Effect of Mn doping on the structural, optical, magnetic properties, and antibacterial activity of ZnO nanospheres

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Abstract
This work investigates the systematic study of the structural, optical, magnetic, and antibacterial properties of Mn-doped ZnO. Zinc oxide (ZnO) and Mn2+ doped zinc oxide (ZnMnO) nanoparticles (NPs), were prepared through the co-precipitation method. The X-ray diffraction studies confirmed that the synthesized nanoparticles did not modify the crystal structure upon Mn doping. However, the microstructural parameters were changed considerably upon the increase of the concentration of Mn dopant. The HRTEM images showed that the ZnO NPs exhibit nanospheres-like morphology, and a reduction in the average particle size from 41 nm to 33 nm was observed upon Mn2+ doping. The elemental composition of Zn, Mn, and O atoms were identified by EDAX spectra. The Zn–O stretching bands were observed at around 550 cm−1 in the FTIR spectra and the zinc and oxygen vacancies defects were confirmed by PL spectra. The estimated band gap of ZnO was 2.95 eV and increased to 3.14 eV for ZnMnO3. In addition, the Mn-doped ZnO NPs showed a more significant antibacterial effect than the pure ZnO NPs. The ZnO and Mn-doped ZnO NPs showed significant changes in the M-H loop where the diamagnetic behavior of ZnO changes to a weak ferromagnetic nature when doped with Mn ions.

Graphical abstract

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Highlights
- Mn$^{2+}$ doped ZnO was efficiently synthesized via wet chemical route.
- Microstructural parameters were altered considerably upon Mn concentrations.
- Bandgap of ZnO were altered significantly with respect to Mn$^{2+}$ doping.
- Mn$^{2+}$ doped ZnO NPs showed greater antibacterial effect than the pure ZnO NPs.

1 Introduction

With the rapid development of nanoscience and nanotechnology in the past two decades, many nanomaterials have been fabricated for various technological industries such as optoelectronics, sensors, energy, and environmental sectors [1, 2]. Among different semiconductor nanostructures, ZnO nanoparticles (NPs) possess a wide band gap of 3.36 eV along with meV exciton binding energy. Thus, ZnO nanostructure materials are suitable for promising applications in the transparent conducting electrodes in optoelectronics, photonics, textiles, paintings, industrial coatings, photo-catalysts, antimicrobial agents, and sunscreen [3–8]. Moreover, the physical and chemical properties of ZnO can be successfully tuned through doping of different transition metal (TM) ions (Cr, Mn, Fe, Co, etc.), and other materials such as carbon and chalcogenides are used to reduce the size [9–14]. The optical properties of ZnO could be controlled via size reduction, and reduction in size leads to tuning the band of materials and enhancing the emission characteristics and is due to the quantum size effects. Doping and adding an impurity in host lattice is a simple and efficient way of controlling the physical and chemical properties of ZnO nanostructured materials [15–19]. The doping of TM ions in the ZnO matrix can be realized through various synthesis routes such as hydrothermal [20], sol–gel [21], and co-precipitation [22] method. Among the available chemical routes, co-precipitation techniques are simple, cost-effective, low temperature, and well-controlled size distribution [23, 24]. The doping of Mn ions in the ZnO matrix leads to enhancement in the optical, magnetic, electrical, and photocatalytic properties. For instance, a significant role in enhancement in the carrier concentration of ZnO nanostructures concerning the concentration of Mn ions [25]. The band gap modification and room temperature ferromagnetism have been realized by doping Mn$^{2+}$ and Mg$^{2+}$ ions in ZnO [26]. A label-free photoelectrochemical sensor has been fabricated using Mn-doped ZnO nanorods and found that sensitivity and selectivity are significantly improved upon Mn doping [27]. In addition, Mn doping could be used to improve the antimicrobial activities in ZnO nanostructures.

