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Green Synthesis Of Zno Nps from Ginger Extract and the Potential Scavenging Activity

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Abstract

Zinc oxide nanoparticles (ZnO NPs) were produced using a simple green method, zinc citrate, and an aqueous solution of ginger extract. The aim of the study is tosynthesize zinc oxide nanoparticles in a simple green way, diagnose their properties، and measure their antioxidants against free radicals. These NPs were investigated using ultraviolet-visible reflectance spectroscopy (UV-VIS), photoluminescence (PL) spectroscopy, X-ray diffraction (XRD), field emission scanning electron microscopy (FE-SEM), and transmission electron microscopy (EDX), respectively. Results showed that the estimated bandgap is 3.51 eV and that the PL intensity has one peak in the ultraviolet region (450 nm) and another in the visible region (590 nm) of the spectrum depending on the geometric shape and size of the ZnO NPs. It was concluded from this study that zinc oxide nanoparticles are synthesized by green synthesis ginger extract, which is a safe and environmentally friendly method. And when these nanoparticles were diagnosed by XRD, EDX, and AFM, it was found that they are of high purity and have a particle size of approximately 23.69 nm. Moreover, the antioxidant activity of ZnO NPs was determined against DPPH, where the particles showed a free radical scavenging capacity of 63.1% at 360 µg/ml, which gives good evidence for the antioxidant activity of ZnO NPs.

Keywords: ZnO Nps, green synthesis, ginger, antioxidant.

1. Introduction

Zinc is a trace element required by many enzymes in the human body, such as carbonic anhydrase, carboxypeptidase, and alcohol dehydrogenase. It is significant for eukaryotes because it indicates several physiological roles [1]. Zinc in nature plays an important role in the metabolic processes of humans, animals, and plants. All living systems necessitate zinc exposure from the biosphere's natural background levels. Zinc oxide is a valuable nutritional additive that is widely used in cosmetic, pharmaceutical, and medical applications. Although zinc oxide dust and fumes are generally considered safe, inhaling them should be avoided [2]. Because of their unique properties such as surface area, size, shape, low toxicity, optical properties, high binding energy, and large bandgap, zinc oxide nanoparticles (ZnO NPs) have a wide range of potential applications ranging from electronics to cosmetics [3]. Because of their wide direct bandgap and high excitation energy of 3.37 eV and 60 meV, respectively, ZnO NPs are ideal materials for many devices, including semiconductor diodes, transistors, and UV photodetectors, These NPs are also excellent candidates for biomedical applications due to their overall bio-safety and variety of morphological shapes and sizes[4], Because of their excellent antibacterial performance, they are used in dental fillers and food packaging materials to prevent bacterial contamination. [5], Because of their ability to generate excess reactive oxygen species (ROS), release zinc ions, and induce cell apoptosis, anticancer and antibacterial fields are involved. Furthermore, zinc is well known for maintaining insulin's structural integrity. ZnO NPs have also been successfully developed for diabetic treatment [6].

Zinc oxide NPS are white powders nearly insoluble in water and have two known crystal structures namely hexagonal wurtzite crystals and zincblende structures Fig 1, with shapes ranging from spheres for zero-

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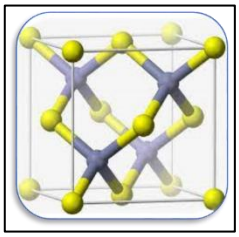
dimensional (0D) structures to dumbbells, nanorods, nanotubes, and needles for one-dimensional (1D) structures, disks and platelets for two-dimensional (2D) structures, and flowers, stars, and flakes for three-dimensional (3D) structures[7].



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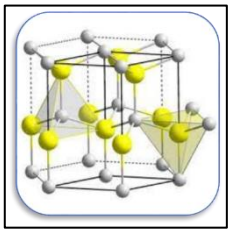

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Figure 1. Structure of ZnO NPs. A) Wurtzite structure of ZnO. B) Zincblende structure of ZnO.

