Semiconductor Physics, Quantum Electronics & Optoelectronics, 2024. V. 27, No 1. P. 064-069.

Semiconductor physics

Green route to prepare zinc oxide nanoparticles using *Moringa oleifera* leaf extracts and their structural, optical and impedance spectral properties

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Abstract. This article investigates biosynthesis of zinc oxide (ZnO) nanoparticles (NPs) from *Moringa oleifera* leaves extract using an eco-friendly preparation method. The crystalline structure, optical properties, morphology and impedance characteristics of ZnO NPs were analyzed using impedance spectroscopy, powder X-ray diffraction (XRD), scanning electron microscopy, Fourier transform infrared spectroscopy (FTIR) and ultraviolet spectroscopy (UV-vis). The powder XRD pattern confirmed the crystallinity of the prepared samples as well as enabled determining their crystallite size and pure phase portion. The FTIR study confirmed the presence of functional groups responsible for reduction metal ions into ZnO NPs. UV-vis absorption spectra contained the absorption peak corresponding to ZnO NPs. Impedance spectroscopy of the prepared ZnO NPs revealed the grain boundaries in them and confirmed their semiconducting nature.

Keywords: frequency, impedance spectroscopy, leaves extract, *Moringa oleifera*, bio-synthesis, absorption spectra.

https://doi.org/10.15407/spqeo27.01.064
PACS 61.46.-w, 72.80.Jc, 78.67.Bf, 84.37.+q

Manuscript received 17.06.23; revised version received 05.12.23; accepted for publication 28.02.24; published online 12.03.24.

1. Introduction

Preparing nanoparticles (NPs) from plant leaves is an exhaustive method mostly applied in medicine. NPs prepared by common techniques have a limited application in the medical field due to their negative impact on living organisms [1]. Chemical studies of the NPs preparation methods from plants leaves contributed to overcoming the limitations of conventional chemical and physical NPs synthesis techniques [2, 3]. Plants possess wealthy genetic varies with respect to most of the bio-molecules and metabolites like vitamins, proteins based intermediates and carbohydrates [4]. These plants metabolites contain hydroxide and amine functional groups that react with metal oxides forming nanoparticles [5]. In particular, flavonoid contains functional groups. It is believed that, the pH value of flavonoids is favorable for the reduction of metal ions into NPs [6]. These molecules not only help in reducing the size to nanorange, but also play an important role in capping the NPs, which is pivotal for their stability and bio-compatibility [7].

Synthesizing processes of NPs from plant leaves are technically the same as described as chemical routes in many research articles. Hence, organic ingredients play the most important role on the preparation of NPs. leaves of the plants such as *Moringa oleifera* (MO), *Aloe vera*, *Limonia acidissima* and *Glycosmis pentaphylla* are used for the biosynthesis of ZnO NPs [8]. Despite great importance of plant leaves for preparing metal oxide NPs, very few investigations in this area were done in Tenkasi, Tamil Nadu, India. Since Tamil Nadu has a wonderful diversity of medicinal plants, the still unveiled properties of which will necessarily be found using the techniques mentioned above. *Moringa oleifera*, which is a medium size tree, belongs to the *Moringaceae* family. The leaves of this tree are elliptically shaped. The tree is a Tamil Nadu cultural and the most important medical plant [9]. Various medical treatments are used at various diseases like epilepsy, herpes simplex virus, blindness, Crohn's disease, arthritis, hyperthyroidism, anemia and rheumatism [10, 11]. MO is also used to supplement nutrition providing important phytochemicals. MO leaves

contain essential substances such as anthraquinones, alkaloids, vitamins, sterols, terpenoids, tannins, flavonoids and saponins [12].

Preparation of NPs from leaf extracts is simple. The plants release no poisons to the environment and are not toxic. Such preparation methods may replace other techniques of NP synthesis. In view of the medical importance of MO leaves, we consider here the green synthesis method of ZnO NPs from MO leaf extract.

2. Experimental

2.1. Chemicals and materials

Zinc acetate dehydrate [$Zn(CH_3COO)_2 \cdot 2H_2O$] and sodium hydroxide pellets [NaOH] were purchased from the Merck (India) Ltd. All chemicals were used without any purification. De-ionized water was used throughout the experiment.

2.2. Preparation of *Moringa oleifera* leaf extract

Moringa oleifera leaves were collected in our village. MO leaves were thoroughly washed in the purified water and allowed to dry in air at room temperature during five days. 20 g of MO leaves powder were mixed with 50 ml of distilled water and sterilized for one hour at 60 °C. The solutions prepared in this way were cooled at room temperature. The leaf extract was filtered with Whatman filter paper. The filtrate was stored in a cool and dry place.

2.3. Synthesis of ZnO nanoparticles

For the green synthesis of ZnO NPs by the chemical method, 10 ml of the MO leaf extract solution was mixed with 10 ml of the prepared zinc acetate solution (0.2194 g in 10 ml of water, 1 M) and stirred for two hours. Then NaOH solutions (0.4 g in 10 ml of water, 1 M) were added dropwise at constant stirring. Pure sodium hydroxide was used for controlling the pH value. After finishing the primary stirring, the prepared solution was stirred for 30 min at room temperature at very high RPM. Finally, the precipitates were filtered and washed with deionized water several times. After that, the precipitates were dried for two days at room temperature. Then the ZnO NPs were collected and stored for further use.

