. Therefore, at high doping concentration, the Ag-substituted Zn^{2+} ions play as an electron acceptor levels, which compensate the donors and decrease the conductivity and photocatalytic activity of ZnO films.

4.2.1.2. Mn-doped ZnO

Manganese is the second interesting material to modify the optical properties and enhance the photocatalytic activity of ZnO nanostructures [16, 96, 106-111]. Mn^{2+} radius is nearly close to Zn^{2+} radius with the same cationic charge, so it can be easily replaced the Zn^{2+} in ZnO lattice without any significant crystal changes. The origin of the broad absorption band via

manganese doping is ascribed to the d–d transition from ZnO 6A_1 ground state to Mn^{2+} excited states of 4A_1 , 4T_2 and 4E . The excited states create as a result of the crystal field splitting of free Mn^{2+} ion (4G state) inside ZnO band gap [108]. Therefore, charge transfer between Mn-induced levels and VB as well as d–d transition in the crystal field can be induced by visible-light irradiation [96]. Both defect-induced and Mn-induced mid-gap states as an intermediate step, cause an electrons excitation from VB to the CB by absorbing two or more visible photons instead of a UV photons [109]. Various possible photo-excitations (and so emissions) of Mn-doped ZnO nanoparticles and the contribution of intermediate steps is depicted in Fig. 9.

The addition of Mn precursors during the preparation procedure of ZnO can affect the final product morphologies [96, 107]. Moreover, Mn induces a large strain during the ZnO nanoparticle growth and results in the formation of small particles and crystallites with higher surface area and enhanced photocatalytic activity [92, 106, 111, 112]. One of the important effect of Mn doping is related to increase in the defect concentrations, especially oxygen vacancies [16, 108, 109]. These defects act as the charge-carrier traps to separate photo-induced electron/hole pair and increase their lifetime. Intensity reduction of the PL spectra of Mn-doped ZnO is another evidence for this phenomenon [96, 111].

Various reports have shown a better photocatalytic activity of Mn-doped ZnO than pure ZnO, however, there has been also some research show a decrease of photocatalytic activity via doping [92, 112, 113]. If the Mn doping concentration is higher than the optimum value, the average distance of trapped carriers reduces, and Mn dopant sites can act as an efficient recombination center to decrease photocatalytic activity [96]. In addition, at high concentrations, Mn^{2+} ions prefer to react more readily with lattice oxygen to form MnO_x species instead of substitution to the Zn^{2+} sites [16]. The MnO_x formation increases the energy band gap of Mn-

doped ZnO and reduces photocatalytic activity under visible light. Therefore, Mn doping increases photocatalytic activity in some reports and decreases in some others.

4.2.1.3. Cu-doped ZnO

Copper is an inexpensive element and its size is near to that of Zn, therefore, Cu^{2+} can simply penetrate in the substitutional sites of ZnO lattice and modify the absorption and emission spectrum into visible-light region [17]. This modification was attributed to the induction of localized Cu 3d states in ZnO band gap [114]. The intra-band transition between Cu 3d and Zn 4s in the conduction band causes visible-light absorption in Cu-doped ZnO [115]. Substitution of Cu^{2+} on the Zn^{2+} sites was confirmed by the shrinkage of ZnO crystal lattice that caused the broadening and shifting of the XRD patterns toward larger 2θ [17]. In addition, the substitution of Cu dopant increases the concentration of interstitial Zn, oxygen and Zn vacancies, which causes the appearance of more intense PL spectra in comparison to pure ZnO [17]. Fig. 10 illustrates band gaps of Cu (1.0 – 5.0 at%)-doped ZnO nanoparticles using Tauc's formula. The band gaps decrease as the Cu doping concentrations increase from 1.0 to 4.0 at% and increases at Cu 5.0 at% doping [17].

