ZnO Nanoparticles Synthesized by a Novel Approach at Room Temperature and Antibacterial activity

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Abstract: Applications of metal oxide nanoparticles in research and health-related applications, metal oxide nanoparticles are increasingly being developed through cheaper and more user-friendly approaches. We have formulated a simple route to synthesize zinc oxide nanoparticles (ZNPs) by a hydrothermal method at near-room temperatures. The results are analyzed by X-ray diffraction, transmission electron microscopy, FTIR and ultraviolet-visible absorption spectroscopy. Highly significant antimicrobial activity against medically important Gram-positive (S.aureus) and Gram-negative (Escherichia coli) bacteria by these ZNPs, we can postulate that our fabricated ZNPs may be useful as antimicrobial agents in antiseptic creams and lotions for the treatment of skin diseases.

Index Terms: Nanoparticles, hydrothermal method, antimicrobial activity etc.

I. Introduction

ZnO Semiconductors with magnitude in the nanometer region are important because their electrical, optical and chemical properties can be tuned by varying the size of particles. Optical properties are of great importance for relevance in optoelectronics, photovoltaics and biological sensing. Various chemical synthetic methods have been developed to prepare such nanoparticles. Zinc Oxide (ZnO) is an exclusive material with a direct band gap (3.37eV) and large exciton binding energy of 60meV. It has been normally used in near-UV emission, gas sensors, transparent conductor and piezoelectric application. Most of the ZnO crystals have been synthesized by conventional high temperature solid state method which is energy consuming and difficult to manage the particle properties as well as similar methods that are used for the fabrication of ZNPs include the sol–gel method, facile hydrothermal method, solution method, electric current heating method; solvothermal method, self-propagating high-temperature synthesis method, spontaneous nucleation method, spray pyrolysis, gas-phase reaction method, laser ablation method and thermal evaporation. Hydrothermal technique is a promising substitute synthetic method because of the low process temperature and very easy to control the particle size. The hydrothermal process have several advantage over other growth processes such as use of simple equipment, catalyst-free growth, low cost, large area uniform fabrication, environmental friendliness and less hazardous. The low down reaction temperatures create this method an gorgeous one for microelectronics and plastic electronics. This method has also been successfully employed to prepare nanoscale ZnO and other luminescent materials. The particle properties such as morphology and size can be controlled via the hydrothermal process by adjusting the reaction temperature, time and concentration of precursors. In this consider, several reports are obtainable that are neither feasible nor cost effective. The hydrothermal preparation of ZnO/Au and ZnO/Ag nanoparticles at 80°C for 5 hours and flower-like ZnO nanorods is masintained at more than 120°C, for several hours, at basic medium chrysanthemum-like ZnO nanorods are formed in the presence of sodium dodecyl sulfate at 120°C for 24 hours and 10 hours and the preparation of flower-like ZnO microstructures was conducted via sonochemical treatment for 1 hour. The present study focuses on the hydrothermal synthesis of ZnO nanopowders. The hydrothermal synthesis of ZnO powders has four advantages (1) powders with nanometer-size can be obtained by this method (2) the reaction is carried out under moderate situations (3) powders with different morphologies by adjusting the reaction situation and (4) the as-prepared powders have different properties from that of the bulk. In this present work, we have reported the synthesis of ZnO nanoparticles using hydrothermal method and characterized its structural, morphological properties. Additionally we have performed the electrochemical activity of the synthesized ZnO.
II. Materials and Experimental Methods:

**Materials:**
Zinc acetate dihydrate Zn(CH₃COO)₂·2H₂O and sodium hydroxide pellets (NaOH) were purchased from Sigma- Aldrich and were all used without further purification and Double distilled water was used as the solvent.

**Synthesis of Zinc Oxide Nanoparticles:** 5g of Zn(CH₃COO)₂·2H₂O and 10ml (5M) of NaOH were dissolved into 100 mL of distilled water. After the mixture are magnetically stirred for 4h at room temperature and then slowly being cooled to room temperature, obtained powders were collected by centrifugation and washed with distilled water and absolute ethanol. The powders were finally dried at 60 °C for 12 h.

