

Review on the Photocatalytic Degradation of Dyes and Antibacterial Activities of Pure and Doped-ZnO

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Abstract: *This paper reviews the recent advances on the photocatalytic and antibacterial activities of ZnO, metal-doped ZnO, non metal-doped ZnO and nano-composite of ZnO synthesized using different methods. Materials with different morphologies and structures have been investigated, by different groups, under UV, visible light and sunlight irradiations. The majority of data reveal superior performance of modified ZnO nanomaterials compared to unmodified ZnO nanomaterials. The nanocomposite of ZnO exhibits highest photocatalytic and antibacterial activity among all nanomaterial. The degradation of the dyes depends on both its concentration as well as the amount of photocatalyst.*

Keywords: Photocatalyst, Degradation, antibacterial activity

1. Introduction

Textile industries are vast sectors especially in developing countries. Among these various textile industries dyeing process use large volume of water for dyeing, fixing and washing. The textile industries use more than 10,000 different dyes and the worldwide annual production of dyestuffs is over 7×10^5 tons [1-2]. Among several classes of textile dyestuffs, reactive dyes contribute about 50% of the total market share and the most common group used as chromophore is the azo followed by anthraquinone. Dyes lost in wastewater could vary up to 50% during manufacturing/processing operations. The release of those colored wastewaters in the ecosystem constitutes a dramatic source of pollution which causes these effluents to be toxic and mostly non-biodegradable. The coloration is visible even in very low dye concentrations [3-4]. As a result, technological systems for the removal of organic pollutants such as adsorption on active carbon, reverse osmosis, ion exchange on synthetic adsorbent resins, ozonation and biological methods are evaluated. All of these methods have advantages and drawbacks but these processes have very high operating costs. However, these conventional treatment methods cannot effectively remove the dyes from effluents so finding an effective technique is necessary [5].

Heterogeneous photocatalysis is a promising technology for the removal of dyes from wastewater. It has great potential as an environmental friendly, low cost and sustainable technology. According to the different scholars there are various semiconductors including TiO_2 [6], Fe_2O_3 [7], ZnO [8] and CuO [9] used as photocatalysts because of their ability to decolorize dye containing wastewater.

Of the various semiconductor materials ZnO stands out due to its properties and wide applications. ZnO has band gap energy of 3.37 eV for efficient absorption in larger fraction of solar energy and has a low cost. Therefore, it is considered as a favorable material with potential use in photocatalysis [10]. The photocatalytic activities of semiconductors are correlated to the morphology, crystalline phase, porosity and surface area of the materials [11]. Additionally, the surface

defect sites of the photocatalysts are thought to be a main factor affecting the electron-hole recombination process during photocatalysis [12-13].

Many researches have focused on addressing issues through different approaches including growing nanostructures with a large fraction of polar surfaces, alloying with low band gap materials, doping with metals and inserting carbon allotropes including graphene, carbon nanotubes (CNTs) and fullerenes to achieve effective electron transport [13-14]. The creation of polar surfaces and doping with metals are particularly promising routes to improve the photocatalytic properties [13]. Unsaturated coordination bonds are highly reactive and are favorable for the adsorption of oxygen molecules resulting in a large number of H_2O_2 radicals which can improve the photocatalytic properties [14]. Wang and co-workers [15] have shown that faceted ZnO prism quantum dots with polar surfaces adsorb OH^- ions resulting in improved photocatalytic activity. They have also investigated hierarchical mixed metal oxide structures grafted onto ZnO and demonstrated improved visible light photocatalytic activity which is attributed to the large fractions of (0001) facets [16].

The advantages of photocatalyst modifications are also to delay electron-hole recombination to broaden the absorption spectrum to facilitate some specific reactions on the surface of photocatalysts and to improve photo-stability. To overcome the problems of anodic photo-corrosion and instability of zinc oxide in acidic or alkaline media, doping of transition metals like Ag, Pd, Pt, Au and Fe with ZnO has proved beneficial [17-19].

ZnO has wide band gap energy ($= 3.37$ eV) which limits light absorption to the UV region. A possible strategy to extend ZnO photo-absorption to visible light may be the modification of its VB position by nonmetal doping such as N, F, S, P etc. Among the nonmetals N is widely acceptable owing to its compatible size to O and the smallest ionization energy [20]. The doping of nonmetal in ZnO may cause band gap narrowing, thus, shifting the photo-absorption edge of ZnO to visible region. Many methods such as chemical-precipitation [21], thermal oxidation process [22],

hydrothermal synthesis [23], sol-gel method [24], and microwave radiation [25] have been used to successfully synthesize the ZnO, metal-doped ZnO nanocrystals. Methods such as molecular beam epitaxy [26], pulsed laser ablation [27] and chemical vapor deposition [28] have been utilized to dope nonmetal into ZnO.

2. Synthesis Methods

(i) ZnO

Li *et al* [29] prepared ZnO crystalline powder solvothermally. Aqueous solutions of zinc nitrate hexahydrate and sodium hydroxide were prepared using de-ionized water. NaOH solution was added drop wise into $\text{Zn}(\text{NO}_3)_2$ solution at room temperature under vigorous stirring which results in the formation of a white suspension. The suspensions were separated with a centrifuge, thrice washed with distilled water and finally washed with absolute alcohol. The separated powders were dried at 60°C in an oven and obtained as the precursor. Subsequently, some amount of the precursor materials and NaCl were added into absolute alcohol, the mixture is sealed in a Teflon-lined autoclave with an interior volume filled in 35%. The autoclave is treated solvo-thermally at 180°C . Then, the resulting white precipitates were washed with distilled water and alcohol several times and ZnO crystallites were obtained [29].

ZnO nanorods were synthesized by Onwudiwe *et al.* [30]. Zinc acetate and polyvinylpyrrolidone (PVP) were dissolved into water. The solution was stirred at room temperature and sonicated. Then, water was removed by slow evaporation and the resulting white solid product was grounded in a mortar and pyrolyzed at 330°C in a tube furnace under nitrogen flow. The resultant white solid powder was washed with de-ionized water and ethanol to remove any remaining ions from the final products and finally dried at 60°C in air. The PVP polymeric network was slowly burned off from the outer surface of the complex below 200°C and decomposition of the zinc acetate at 330°C results in ZnO nanorods [30].

Synthesis of ZnO nanoparticless (NPs) by thermal decomposition of zinc peroxide was demonstrated by Uekawa *et al.* [31]. Aqueous solutions of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and NaOH were reacted and the resultant zinc hydroxide ($\text{Zn}(\text{OH})_2$) precipitates were centrifuged. The precipitates were separated and re-dispersed in distilled water. The solutions were again centrifuged and the precipitates were dispersed in H_2O_2 aqueous solution. The dispersed solutions were heated at 75°C to yield a translucent sol of zinc peroxide and dried at 75°C . ZnO NPs could be obtained by firing the dried sol at temperatures above 473K [27]. The as-synthesized NPs were calcined at 300°C in a furnace to obtain spherical shaped ZnO NPs [31].

Fang *et al* [32] synthesized ZnO NPs by using hydrothermal method. The initial precursor of zinc acetate dihydrate was directly heated to different temperatures (300, 400, 500 and 600°C) in ambient atmosphere with a heating rate of 25°C/hr . Then, the hot intermediate products were taken out and immediately soaked in distilled water in a $5\text{ cm} \times 10\text{ cm}$ quartz boats. Finally, the resulting white powders were

obtained after slow and thorough vaporization of water at 80°C in air and were denoted as 300-ZnO, 400-ZnO, 500-ZnO and 600-ZnO respectively. The effect of cooling rate on ZnO photocatalytic activity was analyzed and same amount of intermediate products at 600°C were soaked in air and cooled naturally to room temperature and denoted as 600(air)-ZnO [32].

