ISSN No:-2456-2165

Zinc Oxide and Titanium Dioxide Nanoparticles Sizes Determined Utilizing Several Characterization Techniques

Fatma Ezzahra BENMOHAMED[1], Sakina Ibrahim Ali Abonaib[2], A.S. Hamid[3] and M.A. Abdalrasool[4]
[1,2] Department of Physics, Faculty of Science and Arts, Albaha University, Almakhwah, The Kingdom of Saudi Arabia
[3] Renewable and Alternative Energy Researches Centre - Al Neelain University, Khartoum, Sudan & Department of Laser & Renewable Energy, Faculty of Science & Technology, Al-Neelain University, Khartoum, Sudan
[4] Department of Physics, College of Science, Sudan University of Science and Technology & Department of Physics, Faculty of Science & Technology, Al-Neelain University, Khartoum, Sudan

Abstract:- In this work, zinc oxide and titanium dioxide nanoparticles were synthesized using the sol-gel method. UV-visible spectroscopy, scanning electron microscopy (SEM), and X-ray diffraction (XRD) were used to calculate the particle size of the synthesized samples. The ZnO had a primitive hexagonal structure with an average particle size of 86.72 nm, according to the XRD data, whereas the TiO_2 crystal structure was body-centered tetragonal with an average particle size of 94.72 nm. The average particle sizes for ZnO and TiO_2 were 85.49 nm and 89.61 nm, respectively, derived from SEM images using the histogram approach. The optical results demonstrate the absorbance ratio (A_{spr} /$A_{absorbance}$) at 300 nm for ZnO and 275 nm for TiO_2 in dependence of the absorbance for ZnO and TiO_2 nanoparticles at the surface plasma resonance peak. The particle sizes were 88.4nm and 97.3 nm for ZnO and TiO_2 respectively. The three methods that were used to determined particle size gave close values.

Keywords:- *Zinc Oxide, Titanium Dioxide, Surface Plasma Resonance, Particle Size, SEM, & XRD*

I. INTRODUCTION

Nanoscience is the study of systems with components on the scale of a billionth of a meter; one nanometer is approximately the length equivalent to 10 hydrogen or 5 silicon atoms aligned in a line [1]. The application of nanoscience toward developing new technologies is known as nanotechnology, which is defined as the engineering or manipulation of functional systems at the molecular scale [2,3]. Materials with individual grain or particle sizes between 1 and 100 nm, at least in one dimension, are referred to as nanomaterials. Because of their large surface-to-volume ratio and intermediate size between bulk and quantum materials, nanomaterials have unique electronic, optical, photonic, and catalytic properties that make them extremely advantageous for a wide range of application fields. [4,5]

The size of the particle has a significant effect on the properties of materials, especially mechanical properties, and is a valuable indicator of quality and performance. Electrical and magnetic properties are important characteristics of the metal for application in various fields. The study of nanoparticle metals shows different properties compared to bulk metals. Bulk metal has some properties, such as the ability to be formed, specific electrical conductivity, and thermal conductivity [6,7]. However, when a metal's size is lowered to the nanoscale, certain changes occur in its properties. These include becoming semiconductors, shifting from superparamagnetic to ferromagnetic, shifting the absorption (Plasmon Absorption), and using nanoscale metals in thermoelectric material applications [8-10]. Metal nanoparticles have varied electrical conductivity depending on their size. Based on this variation, the metal can be used for different applications by controlling its size. The magnetic properties also have a great dependence on the variation of the magnetic particle size. The change in particle size usually produces a more evenly distributed air gap within the core and results in changes in permeability and resistivity. [11-14] The volume fraction dependence of the thermal conductivity of nanofluids has been extensively studied, but there are few systematic studies related to the particle size dependence of the thermal conductivity. The particle size increases were attributed to increases in surface area, which leads to increases in thermal conductivity, as well as to other factors including the Brownian motion of particles, the ordering of liquid molecules near the surface of particles, and interfacial resistance at the fluid-particle interface [15-17]. In fact, there is not a single characterization technique to measure the particle size of nanoparticles accurately. The particle can be estimated using different methods, such as dynamic light scattering, image analysis, diffuse reference, and X-ray diffraction [18-20]. In this paper, the particle sizes of zinc oxide and titanium dioxide have been estimated by different methods.

