



Synthesis, Structural, Optical Properties and Antibacterial activity of co-doped (Ag, Co) ZnO Nanoparticles

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Abstract

In this paper, undoped ZnO and 5 mol% of Ag, 5 mol% of Co individually doped and co-doped (Ag, Co) ZnO nanopowders were synthesized by chemical co-precipitation method and their structural, morphological, optical properties and antibacterial activity were studied. Crystal structure and grain size were characterized by X-ray diffractometer and reveals that all synthesized ZnO samples were hexagonal structure and the sizes of ZnO nanoparticles were 23 nm, 20 nm, 17 nm, and 25 nm for undoped ZnO, 5 mol% of Co doped, 5 mol% of Ag doped and co-doped (Ag, Co) ZnO nanoparticles respectively. Field emission scanning electron microscopy (FESEM) and Transmission electron microscope (TEM) characterizations were used to determine the morphology and size of the ZnO nanoparticles. TEM results were in good agreement with the X-rd results. Energy dispersive analysis of X-rays spectroscopy (EDAX) spectrum indicates that the successful dopants of Ag, Co peaks in the ZnO lattice and which indicates the purity of the samples. Optical properties of the ZnO samples were characterized by UV-Vis Diffuse Reflectance spectrophotometer. The antibacterial activity test was carried out via well diffusion method, and antibacterial activity of the prepared samples of undoped, Co doped, Ag doped and co-doped (Ag, Co) ZnO nanoparticles were reported, against pathogenic organisms like Pseudomonas, Klebshiella, Aspergillus and Candida. The co-doped (Ag, Co) ZnO nanoparticles show twice as potent in killing as against those pathogenic organisms compared to undoped ZnO and was also more effective than the single element Ag doped, Co doped ZnO nanoparticles. The present study indicates that single element doped and co-doped ZnO nanoparticles could potentially be antibacterial reagents to treat diseases caused by bacteria and fungi.

Keywords: Zinc oxide, Nanoparticles, XRD, TEM, Antibacterial activity.

Introduction

In the recent years, a number of investigations have focused on transitional metals doped II-VI compound semiconductor ZnO, because of its direct band gap of 3.37 eV at room temperature with a large excitation binding energy of 60 meV. It has been attracted high intense research efforts for its unique properties and variety of applications such as optoelectronics, transparent electronics, UV-light emitters, piezoelectric devices, chemical sensors, and spintronics¹⁻⁶. Further, nanoparticles play a wide range of applications in biology, food industries and pharmaceuticals like anti-inflammatory, anti-hypersensitive and anti-microbial functions. This type of characters performed because nanoparticles composed of chemical components which allow interacting closely with cell membranes. Doped ZnO shows maximum effect against pathogenic organisms as compared to ZnO, there by using nanoparticles as an antimicrobial agent and was one of the most useful techniques to control pharmacy chemical waste and cost effect. ZnO was also an environmentally friendly material, high chemical stability and low toxicity, and which was widely used as an active ingredient for dermatological applications in creams, lotions and ointments on an account of its antibacterial

properties⁷⁻¹². The microstructure, morphology and size of Ag doped ZnO and Co doped ZnO nanoparticles prepared by various methods such as sol-gel, co-precipitation, hydrothermal, thermal hydrolysis, dc thermal plasma method etc.¹³⁻¹⁹. Among the various methods, the chemical co-precipitation is the best low cost method used for the preparation of large quantity of pure and co-doped ZnO nanoparticles. Recently, our research group synthesized zinc oxide nanoparticles by chemical co-precipitation technique at low cost with a high yield rate²⁰.

Here we report that a simple chemical co-precipitation method for synthesizing undoped and single element of Ag doped, Co doped and co-doped ZnO nanoparticles. The influences of Ag, Co doping on the microstructure, morphology of the ZnO nanocrystallites have also been investigated in detail. Moreover, these nanoparticles were used in against Pseudomonas, Klebshiella, Aspergillus and candida. Pseudomonas and Klebshiella causes pneumonia, recently Klebshiella causes drug resistant pneumonia, Aspergillus was a food poisoning pathogen and candida causes skin allergic diseases. Nowadays metal oxide used as a food preservative agent instead of organic compounds. Zinc used as an ingredient for the purpose of enrichment, and co-doped Zinc oxide inhibits major food pathogenic organisms.

Material and Methods

A simple chemical co-precipitation method can make use of preparing Pure ZnO nanocrystals by using zinc acetate dehydrate ($\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$) and potassium hydroxide (KOH) as precursors and for cobalt and silver doping, cobalt acetate ($\text{Co}(\text{C}_2\text{H}_3\text{O}_2)_2$) and silver nitrate (AgNO_3) have been used. Undoped ZnO, $\text{Zn}_{0.95}\text{Co}_{0.05}\text{O}$, $\text{Zn}_{0.95}\text{Ag}_{0.05}\text{O}$ and $\text{Zn}_{0.90}\text{Ag}_{0.05}\text{Co}_{0.05}\text{O}$ nanostructures were prepared at room temperature by the following procedure. Initially 0.2 M solution was prepared by using zinc acetate and KOH. For the Ag and Co dopants, 5 mol% of silver nitrate and cobalt acetate have been added drop-wise individually and combinedly to the above solution under continuous stirring for 10 hrs. After the precipitate was filtered out separately and repeatedly washed with double distilled water to remove unnecessary impurities formed during the preparation process. Co and Ag doped ZnO nanopowders were obtained after drying at 70 °C for 10 hrs. Then the final products were ground and annealed at 500 °C in the furnace for 1 hr. The prepared undoped, single element doped and co-doped ZnO samples were dissolved in double distilled water (5 mg/ml) by using sterile tubes and mixed the samples with the help of cyclomixture to prepare well mixed nanoparticles solution.

The structural properties including structure and crystallite-size of the samples were determined by Seifert 3003 TT X-ray diffractometer (XRD) using CuK_α radiation by applying voltage and current of 40 kV and 30 mA, respectively. The nanoparticles size and structure confirmations were done by Transmission Electron Microscopy (TEM) and high resolution transmission electron microscope (HRTEM) using JEOL JSM 2100. Morphology of the nano powders was studied by Field Emission Scanning Electron Microscopy (FESEM), (ZEISS ULTRA 55, Model: Gemini). Concentration of dopants in ZnO was estimated by energy dispersive X-ray spectroscopy (EDS) attached with scanning electron microscope (SEM) (Model: CARL-ZEISS EVOMA 15). Spectrophotometer (Model: JASCO V- 670) was employed to record the UV- visible optical spectra of the samples. Pathogenic bacteria and fungi (Pseudomonas, Klebsiella, Aspergillus, and Candida) were used for antibacterial activity testing via well diffusion method.

