



Investigation of structural and optical properties of biosynthesized Zincite (ZnO) nanoparticles (NPs) via an aqueous extract of *Rosmarinus officinalis* (rosemary) leaves

S. K. Noukelag^{b,c}, H.E.A.Mohamed^{a,b}, B. Moussa^{a,b,g}, L.C. Razanamahandry^d, S.K.O. Ntwampe^{e,f}, C.J. Arendse^c, M. Maaza^{a,b}

^aUNESCO-UNISA Africa Chair in Nanosciences & Nanotechnology Laboratories (U2AC2N), College of Graduate Studies, University of South Africa (UNISA), Muckleneuk Ridge, PO Box 392, Pretoria, South Africa

^bNanosciences African Network (NANOAFNET), Material Research Department (MRD), iThemba LABS-National Research Foundation, 1 Old Faure Road, Somerset West 7129, PO Box 722, Somerset West, Western Cape, South Africa

^cDepartment of Physics and Astronomy, University of the Western Cape, Robert Sobukwe Road, Private Bag X17, Bellville 7535, South Africa

^dAfrican Union Development Agency, Economic Integration Division, PO Box 1685, Johannesburg, South Africa

^eBioresource Engineering Research Group (BioERG), Cape Peninsula University of Technology, PO. Box 652, Cape Town, 8000, South Africa

^fSchool of Chemical Engineering, North West University, Potchefstroom Campus Private Bag X6000, Potchefstroom 2520, South Africa

^gUniversité Cheikh Anta Diop de Dakar, Département de Physique, Sénégal

Abstract

Biosynthesized Zincite nanoparticles have been successfully demonstrated by a completely green process mediated aqueous extract of rosemary leaves acting as both reducing and stabilizing agents and zinc nitrate hexahydrate as the precursor. The synthesis was free of solvents and surfactants to adhere to green chemistry principles and the impartation of environmental benignity. To achieve our objective, structural and optical investigations of

ZnO annealed at 500°C for 2hrs were carried-out using complementary techniques. High resolution transmission electron microscopy (HRTEM) revealed the self-assembled, highly agglomerated quasi-hexagonal shaped NPs and the average particle size was found to peak at 15.62 ± 0.22 nm. Selected area electron diffraction (SAED) and X-ray diffraction (XRD) exhibited several diffraction rings with clear diffraction spots confirming their polycrystallinity and the purity of ZnO NPs with a wurtzite structure. Furthermore, the energy dispersive X-ray spectroscopy (EDS) substantiated the presence of Zn and O in the sample and attenuated total reflection-Fourier transform infrared spectroscopy (ATR-FTIR) illustrated the Zn-O chemical bonds. From UV-Vis-NIR, the optical band gap was amounted to 3.2 eV and photoluminescence (PL) emission spectrum to 2.9eV with high surface defects and oxygen vacancies. Through these results, the use of rosemary leaves extract is hereby shown to be a cost-effective and environmentally friendly alternative to synthesize Zincite nanoparticles (ZnO NPs).