Herein, zinc oxide NPs were synthesized by green methods using ginger plant extract, characterized by UV-VIS,XRD, EDX, AFM, PL, and SEM, and used to explore the scavenging activity of 2, 2-diphenyl- 1-picrylhydrazyl (DPPH).

2. Experimental

2.1. Chemicals and reagents

Zinc acetate hexahydrate [$Zn(CH_3.COO)_2.2H_2O$], Sodium hydroxide (NaOH) Sigma-Aldrich It was received from the chemical materials store at the College of Science, Mustansiriyah University. The plant extract was prepared in the lab using Dried ginger and all the solutions were prepared using deionized water. To study the antioxidant activity, we used methanol, ascorbic acid, and 2, 2-diphenyl- 1-picrylhydrazyl (DPPH).

2.2. Collection of plant Preparation of extract

Dried ginger was purchased from a local market and thoroughly washed with distilled water, washed with deionized water well, dried, ground, and was kept in an air-tight container afterward before analysis. A weight of 10 g powdered Zingiber rhizome was mixed with 200 mL of deionized water and the solution was boiled for 15 minutes at 80C until a yellow-colored solution remained. The solution was cooled to room temperature and filtered to obtain a clear yellow-colored plant extract solution. As a reducing and stabling agent, this plant extract was used. The filtered extract was then used to create green ZnO NPs.

2.3. Green synthesis of ZnO NPs using rhizome extracts

A weight of 2.07 g zinc nitrate hexahydrate was dissolved in 150 mL deionized water for a final concentration of 0.1 M. To achieve a homogeneous solution, the solution was agitated on a magnetic stirrer at room temperature for 5 minutes. Then, for 30 minutes, 20 mL of rhizome plant extract was added while continuously stirring. After adding the plant extract, the solution turns yellow. After 30 minutes of stirring, 1 M NaOH was dropped in dropwise until the yellow color solution turned into a pale-yellow color precipitate. For 10 minutes, the solution was centrifuged at 7500rpm. The supernatant solution was removed and washed several times with water before collecting white ZnO nanoparticles on a watch glass and drying at 70˚ C. To remove any evaporable impurities, the dried ZnO NPs were calcined in a furnace at 400 C for 4 hours. The calcined samples were cooled to room temperature before being stored for further analysis[8]

2.4. Characterization of ZnO NPs

for Optical studies, UV spectrum analysis was estimated using a UV-1800 spectrophotometer (Shimadzu, Japan, 210 to 800 nm photoluminescence PL). ZnO NPs were also characterized using XRD, TEM, AFM, EDX, and SEM, zeta potential (ζ-potential) to indicate the molecular structure, shape, size and investigate the surface charge and stability.

3. Result and discussion

3.1. UV–visible spectroscopy analysis

Typically, UV-visible spectroscopy is used to confirm the synthesis of ZnO NPs. Because of the surface plasmon resonance (SPR) effect, conducting electrons begin to oscillate at a specific wavelength range, as shown in Fig 2. The presence of ZnO NPs indicated by a peak at 375.5 nm. This result is consistent with the findings of Santhoshkumar *et al* [9].

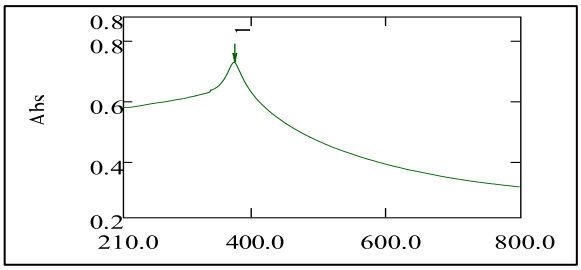

Figure 2. UV-vis spectrum of ZnO NPs synthesized by Zingiber extract.

