Simple Route to Prepare ZnO Nanoparticles and Study Their Optical Properties

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Abstract

A simple electrochemical method called electrolysis was used in this research to create zinc oxide (ZnO) nanoparticles from zinc and gold electrodes in diluted hydrochloric acid solution. The process of electrolysis was performed with a constant voltage of 5 V over 30 minutes in a mixture of HCl and water 12.5 % . The nanoparticles of ZnO were characterized by examining them with XRD, SEM, AFM and UV-Visible spectroscopy. Analysis of the particles showed that hexagonal wurtzite-phase ZnO nanoparticles have an average size between 30 and 50 nm. Approximately 3.3 band gap was estimated for ZnO and the given spectroscopic data revealed another band gap of 4.2 eV which is likely because the sample contained ultra-small particles of ZnO. The procedure uses electrolysis which provides benefits such as low temperatures, friendliness to the environment and scalability, so it has potential for use in photocatalysis, gas sensing and optoelectronics.

Keywords: Zinc oxide nanoparticles, Electrochemical synthesis, Optical properties.

1. Introduction

Zinc oxide is a main transition metal oxide that is known for its unique features. These features include a direct band gap of 3.37 eV, as well as a high exciton binding energy of 60 meV at room temperature [1]. Therefore, ZnO is commonly used in photocatalysis, gas sensing, ultra-violet detection, light-emitting diodes and solar cells [2-4]. Because of the quantum effect and its greater ratio of surface to volume, nanostructured ZnO works better than bulk ZnO [5].

Synthesis techniques for ZnO nanostructures have evolved and exist today as sol-gel, hydrothermal, precipitation, microwave-assisted and electrochemical methods [6-8]. Electrochemical deposition has several benefits due to the easy working methods, requiring low temperatures, being economical and offering exact control over the shape and composition of the nanostructures [9].

Classic electrochemical techniques incline to involve many steps and usually require expensive tools or reagents [10]. Besides, traditional techniques depend on chemicals that effect the environment and / or require a lot of energy. Achieving a route to make ZnO nanoparticles that is easy, eco-friendly and cost-effective is still an important challenge. In nanofabrication, the process of electrolysis is beneficial if factors like the distance between the electrodes, levels of electrolyte solution and applied voltage are properly controlled [11].

2. Experimental work

2.1 Materials

Experiments were performed attached metal plates from pure zinc and gold to electrodes to conduct their experiments. Merck provided the analytical-grade hydrochloric acid (HCl) that was used. Because the resistivity level of the deionized water was 18.2 MΩ cm, it showed that it was very pure. All chemicals in the experiments were kept as they were, without being purified further.

2.2 Synthesis of ZnO Nanoparticles

The nanoparticles of ZnO were produced by electrically driving a metal-to-metal reaction between zinc and gold in the absence of liquid electrolyte, as seen in Figure 1. The length, width and thickness of each electrode were 2.5 cm, 1 cm and 0.1 cm, respectively and they were set up with a 1.5 cm gap between them. Before carrying out electrolysis, the electrodes were cleaned in three different steps: The items were refined using fine sandpaper, immersed in ethanol and deionized water within an ultrasonic bath for 15 minutes, and ultimately air-dried.

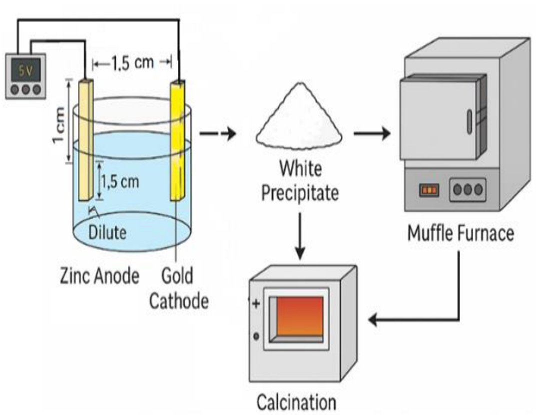

Figure 1: Synthesis of ZnO nanoparticles by electrolysis process.

A solution of electrolyte was made by the addition of one equivalent of concentrated hydrochloric acid to eight equivalents of deionized water to produce 12.5 % HCl solution. The electrolysis process was accumulated at 25 °C with applying a 5 V direct current for 30 minutes.

Followed by a centrifuging process at 6000 rpm for ten minutes to collect the precipitate. Then, the precipitate was rinsed repeatedly with water and ethanol, before drying overnight using oven at 80 °C. The dried powder was heated in a muffle furnace at 400 °C for two hours to produce ZnO nanostructures crystals.

2.3 Characterization

ZnO nanoparticle crystal diffraction was measured using SmartLab instrument, with 1.5406 Å Cu Kα radiation and reflections measured between 20° and 80°. A JEOL JSM-7600F scanning electron microscope (SEM) was utilised to record the appearance of resultant nanocrystals beside the surface structure and details of ZnO NPs shape. A Park Systems XE-100 AFM was used to examine the properties of the ZnO particles at a nanoscale. The resultant ZnO NPs at the nanoscale were located on the surface by scrutinizing the AFM images. Values for the optical character of the nanoparticles were measured with a Shimadzu UV-2600 spectrometer between 200 and 800 nanometres.