Results and Discussion

Structural Analysis: Typical XRD patterns of undoped ZnO and $\text{Zn}_{0.95}\text{Co}_{0.05}\text{O}$, $\text{Zn}_{0.95}\text{Ag}_{0.05}\text{O}$, $\text{Zn}_{0.90}\text{Co}_{0.05}\text{Ag}_{0.05}\text{O}$ powders are shown in figure-1. The diffraction peaks of all samples are quite matching with the hexagonal wurtzite ZnO data [JCPDS. No: 36-1451]. There are no characteristic peaks of impurity phases regardless of the dopant concentrations, confirming the high purity of the synthesized powders. Thus the wurtzite structure is not modified by the addition of Ag, Co into ZnO host material. After annealing the samples at 500 °C for 1 hr, the crystallite sizes of the synthesized powders are estimated from Scherer's equation $D = \frac{0.95\lambda}{\beta \cos\theta}$, and the values are of about

23 nm, 20 nm, 17 nm, and 25 nm for ZnO, $\text{Zn}_{0.95}\text{Co}_{0.05}\text{O}$, $\text{Zn}_{0.95}\text{Ag}_{0.05}\text{O}$ and $\text{Zn}_{0.90}\text{Co}_{0.05}\text{Ag}_{0.05}\text{O}$ nanopowders respectively. But there is no appreciable change of lattice constants because of the ionic radius of cobalt ($\text{Co}^{2+} = 0.745 \text{ \AA}$) and silver ($\text{Ag}^+ = 0.115 \text{ \AA}$) dopants and are almost same as that of Zn site in ZnO (i.e. $\text{Zn}^{2+} = 0.74 \text{ \AA}$). In our studies, Pure ZnO shows highest diffracted intensity than the single element 5 mol% of Ag, 5 mol% of Co doped ZnO nanostructures, but less than the co-doped (Ag, Co) ZnO nanoparticles. The diffracted intensity increases by increasing the size of ZnO nanoparticles due to the substitution of co-dopants silver and cobalt. In earlier, the diffracted intensity decreased by increase of dopants concentrations of Ag, Co in ZnO, as reported in literature^{21, 22}. The diffraction pattern of Ag doped ZnO does not display metallic 'Ag' at 38.2° (111) (or) 44.4° (200) (JCPDS: 03-092) and this is because of the low percentage of Ag^+ doping (5 mol %). Since the doped and co-doped ZnO samples has been obtained by co-precipitation method and Ag_2O decomposes to Ag at 400 °C, silver is unlikely to exist as Ag_2O and also there is no intense peak appear around at 44° for the doped sample. This indicates that 'Co' is well doped in the ZnO lattice, and related impurity phases such as metallic cobalt, cobalt oxides and compounds could not be detected in the doped ZnO samples. This reveals that the Co ions substitute of Zn ions in the ZnO lattice.

Pure ZnO and co-doped (Ag, Co) ZnO have wurtzite structure and are further supported by FT- IR spectra as shown in figure-2. Undoped ZnO, Co doped, Ag doped and co-doped ZnO have the similar spectra and the corresponding broadening peaks at 3440 cm^{-1} is due to OH Stretching vibrations (from KOH, used as a precursor), the band at 2926 cm^{-1} attributed to C-H stretching vibrations; the band arising from the absorption of atmospheric CO_2 on the metallic cations at 2340 cm^{-1} ; the band at 1625 cm^{-1} represents to C = O stretching vibrations; the band at 1404 cm^{-1} indicates ZnO peak and the band observed at 955 cm^{-1} is attributed to C-H bend^{23, 24}. No peaks shifting in FT-IR spectra are observed, which are in good agreement with the results from the XRD.

Morphology and elemental studies: The morphology of the samples was investigated by field emission scanning electron microscope (FESEM) as shown in the figure-3. Undoped ZnO nanoparticles appears like spherical in shape of size ~1 μm and 5 mol% of Co doped and 5 mol% of Ag doped ZnO nanoparticles forms cauliflower shape and co-doped (Ag, Co) ZnO nanoparticles also appears like agglomerated cauliflower shape. All these nanoparticles present in the size range of 100-200 nm. Figure-4 (a) and (b) depicts the energy dispersive spectra (EDS) of undoped ZnO and co-doped (Ag, Co) ZnO nanocrystallites. EDS spectra of undoped ZnO having only two elements, Zn and O indicate the purity of the ZnO sample and that an additional Co, Ag elements exists in ZnO: Ag: Co nanocrystals. Table-1 gives the ratio of Zn: Ag: Co: O elemental composition. The relative error of accuracy is less than $\pm 3\%$. The atomic percentages of the elements are obtained from the

spectra and the doping of cobalt and silver is confirmed. From quantitative analysis, the dopants and atomic concentration in ZnO (atom %), could be found and the Co and Ag contents in the ZnO samples based on the doping levels of 5 mol%.