3.2. Photoluminescence (PL) spectroscopy

For crystalline quality, the photoluminescence (PL) technique was used. All spectra are composed of two emanation peaks which are shown in Fig 3. The ZnO showed one peak in the UV region (450 nm) and another in the visible region (590 nm). The visible region peak appeared because of crystal defects like Zn-interstitials and oxygen vacancies [10].

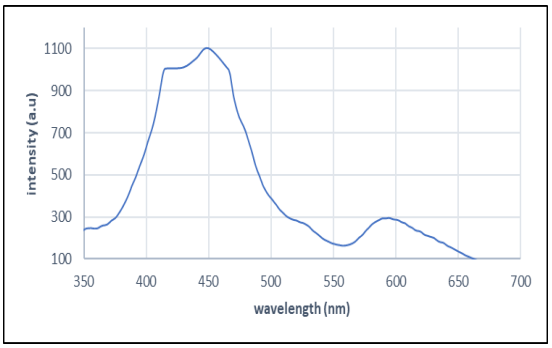

Figure 3: PL spectra of the ZnO NPs prepared from Zingiber extract.

3.3. X-ray diffraction (XRD)

X-ray crystallographic study was performed to confirm the crystalline structure of ZnO NPs after calcination at 400 C. Shimadzu-7000 Powder X-Ray diffractometer with Cu-Kα (λ= 1.54 Å) radiation in the range from 10 to 70 A˚ was used. The particle size was calculated using the Debye -Sherrer equation [11].

$$\mathbf{D = (K*\lambda)/\ \beta*Cos(\theta)}$$

Where D is the crystallite size, K=0.9 Sherrer constant, λ is the wavelength of X-rays, β is the full width half maximum (FWHM) and θ is the Braggs diffraction angle. The XRD pattern of ZnO NPs showed bands at 31.97˚, 34.73˚, 36.53˚, 47.86˚, 62.98˚, 66.44˚, 69.36˚, 74.56˚ and 78.64˚ corresponding reflecting planes are (100), (002), (101), (102), (110), (103), (200) and (112) respectively, all the peaks were well matched with the JCPDS card No. 36-1451[12], as shown in Fig 4.

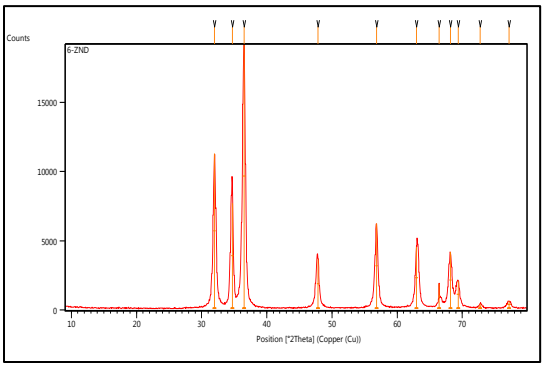

Figure 4. X-ray diffraction pattern of ZnONPs powder.

The sharp diffraction peaks in Table 1 revealed the crystallinity of the particles with particle size ~ 23.69 nm. The ZnO NPs produced is the compound of Zinc Oxide with 63%, in agreement with Fahime Bigdeli *et al*[13].

Table 1. XRD analysis information

Pos. [°2Th.]	Height [cts]	FWHM Left [°2Th.]	d-spacing [Å]	Rel. Int. [%]	Tip Width
31.9763	11164.03	0.3444	2.79894	57.83	0.4133
34.7388	7591.71	0.3936	2.58244	39.33	0.4723
36.5342	19303.62	0.4920	2.45955	100.00	0.5904
47.8646	3538.69	0.3936	1.90047	18.33	0.4723
56.8224	6123.62	0.3936	1.62031	31.72	0.4723
62.9880	4430.93	0.4428	1.47573	22.95	0.5314
66.4431	1775.53	0.1968	1.40713	9.20	0.2362
68.1759	4051.16	0.3444	1.37553	20.99	0.4133
69.3643	1989.86	0.4920	1.35484	10.31	0.5904
72.7452	309.21	0.2952	1.29999	1.60	0.3542
77.1785	509.28	0.5904	1.23600	2.64	0.7085