3. Results and Discussion

3.1 Mechanism of ZnO Formation

Electrode-electrolyte interactions are required for the electrochemical production of ZnO nanoparticles. Zinc metal shows different oxidation state (oxidation process) when electricity is sent between zinc electrode (the anode) and gold electrode (the cathode), resulting in the formation of zinc ions (Zn^{2+}) according to the following reaction:

$Zn \rightarrow Zn^{2+} + 2e^-$ (1)

At the cathode, water molecules are reduced to generate hydroxide ions (OH^-) and hydrogen gas:

$2H_2O + 2e^- \rightarrow H_2 + 2OH^-$ (2)

The generated Zn^{2+} and OH^- ions react in the electrolyte solution to form zinc hydroxide:

$Zn^{2+} + 2OH^- \rightarrow Zn(OH)_2$ (3)

The zinc hydroxide precipitate then undergoes dehydration during the calcination process to form ZnO nanoparticles:

$Zn(OH)_2 \rightarrow ZnO + H_2O$ (4)

Chloride ions from hydrochloric acid in the electrolyte solution change the appearance and size of ZnO nanoparticles by speeding up some crystal growth and affecting their surface energy [11].

3.2 Structural Analysis

Powder XRD pattern obtained from the cooled ZnO nanoparticles as presented in (figure 2). At 2θ angles of 34.4°, 47.5° and 62.9°, diffraction peaks are seen for the (002), (102) and (103) planes respectively.

The resulting spots were fit with the ZnO crystal structure called wurtzite (JCPDS card no. 36-1451) [12]. A lack of impurity peaks was found, proving that the synthesized ZnO nanoparticles had high purity.

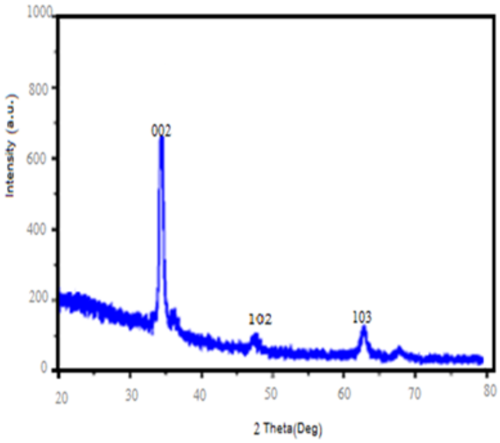

Figure 2: ZnO NSs powder XRD pattern.

The average size of crystallites was obtained using the Debye-Scherrer formula ($D = 0.9\lambda/(\beta\cdot\cos\theta)$)[13]. Where, D represents the size of the crystal, the wavelength of the X-ray is called λ (with a value of 1.5406 Å), the FWHM of the peak is noted β and θ is the Bragg angle. Using the most intense peak (002), the average size of the crystals calculated was roughly 32 nm. The angular dependence of this unit cell was defined by measuring a and c with the help of the expression "$d^2 = 3/4 \cdot [(h^2 + hk + k^2)/a^2 + l^2/c^2]$".
where d is the distance between the layer groups and (hkl) represent the Miller indices. By calculating lattice parameters, a = 3.249 Å and c = 5.206 Å which closely agree with the standard values for ZnO (a = 3.249 Å, c = 5.206 Å) [14].

3.3 Morphological Analysis

AFM reveals, seen in (figure 3) and (figure 4), that the glass surface has a regular layer of nanoparticles, with an average size of about 56 nm. Moderate surface roughness showed that the film was coating well.

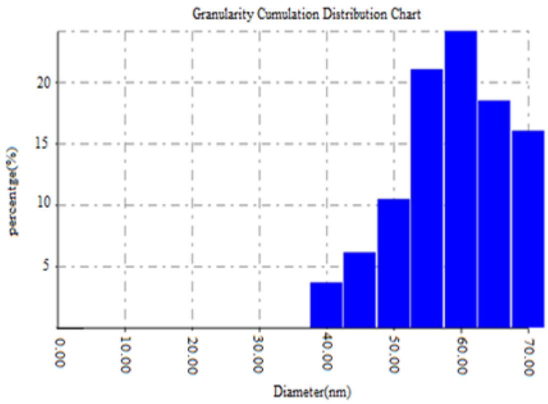

Figure 3: ZnO NSs Granularity Cumulation Distribution Chart.

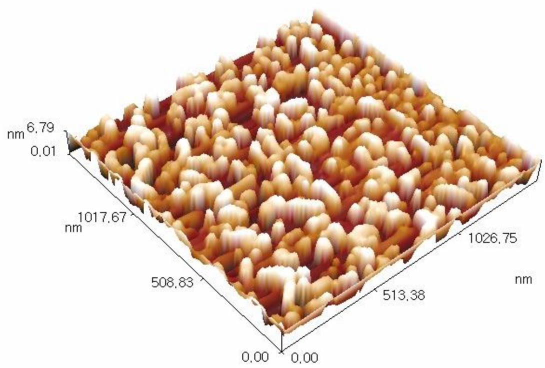

Figure 4: ZnO NSs AFM Image

The scanning electron microscopy was employed to examine the morphology and dimensions of the ZnO nanoparticles. The SEM image, seen in (figure 5), illustrates that ZnO nanoparticles are generally well spread throughout with some small regions of aggregation. A particle scale from 20 to 30 nm was calculated, agreeing with the magnification displayed and the visible scale bar.

