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Effect of Ag Doping on Structural, Optical and Antibacterial Behavior ZnO Nanoparticles

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Abstract:
In the present work, Ag/ZnO nanopowders were synthesized in order to investigate bacterial sensitivity against Gram positive and Gram negative bacteria, comparatively by using well diffusion method. Nanoparticles were synthesized by the Sol-Gel method, using $AgNO_3$, $Zn(CH_3\ CO_2)_2$. NaOH and PVP as capping agent. All the materials were characterized by XRD, SEM, UV, FTIR. The Ag nanoparticles were found attached to crystalline ZnO nanopowder. Ag/ZnO nanopowder were found to be more effective towards Gram positive, and thus contribute to the greater mechanical damage to all functions of bacteria and enhanced bactericidal impact of Ag on ZnO nanoparticles. Sol-Gel method was found to be an effective chemical method to synthesis Ag/ZnO metal semiconductor nanopowder. ZnO was found to be good match for Ag, for enhanced and synergistic antibacterial activities, for both Gram positive and Gram negative bacteria. So, this study provided both theoretical and experimental support for the practical applications of Ag/ZnO nano powders.

Keywords: Nanoparticles, Escherichia coli, Staphylococcus aureus, Bacillus subtilis, polyvinylpyridine.

I. INTRODUTION TO NANO TECHNOLOGY:

The term "nanotechnology" has evolved over the years via terminology drift to mean "anything smaller than micro technology" such as nanopowders, and other things that are nanoscale in size.

Nano technology basically refers to the engineering of functional systems at the molecular scale.

As nanotechnology is a set of techniques which allows manipulation of properties at a very small scale, if can be applied into various areas namely drug delivery,

Fabrics making and synthesis of nano materials due to their extremely small feature size, nano materials have the potential for wide ranging industrial biomedical and electronic applications.

Nano materials can be composed of metals, ceramics, composite materials or polymer materials. Nano materials are defined by their characteristic of having a very small feature size in the range of 1100nm.

At nano scale level, some material properties are affected and thus behaving differently from the bulk materials. A bulk material possesses constant physical properties regardless of its size but at the nano scale level size dependent properties are often observed. This research work focuses on the synthesis of

"**Effect of Ag doping on structural, optical and antibacterial behavior ZnO nanoparticles".**

Methods and Preparation of Nano particles:

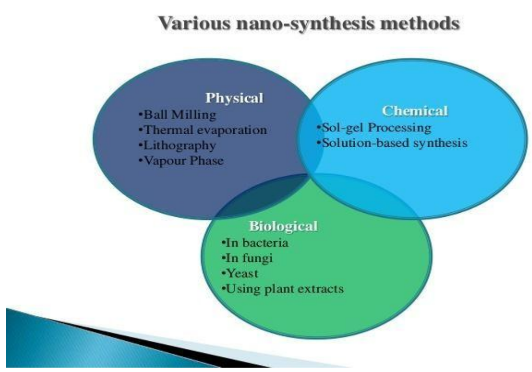


Figure.1. Methods and Preparation of Nano particles

EXPERIMENTAL TECHNIQUES

Materials used:

- Zinc Acetate
- Silver Nitrate
- NaOH
- PVP

Zinc acetate:

Properties	
Chemical formula	- $Zn_4H_6O_4$
Molar mass	- 219.50 g/mol
Appearance	- White solid
Melting point (dehydrate losses water at 100° C)	- Decomposes at 237^{o} C
Solubility	- soluble in alcohol

Sodium Hydroxide:

Properties	
Chemical formula	-NaOH
Molar mass	- 39.9971 g/mol^{-1}
Appearance	- White, waxy, opaque crystal
Melting point	- 318^{o} C
Solubility	- Ethanol

Silver Nitrate:

Properties	
Chemical formula	- $AgNO_3$
Molar mass	- 169.87 g/mol^{-1}
Appearance	- Colourless solid
Melting point	- 209.7^{o} C (409.5^{o}F; 482.8K)
Solubility	- acetone,,ammonia,glycerol

Polyvinylpyrrolidne (PVP):
It is one of the most common water soluble capping agents for use in the synthesis of colloidal particles.