3.4. Energy-dispersive X-ray spectroscopy (EDX)

EDX was used for determining the elemental composition of the NPs surface, which depends on the generation of characteristic X-rays. The EDX results showed that the ZnO powder (Fig 5) was pure as high-intensity peaks of Zn element (81.1%) and low-intensity peaks of oxygen at (18.9 %) and very few

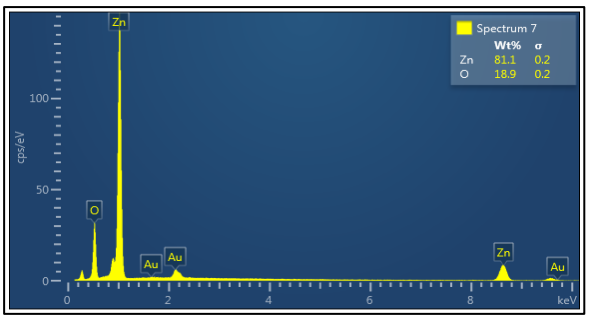

Figure 5. EDX spectrum of ZnO NPs

impurities. The zinc element composition is higher than that of the synthesized ZnO NPs, which agreed previous study [14].

3.5. Atomic Force Microscopy (AFM)

AFM (spm-AA300 contact mode spectrometer, Angstrom) was used to characterize the surface topography, size, and morphology of ZnO NPs. The origin of the surface morphology of the irregularly shaped particle sizes and the size distribution broaden of ZnO-NPs synthesized by ginger plant extract are shown in Fig 6.

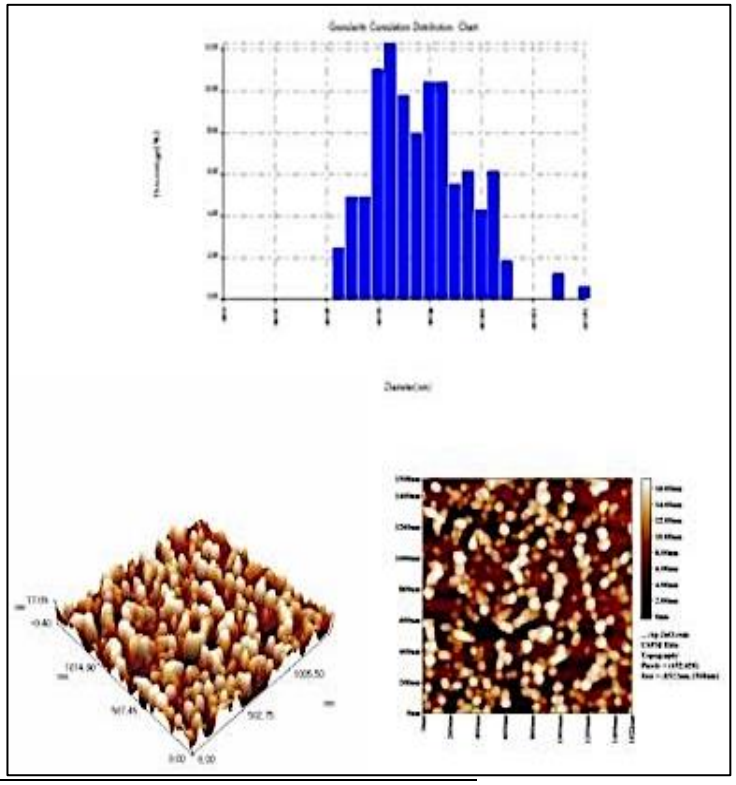

Figure 6. AFM images and size distribution histogram of ZnO NPs.

