An investigation on the synthesis and catalytic activities of pure and Cu-doped zinc oxide nanoparticles

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Abstract: The typical polyol reduction method, where PVP was used as capping agent is aimed to synthesize pure and Cu-doped ZnO nanoparticles (NPs). The spherical morphology of as-synthesized NPs was observed under SEM. The NPs having Zn, O, and Cu as major constituents were observed by SEM coupled with EDX. The EDX confirmed the Zn, O, and Cu as major elements of as-synthesized NPs. The X-ray diffraction (XRD) studies demonstrated crystalline hexagonal structure in all the samples. The band gap of the NPs was determined using UV–vis spectroscopy. The catalytic activities of as-prepared material were investigated for the degradation of dyes like; Methyl Blue (MB), Methyl Red (MR), Thymol Blue (TB), and Alizarine RedS (ARS), in the presence of H2O2. A drastic increase in catalytic activity was observed with the increased concentration of Cu; particularly for MB. All experiments were carried out under mild and environment friendly conditions i.e. without irradiating by sun or UV light. The material was found promising and feasible catalyst for non-photo degradation of dyes, which are present in the wastewaters produced from textile and printing industries.

Subjects: Physical Sciences; Chemistry; Material Science

Keywords: polyol synthesis; ZnO nano catalyst; degradation; dyes

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PUBLIC INTEREST STATEMENT

The nanocatalysis is promising field due to its general potential, energy saving, and rapid achievements. It has also importance due to having the ease of recovery and again having potential to be reused. Therefore, we have designed a strategy to synthesize pure and doped ZnO nanoparticles which were usually studied as photocatalyst. Now our strategy proved that these are non photocatalyst too. Furthermore, dyes used in textile and print industries are usually carcinogenic. These are mixed in wastewater and finally act as poisons for marine diaspora and terrestrial life. These are cause of widespread of cancer diseases. If our reported catalysts could be used by industrial management, these would act for degrading the dyes and save the water from such pollutants. It would help in saving marine and terrestrial life and give us save environment under mild conditions.
1. Introduction
In the previous years, the photo-catalytic degradation of organic dyes/pollutants using nanocatalysts has appealed wide consideration due to low cost, stereoselectivity, and greater turn-over capacity. The nanocatalysts are further advantageous due to ease of recovery and potential of reusability (Tian et al., 2012). Among the semi-conducting metal oxides, zinc oxide is an important material and one of the best candidates due to its promising characteristics like, broader bandgap (3.34 eV at room temperature), high electron portability, luminescent character, and large exciton binding energy (60 MeV) (Jang, Simer, & Ohm, 2006). Furthermore, it has low cost and greater transparency. It possesses more interstitial spaces and oxygen vacancies due to its wurtzite (hexagonal structure) and thus possessed the oxygen binding and trapping ability (Banu Bahşi & Oral, 2007). Similarly, the oxidative catalytic properties are also produced due to surface defects, which acted as active sites for the binding of polar substrate (Rekha, Nirmala, Nair, & Anukalani, 2010; Ullah & Dutta, 2008). Therefore, it has been preferred due to simultaneously binding with atomic oxygen and substrate for effective and reliable catalytic behavior. Doping of ZnO NPs with different metals may further distort its crystal structure and hence improve the oxygen-retaining vacancies and substrate-binding ability. Such structural change may further improve the catalytic properties. Therefore, it was aimed to investigate the effect of doping (transition metal) on the catalytic properties of ZnO, which was produced by the chemical method.