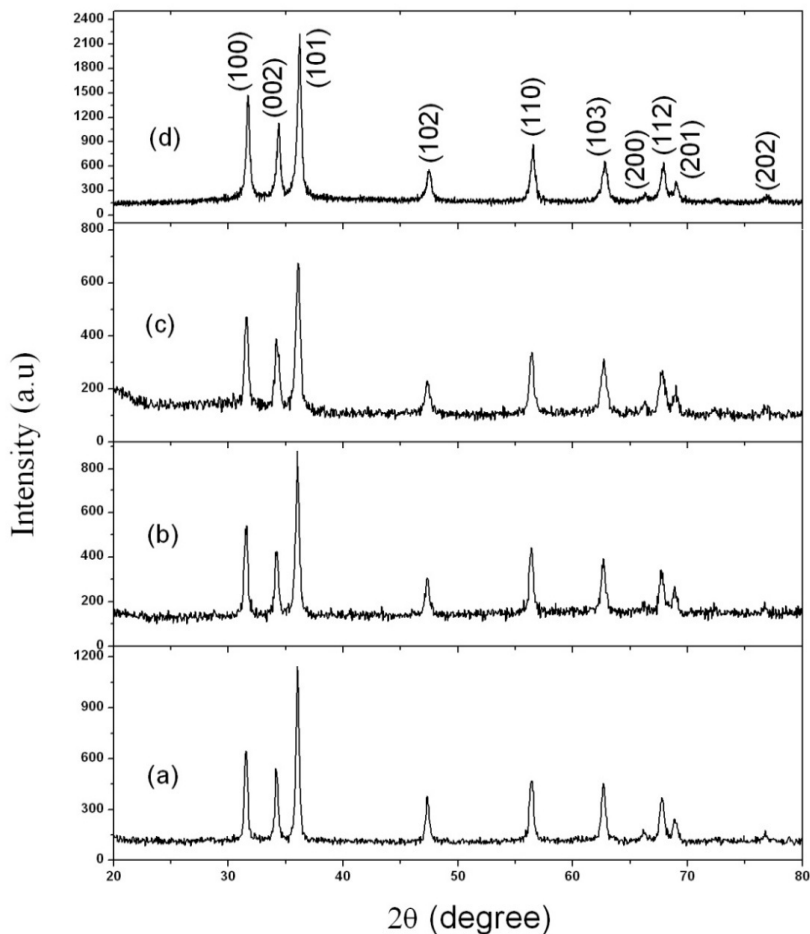
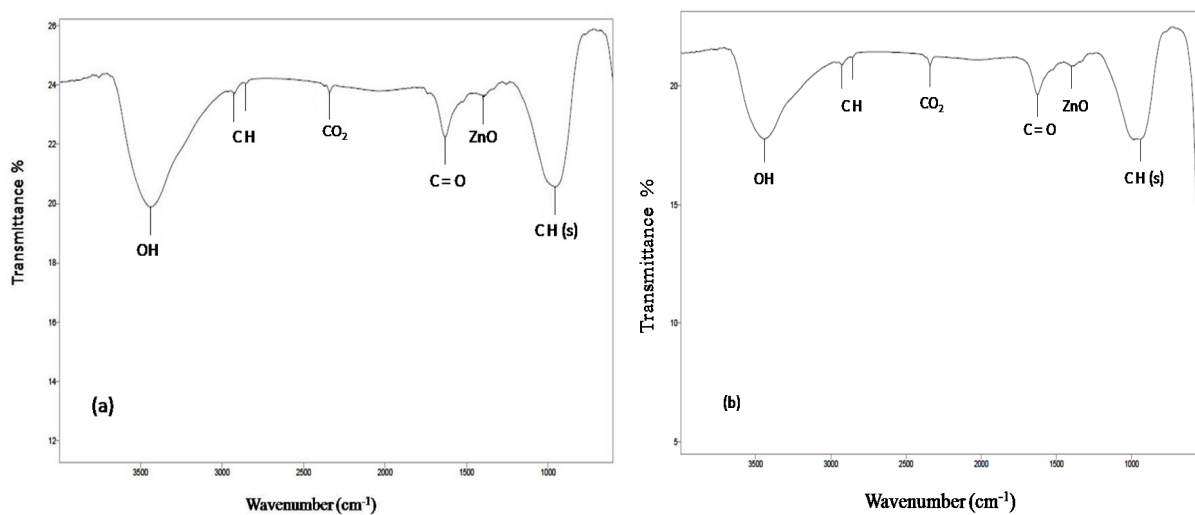


Figure-1

XRD pattern of: (a) Pure ZnO (b) 5 mol% Co doped (c) 5 mol % Ag doped, (d) co-doped (Ag, Co) ZnO nanoparticles



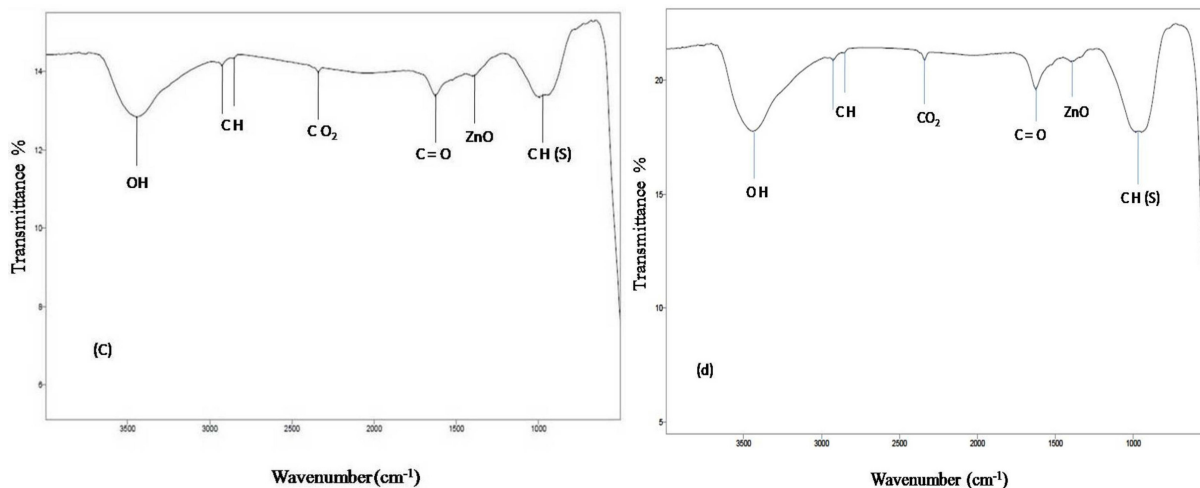


Figure-2
FT -IR Spectra of (a) Undoped ZnO (b) Co doped ZnO (c) Ag doped ZnO (d) co-doped ZnO nanoparticles