Cu-doped ZnO has been prepared by different methods for various photocatalytic degradation reactions and its properties have been studied by different researchers. Polat et al. [114] prepared Cu doped ZnO nanorods on glass substrate by chemical bath deposition for methylene blue degradation. They observed a morphological change from pyramidal geometry to hexagonal rod shape by increasing the Cu contents from 1 to 3 at.%. Fu et al. [116] synthesized Cu-doped ZnO nanoparticles to study the photocatalytic degradation of methyl orange under UV light. The PL results show that increased concentrations of Cu up to 0.5% leads to a decrease in

the recombination rate of photo-generated electrons and holes. Cu^{+2} ions with half-filled electronic configuration act as an electron trap and cause the reduction in e/h recombination. However, the addition of higher amounts of Cu can act as a recombination center to decrease the photocatalytic activity. Mohan et al. [117] prepared Cu-doped ZnO nanorods with narrower band gap using vapor transport method for photo-degradation of resazurin dye. They show that Cu doping in ZnO leads to the creation of more hole trapping centers, surface defects, and surface oxygen vacancies which cause an enhancement in the photocatalytic activity. Jongnavakit et al. [118] used XPS technique and showed that the oxidation states of Cu in Cu-doped ZnO are as a Cu^+ and Cu^{2+} . They determined that Cu^+ improves the formation of $\bullet\text{OH}$ radicals for the photocatalytic degradation by the following mechanism:

In addition, the results show that 0.5 mol% copper performs the best photocatalytic activity for methylene blue degradation due to the higher ratio of $\text{Cu}^+/\text{Cu}^{2+}$ contents.

4.2.1.4. Co-doped ZnO

Cobalt doping has also gained a great attention to prepare highly active ZnO visible-light-responsive photocatalysts. The effective Co^{2+} ionic radius is slightly smaller than the Zn^{2+} , therefore, Co^{2+} can be easily substituted to Zn^{2+} sites without any significant distortion in the lattice structure [93, 119, 120]. The incorporation of Co in ZnO lattice leads to the shift in the optical absorption edge toward visible-light region and band gap energy narrowing [18, 119-125]. The band gap reduction is referred to the s–d and p–d exchange interactions between the localized d electrons of the Co^{2+} ions and ZnO band electrons. The Co^{2+} 3d levels locate within

ZnO band gap, which create a new spectral bands in visible-light region, including the ligand-field (d–d) transitions centered at the dopant and charge-transfer (CT) bands [121, 123, 125-127].

It is found that the addition of Co ion during the preparation process hinders the growth of ZnO nanoparticles and produces smaller particle size with higher effective surface area favored in the photocatalytic activity [18, 93, 121]. Photocatalytic activity enhancement of Co-doped ZnO nanostructures is also related to the combined effects of higher concentration of oxygen vacancies and defects [18, 93, 119, 122]. The oxygen vacancy levels act as electron scavengers and thus, improve charge separation, reduce e/h recombination rate and enhance visible-light photocatalytic activity. It is worthwhile to note that very high concentration of Co doping may create a higher concentration of oxygen vacancies and act as the recombination centers for e/h pair [123]. Kuriakose et al. [18] synthesized Co-doped ZnO nanorods and nanodisks by a facile wet chemical method. They reported 91% degradation of 10 μ M methyl orange and methylene blue dyes in just 8 minutes.

Although many reports have been shown that Co doping increases the photocatalytic activity of ZnO nanostructures; in some reports, it decreases significantly [92, 106, 113, 120, 123, 127]. To find the origin of this discrepancy, some systematic theoretical and experimental investigations have been performed [126, 128]. The results show that there are some major features observed in Co-doped ZnO energy window, including the ZnO band-to-band absorption, the $\text{Co}^{2+/3+}$ donor-type photo-ionization (or metal-to-ligand charge transfer (ML_{CBCT})), the $\text{Co}^{2+/+}$ acceptor-type photo-ionization (or ligand to metal charge transfer ($\text{L}_{\text{VB}}\text{MCT}$)) and the structured $^4\text{A}_2 \rightarrow ^4\text{T}_1(\text{P})$ d-d band transition. These transitions are depicted in Fig. 11. If $^4\text{T}_1(\text{P})$ of the Co^{2+} excited state locates near or in the CB of ZnO, the photo-excited d electrons of Co^{2+}

relax to the $ML_{CB}CT$ band follow by electron transfer into the CB. As a result, the enhancement of visible-light photocatalytic activity achieves. But, if the ${}^4A_2 \rightarrow {}^4T_1(P)$ d–d transition lies below the $ML_{CB}CT$ threshold, d-d photo-conductivity is not observed [126]. Johnson et al. [128] showed experimentally that alignment of these transition levels depends strongly on both Co^{2+} concentrations and the growth temperature. They found that ${}^4T_1(P)$ excited state locates slightly above the $ML_{CB}CT$ state at low Co^{2+} concentrations (~ 0.8 at%), but it is below the $ML_{CB}CT$ state at higher concentrations (~ 11 at%). Therefore, d-d photo-conductivity can be observed in the former but not in the latter. In conclusion, Co substitution induces transition levels, which can increase or decrease the photocatalytic activity of ZnO host depending on the preparation conditions and doping concentrations.