In the current literature, most of the reports related to chemical synthesis of ZnO NPs are hydrothermal, “soak-deoxidize-air oxidation” (Xu et al., 2010), co-precipitation (Aziz, Zahoor, Aysha, Khan, & Aslam, 2016; Liu, Deng, Deng, & Li, 2008; Muthukumaran & Gopalakrishnan, 2012), sol–gel (Fernandes et al., 2009), evaporative decomposition of solution, and gas-phase synthesis with different reagents (Carolin, Manfred, Christian, & Markus, 2014). Few reports were found where poly(vinyl pyrrolidone) (PVP) was used as a capping agent to synthesize ZnO NPs in different methods (Lin & Shihe, 2000; Santi, Paveena, & Vinich, 2006). There was no report in the literature where typical polyol method i.e. glycol and PVP both were employed for the synthesis of pure and Cu-doped ZnO NPs. Therefore, in this study, typical polyol reduction method, i.e. combination of glycol and PVP as capping agent has been reported for the synthesis of pure and Cu-doped ZnO NPs. Moreover, the already reported ZnO nanostructures in pure and doped forms were found to be used for degradation of dyes like; methyl blue (MB) (Ullah & Dutta, 2008), methyl orange (MO) (Liao, Badour, & Liao, 2008), and Rhodamine (6G) by photocatalytic action (Jang, Simer, & Ohm, 2006; Kaur, Bansal, & Singhal, 2013; Kumar, Kumar, & Umar, 2013; Lutic, Coromelci-Pastravanu, Cretescu, Poulios, & Stan, 2012; Yu & Yu, 2008). Herein, the as-synthesized pure and Cu-doped ZnO nanostructures were evaluated for their catalytic activities without light which are environment friendly, under mild conditions at room temperature. The Cu-doped ZnO NPs were found more effective due to having more substrate and reagent binding ability. It was found quite novel to reduce a variety of carcinogenic dyes (Oh, Kang, Cho, & Lee, 1997), like; MB, MR, TB, and ARS. Thus, the study reports the typical polyol reduction for the synthesis of pure and Cu-doped ZnO NPs, which have distorted crystal and finally proved effective catalyst for degradation of industrial carcinogenic dyes. The material may find its applications for the degradation of textile and print industrial wastes which are too carcinogenic, and dangerous for aquatic life.

2. Experimental details
2.1. Materials
Zinc acetate dihydrate Zn(CH₃COO)₂.2H₂O, Mw = 219.5 (Merck), Copper nitrate trihydrate Cu(NO₃)₂.3H₂O, Mw = 241.6 (Merck), Ethylene glycol (EG) 99% (Daejung), Poly (vinylpyrrolidone) PVP (Daejung Reagent Chemicals-Korea), Acetone, Distilled water, Ethanol (Analytical Reagent). Methyl blue (MB), Alzarine red.S (ARS), Methyl red (MR), and Thymol blue (TB) were used as the model dyes for the determination of catalytic activities of as-synthesized NPs.
2.2. Preparation of pure and doped ZnO NPs

Synthesis of ZnO NPs was carried out using a typical polyol reduction method, where EG acted as a solvent and reducing agent, and PVP played the role of capping agent. In this one-pot synthesis, 10 mL of EG was first heated at 170°C for one hour with a constant stirring in a 100-mL three neck round bottom flask. About 15-mL solution of Zn(OAc)2 and PVP having concentration 0.1 M each was injected dropwise in the preheated EG with constant stirring. The temperature was maintained between 160 and 170°C for one hour to complete the reaction. Finally, the white suspension was obtained, which were cooled to room temperature. It was washed with acetone and ethanol, and centrifuged several times to remove EG, PVP, and unreacted reagents. The same method was repeated with adding 1.5-mL copper nitrate solution having concentrations 0.005, 0.007, and 0.01 M to dope the growing crystals of ZnO NPs.

2.3. Catalytic activities

The effect of pure and Cu-doped ZnO NPs as catalysts against dyes like MB, ARS, MR, and TB was determined comparatively taking H2O2 as standard and monitoring the experiment by UV–vis spectrophotometer. In standard experiment, 150 mL of 0.4 mM aqueous solution of each dye was simply treated with 1 mL H2O2 and degradation reaction was monitored by UV–vis spectrophotometer. To investigate the effect of catalyst, 2 mg pure and differently Cu-doped ZnO NPs were added in above solutions of each dye. The mixture was sonicated for 10 to 15 min to obtain the substrate–catalyst binding. Finally, 1-mL H2O2 was added and reaction was again similarly monitored. The reaction was avoided from direct sun light and UV radiation to find its non-photocatalytic activity. The simple degradation by H2O2 and degradation by H2O2 in the presence of each catalyst was observed after specific intervals. The complete reaction with all respects was performed for MB, while for other dyes the representative aspects were performed.

2.4. Characterization

UV–vis absorption spectra were measured on a SHIMADZU UV 1800 Spectrophotometer. The morphologies of the nanostructures were characterized by FESEM TESCAN MIRA3XMU Scanning Electron Microscope (SEM) coupled with EDX. The crystal structures of pure and Cu-doped ZnO NPs were analyzed by D8 ADVANCE XRD with Cu-Kα radiation (λ = 0.154178 nm). The catalytic activities of pure and Cu-doped ZnO NPs were determined against the degradation of different model dyes such as MB, ARS, MR, and TB solutions in the presence of 1 mL H2O2 and 2 mg catalyst at room temperature after specific intervals.

