Synthesis of Honey Mediated Biogenic Zinc Oxide nanoparticles and Structural Parameters Investigations

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Abstract

The advantage of using Honey bee in nanoparticles synthesis is that they are easily available, low cost and safe to handle. The aim of this study was to synthesize and investigate the structural parameters of honey mediated biogenic zinc oxide nanoparticles. The zinc oxide nanoparticles were investigated by Fourier Transform Infrared Spectroscopy (FTIR), X-ray diffraction (XRD) and Transmission Electron Microscope (TEM). We observed that the biogenic honey mediated zinc oxide nanoparticles did not require any external chemicals reagent for stabilization and reduction of nanoparticulate. By XRD the crystallite size was found to 26.29 nm and the dislocation density was 14.46×10^{-4} $(nm)^{-2}$. The volume unit cell was determined and the volume was V= 22.8634 ($Å^3$). The lattice constants (a= b = 3.2369 Angstrom and c = 5.2067 Angstrom, c/a = 1.6024). TEM micrographs also confirmed the particle size of the sample was in the nanoscale range. The present study was carried out to synthesize Zinc oxide nanoparticles by biogenic method using Honey as medium and characterized by different techniques adapted for finding out the morphology, composition, functional group and size.

Key words: Honey bee, zinc oxide nanoparticles, FTIR, XRD, TEM

1. Introduction

Nanoparticles usually ranging in dimensions from 1 to 100 nm have properties unique from their bulk equivalent. The nanoparticles possess unique physicochemical, optical and biological properties which can be manipulated suitably for desired applications [1]. The chemical properties of a material are determined by the type of motion of its electrons. There is a wide range of NPs contributing too many different chemical properties [2]. In recent years, green synthesis of metal nanoparticles is an interesting issue of the nanoscience and nanobiotechnology. There is a growing attention to biosynthesis the metal nanoparticles using organisms [3][4]. Among metal oxide nanoparticles, zinc oxide nanoparticles have been used in various cutting edge applications like electronics, communication, sensor, cosmetics, environmental protection, biology and medicinal industry [5[6][7][8].

Natural honey, documented as the world's oldest food source, is an excellent food with high energy and nutritious value [8]. The concentration of mineral compounds ranges from 0.1% to 1.0%. Potassium is the major metal, followed by calcium, magnesium, sodium, sulphur, and phosphorus.

Trace elements include iron, copper, zinc, and manganese [9]. A variety of enzymes, for example, oxidase, invertase, amylase, and catalase, are constituents of honey; the main enzymes are invertase (saccharase), diastase (amylase), and glucose oxidase[10]. The present study was carried out to synthesize zinc oxide nanoparticles by biogenic method using Honey as medium, characterized by different techniques, and studied structural parameters. Ref [12] studied Honey mediated green synthesis of nanoparticles: New Era of Safe Nanotechnology and reported that honey mediated green synthesis requires relatively low temperatures (generally room temperature) and does not produce any toxic products.

2. Experimental Method

For the reduction of zinc ions natural bee honey (Marthantum, Nagercoil, Tamilnadu) was used. In this method, ZnO nanoparticles were biosynthesized from zinc nitrate as a precursor through a simple ecofriendly route using natural honey, which acted as a reductant and stabilizer simultaneously. For the synthesis ZnO nanoparticles, 20 ml of bee honey was added with 1 N solution of 20 ml zinc nitrate. The mixture was then stirred in a magnetic stirrer at 60^0 C until a paste was formed. This paste was then collected in a ceramic crucible and heated in an air heated furnace at 400^0C for 2 hours. A light yellow colored powder of ZnO nanoparticles was obtained and this was carefully collected and preserved in the airtight vials for further studies.

3. Results and Discussion

Zinc oxide nanoparticles were prepared by Bee honey mediated Biogenic method. The formation of the nanoparticles was confirmed by studying by Fourier Transform Infrared (FTIR) spectra, X-ray diffraction (XRD) and Transmission Electron Microscope (TEM)

3.1 FTIR Studies:

The IR spectrum was taken for Zinc oxide using a Nicolet iS5 FT-IR instrument operating at a resolution of 4000-400 cm^{-1} in the percent transmittance mode. Generally, all the metals and its oxide, give the FTIR peaks at lower wave number ranging from 400 to 800cm^{-1}. The results are shown in Fig.1 and band assignments are given in Table 1.