(ii) Doped ZnO nanocrystals

Singh *et al* [33] prepared N-doped p-type ZnO nanocrystals by chemical route. Aqueous solutions of zinc acetate were mixed with appropriate amount of aqueous solutions of ammonia. Then, stoichiometric amount of tetra methyl ammonium hydroxide (TMAH) were mixed in the solutions and stirred constantly. The mixtures were poured into a reaction vessel and kept on the stirrer at 100°C . The color of the solutions changed from colorless to light milky white due to the formation of colloidal $\text{Zn}(\text{OH})_2$ nanocrystals. The reaction mixtures were kept inside a microwave oven at 250°C . The white precipitates of N-doped ZnO NPs formed were extracted by repeated washings. These precipitates were dried at 60°C [33].

Ag-doped ellipsoid ZnO nanostructures were synthesized by simple low temperature ($\sim 60^\circ\text{C}$) solution process using $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, AgNO_3 and NaOH as precursors. $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and AgNO_3 were dissolved in de-ionized water under continuous stirring at room-temperature followed by drop wise addition of NaOH solution [34]. Few drops of NaOH were added to the resultant solutions under continuous stirring until pH reaches 11. The stirring of the solutions was continued. The final solutions were heated and refluxed. After completing the reaction, the solution was cooled to room-temperature and finally grayish white precipitates were obtained after decanting the supernatant liquid. The precipitates were washed with de-ionized water followed by ethanol and dried in an oven at 50°C [34].

Viswanatha *et al* [35] synthesized tin-doped zinc oxide (Sn-doped ZnO) using zinc sulfate and different concentrations of SnCl_2 . NaOH solutions were added drop wise into a solution mixture containing zinc sulphate and different concentrations of SnCl_2 with constant stirring. Cetyl trimethyl ammonium bromide (CTAB) was added as capping agent which inhibits anomalous growth of crystals. The resulting solutions were stirred constantly at room temperature. The white precipitates obtained were centrifuged, washed with distilled water and alcohol. It was dried at 80°C in an oven. The samples were calcined in a furnace at 600°C to obtain Sn-doped ZnO NPs [35].

Zinc oxide (ZnO) and gadolinium-doped zinc oxide (Gd-doped ZnO) nanostructures were synthesized using a simple sonochemical method. The as-synthesized nanostructures prepared by sonochemical method possessed higher photocatalytic activity than the as-synthesized nanostructures prepared by conventional method [36]. Different amount of $\text{Gd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ was added to the solutions of zinc acetate. NaOH solution was added to the mixtures until the pH reaches 10. Then, the mixtures were sonicated in a bath type sonicator at a frequency of 36 kHz. The resulting white

precipitates were washed thrice with absolute ethanol, distilled water and dried at 80°C [37].

ZnO NPs were synthesized by a modified non-basic solution route [38]. Zinc acetate dihydrate ($\text{Zn}(\text{Ac})_2 \cdot 2\text{H}_2\text{O}$) was dissolved into methanol under continuous stirring till a transparent solution was formed. The solutions were heated at 80°C under reflux to obtain a white colloidal product. It was collected and dried at 80°C in air. The resultant product was semi-crystalline ZnO. The crystalline ZnO NPs were prepared by heating the semi-crystalline ZnO at 400°C in air in a tube furnace. Nitriding process was carried out by heating the semi-crystalline or crystalline ZnO at 400°C in a tube furnace with a flux flow of gaseous NH_3 . Then, N-doped ZnO were formed [39].

Pure ZnO powder and NH_4NO_3 were mixed by grinding with a pestle at room temperature using an agate mortar. Then, the mixture was transferred into a ceramic crucible and calcined at 600°C in a furnace. For comparison, N-doped P_{25} TiO_2 was also synthesized. For preparing N-doped Degussa (P_{25}) TiO_2 , P_{25} TiO_2 powder and NH_4NO_3 were mixed by grinding at room temperature. Then, the mixture was transferred into a ceramic crucible and calcined at 600°C in a furnace and N-doped ZnO, N-doped P_{25} TiO_2 was obtained [40].

(iii) ZnO nanocomposites

Kim *et al* [41] synthesized Ag-doped ZnO/fly ash composite by a hydro-thermal process. Some amount of fly ash (FA) in distilled water was pulverized ultra-sonically in a bath sonicator. Solutions of the following were prepared: Bis-hexa methylene triamine, zinc nitrate hexahydrate and AgNO_3 , all in distilled water. Zinc nitrate and bis-hexamethylene triamine solutions were blended and vigorously stirred. The as-synthesized FA and AgNO_3 solutions were added to the above solutions. The solutions were put into a Teflon crucible and maintained inside the autoclave for hydrothermal treatment at 140°C [42]. Pristine-ZnO flowers and Ag-doped ZnO nanocomposites were synthesized without FA. The hydro-thermal plants were cooled to room temperature. Then, the nanocomposites were filtered and washed many times with distilled water and ethyl alcohol with cellulose acetate membrane filter. The as-synthesized nanocomposites were dried at 120°C and used for further analysis [41].

ZnO NPs, zinc oxide carbon nanotubes (ZnO-CNTs) nanocomposites were synthesized using a sol method [43]. Copper-doped zinc oxide (Cu-doped ZnO) NPs embedded in carbon nanotubes (CNTs) exhibiting enhanced visible light photocatalytic activity was synthesized by Ahmad *et al.* [44]. Zinc acetate and appropriate amount of copper acetate was dissolved in diethyl glycol. Subsequently, de-ionized water was added into the as-synthesized solution. The mixtures were magnetically stirred at 160–180°C in air, forming aged homogeneous sol. Then, purified CNTs were dispersed into the sol with ultrasonication. The solutions were slowly heated to 160–180°C with vigorous magnetic stirring. It was cooled to room temperature and Cu-doped ZnO-CNTs nanocomposites were obtained after centrifuging. It was

washed by absolute ethanol and de-ionized water several times and dried at 80°C [44].

Dou *et al.* [45] reported the microwave synthesis of Ag-ZnO-grapheme nanocomposites. Graphite and NaNO_3 were added in a flask containing H_2SO_4 under stirring in an ice bath. Potassium permanganate (KMnO_4) was added slowly to the mixture. The ice bath was removed and the suspensions were heated to 35°C while stirring. The color of the solution changed to dark. H_2SO_4 was added slowly to the suspension which was kept at 60°C. The solution was cooled to room temperature. The color of the solution changed to luminous yellow after H_2O_2 was added into the mixture. The precipitates were centrifuged and washed with the mixture of H_2SO_4 and H_2O_2 ten times, with HCl five times and with distilled water three times and then, finally dried at 45°C in vacuum [45].

Ag-ZnO-graphene nanocomposites were prepared from graphine oxide (GO). Different amount of graphine oxide (GO) was dispersed in water and kept in a bath type ultrasonicator and then, $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ solution, AgNO_3 , $\text{C}_6\text{H}_{12}\text{N}_4$ were added into the mixture and the mixtures were sonicated at 90°C. All the samples synthesized were centrifuged and washed with distilled water several times and dried at 45°C in vacuum [45].