ISSN No:-2456-2165

II. METHOD

In this experiment, sol-gel was used to synthesize zinc oxide and titanium dioxide nanoparticles. Titanium tetrachloride (TiCl4) and absolute ethanol in a 1:15 ratio was combined to create the base solution, which was stirred for an hour at 80°C. The resultant sol was then allowed to settle at room temperature for a full day before being dried for an hour at 300°C in an oven to produce titanium dioxide nanoparticles. Zinc oxide nanoparticles (ZnO-NPs) were prepared by dissolving 12.6g of zinc acetate dihydrate in 400 ml of double-distilled water while stirring constantly. After heating the mixture to 50°C, 600 ml of pure ethanol was gradually added while being stirred. After this, 6 ml of H2O2 (47%) was added dropwise and mixed using a stirrer to get a clear solution. This solution was kept for 24 hours, and the solution was dried at 80 °C for one hour to obtain white nano zinc oxide. Nano zinc oxide was washed several times with double-distilled water to remove the byproducts. After washing, the ZnO nanoparticles were dried at 80 °C in a hot air oven. The complete conversion of zinc oxide will occur during the drying. The particle size of the obtained materials was estimated using a scanning electron microscope (SEM), XRD powder diffraction, and a UV-VIS spectrometer.

III. RESULTS & DISCUSSION

After the synthesis of zinc oxide and titanium dioxide nanoparticles, particle size was investigated, as shown in the results below:

A. X-ray Diffraction (XRD) Results

In nanoparticle research, X-ray diffraction is thought to be the main characterization technique for obtaining crucial properties, including crystal structure and crystallite size. The random orientation of crystals in nanocrystalline materials results in a broadening of diffraction peaks since there are no total constructive and destructive X-ray interferences inside a finite-sized lattice [21]. The Debye-Scherrer's formula is the most widely used method for estimating the particle size from the full width at half maximum (FWHM) of a diffraction peak broadening. Where d is the particle size in nm, λ is the X-ray wavelength (λ=1.5405950595 Å), β is the full width at half maximum (FWHM) of the peak in radian, θ is the X-rays incident angle degree, and K is the Scherrer constant that is close unity (K =2√((ln 2)⁄π) [22].