Table 2. (ZnO NPs) size and distribution histogram obtained from the AFM images

Diameter (nm)<	Volume (%)	Cumulation (%)	Diameter (nm)<	Volume (%)	Cumulation (%)	Diameter (nm)<	Volume (%)	Cumulaion (%)
33.00	0.61	0.42	66.00	13.65	58.96	96.00	5.67	96.92
41.00	6.12	6.13	72.00	9.57	67.53	110.00	1.82	97.73
45.00	11.65	19.7	77.00	11.80	78.33	115.00	2.22	98.96
51.00	7.53	24.71	83.00	9.35	85.67	125.00	1.41	99.37
57.00	9.57	36.29	87.00	6.49	89.16	130.00	1.41	99.78
60.00	13.02	47.31	90.00	5.08	92.24	140.00	2.22	102.00

The images confirmed the uniform distribution of ZnO NPS because the majority of the particles were 20–100 nm in diameter, with the greatest number of NPs between 33 and 102 nm, Table 2. After two weeks, the sample of ZnO NPs was examined. However, the particle size of ZnO NPs almost agreed with other studies [15],[16],[17]. Different particles size could be obtained by changing the type of plant as well as, the conditions of synthesis [18].

3.6. Scanning electron microscopy (SEM)

The morphology, shape, and size of green synthesized NPS were successfully depicted using SEM micrographs. According to the current study, the shape of ZnO NPs was spherical, however, SEM images in Fig 7 showed irregular shapes of NPs, which could be resulted from the harsh conditions of preparation, in line with another study [19].

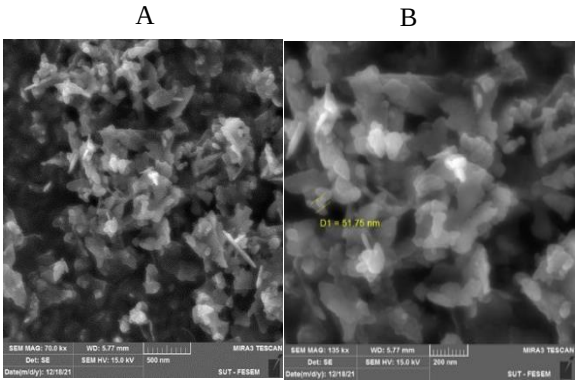

Figure 7. SEM images of ZnO NPs of different magnification. A) 500 nm, B) 200 nm

3.7. Zeta potential analysis (ζ-potential)

The ζ-potential analysis was use d to study the net charge on the surface of ZnO NPs and calculate the charge to understand their stability. ζ-potential value of ZnO NPS was observed as 13.6 mV (Fig 8) which indicated an increase in the stability of the NPs, Snehal Yedurkar *et al* [20], concluded that "if the particles in a suspension have large negative or positive (ζ-potential values, particles will repel each other and there will be no aggregation of NPs. On the other hand, if particles have small ζ-potential values there is no force to prevent particles from coming together and aggregating"[21].

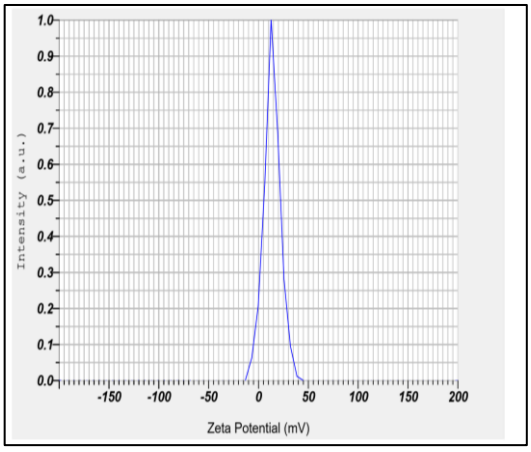

Figure 8. ζ-potential of ZnO-NPs

3.8. Antioxidant Activity

In the metabolism of a healthy living system, antioxidants and free radicals are in balance. Because antioxidants act as free radical scavengers, they boost the effectiveness of the immune system and lower the risk of disease [22]. The antioxidant status of various NPS was estimated by inhibiting the effect of DPPH by 50%, which is called half inhibitory concentration (IC_{50}). The lower IC_{50} value the greater is the scavenging potency. The current results showed the scavenging activity of ZnO NPs compared with Vitamin C as a standard.

