Journal of Nanosciences: Current Research

Sarkar et al., J Nanosci Curr Res 2017, 2:1
DOI: 10.4172 /2572-0813.1000109

Research Article Open Access

Sol-gel Synthesis and Meticulous Characterization of Zinc Oxide Nanoparticles

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Received date: May 10, 2017; **Accepted date**: May 15, 2017; **Published date**: May 22, 2017

Abstract

This work presents and discusses the study of ZnO (zinc oxide) as nanoparticles and its idiosyncratic characteristics. Zinc oxide nanoparticles were synthesized employing a simple sol- gel method, with zinc chloride, zinc nitrate and sodium hydroxide as starting materials at room temperature. The synthesized ZnO nanoparticles were then characterized by X-ray diffraction (XRD), Scanning electron microscopy (SEM), Transmission electron microscope (TEM) and UV-Visible spectroscopy. SEM and TEM images reveal hexagonal morphology of ZnO obtained, with average crystalline size. This was determined from the full width at half maximum of XRD peaks by using Debye-Scherrer's Formula. Moreover, interpretation through UV-Visible absorption spectra supported a high absorption confirming its transcendent electrical and optoelectronic properties. It was further mathematically showed that ZnO nanoparticles can be efficiently utilized as additives in base lubricants to diminish abrasion and wear, enhancing tribological properties.

Keywords: Nanoparticles; ZnO nanoparticles; Hexagonal morphology; Additive; Optoelectronic

Introduction

Nanotechnology is a branch of science which studies fabrication and designing with immense augmentation of nanostructural materials. It is a discipline of matter in size regime of nanometers. In nanolevel, material exhibits unique features with variation in physio-chemical attributes [1-11]. Between year 1997 and 2005, investment in nanotechnology research and development by governments around the world soared from $432 million to about $4.1 billion, and corresponding industry investment exceeded that of governments by 2005 [12-15]. There are diverse sorts of nanoparticles reported in the scope of entire nano literature, e.g., metal nanoparticles, metal oxide nanoparticles, and polymer nanoparticles. Among all these, metal oxide nanoparticles stand out as one of the most versatile materials, owing to their diverse characteristics and functionalities is Zinc oxide nanoparticles [1,2,13,14]. The investigation on ZnO is catching fire right from the beginning of 1950 to recently, with some reviews on electrical [16], mechanical [1] and optical properties [16] like N-type conductivity, absorption spectra and electroluminescence decay parameter. ZnO has now become one of most studied material in the last seven years as it presents very interesting properties in nano range synthesis. We recently, carried and studied the synthesis ZnO nanoparticles along with characterization through XRD, SEM, TEM and UV-Visible spectroscopy. We further studied the influence of ZnO as additives in base oil and as effective semiconductor.

Experimental Details

Materials

Zinc chloride (ZnCl, 99%, Sigma Aldrich, Mumbai, India) Zinc nitrate (Zn(NO3)2, 99%, Merk and Co., Mumbai, India) and Sodium hydroxide (NaOH, 99%, Sigma Aldrich, Mumbai, India were used in the synthesized experiments. All the chemicals used were of analytical reagent grade obtained from Merck, India. Deionised water (18.2 MΩ.cm), obtained from a Milli-Q water purification system, is used throughout the experiment.

Synthesis of zinc oxide (ZnO)

In a typical synthesis procedure, ZnO (Zinc Oxide) nanoparticles were prepared by sol-gel method by mixing 0.5 M Zinc chloride, and 0.5 M Zinc nitrate. To this was added 2 M sodium hydroxide solutions slowly, drop wise with vigorous stirring which was continued for 45 min. The resulting white gel (precipitate) obtained was filtered, and washed thoroughly with deionised water for 3 to 4 times. After washing, the gel was allowed to dry at 100°C for 10 hours on hot plate in BP110 Laboratory Grade Microwave. This caused Zinc hydroxide (ZnOH) to decompose into Zinc Oxide (ZnO). The obtained product was calcined at 400°C for 5 hours in a muffle furnace (C-601 version), to remove volatile impurity, which was later then grind to fine powder using a gate mortar for 15 hrs to obtain the desired ZnO nanoparticles.