In recent years, significant efforts have been paid to understand and utilize the semiconductor (SC) nanostructures for biomedical applications such as antimicrobial and anti-cancerous treatment due to their biocompatibility and low toxicity in nature. Among all other SC, ZnO nanostructures exhibited the capability to produce reactive oxygen species (ROS) at their surface of particles. The creation of ROS levels is greater than the antioxidant capacity of the cell that causes cell death [28]. An investigation has been demonstrated to evaluate the antimicrobial activity of ZnO nanostructure against *Vibrio cholerae* with a particle size of 7–10 nm. It is found that ZnO NPs produces a significant number of ROS, which leads to disruption of bacterial cell wall membrane [29]. Similarly, a detailed investigation has been performed on the toxicity of ZnO and TiO$_2$ NPs where *Escherichia coli* (*E. coli*) are used as a model organism. Results revealed that upregulation of ROS-related proteins on toxicity need not correlate with one another [30]. Prasanna and Vijayaraghavan carried out the antibacterial study in both dark and light conditions. It has been observed that ROS such as ‘OH, ‘O$_2$-, and H$_2$O$_2$ are significantly produced from the aqueous suspension of ZnO mainly responsible for the activity in the dark [31]. Akhavan et al. investigated photo-inactivation of *E. coli* bacteria on the surface of unfunctionalized and functionalized multi-wall carbon nanotubes (MWCNT–ZnO nanocomposites. The results revealed functionalized MWCNT–ZnO nanocomposites showed significantly stronger photo-inactivation due to charge transfer through Zn–O–C bands formed between the Zn atoms of the ZnO film and oxygen atoms of the carboxylic functional groups [32]. Wang et al. prepared ZnO/graphene oxide composites were evaluated with *E. coli* and HeLa cells and found that zinc concentration pitting and permeability of the bacterial membrane, thus inducing bacterial death [33]. Akhavan et al. observed ZnO nanorod arrays to show an excellent UV-induced photocatalytic degradation of *E. coli* bacteria [34]. Raghupathi et al. reported the antibacterial activity of ZnO NPs involve both the production of ROS and the accumulation of NPs in the cytoplasm or on the outer membranes [35]. Mesaros et al. identified ROS generation by using EPR studies and reported that Mn dopant with ZnO
NPs improves the antibacterial efficiency against E. coli and Bacillus cereus [36]. However, the present work mainly focused to improve the antibacterial activity using pure and Mn-doped ZnO.

Due to TM-doped ZnO importance in various technological fields, the present investigation includes the synthesis of pure and Mn-doped ZnO NPs by co-precipitation process and their characterization of structural, optical, and magnetic properties depending on concentrations of Mn ions. It also explains their performance of antibacterial activities against the Staphylococcus epidermidis (S. epidermidis) and Pseudomonas aeruginosa (P. aeruginosa) bacterial strains.

2 Experimental

2.1 Material synthesis

Chemicals used in the synthesis were analytically pure and used as received without any additional purification. Briefly, pure ZnO NPs synthesized by slow addition of NaOH solution (3.2 g in 100 ml) to Zn(CH3COO)2·2H2O (0.1 M) until the zinc acetate dehydrate solution became white milky precipitates. The formed precipitated is subjected to centrifugation process for 5 min at 3000 rpm, and the process was repeated five times and washed thoroughly with distilled water. A similar procedure was repeated to synthesis Mn-doped ZnO NPs. The NaOH (3.2 g in 100 ml) solution was slowly added to the solution mixtures containing 0.024 g (1%), 0.049 g (2%) and 0.073 g (3%) of manganese acetate (100 ml distilled water), and 2.17, 2.15 and 2.12 g of zinc acetate (100 ml distilled water). The formed precipitates appeared as black-colored for all Mn-doped ZnO samples. The final precipitates were collected to dry in a hot air oven at 90 °C for 5 h to obtain pure and Mn-doped ZnO NPs. Furthermore, all the samples were subjected to annealing at 700 °C for 2 h. The prepared pure and Mn-doped ZnO samples are codenamed as ZnO, ZnMnO1, ZnMnO2, and ZnMnO3 for 0%, 1%, 2%, and 3% of Mn concentrations, respectively (Table 1).

2.2 Instrumentation

The phase purity and doping induced microstructural properties of ZnO NPs were identified using X-ray diffraction (XRD model: X’PERT PRO PANalytical). The diffraction patterns were recorded in the range of 20–80° and X-ray of wavelength 1.54 Å was used. The morphology and reduction in size of ZnO upon doping was examined by using high-resolution transmission electron microscopy (Tecnai F20 model) instrument and operated at an accelerating voltage of 200 kV. The elemental composition and presence of dopant in ZnO were identified through energy-dispersive X-ray spectroscopy (EDAX model: AMETEK) with FEI-QUANDA 200F HRSEM operated at 30 kV. The vibrational properties of ZnO were acquired through FTIR spectral measurement and spectra were recorded by using Perkin-Elmer spectrometer through KBr pellet technique. The modification of band gap and emission characteristics was analyzed through UV–Vis-NIR spectra (Lambda 35) in the wavelength range 190–1110 nm and photoluminescence (FLUROLOG-3-11, HORIBA Jobin Yvon, USA) measurement with the excitation wavelength of 330 nm.