**Optical Properties:** Ultraviolet-visible spectroscopy (UV-Vis) refers to absorption spectroscopy in the UV-Visible spectral region. That means it uses beam in the visible and adjacent (near-UV and near-infrared (NIR)) ranges. The absorption in the visible range openly affects the perceived colour of the chemicals involved. In this form of the electromagnetic spectrum generate by the electronic transitions. In this time uv-vis absorption spectra was taken using a (LABINDIA Uv- Visible 3000) spectrophotometer where the cuvette path length was set to 1.0 cm. The particles were dissolved in methanol, and solution was placed in a quarts cuvettes.

**pH Analysis**
The pH was determined by using Digital pH meter Systronics. The pH of the reduced solution with Nanoparticle synthesized was found to be basic. After reduction the pH of sample was found to increase and move towards the basic range.

**Structure and morphology:**

**Powder X-Ray Diffraction:** XRD patterns of the powdered samples were obtained on a Phillips X’Pert materials research diffractometer using secondary monochromated Cu Kα radiation (λ = 1.54060 Å°) at 40 Kβ/50mA. Samples were supported on a glass slide. Measurements were taken using a glancing angle of incidence detector at an angle of 2 for 2θ values over 10–80 in steps of 0.05 with a scan speed of 0.012.

**TEM analysis:** The TEM measurement was done with JEOL model 1200Ex instrument operated at an accelerating voltage of 80kV. Samples were prepared by placing 3-4 drops of the well dispersed Zn nanoparticles samples on a 300-mesh, carbon coated Cu grid (EM sciences) and allowing the liquid to evaporate in air. For Zn nanoparticles the particle size distribution was based on 30 randomly selected particles. The TEM image was taken with very high resolution and MATLAB analysis gives the pixel depth of the image equal to 24bits and the image format as JPEG. The TEM Images have been taken from National Chemical Laboratory, Pune, India.

**Fourier Transform Infrared (FTIR) Spectroscopy:** FTIR analysis range 4000 to 400 cm⁻¹ using Bruker -Tensor Spectrum in the diffuse reflectance mode at a resolution of 4cm⁻¹ in KBr pellets. The powder sample was placed on a sample holder and the spectrum was recorded.

III. Results and discussions

**Synthesis of silver nano particles:**

**Structural Characterization:**
XRD patterns of the ZnO nanoparticles prepared by hydrothermal method is shown in Figure 1, which indicates the ZnO has hexagonal wurtzite phase structure. The peak and relative intensities obtained for the ZnO competition with the reported JCPDS data and no other attribute peaks were observed other than ZnO. The x-ray diffraction information were recorded by using Cu Kα radiation (1.5406 Å°). The intensity data were collected over a 20 range of 20-80°. In addition, the peaks (100), (002), and (101) clearly indicate formation of pure wurtzite structure of ZnO. Therefore, the XRD pattern showed that samples were formed in single phase. The high intensity of (100) peak at 31° suggested the growth of ZNPs along the easy direction of crystallization. No other peaks related to impurities were detected in the XRD spectra, confirming the pure form of the synthesized ZNPs. The expected grain size of the ZnO nanoparticles was estimated with the help out of Scherrer equation using the diffraction intensity of (101) peak. x-ray diffraction studies confirmed that the synthesized materials were ZnO nanoparticles with wurtzite phase and all the diffraction peaks agreed. The mean grain size (D) of the particles was resolute from the XRD line broadening measurement via Scherrer equation.

\[ D = \frac{0.89\lambda}{(\beta \cos \theta)} \]

Where \( \lambda \) is the wavelength (Cu Kα), \( \beta \) is the full width at the half- maximum (FWHM) of the ZnO (101) line and \( \theta \) is the diffraction angle. A specific line broadening of the diffraction peaks is suggested that the synthesized materials are in nanometer series and the average grain size of ZnO is determined using Scherrer equation and it was found to be around 50 nm.
Figure 1. XRD pattern of ZnO nanoparticles

