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Characterization and Antibacterial activity of Undoped ZnO and Copper doped ZnO thin film prepared by Sol–gel Dip Coating Method

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Abstract:- *This paper reports on antibacterial study of undoped and Cu doped ZnO thin film prepared by the Sol-gel dip coating method. The prepared undoped and Cu doped ZnO films are characterized by SEM, FTIR, UV-Vis and XRD analysis. Amorphous and nano cluster shapes are observed in SEM analysis. The presence of different chemical functional groups is confirmed by FTIR analysis. The optical properties of undoped ZnO and Cu doped ZnO nanostructures are analyzed by UV-Vis analysis. The average particle size for undoped ZnO is estimated as 15 nm using the Scherrer's formula by XRD analysis.*

***Keywords**: Antibacterial activity, Undoped ZnO nanostructures, Cu doped ZnO, UV- Vis, FTIR, SEM analysis*

Introduction

Zinc oxide is a significant metal oxide semiconductor. It has novel scientific applications in diverse fields. ZnO has multifunctional properties such as piezoelectrics, optoelectronics, catalysis and antibacterial activity [1-2]. ZnO is an n-type extrinsic semiconductor with extensive direct band gap and large exciton binding energy (3.3 eV and 60 meV) [3,5]. ZnO nanostructures are synthesized by different methods, such as sol-gel method, hydrothermal method, co-precipitation method, solvo-thermal method, thermal evaporation technique, chemical vapour deposition and vapour transport technique [3-4]. ZnO is doped with different elements for the variation of electrical and optical properties. The most common elements which are doped with ZnO are Al, Ni, Fe, Mg, Co, Mn and Ce [5-6]. Among the different elements, Cu has numerous physical, chemical and antibacterial properties with Zn. The addition of Cu in ZnO lattice enhances the micro structure and antimicrobial properties of ZnO [7]. ZnO is extensively used in the fields such as solar cell, biosensor and anti-cancer activities [8-9]. The diverse morphologies of ZnO nanostructures are nanoflower, nanobelt and nanowire [10-11].

In this, the ZnO thin films were prepared by sol-gel dip-coating method. The prepared undoped and Cu doped ZnO films are characterized by SEM, FTIR, UV-vis and XRD Analysis. The change in the morphology of ZnO due to the addition of Cu is reported. The antibacterial activity was determined by testing the inhibit growth of S.typhi, S.aureus, B.subtilis, E.coli and P.aeruginosa bacteria.

Experimental Procedure

Preparation of Undoped ZnO thin film

The sol of 0.5M concentration was prepared by dissolving the required amount of Zinc acetate dehydrate [Zn (CH3 COO2).2H2O] into 20ml of iso-propanol which contains monoethanolamine (MEA) acting as a stabilizer. The molar ratio of Zn2+ to MEA is kept as 1:1 throughout the synthesis. Then homogeneous solution was stirred at 70^0C for 1hr to accelerate hydrolysis reaction to obtain a transparent sol-gel, which is used for coating after cooled to room temperature and also aged for 24hrs. ZnO thin films are prepared by depositing sol on the glass substrate by using dip-coating method, that time duration as 30sec of dip and 1 minute dry at 75^0C and this is repeated for 10 times. Then subsequently coated films are calcinated by annealing at 400^0C for 1hr to achieve the pure ZnO thin films. Finally the ZnO thin films are allowed to cool to room temperature and further it has taken for various studies.

Preparation of Cu doped ZnO thin film

The sol of 0.3M concentration was prepared by dissolving the required amount of Zinc nitrate hexahydrate ($Zn(NO_3)_2.6H_2O$) and copper nitrate hexahydrate (Cu(NO3)2.6H2O) into 20ml of ethanol is used as the host and dopant precursors. Then homogeneous solution was stirred for 1hr to accelerate hydrolysis reaction to obtain a blue coloured sol-gel, which is used for coating. ZnO thin films are prepared by depositing sol on the glass substrate by using dip-coating method, that time duration as 1 minute of dip and 5 minute dry at 75^0C and this is repeated for 5 times. Then subsequently coated films are calcinated by annealing at 350^0C for 1hr to achieve the Cu doped ZnO thin films. Finally the Cu-ZnO thin films are allowed to cool to room temperature and further it has taken for studies.