2.3 Testing of antibacterial activity

All the media and disk used in this experiment were purchased from Hi-Media (Mumbai, India). Antibacterial activity of ZnO and Mn-doped ZnO were studied against a gram-positive (S. epidermidis) and a gram-negative (P. aeruginosa) bacteria by disk diffusion method. A disk diffusion technique is well understood to test the bacterial sensitivity against antibiotics. A similar method was employed with pure and Mn-doped NP laden disks in the present investigations. Briefly, 3.8 g of Muller Hinton Agar (MHA) powder was dissolved in 100 ml of water in ambient temperature, followed by sterilization in an autoclave under 15 lbs pressure at 121 °C over 15 min. Then the solution was allowed to cooled to 40–45 °C. Similarly, all the petri dishes had been thoroughly sterilized to avoid contamination and 20 ml of the agar medium was added into all petri dishes, separately. The dishes were allowed (around 30 min) to cool to become solidify. The MHA plate was constantly rotated for every 60 min to ensure homogeneous growth. The pure and Mn-doped ZnO NPs coated disks (6 mm diameter) were placed in each dish were made by sterilized forceps. Twenty microlitres of test solution of different

| Sample coding and sample composition |
|-------------------------------------|
| **S.no** | **Sample coding** | **Sample composition** |
| 1. | Pure ZnO (Zn-100%) | 0.100 M Zn(CH3COO)2·H2O + 0.8 M NaOH |
| 2. | ZnMnO1 (Zn-99% & Mn-1%) | 0.099 M Zn(CH3COO)2·H2O + 0.8 M NaOH + 0.001 M Mn(CH3COO)2·H2O |
| 3. | ZnMnO2 (Zn-98% & Mn-2%) | 0.098 M Zn(CH3COO)2·H2O + 0.8 M NaOH + 0.002 M Mn(CH3COO)2·H2O |
| 4. | ZnMnO3 (Zn-97% & Mn-3%) | 0.097 M Zn(CH3COO)2·H2O + 0.8 M NaOH + 0.003 M Mn(CH3COO)2·H2O |
concentrations were poured in each disk in two dishes. Each petri dish contained two different concentrations (0.6 and 1.20 mg) of pure and Mn-doped ZnO NPs and the petri dishes were covered with paraffin film to avoid contamination from the surroundings. All dishes were incubated at 35 °C over one day and inhibition zone was measured. In the present investigations, methicillin was used as a positive control.

3 Results and discussion

3.1 XRD analysis

Figure 1 shows the XRD patterns of pure ZnO and 1%, 2%, 3% Mn-doped ZnO NPs. The diffraction patterns show strong and sharp peaks located at the angle (2θ) of 31.8°, 34.4°, 36.3°, which correspond to (100), (002), (101) planes which confirm the hexagonal wurtzite structure of ZnO with lattice constants of \( a = b = 3.249 \, \text{Å} \) and \( c = 5.206 \, \text{Å} \) (JCPDS card No. 36-1451). Similarly, other peaks are located at the angles of 47.4°, 56.7°, 62.9°, 66.2°, 68.0°, 69.2°, 72.4° and 77.3°, corresponding to (102), (110), (103), (200), (112), (201), (004) and (202) planes of the wurtzite structure, respectively. Interestingly, Mn-doped ZnO samples did not show any secondary peaks, which further confirms that there is no secondary phase formation in ZnO. However, Mn doping on ZnO lattice causes slight lower angle shift compared to pure ZnO and intensities of diffraction are decreased upon increasing the concentration of Mn.

3.2 Particle size determination

The particle size of the pure and Mn-doped ZnO could be extracted by using Debye-Scherer’s formula [37]

\[
D = \frac{k\lambda}{\beta_{hkl}\cos\theta}
\]

where the constant \( k \) is the shape factor = 0.94, \( \lambda \) is the wavelength of X-rays (1.5418 Å for Cu \( K\alpha \)), \( \theta \) is diffraction angle, and \( \beta \) is the full width at the half-maximum. The crystallite size of the pure ZnO is calculated as 41.6 nm and it is decreased to 40.1 and 33.8 nm for ZnMnO2 and ZnMnO3, respectively (Table 2). Staumal et al. [38] investigated that the decrease of crystallite size is due to increase of Mn solubility in ZnO. The reduction in the particle size is mainly due to the distortion in the host ZnO lattice by foreign impurities i.e., Mn\(^{2+}\) which decrease the nucleation and the subsequent growth rate of the ZnO NPs.

