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Synthesis and Characterization of Pure and Manganese (Mn) Doped Zinc Oxide (ZnO) Nanocrystallites for Photocatalytic Applications

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Abstract

In this work, pure and manganese (Mn) doped zinc oxide (ZnO) nanocrystallites are synthesized using a sol-gel technique. 0.25 M solution of zinc nitrate hexahydrate is prepared in 50 ml of DI water with stirring condition. An equimolar citric acid (0.25 M) solution is added slowly into the above solution and stirred for 2 hrs. at 70ºC. The obtained gel is dried for 3 hrs in hot air oven at 120°C. Further, the nanoparticles are annealed at 400°C and the samples are characterized by X-ray diffraction (XRD), Field emission scanning electron microscopy (FESEM), Fourier transform infrared (FTIR) spectroscopy, photoluminescence spectroscopy (PL) and photo catalytic studies. XRD analysis deciphered the polycrystalline hexagonal of the samples and the crystallites sizes are observed to be 18 nm and 42 nm for the pure and Mn doped ZnO particles, respectively. FE-SEM studies demonstrate that the crystallites are spherical in shape with agglomeration. PL studies reveal the emission bands at 490 nm for pure ZnO and 530 nm for Mn doped ZnO. The photocatalytic studies determine the photocatalytic performance of pure ZnO NPs and Mn doped ZnO NPs under the UV light irradiation (365 nm and 125 W) in which, the pure ZnO degrades MB dye more efficiently than Mn doped ZnO.

Keywords: ZnO • Mn doped ZnO • XRD • FESEM • Photocatalytic studies

Introduction

Nanoscience is the manipulation and study of materials with nanoscale structure. It mainly deals with the synthesis, analyses, exploration, and development of nanomaterials. Nanomaterials have gained much attention in various fields because of its potential optical, electrical, magnetic and mechanical properties. Zinc oxide (ZnO) exhibits hexagonal structure (a=3.246 Å, c=5.207 Å), wide energy gap (3.37 eV), high melting point (2250 K), refractive index of 2 with 60 meV exciton binding energy. ZnO has outstanding properties and widely used in acoustics, piezoelectric devices, ultraviolet (UV) lasers, gas sensors, and solar cells. In addition, ZnO possesses various applications in electronics, magnetic devices, sensors and photocatalysts [1-4]. ZnO nanostructures improve catalytic reaction process due to their large surface area. Therefore, synthesis of nanostructured ZnO materials with different microstructures is important for different applications [5]. Several methods are used for the ZnO NPs synthesis such as hydrothermal, sol-gel, solution combustion, precipitation and solid-state reactions. The sol-gel method is preferred over other techniques, owing to its good homogeneity of the products with superior properties. Moreover, sol gel is a simple, cost effective, low temperature processing and morphological control process. Several factors influence the properties of the gel, such as precursor concentration, surfactant, temperature, solvent content, acid or base content and water percentage [6].

Several synthetic techniques are employed to obtain different morphologies of ZnO, like nanowires, nanotubes, nanorods, and nanodisks [7]. The surface topography and crystallites size of ZnO nanoparticles are important for photocatalytic activity. Morales et al. [8] prepared ZnO nanoparticles with diverse morphologies and analyzed the photocatalytic behaviour using UV light. Xu, Linping et al. [9] synthesized ZnO by solvo-thermal method with various solvents and found degradation activities of phenol. They observed that there is no link between the catalytic activity and surface area, representing that there are other key parameters to decide the photocatalytic activity [10]. In this work, pure and doped ZnO nanocrystallites are synthesized by a sol-gel method and microstructural, optical and photocatalytic properties are investigated.

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Experimental Details

Synthesis of pure and Mn doped ZnO nanocrystallites using sol-gel method

The precursor materials of AR grade are used directly for the synthesis of nanocrystallites. In this work, pure form of ZnO is prepared as follows: 0.25 M solution of zinc nitrate hexahydrate is prepared in DI water under constant stirring. Then, 0.25 M solution of citric acid is added slowly to the above solution and stirred for 2 h continuously at 70-80°C. Similarly, for dopant, an equimolar concentration of zinc nitrate hexahydrate ($Zn(NO_3)_2.6H_2O$) and manganese nitrate hexahydrate ($Mn(NO_3)_2.6H_2O$) is prepared in DI water under stirring. Subsequently, 50 ml of 0.25 M citric acid is added slowly in the above solution and stirred for 2 h continuously at 70-80°C temperature. The gel obtained via both the process is dehydrated in an oven at 120°C for 3 h for dehydration. The nanocrystallites are ground using mortar and pestle and annealed at 400°C, which is used for further characterization.