3. Results and discussion

SEM was used to study the morphology of pure and Cu-doped ZnO NPs. Figure 1(A)–(D) presents the images of pure and Cu-doped ZnO NPs with copper nitrate concentration; 0.005, 0.007, and 0.01 M, respectively. According to the Figure 1(A), the morphology of pure ZnO NPs is spherical having diameter less than 20 nm. These NPs are observed as isolated and merged form forming the nano agglomerates. However, when it was doped with 0.005, 0.007, and 0.01 M Cu(NO3)2 solution, the particle size was not affected, but their merging ability significantly increased as demonstrated by Figure 1(B)–(D), respectively. The NPs gradually transformed into nano agglomerate and their reflection is quite dominant as expressed in Figure 1(B)–(D). The diameter of Cu-doped ZnO agglomerates increased from below 40 nm to above 60 nm. The formation of nano agglomerates is attributed to the crystal distortion of ZnO, which was produced by doping of Cu whose atomic size is larger than Zn. The formation of nano agglomerates from constrained crystal is thermodynamically favored (William, 1992). Resultantly, the distortion of ZnO crystal developed cavities and oxygen vacancies which are helpful to bind with substrate and reagent for reliable catalytic activities as it was demonstrated by this material, which will be discussed in relevant section.
The elemental analysis of pure and Cu-doped ZnO nano agglomerate was assessed by EDX and reflected in Tables 1a and 1b. Table 1a reflected Zn, and O, and not Cu, while Table 1b expressed Cu along with Zn and O. In both samples, the large amount of O is due to the background of SiO2 that is from glass slides. The other elements from background were omitted to make pronounced effect over desired elements for clarity. The omission of other elements like Si, Ca further contributed in reflection of higher weight % of oxygen. Table 1b gives the evidence that Cu is present within the crystal of ZnO, possibly in a doped form. The possible doping of Cu was found in each concentration of Cu(NO3)2; however, EDX data are always qualitative, therefore, the only representative table of Cu-doped sample was appended.

UV–visible spectroscopy was performed to determine the transitory energy levels of pure and Cu-doped ZnO NPs and expressed in Figures 2a and 2b, respectively. Figure 2a focuses on the energy gaps of pure ZnO NPs, synthesized within one hour. The $\lambda_{\text{max}}$ of ZnO NPs was observed at 358 nm. Similarly, Cu-doped ZnO NPs demonstrated their optical gap at $\lambda_{\text{max}}$ 369, 374, and 381 nm for Cu+ concentrations 0.005, 0.007, and 0.01 M, respectively, as given in Figure 2b. All these electronic
transitions are corresponded to ZnO NPs with some shifting. Such electronic transition of ZnO NP in the presence of Cu supported the phenomenon of its doping, otherwise Cu or its cation may express its own absorption that occur at 350 nm (Anna, Claudia, Mirko, Fabio, & Bernardo, 2013). The non-existence of such absorption in Figure 2b suggested the non-existence of independent or composite Cu or CuO NPs. Therefore, it was perceived that Cu is not present in a composite or independent form, but it is the part of ZnO crystal, which is due to its doping. On comparing the data of UV–vis spectroscopy with SEM, expressed in Figure 1, it became clear that red shift in optical gap is related with the size of nano agglomerates. The optical absorption became gradually red shifted as the size of nano agglomerates increased which resulted in decrease of electronic transitions gaps. The formation of nano agglomerate was prominently observed in Figure 1(B)–(D), respectively.

The optical gap for the different concentrations in pure and Cu-doped ZnO samples is shown in Table 2, which was calculated by the relation given as;

\[
E_g = \frac{1240}{\lambda_{\text{max}}} 
\]

(1)

where \(E_g\) stands for the energy of band gap or optical transition for bulk semi conducting or nano materials, \(1,240 = hc\), and \(\lambda_{\text{max}}\) is taken from above plot. \(E_g\) of pure ZnO NP or nano agglomerate is 3.4 eV and it is closely in accordance with the already reported values (Chen & Xu, 2011; Kanade et al., 2007; Reddy et al., 2011; Sharma et al., 2003; Viswanatha, Chakraborty, Basu, & Sarma, 2006; Viswanatha et al., 2004). However, doping of Cu decreased the band gap and produced gradual red