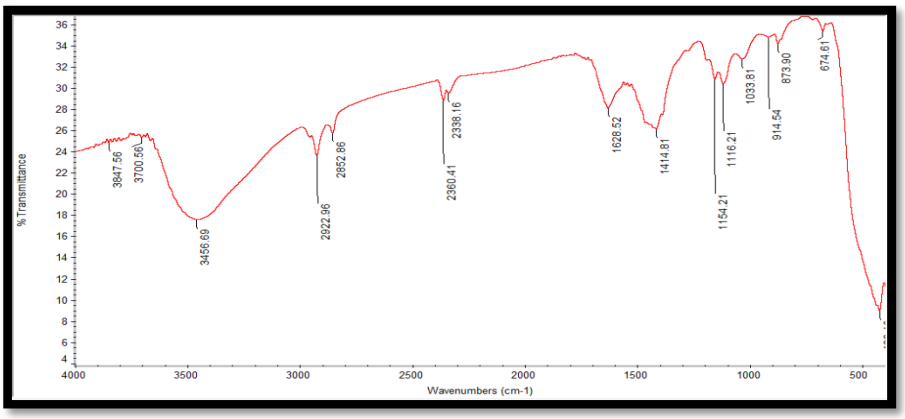


Fig.1 FTIR spectrum of ZnO nanoparticles synthesized using Honey medium.

Table 1. Band assignment for zinc oxide nanoparticle

Frequency (cm^{-1})	Tentative Assignment
3432.86	O-H stretching vibration
2922.95	aliphatic asymmetric C-H stretching vibration
2361.34	O-H stretching in carboxylic acid
1628.11	N–H bend of amines,
1463.72	C–C stretch (in–ring) of aromatics,
1384.32	-C=N- stretching vibrations as well as amide bands of proteins
914.35	O–H stretch of carboxylic acids,
870.47	tetrahedral coordination of Zn ion
754.61	C – H bending of aromatic

3.2. X-Ray Diffraction Studies (XRD)

Structural parameters of Zinc oxide nanoparticle prepared from Honey was calculated from XRD pattern. Calcination at 400^0 C is essential for complete removal of water and to obtain higher crystallinity. The average crystallite size (D) was calculated using the well-known Scherrer's formula, $D = k\lambda / \beta\cos\theta$.

Presence of several peaks indicates random orientation of the crystallites, confirming the hexagonal wurtzite structure of the ZnO nanoparticles [13]. The average crystallite size (D) was calculated using the well-known Scherer's formula.

$$D = k\lambda / \beta\cos\theta$$

The X-ray diffraction pattern of ZnO nanoparticles synthesized using Honey as medium is shown in Fig.2. The spectrum of ZnO nanoparticles exhibits sharp peaks at 2θ equal to 31.88^0, 34.40^0, 36.32^0, 47.60^0, 56.63^0, 62.92^0, 66.38^0, and 69.20^0. These peaks are identified to originate from {100}, {002}, {101}, {102}, {110}, {103},{200},and {201} planes of the hexagonal ZnO phase respectively. This XRD pattern was well matched with standard JCPDS Card No. 361451[14]. The above mentioned XRD parameters were depicted in Table 3. The average crystallite size (D) of synthesized nanoparticles was 26.29 nm.

$\delta=1/D^2$

Where ***D*** is the crystallite size. The dislocation density (***δ***) is 14.46×10^{-4} $(nm)^{-2}$.

The lattice constant **a** for (100) plane was calculated by [15]

$$\mathbf{a = \lambda / \sqrt{3}\ Sin\theta}$$

For the (002) plane, the lattice constant c was calculated by

$$\mathbf{c = \lambda / Sin\theta}$$

The lattice constants (a = b = 3.2369 Angstrom and c = 5.2067 Angstrom, c/a = 1.6024) and diffraction peaks corresponding to the planes (100), (002), (101), (102), (110), (103) obtained from X-ray diffraction data are consistent with the JCPDS data of ZnO. The dislocation density (δ), which represents the amount of defects in the sample, is defined as the length of dislocation lines per unit volume of the crystal. The volume (V) of the unit cell for hexagonal system and the number of unit cells (n) in the particle (considering it spherical in shape) were estimated from the relations

$$V = \sqrt{3}/2\, a^2 c$$

Significant degrees of strains were associated with nanoparticles, because they are known to have a number of surface atoms which have unsaturated co-ordinations, various structural parameters namely dislocation density (δ) microstrain (ε), stress and stacking fault (SF) were estimated by the following relations [16][17].The estimated structural parameters are shown in Table 3.

$$\varepsilon = \beta \cos \theta / 4$$

$$\sigma \text{ stress } = \varepsilon E$$

The Bragg's angle and E the elastic constant or generally known as Young's modulus of the material. Young's modulus of the zinc oxide is 128 GPa.

