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Synthesis, Characterization of ZnO Nanoparticles and the Impact of Changing the Proportion of Precursor on their Morphology, Average Formation, and Its Antimicrobial activity

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ABSTRACT

In this communication, we report the simple, Eco-friendly, cost effective, single step formation of ZnO nanoparticles in polymer matrix (PPS). Polyphenylene sulphide as a polymeric material for nonwoven bag filter as it has good mechanical and high resistance property to high temperature, also this is high-performance thermoplastic, tremendously strong, tough, and rigid. PPS play dual role–as a chalcogen (S) source and stabilizing matrix. We observed the effect of change of molar ratio of ZnO:PPS precursor on the formation of ZnO nanoparticles and formerly on the applications of nanostructures. The produced nanoparticles were characterised by XRD, SEM, FTIR and antibacterial activity. XRD report shows the presence of Hexagonal ZnO nanoparticle corresponding to zincite mineral. Supported by SEM. Additionally, 1:5 and 1:20 shows effective enhanced antibacterial activities.

Keywords: PPS, ZnO nanoparticles, Structural analysis, Histogram, Polymer matrix, XRD analysis, SEM, Antimicrobial activity, Eco-friendly synthesis.

INTRODUCTION

Nanostructures of different metal oxide have already proved their revitalization importance for the production of energy saving and harvesting devices, viz fuel cells, light emitting devices, solar cells, transistors, humidity, lithium batteries, and temperature sensor, UV-screening, photoelectrodes etc. Nevertheless, they have fabulous applications in biological and medical sciences like cancer treatment, drug delivery, bio tagging, bio labelling, fluorescent imaging etc. Transition metals like Zn doped metal oxide (ZnO) called as diluted magnetic semiconductors (DMS). Nowadays ZnO nanomaterials have garnered significant research attention for potential applications as it is cheap replacement for Si and GaN, and hence recommended as “Future promising material”. Crystalline ZnO possess wurtzite crystal structure at normal temperature and pressure and has a hexagonal unit cell Fig.1. Zinc oxide as it has polar nature exhibits variety of unique properties. ZnO change its physical properties with the dimension of nanostructures. ZnO nanoparticles reported vital important metal oxides as popularly employed in different field promising its vast useful properties like physical and chemical. The direct band gap 3.37 eV showing the transparency in visible region[1-6]. As it has shown distinctive optical and electrical properties, ZnS Co-doped with Cd and Fe showed magnetic properties[7], hybrid Fe_2O_3–ZnO/PS-PEG Nanocomposites showed optomagnetic properties[8] it is considered as important material in the field of optoelectronics applications for visible and very near to ultraviolet spectral regions. ZnO nanoparticles are vastly used in various industries as UV-Visible light emitting devices and also in different pharmaceuticals and cosmetic industries. It further includes non-toxic and compatible property with skin, antimicrobial and dermatologic associate degreed are dynamically used in sunscreen.[9-11] Zinc oxide (ZnO) nanoparticles have been fabricated by using numerous methods like laser ablation, hydrothermal synthesis, electrochemical deposition, Sonochemical method, thermal evaporation, electrophoretic deposition, sol-gel, anodization.[12] Moreover, development of inorganic/polymer hybrid material on nanoscale obtains more consideration for their potential applications in optoelectronics field. A doped ZnO variants for the development of latent finger print.[13-14] Earlier investigation between inorganic fillers and organic polymer reveals the changes in mechanical properties due to addition of inorganic filler in polymer matrix, and functional properties like antibacterial activities and UV -protection are largely explored.[15] PANI@ZnO hybrid materials in Adsorption of Congo Red and Methylene Blue Dyes have good adsorption property[16]. Zinc Oxide Nanoparticles, for dye-sensitive solar cells[17]. Novel green synthesis of Zinc Oxide nanoparticles using orange waste also showed Antibacterial Activity[18]. ZnO nanoparticles induced by surface stabilization due to positive aging effect.[19]