4.2.1.5. Fe-doped ZnO

Similar to the other transition metal doping, sp-d orbitals exchange interactions between localized Fe d electrons and ZnO band electrons, cause band gap narrowing and increase in electron excitation rate [129, 130]. Presence of Fe species during ZnO preparation procedure show strong influence on the nanostructure morphologies and commonly reduce the crystallite and particle sizes with higher surface area [95, 131-134]. In addition, Fe incorporation in ZnO crystal lattice induces defects, especially increases oxygen vacancies. Appropriate concentrations of defects act as electron-trap centers and increases electron/hole separation efficiency [19, 95, 135, 136].

Ferromagnetic properties of Fe-doped ZnO nanostructures is another interesting issue which enable doped products gather by simple magnetic routes from aqueous solutions after the photo-degradation process [135, 137]. Another important property of Fe dopant is different

oxidation states, namely Fe^{2+} , Fe^{3+} and Fe^{4+} [19, 95, 133, 135]. The redox potential of $\text{Fe}^{3+} / \text{Fe}^{2+}$ is 0.771 V, which locates between the VB and CB of ZnO and act as charge-carrier trap [19]. The photocatalytic degradation of water pollutants in the presence of Fe-doped ZnO nanostructures can be described as follows [19, 133]:

The produced $\bullet\text{OH}$ and $\text{O}_2^{\bullet-}$ radicals are extremely active oxidant species to decompose the pollutants. If Fe is doped higher amounts than the optimum concentration, the availability of Fe-induced traps increase. In this situation, Fe sites act as recombination centers because the Fe^{4+} reacts with electrons to produce Fe^{3+} and Fe^{2+} , then, Fe^{2+} reacts with hole to give Fe^{3+} (see Fig. 12). Thus, the photo-induced electron/hole cannot produce active oxidant species and photocatalytic activity reduces [19, 95].

Similar to the other metal doping, there are also some reports showing that Fe doping reduces photocatalytic activity [19, 129, 131]. In these reports, defects, crystal distortion, and also high concentration of Fe-induced mid-gap states have been correlated to the reduction of doped ZnO photocatalytic activity.

4.2.2. Rare-earth metal doping

The incorporation of rare-earth (RE) elements in ZnO structure is also explored as an attractive strategy to modify the electronic structure and extends the absorption to visible light. Changes in the band gap energy are attributed to i) localized impurity level band formation by RE metals, ii) potential fluctuation introduced by the ionized impurities, iii) charge transfer between ZnO valence or conduction band and the 4f and 5d states of RE metals [138]. In addition, due to the RE metal's ability to trap the electrons, doping leads to efficiently suppress the photo-generated electron/hole recombination. Despite the advantages of the RE-doping in ZnO lattice, they may have some problems such as low saturated concentration of RE ions in ZnO lattice due to the difference in ionic size, charge and unsuitable energy level position of RE ions relative to the VB and CB of ZnO [139]. In this review, doping of ZnO with cerium (Ce), europium (Eu), lanthanum (La), and dysprosium (Dy) and their photocatalytic applications will be considered. These RE metal dopants are more investigated based on the recent published papers and are useful from practical applications due to the absorption of visible-light region.