Characterization

The crystalline nature of the prepared nanoparticles is investigated using X-ray diffractometer with CuKα radiation (Rigaku/1.5418 Å). The nanoparticles are analyzed in the 20-90º (2θ) range with 0.02º step size. FTIR spectrometer, (FTIR/ATR) is used to analyze the chemical bonds present in the samples. The Spectrofluorimeter (Model: LS 45) is executed at 350 nm excitation wavelength to study the optical properties of the materials. The morphology is analyzed

using FE-SEM (Carl: Zeiss). The photocatalytic performance of the samples is studied using the photo reactor (HEBER, MODEL HVAR-MP400) under UV light (365 nm and 125 W).

Results and Discussion

Structural properties using XRD

XRD pattern shows many distinct diffraction peaks for ZnO nanoparticles (Figure 1). These peaks are indexed at 2θ angles, 31.82°, 34.40°, 36.3°, 47.55°, 56.45°, 62.90°, 66.4°, 67.9°, 69.15°, 72.70° and 77.01°, which belongs to (100), (002), (101), (102), (110), (103), (200), (112) and (201) planes, respectively. These peaks are indexed with the help of powder diffraction file JCPDS No.00-005-0664 and indicating that the ZnO structure belongs to Wurtzite hexagonal structure. Within the diffractometer detection limit, there is no impurity peaks observed. Furthermore, crystallites sizes of the samples are calculated from the Scherrer formula:

$$D = \frac{}{ii}$$

Where K-Scherrer constant, λ-wavelength of X-rays used (1.5418 Å), β-Full width at half maximum and θ- angle of diffraction. The (101) peak is chosen for the calculation of crystallite size and found to be 18 nm and 42 nm for pure and Mn doped ZnO samples respectively [11].

Shunmuga sundaram et al. used precipitation method to synthesize Mn doped ZnO nanopowders and the XRD analysis indicating ZnO wurtzite structure [12]. Seval Aksoy et al. prepared doped ZnO nanoparticles using hydrothermal technique and XRD results revealed the hexagonal structure [13]. Shatnawi et al. produced Mn doped ZnO particles and the XRD analysis revealed that the Mn doped samples possess wurtzite structure [14].

Field emission scanning electron microscopy (FE-SEM) analysis

FESEM is mainly used to analyze the surface topography of the sample. (Figure 2) shows the FESEM images of pure ZnO nanoparticles. It shows that the ZnO nanocrystallites are spherical in shape and are uniform size. The agglomerated ZnO nanoparticles yield bigger size ZnO. There is a very minimal interparticle pore formation. This might be attributed to the annealing temperature and the molar concentration of the precursor used for synthesis. Murugesan silambarasan et al. synthesized Mn doped ZnO particles using solution combustion process and the SEM studies revealed the presence of big size crystallites, it might be attributed to the aggregation of smaller particles [15].

Fourier Transform Infrared Spectroscopy (FT-IR) studies

FT-IR spectroscopy deals with the molecular vibrations of the ZnO nanostructures (Figure 3) shows the FT-IR peaks at 875, 1420, 1980, 2050, 2324 and 3400 cm^{-1}. The absorption band in the finger print region 875 cm^{-1} is from the inter-atomic vibrations. The broad band is recorded ~3400 cm^{-1} due to O-H stretching in hydroxyl group and the 2324 cm^{-1} peak occurs due to C=O formation. Thus, the formation of Zn-O is confirmed from the earlier studies [11].

Chadia Belkhaoui et al., synthesized Mn doped ZnO nanocrystallites using precipitation technique and investigated its structural properties, in which the band observed at ~ 3500 cm^{-1}, is from OH stretching vibration [16]. Kalita et al. studied the properties of Mn doped ZnO NPs and found that the FTIR spectrum shows the peak ~3408 cm^{-1} due to O-H stretching vibrations [17].