Antimicrobial Assay

The antibacterial effects of prepared undoped and Cu doped ZnO films are studied by using disc-diffusion method. Inoculums are prepared by, that the stock cultures are stored at 4^0C on slope of nutrient agar. Active cultures of experiment was prepared by shifting a loopful of cells from the stock cultures to the test tube of Muller-Hinton broth(MHB), that are incubated without agitation for 24 hours at 37^0C and 25^0C. Then the cultures are diluted with the fresh Muller-Hinton broth to gain optical densities approximately to 2.0 x 106 CFU/ ml for bacteria.

Here the disc diffusion method (Bauer *et al.*, 1966) was used to screen the antibacterial activity. In *vitro*, the microbial activity has been screened by using Muller-Hinton Agar (MHA) from Hi-media, Mumbai. The MHA plates are prepared using 15 ml of molten media into sterile petri plates. The plates are dried for 5 minutes and 0.1 %, inoculums suspension was swabbed throughout the plate and dried for 5 minutes. The concentration of extracts is 4 mg/disc was loaded on 6 mm sterile disc. The loaded disc was placed on the surface of the medium and extract was allowed to diffuse for 5 minutes and the plates are kept in incubator for 24 hours at 37^0C. As a result, the incubation zones on the disc were measured with the help of transparent ruler. The inhibition zones are obtained in the range of millimeter.

Result and Discussion

FTIR

The FTIR spectrum of Cu doped ZnO nanostructure is shown in Fig. 4. The spectrum is recorded in the range 3500 cm^{-1} – 500 cm-1. The characteristic peaks are observed at 3216 cm $^{-1}$, 2964 cm^{-1}, 2859 cm^{-1}, 1638 cm^{-1}, 1439 cm^{-1} and 631 cm^{-1}. The peaks at 3450 cm^{-1} and 1630 cm^{-1} are assigned to O-H stretching and O-H bending vibration [21]. The characteristic peaks at 631 cm^{-1} and 968 cm^{-1} indicate, the formation of Cu-O bond and stretching mode of Zn-O bond. The presence of various chemical functional groups proves the formation of Cu doped ZnO.

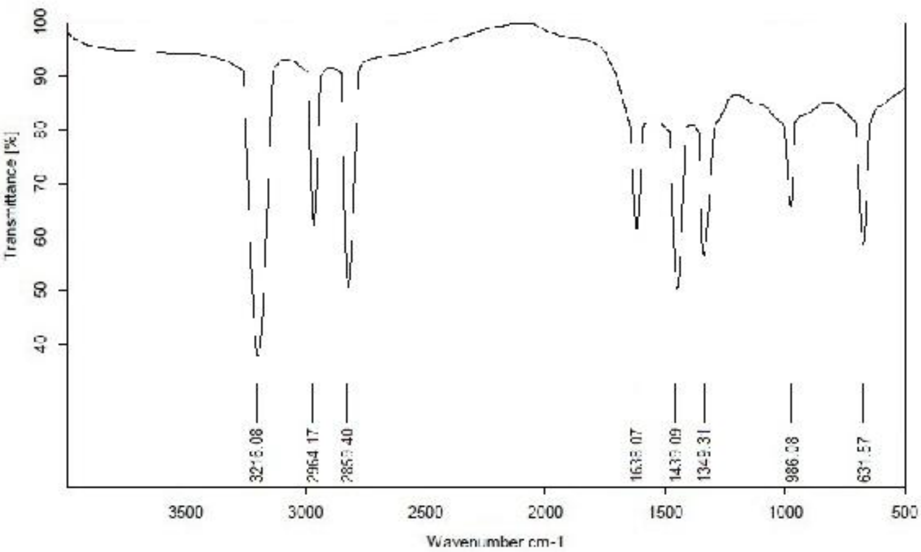

Figure 1: FTIR Spectra of Cu doped ZnO thin film

SEM Imaging

This analysis was performed by using Hitachi S-4500 Scanning Electron Microscope. SEM images Figure 2a and 3b shows that the nanoparticles of undoped ZnO are in amorphous form and Cu doped ZnO particles are in cluster form.