Table.2 XRD parameters of ZnO Nanoparticles

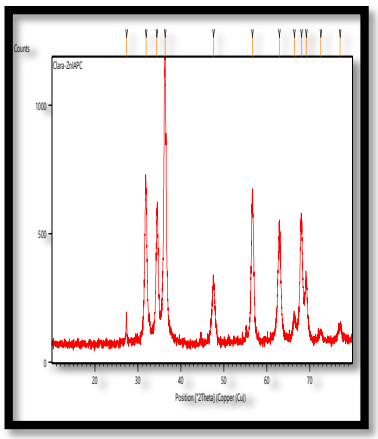


Fig.2 FTIR spectrum of zinc oxide nanoparticle

2-Theta	FWHM	Size	Plane
31.8853	0.4684	99.765	100
34.4064	0.4349	71.386	002
36.3285	0.3680	75.958	101
47.6099	0.4684	56.150	102
56.6326	0.6022	46.215	110
62.9261	0.6691	73.743	103
66.3838	0.6691	26.821	200
69.2091	0.4015	34.256	201

Table 3. Estimated structural parameters of ZnO NPs

Parameters	(100)	(002)	(101)	(102)	(110)	(103)
θ	15.9426	17.2032	18.1642	23.8049	28.3163	31.4630
$\beta x10^{-3}$	8.169	7.585	6.418	8.169	43.02	47.8
D	26.32	29.65	39.14	27.66	20.16	18.10
a(Å)	3.2369	3.0061	2.8520	2.2028	1.8744	1.7050
c(Å)	5.6066	5.2067	4.9399	3.8154	3.2466	2.9504
$\delta\ 10^{-15}$ (kg m^{-3})	1.4435	1.137	0.6527	1.3070	2.4604	3.0524
d(Å)	2.8067	2.6066	2.4729	1.9100	1.6252	1.4770

$\varepsilon x10^{-3}$	1.9632	1.8114	1.5245	1.8685	9.4680	10.1932
σ x 10^8 (Pa)	2.512	2.318	1.951	2.391	12.11	13.04
SF	0.4734	0.5108	0.5394	0.7068	0.8408	0.9343
V ($Å^3$)	22.8634					

3.3 Scanning Electron Microscope (SEM)

A Scanning Electron Microscope (SEM) (model-JEOL-JSM-6380LA) with energy dispersive X-ray Spectroscopy (EDXS) was used to evaluate the texture, morphology of Zinc oxide nanoparticle (1N) SEM were recorded at different magnifications, i.e., X10,000, X20,000, X30,000, X40,000, X55,000. The SEM analysis of the zinc oxide nanoparticles revealed that their shape and sized less than 1 µm. Exhibited irregular particle shape of plate like structure and noticeable aggregation with particle size ranging from 0.2µm -1 µm. Sample consists of small irregular particle aggregates with a rod-like shaped structure.

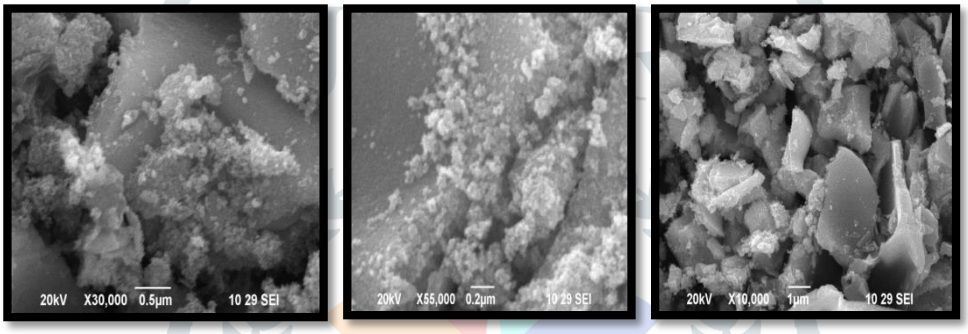


Fig.3-5 represents the SEM image of ZnO nanoparticles synthesized using Honey.