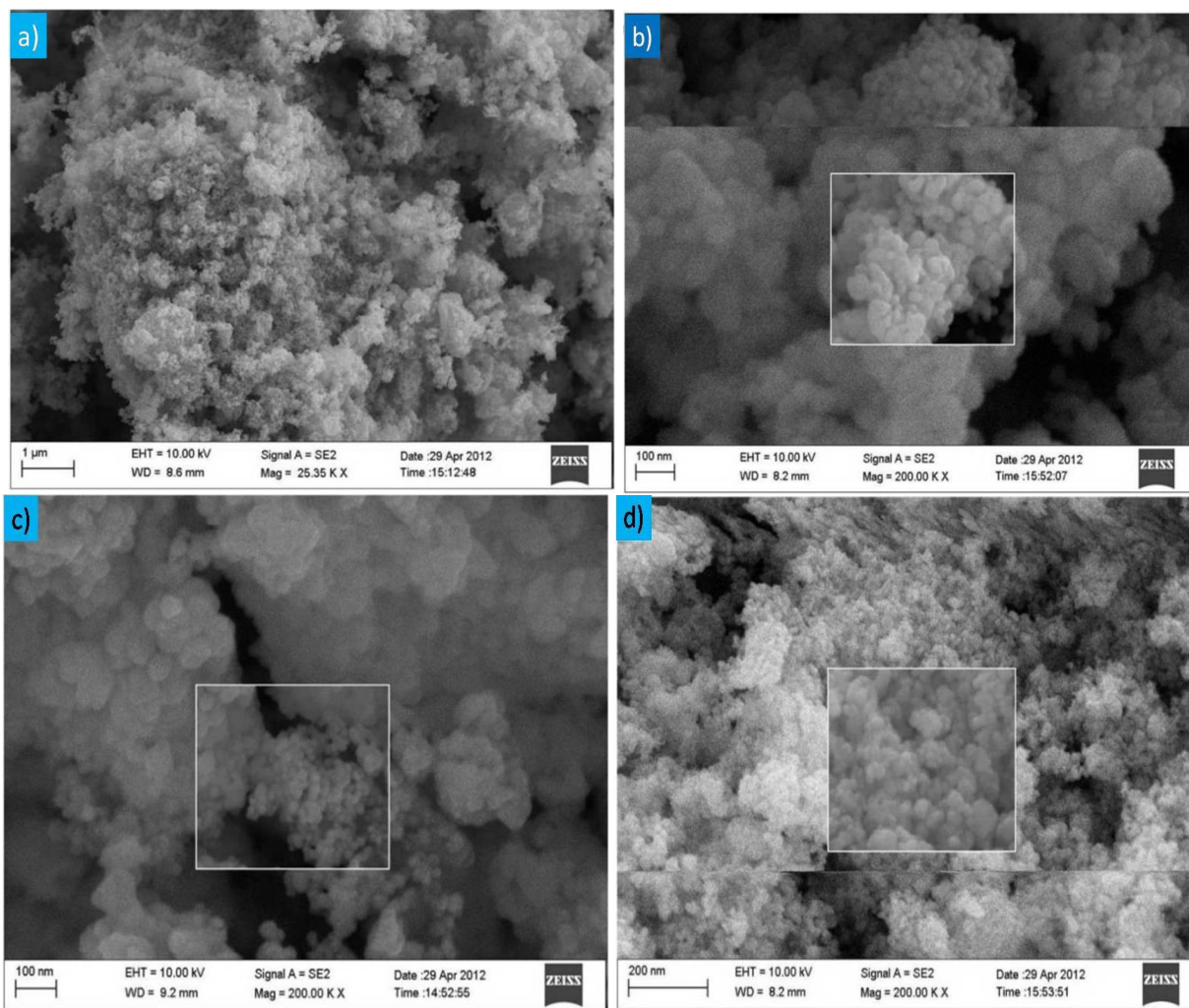


Figure-3
FESEM images of: (a) Undoped ZnO, (b) 5 mol% of Co, (c) 5 mol% of Ag (d) co-doped (Ag, Co) ZnO nanoparticles

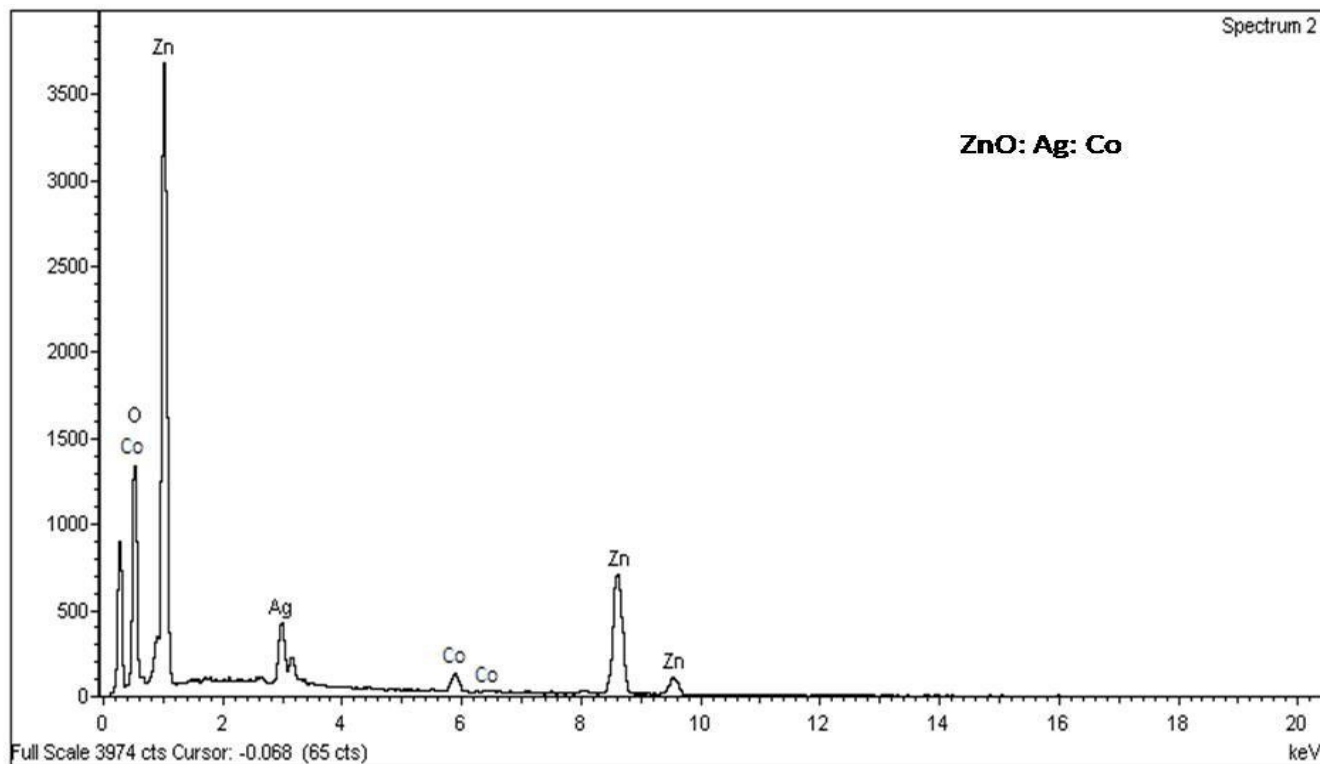
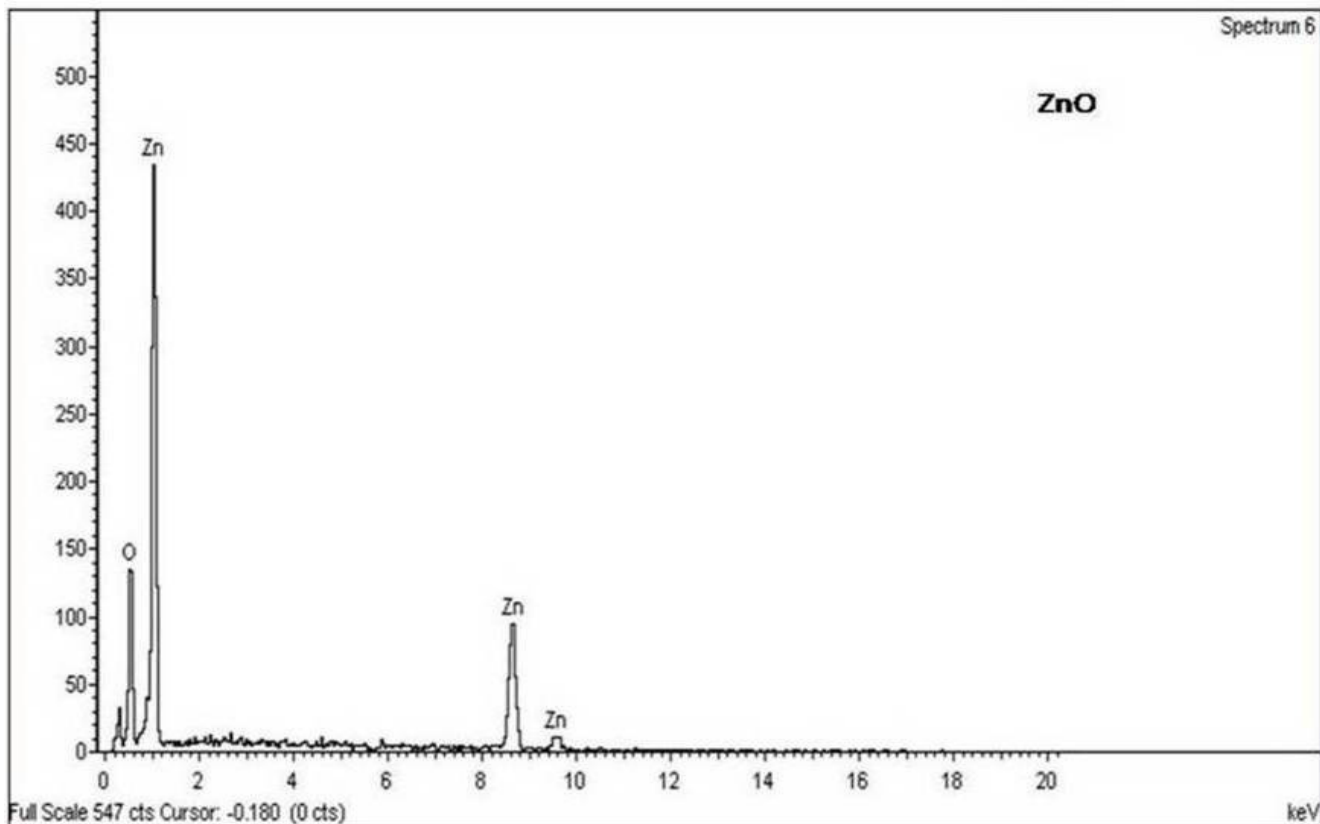