These results agree with the present results:

Photoluminescence (PL) Studies

The absorption peak for the ZnO nanomaterials is analyzed using spectroflurometer. ZnO is excited using laser light at 350 nm wavelength and the PL emission spectra are recorded. Five distinct peaks are observed for

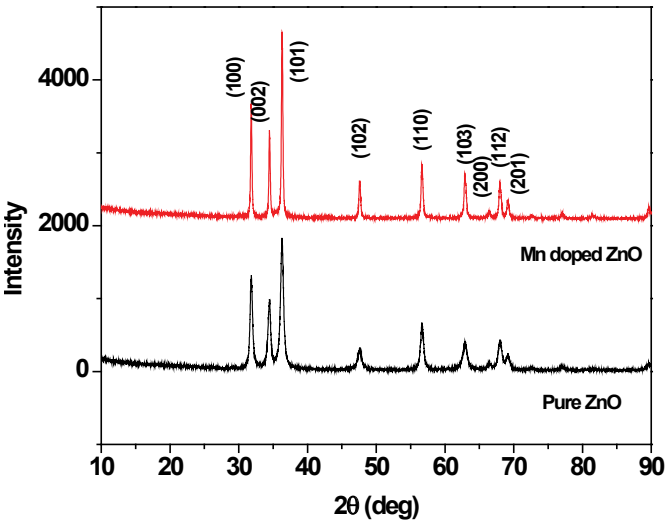

Figure 1. XRD pattern of the pure and Mn doped ZnO nanoparticles.

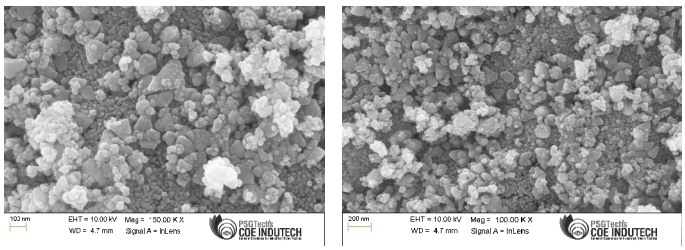

Figure 2. FE-SEM images of pure ZnO nanostructures.

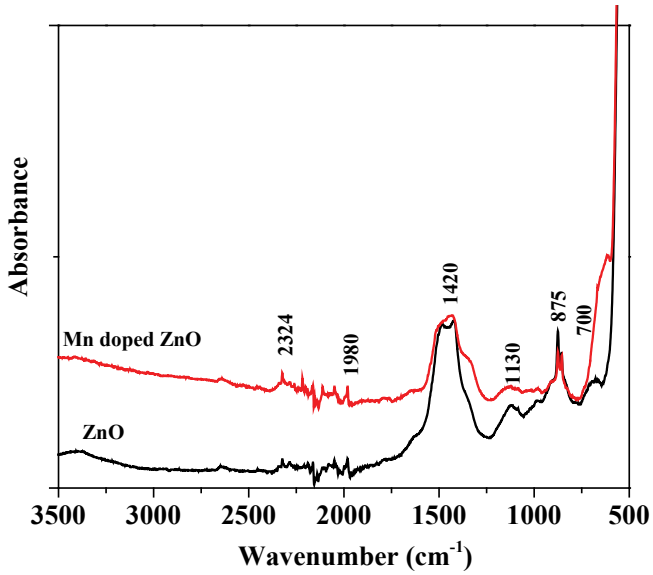

Figure 3. FT-IR spectra of pure and doped ZnO nanoparticles.

the sample at 334 nm, 344 nm, 387 nm, 428 nm and 676 nm (Figure 4). The peak ~ 387 nm is the UV emission peak, corresponding to the energy gap of 3.21 eV and attributes to the phonon replica of free exciton luminescence. The peak ~ 428 nm corresponds to band gap of 2.9 eV, which contributes to the oxygen vacancy or the presence of zinc at interstitial site. In addition, the red emission peak ~ 676 nm is observed [18]. Photoluminescence spectrum of Mn doped ZnO sample shows the high intense peak ~530 nm, corresponding to the energy gap of 2.33 eV.

Benze Wu et al., prepared Mn doped ZnO sample and studied its photoluminescence properties, where emission bands are found to be from 365 to 432 nm, visible emission bands are located at 450, 625 nm and are generated by defect level band edge emission [19]. Arup Dharaa et al, [20]

used mechanical alloying to synthesize Mn doped ZnO nanocrystallites and the results indicated two broad peaks ~ 465 nm and 540 nm with reduced intensity. In the present work, UV band is located at 387 nm, red emission peak at 676 nm, Mn doping affect the bandgap of ZnO nanoparticles and peaks clearly indicating energy gap of 2.33 eV, which is less as compared to pure ZnO nanoparticles.

