ENHANCED PHOTOCATALYTIC ACTIVITIES OF F DOPED ZINC OXIDE NANOPARTICLES BY COPRECIPITATION METHOD

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Abstract

Fluorine (F) doped ZnO nanoparticles synthesized by simple and cost effective co-precipitation method. Optical, structural, and morphological activities of F doped ZnO nanoparticles were investigated. The measured band gap energy of F doped ZnO nanoparticles showed a blue shift of approximately 0.08 eV in comparison to the 3.33 eV of the bulk band gap energy. The wurtzite structure of the produced ZnO nanoparticles was revealed by the XRD results. The particle size of of F doped sample was calculated as 15 nm. By degrading the three dyes methyl orange, rhodamine B, and congo red in the presence of nano catalysts, the photocatalytic activity of synthesized nanoparticles has been assessed.

Key words: ZnO; Fluorine; co-precipitation, photocatalysis; decomposition.

Introduction

Zinc oxide nanoparticles (ZnO NPs) have gained significant attention due to their unique properties such as high surface area, tunable bandgap, and excellent catalytic and electrochemical activity. The textile business produces a significant amount of organic dyes each year, which has detrimental effects on the environment. Doping of ZnO NPs is often favoured over undoped configurations due to the synergistic effects of piezoelectric, optical, electrical, magnetic, and photocatalytic properties, that arise from the incorporation of metals or non-metals [1]. Fluoride (F^-) serves as a non-metallic dopant in ZnO structure, attributed to its ionic radius (1.36 Å) that allows potential substitution at oxygen sites (ionic radius 1.40 Å) or occupancy of oxygen vacancies within the ZnO lattice [2, 3]. The ZnO lattice's significant increase of oxygen vacancy is achieved by substituting F^- for O. Doping of ZnO NPs with F can enhance their photocatalytic efficiency by modifying their electronic band structure, surface properties, and charge carrier dynamics, thereby improving their ability to generate reactive oxygen species and degrade

organic pollutants under visible light [4]. Thus, F doped ZnO NPs synthesized through co-precipitation method for addressing environmental challenges.

1. Materials and methods

In this investigation, F doped ZnO nanoparticles were synthesized by co-precipitation method. 0.4 M of zinc acetate was added to 0.2 M NaOH solution and 5 wt% NH_4F with constant stirring. The solution was stirred well at 80°C until the precipitate was formed. Then it was filtered and washed continuously using distilled water. To dry the precipitate, it was then kept in oven for 2h at 120° C. Finally, it was annealed at 500 °C for 4 h to enhance the crystallinity.

2. Results and discussion

Figure 1 (a) depicts the XRD pattern of F doped ZnO nanoparticles. It showed a polycrystalline hexagonal wurtzite structure (JCPDS card: 36-1451). The obtained peaks correspond to (1 0 0), (0 0 2), (1 0 1), (1 0 2), (1 1 0), (1 0 3), (1 1 2) and (2 0 1) planes, confirming the purity of the samples. The crystallite size of the powders are estimated using the Scherrer's formula [5]

$$D = \frac{0{\cdot}9\lambda}{\beta \cos\theta} \qquad (1)$$

where λ is the wavelength used, β is the full width half maximum and ,θ is the Bragg's angle. The average crystallite size of the sample is 11 nm calculated using Debye Scherrer's formula. The lattice constants 'a' and 'c' are calculated using the formula [5]

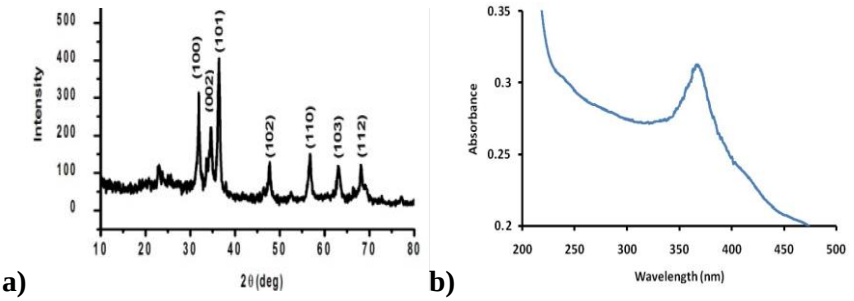
$$\frac{1}{d^2} = \frac{4}{3}\left(\frac{h^2+hk+k^2}{a^2}\right) + \frac{l^2}{c^2} \qquad (2)$$

