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Facile Biomimetic Synthesis and Spectral Characterization of Nano Zinc Oxide Using Gelatin

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ABSTRACT:

Among the metal oxides, zinc oxide is one of the most attractive materials, because of their excellent performance in fields such as high corrosion resistant nano coating, highly transparent composites, semiconductors, cosmetics, sensors etc. The present work, attempted the synthesis and characterization of zinc oxide nanoparticles using a cost-effective and low temperature aqueous sol-gel method via, a facile biomimetic process using gelatin. X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), UV- visible absorption spectroscopy, Scanning electron microscopy (SEM) and Energy dispersive X-ray spectrometry (EDX) were employed for sample characterization. The average crystallite sizes of the samples were calculated from FWHM of XRD peaks using Debye-Scherrer's formula and were found to be in the nano range. All the diffraction peaks were indexed to the hexagonal wurtzite structure of ZnO. EDX showed that the above route produced highly pure ZnO nanoparticles. A flower- like morphology was observed for the ZnO samples. The formation of zinc oxide was confirmed by FTIR and UV- visible absorption studies.

Keywords: zinc oxide, sol-gel, gelatin, nano particles, synthesis

[I] NTRODUCTION

Among the various semiconductor oxide nanomaterials, zinc oxide (ZnO) is a versatile and an important material having unique position due to its piezoelectric and transparent conducting properties. It has a high electrical conductivity and optical transmittance in the visible region. These properties make it an ideal candidate for applications like transparent conducting electrodes in flat panel displays and window layers in solar cells [1-4]. ZnO has wide band gap energy (3.37 eV) and a large binding energy (60 meV) and exhibits many potential applications in areas such as laser diodes, solar cells, gas sensors, optoelectronic devices. Apart from this, bio-safe characteristics of ZnO make it very attractive for biomedical applications. A method for economical mass production of ZnO nanostructures would therefore be very useful. This is why, to study the

synthesis of ZnO nanostructures and understanding the ZnO nanostructures is of great interest [5-7].

Physically, ZnO has the appearance of a white powder and is referred to as Zinc white or zincite. It is almost insoluble in water and alcohol but readily soluble in acids like HCl. Crystalline form of ZnO is thermo chromic in nature and due to this it changes from white to yellow on heating and vice versa on cooling. ZnO has three crystal forms: the hexagonal wurtzite, the cubic zinc blende and the cubic rock salt which is rarely observed. The wurtzite structure is most commonly used as it has the highest stability under normal working conditions. ZnO is considered to be a soft material and its elastic constants are not that impressive. But ZnO has got very good thermal properties like high melting point, high thermal capacity and conductivity and a low coefficient of thermal expansion which makes it suitable for use as a ceramic [8].

Many methods have been described in the literature for the production of ZnO nanostructures such as laser ablation [9], hydrothermal methods [10], electrochemical depositions [11], sol–gel method [12], chemical vapor deposition [13], thermal decomposition [14], and combustion method [15, 16]. Recently, ZnO nanoparticles were prepared by ultrasound [17], microwave-assisted combustion method [18], mechano-chemical-thermal synthesis [19], anodization [20], co-precipitation [21], and electrophoretic deposition [22]. Rodrigues - Paez *et al*. synthesized zinc oxide nanoparticles with different morphologies by controlling different parameters of the precipitation process such as solution concentration, pH, and washing medium [21]. Muhammad *et al.* synthesized zinc oxide thin films by sol-gel method on glass substrate [23].

In the present study, ZnO nanostructures were synthesized using a simple sol-gel method. Zinc nitrate hexahydrate and gelatin were used as precursors to formulate ZnO nanoparticles. Gelatin is a translucent, colourless, brittle (when dry), flavourless foodstuff, derived from collagen obtained from various animal by-products. It is a mixture of peptides and proteins produced by partial hydrolysis of collagen extracted from the skin, bones and connective tissues of animals such as domesticated cattle, chicken, pigs and fish. The prepared samples were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM) and the purity of the sample was tested using energy dispersive X-ray spectroscopy (EDX) analysis. The formation of ZnO was confirmed from FTIR spectroscopy and the band gap energies of the samples were calculated from UV-visible absorption spectroscopy. The morphology and crystallite size of ZnO nanostructures were investigated and the results of synthesized zinc oxide samples were correlated with the commercial zincite.