### Table 1a. EDX data of pure ZnO NPs

<table>
<thead>
<tr>
<th>Element</th>
<th>Weight (%)</th>
<th>Atomic (%)</th>
</tr>
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<tbody>
<tr>
<td>O K</td>
<td>85.01</td>
<td>95.86</td>
</tr>
<tr>
<td>Zn K</td>
<td>14.99</td>
<td>4.14</td>
</tr>
<tr>
<td>Totals</td>
<td>100.00</td>
<td></td>
</tr>
</tbody>
</table>

### Table 1b. EDX data of Cu-doped ZnO NPs

<table>
<thead>
<tr>
<th>Element</th>
<th>Weight (%)</th>
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</tr>
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<tbody>
<tr>
<td>O K</td>
<td>57.96</td>
<td>84.91</td>
</tr>
<tr>
<td>Cu K</td>
<td>1.48</td>
<td>0.55</td>
</tr>
<tr>
<td>Zn K</td>
<td>40.55</td>
<td>14.54</td>
</tr>
<tr>
<td>Totals</td>
<td>100.00</td>
<td></td>
</tr>
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</table>

Figure 2a. UV–vis spectrum of pure ZnO NPs.
shift due to p–d spin exchange interactions that occurred between the localized d-electrons and the band electrons of transition metal ion replacing the cation, as reported by Diouri, Lascaray, and El Amrani (1985), Elilarassi and Chandrasekaran (2010), Li et al. (2011) and Muthukumaran and Gopalakrishnan (2012). The decrease in band is also due to the strong mixing of p–d of O and Cu, and it was further consolidated by second-order perturbation theory that confirms the complete substitution of Zn cation by Cu cation (Muthukumaran & Gopalakrishnan, 2012). Moreover, the formation of nano agglomerate is also responsible for the decrease in Eg values.

Finally, Figure 3(A)–(D) displayed the XRD pattern of pure and varying Cu-doped ZnO NPs in due course. Data are well indexed in card JCPDS No. 36-1451, which stands for wurtzite or hexagonal unit cell of ZnO crystal phase (Li et al., 2011). The different phases of crystal growth are expressed over relevant peak. Pure ZnO NPs demonstrated all its peaks quite intense with little anisotropy along 101 phase of orientation as shown in Figure 3(A). The sharpness, strong intensity, and narrow width in diffraction peaks indicated that as-synthesized ZnO is well-defined crystalline nanomaterial having high degree of purity. As the material was doped with Cu ions from 0.005, 0.007, and 0.01 M, the diffraction peaks were broadened as indicated in Figure 3(B)–(D), respectively. The anisotropy at 101 phase also decreased. It suggested the decrease in crystallite size of NPs due to incorporation of Cu cation, which has slightly greater size than Zn. It produced distortion in crystal which slows down the anisotropic growth at 101 phase and increased the merging potential of particles. It increased the extent of nano agglomeration with increasing the dopant concentration, which was already reflected by SEM in Figure 1(A)–(D). The enclosure of Cu further developed more space for O vacancy and made it stronger catalyst. Moreover, there is no separate peak for Cu at concentration 0.005 and 0.007 M as expressed in Figure 3(B) and (C), which indicated the successful doping of Cu at ZnO crystal lattice points. However, the XRD spectrum displayed in Figure 3(D) reflected the appearance of separate peak of Cu around 2θ = 38º, which dictates that 0.01 M for Cu ions was the critical concentration, which produced separate CuO nano coating over ZnO NPs. It further specified that less than 0.01 M for Cu ions is sufficient for lattice points’ substitutions and at least more than this

<table>
<thead>
<tr>
<th>Sample</th>
<th>At 10%</th>
<th>Eg (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu-doped ZnO</td>
<td>0</td>
<td>3.4</td>
</tr>
<tr>
<td>0.005 M</td>
<td></td>
<td>3.10</td>
</tr>
<tr>
<td>0.007 M</td>
<td></td>
<td>3.02</td>
</tr>
<tr>
<td>0.01 M</td>
<td></td>
<td>2.84</td>
</tr>
</tbody>
</table>
concentration of copper would also produce composite structure. Thus, XRD confirmed that ZnO is well-defined crystalline material and it upon doping with Cu decreased the nanoparticle size which resulted in developing nano agglomerates.