4.2.2.1. Ce-doped ZnO

Cerium doping in ZnO nanostructures increases photocatalytic activity and stability [140, 141]. Ionic radii of both Ce^{4+} and Ce^{3+} are much bigger than Zn^{2+} ion. So, the Ce substitution instead of Zn leads to increase unit cell volume and peak shift toward lower XRD 2θ values. Due to compensation of electrical neutrality after doping, the discrete impurity states create below ZnO conduction band. Therefore, some new electronic transition states are induced from the ZnO valence band to various new energy levels, and visible-light absorption obtains [20]. Recently, Moshfegh's group found more information about the electronic and oxidation states of Ce in ZnO lattice by high-resolution XPS analysis [56, 142]. They show the co-existence of both Ce^{3+} and Ce^{4+} by analyzing C 3d core level of XPS spectrum [142]. Their results indicate that the

Ce/Zn and $\text{Ce}^{3+}/\text{Ce}^{4+}$ ratio strongly depend on the preparation conditions. Both Ce/Zn and $\text{Ce}^{3+}/\text{Ce}^{4+}$ ratios increase by annealing temperature from 180 to 500 °C. Detail of the XPS analysis of Ce 3d core level spectra of samples prepare under different annealing temperatures are compared in Fig. 13(a). Increase in the Ce/Zn ratio indicates that Ce atoms diffuse into the sample surface via annealing at higher temperatures. Deconvolution of Ce 3d core level in Fig. 13(b) provides useful information and obviously indicates ten fitted peaks [56]. The complexity of XPS spectra attributes to the hybridization between the Ce 4f levels and the O 2p states. The two sets of spin–orbital multiplets corresponding to the Ce $3d_{3/2}$ and Ce $3d_{5/2}$ contributions are labeled as “U” and “V”, respectively. The peaks are labeled as V and V’ attribute to mixing of $\text{Ce}(3d^9 4f^2)\text{O}(2p^4)$ and $\text{Ce}(3d^9 4f^1)\text{O}(2p^5)$ Ce(IV) final states, and the peak denotes as V’’ is corresponded to the $\text{Ce}(3d^9 4f^0)\text{O}(2p^6)$ Ce(IV) final state. On the other hand, V_0 and V' assign to $\text{Ce}(3d^9 4f^2)\text{O}(2p^5)$ and $\text{Ce}(3d^9 4f^1)\text{O}(2p^6)$ of Ce(III) state. The same assignment can be applied to the “U” structures, which corresponds to Ce $3d_{3/2}$ levels.

Ce doping causes crystallite and particle size decrease and surface area increase, which is favored for the photo-degradation reactions [141, 143]. In addition, blue shift [141] or red shift [143] in the optical absorption edge of ZnO occur via doping. Kannadasan et al. [141] proposed a mechanism for the photocatalytic degradation of Ce-doped ZnO as shown in Fig. 13(c). Upon illumination, the incorporated Ce^{4+} ions absorb photo-excited electrons and change into the Ce^{3+} ions. After that, the Ce^{3+} ions react with O_2 molecules and produce $\text{O}_2^{\bullet-}$ radicals and Ce^{4+} ions. Moreover, photo-generated holes react with water to produce $\bullet\text{OH}$ radicals. The produced $\text{O}_2^{\bullet-}$ and $\bullet\text{OH}$ radicals are extremely active species toward degradation of various pollutants.

4.2.2.2. Eu-doped ZnO

Korake et al. [144] prepared Eu (0.1, 0.2, 0.5 mol.%)-doped ZnO nanorods by microwave assisted method and approved the Eu incorporation in ZnO by broadening and shifting of XRD patterns toward lower angle. They estimate the direct band gap energy of samples, which show decrease with an increase of Eu dopant concentrations. In addition, 0.2 mol.% Eu-doped ZnO sample shows the highest photocatalytic activity for methyl orange degradation. Sin et al. [21] utilized diffuse reflectance spectroscopy (DRS), XRD, XPS, and PL techniques to study the Eu incorporation in ZnO lattice and determined the formation of the Eu–O–Zn bond. Their XPS analysis reveals that the chemical state of Eu is in the form of Eu^{+3} . The intensity of the PL emission spectra decreases with increase of Eu contents, which attributes to the reduction in e/h recombination rate. Also, they studied the photocatalytic performance in the presence of charge-carrier scavengers and identified that $\bullet\text{OH}$ radicals are the main active species responsible for the phenol degradation. Their proposed mechanism for the photocatalytic degradation of phenol is shown in Fig. 14. Formation of $\bullet\text{OH}$ radicals during the photocatalytic reactions and degradation mechanism for Eu-doped ZnO are described in the following reactions [21]:

Eu³⁺ ion with partially filled f-orbital is a strong Lewis acid and can trap the e_{CB}⁻ to produce Eu²⁺ (Eq. 18). The reduced state of Eu²⁺ is very unstable and consequently trapped e_{CB}⁻ to transfer to the O₂ molecules to generate O₂^{-•} (Eq. 19). Then O₂^{-•} species change to •OH radicals through the equations 20-22. In addition, the remained VB holes generate •OH radicals as shown in equations 23 and 24.