3.4 Energy Dispersive X-Ray Analysis:

The elemental composition of ZnO nanoparticle was carried out by EDAX spectroscopy. Fig.6 showed the EDAX spectrum of Zinc oxide nanoparticles synthesized using Honey bee. Zinc oxide nanoparticles were found to have atomic percentage 48.42 of Zn, 11.85 of O, as shown in Table 4. This confirmed the presence of Zn and O.

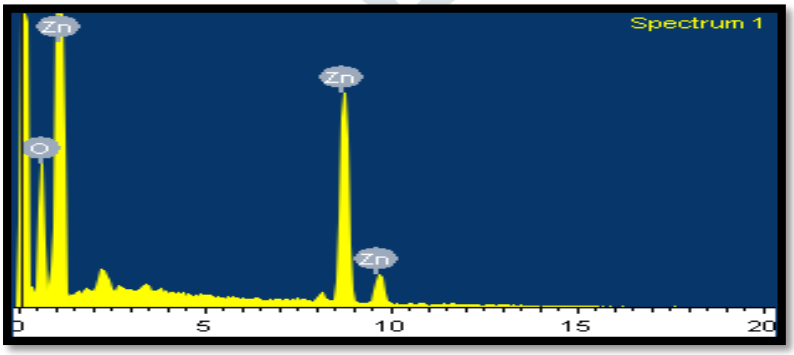
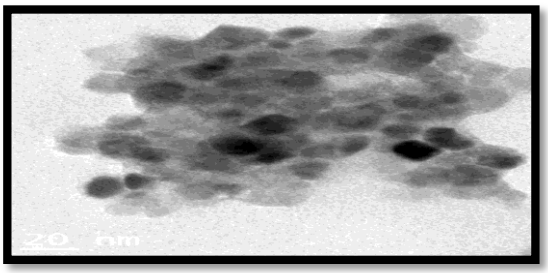


Fig.6 EDAX spectrum of ZnO nanoparticles synthesized using *Honey*

3.5 Transmission Electron Microscope (TEM)

The size of the synthesized ZnO nanoparticle using honey medium was further confirmed by TEM. The TEM monograph (Fig.7 & 8) clearly shows the distribution of spherical and rod like appearance for ZnO nanoparticles synthesized. The low-resolution TEM micrograph exhibited spherical nanoparticles with diameters of 20 nm in size. The selected area electron diffraction (SAED) pattern

in Fig. 8 shows distinct bright rings which confirmed the preferential orientation of nanocrystals instead of irregular. The narrow ring of SAED pattern confirms the nanocrystalline nature of the sample and size of nanoparticle was 21 nm. The average crystallite size (D) of synthesized nanoparticles found by XRD was 26.29 nm. The particle size calculated from TEM measurement was in good agreement with the particle size calculated from the Debye-Scherrer formula.



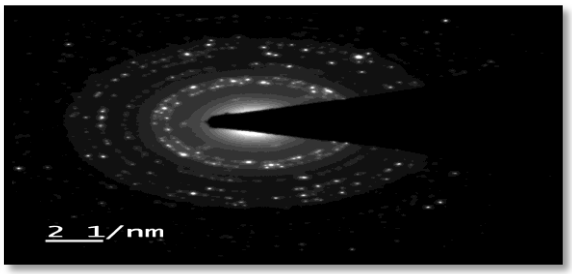


Fig. 7 TEM image of nanoparticle **Fig. 8 SAED pattern of nanoparticle**

4. Conclusion

Zinc oxide nanoparticles are synthesized by biogenic method (simple and cost effective) method using natural Honey bee. By XRD the crystallite size was found to 26.29 nm for ZnO nanoparticles, the dislocation density was 14.46×10^{-4} $(nm)^{-2}$. The volume unit cell was determined and the volume was V= 22.8634 ($Å^3$). The lattice constants (a = b = 3.2369 Angstrom and c = 5.2067 Angstrom, c/a = 1.6024). TEM micrographs also confirmed the particle size of the sample was in the nanoscale range.

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