The concentration of dopant in ZnO matrix significantly alter the lattice parameters and is due to the difference of ionic radius of dopant ions with respect to the ZnO

\[
\frac{1}{d_{hkl}^2} = \frac{4h^2 + hk + k^2}{a^2} + \frac{l^2}{c^2}
\]

the lattice constant ‘\( a \)’ is calculated through the relation

\[
a = \frac{\lambda}{\sqrt{3}\sin\theta}
\]

for (100) plane and the lattice constant ‘\( c \)’ can be extracted through the relation

\[
c = \frac{\lambda}{\sin\theta}
\]

for plane (002). The unit cell volume could be deduced from the formulae [39]

\[
v = \frac{\sqrt{3}a^2c}{2}
\]
and the change in the bond length upon Mn doping is calculated through the relation [40]

\[ L = \left( \frac{a^2}{3} + \left( \frac{1}{2} - u_p \right)^2 \right)^{1/2} \]  

(6)

where, ‘a’, and ‘c’ are lattice parameters and ‘u_p’ is the positional parameter and it can obtained by applying formula

\[ u_p = \left( \frac{a^2}{3c^2} \right) + 0.25 \]  

(7)

The calculated lattice constants and bond length is shown in Fig. 2a, b. It clearly shows an increment in lattice constant due to Mn doping. The lattice constants of Mn-doped ZnO are more than that of undoped ZnO, because of the ionic radius of Mn$^{2+}$ (0.66 Å) is larger than that of Zn$^{2+}$ (0.74 Å) [41].

The dopant-induced lattice strain can be simply extracted from the peak broadening of diffraction line analysis. The broadening of diffraction line is formed due to the addition of the two components namely; lattice strain and the particle size with respect to diffraction angle and it can be written as [42]

\[ \beta_{hlk} = \beta_t + \beta_e \]  

(8)

where \( \beta_t \) is the particle size contribution and \( \beta_e \) is due to the strain contribution which induced by dopant ions. The strain-induced line broadening can be obtained through this relation

\[ \beta_e = 4\varepsilon \tan \theta \]  

(9)

where \( \varepsilon \) is the microstrain. So the total peak broadening including the contribution from particle size as well as microstrain can be written as [43]

\[ \beta_{hlk}\cos \theta_{hlk} = \frac{k\lambda}{D} + 4\varepsilon \sin \theta \]  

(10)

The value of microstrain with respect to Mn concentration is extracted from the plot of \( \beta_{hlk}\cos \theta_{hlk} \) vs \( 4\sin \theta \) (Fig. 3a). The variation in the microstrain upon Mn concentration is plotted and shown in Fig. 3b. The results reveal that the microstrain is decreased for 1% and 2% of Mn.
concentration with respect to pure ZnO. However, the microstrain is slightly increased to 3% Mn concentration due to lattice mismatch when the concentration of Mn is large [43].

3.3 Morphological and compositional analysis

The morphology and size of NPs were observed through HRTEM images, which are shown in Fig. 4.1(a–d) and 4.2 (a–d). The results clearly revealed that the pure ZnO NPs are spherical in shape and size of particle is found to be 45 nm which is consistent with our XRD results. Fig. 4.2 represents the Mn-doped ZnO NPs, and it also exhibited nearly spherical in nature. It can seen from this Fig. 4.2 reduction in particle size (42 nm) was observed upon the 3% of Mn-doped ZnO sample. The distance between two parallel planes was observed at ~0.26 nm. The corresponding selected area electron diffraction (SAED) pattern of the pure and Mn-doped ZnO NPs is shown in Fig. 4.1(d) and Fig. 4.2 (d). The superimpositions of the bright spots demonstrate the good crystalline nature of the particles. The presence of Mn dopant and composition of Mn ions in ZnO matrix was identified from EDAX analysis. The EADX spectra of pure and Mn-doped ZnO shown in Fig. 5(a–d), the peaks located at energies 1 and 8.6 keV, are corresponds to Zn ions and O ions peak appeared at 0.5 keV and chemical compositions of Zn and O were observed at 59.25 and 40.75%. Similarly, for Mn-doped ZnO NPs, the peaks are located at energies 0.6 and 5.9 keV are corresponds to Mn ions and it further confirms the presence of Mn doping in ZnO matrix. Further, Mn concentrations are found to be 0.53, 1.04, and 1.91% for ZnMnO1, ZnMnO2, and ZnMnO3 NPs, respectively (Table 3).