In contrast, Zong et al. [145] synthesized Eu-doped ZnO nanoparticles with a wider band gap in comparison with pure ZnO. Their PL emission spectra show a slower e/h recombination rate, which leads to the improved photocatalytic activity under UV light.

4.2.2.3. La-doped ZnO

Anandan et al. [146] synthesized La-doped ZnO nanoparticles by coprecipitation method for degradation of 2,4,6-trichlorophenol (TCP). Increase in La dopant concentrations leads to crystal size decrease and band gap broadening due to the La–O–Zn bond formation on the surface which hinders growth of crystal grains. Therefore, smaller particle size provides higher surface area and enough active sites for the pollutant adsorption, which is desired for the photocatalytic degradation. Higher production of •OH radicals and decrease in e/h recombination rate are also correlates with better photocatalytic activity. Iqbal et al. [138] showed the production of a large number of oxygen vacancies on La-doped ZnO, which strongly adsorb OH⁻ and causes improvement in photocatalytic activity. Enhancement in the photocatalytic activity of La-doped ZnO due to the presence of more surface defects and space charge formation is also reported by Jia et al. [147]. XPS technique used to study the chemical state of La in La-doped ZnO and results show the oxidation state of +3 for La [138, 147]. Zheng et al. [148] prepared

La(III)-doped ZnO/C core shell nanofibers by electrospinning technique for rhodamine B decomposition under UV light. The highest efficiency for the decolorization is obtained for 2 wt% optimum doping dosage.

4.2.2.4. *Dy-doped ZnO*

Khataee et al. [149] prepared Dy-doped ZnO nanoparticles by the sonochemical method for C. I. acid red 17 degradation. 3 wt% Dy-doped ZnO reveals the highest photocatalytic decolorization under visible-light irradiation. They associate the better photocatalytic activity of Dy-doped ZnO to the correlation between two oxidation states of Dy namely Dy^{4+} and Dy^{3+} . Dy^{3+} ions transfer electrons to the adsorbed O_2 to produce $\text{O}_2^{\bullet-}$ radicals and Dy^{4+} ions. Then, the Dy^{4+} ions transform to Dy^{3+} by receiving photo-generated electrons of ZnO conduction band. These repeated cycles cause a prevention in the electron/hole recombination process, which leads to photocatalytic activity enhancement.

4.2.3. *Other metals doping*

Aluminum doping in ZnO has demonstrated a lot of attention because of its remarkable conductivity and chemical stability. Al-doped ZnO (AZO) is considered as a perfect photocatalyst, because it is inexpensive, nontoxic, chemically and thermally stable and possess high carrier concentrations [150, 151]. Substitution of Zn by Al is proven by broadening and slightly red shifting of XRD peaks [22, 150]. The optimum content of Al 4 at.% in Al-doped ZnO for the enhanced photocatalytic activity was investigated [22]. It has been reported that the synthesis methods and process parameters influence on the properties of Al-doped ZnO and formation of the wider [153, 154] or narrower AZO band gap [152, 155].

Modification and co-doping of AZO nanocrystals with other elements have been used for visible-light-active photocatalysts [150, 156]. Huo et al. [156] synthesized Y-doped AZO (Y-AZO) by sol-gel method for photocatalytic hydrogen production. Their results show that the Y-AZO nanoparticles exhibit higher optical absorption than pure ZnO in the whole light region. Wang et al. [150] prepared visible-light-active AZO nanocrystals modified with nitrogen atoms (N-AZO) and used them for the photocatalytic degradation of rhodamine B. Enhanced visible-light photocatalytic activity of N-AZO is correlated to creation of new VB after nitridation of AZO, which leads to band gap narrowing.