Reactions

$$ZnCl_2 + Zn(NO_3)_2 + 2NaOH \rightarrow Zn(OH)_2 + 2HNO_3 + 2NaCl$$

$$Zn(OH)_2 \quad ZnO + H_2O$$

$$ZnO \xrightarrow{400°C} ZnO\ (calcined)$$

Results and Discussion

X-Ray diffraction spectroscopy analysis

The XRD patterns of the prepared sample is shown in Figure 1. The characterization was carried out using Siemens D500 X-ray Powder Diffraction (XRD) System. The diffraction peaks of all samples exhibited a ZnO hexagonal wurtzite structure (P63mc structure) with high quality crystallinity in good agreement with JCPDS standard number of 36-1451 (Table 1). Shows the average crystalline size of the sample using Debye –Scherrer's equation (Equation 1) and using the full-width at half maximum of (100), (002) and (101) of the X-ray diffraction peaks.

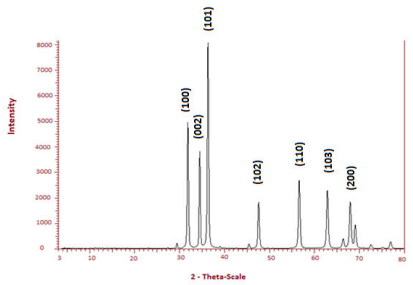

Figure 1: X Ray diffraction pattern of ZnO nanoparticles.

$$D = \frac{0.9\lambda}{\beta\cos\theta} - (Equation\ 1)$$

Where D is the crystallite size (nm), λ is the wavelength of incident X-ray (nm), β is the full width at half maximum (FWHM) in radians and θ is the diffraction angle (Half Bragg angle) in degrees. In Figure 1 the diffraction line (0 0 2) is narrower than the line (1 0 1), and (1 0 1) is narrower than the line (1 0 0) this indicated an asymmetry in the crystallite shape. The lattice parameters of the crystalline structure was estimated from the following relation (Equation 2) and calculated results are shown in Table 1.

$$\frac{1}{d_{hkl}^2} = \frac{4}{3}\left[\frac{h^2+hk+k^2}{a^2}\right] + \frac{l^2}{c^2} - (Equation\ 2)$$

Where *dhkl* is the lattice spacing of the (hkl) plane and a and c are the lattice parameters. From the Table 1 it also confirms the porosity of ZnO nanoparticles since the Bulk density is much lower than X-ray density [8].

SEM (Scanning Electron Microscopy)

The synthesized nano ZnO particles where characterized using Scanning electron microscope (Philips XL 30 ESEM scanning electron microscope), and its morphology was inspected. It demonstrates clearly the formation of spherical ZnO nanoparticles. The subservient ZnO particles exhibiting size of 1 μm, as observed by SEM images, inhere primary ZnO nanocrystallites having size of about 20 μm was estimated by line intersecting method. The primary nanocrystallites are combined to form a larger particle (secondary) by the following two routes [16]: (1) Fusion of one primary crystallite into another. (2) Aggregation of the primary crystallite. The first mechanism gives large crystallite size of micrometer scale. The second route results a bigger particle consisting of primary subunits with less porosity. Nucleation and growth rate increases with increase in annealing temperature. In the present work it appears that the aggregation is the dominant mechanism which occurred during the crystallization of gel-network leading to macroscopic ZnO particles.

TEM (Transmission Electron Microscopy)

In order to study deeply the shape and crystallinity of ZnO nanoparticles, prepared in sodium hydroxide and de-ionised water and to further confirm the XRD patterns, high resolution TEM was performed. Figure 2 shows the TEM images and selected area electron diffraction patterns of ZnO nanoparticles annealed at 400oC. This image reveals that the product consist of hexagonal particles with the average size of 21-26 nm which is in close agreement with that estimated by Scherer formula based on the XRD pattern. From the Figure 3 the selected area electron diffraction(SAED) shows the crystalline structure and it indicates that the synthesized ZnO nano particles are not single crystal, rather are the aggregates of several singla crystals.