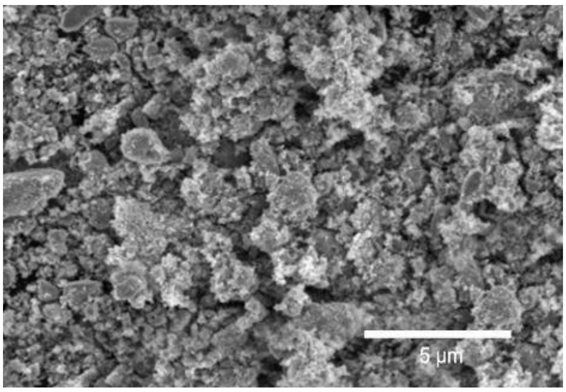

Figure 2a: SEM image of Undoped ZnO thin film

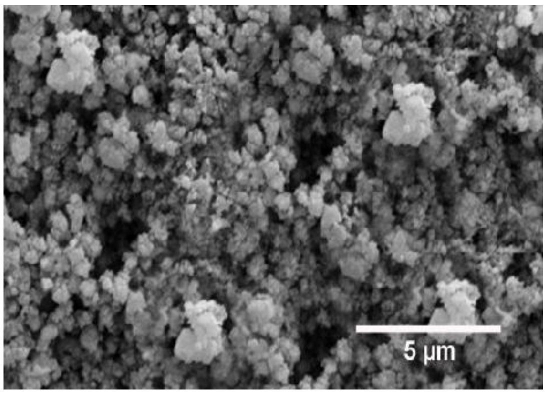

Figure 2b: SEM image of Cu doped ZnO thin film

X-Ray Diffraction

By scattering the X-ray beam on the sample, we get the information about the crystallographic structure, chemical and physical properties of the ZnO nanoparticles.

For undoped ZnO film the 2θ values 32.04, 34.97, 36.52, 47.81, 56.90, 62.64, 68.39, and 69.27 is corresponding to the plane of (100), (002), (101), (102), (110), (103), (112) and (201) respectively according to JCPDS No. 036-1451 shown in Figure 3a.

For Cu doped ZnO film the 2θ values 39.26.04, 46.18, 64.51, 74.39 is corresponding to the plane of (400), (002), (222), (003) respectively according to JCPDS No. 075- 1553 shown in Figure 3b. The particle sizes are obtained in the range of 3.86, 4.64, 6.8 and 8.03nm. The nanoparticle sizes are calculated by using Debye Scherrer's formula.

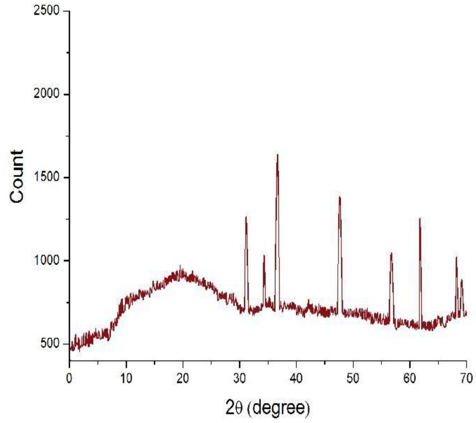

Figure 3a: XRD pattern of ZnO thin film

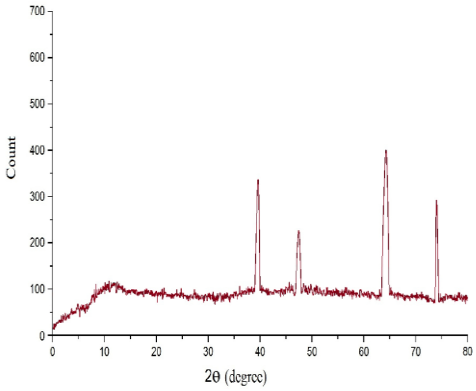

Figure 3b: XRD pattern of Cu doped ZnO thin film

UV-Vis

The optical properties of undoped ZnO and Cu doped ZnO films are analyzed by UV-Vis analysis. Fig. 5a and 5b shows the UV-Vis spectra of undoped and Cu doped ZnO nanostructures. The peaks are observed at 362 nm (undoped ZnO) and 437 nm (Cu doped ZnO). The observed peaks are endorsed to large exciton binding energy and better optical properties of the prepared nanostructures [12]. The addition of Cu in ZnO lattice increases the absorption wavelength from 362 nm to 437 nm.