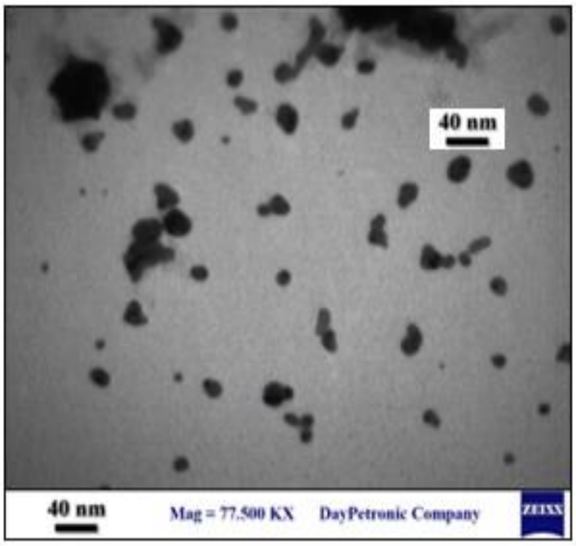

Figure 5: ZnO nanostructures by SEM imaging.

3.4 Optical Properties

Optical properties of the man-made ZnO nanoparticles were analysed by UV-visible and photoluminescence spectroscopy. The UV-visible spectrum seen in (Figure 6) is of ZnO nanoparticles suspended in ethanol. A clear absorption peak is seen at 325 nm and it is due to electron motions within the band gap of ZnO [15].

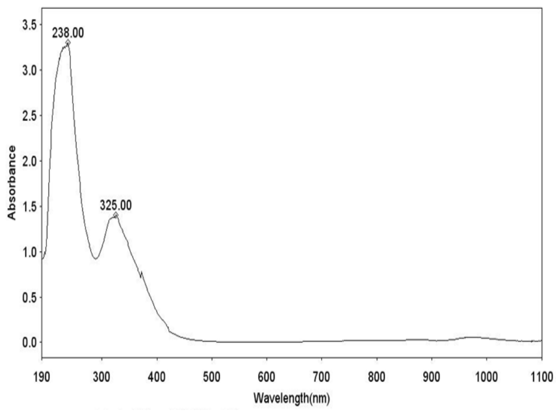

Figure 6: ZnO nanoparticle absorption spectrum.

The Tauc plot method enabled us to determine the optical band gap (Eg) of ZnO nanoparticles, employing the equation ($(\alpha h\nu)^2 = A(h\nu - Eg)$), The absorption occurs when we use α for absorption coefficient, hv stands for photon energy, A refers to a constant and Eg represents the optical band gap. The linear part of the curve is drawn up unto the energy scale in a Tauc plot to determine the optical band gap (Eg). The synthesized ZnO nanoparticles showed a main optical band gap of 3.3 eV as shown in (figure 7). Matching the documented band gap of bulk ZnO. A second band gap of approximately 4.2 eV was detected which may be due to the small ZnO nanoparticles present in the sample. Usually, this type of behaviour is due to the quantum confinement effect, during which a smaller particle size brings about a rise in the band gap energy. According to the analysis, the nanoparticles have a wide distribution size range which is consistent with prior results regarding ZnO nanostructures [16].

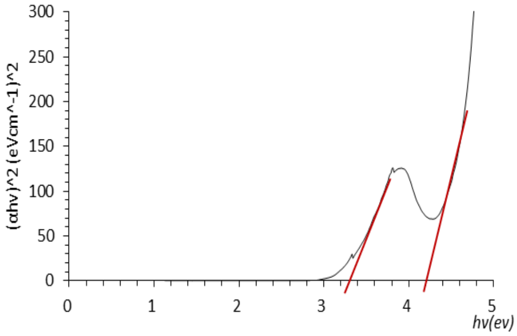

Figure 7: "(αhν) 2 versus optical energy gap of ZnO NPs".

4. Conclusion

An efficient and low-cost process was utilised to produce ZnO nanoparticles by using zinc and gold electrodes in a diluted hydrochloric acid solution at a normal room temperature. Structural and optical testing confirmed that ZnO nanoparticles formed with a hexagonal wurtzite structure, were roughly 30 to 50 nm in size, with a quasi-spherical morphology. The analysis of light transmission showed that the medium has different band gaps of 3.3 eV and 4.2 eV, probably indicating various transitions between energy levels or quantum clearance effects. These results indicate that the synthesized ZnO nanoparticles have promising uses in optoelectronics. A scalable and environmentally friendly process is applied to create ZnO nanomaterials useful for photocatalysis, gas sensing and similar areas.

5. References

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