In our previous work, we presented the research work for the synthesis of ZnO nanoparticles in polymer matrix by using zinc nitrate as an inorganic salt and polyphynelene sulphide (PPS) as a polymer. In this research we observed typical 1:1 molar ratio only (zinc nitrate: PPS) to produce ZnO nanoparticles[20]. This study investigates cost effective, eco-friendly, synthesis and real-world applications of ZnO nanoparticles in polymer matrix by changing the molar ratio of inorganic salt zinc nitrate to PPS as 1:5,1:10.1:15, and 1:20. For the present work we kept the fixed ratio of zinc nitrate and variable ratio of PPS. Polyphenylene sulphide has been broadly used polymeric material for nonwoven bag filter as it has good mechanical and high resistance property to high temperature, also this is high-performance thermoplastic tremendously strong, tough, and rigid and does not change these properties above the temperature 200°C. Melting range of PPS ranges from 280°C to 290°C has good resistance to chemicals, fluids and oils. Furthermore, it has fabulous property to change upon heating in the presence of ambient oxygen.[21]

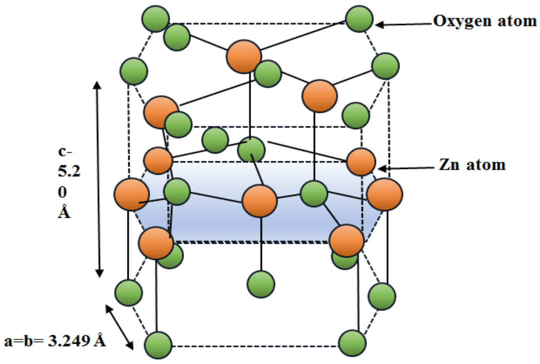

Fig. 1. Tetrahedral structure of ZnO

EXPERIMENTAL

Materials

Analytical grade reagents Poly-phenylene sulphide $(C_6H_4S)n$, zinc nitrate $(ZnNO_3)_2$ and acetone (CH_3COCH_3) from Sigma Aldrich (99% purity) were directly used for the synthesis for ZnO nanoparticles.

Synthesis procedure

ZnO nanoparticles were synthesized by using one step, very simple, ecofriendly solid-state method. In this procedure zinc nitrate to variable ratio of PPS were admixed physically in agate mortar pastel for minimum 20 min with acetone. Further admixed sample was dried under IR lamp and then subjected to melting temperature of PPS at 285°C in muffle furnace for five hours under normal atmosphere condition in alumina crucible. After 5 h the synthesized product was cooled at room temperature. The received shady brown coloured product was then crushed to fine powder to study the different properties of ZnO nanoparticles.

Characterization

The ZnO nanoparticles were characterised by various physicochemical techniques. To obtain the UV-Visible analysis sample were dispersed in methanol and sonicated for about 20 minutes. The solution then transferred in a quartz cuvette. The optical spectrum then recorded within the range of 200-800 nm.

The structural analysis was accomplished via X-ray diffraction analysis. The Rigaku Miniflex X-ray diffractometer armed with copper target (CuKα1, λ = 1.5406Å) nickel filter. The sample was placed on stub and diffraction pattern 2θrecorded ranging from 20°- 80° angle.

The morphology of ZnO nanoparticles were studied through scanning electron microscopy (SEM) (FEI Nova SEM450). For this analysis the sample was prepared as given below; the product was dispersed in acetone and sonicated for about 20 minutes.

Antimicrobial activity test was performed by the commonly used Agar diffusion method which is designed to determine the smallest amount of the antibiotic needed to inhibit the growth of micro-organism. Antimicrobial activity was tested using Kirby-Bauer Method. Plates were incubated at 37°C for 24-48 hours. in an incubator and the diameter of zone of inhibition in mm was measured using a ruler on the underside of the plate.

FTIR spectrum of ZnONP solid sample was performed in the spectral range from 500-4000 cm^{-1}. The IR Affinity-1 Shimadzu interferometer with High-energy ceramic light source was used for the analysis of product.