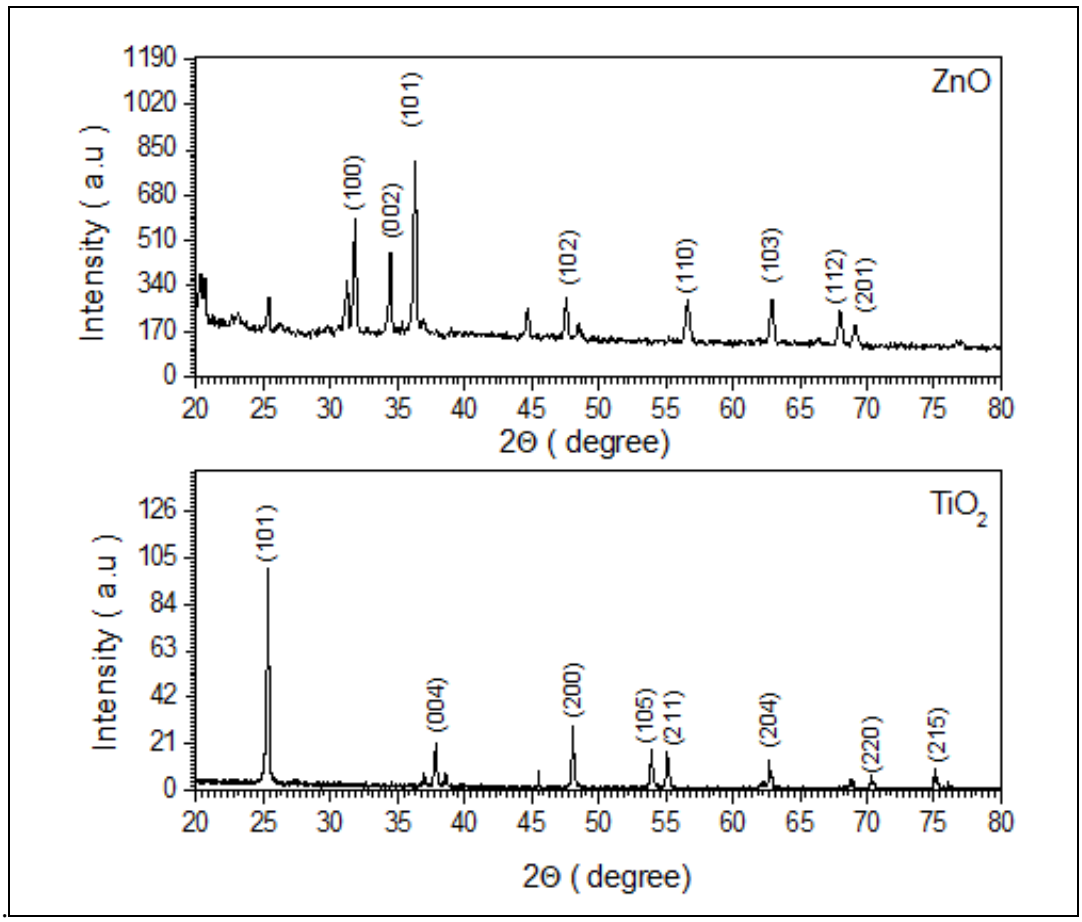

Fig. 1: XRD Pattern of (ZnO and TiO2) nanoparticles

The crystal structure of zinc oxide and titanium dioxide samples was performed using XRD at room temperature using a Philips PW1700 X-ray diffractometer (operated at 40 kV and current of 30 mA), and samples were scanned between 20°C and 80°C at a scanning speed of 0.06°C/s using Cu Kα radiation with λ = 1.5418Å

ISSN No:-2456-2165

Table 1: Crystal Planes and Particle Size Details from the XRD Analysis of (Zno And Tio_2) Nanoparticles Synthesized Using Sol-Gel Method

ZnO nanoparticles				***TiO_2 nanoparticles***			
Peak Position 2θ(degree)	***(FWHM) (β(Radians))***	***Crystallite size (D(nm))***	***Average (D(nm))***	***Peak Position 2θ(degree)***	***(FWHM) (β(Radians))***	***Crystallite size (D(nm))***	***Average (D(nm))***
31.8	0.171	84.4	86.72	25.3	0.171	83.3	94.72
34.5	0.200	72.9		37.8	0.200	73.7	
36.4	0.200	73.6		48.1	0.172	88.8	
47.6	0.200	76.1		53.9	0.172	90.8	
62.9	0.257	63.3		55.1	0.172	91.8	
69.2	0.114	147.7		62.5	0.200	81.4	
				75.2	0.114	153.3	

From the XRD analysis of ZnO and TiO_2 nanoparticles, the crystal planes were indexed as shown in Figure 1. The results display that ZnO nanoparticles have a primitive hexagonal crystal structure [23-24], while TiO_2 nanoparticles have a body-centered hexagonal crystal structure in the anatase form [25-26], which corresponds to the lattice planes (hkl) labeled as (100), (002), (101), (102), (110), (103) (112), and (201) respectively for ZnO and (101), (004), (200), (105), (211), (204), and (215) for TiO_2, respectively, as shown in Fig-1. The average particle size was determined to be around 86.72 nm for ZnO and 94.72 nm for TiO_2 (table 1).

