Enhanced antibacterial activity of transition metal doped ZnO nanorods on thin films

G. Poongodi¹,², R. Mohan Kumar²*, R. Jayavel³

¹Department of Physics, Quaid-e-Millath Govt. College for Women, Chennai –600 002 , India.
²Department of Physics, Presidency College, Chennai – 600 005, India.
³Centre for Nanoscience and Technology, Anna University, Chennai – 600 025, India.

*Corres. Author: mohan66@hotmail.com

Abstract: Transition metal (Mn, Co and Cu) doped ZnO nanorods were prepared on thin film by hydrothermal method. The structural, morphological, optical and antibacterial properties of thin films were studied by using X-ray diffraction (XRD), Field emission scanning electron microscopy (FE-SEM) with energy dispersive X-ray spectroscopy (EDAX) and UV-Vis spectroscopy. Formation of hexagonal wurtzite phase of ZnO was confirmed by XRD analysis. The band gap of TM doped ZnO was estimated from the optical transmission spectra recorded in the wavelength range, 300-800 nm. FE-SEM images showed the well-defined hexagonal shape ZnO nanorods and it was confirmed that TM doping decreases the aspect ratio of ZnO nanorods. The bactericidal efficiency of TM doped ZnO nanorods were investigated against a Gram negative (Escherichia coli) and a Gram positive (Staphylococcus aureus) bacteria. The result showed that TM doped ZnO nanorods enhances the antibacterial activity of pure ZnO nanorods.

Keywords: Transition metal doped ZnO, Thin film, hydrothermal method, FESEM, Antibacterial activity.

Introduction and Experimental

Recently, inorganic antimicrobial agents have been attracted for the effective control of microorganisms. Among the metal oxide semiconductors, ZnO shows biocompatibility and antibacterial activity in the neutral region (pH = 7) [1]. The antibacterial activity of ZnO is considered due to the generation of reactive oxygen species (ROS) O₂⁺, •OH and H₂O₂ from its surface by photocatalytic activity. Doping of ZnO with transition metals (TM) can modify its photocatalytic and antibacterial activity which are all crucial for its environmental applications. Furthermore, one dimensional (1D) ZnO nanostructures such as nanorod, nanowire, and nanotube can reduces the carrier scattering due to the carriers being confined in a certain direction which improves the complete elimination of pollutants. In this study, pure and transition metals (Co, Mn and Cu) doped ZnO nanorod arrays were synthesised by hydrothermal method on ZnO seed coated glass substrates and studied its properties.

Synthesis of pure and TM doped ZnO thin films

ZnO seed thin films were prepared on glass substrates by sol-gel spin coating method. ZnO nanorod arrays were prepared by placing ZnO seed coated substrates in an aqueous solution containing 0.05M zinc...
nitrate hexahydrate (Zn(NO$_3$)$_2$.6H$_2$O) and 0.05M hexamethylenetetramine (HMT) at 90°C for 3h. Transition metals (TM) doped ZnO (Co:ZnO, Mn:ZnO and Cu:ZnO) nanorods were formed by adding 0.05M manganese (II) acetate tetrahydrate, cobalt(II) acetate tetrahydrate and copper(II) acetate monohydrate in the above reactant solution separately. The grown pure and TM doped ZnO nanorod arrays were rinsed with deionized water and dried at 100°C for 2h.

**Antibacterial activity studies**

Antibacterial activity of pure and TM doped ZnO thin films against a Gram negative bacterium Escherichia coli (E.coli) and a Gram positive bacterium Staphylococcus aureus (S.aureus) was investigated using liquid culture test. The thin film samples of 1cm$^2$ were immersed in the bacteria culture medium and the optical density at 600 nm of this medium (the bacteria and sample) was measured after 24 h using a digital spectrophotometer. The same procedure was also followed for the control plain glass plate. The decrease in absorbance was considered as the effect of thin films against the bacterial growth. The bacterial inhibition by thin films was calculated using,