Result and Discussion

Synthesis

ZnO-pps nanoparticles were synthesised by mixing zinc nitrate with various proportions of PPS. Poly-phenylene sulphide has glass transition temperature (T_g) approximately 85°C and melting temperature 285°C (approximately) (average molecular weight 10,000). The reaction temperature of 285°C was selected because PPS thermally decomposition at ~450°C and melting temperature of polymer is 285°C. The loosely bound sulphur in PPS reacts with Zn to produce ZnO in polymer matrix which gives desired product. The synthesised nanoparticle was characterised by various physicochemical techniques. The chemical and electrolysis route for the synthesis is shown in Figure 2.

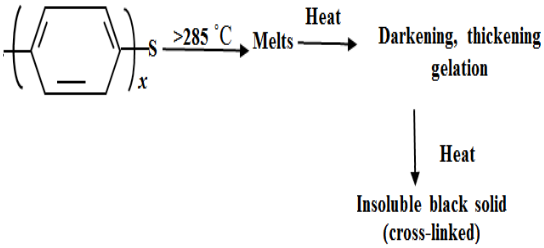

Fig. 2. Procedure for the synthesis of ZnO nanoparticles

XRD

To get insight into crystalline nature and size of synthesised X-ray diffraction studies were carried out. X-ray Diffraction patterns of ZnO nanoparticles in polymer matrix with different molar ratio as 1:5, 1:10, 1:15, and 1:20 were recorded and shown in Fig. 3. The peaks at 2θ, 31.7, 34.4, 36.2, 47.5, 56.6, 62.8, 66.3, 67.9, 69.09 are attributed to the presence of Hexagonal ZnO nanoparticle corresponding to zincite mineral according to JCPDS: 36-1451. The very strong and peak broadening at 36.2 derive the good crystallinity of the nanoparticles.

The average crystallite size of nanoparticles was calculated from Scherrer equation.

$$D=(K\lambda/\beta\cos\theta) \quad (1)$$

Where D-Crystallite size, K is shape factor, λ is wavelength, β is full width at half maximum (FWHM) and θ is angle of diffraction (Bragg's angle).

The crystallite sizes obtained from above equation are tabulated in Table 1.

It has been observed that the crystallite size varies from 12-22 nm as proportion of Zn nitrate to PPS is changed.

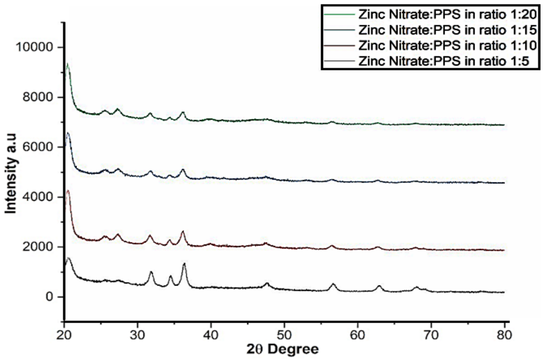

Fig. 3. XRD pattern of ZnO nanoparticles at different molar ratios (1:5, 1:10, 1:15, 1:20)

Table 1. Crystallite size of nanoparticles prepared

Proportion	Particle size nm
1:5	12.27
1:10	14.74
1:15	14.08
1:20	22.38

FTIR

The nanoparticles of ZnO in polymer matrix was examined via FTIR for different molar ratios of ZnO in PPS i.e. 1:1, 1:5, 1:10, 1:15 & 1:20 can be seen in Fig. 4. In the Fig. 4, for the molar ratio 1:1 (ZnO:PPS) the absorption peak at 547.78 represents the ZnO stretching frequency, the peaks at 640.36, 740.66 and 1002.9 represents C=C bending and 1465.9 and 1566.1 represents C-H bending frequencies of polymer.