Zinc acetate [$\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$] was first dissolved in a 2-methoxyethanol ($\text{C}_3\text{H}_8\text{O}_2$) and monoethanolamine (MEA, $\text{C}_2\text{H}_7\text{NO}$) solution at room temperature. The solution was stirred at 60°C until it become clear and homogeneous. Aluminum nitrate [$\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$] and/or cadmium nitrate [$\text{Cd}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$] were added into some of the previous solutions in an appropriate ratio. Then, it was stirred vigorously at 60°C. The resulting mixtures were dried at 180°C. The gel was first heated at 300°C and calcined in an oven at 800°C to obtain (Cd, Al)-co-doped ZnO NPs [46]. Pure and doped ZnO nanostructures have been synthesized and reported by many groups. Reddy *et al.* [47] have carried out antibacterial studies on (Ag, Co) co-doped ZnO NPs. ZnO nanorods doped with Mn^{2+} , Co^{2+} and Ni^{2+} were synthesized and characterized by Murugadoss [48]. Rajkumar *et al.* [49] have presented a simple method for synthesis of dumbbell shaped ZnO nanorods. Mechano-chemical method was adopted by Wang *et al.* [50] to synthesize S and N-doped ZnO NPs. Yang and co-workers [51] succeeded in synthesizing corn-like ZnO nanostructures and investigated their photoluminescence. N-doped ZnO bundle-like nanostructures were synthesized and studied by Zong *et al.* [52]. A solvo-thermal treatment approach yielding mesoporous ZnO nanospheres with enhanced photocatalytic activity was reported by Zhang *et al.* [53]. Er-N co-doped ZnO nanowires were synthesized by ion implantation [54]. Al-doped conductive powders of ZnO [55], Sb-doped NPs [56] prepared by different methods have also been reported.

3. Characterization Techniques

Reddy *et al* [47] characterized pure ZnO, $\text{Zn}_{0.95}\text{Co}_{0.05}\text{O}$, $\text{Zn}_{0.95}\text{Ag}_{0.05}\text{O}$ and $\text{Zn}_{0.90}\text{Co}_{0.05}\text{Ag}_{0.05}\text{O}$ NPs using x-ray diffraction (XRD). The diffraction peaks of all samples were

matched with the hexagonal wurtzite ZnO data. There were no characteristic peaks of impurity phases regardless of the dopant concentrations, confirming high purity of the as-synthesized NPs. Thus, the wurtzite structures were not modified by addition of Ag and Co into ZnO host material. After the samples were annealed at 500°C, the crystallite sizes of the as-synthesized NPs were estimated from Scherer's equation

$$D = \frac{0.89\lambda}{\beta} \times \frac{1}{\cos\theta} \quad (1)$$

λ is X-ray wavelength, θ is the Bragg angle, β is the full width at half maximum (FWHM) of the prominent diffraction peak.

Quantitative analyses were made for Co and Ag contents in ZnO samples at different doping levels [47].

The crystallinity of ZnO nanorods synthesized by Murugadoss [48] was investigated by XRD pattern. The peaks at scattering angles (2θ) of 31.4, 33.2, 35.1, 46.3, 55.4, 61.6 and 66.6 corresponding to the reflection from (100), (002), (101), (102), (110), (103) and (112) crystal planes were observed respectively. The peaks were assigned to diffractions from various planes corresponding to hexagonal structure of ZnO. The crystallite sizes of Mn^{2+} , Co^{2+} and Ni^{2+} doped ZnO were determined by means of X-ray line-broadening method [48].

The size of the crystallites estimated from XRD patterns are of the order of 8-12 nm. The full width at half maximum (FWHM) of the diffraction peaks of pure ZnO NPs are broader than that of the doped nanocomposites. No diffraction peaks of other compounds are observed. The ZnO nanorods prepared by chemical method have high crystallinity and high purity. The observed interplanar spacing of pure ZnO are indexed to hexagonal wurtzite with lattice constant of about 0.2476 nm (d_{101}). When dopant ions were introduced in ZnO lattice, the interplanar spacing of ZnO changed. The interplanar spacings were 0.2504, 0.2397 and 0.2392 nm for Mn^{2+} , Co^{2+} and Ni^{2+} doped ZnO nanostructures respectively. The doped ions were successfully incorporated into ZnO lattice sites [48].

However, the crystal quality of Co and Ni-doped ZnO is significantly better than that of Mn-doped ZnO. The substitution of the Zn ions by Co and Ni into ZnO lattice is due to smaller ionic radius of Co and Ni than Zn though the crystal quality of doped ZnO is decreased by impurity ions of Mn, Co and Ni, [48].

The ultraviolet visible (UV-Vis) spectra of Sn-doped ZnO NPs were obtained by precipitation method and showed a small red shift in the absorption peaks with increasing Sn concentration [35]. The small shift in the absorption band is attributed to the doping of Sn into ZnO. The band gaps of Sn-doped ZnO are calculated by using the formula

$$E = hc/\lambda \quad (2)$$

Where E is band gap energy, h is Planck's constant, C the speed of light and λ is the wave length.

The band gaps of Sn-doped ZnO at different concentrations are found to be in the range 3.40 to 3.33 eV. With increasing

concentrations of Sn the optical absorption edge slightly shifted towards the longer wavelength region which is attributed to the change in the grain size [35].

ZnO and nitrogen-doped ZnO (ZnO:N) were characterized from XRD data [33]. The sharp intense peaks of ZnO confirmed good crystalline nature of ZnO:N. The peaks originating from (100), (002), (101), (102), (110), (103) and (112) reflections are of hexagonal ZnO doped with N. All the diffraction peaks are in good agreement with that of the hexagonal wurtzite structure of ZnO. The relative intensity of peaks (100)/(002) in all three samples are nearly 1.2 which clearly supports the formation of non spherical ZnO:N NPs and indicating the formation of rod shaped ZnO nanostructures[33].

Increasing nitrogen concentration increases the 2θ value and crystallite size. The slightly larger 2θ values for ZnO:N is due to the bond length of Zn-N (1.88 \AA) being smaller than that of Zn-O (1.93 \AA). These results clearly support the incorporation of nitrogen into the ZnO lattice forming Zn:N i.e. substituting oxygen with nitrogen in ZnO [33].

The dependence of absorption coefficients on the photon energy for the ZnO:N NPs have also been carried out [33]. A change in the energy gap with N concentration is observed, caused by the variation in size of the particles with nitrogen concentration. As the nitrogen concentration increases from 3 at% to 6 at%, there is an increase in band gap energy by 0.38 eV but as concentration is further increased to 9 at% there is a decrease in band gap energy by an amount of 0.1eV with respect to 3 at% concentration. An increase in nitrogen concentration from 3 at% to 6 at% also increases the carrier concentration which cause a blue shift in absorption spectra while a further increase in nitrogen concentration i.e. up to 9 at%, causes decreasing carrier concentration. This result agrees well with the result of Hall measurements. The as-synthesized ZnO:N NPs have very large direct band gap energy [33].

Wang et al [50] investigated the UV-visible absorbance of S-doped ZnO. Compared with ZnO in which absorbance occurs only in the UV range under 400 nm, extension of the absorbance is clearly observed in these samples into the visible range for wavelength as long as 500 nm. The extension of absorbance reflects doping effects of sulfur and is confirmed by XRD [50].

The UV-Vis absorption spectra of pure ZnO, calcined zinc oxide at 600°C (ZnO-600), N-doped P_{25} TiO_2 and N-doped ZnO were evaluated [40]. Pure ZnO and ZnO-600 exhibited band edge absorption at around 390 nm but with little absorption of visible-light [40]. However, for N-doped ZnO, it displayed a distinct tailing absorption covering the whole visible region. Photo-absorption feature reported for N-doped ZnO suggests that the as-synthesized N-doped ZnO have the potential to be a visible light driven photocatalyst. Furthermore, the visible-light absorption ability of the as-synthesized N-doped ZnO is better than those of pure ZnO, ZnO-600 and N-doped P_{25} [40].