B. Scanning Electron Microscope (SEM) Results

Scanning electron microscopy is a powerful imaging technique that enables high-distinguishability imaging and analysis of materials' surface morphology, structure, and composition. The morphology and composition of nanomaterials play a decisive role in the overall properties of materials, while SEM has tremendous advantages in investigating the microscopic morphology of materials and is indispensable, especially in materials analysis and preparation [19,28]. The images obtained from SEM were processed using an open-source Java-based framework known as ImageJ software to construct the computer vision methodology. ImageJ offers several tools for image enhancement, segmentation, and feature extraction, including scripting capabilities that ease the analysis of microscopic images. OriginPro 9 software was used to generate histograms from data extracted from images through ImageJ.

Figure 2 shows SEM images of ZnO and TiO_2 nanoparticles and their respective size distributions. The average particle size and distribution are statistically measured by using the histogram method. The particle size distribution histograms show that ZnO and TiO_2 nanoparticles were inhomogeneous, with average particle sizes of 85.49 nm for ZnO and 89.61 nm for TiO_2.

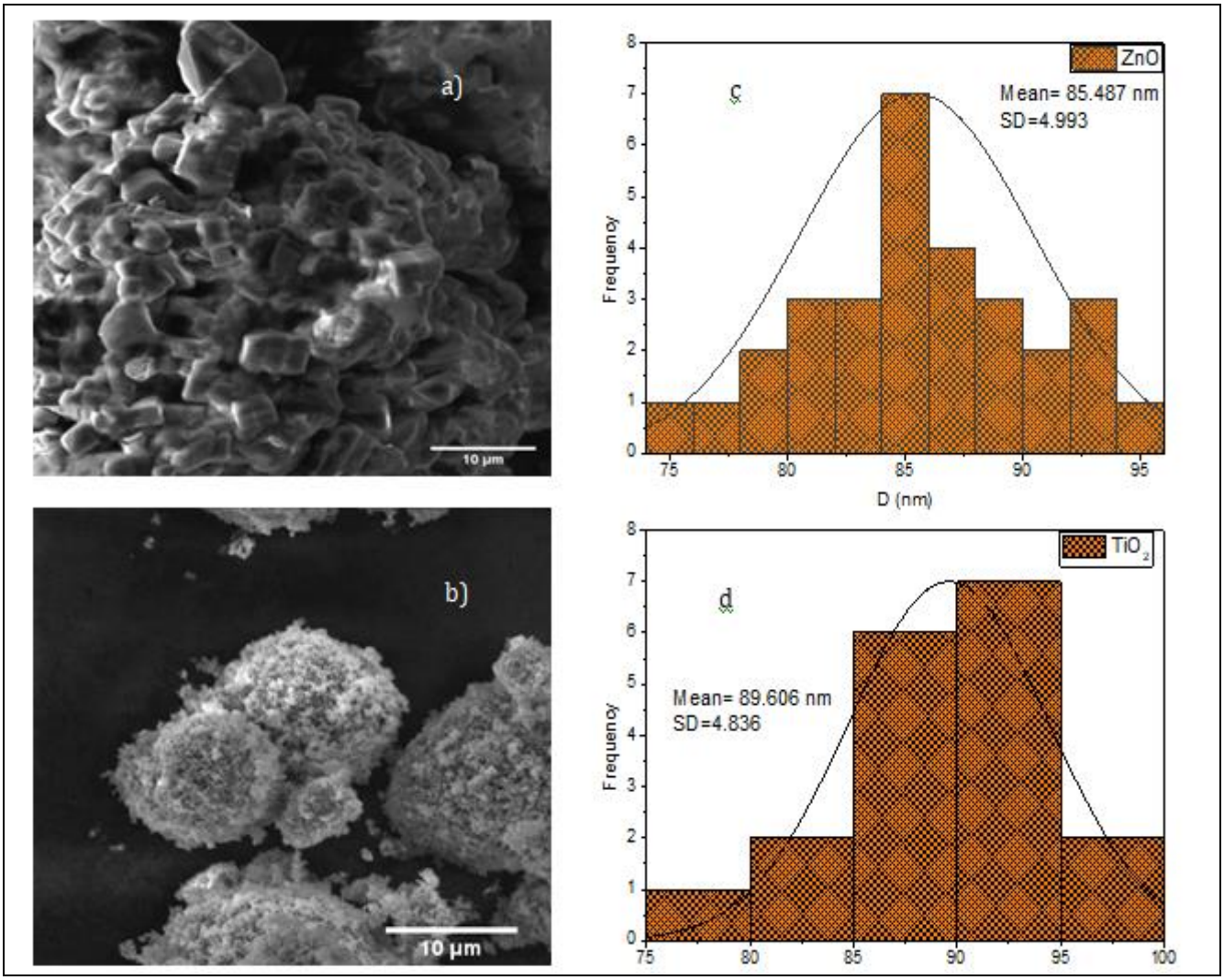

Fig. 2: SEM images (a, b) and particles size distribution (c, d) of (ZnO and TiO_2) nanoparticles

C. The Optical Method Results

The dependence of the optical properties of nanoparticles on particle size and wavelength was analyzed using multipole scattering theory. Localized surface plasmons are charge density oscillations confined to metallic nanoparticles. Excitation of localized surface plasmons by an electromagnetic field at an incident wavelength where resonance occurs results in strong light scattering and an enhancement of the local electromagnetic fields. According to the quasi-static approximation for small particles, the surface plasmon resonance peak occurs when the particle's polarizabi2lity is maximized [28,29].