1. INTRODUCTION

Metal oxides represent a bright domain of research due to their attractive physico-chemical, electronic and optical characteristics. Their interface and their low-dimensionality provide exciting paths for fabricating nano-scaled matter with special properties, i.e., high reactivity, high specific surface area, controlled size, and distribution [1-2]. Common metal oxides such as CuO, NiO, ZrO₂, CeO₂, PbO, and Sm₂O₃ are highly efficient and active adsorbents for many toxic chemicals including air pollutants, chemical warfare agents, acidic gases, and water pollution [3-5]. Particularly, ZnO is characterized by its wide direct band gap of 3.37 eV and high excitation energy of 60 meV. It is also the most exploited n-type semiconducting metal oxide materials due to its tunable, multifunctional morphological, photonic and spintronic properties and therefore there is a growing interest in ZnO NPs synthesis [6-9]. Nevertheless, the use of chemical and physical methods to synthesize ZnO NPs is disadvantageous due to cost and the generation of hazardous waste [10-14]. The use of plant extracts for the synthesis of NPs is potentially advantageous as it is imparting environmentally friendly, rapid, simple and less energy-intensive with minimal waste generated, so an economical synthesis route to produce the desired metal oxides nanoparticles [15-20]. Plant extracts such as those from *Callistemon viminalis* (Weeping bottlebrush), *Sageretia thea* (Osbeck), *Aspalathus linearis* (Rooibos), *Agathosma betulina* (Buchu), *Azadirachta indica* (Neem), *Aegle marmelos* L. (Bael), *Artocarpus gomezianus* (Sampang), *Punica granatum* (pomegranate), *Lycopersicon esculentum* (tomato), *Ocimum Tenuiflorum* (Basil) and *Hibiscus Sabdariffa* (Roselle) have been used as capping, reducing and stabilizing agents for the synthesis of ZnO nanoparticles via green chemistry [21-29]. To the best of our knowledge, rosemary leaves have not been used for the green synthesis of ZnO NPs.

In fact, rosemary is an aromatic medicinal and valuable plant which belongs to the family Labiate. Although it is a native plant of the Mediterranean region, it can be cultivated around the world due to its hardiness [30]. Its small green leaves are important in the treatment of jaundice, hepatitis, circulatory, and cardiovascular diseases [30-31]. Bioactive components in rosemary leaves extract (see table 1) can play a critical role in the capping and stabilization of nanoparticles [32-33].

In this work, we report on the synthesis of ZnO NPs, using mediated rosemary leaves extract as reducing and stabilizing agents by green chemistry. Furthermore, we report on their main physical properties using complementary techniques.

Table 1. Major chemical composition of rosemary leaves natural extract [30]

Chemical composition	Explanation
FLAVONOIDS	PELARGONIDIN-3,5-DIGLUCOSIDE (I) CYANIDIN-3,5DIGLUCOSIDE(II) KAEMPHEROL (III)
MONOTERPENOIDS	α - PINENE (IV) 1,8-CINEOLE CAMPHOR
PHENOLIC ACIDS	ROSMARINIC ACID CAFFEIN ACID
DITERPENOIDS	CARNOSOL METHYL CARNOSATE 12-METHOXYCARNOSIC ACID EPI- AND ISO-ROSMANOL

2. EXPERIMENTAL SECTION

2.1 Biosynthesis: green process via rosemary leaves natural extract

Rosemary leaves were purchased from Western Cape Province-South Africa. Zinc nitrate hexahydrate $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ was purchased as an analytical grade reagent (Sigma Aldrich, Modderfontein, South Africa) and used without any further purification.

6g of rosemary leaves were immersed in 200 mL of boiled deionized water at 80°C for 2 hrs. The resultant extracts' pH was found to be 5.7. The extract solution was filtered twice with Whatman paper (N°5) to eliminate residual solids. Thereafter, 6g of zinc nitrate hexahydrate i.e., the precursor salt was mixed homogenously in 100mL of rosemary extract, under the magnetic stirrer at 60 °C for 1 hr. After homogenization, the slight acidification of the resultant solution was observed with a final pH of 4.8. This greyish-brown solution was dried in the oven at 100 °C for one day. Hence, the dried greyish-brown powder was annealed at 500 °C in an open-air furnace for 2hrs leading to the formation of ZnO nanoparticles with a change of color from greyish-brown to white powder.