4. Catalytic degradation of dyes
Degradation of different dyes like methyl blue, alizarine red S, thymol blue, and methyl red, using the nano-catalysts in the presence of hydrogen peroxide at room temperature, was also studied. All of these model dyes are equally hazardous to the environment and health (Oh et al., 1997). The complete experiment for the degradation of MB was carried out with H₂O₂ as reference and H₂O₂ with pure ZnO and Cu-doped ZnO catalyst as experimental. The reactions were monitored by UV−vis spectrophotometer by observing the decrease in absorbance. The findings of MB degradation experiments are presented in Figure 4(A)–(E). In reference experiment, which was carried out with pure H₂O₂, there is negligible and unreproducible effect of pure H₂O₂. The MB could not be degraded even after 24 h as it is demonstrated in Figure 4(A). However, the similar experiment in the presence of pure ZnO nano catalyst started degradation after 5 min and within 90 min whole MB solution was decolorized as its gradual decrease in absorbance is displayed in Figure 4(B). Similarly, when Cu was doped with increasing concentration, like 0.005, 0.007, and 0.01 M, and the degradation of MB was further found to be increased, which is given in Figure 4(C)–(E). The Cu-doped ZnO nano agglomerates showed complete degradation for MB. It was achieved within 70 min for 0.005 M Cu-doped ZnO.
Figure 4. (A–E) Degradation spectra of MB with pure H₂O₂, pure ZnO and differently Cu-doped ZnO nano catalyst.
and within 45 min 0.007 and 0.01 M Cu-doped ZnO. The Cu-doped ZnO nano catalyst exhibited higher catalytic activities than those of the pure and proved efficient under mild condition as compared to its photocatalysis reported by Zahira Yaqoob, where only MB was focused (Manoj & Zahira, 2014, 2015).

The degree of degradation of dyes was evaluated using the following equation:

\[
\text{% Degradation} = \frac{(C_i - C_0)}{C_0}
\]

where \(C_0\) = initial absorbance and \(C_i\) = absorbance at time “t”.

The bar graphs show the concentration of MB which was left after the degradation during reaction with pure and Cu-doped catalyst. The concentration of pure dye without reagent and catalyst was initially observed under UV–vis spectrophotometer and again after 24 h but noticed no change in absorbance. It was referenced as 100% pure without having any environmental effect. However, when it was treated with only H₂O₂, it degraded 17% and left over concentration was 83% after 24 h, and pure catalyst degraded 92% within 90 min. Similarly, increasing the doping level of catalyst, the catalytic activity significantly enhanced, as 0.05 M Cu-doped degraded MB to 94% within 70 min, 0.07 M Cu-doped did the same 96% within 45 min and finally 0.01 M Cu-doped ZnO degraded 99% MB within 45 min. Thus bar graph explained the effectiveness of doping, which appeared in improving its catalytic behavior (see Figure 5).

Furthermore, the representative degradation reactions against different dyes like ARS, MR, and TB with varying Cu-doped ZnO nano agglomerates were also analyzed and given in Figure 6(A)–(C), respectively. These results denote that Cu-doped catalyst is again capable for degrading other hazardous dyes like ARS, MR, and TB. The representative study is validating that the doped catalyst with every doping extent is fully able to degrade each dye.

The procedure involved in the degradation is the adsorption–oxidation–desorption mechanism as reported by Zhang and Kerr (2007) for MnO₂. Firstly, MB molecule along with H₂O₂ was adsorbed on the nano-catalyst surface and then free radical species (HO•, HOO• or O₂⁻) were produced by the catalytic disintegration of H₂O₂. These generated free radicals are responsible for the destructive oxidation of the (organic) dye(s). Soon after the degraded parts of dye molecules desorb from the surface of nano-catalyst which proved helpful in its recovery (Zhang, Feng, & Zhang, 2008; Zhang et al., 2006).
5. Conclusion
The pure single phase of ZnO having a hexagonal wurtzite crystal was successfully synthesized by typical polyol reduction method having particle size less than 20.00 nm. These were successfully in situ doped with Cu ions with different concentrations which produced nano agglomeration of different size. The band gap of as-synthesized NPs was found 3.4 eV which gradually decreased to 2.84 eV as Cu-doping concentration was increased. The catalytic activities of pure and Cu-doped ZnO nanoparticles were determined against different dyes like MB, ARS, MR, and TB. The potential of catalyst in degrading MB was found more appropriate as compared to other dyes as it degraded MB up to 99%. Therefore, these NPs can be effectively used as degrading agents for various carcinogenic dyes which were produced in print and textile industries.
Supplementary material
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