Figure-4
EDAX Spectrum of: (a) Pure ZnO (b) co-doped ZnO nanoparticles. (ZnO: Ag: Co)

Transmission electron microscopy images of the undoped ZnO and Zn_{0.90}Co_{0.05}Ag_{0.05}O samples are depicted in figure-5 (a) and (b) respectively. From the TEM images, the pure and co-doped ZnO nanoparticles are nearly in equal size of 20 nm. The evaluated particles size from the X-rd pattern, which were in good agreement with the TEM (20 nm) results. In figure 5 (c), the corresponding selected area electron diffraction (SAED) pattern indicates the crystallinity and preferential orientation of

the ZnO: Co: Ag samples pattern without any additional diffraction spots of Ag and Co clusters, and which is in good agreement with the wurtzite structure of the XRD results and the standard data card JCPDS: 36-1451. HRTEM lattice images are presented in Figure-5 (d), which shows a nice crystallinity and clear lattice fringes of a single nanocrystal. The fringe spacing is about 2.47 Å, corresponding to the (101) crystal planes of ZnO.

Table-1
Compositional analysis of ZnO and ZnO: Ag: Co nanostructures

Dopants concentration (at %)	Experimental results (at %)			
	Zn	Co	Ag	O
0	49.63	---	---	50.37
5	47.04	2.01	---	50.95
5	46.83	---	1.85	51.32
5	46.27	1.87	1.76	50.10