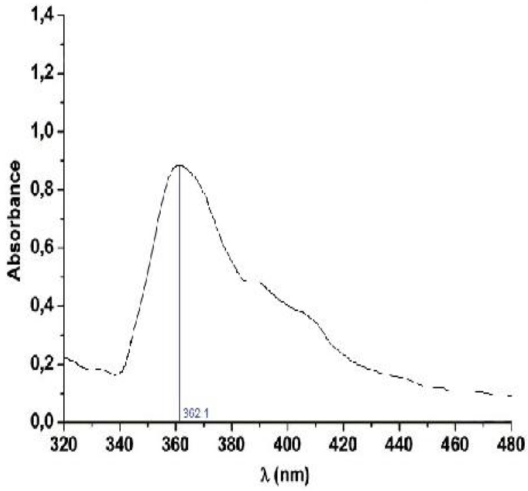

Figure 4a: UV-Vis Spectra of ZnO thin film

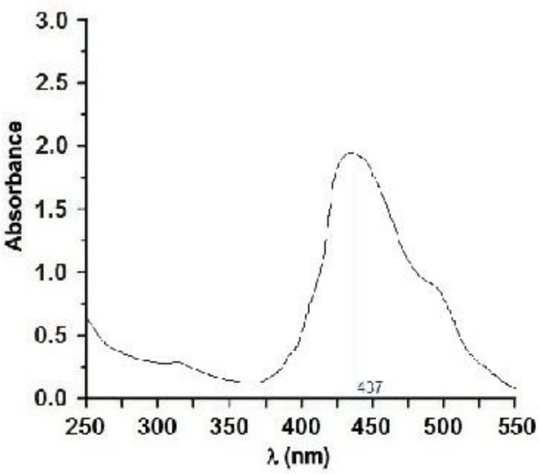

Figure 4b: UV-Vis Spectra of Cu doped ZnO thin film

Antibacterial Activity

Undoped ZnO

The antibacterial activity of undoped ZnO thin film shows better effect against *P.aeruginosa, S.typhi, S.aureus, E.coli* and *B.subtilis* shown in **Figure 5**. The maximum zone of inhibition obtained for 50µl concentration was observed that *P.aeruginosa* (26mm), *S.typhi* (23mm), *S.aureus* (19mm), *E.coli* (18m) and *B.subtilis* (16mm) shown in **Table 1**.

Table 1: Antibacterial activity of ZnO thin film

P.aeruginosa is a gram-negative bacterium, which causes serious illnesses – hospital acquired infections such as ventilator associated pneumonia and various sepsis syndromes. Hence the prepared ZnO thin film has shown the highest inhibition zone against this bacterium.

S.NO.	***Organisms***	***Gram***	***Zone Of Inhibition (mm)***				
			Control	**Concentration of Sample *20µl***	**Concentration of Sample *30µl***	**Concentration of Sample *40µl***	**Concentration of Sample *50µl***
1	*P.aeruginosa*	-ve	24 mm	12 mm	16 mm	19 mm	26 mm
2	*S.typhi*	-ve	19 mm	10 mm	15 mm	18 mm	23 mm
3	*S.aureus*	+ve	22 mm	11 mm	13 mm	16 mm	19 mm
4	*E.coli*	-ve	20 mm	12 mm	13 mm	15 mm	18 mm
5	*B.subtilis*	+ve	21 mm	9 mm	12 mm	14 mm	16 mm

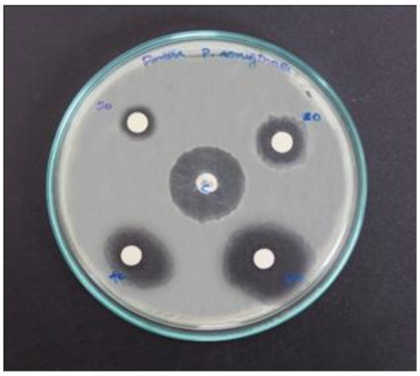

Figure 5(a)

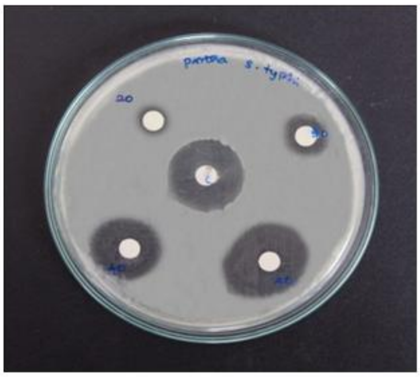

Figure 5(b)

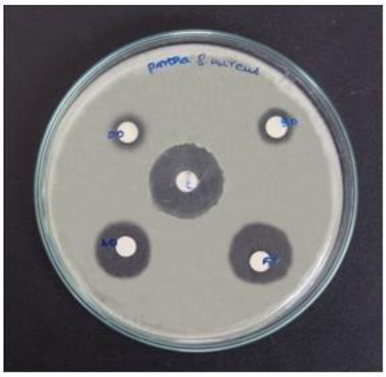

Figure 5(c)

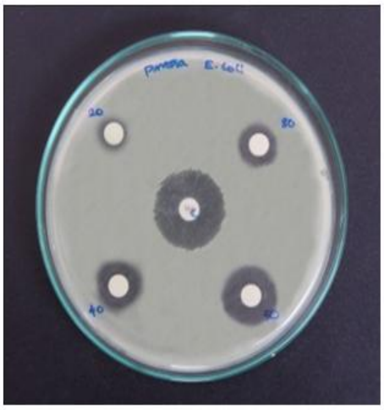

Figure 5(d)