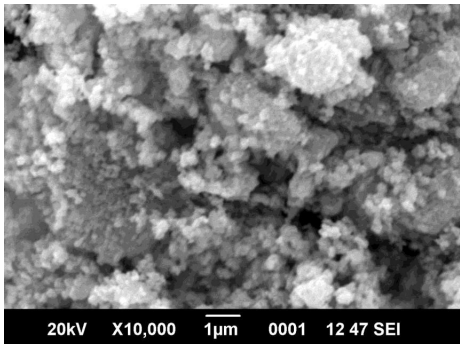

Figure 2: SEM characterization of ZnO nanoparticles confirming circular morphology and presence of overlapped nanoparticles.

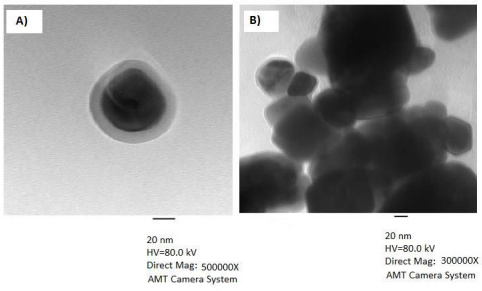

Figure 3: TEM images of ZnO nanoparticles showing regular and hexagonal morphology at 400°C.

UV-visible spectroscopy

In order to explore the optical properties of calcined ZnO nanoparticles, the optical absorption spectrum was taken using a Beckman DU640 UV/Visible spectrophotometer. The considerable

high absorbance attributes towards smaller size of the sample which in turn shows less Rayleigh scattering. Rayleigh scattering (RS) intensities from ZnO nanoparticles arise from electric–dipole and electric–quadrupole plasmon resonances at the emitted wavelength [16,17].

Considerable conclusions associated with ZnO nanoparticles can be made by studying its optical properties using UV –visible spectrophotometer [3,8,9]. The sample showed absorbance between 300 and 500 nm. The behavior obtained in UV/Vis spectrum can occur for variety of reasons, such as inner electrical fields within the crystal, strain caused by imperfection causing deformation of lattice and due to photons carrying inelastic scattering of charge. By considering the wavelength equivalent to the strong cutoff region in the UV/Vis Absorption measurement graph for ZnO (Figure 4). The band energy gap of the sample was premeditated (Equation 3) [8,9].

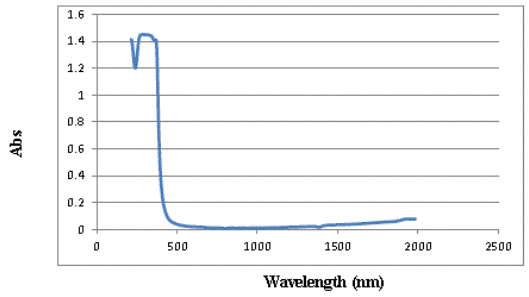

Figure 4: UV- visible spectrum of ZnO nanoparticles.

Calculations

$E = \frac{h*c}{\lambda} - (Equation\ 3)$here;

E: $Band\ gap\ energy$, h: $Plank's\ constant = 6.626*10^{(-34)}$,

c : $velocity\ of\ light = 3*10^{8} m/s$

$Now,\ \lambda =\ \ (from\ graph\ Figure\ 2) \simeq 425*10^{(-9)} m$

$We\ get, E = 4.6772*10^{(-19)} J = 2.92eV$

Consequently, from above it can be inferred that ZnO is an exceedingly fine II-VI semiconductor compound. Single crystal exhibits directionally dependent optical properties owing to which it can be brought to bear for modulation of UV radiation. The contemporary example of it is the intended model of ZnO modulator with a contrast of 70:1 and execution speed of 100ps [18]. This band gap can further be augmented by associating effective doping techniques. Magnesium doped zinc oxide possesses a wide array of sensing spectra between (200-280) nm which makes it convenient to tune for UV-B and UV-C and can be made pertinent for numerous fields such as solar UV radiation monitoring, ultra high temperature flame detection etc. [18]. The most important factor responsible for a material to show a better optoelectronic property is the large binding energy, and this property is possessed by Zinc oxide having binding energy of 60 mev which could be attended to and above room temperature due to excitonic recombination [19]. Dye Sesitized Solar Cell (DSSC) is an optoelectronics device that converts light to electrical energy via charge separation in sensitizer dyes absorbed on a wide band gap semiconductor [20], thus it opens up a wide scope for the application of ZnO nanoparticles for utilizing solar energy.