[II] MATERIALS AND METHODS

2.1 Synthesis of ZnO nanoparticles

The nanoparticles were prepared by simple the sol-gel technology. All chemicals used were analytical reagents. Zinc nitrate hexahydrate (s.d. fine-CHEM Ltd., Mumbai) and gelatin (s.d. fine-CHEM Ltd., Mumbai) were used as raw materials to prepare nano zinc oxide.

Zinc oxide nano particles were prepared by sol-gel process employing the biopolymer, gelatin. 15 wt% aqueous solution of gelatin was prepared and kept under constant stirring using magnetic stirrer. 10 wt% zinc nitrate hexahydrate $Zn(NO_3)_2 \cdot 6H_2O$ was added to it slowly. The resulting mixture was refluxed at 100 ^{0}C for several hours and left to cool down naturally. The resulting gel obtained was calcined for 5 hours at 500 ^{0}C. The nano powders were collected and washed first with deionized water and then with ethanol several time to remove the impurities. The characterizations were done and the reults were compared with the commercial zinc oxide.

2.2 Characterization

The structure of particles was investigated using X-ray diffraction using PANalytical, XRD

machine (DY-1656). Monochromatic CuKα radiations were used as a source of 40 kV/35 mA power and the pattern was recorded in the 2θ range of 3^o– 80^o with a scan step of 0.02 in a scan time of 65.6seconds. IR spectrophotometer (Shimadzu, FTIR-8900, Japan) was used for obtaining IR spectra (KBr) operating in the 400–4000 cm^{-1} range. The transmission spectra of the films were measured by an ultraviolet-visible spectrophotometer (Shimadzu, UV-1800) with a wavelength range 200 nm - 1100 nm and the optical band gap was measured from the transmission spectra. The morphology of particles was investigated using Scanning Electron Microscopy (Hitachi, JEOL-JSM 5800). The elemental analysis or chemical characterizations of the samples were done by taking the EDX of the samples (JEOL-JSM 5800 machine).

[III] RESULTS AND DISCUSSIONS

3.1 XRD Analysis

X-ray diffraction patterns were taken to examine the crystal structure of the synthesized nano zinc oxide particles. The reflections were obviously observed at 2θ angles around 31^0 (100), 34^0 (002), 36^0 (101), 47^0 (102) and 56^0 (110). All the diffraction peaks were in good agreement with the JCPDS file for ZnO (JCPDS 89–1397), which can be indexed to the hexagonal wurtzite structure of ZnO. The strong and sharp diffraction peaks indicated that the ZnO nanoparticles were well crystallized.

The average crystallite sizes of synthesized samples were calculated from the full width at half maximum (FWHM) of the peaks using Debye-Scherrer formula:

$$D = 0.9\lambda / \beta \cos \theta$$

where, D - crystallite size, λ - wavelength of CuKα radiation, β - corrected full width at half maximum (FWHM) of the diffraction peak, θ – Bragg's angle of the X-ray diffraction peak. The average crystalline size of synthesized nano particles was in the range of 15 - 25 nm and for commercial zinc oxide the range was 35 – 40 nm. Figure 1(a) and 1(b) shows XRD pattern of commercial and synthesized nano particles respectively.

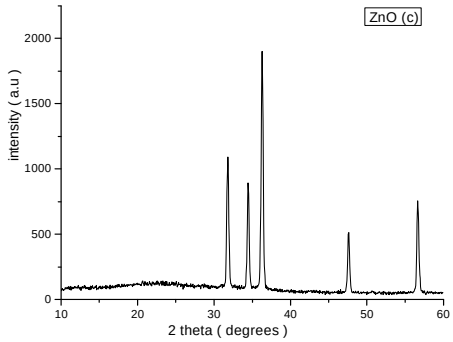

Fig: 1(a). XRD pattern of commercial ZnO

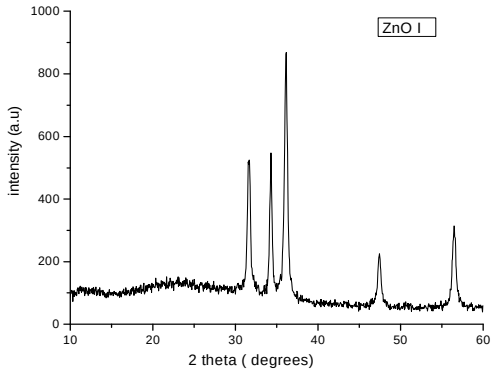

Fig: 1(b). XRD pattern of synthesized nano ZnO

3.2 FTIR analysis

The wide band between 400 cm^{-1} and 500 cm^{-1} indicated the presence of vibrational frequencies of Zn-O bond. For commercial and synthesized ZnO, an intense band centered around 3500 cm^{-1} and the other around 1600 cm^{-1} was assigned to O–H stretching and bending modes of water or alcohol respectively.