5. Comparative remarks for doped ZnO photocatalysts

As reviewed in the section 4, doping strategy is a good approach to modify the photocatalytic activity of ZnO nanostructures for visible-light-responsive photocatalysts. Changing the morphology of the products, generation of various defects such as oxygen vacancies, dislocation and crystal deformation are general features of doping process. These defects can enhance greatly photocatalytic activity of ZnO with an appropriate dopant type and doping concentration. As discussed in detail earlier, the concentration of dopant elements is a key factor to improve the ZnO photocatalytic activity under visible light, which depends on the preparation procedure and ionic radius of the dopants.

Metal doping does not change the conduction and valence band position of ZnO host, but create new intra-band energy levels, which are desired in some applications such as generation of high oxidant holes. Nonmetal doping causes band gap reduction by elevating valence band of ZnO. Protection of ZnO against photo-corrosion is an important issue which can be achieved by doping process, especially by metal doping. Inhibition of ZnO crystal growth leads to the formation of smaller particles and crystallites with higher surface area as a consequence of metal

doping. The important effects of doping process to enhance photocatalytic activity of doped ZnO under visible light are depicted in Fig. 15.

Concerning ZnO doping strategies to fabricate visible-light-responsive photocatalysts and after reviewing many published reports, we classify and summarize some of the important dopants and their significant information in Table 2. It should be noted that the reported values in Table 2 are the average data of the published reports with excluding some unusual ones.

6. Summary and outlook

Effective metals and nonmetals doping of ZnO nanostructures have been extensively used as an effective approach for the photocatalytic activity under visible light. This approach provides utilization of sunlight as a cheap and clean energy source for photocatalytic reaction performance. Metals and nonmetals have been explored to modify the electronic structure of ZnO to generate a shift in the absorption edge. Depending on the dopant type, its concentrations, as well as preparation conditions, different properties such as crystal structure, surface area, pore size, and photocatalytic activity of doped ZnO have been reported. In metal doping, metal cations replace by Zn^{2+} ions, which leads to the reaction of dopant cation states with the VB or CB of ZnO, or creation of intra-band gap levels. Although, these new band states extend response in visible-light range, but, they can act as recombination centers to decrease the photocatalytic activity, depending on the nature of the metal dopants and its concentrations. In nonmetals doping case, the anionic dopants are expected to substitute the oxygen atoms; therefore, their lower electronegativity and size similarity to lattice O atoms require. With this strategy, the valence band maximum elevates upward to shift the optical response toward visible-

light absorption. In this review, a comparative study was carried out to evaluate nonmetal and metal dopant materials for photocatalytic reactions under visible light.

Based on the experimental and theoretical results, doping of ZnO photocatalysts, which absorb the extended part of visible-light wavelengths, are recognized as an appropriate method to tune the photocatalytic activity. However, the photocatalytic applications of doped ZnO nanostructures have still number of important issue, including the following:

- i) Most of the published work of doped ZnO nanostructures have performed only on dye degradation reactions, further investigation should be carry out to elucidate the detail of photo-degradation pathway and mechanism.
- ii) The antibacterial properties and detoxification of harmful compound beyond dyes on doped ZnO photocatalysts should be also taken into consideration.
- iii) There is a lack of research on the photocatalytic oxidization of volatile organic compounds and indoor and outdoor air purification on doped ZnO photocatalysts.
- iv) Photoelectrochemical solar water splitting to generate hydrogen and artificial photosynthesis to recycle CO₂ are critically important issue of future sustainable society. Much research on these topics requires for doped ZnO nanostructures both from experimental and theoretical viewpoints.

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Figure Captions

Fig. 1. Schematic representation of ZnO wurtzite crystal structures: (a) side view and (b) top view and (c) Band structures of wurtzite ZnO obtained from density-functional theory calculations.

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Fig. 2. (a) The photocatalytic applications of the ZnO nanostructures in the environment and energy fields. (b) The number of publications of ZnO and doped ZnO as a photocatalyst from 1 January 2000 to 22 May 2015 in the Scopus citation database using keywords in title section "photocataly*" and "Zinc Oxide" or ZnO.

Fig. 3. Schematic illustration of the formation of charge carriers (e^- and h^+) and photocatalytic degradation of pollutant on the ZnO nanostructured surface.