Properties	
Chemical formula	- $AgNO_3$
Molar mass	- 169.87 g/mol^{-1}
Appearance	- Colourless solid
Melting point	- 209.7^{o} C (409.5^{o}F; 482.8K)
Solubility	- acetone, ammonia, glycerol

Synthesis of Zno and Ag doped Zno:

High purity zinc acetate $Zn(CH_3CO_2)_2$, silver nitrate $Ag(NO_3)_2$, sodium hydroxide (NaOH) and poly vinylpyrrolidone (PVP) as capping agent, were used for chemical processing.

Procedure for the synthesis of pure ZnO
0.05 M(1.097g) zinc acetate was dissolved in 100 ml of de-ionized water and 0.1 M (4g) NaOH was dissolved in 100 ml de-ionized water.

NaOH solution

↓

(dropwise added to zinc acetate)
White coloured gel is produced

↓

(kept overnight)
Annealed at 500°C for 2 hrs in muffle furnace

↓

Zinc Oxide

Figure.2. Flow chart for the preparation of ZnO

Similarly for the synthesis of Ag doped ZnO nanorods:

0.1 M (2.194g) zinc acetate solution with milli molar (0.0169g) silver nitrate and aqueous ammonia (1:1) was added drop wise to reach a pH ~ 7, and the stirring was continued for another 30 minutes.

Zinc acetate + Silver nitrate
[1:1] aqueous ammonia

↓

During stirring
(Few drops of PVP were added)
Glassy like **white gel** formed

↓

(Allowed to age overnight)
(Dried at 100°C for 12hrs)

↓

Annealed at 500°C for 2 hrs

↓

Ag doped zno

Figure.3. Flow chart for the preparation of AgZnO

II. CHARACTERIZATION

CHARACTERIZATION TECHNIQUES:
Various characterization techniques were performed in order to study the properties of the samples which were prepared by performing the above experimental techniques.

1. X-RAY DIFFRACTION
2. SCANNING ELECTRON MICROSCOPY
3. UV /VISIBLE SPECTROSCOPY
4. FTIR SPECTROSCOPY

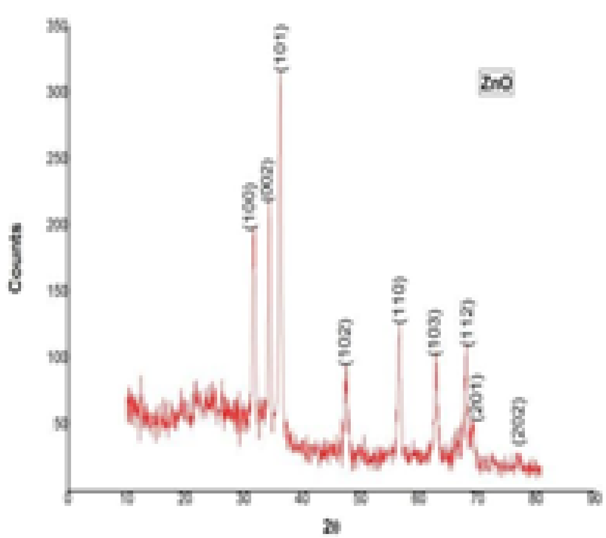
ANTI-BACTERIAL STUDIES:
Escherichia coli is an enterobacter belongs to gram negative organisms. (Rod Shaped) . It is most widely used "vector" and other biotechnological organisms. Human Insulin known as humulin were produced artificially by E.coli using gene manipulation. Anti-Bacterial testing was performed against Staphylococcus aureus (MTCC 3160) and Bacillus subtilis (MTCC 441) by agar well diffusion method. Bacterial strains were obtained from MTCC (Microbial Type Culture Collection) Chandigarh. For bacterial growth nutrient agar medium is used which contains beef extract, peptone, sodium chloride, and yeast, distilled water at pH 7.2 and incubated at 37 _C for overnight. Wells were then bored into the plates with seeded organisms using sterile cork borer of 6 mm in diameter. 50 ml of different samples of concentration 200 mg/ml were placed in the wells in different plates for study. All bacterial plates were incubated at 37 _C for 24 h. Average values were used for calculation of the inhibition zone area, which was the measure of the antibacterial activity of the studied samples. The diameter of the minimum zone was measured in mm