3.4 UV spectroscopy analysis

The UV–Vis absorption spectra of the pure and Mn-doped ZnO NPs samples were performed by dispersing 3 mg of prepared samples in 10 ml distilled water and the obtained spectra is shown in Fig. 6. The absorbance peak edges located at 3.29 eV were free excitons of ZnO NPs and spectra did not show any bands from Mn ions. The higher energy shifts in absorption band edge were identified upon increase of Mn concentrations. The excitonic absorption peaks located at 3.31, 3.31, and 3.324 eV were corresponded to 1%, 2%, and 3% Mn-doped ZnO, respectively.

3.5 Estimation of optical band gap

The optical band gap of the synthesized ZnO and Mn-doped ZnO NPs can be calculated using from this relation,

\[
\alpha = \frac{2.303 A}{\lambda}
\]

(11)

where \(A\) is the absorbance and \(\lambda\) is the path length of the cuvette. The Mn doping induced changes of optical band gap was calculated by using Tauc relationship [44]

\[
(\alpha h \nu)^n = A(h \nu - E_g)
\]

(12)

where \(A\) is a constant, \(h\) is Planck’s constant, \(\nu\) is the photon frequency, \(E_g\) is the optical band gap and \(n = 2\) for direct band gap SC. An extrapolation of the linear region of a plot of \((\alpha h \nu)^2\) vs Photon energy \((h \nu)\) would give the value of optical band gap \((E_g)\) of the materials [40]. Figure 7 displays the band gap energy diagram for pure and Mn-doped ZnO NPs. The calculated band gap of pure ZnO NPs was found to be 2.95 eV. The band gap energy of ZnO increases to 3.14 eV with the addition of Mn. This is attributed to the decrease in particle size of doped ZnO. It’s clear that more level of doping causes the blocking of low energy transition which lead to an increase in the exitonic band gap confirms the Burstein–Moss effect [40, 45]. It concludes that the increase of band gap upon doping is a combined effect of size and Burstein–Moss effect. Similar kind of observation has been reported in Mn-doped ZnO nanostructures [46].

3.6 Photoluminescence (PL) analysis

Generally, the densities of defects and oxygen vacancies affect the optical properties of oxide SC nanostructures significantly. The correlation between the structure and the property is investigated by measuring PL spectra of undoped and Mn-doped ZnO NPs at the excitation wavelength of 325 nm which is shown in the Fig. 8a. The PL spectra of the samples ZnO, ZnMnO1, ZnMnO2, and ZnMnO3 NPs demonstration of UV emission peak at ~387 to 397 nm and broad visible emission peaks including violet emission at ~416 to 418 nm, blue-green emission at ~480 to 479 nm, and green emission at ~523 to 524 nm. The UV emission band is associated to the near band-edge (NBE) emission of the ZnO NPs due to the recombination of free excitons by exciton-exciton collision process [47, 48]. Several authors have investigated the PL properties of ZnO nanostructures [47–54]. Generally, visible emission in ZnO contains of blue, violet, green, and yellow region, this may be ascribed to many intrinsic defects such as oxygen vacancies \((V_o)\), zinc vacancies \((V_{Zn})\), oxygen interstitials \((O_i)\), zinc interstitials \((Z_i)\) and oxygen antisites \((O_{Zn})\) [45]. UV peak is shifted from 394 to 387 nm with respect to the Mn concentrations (Fig. 8b), that shows the result is consistent with UV absorption spectra. The violet emission in synthesized ZnO NPs centered at ~416 to ~418 nm is attributed to an electron transition from a shallow donor level of the neutral Zn to the top level of the valence band [55]. A blue–green emission observed at ~480 to 479 nm is
due to a radiative transition of an electron from the shallow donor level of Zn$_i$ to an acceptor level of neutral V$_{zn}$ [47]. The green emission at 524 nm is attributed to radiative transition from conduction band to the edge of the acceptor levels of O$_{zn}$ caused by oxygen antisites (O$_{zn}$) [47, 56]. The UV emission and reduced visible emission shows that the
undoped and Mn-doped ZnO NPs have a good crystal structure with fewer oxygen vacancies.