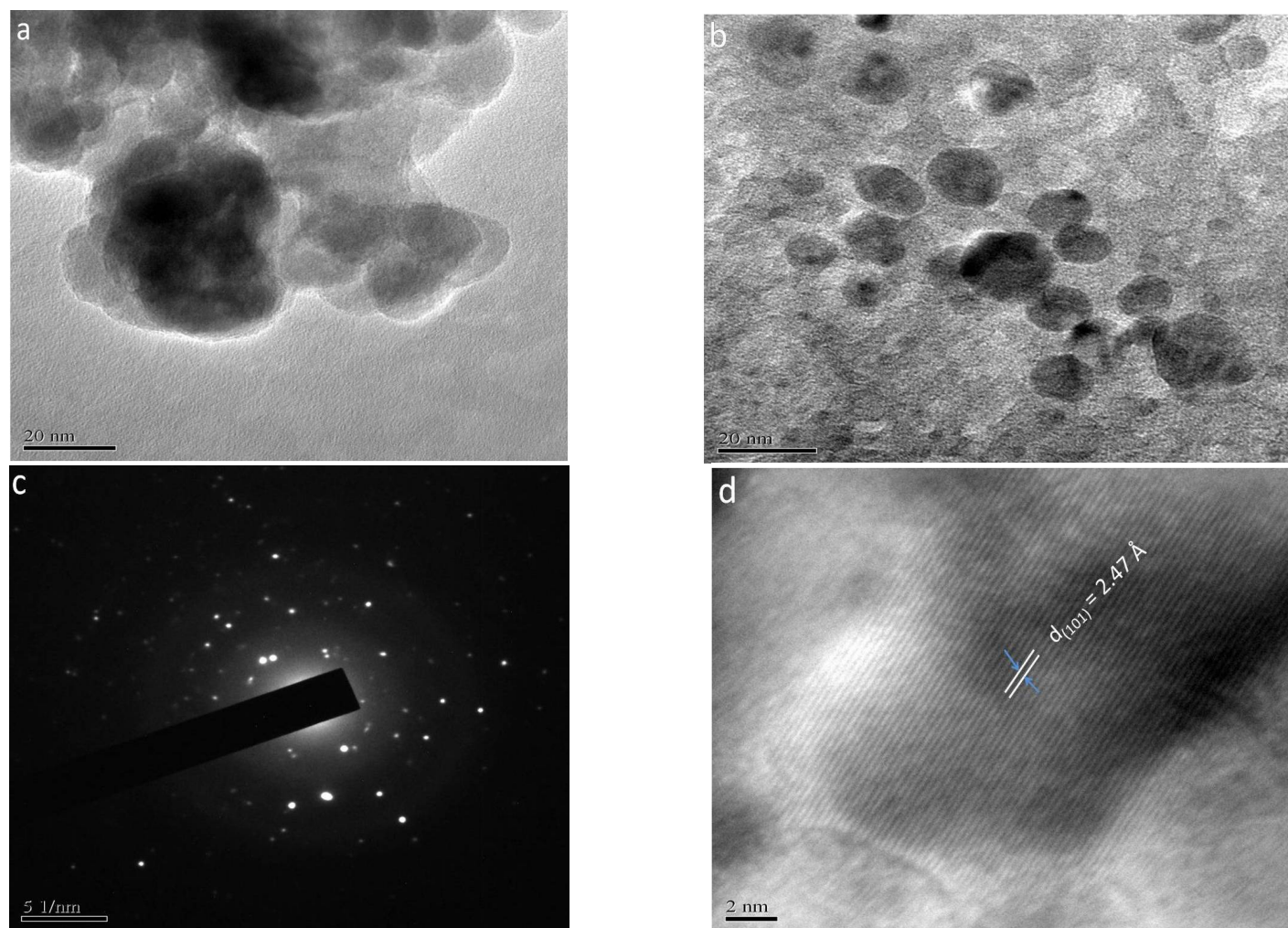


Figure-5
 TEM micrographs of (a) pure ZnO (b) Zn_{0.90}Co_{0.05}Ag_{0.05}O nanoparticles (c) SAED pattern of Zn_{0.90}Co_{0.05}Ag_{0.05}O nanoparticles (d) HRTEM lattice image of single ZnO nanoparticle

Optical Studies: UV-Visible diffuse reflectance spectroscopy (UV/DRS) was used to study the optical properties of ZnO, $Zn_{0.95}Co_{0.05}O$, $Zn_{0.95}Ag_{0.05}O$ and $Zn_{0.90}Co_{0.05}Ag_{0.05}O$ nanoparticles and measured at room temperature in the wavelength range of 200 – 800 nm as shown in Figure-6. For undoped ZnO nanoparticles, the band edge absorption is appeared at 3.20 eV (370 nm). In the visible region, the undoped ZnO nanoparticles showed high reflectance about 80 %. The reflectance decreases in 5 mol% of Ag doped, 5 mol% of Co doped and co-doped (Ag, Co) ZnO samples. Three additional absorption bands are observed at 565 nm, 612 nm and 658 nm in the spectra of Co doped and co-doped ZnO samples when compared with the spectra of undoped ZnO and Ag doped ZnO samples. Further, Co doped ZnO powders shows high intensity bands than the co-doped ZnO samples. All these three absorption bands are attributed to the $^4A_2(F) \rightarrow ^2E(G)$, $^4A_2(F) \rightarrow ^4T_1(P)$, and $^4A_2(F) \rightarrow ^2A_1(G)$ transitions involving 3d levels in Co^{2+} ions in ZnO, and which are mainly due to the sp-d exchange interactions between the band electrons and the localized d electrons of the dopant²⁵. Kubelka-Munk treatment has been applied to the DRS spectra of all ZnO samples and estimates the band gap energy of those samples. Band gap energies of the pure, Co doped, Ag doped and co-doped ZnO nanoparticles are determined from the Kubelka – Munk plots (Figure-7), and the band gap energy values are 3.20 eV, 2.74 eV, 3.17 eV and 3.01 eV for ZnO, ZnO: Co, ZnO: Ag and ZnO: Ag: Co samples respectively. Band gap energy values of ZnO were decreased by the doping of transitional elements like cobalt and silver, as reported in the literature^{22, 26}.

nanoparticles were subjected to antibacterial activity for two pathogenic bacteria and two pathogenic fungal strains. Well diffusion test was carried out on Nutrient agar and Czapek-Dox agar plates to observe the antimicrobial activity against pathogenic organisms. For bacteria, 100 ml Nutrient Agar Medium (NAM) was prepared by maintaining the value of pH 6.8 - 7.0. Nutrient agar medium was poured in the sterile petriplates and it was solidified bacterial suspension spreading on petriplates. 50 μ l of nanoparticles solution was loaded into each well. The inhibition zones were appeared, when the plates are allowed to incubation for 24 - 48 hours. For fungal cultures using Czapek-Dox Media in place of Nutrient agar media, the inhibition zones are appeared after the incubation period from 3 to 5 days. Undoped ZnO shows minimum inhibition effect against pathogens, 5 mol% of Co doped ZnO, 5 mol% of Ag doped ZnO shows better activity compared to undoped ZnO, and $Zn_{0.90}Ag_{0.05}Co_{0.05}O$ shows maximum range effect against pathogenic bacteria and fungi. Table-2 illustrates the results of the antimicrobial test performed by undoped ZnO, Co doped ZnO, Ag doped ZnO and co-doped (Ag, Co) ZnO nanoparticles. So, co-doped (Ag, Co) ZnO enhances the antibacterial activity than single element doped and undoped ZnO. Our results explain ZnO nanoparticles which act against the water contamination, allergic reactions, food poisoning and also act as drug resistant pneumonia. Hence, co-doped ZnO nanoparticles are used in pharmaceuticals to prepare best anti-drug against pneumonia. Antibacterial activity of co-doped ZnO gives the better results when compared to the antibacterial activity of undoped ZnO, nano ZnO, Ag doped and Co doped ZnO nanoparticles as reported in the literature^{18, 27-29}.

Antibacterial activity: Undoped ZnO, 5 mol % of Co doped ZnO, 5 mol% of Ag doped ZnO and co-doped (Ag, Co) ZnO

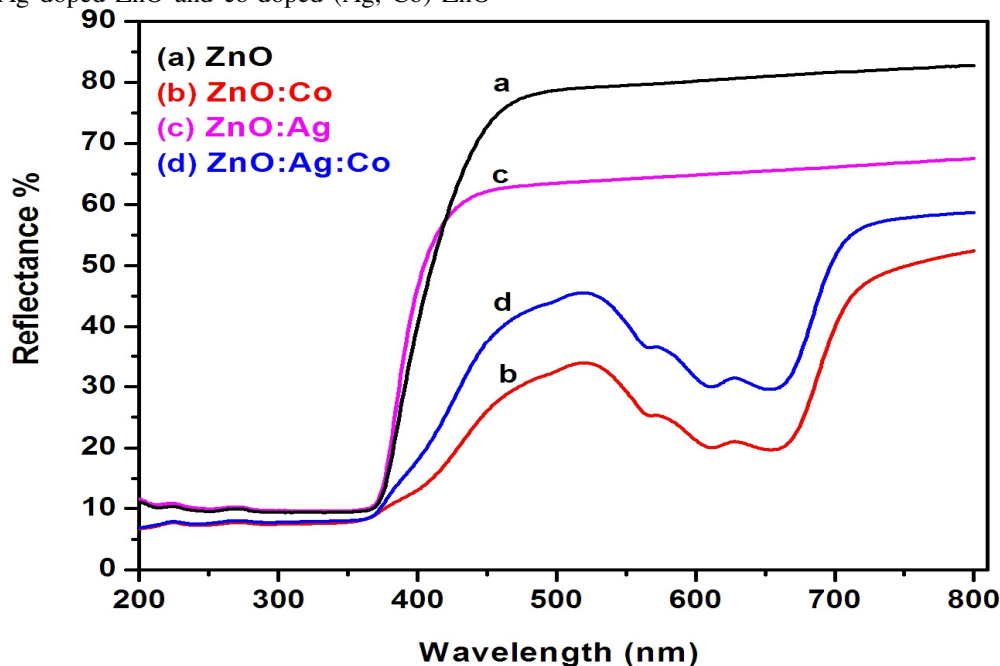


Figure-6
 Diffuse reflectance spectra of the (a) undoped (b) Co doped (c) Ag doped (d) co-doped (Ag, Co) ZnO nanoparticles