However, the prominent difference between the two kinds of powders was in the depth of the bands. For the synthesized nano powders, the peaks were much sharper than in the commercial ZnO suggesting that, the synthesized nano ZnO was crystalline in nature. Figure 2(a) and 2(b) showed FTIR spectra of commercial and synthesized nano ZnO respectively.

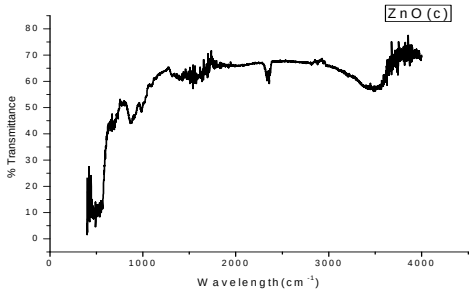

Fig: 2(a). FTIR spectrum of commercial ZnO

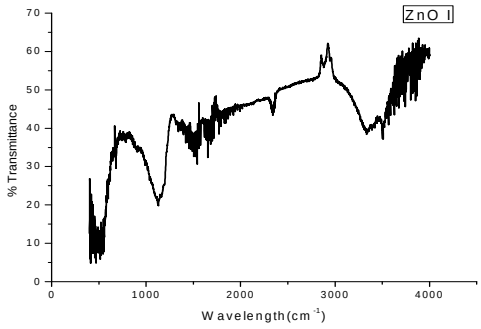

Fig: 2(b). FTIR spectrum of synthesized nano ZnO

3.3 UV-visible analysis

Figure 3 showed the UV-visible absorption spectra of ZnO nano particles suspended in deionized water. The spectra of ZnO nanoparticles were measured and the absorptions were observed in the wavelength range of 200-400 nm. Band gap energy of the nanoparticles was calculated from

$$E = hc / \lambda$$

where, E is Band gap energy, h is Planck's constant, c is velocity of light; λ is wavelength of absorption edge in reflectance spectra. The wavelength of 391 nm corresponds to the band gap energy of 3.17 eV for commercial ZnO. The absorbance at wavelength of 362 nm indicated a blue shift and showed band gap energy of 3.43 eV. These results clearly indicated the effect of gelatin on the particles size for the synthesized nano ZnO. Greater the band gap energy, smaller will be the particle size.

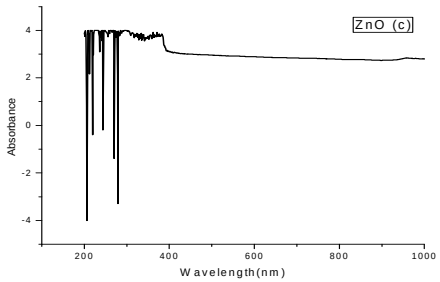

Fig: 3(a). UV- visible Spectra of commercial ZnO

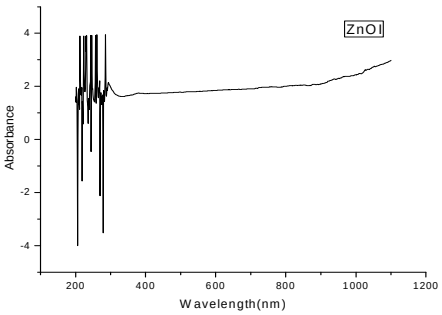

Fig: 3(b). UV- visible Spectra of synthesized nano ZnO

3.4 SEM Analysis

Scanning electron microscope is a very useful tool for studying morphology of nano powders. Figure 4(a) and 4(b) shows SEM pictures of commercial ZnO and synthesized ZnO nanoparticles respectively. It was clear from the images that surface morphology had been greatly affected. For commercial ZnO irregular spherical shaped particles were obtained. But for the synthesized nano ZnO using gelatin as precursor flower shaped particles were observed.