FT-IR spectrum of ZnO nanoparticles (Figure 2) showed significant absorption peaks at 3372 and 1577, 573 cm\(^{-1}\). The absorption band at 573 cm\(^{-1}\) was assigned to Zn-O stretching vibration. The weak band near 1577 cm\(^{-1}\) is assigned to H-O-H bending vibration mode were presented due to the adsorption of moisture, when FTIR sample disks were prepared in an open air atmosphere. These observations provided the evidence for the presence of hydration in the structure and intense broad band near 3372 cm\(^{-1}\) represents the hydrogen bonded O-H stretching vibration.

Figure 2. FT-IR spectrum of ZnO nanoparticles

Figure 3 shows the TEM image and equivalent selected-area electron diffraction (SAED) pattern of the ZnO nanoparticles synthesized at room temperature for 4h from 5M NaOH. TEM image confirms the formation of ZnO nanoparticles and it has an average size about 50 nm.

Figure 3 TEM Images of ZnO Nanoparticles

Size evolution of semiconducting nanoparticles become very essential to explore the properties of the materials. UV-Visible absorption spectroscopy is widely used technique to examine the optical properties of nano sized particles. The prepared zinc oxide white Crystalline powder was not soluble in water and almost in all organic solvents. ZnO nano particles UV-Visible spectra recorded by dispersed in methanol solution and sonicated for 5 to 10 min. Fig. 4 shows the absorption spectroscopy of the ZnO nanoparticles in the uv-spectral region. ZnO
exhibits a sharp band at 354 nm, which corresponds to the formation of ZnO nanoparticles. From the absorption spectrum of ZnO nanoparticles an approximate optical band gap can be derived using the following equation:

\[ \alpha E_p = K(E_p - E_g)^{1/2} \]

where, \( \alpha \) stands for the absorption coefficient, \( K \) is a constant, \( E_p \) is the discrete photo energy, and \( E_g \) is the band gap energy. A classical Tauc approach is further employed to estimate the \( E_g \) value of ZnO nanoparticles. A plot of \( (\alpha E_p)^2 \) vs. \( E_p \) is shown within the inset of Fig. 4. The extrapolated straight line of this plot meets the \( E_p \) axis. Which represents the absorption edge energy corresponds to the band gap (\( E_g \)) of the material. The band gap value of ZnO from the experimental data was calculated to be 3.12 eV, which is in good agreement with the value reported in the literature.

IV. Antibacterial Activity

The antibacterial property of the ZnO was evaluated against Gram-ve Escherichia coli and Gram +ve bacteria S. aureus using agar well diffusion method. In agar well diffusion method the ZnO nanoparticles showed significant antibacterial activity on bacterial strains Gram-ve and Gram +ve bacteria and Table 1 represents the comparative activities in terms of inhibition zone i.e 16 and 14, respectively. Study demonstrated that the ZnNPs show best antagonistic activity of Zinc nanoparticles against Escherichia coli.

<table>
<thead>
<tr>
<th>Organism</th>
<th>Zone of inhibition (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Escherichia coli</td>
<td>16</td>
</tr>
<tr>
<td>Staphylococcus aureus</td>
<td>14</td>
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Table: 1 Antagonistic activity of silver nanoparticles against bacteria

V. Conclusion

ZnO powder was successfully synthesized by novel approach at room temperature. The crystallite size calculated from the XRD is 50 nm is in good agreement with TEM results. FT-IR results confirm that the presence of Zn-O at 573 cm\(^{-1}\) as well as UV-visible Spectroscopy, the absorption spectrum was 354 nm show the blue shift compared to bulk ZnO. The antibacterial activity of ZnO Nanoparticles was confirmed by Zone of inhibition. As the diameter of the zone of inhibition is high, we can conclude that ZnO is also a very effective antibacterial agent. ZnO Nanoparticles are effective against both the bacteria which gives a conclusion that it is effective against gram +ve and gram –ve bacteria. Therefore we can conclude that ZnO Nanoparticles is a very effective antibacterial agent.

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