SEM

The synthesised nanoparticles were analysed by SEM for further characterisation and to get the information of morphology of ZnO nanoparticles. The photomicrographs of SEM [recorded with secondary electron (SE) mode] of the stated molar ratios sample product are presented in Fig. 5. All the images of SEM of all ratios depict the formation of globular morphology of size between 10-25 nm. These values are also in accordance with particle size calculated from powder XRD using Scherrer formula. Further, SEM study revealed globular morphology in molar ratio 1:5 with intense unequal dispersion of globular particles in polymer matrix. Whereas, less distribution of globular particles observed as the molar ratio increases can be attributed to less percentage of availability of zinc compare to PPS. In addition, chunk like morphology is observed for all samples, such features appeared to be characteristics property of PPS. The average particle size distribution (histogram) from SEM image is shown in figure Figure 6.

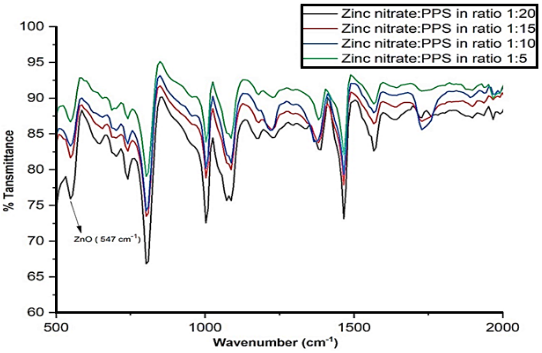

Fig. 4. IR spectrum of PPS and zinc nitrate mixture heated at different molar ratio

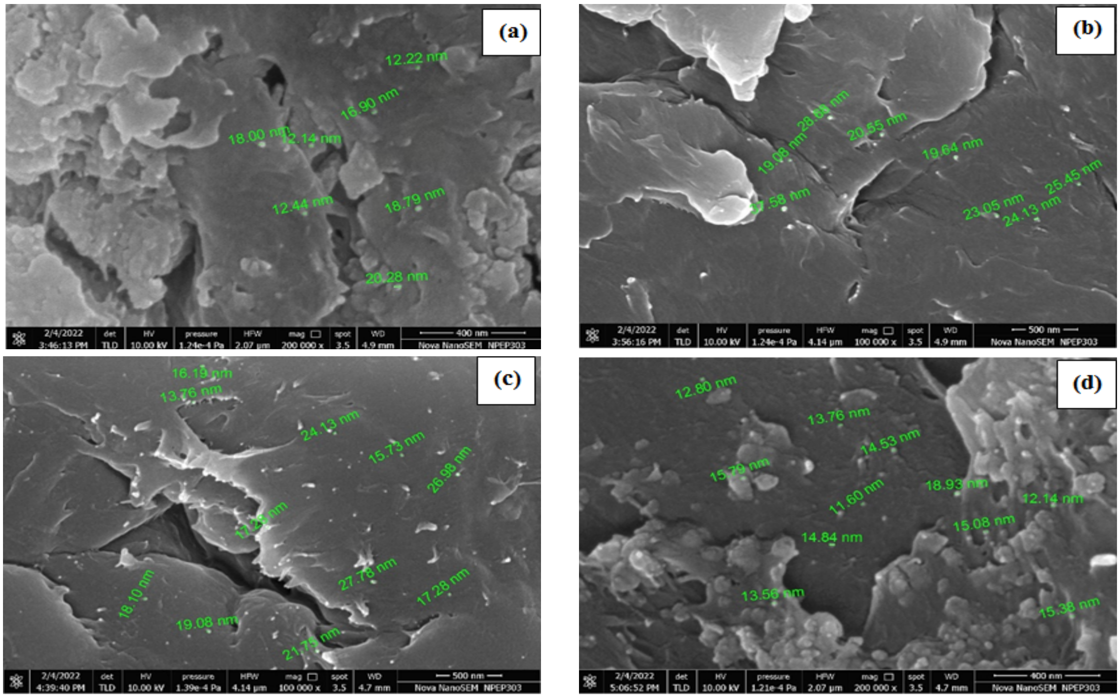

Fig. 5. SEM photomicrographs (SE mode) corresponding to zinc nitrate and PPS heated admixture of (a) 1:5, (b) 1:10, (c) 1:15, (d) 1:20 molar ratios