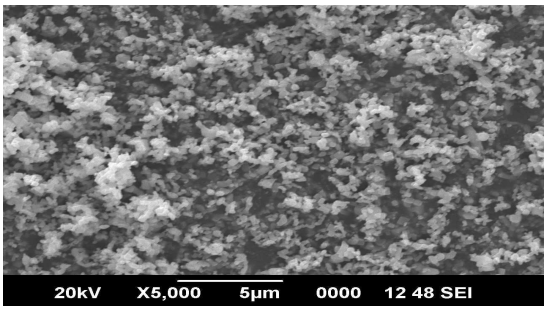

Fig: 4(a). SEM of commercial ZnO

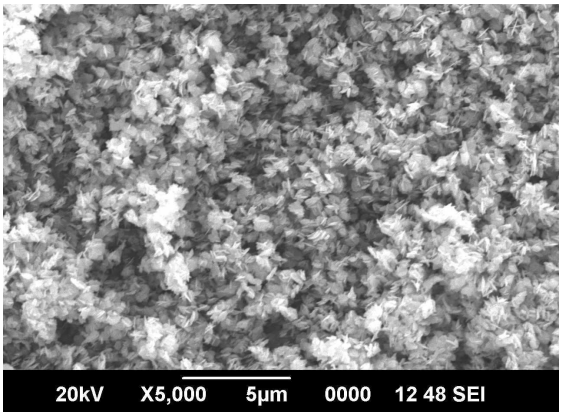

Fig: 4(b). SEM of synthesized nano ZnO

3.5 EDX Analysis

The energy dispersive X-ray spectra of the samples obtained from the EDX analysis for commercial and synthesized nano ZnO was shown in Figure 5(a) and 5(b) respectively. The results clearly showed that the sample prepared by the above route had pure ZnO with no other contaminants and the elemental composition was in good agreement with the commercial zinc oxide.

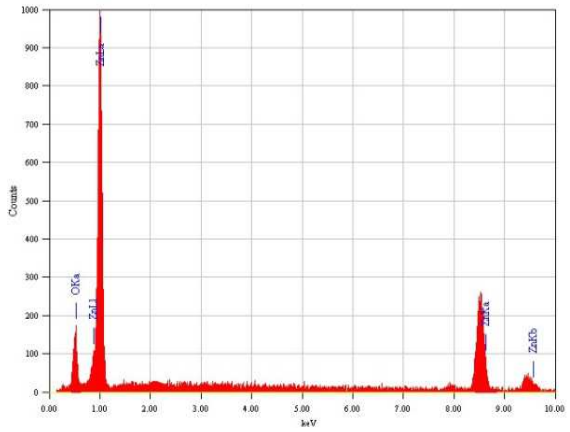

Fig: 5(a). EDX patterns of commercial ZnO

Element	Element %	Atomic %
O	5.55	19.36
Zn	94.45	80.64
Total	100	100

Table: 1. Elemental compositions of commercial ZnO

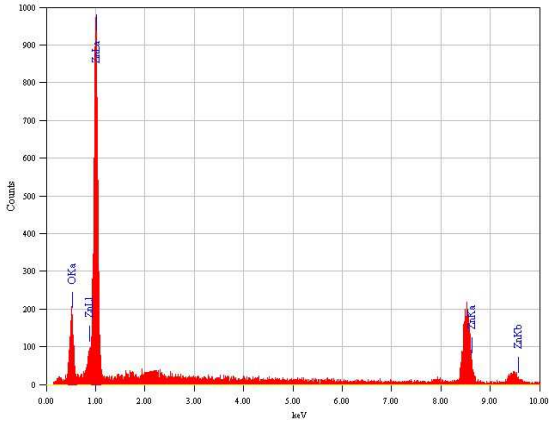

Fig: 5(b). EDX patterns of synthesized ZnO

Element	Element %	Atomic %
O	6.79	22.93
Zn	93.21	77.07
Total	100	100

Table: 2. Elemental compositions of synthesized ZnO

[IV] CONCLUSIONS

ZnO nanoparticles were prepared using a simple sol – gel method using gelatin as precursor. The XRD pattern revealed that the synthesized nano zinc oxide particles were crystalline in nature and had a hexagonal wurtzite structure. The average particle size for the synthesized nano ZnO was about 20 nm and for commercial ZnO, it was about 35 nm. FTIR analysis confirmed the formation of nano zinc oxide powder. UV-visible absorption peaks below 400 nm was also clearly observed which supported the formation of zinc oxide nano particles. The band gap energy of synthesized nano ZnO was increased which revealed the decrease in particle size. SEM images of nano ZnO showed that the morphology was changed with the use of the biopolymer, gelatin from irregular to flower shaped ZnO. EDX analyses clearly indicated that highly pure ZnO was formed .Zinc oxide powders obtained at the nano metric scale, may have superior properties as compared to the powders obtained in larger particle sizes and can be used in medical applications as a biomaterial.

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