3.7 FTIR analysis

FTIR spectra of pure and Mn-doped ZnO NPs are shown in Fig. 9. The Zn–O vibrational band located at 550 cm⁻¹ for pure ZnO and is shifted to lower frequency of 548 cm⁻¹ for Mn = 0.01 M, 546 cm⁻¹ for Mn = 0.02 M and 541 cm⁻¹ for Mn = 0.03 M. The O–H bending vibration bands were identified at 1500–1650 cm⁻¹. The band at 900 cm⁻¹ and 1405 cm⁻¹ is attributed to =C–H bending vibrations and C–H bending vibrations, respectively [57]. The small peaks observed at 2344, 2330, 2358 cm⁻¹ which are arising from the absorption of atmospheric CO₂ [58]. The bands around 1200 and 1100 cm⁻¹ are attributed to the characteristic frequency of inorganic ions. The wide absorption peaks in the range of 3410–3465 cm⁻¹, related to the –OH group, may due to the water adsorbed on the surface of NPs.

Table 3 Compositional Analysis of ZnO and ZnMnO NPs

| Sample   | Dopant concentration (Atomic %) | Experimental results (Atomic %) |
|----------|---------------------------------|--------------------------------|
| ZnO      | 0                               | Zn 59.25 Mn – 40.75 O           |
| ZnMnO1   | 1                               | Zn 40.22 Mn 0.53 O 59.25        |
| ZnMnO2   | 2                               | Zn 44.81 Mn 1.04 O 54.15        |
| ZnMnO3   | 3                               | Zn 40.60 Mn 1.91 O 57.48        |

Fig. 5 (a–d) EDAX spectrum for pure ZnO and different concentration of Mn-doped ZnO NPs

Fig. 6 UV absorption spectra of pure ZnO and different Mn concentration of ZnO NPs
3.8 Antibacterial properties

The antimicrobial activity of pure and Mn-doped ZnO is performed against S. epidermidis and P. aeruginosa pathogens using the disk diffusion method. The antimicrobial activity of NPs is found to vary with respect to type of microorganism and concentration of NPs. Figure 10 represents disk diffusion results of (a) S. epidermidis and (b) P. aeruginosa. Figure 11 shows zone of inhibition graph against the bacterial strains (a) S. epidermidis, and (b) P. aeruginosa respectively. The higher ROS is generally produced due to the decreasing particle size, larger surface area, diffusion ability of the reactant molecules, and an increase in oxygen vacancies. In the present work, the antimicrobial activity of the ZnO NPs is essentially attributed to the combination of several factors such as ROS, and the release of Zn$^{2+}$ [37].

Gram-positive and gram-negative bacteria both have amine and carboxyl groups on their cell surfaces, and Zinc has a strong affinity for these groups [59]. Figure 10(c) shows the ZnMnO attached to a carboxyl group in a bacterial species is depicted schematically. The Zn$^{2+}$ is connected to the bacterial cell wall membranes by cross-linking within and between nucleic acid strands, Zn$^{2+}$ ions released later may connect with macromolecules such as DNA, protein, and lipid molecules, causing helical structural disruption. Then ZnMnO NPs bind to the cell membrane and become adsorbent on the surface of the deceased bacterium, preventing further antibacterial activity. The release of a higher number of oxygen species during H$_2$O$_2$ production from the NP surface could thus explain the increased bacterial activity of Mn-doped ZnO compared to pure ZnO. The generation of oxygen species is reduced in ZnO NPs due to recombination of electron-hole pairs. By contrast, because of the trapping of electrons by Mn ions, this recombination is reduced in Mn-doped ZnO NPs, resulting in the production of more reactive species and improved antibacterial activity. It’s also possible that the NPs release ions called Zn$^{2+}$, which may stick to the bacteria’s negatively charged cell wall and break it, causing proteins to break down and cell death [60].