The volume of the unit cell (V) is estimated using the formula [5],

$$V = \frac{\sqrt{3}}{2} a^2 c\ A^\circ \qquad (3)$$

The calculated lattice constants 'a' and 'c', and cell volume (V) are found to be a= 3.231Å, c=5.19 Å and V= 47.153 $Å^3$. The acquired lattice parameters and cell volumes are comparable to the standard value (a=3.2498Å, c=5.20661Å and V=47.62 $Å^3$) in the JCPDS no: 36–1451. The observed lattice constant and cell volume values decreases with respect to bulk, which is strong supporting evidence for the progressive increase in the substitutional incorporation of F^- in the ZnO lattice sites.

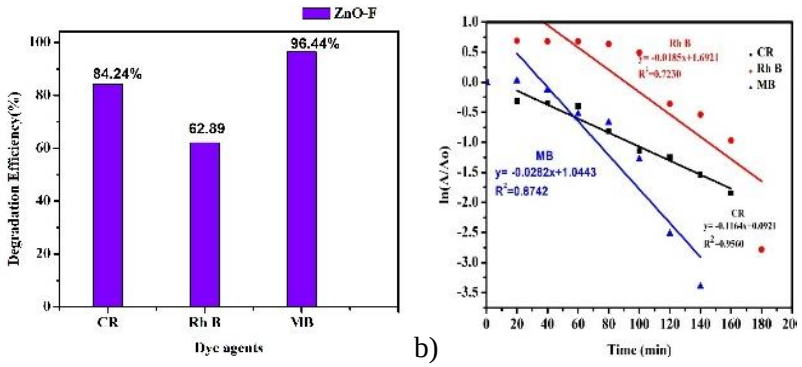
Figure 1 (b) shows the UV-visible spectra of F doped ZnO nanoparticles. ZnO is shown to absorb light at a wavelength of 377 nm. The measured band gap energy of F doped ZnO nanoparticles (3.41 eV) showed a blue shift of approximately 0.08 eV in comparison to the 3.33 eV of the bulk band gap energy [6]. The inclusion of F is confirmed by blue shifting the wavelength in F doped ZnO nanoparticles [5].



a) b)

Figure. 1 a) XRD pattern, b) UV-vis spectra of F doped ZnO nanoparticles

The photocatalytic degradation of CR, Rh B, and MB dyes in the presence of F doped ZnO nanoparticles, under the illumination of an ultra violet (UV) light simulator is conducted for 160, 180, and 140 minutes, respectively. The nano catalyst, F doped ZnO nanoparticles demonstrated significant photocatalytic activity, as evidenced by the decrease in dye absorption. With increasing UV radiation exposure duration, the concentrations of CR, Rh B, and MB dyes gradually decreased. **Figure. 2 (a) and (b)** illustrate the degradation rates and efficiency of CR, Rh B, and MB dyes over time under UV light using these photocatalysts. The F doped ZnO catalyst that has been demonstrates optimal degradation efficiency, resulting in 96% degradation of the MB dye in 140 min. According to **Figure. 2**, MB demonstrates higher degradation efficiency compared to CR, and Rh B due to differences in their physicochemical characteristics and structural composition. The maximal degrading efficiency can be ascribed to the introduction of impurity levels closer to the conduction band, which causes ZnO's band gap to contract. Therefore, electrons can be excited from the valence band to the conduction band or the impurity level with a modest amount of energy, which means that ZnO sites' ability to absorb UV light may have improved. Furthermore, by preventing the recombination of photogenerated charge degradation efficiency, F^- ions which can act as electron trapping sites promote charge separation.



a) b)

Figure. 2. a) Degradation efficiency, b) Kinetic plot of ln A_t/A_0 vs. irradiation time of the F doped ZnO nanoparticles

3. Conclusion

F doped ZnO nanoparticles have been successfully prepared by co-precipitation method. The optical, and structural activities of ZnO nanoparticles by the influence of F doping were investigated. XRD shows crystallite size decreases with increasing Sb/F cont. The photocatalytic activities were studied by applying CR , Rh B, MB dyes under UV light. Photocatalytic decomposition process of CR , Rh B, MB dyes follows the first-order reaction. The F doped ZnO catalyst that has been demonstrates optimal degradation efficiency, resulting in 96% degradation of the MB dye in 140 min.

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