RESULT AND INTERPRETATION

XRD ANALYSIS:
ZnO, 0.05 M zinc acetate was dissolved in 100 ml of de-ionized water and 0.1 M NaOH was dissolved in 100 ml deionized water. NaOH solution was added drop wise to zinc acetate solution. Then, a white colored gel is produced and this gel was

kept for ageing overnight. Similarly for the synthesis of Ag doped ZnO nanorods, 0.1 M zinc acetate solution with milimolar silver nitrate and aqueous ammonia (1:1) was added drop wise to reach a pH ~ 7, and the stirring was continued for another 30 minutes. A few drops of PVP were also added during stirring for controlling growth. The formed glassy like white gel was allowed to age overnight. It was filtered, washed, dried at 100°C for 12 hrs and annealed at 500°C for 2 hrs in a muffle furnace, fitted with a proportional-integral-derivative (PID) temperature controller, and the heating rate was set at 100°C per minute. The prepared sample of zinc oxide and Ag doped zinc oxide nano particles were characterized by XRD for micro structural study the diffraction pattern were recorded using the XPERT-PRO diffract meter system. The diffraction intensity is detected and recorded with the counter and computer facility attached with instrument. Finally X-ray diffraction pattern is drawn by computer with the diffraction 2Ɵ in degrees along the x- axis and the intensity Counts per second along y – axis. Then from the obtained spectrum corresponding values of 2Ɵ and the intensities for the peak obtained or noted and tabulated. In the obtained spectrum ,the Bragg peak position and their intensities are compare with the standard Join Committee on Powder diffraction Standards(JCPDS) files to identify the crystal structure. The interplanar spacing (d-values) of respective miller planes responsible for the peak obtained are also determined and compared. The XRD patterns and hence the Bragg peaks obtained are shown in fig. A series of characteristic peaks in spectrum agree with standard ZnO and AgZnO XRD spectrum. The average crystalline size D of the particles calculated from the scherrer equation: $D=K\lambda/\beta\cos\theta$, where K is scherrer constant, λ is the X-ray wavelength , β is the full width of half maximum and θ is the Bragg diffraction angle. The particle sizes of the ZnO and AgZnO range The strongest peaks were detected at 2θ values are: 31.7°, 34.4°, 36.17°, 47.5°,56.6°, 62.2°, 66.4°, 68° and 69.1°, corresponding to the following lattice (hkl) planes: (100), (002), (101), (102), (110),(103), (200), (112), and (201), respectively. Two additional weak peaks are obtained at 38.18° and 44.36°, as shown in figure

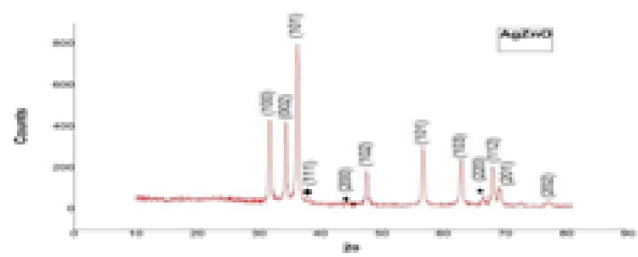
XRD PATTERNS OF ZnO



	Observed		JCPDS 36-1451		
(h k l)	2Ɵ(°)	d value (Å)	2 Ɵ(°)	d value (Å)	FWHM
100	31.8252	2.81189	31.770	2.8143	0.3936
002	34.4149	2.60600	34.422	2.6033	0.2460
101	36.2982	2.47499	36.253	2.4759	0.3444
102	47.5170	1.91355	47.539	1.9111	0.4920
110	56.5697	1.62695	56.603	1.6247	0.5904
103	62.8941	1.47771	62.864	1.4771	0.4920

The XRD pattern of ZnO and observed and JCPDS values of 2θ and d spacing values.