The above mechanism of light induced generation of ROS can be given in equation form as following [61],

$$\text{ZnO} + \text{hv} \rightarrow \text{e}^- + \text{h}^+ \quad (13)$$

$$\text{h}^+ + \text{H}_2\text{O} \rightarrow \text{OH} + \text{H}^+ \quad (14)$$

$$\text{e}^- + \text{O}_2 \rightarrow \cdot\text{O}_2^- \quad (15)$$
From the result of PL studies for ZnO and Mn-doped ZnO NPs, the violet and blue-green emissions can have the possibility of interstitial incorporation of Mn and Zn ions into the ZnO lattice. The second reason for the antibacterial activity is that when Zn\(^{2+}\) released by ZnO contacts with the cell membranes of microbe, the cell membranes with negative electricity and Zn\(^{2+}\) with positive electricity attract mutually and then the Zn\(^{2+}\) would penetrate into the cell membranes and react with sulfhydryl inside the cell membranes. Thus causes the cell wall rupture and leads to death of microorganism. The antimicrobial ability of the ZnO NPs is closely related to the disruption of the membrane integrity through direct contact with bacterial cells. The intrinsic toxic properties of ZnO play an important role in causing structural changes and degradation of cells [62]. The antibacterial effects of the NPs supernatants and the NPs suspensions suggest the contribution of the released ions to the ZnO NPs antibacterial effects. The antibacterial effects of Mn\(^{2+}\) ions cannot be accountable for the biocide activity of the Mn-doped samples [37]. But the replacement of Mn in the Zn site enhanced the photoactivity of the particles as related to ZnO NPs because of the similarity in ionic radii between Mn\(^{2+}\) (0.66 Å) and Zn\(^{2+}\) (0.74 Å). From the PL spectra of pure and Mn-doped ZnO, the wavelengths of green emissions are at 523 and 524 nm. These indications increased the oxygen vacancies in the Mn-doped ZnO NPs leading to more ROS as compared to that of ZnO NPs [64].

The NPs with uneven surfaces and rough edges have adhered to the bacterial wall and these causes damage to the cell membrane [65]. From the field emission scanning electron microscopy image, the Mn-doped ZnO NPs have uneven ridges and cluster formations at their outer surface leading to antibacterial activity.

Interestingly, the zone of inhibition in this investigation corresponds to the microorganism’s susceptibility level. The disinfectant-included strains have a higher inhibition zone, whereas resistant strains have a smaller inhibition zone (see Fig. 11). For both pure ZnO and Mn-doped ZnO NPs, all bacterial strains are more sensitive at higher concentrations (1.2 mg/ml). S. epidermidis, and P. aeruginosa showed similar zones of inhibition to the positive control (methicillin) for pure ZnO and Mn-doped ZnO NPs when compared to the positive control.

The present antibacterial activity results are compared with previous reported literature [31–36], are given in Table 4. Previous works [31–36] have shown promising results to enhance the antibacterial efficiency against various pathogenic microorganisms and they found that cell death mainly due to ROS. In the present investigation, compared to the pure ZnO NPs, Mn-doped ZnO NPs have the highest antibacterial activity and increasing the concentration of Mn\(^{2+}\) ions in the ZnO matrix significantly increased antibacterial activity.

### 3.9 Magnetic properties

The influence of Mn doping on ZnO NPs on the magnetic properties is observed through vibrating sample magnetometer measurements. The ZnO NPs exhibit diamagnetic behavior with a magnetic moment of 0.0096 emu/g and magnetic moments of 0.00809, 0.0304, and 0.0408 emu/g are observed for 1%, 2%, and 3% Mn-doped ZnO NPs (Fig. 12). It is clearly visible that the Mn content significantly influences the magnetic parameters of the ZnO

\[ \cdot O_2^- + H^+ \rightarrow HO_2^\bullet \]  
\[ HO_2^\bullet + H^+ \rightarrow H_2O_2 \]
matrix. Magnetic parameters change due to various factors, including variation in particle size/crystallite size with Mn doping level and creation of lattice strain [66–70]. In the present work, the XRD results revealed that the average crystalline size of synthesized ZnO, ZnMnO1, ZnMnO2 and ZnMnO3 NPs was observed at 41.8, 41.2, 40.1, and 33.8, respectively. From the EDAX spectrum, the 0.53%, 1.04%, and 1.91% for ZnMnO1, ZnMnO2, and ZnMnO3 NPs, increasing the doping concentration of Mn ions also increased the atomic percentage of Mn$^{2+}$ ions. An increase in Mn doping concentration, enhances the linear behavior of the M–H loop. Due to the decreasing crystalline size of prepared Mn-doped ZnO NPs and also increasing Mn$^{2+}$ ion concentration in the ZnO surface matrix, these effects the enhanced weak ferromagnetic behavior of Mn-doped ZnO NPs [71].