The transmission electron microscopy (TEM) image of ZnO revealed a tetrapod structure with a size distribution of 200–500 nm in diameter and of $\sim 3 \mu\text{m}$ in length [54]. The branch of tetrapods displayed a conjunctive shape whose radial size at the middle is less than that at the two ends. The growth mechanism is interpreted as vapor-liquid-solid (VLS) process which generally involves nucleation which induces the epitaxial growth. The estimated interatomic spacing is about 0.52 nm which is consistent with the lattice constant c of ZnO. After ion implantation of Er^{3+} , the crystalline quality is found to degrade gently [54]. Similarly, the solubility of Er^{3+} in ZnO host is low because the radius of Zn^{2+} is smaller than that of Er^{3+} ion and their formal valences are different. The studies showed that ion implantation offered the possibility of controlling the number of atoms and their depth profile by changing the implantation parameters [54].

Viswanatha et al [35] evaluated the morphology of the Sn-doped ZnO NPs using TEM. The sizes of the Sn-ZnO NPs are found to be in the range ~ 60 nm. Although the NPs are slightly agglomerated, their grain boundaries are clearly distinguishable and the crystal images of the product are clearly observed. Nanosize crystallites are seen as closely grouped together and formed a small flake like morphology. Doping of Sn does not change the shape of the NPs. The selected area electron diffraction (SAED) pattern showed the crystalline nature of Sn-doped ZnO NPs [35].

Scanning electron microscopy (SEM) is one of the promising techniques for the morphology studies of the samples and gives important information regarding the shape and size of the particles. The morphologies of samples are approximately hexagonal in accordance with the XRD analysis [55]. The average grain size and surface roughness of aluminum-doped zinc oxide (AZO) particles decrease as reducing the amount of oxygen present in AZO which surrounds the atmosphere in post-calcined. Al-doped ZnO showed that the as-synthesized particle sizes are uniformly distributed on the surface. This result is attributed to the AZO post calcined under reduced atmosphere (CO). This kind of atmosphere causes more defects such as oxygen vacancies, Zn interstitial and Al^{3+} substituted Zn^{2+} . The existence of more defects greatly decreases the grain size and the surface roughness due to Al^{3+} substituting Zn^{2+} completely and uniformly [55].

SEM images of ZnO:N nanostructures synthesized at different nitrogen concentrations showed the formation of uniform size dumbbell shaped ZnO:N nanorods. In the sample in which the concentration of nitrogen relative to ZnO is 3 Atm% the length is about $1.7 \mu\text{m}$ and central width about 250 nm. It was found that as the relative concentration of nitrogen is increased it gives rise to the formation of nanorods of ZnO i.e. there is a decrease in the aspect ratio of the nanorods with increasing nitrogen concentration [33].

The morphology of nanocrystalline pure ZnO and Sb-doped ZnO nanopowders were studied by SEM [56]. The SEM images revealed that the surface morphologies of ZnO NPs are affected by concentration of doped-Sb. The SEM images of pure ZnO NPs are well defined and distinguishable from each other. At 1% composition of Sb-doping in ZnO NPs, the particles are smaller, darker and have a homogeneous

morphology. Almost the same homogeneous structures are obtained for ZnO doped with 3% Sb. But when doping is increased from 3% Sb to 5% Sb, finer particles are observed with heterogeneous morphology. [56]

From SEM observations the Segmented Flow Tubular Reactor (SFTR) process is found to produce particles homogeneous in size with narrow particle size distribution (PSD) and equiaxed morphologies [57]. The average size of SFTR produced particles with polyacrylic acid (AlO-PAA) at the initial point of Al addition is $d_{v,50} = 64$ nm. The addition of very small amount of Al (Al/Zn = 0.01) decreases the size to $d_{v,50} = 46$ nm. The power of the SFTR allowed a continuous production of very homogeneous ZnO nanocrystals in a very reproducible way [57]. The investigation showed that this behavior is extended to Al-doped ZnO with different Al amounts.

NPs are also formed via the microwave-assisted hydrothermal method. By adding some amount of Al an elongation is observed in many particles obtained by microwave-assisted hydrothermal method (MW-AlO) [57]. The addition of polyacrylic acid (PAA) is found to inhibit the elongated growth and lead to smaller and more homogeneous particles (150–200 nm) with equiaxed morphologies. Without any additive/dopant the microwave-assisted hydrothermal method led to a chaotic nucleation and growth which led to less control on the final particle size and PSD than when using the SFTR. This is mainly explained by the use of a micro-mixer in the SFTR which controls the initial supersaturation and the smaller reaction volume which ensures a more homogeneous heating and concentration profile [57].

SEM images of Eu-doped ZnO NPs revealed smaller crystalline size as compared to pure ZnO NPs [58]. Introduction of Eu^{3+} ions into the ZnO lattice decreases the aggregation of NPs and consequently decreases the size of the particles. Using manual microstructure distance measurement software, the size distribution of the Eu-doped ZnO NPs is found to be in the range of 30–40 nm which is much smaller than that of pure ZnO NPs which have sizes in the range 200–250 nm [58].

4. Photocatalytic Degradation of Dyes

The degradation of methylene blue (MB) was evaluated in the presence and absence of ZnO nanoflowers under UV irradiations [59]. In the absence of ZnO, there is no degradation of MB. The characteristic peak of MB ($\lambda = 664$ nm) is taken as a standard for evaluation of photocatalytic activity. As irradiation time is increased, the intensity of absorbance peak declined. 83% degradation of MB is achieved in the presence of ZnO nanoflowers [59]. Principally, the generation of electron-hole pairs by ZnO nanoflowers and its destination is the basic mechanism behind photo-degradation in the presence of ZnO nanoflowers. The degradation reaction kinetics followed a first order at a low concentration of the dye [59].

The photo-degradation of MB under UV irradiation and without UV irradiation was studied both in the presence and absence of ZnO. The photocatalytic degradation of MB is found to be 37.15% by using CdS NPs whereas ZnO nanoflowers showed 83% degradation. This showed that ZnO nanoflowers are better photocatalysts than CdS NPs. The degradation of MB using ZnO NPs by Barnes et al. [60] showed only 18% degradation of MB thus suggesting a greater efficacy of ZnO nanoflowers for photo-degradation of MB [59].

The authors also examined the photo-stability of ZnO nanoflowers. The photo-degradation efficiency after 3 consecutive recycles is found to be 74% indicating good photo-stability of the nanoflowers. The rate of recovery is found to be about 90%; this shows great applicability of ZnO nanoflowers in industrial photocatalysis processes.

The mechanism responsible for the photocatalytic activity suggested was the one proposed by Sun and co-workers [61]. The electron-hole pairs are produced under UV light, when ZnO are illuminated with UV light irradiations having larger photon energy than the band gap of the ZnO nanoflowers. These act as powerful oxidizing and reducing agents. The photo-generated electrons and holes are transferred to the surface of the crystal where the water adsorbed on the ZnO nanoflowers trapped the holes leading to the formation of hydroxyl radicals ($\cdot\text{OH}$). The presence of oxygen (O_2) prevents the recombination process of electron and hole pair, and initiates the formation of an anion radical (O_2^-) by accepting electrons from the conduction band (CB) associated with the proton, to give $\cdot\text{OH}$. The $\cdot\text{OH}$ and O_2^- degrade the aromatic ring of MB by opening it at the azo bond and the hydroxylated ring. The oxygen vacancy on the surface acts as an active center which captures the photo-induced electrons. These inhibited the photon-electron recombination thereby increasing the photocatalytic activity.