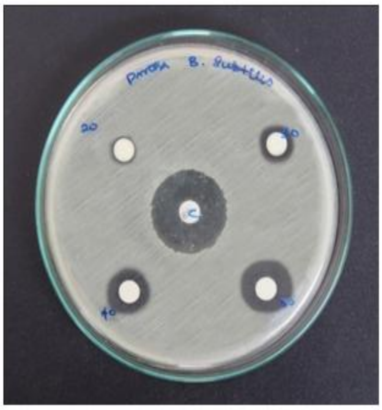

Figure 5(e)

Figure 5: Antibacterial activity of Undoped ZnO thin film against multiple pathogens

Antibacterial Activity
Cu doped ZnO

The antibacterial activity of Cu doped ZnO thin film shows better effect against *P.aeruginosa*, *S.typhi*, *S.aureus*, *E.coli* and *B.subtilis* shown in **Figure 6**. The maximum zone of inhibition obtained for 50µl concentration was observed that *P.aeruginosa* (24mm), *S.typhi* (20mm), *S.aureus* (18mm), *E.coli* (20m) and *B.subtilis* (20mm) shown in **Table 2**.

Table 2: Antibacterial activity of Cu doped ZnO thin film

P.aeruginosa, S.typhi and E.coli is a gram-negative bacterium, which causes serious illnesses – hospital acquired infections and various sepsis syndromes. Hence the prepared Cu doped ZnO thin film has shown the highest inhibition zone against this bacterium.

S.NO.	*Organisms*	*Gram*	*Zone Of Inhibition (mm)*				
			Control	Concentration of Sample *20µl*	Concentration of Sample *30µl*	Concentration of Sample *40µl*	Concentration of Sample *50µl*
1	*P.aeruginosa*	-ve	21mm	10 mm	15 mm	18 mm	24 mm
2	*S.typhi*	-ve	22 mm	9 mm	12 mm	16 mm	20 mm
3	*E.coli*	-ve	19 mm	8 mm	13 mm	17 mm	20 mm
4	*S.aureus*	+ve	18 mm	10 mm	12 mm	15 mm	18 mm
5	*B.subtilis*	+ve	20 mm	7 mm	10 mm	14 mm	16 mm

Figure 6(a)

Figure 6(b)

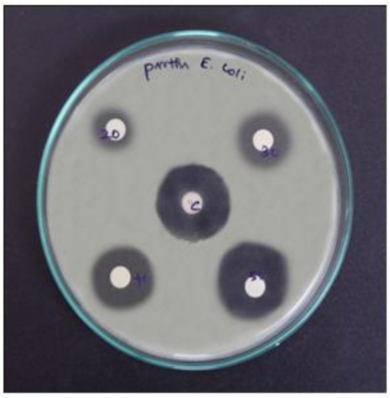

Figure 6(c)

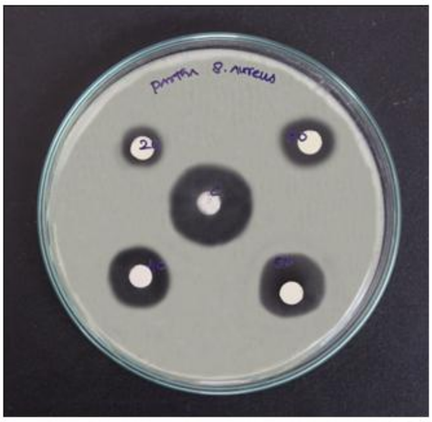

Figure 6(d)

Figure 6(e)

Figure 6: Antibacterial activity of Cu doped ZnO thin film against multiple pathogens

Conclusion

Undoped and Cu doped ZnO films are synthesized by Sol-gel dip coating method. SEM images show the amorphous and cluster shape nanostructures for undoped and Cu doped ZnO nanostructures respectively. The presence of various chemical functional groups proves the formation of Cu doped ZnO nanostructure. The peaks are observed at 362 nm (undoped) and 437 nm (Cu doped ZnO) in UV-Vis Analysis. XRD analysis of undoped ZnO confirms the formation of hexagonal wurtzite structure with primitive lattice. From the results, Therefore, based on the reported antibacterial activity, it can be concluded that the ZnO thin film constitute an effective antimicrobial agent against pathogenic microorganisms. The prepared nanostructures are the potential candidates in the field of energy and medicine.

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