Photocatalytic studies

The dyes being used in industries are resistant to most of the degradative environmental conditions because of their complex structure. Therefore, the conventional wastewater treatment methods remain ineffective. There are two main methods available for treating dye wastewater, namely, adsorption and biological treatment. Adsorption method is a constructive procedure due to simple design, recycling of catalyst, economic feasibility and absence of harmful residues. (Figures 5a and 5b) shows the MB dye degradation with ZnO catalyst. The ultraviolet light emitting the wavelength at 365 nm is placed at the centre of the photo reactor. Continuous water flow is arranged to keep the temperature 25-30°C in the photoreactor. The catalyst is dissolved in MB dye aqueous solution and placed in the photo reactor [21].

The photocatalytic performance of MB dye using ZnO catalyst and 1 g/L catalyst is mixed with 10 ppm dye solution. The solution is kept under

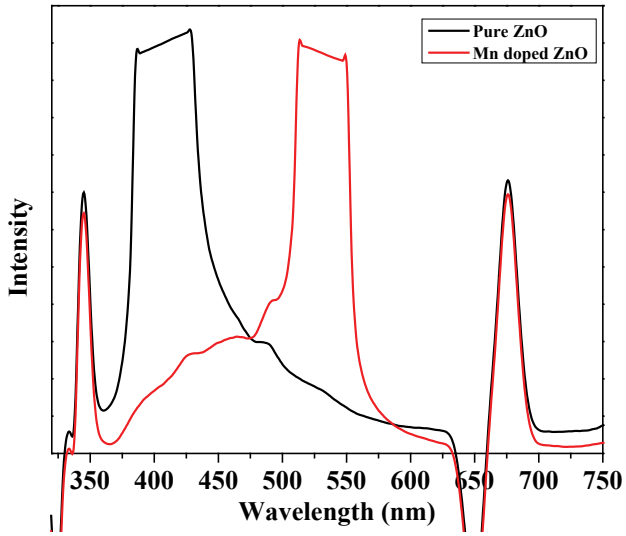

Figure 4. Photoluminescence spectra of pure and Mn doped ZnO nanoparticles.

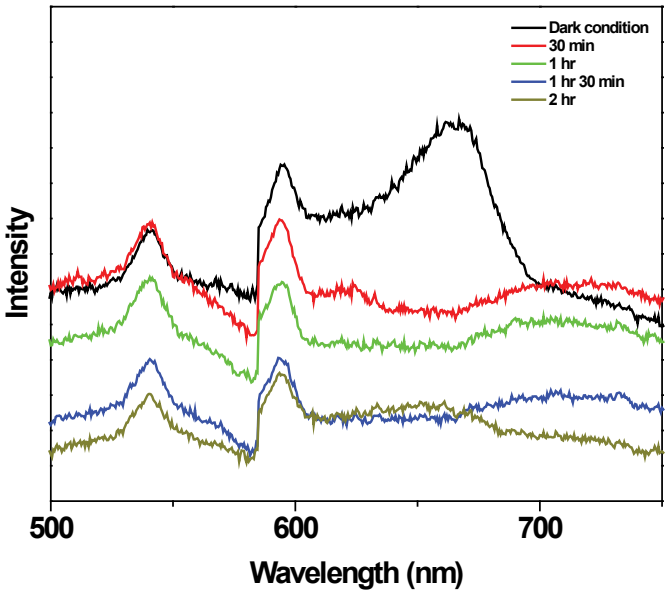

Figure 5a. MB dye degradation of pure ZnO nanoparticles under UV light irradiation.