2.2 Characterizations

High resolution transmission electron microscopy (HRTEM) measurements were performed using a Joel JEM 4000EX electron microscopy unit with a resolution limit of about 0.12 nm at an accelerating voltage of 200 kV, combined with selected area electron diffraction (SAED). X-ray diffraction (XRD) measurements were performed using a Bruker AXS D8 diffractometer with an irradiation line $\text{K}\alpha_1$ of copper ($\lambda_{\text{CuK}\alpha_1}=1.5406 \text{ \AA}$) operating at a voltage of 40 kV and a current of 35 mA, in the angular range of 20 to 90°. Energy dispersive X-ray spectroscopy (EDS) spectrum was collected with an EDS Oxford instrument X-Max solid-state silicon drift detector operated at 20 kV. A Thermo Nicolet 8700 FTIR spectrometer was used to measure the ATR-FTIR absorption spectrum in the spectral range 400 to 4000 cm^{-1} . UV-VIS-NIR measurements were performed using a Nicolette Evolution 100_Spectrophotometer in the spectral range 200 to 800 nm whereas the photoluminescence (PL) spectrum was recorded from 200 to 800 nm using Varian Cary Eclipse Fluorescence Spectrophotometer at an excitation wavelength of 372 nm.

3. RESULTS & DISCUSSIONS

3.1 Morphology and microscopy observations

The morphology, internal structure and the crystallinity of ZnO NPs annealed at 500°C were investigated using HRTEM combined to SAED, as presented in figure 1.

From HRTEM micrographs, highly agglomerated quasi-hexagonal shaped nanoparticles are depicted. SAED exhibits several diffraction rings with clear diffraction spots confirming the polycrystalline nature of the formed NPs [22,24,27]. By fitting the histogram data with a Gaussian distribution, the average particle size amounts to 15.62 ± 0.22 nm.

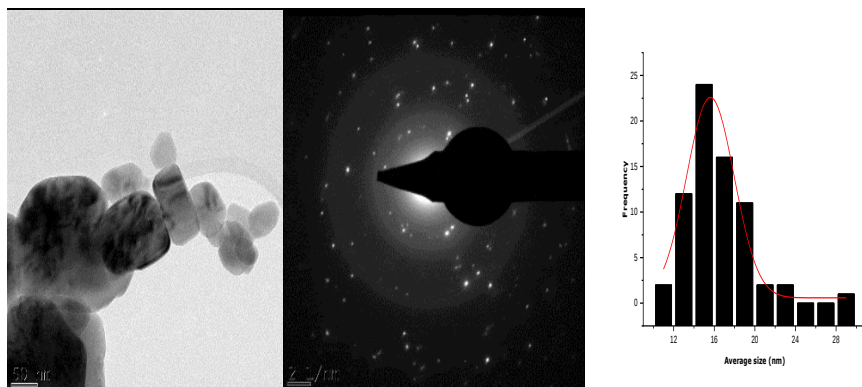


Figure 1. HRTEM, SAED and average size distribution of ZnO NPs annealed at 500°C for 2hrs.

3.2 Crystallographic analysis

XRD of the ZnO nanoparticles was employed to study their structural properties annealed at 500°C for 2hrs. As depicted from figure 2, the presence of intense and well defined diffraction peaks were observed with their maxima centered at $2\theta(^{\circ}) = 31.770; 34.422; 36.253; 47.539; 56.603; 62.864; 66.380; 67.963; 69.100$ and 72.562 , assigned to the reflections planes of the Zincite (100); (002); (101); (102); (110); (103); (200); (112); (201) and (004) which correspond to wurtzite crystalline with the hexagonal crystallographic reflections of ZnO having standard lattice parameters of ($a = 3.2498$ and $c = 5.20661$). This is consistent with the JCPDS pattern No.036-1451. The sharper and narrow peaks in the XRD spectrum indicate the highly crystalline nature of the ZnO NPs [20,21,23]. Therefore, it can be concluded that the biosynthesized ZnO NPs have a good degree of crystalline structure. Using the Debye-Scherrer formula, the average particle size of the annealed ZnO nanoparticles was found in the range of 8.894-20.852 nm which corresponds to HRTEM observations.