The photocatalytic degradation of methyl orange (MO) was assessed by using ZnO nanosheets and nanotubes after prolonged exposure to UV light in aqueous solution [62]. The optical absorption spectra of MO solution at different time intervals of the photo-degradation reactions over ZnO nanosheets and ZnO nanotubes were taken. For both samples, the degradation behaviors are found to be similar but the time consumed for degradation is different. These results showed that the degradation efficiency depends on the morphology of ZnO. The effect of morphology on the photo-degradation efficiency is ascribed to the following reason: when the size of ZnO crystals decreases, the amount of the dispersion of particles per volume in the solution increases resulting in the enhancement of photon absorbance. ZnO nanosheets are found to be more effective on the degradation of MO than the nanotubes, possibly due to their higher surface area and consequent larger contact area between photocatalyst and target material [62].

The degradation of organic azo-dye N, N, N', N'-tetra ethylated rhodamine (RhB) was examined under UV irradiation [63]. The degradation of RhB was done with different amounts of ZnO photocatalysts. In the absence of a catalyst, only a slow decrease in the concentration of RhB is

observed under UV irradiation. The photocatalytic activity is dependent on the morphology of ZnO films. The activity showed the following order: ZnO films deposition at 2 days time (3#) > ZnO films deposition at 1 day time (2#) > ZnO films deposition at 3 days time (4#) > ZnO films deposition at 5 hours time (1#). After irradiations, the aqueous solution of RhB is almost eliminated by film 3#. After the degradation experiments, the regenerated photocatalyst were washed and dried before further run. After 5 runs, 87% degradation is completed [63].

Solar energy absorption is more effective in film 3# with ZnO cages on the surface which plays the role of RhB molecules traps. Under UV irradiation, as long as photons entered into ZnO cages, they are reflected by the cage bars many times before escaping. The increase in reflecting times in cages led to absorption of photons by ZnO cages [63]. Once an RhB molecule enters into ZnO cages, they have more opportunity to contact the surface of ZnO materials than on other films. RhB molecules react with hydroxyl radicals on the surface of ZnO more smoothly. Therefore, most of RhB molecules are completely degraded before they diffuse out of cages [63].

4.1. Degradation of Dyes Using Metal-Doped ZnO

The degradation of MO was investigated using ZnO and silver-doped zinc oxide NPs in aqueous solutions under UV irradiations [64]. The studies were carried out with Ag-doped ZnO NPs prepared with various molar ratios of $\text{Zn}(\text{NO}_3)_2$ to AgNO_3 ratios, viz. 0, 0.01, 0.03, 0.05 and 0.07 labeled as AZ₀, AZ₁, AZ₃, AZ₅ and AZ₇. Ag-doped ZnO NPs possessed higher photocatalytic activities than pure ZnO. The photocatalytic activities of Ag-doped ZnO first increased with increasing Ag content up to 3% (AZ₃), and slightly decreased with further increase in content of Ag. AZ₃ is found to be the most active which shows a photocatalytic activity about 2 times higher than pure ZnO (AZ₀). Further, it is also found that the degradation rate of MO under the real sunlight irradiation is complete after irradiation for 100 min by adding sample AZ₃.

The enhanced photocatalytic activity of Ag-doped ZnO, as suggested by Zheng et al. [65], is attributed to the better charge separation formed as a result of Ag hindering the recombination of photo-induced electrons. When the content of Ag is below the optimal value, the higher the content of Ag in composite is, the higher the photocatalytic activity of Ag-doped ZnO heterostructure photocatalyst. When the content of Ag is above the optimal value, metallic Ag act as recombination centers which is caused by the electrostatic attraction of negatively charged Ag and positively charged holes. Furthermore excessive Ag reduced the number of photons absorbed by the photocatalyst because of light-filtered effect.

Aluminum-doped zinc oxide (AZO) was prepared with different electrical conductivities under different post-calcined atmospheres [55]. AZO possessed more photocatalytic activity than pure ZnO which is ascribed to the Al^{3+} entering into the ZnO lattice substituting the Zn^{2+} site which made the particle size small and caused an increase in

the carrier concentration. The photocatalytic activities of AZO in different post-calcined atmospheres are different, with the sample post-calcined under reduced atmosphere (CO) showing highest photocatalytic activity. This is because under reduced atmosphere the generated oxygen is consumed, prompting the larger generation of oxygen vacancy which makes the Al^{3+} effectively substitute the Zn^{2+} sites. So the carrier concentration increases, causing a reduction in resistivity. As the carrier concentration increases, the intermediate energy gap between VB and CB become more active. Therefore, during light irradiation the free electrons are easily decomposed from the AZO, resulting in the formation of positively charged hole allowing better electrical conductivity. The hole generates H^+ and $\cdot\text{OH}$ from H_2O whereas the electrons activate O_2 to become superoxide anion radicals $\cdot\text{O}_2$ in air. This reacted with H_2O , forming H_2O_2 which further yielded reactive $\cdot\text{OH}$ [55]. The generated radicals caused MO dye decomposition.

Photocatalytic degradation of cresols was studied under visible light irradiation using commercial zinc oxide (C-ZnO), manganese-doped zinc oxide (Mn-doped ZnO) and uncalcined zinc oxide (U-ZnO) [66]. The photocatalytic activities of the nanomaterials depend on the adsorption of the amount of removable pollutants over nanomaterials. The amount of adsorbed cresols on the C-ZnO, U-ZnO and Mn-doped ZnO were evaluated. The results are given in increasing order $\text{C-ZnO} \leq \text{U-ZnO} \leq 0.5\% \text{ Mn} \leq 1\% \text{ Mn-doped ZnO}$. However, the adsorption decreases above 1% Mn. The adsorption of cresols on 1% Mn-doped ZnO is the highest attributing to it has the highest Brunauer-Emmett-Teller (BET) surface area.

The reaction rates and degradation efficiency are given in the order $1\% \text{ Mn-doped} > \text{U-ZnO} > \text{C-ZnO}$. This is attributed to characteristics of the photocatalyst such as decreasing particle size, agglomeration size and increasing surface area. Another reason is related to overlap of the t_{2g} of Mn with the VB of ZnO. Average particle size of as-synthesized ZnO is 30–40 nm while C-ZnO particle size is 400–500 nm and surface area of pure ZnO is greater than the surface area of C-ZnO. Therefore, the improvement of degradation efficiency and rate of reaction is due to the surface area difference [66].

The percentage degradation of phenol was evaluated as a function of time using pure and Nb-doped ZnO NPs by loading different amounts of Nb [67]. A 0.50 mol% Nb-loaded ZnO NPs possessed the highest photocatalytic activity among all samples and took shortest time to complete phenol degradation process. The results clearly suggested that the photocatalytic activities of ZnO NPs are greatly improved by loading an appropriate amount of Nb. The optimal amount of Nb is found to be 0.50 mol% for degradation of the organic compound tested. It was also reported that increasing Nb loading results in an enlarged surface area of the Nb-loaded ZnO nanomaterials. However, an increase in surface area is likely not the main factor affecting the photocatalytic activity of Nb-loaded ZnO. This is supported by the facts that although the surface area of 1 mol% Nb-loaded ZnO NPs are higher than 0.5 mol% Nb-loaded ZnO NPs, its photocatalytic activity is lower [67].

The enhanced photocatalytic activity of Nb-loaded ZnO NPs found in the study is thus, ascribed to Nb acting as electron trap centre which decreases electron-hole pair recombination rate. If the amount of Nb-loading is higher than the optimal value, the activity of ZnO NPs decreases probably because an excess amount of Nb become the center for recombination of photo-induced electron and hole pairs [67].