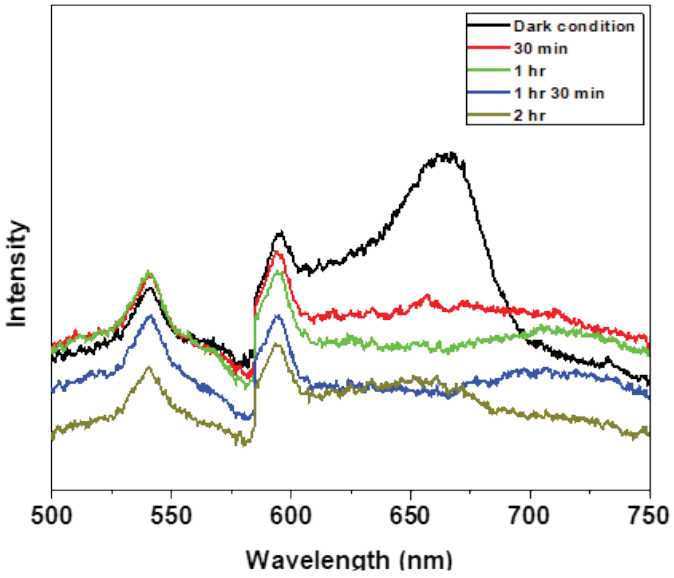

Figure 5b. MB dye degradation using Mn doped ZnO nanoparticles under UV light irradiation.

dark atmosphere for 30 minutes to attain equilibrium. After the UV light is on, absorbance is noticed for every 30 min using the UV-Visible spectrophotometer. Figures show the linear increase of MB dye adsorption by the catalysts. The percentage of adsorption of the sample is calculated from the following expression

Degradation percentage $\%=(A_0-A)/A_0 \times 100\%$

Where A_0 and A are the absorbance at time *t=0* and after time *t* of the dye solution

The adsorption capacity of specific catalyst Q can be given as

$Q=(C_0-C)\ V/m$

V and m denote the volume of the solution and mass of the catalyst respectively.

The experiments are carried out to estimate the effect of degrading the MB dye using nano-catalyst under UV irradiation. The figure clearly shows that the MB dye solution has maximum absorption intensity at dark condition and the intensity of absorbance of MB dye decrease with increase of time. After 120 min, the absorbance intensity is reduced, due to the MB dye degradation and the solution becomes colourless.

Figure 5a shows the photocatalytic behavior of the pure ZnO sample and adsorption increased for every 30 mins and after 120 minutes, the blue colour solution of the dye changes to colourless, which indicates strong catalytic activity of pure ZnO nanoparticles and it shows 77% degradation efficiency. (Figure 5b) shows reduced photocatalytic activities of Mn doped ZnO sample show 72% degradation efficiency, which are attributed to their larger crystallites size. The pure ZnO nanoparticles showed better photocatlytic activity than the Mn doped ZnO NPs [8,9].

Mostafa Khaksar et al. examined the degradation performance of Mn doped ZnO particles in presence of H_2O_2 [22]. Jagpreet singh et al. analyzed the photocatalytic performance of Mn doped ZnO NPs using MB, CR, MO dyes and showed that Mn doped ZnO shows a higher degradation efficiency as compared with pure ZnO [23]. But in present study, high photocatalytic performance is observed in pure ZnO, having 77% of degradation efficiency. Anju Chanu et al. prepared Mn doped ZnO crystallites using precipitation technique. The 2% Mn doped ZnO particles showed the maximum photocatalytic performance with MB dye under UV light [24]. Faouzi Achouri et al. prepared the porous Mn doped ZnO crystallites by solvothermal method. The 3 mol % Mn doped sample showed the maximum photocatalytic activity for orange dye using solar light irradiation [25]. Qun Ma et al. prepared the Mn

doped ZnO structures using ion-exchange method and the results indicate the highest photocatalytic activity for the Mn doping [26].

Conclusion

The pure and Mn doped ZnO nanocrystallites are synthesized using a sol-gel process. The synthesized particles are annealed at 400°C and utilized for characterization. XRD patterns of ZnO and Mn doped ZnO nanoparticles represent the wurtzite hexagonal structure. The average crystallites size of pure ZnO is 18 nm, whereas, Mn doped ZnO nanocrystallites are 42 nm in size. FESEM studies illustrate that the ZnO nanocrystallites are spherical in shape, uniformly distributed with agglomeration. In PL spectra, the emission bands are observed at ~ 490 and 530 nm for the pure ZnO and Mn doped ZnO respectively corresponding to the band gap energy of 2.53 eV and 2.33 eV. The additional peaks in the PL spectra refers to the oxygen related vacancies and red emission. The photocatalytic studies demonstrate the degradation of MB dye pollutant using pure and Mn doped ZnO samples under the exposure to UV light irradiation. The photocatalytic performance of the pure ZnO NPs is ~ 77%, while for the Mn doped ZnO is 72% after 120 min time of irradiation. The ZnO NPs can be used for the degradation of pollutants and other environmental related applications.

Declaration of Competing Interest

The authors declare that there is no conflict of interest.

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