Fig. 4. Schematic representation of the doped ZnO energy levels: (a) acceptor level and (b) donor level with metal doping, (c) new valence band formation by nonmetal doping.

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Fig. 5. (a) Schematic representation of the Kohn–Sham levels in the band gap of the N-doped ZnO (top) and ball-and-stick representation (bottom) with spin density plot (yellow) for substitutional (left) and interstitial doping (right). (b) High-resolution of the N 1s XPS spectra of the N-doped ZnO nanospheres. (c) Photocatalytic activity for the degradation of methyl orange solution by using pure ZnO, TiO_2 , N-doped TiO_2 and N-doped ZnO. (d) Schematic diagram illustrating the mechanism for photo-induced charge carrier transfer in the N-doped ZnO/g- C_3N_4 core–shell under the visible-light irradiation.

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Fig. 6. (a) Raman spectrum of the pure and MWCNT-doped ZnO nanofibers. (b) Variation of $(\alpha h\nu)^2$ vs. $h\nu$ for pure and MWCNT-doped ZnO nanofibers. (c) Photo-sensitized mechanism of MWCNT in the MWCNT-doped ZnO nanofibers under the visible-light irradiation.

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Fig. 7. (a) Variation of $\ln(C_0/C)$ vs. visible-light irradiation time for the ZnO, ZnO-carbon, and dye solution (no photocatalyst). (b) Photoluminescence (PL) spectra of the ZnO and ZnO-carbon nanofibers.

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Fig. 8. XRD patterns of the samples and comparison of (100), (002), and (101) peaks of pure ZnO and Ag-doped ZnO with various Ag amounts.

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Fig. 1. Schematic diagram shows the estimated position of the quasi-stable mid-gap energy states in the form of zinc interstitials ($Zn_i^\bullet$), singly and doubly charged oxygen vacancies ($O_v^\bullet$, $O_v^{\bullet\bullet}$) and manganese (Mn) states to explain the possible sources of luminescence from the ZnO nanocrystals with different types of point defects. The emissions are shown as $h\nu_{em1-4}$ and the excitation as $h\nu_{ex}$.

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Fig. 10. The Tauc's plot for the undoped and Cu (1.0–5%)-doped ZnO nanoparticles.

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Fig. 11. Schematic illustration of the optical transitions observed in the Co-doped ZnO.

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Fig. 12. Schematic representation of the photocatalytic processes on highly Fe-doped ZnO surfaces under the UV irradiation. The red line represents the main process and the blue line represents the secondary process.

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Fig. 13. (a) Ce 3d core level XPS spectra of the Ce (10 at.%)–ZnO nanocomposite thin film. (b) Deconvoluted XPS spectra of the Ce 3d core level of the Ce-ZnO nanocomposite films annealed at the different temperatures. (c) Illustration of the photo-degradation mechanism of MB over Ce^{4+} -doped ZnO photocatalysts.

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Fig. 14. Possible photocatalytic mechanism of phenol degradation for the Eu-doped ZnO under the natural sunlight.

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Fig. 15. General features of metal and nonmetal doping to enhance activity of ZnO photocatalyst under the visible-light.

Table 1

Overview of the most abundant dopants in the ZnO nanostructures with their synthesis methods and operated photocatalytic conditions