Reactive oxygen species (ROS) generations by pure and Se-doped ZnO NPs were investigated for degradation of trypan blue (TB) under UV light (340–360 nm). This wavelength region corresponds to the order of band gaps of the doped and pure ZnO NPs. The degradation of TB was examined by oxidative processes. Compared to the control batch which is not treated with ZnO NPs, the degradation of TB dye is more for the batches treated respectively with 5 wt% Se-doped ZnO NPs and pure ZnO NPs in the presence of UV light illumination [68]. The dye degradation efficiency is several folds higher for Se-doped ZnO NPs than that of pure ZnO NPs. Such high efficiency of dye degradation by Se-doped ZnO NPs is attributed to higher ROS generation. The results on ROS induced dye degradation are consistent with the literature [69]. The doping of Se in ZnO NPs enhanced ROS generation and this led to higher dye degradation than pure ZnO NPs [68].

4.2. Degradation of Dyes Using Non-Metal Doped ZnO

The as-synthesized N-doped ZnO microcrystals possessed much higher photocatalytic activity than commercial pure ZnO in the decomposition of formaldehyde under visible-light ($\lambda > 420 \text{ nm}$) [40]. Zinc oxide doped with nitrogen (N-doped ZnO) at the interstitial sites creates intra-band gap N related defects about 1.2–1.3 eV above the VB edge which are responsible for the absorption of visible light. The intra-band gap N related defects (NO) is stable in either the neutral (NO^0) or -1 charge states (NO^-). The existence of NO^- and NO^0 intra-band gap states allow N-doped ZnO to absorb the needed photon energy for moving electrons from VB to CB via two different steps of electron excitation i.e. the electron excitation from NO^- to CB and from VB to NO^0 in which the intra-band gap N related defects plays the role of electron transfer intermediate.

The degradation of formaldehyde is carried out in the presence pure ZnO and N-doped ZnO and described in terms of Langmuir Hinshel wood model [40]. The degradation of formaldehyde followed a first order kinetics. The photocatalytic activities of N-doped ZnO NPs deteriorated with recycling. The photocatalysts are separated from the suspension by filtration and washed with de-ionized water to remove the suspensions. The photocatalysts were dried and weighed after each cycle. Moreover, the mass lost during each cycle is lower than 3 wt. % which meant the recovery efficiency of N-doped ZnO is above 97 wt. % for each cycle [40]. The as-synthesized N-doped ZnO NPs is easily recovered from the suspension by filtration after the photocatalysis reaction, and further used for another photocatalysis reaction. 94% degradation ratio of formaldehyde is achieved in the first three cycles and 91% in the fifth cycle. This is because of the high photocatalytic activity of N-doped ZnO and excellent photochemical

stability. The as-synthesized N-doped ZnO micropolyhedrons are therefore, promising photocatalysts in removing formaldehyde pollutants from wastewater due to its high visible light photocatalytic activities and excellent photochemical stability [40].

4.3. Photocatalytic Degradation of Dyes Using Nanocomposite

The photocatalytic activities of ZnO–CdS core–shell nanostructure coated on glass were investigated by degradation of Congo red (CR) dye in aqueous solutions [70]. The photocatalytic degradation of organic pollutants takes place on the surface and the solution pH play an important role in the process. The absorption spectra of CR is taken at different irradiation times using ZnO/CdS which is coated on glass, at a solution of pH = 3, 7.4 and 9. The maximum degradation of CR at solution pH = 3, 7.4 and 9 occurred at 75 min, 107 min and 90 min respectively.

The pH of the solutions thus, seems to affect the rate of reaction on photocatalyst surfaces which is related to the surface charge properties of the semiconductors. The point of zero charge (pzc) for ZnO is at pH 9 [70]. The photocatalyst is positively charged at pH < pzc which favored adsorption of the negatively charged CR due to the interaction of holes or hydroxyl radicals with Congo red. At pH > pzc, the photocatalyst surface become negatively charged and adsorption of CR is not favorable [70].

The studies showed that under dark conditions, the degradation of CR is negligible. The presence of both light irradiation and photocatalysts are necessary for the efficient photocatalytic degradation of CR [70]. Pure ZnO possessed a lower photocatalytic activity under the same conditions. When ZnO and CdS are coupled together then, they form core–shell nanostructures and photons are absorbed in both ZnO and CdS surface, and electron-hole pairs are formed. The electrons are transferred from CdS to ZnO with formation of a hole on CdS. The electron and hole pairs are efficiently separated which is regarded as the key factor for the improvement of photocatalytic activities of the ZnO–CdS core–shell nanostructures [70].

Another factor affecting the photocatalytic activities of the core–shell is the loading content of the active components. The photocatalytic degradation rate of CR is enhanced with increasing content of ZnO up to ZnO(0.2 M)/CdS(0.075 M) which is reached at 88.0% irradiation [70].

The photocatalytic activity of the Ag-ZnO-graphene with different amounts of graphene loading is investigated for the degradation of MO [45]. In the absence of photocatalysts, no significant decrease is observed in the concentration of MO under UV irradiations. The photocatalytic activity of ZnO is improved by incorporation of Ag [71]. The addition of graphene enhanced the photocatalytic performance significantly. In addition, Ag-ZnO-graphene photocatalyst with different amount of graphene loading shows different photocatalytic activities. Ag-ZnO-graphene nanocomposites exhibited the highest photocatalytic activity when the content of graphene is 1.0 wt%. When the loading amount is below 1.0 wt%, the photocatalytic activities improved with

increasing of graphene amount. However, when the loading amount exceeded 1.0 wt%, the photocatalytic activities of Ag-ZnO-graphene samples decreases as the amount of graphene is increased. For MO solution in the presence of Ag-ZnO-graphene, almost all of MO is degraded under UV irradiation. The maximum absorbance at 464 nm almost disappeared after irradiation [45].

Kinetic analysis of MO degradation is conducted to understand the photocatalytic efficiency of the Ag-ZnO-graphene composites. The reaction kinetics is described in terms of Langmuir Hinshel Wood model:

$$-\frac{dC}{dt} = k \frac{KC}{1 + KC} \quad (3)$$

where $(-dC/dt)$ is the degradation rate of MO, k is the photocatalysis rate constant, C is the concentration and K is the equilibrium adsorption coefficient of MO. KC is negligible when value of C is very small. The above equation can be described as first-order kinetics model:

$$\ln\left(\frac{C_0}{C}\right) = k \cdot K \cdot t = K_{app} \cdot t \quad (4)$$

Where C_0 is the initial concentration and k_{app} is the apparent rate constant. k_{app} determines a photocatalytic activity independent of the adsorption period in the dark and the concentration of MO remaining in the solution. k_{app} of Ag-ZnO-graphene with 1.0 wt% GO addition is about 3.1 times that of Ag-ZnO and nearly 4.8 times of pure ZnO.

Photoluminescence (PL) studies on these samples showed that there are a great number of surface deep traps or intrinsic defects such as oxygen vacancies and interstitial zinc. The PL intensities of these samples increase in the following order: Ag-ZnO-graphene, Ag-ZnO, ZnO. The orders of PL intensities of the samples are in accordance with the photocatalytic activities [45].

The authors explain the enhancement of the photocatalytic activity based on the lifetime of photo-excited electron-hole pairs. The work functions of Ag and ZnO are about -4.26 eV and -5.2 eV [45]. The Fermi energy of Ag being higher than that of ZnO favored the transfer of electrons from Ag to ZnO, reached equilibrium, and formed the new Fermi energy [71]. When the Ag-ZnO nanocomposites were illuminated under UV light with photon energy higher or equal to the band gap of ZnO, electrons in the VB were excited to the CB and left the corresponding holes in the VB. Since the bottom of the CB of ZnO is higher than the new equilibrium Fermi energy level of Ag-ZnO, the photo-induced electrons are transferred from the CB of ZnO to the Ag and holes remained in VB of ZnO [71]. Therefore, the recombination of electrons and holes are effectively delayed. Graphene is a zero band gap semiconductor having a work function of -4.42 eV. The photo-induced electrons are also transferred from ZnO to graphene which left holes in VB of ZnO. Therefore, the most effective electron-hole separation of Ag-ZnO-graphene nanocomposites achieves the highest photocatalytic activity [45].