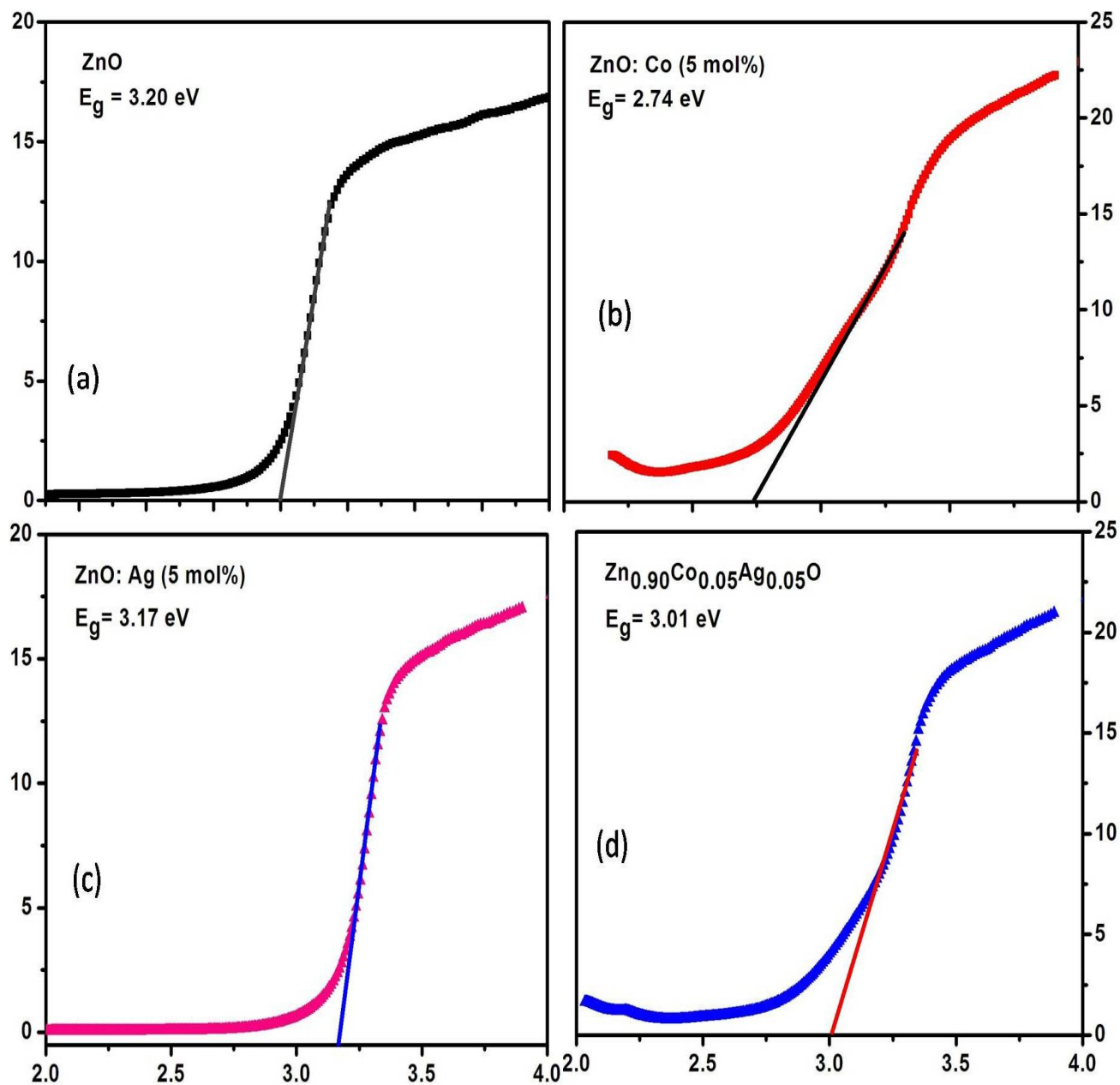


Figure-7

Kubelka-Munk plots and band gap energy estimation for the (a) undoped (b) Co doped (c) Ag doped (d) co-doped (Ag, Co) ZnO nanoparticles

Table-2

Antibacterial activities of undoped, doped and co-doped ZnO nanoparticles against pathogenic bacteria and fungal strains

S.No	Type of nanoparticles	Diameter of Inhibition Zone (mm)			
		Bacterial Strains		Fungal Strains	
		Pseudomonas	Klebshiella	Aspergillus	Candida
1	ZnO	6.0	5.0	5.0	8.0
2	Zn _{0.95} Co _{0.05} O	7.0	8.0	6.0	9.0
3	Zn _{0.95} Ag _{0.05} O	9.0	8.0	9.0	8.0
4	Zn _{0.90} Ag _{0.05} Co _{0.05} O	13.2	14.0	13.0	13.9

Conclusion

Undoped, Co doped, Ag doped and co-doped (Ag, Co) ZnO nanoparticles were synthesized by chemical co-precipitation method. The prepared ZnO samples have hexagonal structure when characterized by XRD and the evaluated average particle sizes are 23 nm, 20 nm, 17 nm and 25 nm respectively. TEM results of the particles size 20 nm are in good agreement with the XRD results. The morphology of the samples was observed as spherical and cauliflower shapes by FESEM. Co-dopant elements (Ag, Co) in ZnO were clearly confirmed by EDS. The zone of inhibition was observed against pathogenic bacteria and fungal strains, and suggests that the co-doped (Ag, Co) ZnO nanoparticles exhibit excellent antibacterial activity than the Ag doped, Co doped and undoped ZnO nanoparticles. Hence, these ZnO nanoparticles may be the promising antimicrobial agents. Thus, the present study clearly indicates that co-doped ZnO nanoparticles were potentially used in food preservation, water purification and pharmaceuticals to prepare anti-drug against pneumonia.