The experimental results for the ZnO and TiO_2 nanoparticles predicted particle sizes using the optical technique are displayed in Fig. (3). Figure 3-A displays both samples' absorbance in the range of 190-450 nm. It is noted that both samples have the same peak absorbance value, 1.02 (a.u.) at 235 nm for ZnO and 205 nm for TiO_2 (in the UV area). The ZnO sample's maximum reflection value was 0.2055 (a.u). at 300 nm wavelength, whereas the TiO_2 sample had the same value of reflection at 275 nm, as indicated in fig (3-B). Both samples' reflections fell within the same absorbance range.

The ratio of absorbance for ZnO and TiO_2 nanoparticles at the surface plasma resonance peak to the absorbance (A_{spr} / $A_{absorbance}$) at (300 nm for ZnO and 275 nm for TiO_2) in dependence of the logarithm of the particles size as show in fig (3-C), in fig (3-D), the ratio (Aspr / A300) equal 0.99995 for ZnO and (A_{spr} / A_{275}) equal 0.9972 for TiO_2 can be used to calculate the particles size (in nanometers) as following equation

$$d = exp\left(B_1 \frac{A_{spr}}{A_{Absorbace}} - B_2\right)$$

Where B_1 is the inverse of the slope (m) of the linear fit in Fig (3-D) and B_2 equal B_0/m where B_0 is the intercept [30]. From fig (3-D) the slope of linear fit (m) for ZnO equal 0.3124 then B_1 equal 3.201 and the intercept B_0 equal (-0.410) then B_2 equal1.312 while for TiO_2 the slope of linear fit equal 0.31374 then B_1 equal 3.187 and the intercept B_0 equal (-0.507) then $_{B2}$ equal 1.623, according to above mention the particles size of ZnO and TiO_2 were 88.40 nm and 97.30 nm respectively.