Zinc oxide nanoparticles as additives in lubricants

Efficiency of machines can be added on by reduction in energy loss due to friction. Advances in tribology have lead to saving of 11% of total energy loss in major areas of power generation, transportation and industrial process.

Zinc oxide nanoparticles when employed as lubricant additives have significantly contributed towards better tribological properties [7,11] by exhibiting good attrition and wear reduction features [5].

A very important feature confederated with effective lubricants is the presence of high homogeneity. This is because homogeneity is a direct consequence of the colloidal stability of the lubricant which assists towards reducing erosion between shearing surface [5]. Colloidal stability inversely depends on the deposition rate of the additives at the shearing surface. Hence low deposition rate plays a significant role in imparting better tribological characteristics.

The time taken for ZnO nanoparticles to deposit is higher than usual micrometer (μm) sized particles that are used as additives.This can be interpreted through theoretical analysis using Stokes Law.

Conceding to the XRD and SEM analysis the morphology of ZnO nanoparticles is spherical which serves as an essential facet for the application of Stoke's Law.

$According\ to\ Stoke's\ Law$;

$$v_d = \frac{2gr^2\left(\rho_{np} - \rho_f\right)}{9\mu_f} - \ (Equation\ 4)$$

$Where$; v_d : $velocity\ of\ deposition$

μ_f: $Dynamic\ viscosity\ of\ fluid$

g: $acceleration\ due\ to\ gravity$

r: $Size\ of\ the\ particle$

ρ_{np}: $Density\ of\ the\ nanoparticle$

ρ_f : $Density\ of\ the\ fluid$

$Also;$

$v_d\ \alpha\ \frac{1}{t}(Equation\ 5)\ i.e.,\ velocity\ is\ inversely$

$proportional\ to\ the\ time\ of\ deposition\ (Equation 2)$.

$From\ the\ above\ two\ equations\ (Equation\ 1\ and\ 2\ )$
$it\ was\ concluded\ that;$

$Time\ of\ deposition\ of\ the\ additives\ is\ inversely\ proportional$
$to\ the\ square\ of\ the\ particle\ size\ i.e\ \ (\ Equation\ 4)$

$t\alpha 1/r^2 - \ (Equation\ 6)$

From the above theoretical evaluation (Equations 1, 2 and 3) it can be consummated that for a given base lubricant (fluid) as size of the additive decreases 10 folds i.e., from μm to nm the deposition time increases 100 folds contributing towards more colloidal stability hence better tribological limits are attained.

The above hence illustrates that lubricant having ZnO nanoparticles as additives, which has an average size of 25 nm from XRD (Table 1).

involves much more homogeneity in lubricant than any other additives and hence diminishes the abrasion between the shearing surface.

Compound	a (A°)	c (A°)	v (A°3)	X-ray Density g/cm3	Bulk Density gm/cm3	Porosity %	Particle Size
ZnO	3.2449	5.203	47.4443	5.6986	1.75	69.2907	25 nm

Table 1: XRD chart.

Through experimental conclusions and setting it has been ascertained that lubricant with 0.5% ZnO nanoparticles showed lower deposition and had the best general tribological behavior, but an increase in concentration caused fast deposition which exacerbated the case [4].

Conclusion

The following conclusions can be drawn from the results presented above:

- SEM characterization confirmed the aggregation as the prevailing agency which ensued during the crystallization of gel-network contributing to celestial overlapping ZnO particles.
- TEM outcomes reveal that Zinc oxide nanoparticles displays hexagonal morphology confirming the crystalline wurtzite structures with space group P63mc.
- XRD analysis confirms formation of pure ZnO from sol- gel process with the diffraction peaks corresponding to ZnO hexagonal wurtzite structure. High quality crystallinity with lattice parameters a=3.2449() and c=5.2030() and affirmative porosity is ascertained.
- ZnO nanoparticles when employed as additives in lubricants shows diminution in depreciation and attrition under controlled concentr ation. Decrease in the deposition rate of the nano-additives contributed towards better tribological properties.
- UV-spectrometer evaluation confirmed that ZnO can be drawn on as excellent semiconducting composite as it possesses a promising band gap of 2.92 eV also permitting it to be applied in electrical and optical industries.

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