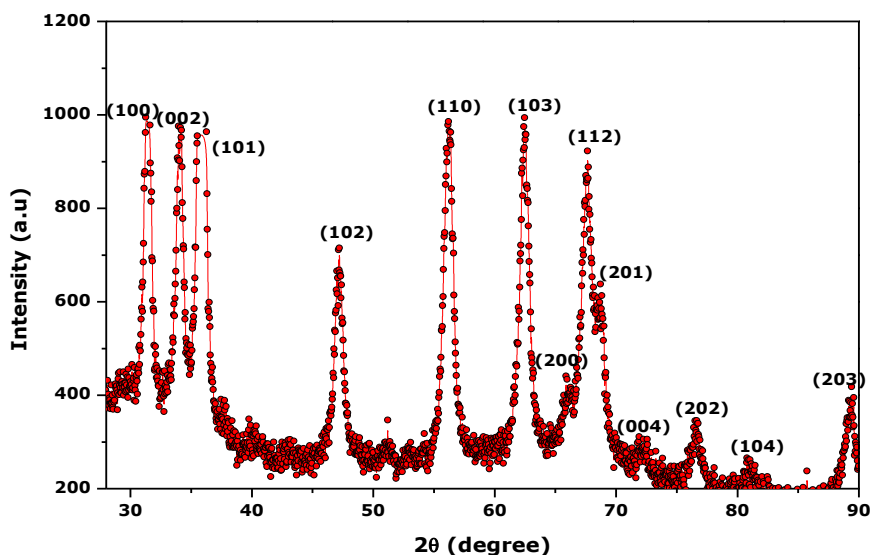


Figure 2. XRD of ZnO NPs annealed at 500°C for 2hrs.

The d-spacing for each plane and its comparison to the bulk value and the corresponding crystal size obtained from Scherrer approximation are reported in table 2.

Table2. XRD Values and crystalline size of ZnO NPs annealed at 500°C for 2hrs.

hkl	2θ ($^{\circ}$)	θ (rad)	$d_{bulk}(\text{\AA})$	$d_{exp}(\text{\AA})$	$\Delta d/d_{bulk}$	FWHM(rad)	$\langle\phi\rangle$ (nm)
(100)	31.770	0.277	2.8143	2.8144	0.0035	0.0081	19.775
(002)	34.422	0.300	2.6033	2.6033	0.0000	0.0113	14.272
(101)	36.253	0.316	2.4759	2.4760	0.0040	0.0169	09.592
(102)	47.539	0.414	1.9111	1.9111	0.0000	0.0114	14.766
(110)	56.603	0.494	1.6247	1.6250	0.0180	0.0136	12.838
(103)	62.864	0.548	1.4771	1.4772	0.0067	0.0203	08.894
(200)	66.380	0.579	1.4071	1.4073	0.0142	0.0137	13.123
(112)	67.963	0.593	1.3782	1.3784	0.0145	0.0158	11.697
(201)	69.100	0.603	1.3582	1.3585	0.0220	0.0089	20.852
(004)	72.562	0.633	1.3017	1.3016	-0.0076	0.0153	12.443

3.3 Elemental analysis

For elemental composition, energy dispersive X-ray spectroscopy (EDS) was used to obtain the profile of the annealed ZnO nanoparticles at 500 °C for 2hrs as shown in figure 3, which confirms the presence of zinc and oxygen atoms in the sample. The carbon peak is due to the carbon tape used as grid support to immobilize the

biosynthesized ZnO nanoparticles and to minimize charging effects [21,25]. The peaks due to K, Cl, and Na were hypothesized to emanate from the rosemary leaves extract.

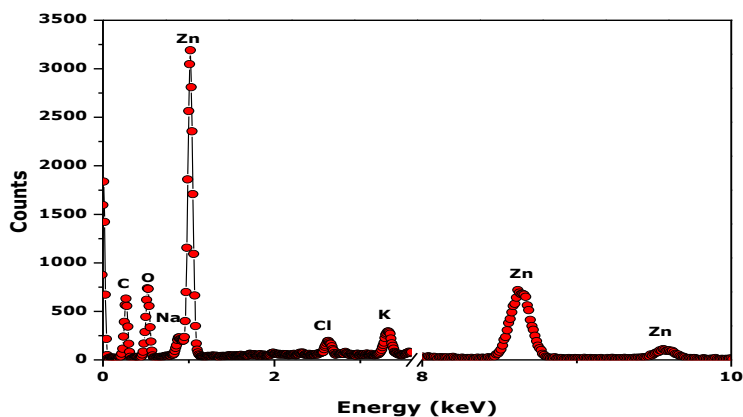


Figure 3. EDS spectrum of ZnO NPs annealed at 500°C for 2hrs.