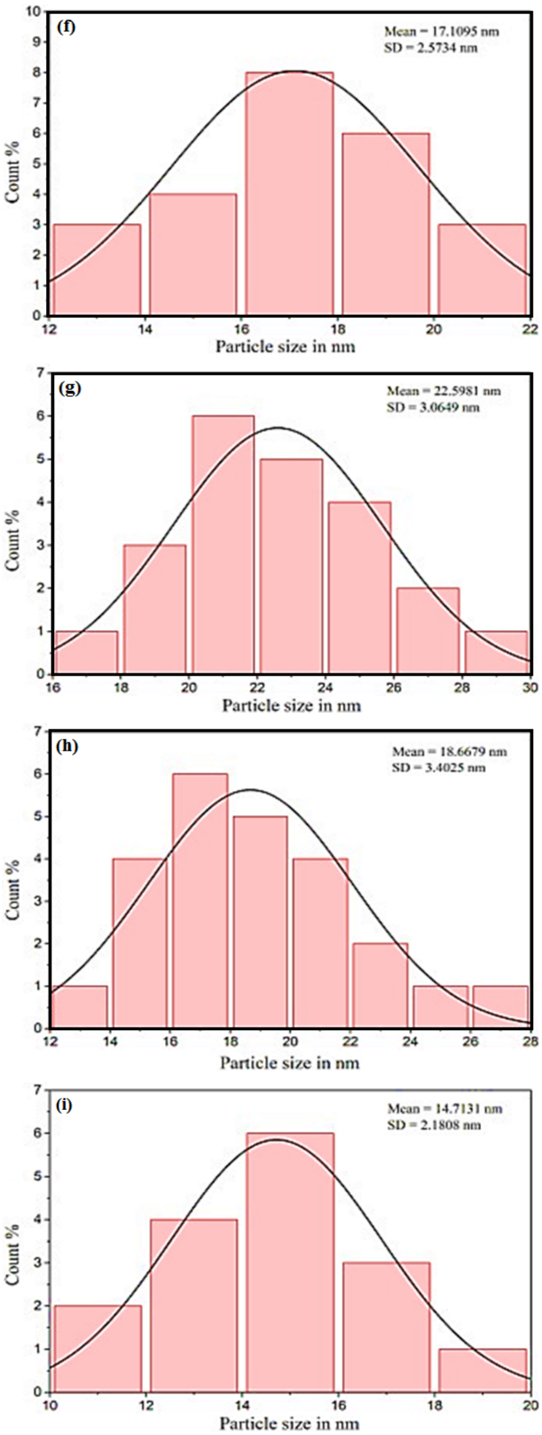

Fig. 6. Average particle size distribution (histogram) from SEM image by Image J software for Zinc nitrate and PPS heated admixture of (f) 1:5, (g) 1:10, (h) 1:15, (i) 1:20 molar ratios

Antimicrobial activity

Since ZnO has been found to exhibit antimicrobial activity, we have tested the antimicrobial activity of ZnO enforced polymer matrix against *E. coli* and *S. aureus* Fig. 7. It has been found that the ZnO enforced polymer matrix with 1:5 proportion exhibited efficient antimicrobial activity or inhibitory action. Antimicrobial activity for ratios 1:5 and 1:20 reveals the similar trends as we increase the proportion of PPS activity report is supressed as less availability of ZnO nanoparticles and more entrapment in polymer matrix.