4.4. Effect of Concentration of Dyes on Photocatalytic Activity of Photocatalysts

The reaction rate was performed by varying the concentrations of indigo carmine at a fixed amount of Se-doped ZnO NPs [72]. The reaction rate was found to decrease with increasing concentrations of indigo carmine. This is because with increase in the dye concentration, the solution become more intense in color and the path length of the photons entering the solution is decreased resulting in only a few photons reaching the catalyst surface. Hence, the productions of hydroxyl radicals are reduced. Therefore, the degradation efficiency is reduced [72].

The mineralization of chemical oxygen demand (COD) was determined at different stages. The dye is mineralized into H₂O, CO₂ and simpler inorganic salts after it was irradiated in presence of Se-doped ZnO photocatalysts [72]. The degradation efficiency of the photocatalyst is calculated by the following formula.

$$\text{photodegradation efficiency} = \frac{\text{initial COD} - \text{final COD}}{\text{initial COD}} \times 100\% \quad (5)$$

The effect of initial acid orange 7 (AO7) concentrations on its sonocatalytic decolorization efficiency was investigated by varying initial dye concentrations [37]. The decolorization efficiency of AO7 is inversely proportional to its initial concentrations. As the initial concentrations of the dye were increased, the sonocatalytic decolorization of AO7 decreases [37]. This negative effect is because of the following reasons:

The number of dye molecules that are adsorbed on the surface of photocatalyst increases because of the increment in dye concentration. In addition, at a high dye concentration a significant amount of UV light is absorbed by the dye molecules [37]. The generation of OH[•] radicals on the surface of catalyst is likely be reduced since active sites on the surface of the catalyst are occupied by the dye ions [37].

With increasing dye concentration the numbers of hydroxyl radicals required for decolorization of dye molecules increases. However, the formation of hydroxyl radicals remain constant for a given catalyst dosage, irradiation time and intensity. The catalytic degradation process is therefore promising at low concentration of pollutants [37].

The effect of initial concentration of direct blue 71 (DB71) on the catalytic degradation of DB71 was investigated using ZnO NPs [73]. DB71 oxidation process was tested by treating at different initial concentrations of DB71 at pH 2.5 with photocatalysts [73]. The color removal efficiency is found to decrease as initial dye concentration increased. As the initial concentration of dye is increased, more and more dye molecules are adsorbed on the surface of ZnO powder [73]. The large amount of adsorbed dye is thought to have an inhibitive effect on the reaction of dye molecules with sonocatalytic holes or [•]OH radicals because of the lack of any direct contact between them. The removal rate decreases because the concentration of dye increases with no increase in the [•]OH radical concentration responsible for their reduction [73].

The effect of initial concentration of the dye on degradation under sunlight and UV light irradiation was performed by varying the dye concentration from 1 mgL⁻¹ to 25 mgL⁻¹ with constant catalytic loading of 100 mg [76]. The degradation of MB increases with concentration up to 5 mgL⁻¹ and 3 mgL⁻¹ under sunlight and UV light irradiation respectively, and shows a steady decrease in the degradation[74]. In low concentrations reverse effect is observed. The optimal concentration of degradation is 5 mgL⁻¹ under sunlight and 3 mgL⁻¹ under UV light. As the reaction under sunlight and UV light proceeded to completion at 120 min, the comparison of efficiency is done based on the percentage degradation at 15 min. 93% of MB degradation is observed for 15 min in sunlight whereas only 69% was observed under UV light. Degradation of MB occurs faster in sunlight than UV light. The results are in good agreement with earlier reports [75] that ZnO-TS (tapioca starch) NPs could harvest maximum solar energy by making use of sunlight for degradation of water bound organic compounds [76].

4.5. Effect of Photocatalyst Loading

Sowbhagya and Ananda, [72] investigated the effect of photocatalyst loading by varying the amount of photocatalysts. An increase in photocatalyst loading increases dyes removal efficiency. Further increase in the amount of the photocatalyst decreases the photocatalytic activity of the catalyst. The reason for the decrease in degradation rate is due to the aggregation of Se-doped ZnO NPs at high concentrations causing a decrease in the number of surface active sites which increases the opacity and light scattering. This decreases the passage of light through the sample. Therefore, there is an optimized photocatalyst loading [72].

The catalyst dosages of Gd-doped ZnO increased by increasing the catalytic decolorization of acid orange 7 (AO7) within a reaction time for some range [37]. A high amount of catalyst dosages favored the decolorization of AO7. An increase in catalytic decolorization of AO7 increased with photocatalyst dosage and these results from increasing the available surface area containing active reaction sites. Consequently, it generates more OH[•] radicals for the degradation of AO7 [37]. Ultrasonic irradiation is diminished due to the blockage of active reaction sites of the photocatalyst and aggregation of the as-synthesized photocatalyst in the solution [37].

Excessive amount of catalyst in the solution results in the scattering of ultrasound and blocked the transmission of ultrasound waves and energy near the surface of the catalyst thus decreasing the rates of catalytic degradation reactions [37]. In addition, excessive catalyst dosage causes: (i) increasing OH[•] consumption at the interface of bubble and solution (ii) accumulation of byproducts in the cavity bubbles for lower collapsed temperatures and lead less powerful collapse.

Ramasami *et al.* [76] studied the optimal catalyst loading under both sunlight and UV irradiations by varying the amount of ZnO NPs. The degradation of MB is completed at around half-time (30min) for all ZnO NPs concentrations. Initially the degradation of MB increases with increase in the

catalytic load under sunlight and UV light illuminations. Increasing load of catalyst increases the surface area of the catalyst exposed to the radiation, thereby increasing the degradation [74]. Further increase in catalytic loading led to aggregation according to Ramasami *et al.* [76] shielding of the photocatalyst and deactivation of the excited state molecules due to collision with ground state molecules as observed by Neppolian *et al.* [74] and increasing turbidity of the suspension (Kansal *et al.* [77]) which finally results in decreasing degradation [76].

5. Antibacterial Activities of Photocatalysts

The antibacterial activities of ZnO and Ag-doped ZnO suspensions of particles of different sizes around 17 nm and 12 nm towards Gram positive (*M. leutus*) and Gram negative (*K. pneumonia*) bacteria were investigated in aqueous Luria broth (LB) by the well diffusion method [78]. The antibacterial activity increases with decreasing particle size; this is due to greater penetrating ability and reactivity of smaller particles arising as a result of an increase in the surface area to volume ratio of small sized particles. The observed mean inhibition zones for ZnO are around 14 and 18 mm against *M. leutus*. When Ag-doped ZnO nanorods were studied against the same bacteria and these values are increased to 19 and 23 mm [78]. The observed antibacterial activity of NPs could either be a consequence of direct interaction with the microbial cells (e.g. interrupted trans membrane electron transfer, disrupted/penetrated the cell envelope and oxidized cell components)/due to secondary products (e.g. reactive oxygen species (ROS)). The creation of active species by photo-induced reaction is the main source towards the bacterial toxicity in the case of metal - transition metal oxide compounds (MTMC). A possible mechanism for the creation of active species has been put forwarded by Padmavathy and Vijayaraghavan [79] who reported that holes produced when ZnO activated by white lights split the H₂O molecule from the suspension of ZnO into hydroxyl radicals (OH[•]) and hydrogen ion (H⁺). The dissolved oxygen molecules are converted to superoxide radical anions (O₂^{•-}) which reacts with hydrogen ion (H⁺) and produce HO₂[•] radicals. These hydroxyl radicals produce hydrogen peroxide anions HO₂⁻ which react with hydrogen to produce H₂O₂ molecules. The generated H₂O₂ molecules penetrate the cell membrane and kill the bacteria [79].