Dopant	Dopant precursor	Synthesis method	Pollutant	Photocatalytic condition	Source	Ref.
N	Urea	Sol-gel	2,4-D and Picloram	20 mg L ⁻¹ of 2,4-D 5 mg L ⁻¹ of picloram	25W tungsten-halogen lamp	[12]
C	MWCNT	Electrospinning	Methylene blue (MB)	20 mL of 10 ⁻⁵ M MB, 10 mg of photocatalyst	Solar simulator	[13]
S	Thiourea	Hydrothermal	Methylene blue (MB)	10 ⁻⁵ M MB , 1cm ² of photocatalyst	100W halogen-tungsten lamp	[14]
Ag	AgNO ₃	Sol-gel	Methylene blue (MB)	150 mL of 10 ⁻⁵ M MB, 150 mg of photocatalyst	15W fluorescent tubes	[15]
Mn	MnCl ₂	Wet-chemical	Rhodamine B (RB)	100 ml of 10 ⁻⁵ M RB, 40 mg of photocatalyst	300 W xenon lamp	[16]
Cu	Cu(CH ₃ COO) ₂	Co-precipitation	Crystal violet (CV)	100 ml of 10 mg/L CV, 0.25 g of photocatalyst	Mercury lamp	[17]
Co	CoCl ₂ .6H ₂ O	Wet-chemical	Methylene blue (MB)	10 ⁻⁶ M of MB, 5 mg of photocatalyst	Natural sunlight	[18]
Fe	Fe(NO ₃) ₃ .9H ₂ O	Hydrothermal	Rhodamine B (RB)	20 mL of 10 mg/L RhB, 20 mg of photocatalyst	500W xenon lamp	[19]
Ce	Cerium(III) acetate hydrate	Hydrothermal	Acetaldehyde	0.1 g of photocatalyst	Blue-LED	[20]
Eu	Eu(Cl) ₃ .6H ₂ O	Wet-chemical	Phenol	100 mL of 20 mg/L phenol, 100 mg of photocatalyst	Natural sunlight	[21]
Al	AlCl ₃ .6H ₂ O	Sol-gel	Rhodamine 6G (R6G)	100 ml of 10 ⁻⁵ M R6G, 3.5 cm ² of photocatalyst	200 W tungsten lamp	[22]

Table 2

A comparative overview of some important issues on the doped-ZnO visible-light photocatalysts.

Dopant	Ionic radius (pm) ^{a,b}	Chemical state	Doping concentration range	Band gap reduction (eV) ^c	Doping signature
N	146	N ³⁻	15-30 wt %	0.3	<ul style="list-style-type: none"> • XRD peaks broadening and shifting slightly towards a higher 2θ angles. • Appearing peaks at 398.7, 399.7 eV in XPS spectrum. • Presence of 585 and 642 cm⁻¹ peaks in the Raman spectrum.
C	260 16	C ⁴⁻ C ⁴⁺	0.4 -2.7 at% —	0.4	<ul style="list-style-type: none"> • XRD peaks broadening and shifting slightly towards a higher 2θ angle in the case of C⁴⁺ doping and towards lower angles in the case of C⁴⁻ doping. • Presence of the C(1s) peak at 282.5 eV in the XPS spectrum. • Downward shift in the ZnO Raman peak positions.
S	184	S ²⁻	2.78-5.56 at%	0.12	<ul style="list-style-type: none"> • XRD peaks shifting slightly towards a lower 2θ angles.
Ag	115	Ag ⁺	2.08-4.16 at%	0.35	<ul style="list-style-type: none"> • XRD peaks shifting slightly towards a lower 2θ angles. • Appearing peak at 531.1 eV in the O 1s XPS spectrum.
Mn	83	Mn ²⁺	1- 3 wt%	0.25	<ul style="list-style-type: none"> • XRD peaks broadening and shifting slightly towards a lower 2θ angles.
Cu	73	Cu ²⁺	1-3 at%	0.5	<ul style="list-style-type: none"> • Observation of a new PL peaks around 500 nm. • XRD peaks shifting slightly towards a higher 2θ angles.
Co	74.5	Co ²⁺	1-10 mol%	0.6	<ul style="list-style-type: none"> • XRD peaks shifting slightly towards a higher 2θ angles.
Fe	78 65	Fe ²⁺ Fe ³⁺	1-5 at%	0.1	<ul style="list-style-type: none"> • XRD peaks broadening and shifting slightly towards the higher angle in the case of Fe³⁺ doping and towards a lower 2θ angles in the case of Fe²⁺ doping. • Appearing of the Fe 2p1/2 and Fe 2p3/2 peaks at 718.4 and 704.8 eV with doublet separation of 13.6 eV.
Ce	92 103	Ce ⁴⁺ Ce ³⁺	0.5-10 wt% —	0.2	<ul style="list-style-type: none"> • XRD peaks shift toward a lower 2θ angles.

^a Please see ref. [157]

^b Zn²⁺ radius is 74 pm.

^c With reference to the bulk ZnO.

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8

Figure 9

Figure 10

Figure 11

Figure 12

Figure 13

Figure 14

Figure 15