ISSN No:-2456-2165

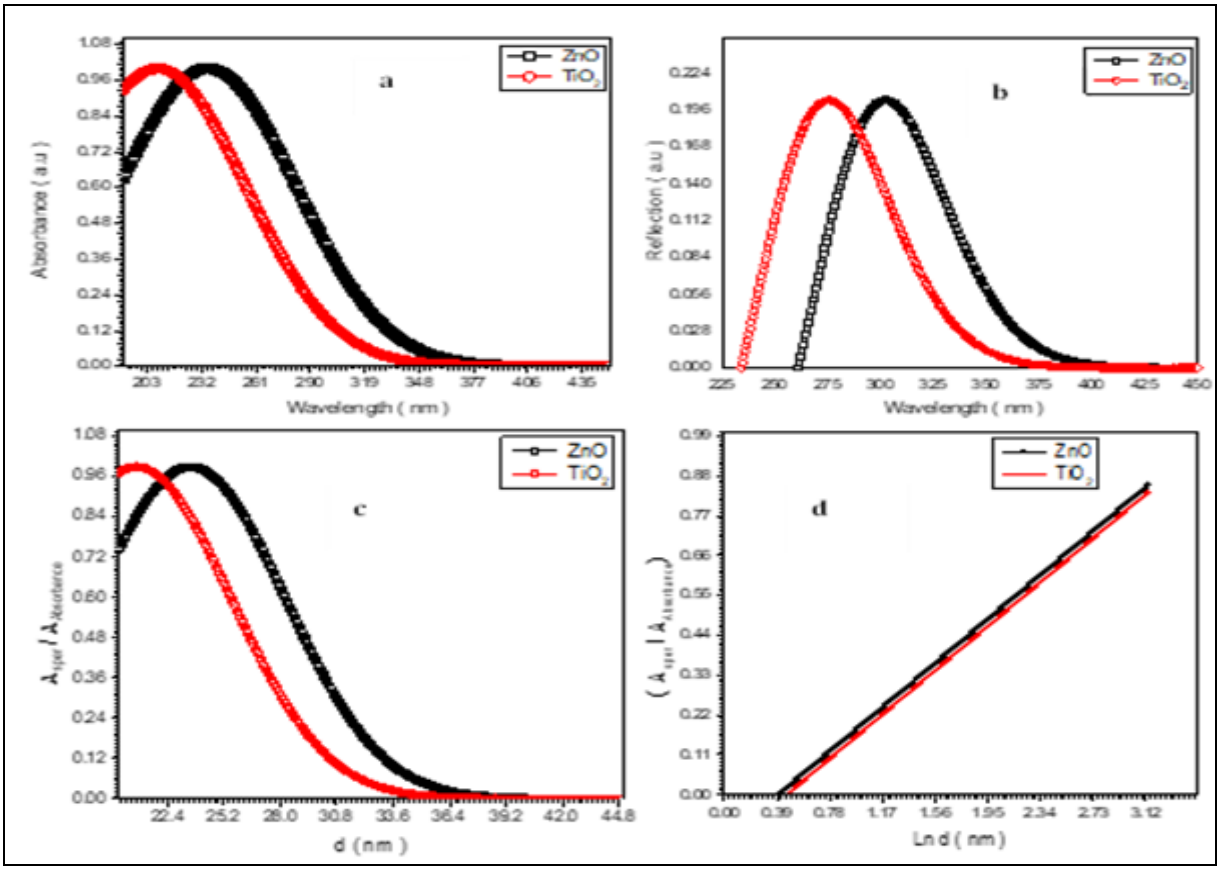

Fig. 3: Calculated particle size of ZnO and TiO_2 nanoparticles by optical method

Table 2: Particle Size Of ZnO And Tio2 Calculated By Different Methods

Samples	Particle Size (nm) Calculated Via		
	XRD	SEM	Optical Method
ZnO	86.72	85.49	88.40
TiO_2	94.72	89.61	97.30

It was observed that the three methods (XRD, SEM, and optical method) that were used to calculate the particle size of ZnO and TiO_2 gave close values for each sample; for ZnO, the values ranged from 85.487 nm by SEM to 88.40 nm by optical method, while for TiO_2, they ranged from 89.606 nm by SEM to 97.30 nm by optical method.

IV. CONCLUSIONS

The particle sizes of zinc oxide and titanium dioxide, which were synthesized through the sol-gel process, were estimated by SEM, XRD, and UV-VISS spectroscopy. For XRD, the grain size was estimated using the Debye-Scherrer formula, while it was calculated statistically by the histogram method; however, in the optical method, it was estimated by multipole scattering theory. All values obtained from the three methods are approximately close for each sample**.**

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