![Fig. 10](image_url) The pictures demonstrate the disk diffusion results of a *S. epidermidis*, b *P. aeruginosa*, and c Schematic diagram of ZnMnO attached to a carboxyl group in a bacterial species.

![Fig. 11](image_url) Zone of inhibition graphs for a *S. epidermidis* and b *P. aeruginosa* bacterial strains.
| Materials                        | Concentration | Bacterial Name | Efficacy   | Mechanism                                                                                                                                 |
|---------------------------------|---------------|----------------|------------|--------------------------------------------------------------------------------------------------------------------------------------------|
| **Present work**                | ZnO           | *S. epidermidis* | 10–21 mm   | The antimicrobial activity of the ZnO NPs is essentially attributed to the combination of several factors such as ROS, and the release of Zn$^{2+}$ ions. |
|                                 | ZnMnO1        | *P. aeruginosa* |            |                                                                                                                                            |
|                                 | ZnMnO2        |                |            |                                                                                                                                            |
|                                 | ZnMnO3        |                |            |                                                                                                                                            |
| **ZnO**                         | 0.6 mg and 1.20 mg | *S. aureus* | 17 mm     |                                                                                                                                            |
| **MWCNT–ZnO nanocomposites**    | 0.1 g/L       | *E. coli*      | 23 and 31% | The reactive oxygen species (ROS) such as ‘OH, ‘O$_2^−$, and H$_2$O$_2$ are significantly produced from aqueous suspension of ZnO even in the dark which are mainly responsible for the activity in the dark up to 17%, rather than Zn$^{2+}$ ion leaching [31]. |
| **Zinc Oxide/Graphene Oxide Composites** | 0–30 wt% | *E. coli* |            | The electrons photoexcited in the space-charge regions of the MWCNT–ZnO composite are transferred from the valence band of the ZnO into the MWCNTs (as electron sinks) through the Zn–O–C bonds. The holes on the ZnO can contribute to redox reactions to inactivate the bacteria [32]. |
| **ZnO nanorod**                 | 100 $\mu$g mL$^{-1}$ | *E. coli* | 10 $\mu$g mL$^{-1}$ | The ZnO/GO composites exhibit a concentration- and composite-dependent bactericidal activity [33]. |
| **ZnO**                         | 10 mm × 10 mm | *E. coli*      | 2.40 (h$^{-1}$) NaOH concentration of 0.10 M | The ZnO nanorods with the highest surface area ratio showed the best antibacterial activity compared with the other grown samples. However, the surface area ratio may not be the only significant factor for increasing the antibacterial activity of the grown ZnO nanostructures [34]. |
| **ZnO**                         | 60–420 $\mu$L | *S. aureus*, *E. coli* and *B. subtilis* | 4–7 mM     | The antibacterial activity of ZnO nanoparticles is dependent on the size of the nanoparticles. It is mainly due to the particulate ZnO releasing free Zn$^{2+}$ ions from the ZnO colloidal solution [35]. |
| **ZnO**                         | 1, 2, 4, 6 and 8 mM | *E. coli* | 1–11 mm   | The improved bacterial activity of Mn-doped ZnO over pure ZnO could be explained by the release of more oxygen species during H$_2$O$_2$ generation from the surface of the NPs [36]. |
Mn$_2$ doped ZnO NPs have the highest antibacterial activity than Mn concentrations. The band gap of ZnO NPs was 
grown and a reduction in the particle size with respect to the 
impurity. HRTEM images showed nanospheres morphology 
and a reduction in the size with respect to the Mn concentrations. The band gap of ZnO NPs was 
increased from 2.95 to 3.14 eV upon Mn doping. The Mn-
doped ZnO NPs have the highest antibacterial activity than 
the pure ZnO NPs. In order to increase the concentration of 
Mn$^{2+}$ ions in the ZnO matrix, significantly increased anti-
bacterial activity.

**Author contributions** EJ: conceptualization, methodology, investigation, writing – original draft. KAC: methodology, investigation. PT: resources, investigation. KC: methodology, investigation. RVM: supervision, editing.

**Compliance with ethical standards**

Conflict of interest The authors declare no competing interests.

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