3.4 Vibrational spectroscopy

To validate again and to conclude on the purity of the Zincite nature biosynthesized, ATR-FTIR studies were carried out to identify the possible biomolecules involved in the biosynthesis of ZnO NPs as depicted in figure 4.

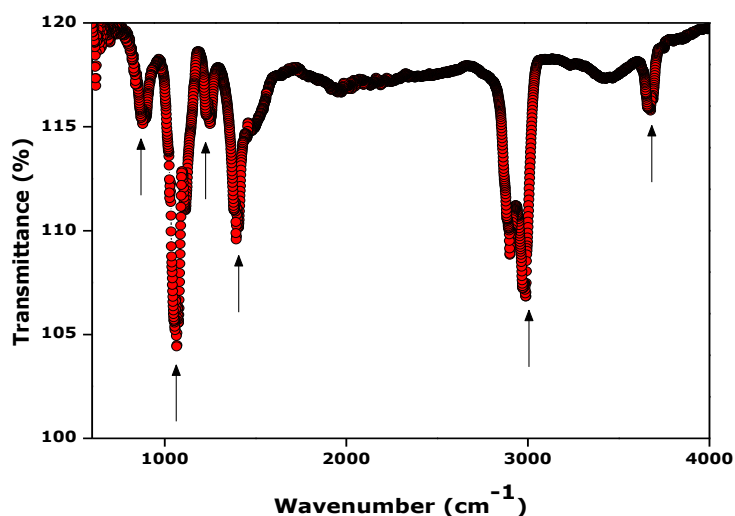


Figure 4. ATR-FTIR spectrum of ZnO NPs annealed at 500°C for 2hrs.

As one can observe on the ZnO NPs annealed at 500 °C for 2hrs, an intense peak at 600 cm^{-1} which is specific to hexagonal phase ZnO NPs. The absorption band at 1063 cm^{-1} and the low absorption band located at 1270 cm^{-1} correspond to the C-O stretching of amino acid and esters, respectively. The absorption band centred at around 1396 cm^{-1} may arise from the C–O–C stretching modes of vibration. The peak at 880 cm^{-1} corresponds to O-H functional group and the absorption band at 1118 cm^{-1} is attributed to C-N of aliphatic amines or alcohols/phenols in rosemary leaves extract. Finally, the 2 broad peaks centred approximately at 2845 and 2993 cm^{-1} are associated respectively to standard H₂O bending modes and OH stretching [4,22,25]. Therefore, the active bio compounds from the leaves evidenced by the FTIR spectrum could be responsible for the reduction and stabilization of the ZnO nanoparticles.

3.5 Optical properties

UV-Vis spectroscopy was carried out to ratify the presence of the semiconductor nanomaterial ZnO NPs annealed at 500°C for 2hrs. Figure 5 shows an absorption edge in the region of 388 nm giving a bandgap value of 3.2 eV, which confirms the ZnO structure and is associated with a charge transfer from the band of conduction to the band of valence cations. The band-to-band excitation of ZnO promotes electrons from the valence band to conduction band, leaving holes in the valence band.