NPs rendered an effective antibacterial agent when compared to pure ZnO [78]. Both the samples have strong antibacterial activity against both Gram negative and gram positive. Similar results are observed on the antibacterial activity of Ag doped ZnO NPs against *E.coli* by Venkatasubramanian and Sundaraj [80]. The inhibitory effect increases, as the concentration of ZnO NPs increases with Ag-doped ZnO NPs exhibiting much enhanced antibacterial activity compared to ZnO NPs. The studies were conducted on Ag doped ZnO NPs in different Ag concentrations. The results showed increasing inhibition rate at both higher Ag concentrations and catalyst concentrations.

Dutta *et al* [68] reported an anomalous behaviour in the antibacterial activity of Se-doped ZnO NPs against *E. coli*.

Culture media containing this bacterial strain was treated with Se-doped ZnO NPs in a wide range of concentrations. They observed a delay in the onset of bacterial growth as also an enhancement in the inhibition of bacterial growth with increasing concentration of NPs. Surprisingly, although bactericidal condition could be achieved with pure ZnO NPs, only 51% growth inhibition was observed for the same concentration of Se-doped ZnO NPs.

Therefore, the possibility of Se acting as additional micronutrients for bacterial growth and ROS scavenging capability was explored. Inductively Coupled Plasma Mass Spectrometry (ICP-MS) measurements on culture media treated with Se-doped ZnO NPs revealed that 30% of the total Se content in the Se-doped ZnO NPs is released into the media. The effect of Se content on the antibacterial activity was studied by spiking the equivalent Se concentration in the culture media pre-treated with pristine ZnO NPs. These studies revealed that the Se release from the Se doped ZnO NPs were used as micronutrients and they may also take part in scavenging ROS from the culture media.

Ag-doped ZnO [81] showed a much stronger antibacterial activity on Gram-positive bacteria than on Gram-negative bacteria. The difference in activity against these two types of bacteria is explained as due to the presence of an outer membrane covering the peptidoglycan layer in Gram negative bacteria. The antibacterial activities for *S. aureus* of Ag-doped ZnO powders were higher than for commercial ZnO NPs [81].

The antibacterial activity is suggested to be through the release of Zn²⁺ from the ZnO powders by mechanical destruction of the cell membrane by penetration of NPs through the production of active oxygen species generated from the surface of ZnO. These reactive species may be generated by photocatalytic reactions of ZnO under UV light.

The antibacterial activity of sulphated cyclodextrin (sb-cd) cross linked cotton fabric treated with Ag, ZnO and TiO₂ against Gram positive bacteria (*S. aureus*) and Gram negative bacteria (*E. coli*) was carried out by Selvam *et al.* [82]. The untreated cotton fabrics have no antibacterial effect. But sb-cd cross linked fabric exhibited maximum of 85% reduction for *S. aureus* and 78% reduction for *E. coli*. The sulfur and nitrogen units in the sb-cd endow it with the antibacterial activity. 100% activity against both *S. aureus* and *E. coli* at 30 min is exhibited by the sb-cd cross linked ZnO NPs coated fabric.

The ZnO band gap is believed to play a role in the generation of ROS. The generated ROS brings about oxidant injury to the surface of the membrane of the microorganism [83]. Because of its positive zeta potential, ZnO NPs rupture the cell membrane of *E. coli* (Gram negative) on contact and releases Zn²⁺ ions. This causes lysosomal and mitochondrial damage which leads to the death of bacterial cells [25].

Ramasami *et al.* also carried out antibacterial studies of ZnO-TS (Tapioca starch) NPs against Gram negative bacteria *K. aerogenes*, *E. coli*, *P. aeruginosa* and Gram positive bacteria *S. aureus* using agar well diffusion method. The ZnO NPs

showed activity against *P. aeruginosa* and *S. aureus* but not against *K. aerogenes* and *E. coli*. [76].

Ag/ZnO composites are synthesized by a solution method. Their antimicrobial activities under UV irradiation were tested as powders and after deposition on cotton and cotton/polyester blended textile fabrics [84]. Whereas the untreated fabrics have no antibacterial activities, the antibacterial activity of Ag/ZnO NPs is found to increase with increasing concentration of silver. Increasing antimicrobial activity of NPs with Ag is attributed to an increase in active surface area with decreasing crystallite size.

Sawai et al. [85] proposed the generation of hydrogen peroxide from the surface of ZnO as an effective means for the inhibition of bacterial growth. With decreasing particle size, the number of ZnO NPs per unit volume of the powder increases and results in an increase the surface area and increasing the generation of hydrogen peroxide. The differences in the reactivity of cell walls of the two bacteria are submitted to the antimicrobial effect of Ag-ZnO NPs. The better antimicrobial activity against Gram positive *M. luteus* as compared to Gram negative *E. coli* is accounted by considering the difference in the composition and structure of the cell walls of Gram-positive and Gram-negative bacteria. The cell wall of the Gram-negative bacteria consists of lipids, proteins and lipopolysaccharides that provide effective protection against biocides which is not the case of Gram-positive bacteria [85].

The antibacterial property of ZnO coated cotton fabrics was evaluated by measuring the value of the zone of inhibition [86]. No inhibition zone is seen surrounding uncoated cotton fabric against two types of bacteria [86]. However, the ZnO-SiO₂ hybrid nanocomposite-coated cotton fabrics present a clear inhibition zone, and its width is larger against *S. aureus* compared to *E. coli*. The greater sensitivity of Gram-positive compared to Gram-negative bacteria to ZnO NPs is probably due to their difference in the cell membrane structure [87]. The antibacterial properties of ZnO NPs is due to reactive oxygen species, probable production of free radicals, and metal ions release. It is reported that the antibacterial activity of ZnO NPs depends on their morphology [88]. The coated cotton sample at method B (zinc acetate added directly to sol solution) with a lower ZnO content presents a larger inhibition zone width compared to method A (zinc acetate added indirectly to sol solution) because the synthesized ZnO NPs in method B presents a stabilized and uniform structure. [89].

The N-doped ZnO was tested for antibacterial activity using photo irradiation film covering method. The killing effect of the sample on *E. Coli* and *S. aureus* was examined. When the doped ZnO is used the existence of remaining bacteria are hardly detected compared with the tremendous numbers of bacteria left in the reference test [90].

6. Conclusion

Nanomaterials of metal and non metal doped, and nanocomposite of ZnO have been synthesized and studied by many researchers. The as-synthesized nanomaterials were used for photo-degradation of organic pollutants in aqueous media under UV, Visible and sun light irradiation. Doping of non metals into ZnO modified the electronic absorption properties ZnO. The band gap narrows thus, extending the optical absorption of ZnO into the visible light region. Non-metal doping enabled ZnO to harvest more photons thereby improving their photocatalytic activity. Metal-doped ZnO shows an enhanced photocatalytic activity for degradation of the organic pollutants possibly by facilitating the electron-hole separation. The photocatalytic activity of nanocomposites of ZnO is also found to increase due to increased active sites.

The concentration of the dye and the amount of the photocatalyst had an effect on the photocatalytic degradation of the dyes. As the concentration of the dyes increased the photocatalytic activity of the photocatalyst decreased. The vast amount of data surveyed suggest that the antibacterial potential of modified ZnO and nanocomposite is higher than the unmodified ZnO.

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