XRD PATTERNS OF AgZnO:



	observed		JCPDS 36-1451[1]		
(h k l)	2Ɵ(°)	d value (Å)	2 Ɵ(°)	d value (Å)	FWHM
100	31.7624	2.81730	31.74	2.81645	51.90
002	34.4313	2.60479	34.371	2.60686	50.40
101	36.2694	2.47689	36.20	2.478	100.00
102	47.5624	1.91183	47.45	1.91314	18.66
110	56.5819	1.62662	56.55	1.62808	35.13
103	62.8905	1.4779	62.80	1.479	28.97
112	67.9167	1.37901	67.96	1.37967	25.15

The XRD pattern of Ag ZnO and observed and JCPDS values of 2θ and d spacing values.

	a(Å)	c(Å)	c/a ratio	Unit cell volume$(Å)^3$
ZnO	3.243	5.206	1.6053	47.416
AgZnO	3.249	5.203	1.6014	47.565
JCPDS	3.250	5.207	1.6020	47.630

Unit cell parameters, cell volume and c/a ratio of ZnO and AgZnO nanopowders. ZnO and AgZnO shows hexagonal wurtzite structure with crystallite size 24.28 nm and 28.32 nm respectively. There are no larger shifts in the position of diffraction peaks in AgZnO pattern only with the two additional peaks at 38.12^0 and 44.36^0.

SEM ANALYSIS:

The Scanning Electron Microscopy (SEM) was used to investigate the morphologies of ZnO and AgZnO nano particles prepared by Sol-Gel method as shown in the figure (a) & (b), reveals that the ZnO consists of crystalline structure.

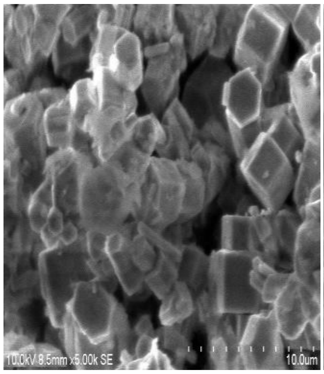


Figure.4. (a)

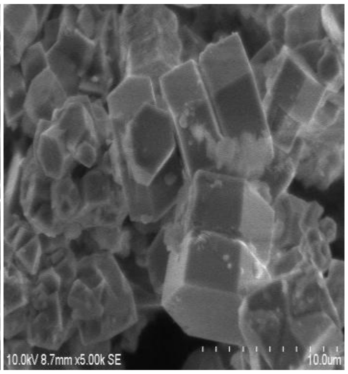
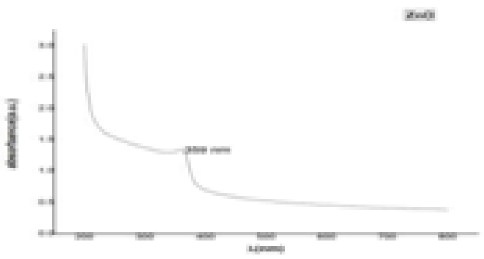


Figure.5. (b)

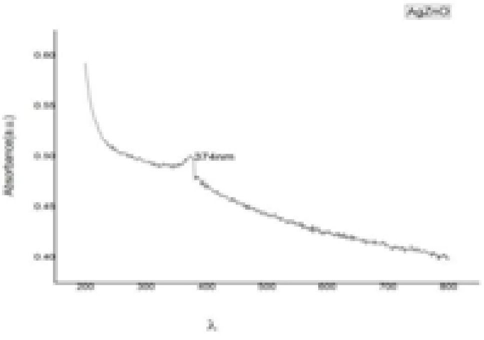
SEM image of Zinc oxide

- ❖ Hexagonal structure of ZnO is confirmed from the SEM image

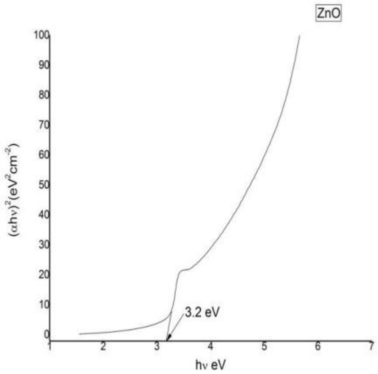
UV-VISIBLE SPECTROSCOPY ANALYSIS:



Optical absorption spectra of undoped ZnO Nanoparticles



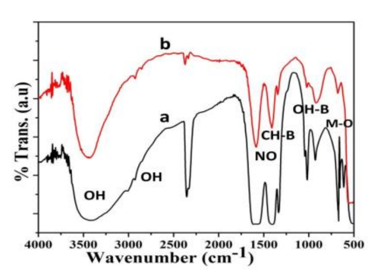
Optical absorption spectra of silver doped ZnO Nanoparticles



Tauc plot for ZnO

- ❖ From the absorption edge and Tauc plot band gap for ZnO and AgZnO is 3.2 eV and 3.3 eV respectively.

FTIR SPECTROSCOPY:

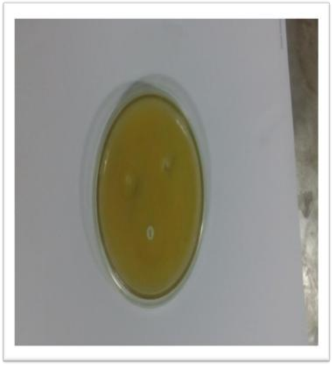


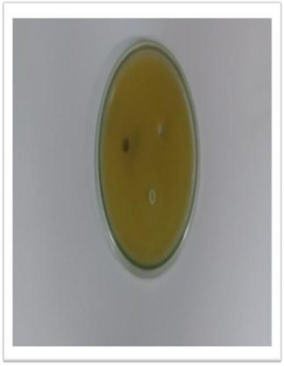
ZnO	Ag doped ZnO
OH-3404cm-1	OH-3443cm-1
NO-1566cm-1	NO-1566cm-1
CH-1412cm-1	CH-1390cm-1
CH bend-890cm-1	CH bend-919cm-1
M-O - 632cm-1	M-O-677cm-1

Fig a. shows all the peaks are appeared broad peak and (b) shows all peaks are very sharp compared to fig.(a) due to doping of Ag.

ANTI-BACTERIAL STUDIES:

In our study, the relative antibacterial activity of ZnO and Ag/ZnO suspensions of particles Gram positive and Gram negative (*E.COLI*) bacteria were studied. The well diffusion method is used to test the ability of the antibacterial agent to rupture the bacterial cells, and inverse relationship has been found between the particle size and its activity. The reason may be due to the increase in the surface-to-volume ratio of small size particles, and hence, a greater penetrating ability and reactivity. At the concentration of 1 mg/ml, the antibacterial activity studied against Gram negative and positive bacteria, as shown in figure.





Anti bacterial behavior of ZnO against Anti bacterial behavior of AgZnO against E.coli

E.coli

- ❖ Colonies of bacteria are more susceptible in AgZnO than in ZnO.
- ❖ The zone diameter of ZnO and AgZnO were 14mm and 17mm respectively.

III. CONCLUSION

Ag/ZnO nanopowders were synthesized by the simple wet chemical sol-gel method. The grain size was controlled by using polyvinyl pyridine as capping agent. Nanoparticle crystallinity, quality of the samples, chemical composition, and the optical properties were investigated by XRD, UV, FTIR, and SEM. The enhanced bioactivity was demonstrated by studying the antibacterial activity of ZnO and Ag/ZnO samples. These improved bioactivities of smaller particles were attributed to the higher surface to volume ratio. The smaller particles need more particles to cover a bacterial colony, which results in the generation of active oxygen species, which will kill bacteria more effectively. Therefore, Ag/ZnO nanoparticles were found to be more effective towards Gram negative and thus, contribute to the greater mechanical damage for all the functions of bacteria, and enhanced bactericidal impact of uniform fine structured Ag/ZnO nanoparticles.

IV. REFERENCE

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