References

1. Ezenwa I.A., Synthesis and optical characterization of zinc oxide thin film, *Research Journal of Chemical Sciences*, **2(3)**, 26-30 (2012)
2. Yang H.M., Nie S., Preparation and characterization of Co-doped ZnO nonmaterial's, *Mater. Chem. Phys.*, **114**, 279-282 (2009)
3. Yang M., Guo Z.X., Qiu K.H., Long J.P., Yin G.F., Guan D.G., Liu S.T., Zhou S.J., Synthesis and characterization of Mn-doped ZnO column arrays, *Appl. Surf. Sci.*, **256**, 4201- 4205. (2010)
4. Irimpan L., Nampoori V.P.N., Radhakrishnan., Spectral and nonlinear optical characteristics of nanocomposites of ZnO- Ag, *Chemical Physics Letters.*, **455**, 265-269 (2008)
5. Nakada T., Hirabayashi Y., Tokado T., Ohmori D., Mise T., Novel device structure for Cu (In, Ga) Se thin film solar cells using transparent conducting oxide back and front contacts, *Sol. Energy.*, **77**, 739 -749 (2004)
6. Konenkamp R., Word, R.C., Schlegel, C., Vertical nanowire light-emitting diode, *Appl. Phys. Let.*, **85**, 6004-6006 (2004)
7. Jones, N., Ray, B., Ranjit, K.T., Manna, A.C., Antibacterial activity of ZnO nanoparticle suspensions on a broad spectrum of microorganisms, *Fem. Microbial. Lett.* **279**, 71-76 (2008)
8. Tam, K.H., Djuricic, A.B., C.M.N. Chan, C.M.N., Xi, Y.Y., Tse, C.W., Leung, Y.H., Chan, W.K., Leung, F.C.C., Au, D.W.T., Antibacterial activity of ZnO nanorods prepared by a Hydrothermal method, *Thin Solid Films.*, **516**, 6167 -6174 (2008)
9. Zhang, L., Ding, Y., Povey, M., York, D., ZnO nanofluids a potential Antibacterial agent, *Prog. Nat. Sci.*, **18**, 939-944 (2008)
10. Sehili, T., Boule, P. Lemaire, J., Photocatalysed transformation of chloroaromatic derivatives on zinc oxide II: Dichlorobenzenes, *J. Photochem. Photobiol. A* **50**, 103-116 (1989)
11. Villasenor, J., Reyes, P., Pechhi, G., Photodegradation of Pentachloro Phenol on ZnO, *J. Chem. Technol. Biotechnol.*, **72**, 105-110 (1998)
12. Driessen, M.D., Miller, T.M., Grassian, V.H., Photocatalytic oxidation of trichloroethylene on zinc oxide: characterization of surface-bound and gas-phase products and intermediates with FT-IR spectroscopy, *J. Mol. Catal.*, **A131**, 149-156 (1998)
13. Georgekutty, R., Seery, M.K., Pillai, S.C., A Highly Efficient Ag-ZnO Photocatalyst: Synthesis, Properties, and Mechanism, *J. Phys. Chem. C.*, **112**, 13563-13570 (2008)
14. Zheng, Y., Chen, C., Zhan, Y., Lin, X., Zheng, Q., Wei, K., Zhu, J., Photocatalytic Activity of Ag/ZnO Heterostructure Nanocatalyst: Correlation between Structure and Property, *J. Phys. Chem.C.* **112**, 10773 - 10777 (2008)
15. Ye X-Y., Zhou Y-M., Sun Y-Q., Chen J., Wang Z-Q., Preparation and characterization of Ag/ZnO composites via a simple hydrothermal route, *J. Nanopart. Res.* **11**, 1159-1166 (2009)
16. Palkar, V.R., 1999, Sol-gel derived nanostructured γ -alumina porous spheres as an adsorbent in liquid chromatography, *Nanostruct. Mater.*, **11**, 369-374 (1999)
17. Park, H.K., Kim, D.K., Kim, C.H., Effect of Solvent on Titania Particle Formation and Morphology in Thermal Hydrolysis of $TiCl_4$, *J. Am. Ceram. Soc.*, **80**, 743-749 (1997)
18. Nirmala, M., Anukaliani, A., Characterization of undoped and Co doped ZnO nanoparticles synthesized by DC thermal plasma method, *Physica B*, **406**, 911- 915 (2011)
19. Zhang, Y., Shi, E.W., Chen, Z.Z., Magnetic properties of different temperature treated Co- and Ni-doped ZnO hollow nanospheres, *Mater. Sci. Semicond. Process.*, **13**, 132-136 (2010)
20. Sankara Reddy B., Venkatramana Reddy S., Venkateswara Reddy P., Koteeswara Reddy N., *Optoelectronics and Advanced Materials – Rapid Communications*, **6**, 953 - 959 (2012)
21. Pal, B., and Giri, P.K., High temperature ferromagnetism and optical properties of Co doped ZnO nanoparticles, *J. Appl. Phys.* **108**, 084322-1 - 084322- 8 (2010)
22. Zeferino, R.S., Flores, M.B. and Pal, U., Photoluminescence and Raman scattering in Ag-doped

- ZnO nanoparticles, *J. Appl. Phys.* **109**, 014308-1 - 014308-6 (2011)
23. Ahmed F., Kumar S., Arshi N., Anwar M.S., Koo B.H., Lee C.G., Doping effects of Co^{2+} ions on structural and magnetic properties of ZnO nanoparticles, *Microelectronic Engineering* **89**, 129-132 (2012)
24. Ullah R., Dutta J., Photocatalytic degradation of organic dyes with manganese-doped ZnO nanoparticles, *Journal of Hazardous Materials*, **156**, 194-200 (2008)
25. Xiao Q., Zhang J., Xiao C., Tan X., Photocatalytic decolorization of methylene blue over $\text{Zn}_{1-x}\text{Co}_x\text{O}$ under visible irradiation, *Materials Science and Engineering: B*, **142**, 121-125 (2007)
26. Li P., Wang S., Li J., Wei Y., Structural and optical properties of Co doped ZnO nanocrystals prepared by a one step solution route, *Journal of Luminescence*, **132**, 220-225 (2012)
27. Sharma V.K., Yngard R.A., Lin Y., Silver nanoparticles: Green synthesis and their antimicrobial activities, *Advances in colloid and Interface Science.*, **145**, 83-96 (2009)
28. Narayanan P.M., Wilson W.S., Abraham A.T., Sevanan M., Synthesis, Characterization, and Antimicrobial Activity of ZnO Nanoparticles Against Human Pathogens, *BioNanoSci.* DOI 10.1007/s12668-012-0061-6
29. Gondal M.A., Alzahrani A.J., Randhawa M.A., Siddiqui M.N., Morphology and antifungal effect of nano ZnO and nano pd doped ZnO against *Aspergillus* and *Candida*, *J. Environ. Sci and Health, Part A* **47**, 1413 -1418 (2012)