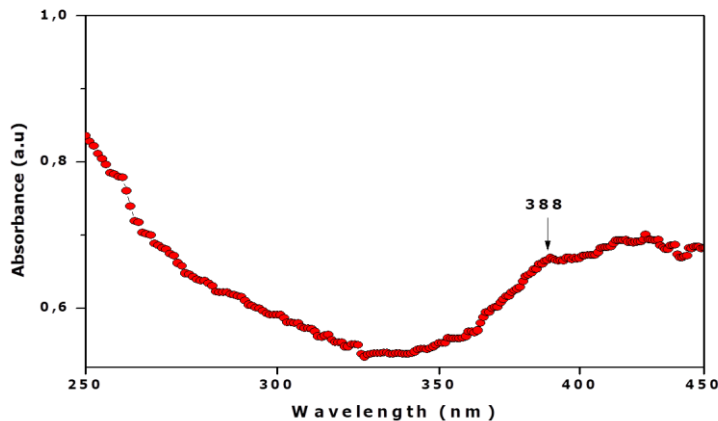


Figure 5. UV-Vis-NIR spectra of ZnO NPs annealed at 500°C for 2hrs.

The holes migrate from the valence band to deep levels and recombination occurs between electrons from either the conduction band or shallow donor levels and trapped holes on deep levels [8,23,25].

As a continuity of the UV-Vis-NIR, the photoluminescence spectrum of the ZnO NPs annealed at 500°C for 2hrs depicted in figure 6, was also performed to understand the extrinsic and the intrinsic defects in ZnO NPs and ion deficiencies if any. One can notice an intense UV emission peak at 428 nm, which can be ascribed to band edge emission that results from the recombination of electrons and holes of ZnO free

excitons. The appearance of this visible emission of the visible spectrum suggests that ZnO NPs have a high surface-to-volume ratio with numerous surface-states and native defects (vacancies and interstitials) which create trap levels responsible for the emissions observed [9,12,13]. The color change of the biosynthesized ZnO nanoparticles (greyish-brown to white) can also be justified by the existence of oxygen vacancies and high surface defects.

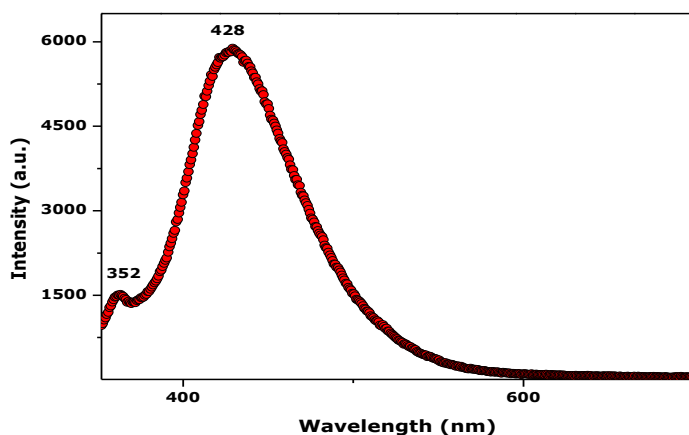


Figure 6. Photoluminescence (PL) spectrum of ZnO NPs annealed at 500°C for 2hrs.

4. CONCLUSION

High-quality ZnO nanoparticles were successfully obtained by an entirely green process using the natural extract of *Rosmarinus officinalis* leaves as an effective reducing agent. The obtained ZnO NPs were annealed at 500°C for 2hrs under air and characterized by HRTEM, SAED, XRD, EDS, ATR-FTIR, UV Vis and PL.

The XRD and HRTEM results confirmed the hexagonal structure with the average size in the range of 8.894-20.852 nm for XRD and 15.62 ± 0.22 nm for HRTEM. SAED results confirmed the polycrystalline nature of the pure hexagonal structure of ZnO NPs. All results from HRTEM and SAED were found in agreement with the XRD study. EDS confirmed the presence of Zn and O in the sample, while ATR-FTIR depicted the Zn-O chemical bonds. From the optical properties, the bandgap energies of Zincite NPs were found to be 3.2 eV for UV-Visible and 2.9 eV for photoluminescence. It was proved the existence of high surface defects and oxygen vacancies. Hence, it can be concluded that this green synthesis pathway has demonstrated the importance of rosemary leaves extract as cost-effective, cheap and environmental benignity to facilitate the synthesis of ZnO nanoparticles.

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