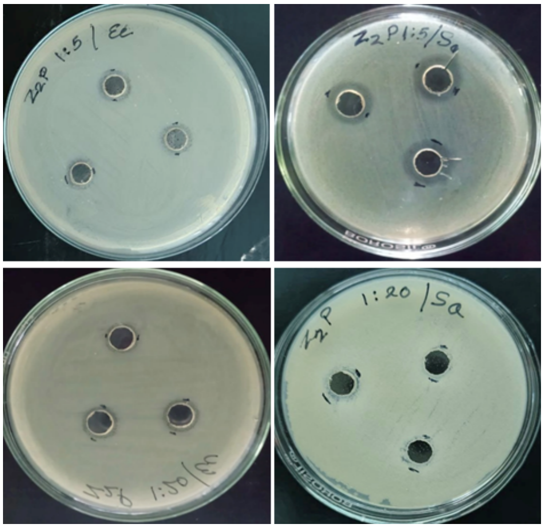

Fig. 7. Zone of inhibition of ZnO enforced in polymer matrix against (A) *S. aureus* and (B) *E. coli* for (a) 1:5 and (b) 1:20 respectively

Table 2 shows zone of inhibition of these compounds against *E. coli* and *S. aureus*. This result indicates the antimicrobial potential of ZnO enforced polymer matrix. These results are also compared with streptomycin and gentamycin as reference drug. The graph of antimicrobial activity of ZnO enforced polymer matrix against *E. coli* and *S. aureus* is presented in Figure 8.

Table 2: Antimicrobial activity of ZnO enforced polymer matrix against *E. coli* and *S. aureus*

Sr. No	Compound	Zone of inhibition (mm)	
		E. coli	*S. aureus*
1	ZnO:PPS (1:5)	11	13
	DMSO	9	--
	Streptomycin	31.6	29.6
	Gentamycin	36	33.5
2	ZnO:PPS (1:20)	10.6	11.6
	DMSO	9	-
	Streptomycin	31.6	29.6
	Gentamycin	36	33.5

Ec:-*Escherichia coli* (NCIM2065)
Sa:-*Staphylococcus aureus* (NCIM2178)

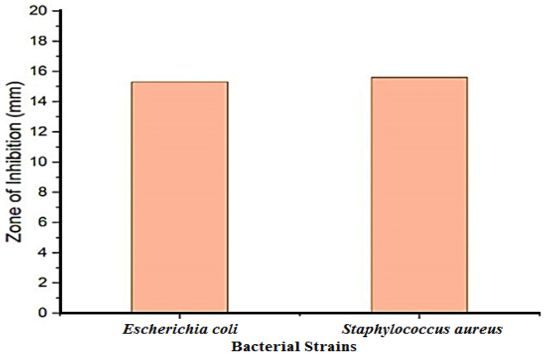

Fig. 8. Graph of Zone of inhibition of ZnO nanoparticles enforced in polymer matrix against *E. coli* and *S. aureus*

CONCLUSION

To the extent that, ZnO nanoparticle can be produced by chemical methods with the evolution of many hazardous and environment polluting gases but recently more standards are focused on eco-friendly production of such nanoparticles. In this research we have demonstrated, cost effective, single step, eco-friendly formation of ZnO nanoparticle in PPS matrix at various proportions of zinc nitrate and PPS with real-world applications. As proportion of PPS was increased, formation of ZnO nanoparticles was found to be decreased due to less availability of Zn. The prominent diffraction peaks revealed, and confirmed the formation of ZnO nanoparticles which are strongly supported by SEM images. Flower like morphology in molar ratio 1:1 with intense unequal dispersion of globular particles in polymer matrix. Whereas, as the percentage of PPS increases less distribution of globular particles observed which can be attributed to less percentage of availability of zinc compare to PPS. The 1:5 ratio showed optimal properties due to ZnO availability in higher PPS ratios. The representative investigation of antimicrobial activity for ZnO enforced polymer matrix with 1:5 and 1:20 proportion exhibited efficient antimicrobial activity or inhibitory action. This result indicates the antimicrobial potential of ZnO enforced polymer matrix. These ZnO nanoparticles may be useful as UV absorber in different cosmetics as sunscreen lotion, catalysis in various organic reaction to produce bioactive compounds, optics and in electrical engineering.

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Conflict of Interest

All the author declares that there is no conflict of interest for the publication of this paper.

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