Vitamin C exhibited a powerful antiradical activity against DPPH with IC_{50} = 19 µg/mL, Table 3, Figure 9.

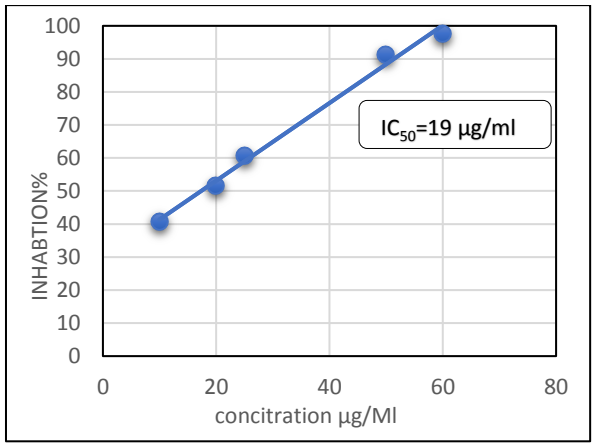

Figure 9. Vitamin C antiradical inhibition plot against DPPH

ZnO NPs showed a scavenging potency against DPPH with IC_{50} = 150 µg/mL, Figure 10. The inhibition activity of ZnO NPs was significantly lower than vitamin C. With increasing the concentration of NPs, the antioxidant activity is increased [23], The highest scavenging % presented with 360 ppm of ZnO NPs has 63.1% Table 3.

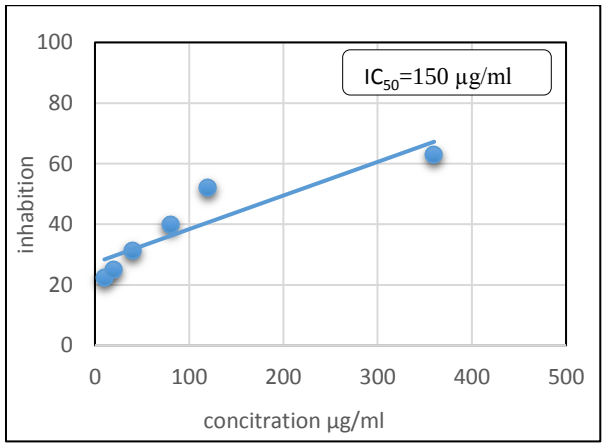

Figure 10. Radical inhibition% of ZnO NPs

The particles have a free radical scavenging capacity of up to 52% in 120 µg/mL, indicating strong antioxidant activity. Because the green synthesized ZnO NPs can be used as antioxidants, these NPs could have the potential to be used as a promising antioxidant in a biological system.

Table 3. vitamin C and ZnO NPs inhibitory percentage against DPPH.

	Inhibition %	Concentration µg/mL
Vit C	40.8	10
	51.66	20
	60.6	25
	91.3	50
	97.6	60
ZnO NPs	22.5	10
	25.0	20
	31.3	40
	39.7	80
	52.0	120
	63.1	360

4. Conclusions

This study demonstrated the use of a natural, low-cost biological reducing agent, ginger plant extracts to produce ZnO NPS. UV-Vis spectral analysis confirmed the surface plasmon resonance of biosynthesized ZnO NPs. Further, the biosynthesized ZnO NPs using ginger extract showed good catalytic activity. The ζ-value of ZnO NPS (13.6 mV) indicated the high stability of the NPS. In addition, the present study suggests that ZnO NPs have good antioxidant activity.

5. Acknowledgments

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