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\% \text{ of bacterial inhibition} = \frac{\text{Absorbance of control} - \text{Absorbance of sample}}{\text{Absorbance of control}}
\]

**Results and Discussion**

Figure 1(a) shows the powder XRD patterns of pure and TM doped ZnO nanorods grown on seed thin films. The XRD pattern reveals the phase pure wurtzite ZnO structure and very well agrees with the reported data (JCPDS card No.36 –1451). The XRD pattern of TM doped ZnO was assigned to that of the hexagonal wurtzite ZnO structure and no extra diffraction peaks were observed for Mn, Co and Cu related secondary phases or impurities. But a small shift towards lower angle for Co and Cu doped ZnO samples and higher angle shift for Mn doped ZnO sample were observed which may be caused by the substitution of TM in ZnO (inset of Fig.1). This slight variation indicates that the incorporation of transition metal ions into the ZnO lattice.

![Fig. 1](image)

**Fig. 1(a)** XRD pattern of pure and doped ZnO microrods (Inset: shift in 20) and FE-SEM images with EDAX spectra of (b) Pure ZnO, (c) Mn:ZnO, (d) Co:ZnO and (e) Cu:ZnO.

FE-SEM images of pure and TM doped ZnO thin films are shown in Fig. 1(b – d). It showed that the ZnO nanorods are well faceted with flat hexagonal symmetry at the top ends and the TM doping influences the aspect ratio of ZnO nanorod arrays. Energy dispersive X-ray spectra (EDAX) of pure and TM doped ZnO are shown in the inset of FESEM image of Fig.1 (b-d). It showed the peaks corresponding to Zn, O, Mn, Co and Cu. No trace of other impurities could be observed in the detection limit of the EDAX, which also confirmed the doping of TM in ZnO.

The optical UV-Vis transmittance spectra of pure and TM doped ZnO thin films were recorded in the wavelength range 300 – 800 nm are shown in Fig 2(a). The optical band gap energy values ($E_g$) were calculated by extrapolation of the linear part of $(\alpha h\nu)^2$ versus h$\nu$ plot as shown in inset of Fig. 2(a). It was observed that the band gap values of pure, Mn, Co and Cu doped ZnO thin films are 3.189eV, 3.096eV, 3.129eV and 3.029eV respectively. The reduction in the band gap is mainly due to the sp–d exchange interaction between the localized d-electrons of metal ions and band electrons of ZnO [2].
Bacterial inhibition of pure and TM doped ZnO thin films were shown in Fig.2 (b). The results reveal that the TM doping enhances the antibacterial activity of ZnO and higher activity was observed against S.aureus bacteria than E.coli. This difference can be attributed to the difference in the cell wall structure and resistance of outer membrane to the reactive oxygen species produced at the surface of the thin films. According to the mechanism related to the antibacterial activity of TM doped ZnO thin films, the release of ROS which kills bacteria can be enhanced by doping since the metal ions acts as a trapping centre of photogenerated electrons and reduces the recombination. The lattice distortion due to doping may create more oxygen vacancies and defects which increases generation of ROS and enhances the antibacterial activity of TM doped ZnO. Among the transition metals, Cu doped ZnO film shows higher bacterial inhibition, since the sizes of Cu doped ZnO nanorods were smaller than Co and Mn doped ZnO nanorods which may cause serious disruptions to amino acid synthesis and DNA [3].

**Conclusion**

Pure and transition metal (Mn, Co, and Cu) doped ZnO nanorods were grown on glass substrates by hydrothermal method. The XRD analysis showed that all the films possess hexagonal wurtzite structure. FE-SEM images revealed that the grown ZnO nanorods are well facetted with flat hexagonal symmetry at the top ends and the TM doping changes the aspect ratio of nanorod arrays. The optical studies showed the reduction in the band gap values. TM doping in ZnO act as electron trapping centres and inhibit electron hole recombination, which led to the generation of ROS and enhances the antibacterial activity of ZnO films.

**References**


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