2.4. Characterization of the green synthesized ZnO NPs

Various methods were used to analyze structural, optical, morphological and impedance properties of the ZnO NPs. The crystalline structure of the prepared ZnO NPs was analyzed using a powder X-ray diffractometer Bruker D2 Phaser with CuKα emission (l = 1.5405 Å) as a radiation source. The average NP size was determined from the full-width at half-maximum (FWHM) of the XRD peaks using the Debye–Scherrer formula. A Fourier-transform infrared (FTIR) spectrometer (Perkin Elmer, Spectrum two, spectrophotometer, 400…4000 cm^{-1}) was used to confirm presence of the functional groups and their chemical bonding. Optical absorption spectra of the ZnO NPs were recorded using a UV-vis spectrophotometer (Perkin Elmer, Lanbda 35, Range: 190…1100 nm). From these spectra, the absorption peak of the NPs was determined. Scanning electron microscopy (SEM) investigations were carried out at the applied voltage of 10 kV using the Model CAREL ZEISS, EVO 18 device. The NP morphology was analyzed. The impedance characteristics were studied by impedance spectroscopy in the frequency range of 1 Hz to 1 MHz using a Princeton Applied Research, Versa STAT MC device.

3. Results and discussion

3.1. XRD analysis of ZnO nanoparticles

An apparent broadening of the peaks was observed in the XRD spectra of the prepared ZnO NPs (see Fig. 1) indicating the NP sizes in the nanoscale range (1 to 100 nm). The obtained XRD peaks matched the standard JCPDS card No. 89-1397 [13]. Fig. 1 shows the correspondence between the powder XRD spectra of our NPs and the standard spectra of ZnO NPs confirming that our NPs were spherical and had the hexagonal crystalline structure. The XRD peak intensity, angle position (2θ) and the FWHM values were obtained from the measured spectra. The diffraction peaks were detected at the values of 2θ equal to 31.14°, 33.92°, 36.20°, 60.77° and 69.52° [14], which corresponded to the lattice parameters a = 3.253 Å and b = c = 5.213 Å (see also the JPCDS card). These peaks could be attributed to the diffractions from the (100), (002), (101), (103) and (201) planes. The size of the crystallites was found using the Scherrer formula [15, 16]:

$D = 0.9\,\lambda/(\beta \cos\theta)$,

where 0.89 is the Scherrer constant, λ is the X-rays wavelength, θ is the Bragg diffraction angle and β is the FWHM of the diffraction peaks, respectively. The average size of crystalline ZnO NPs was calculated to be 12 nm.

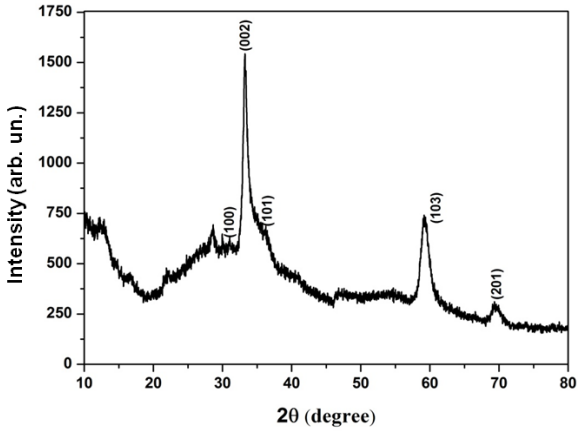

Fig. 1. Powder XRD spectra of ZnO NPs.

3.2. Analysis of FTIR spectra

To identify functional groups in the *Moringa oleifera* leaves extract and ZnO NPs, we measured FTIR spectra in the range of 400 to 4000 cm^{-1}. These spectra are shown in Fig. 2. The FTIR spectra of the MO leaf extract exhibited several peaks at 3435, 2928, 2020, 1600, 1394, 1267, 1126, 1020, 690 and 566 cm^{-1}. The low-intensity band at about 3435 cm^{-1} is related to hydroxyl (−OH) stretching vibrations. The peak at 2928 cm^{-1} was identified as corresponding to the asymmetric stretching vibrations of $-CH_2$ functional groups. The peak at 1600 cm^{-1} is the stretching band of –C=O bending vibrations in acid groups [19]. The peak at around 1394 cm^{-1} is the amide band of the random protein coil [17]. The peak at 690 cm^{-1} corresponds to the stretching vibrations within ZnO NPs [18]. A low-absorbance peak around 1126 cm^{-1} indicates the presence of carbohydrate (C–O), (C=C) rings (cellulose, pectin, and polysaccharides) [20]. The low-absorbance peak around 566 cm^{-1} is characteristic for Metal-O vibrations and is related to the ZnO NPs [21]. Different types of polysaccharides present in the gum and biosynthesized NPs were evidenced by the peaks at 2020, 1267 and 1020 cm^{-1} [22].

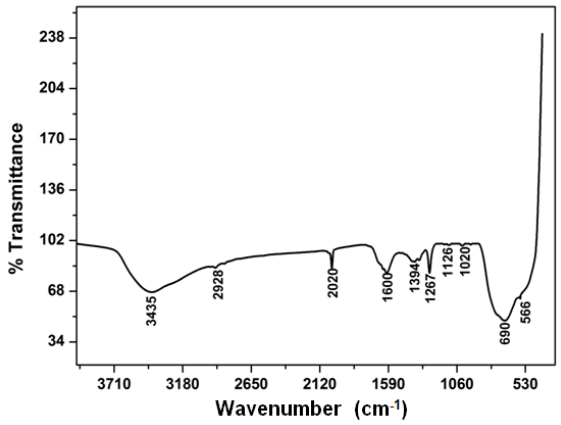

Fig. 2. FTIR spectum of ZnO NPs.

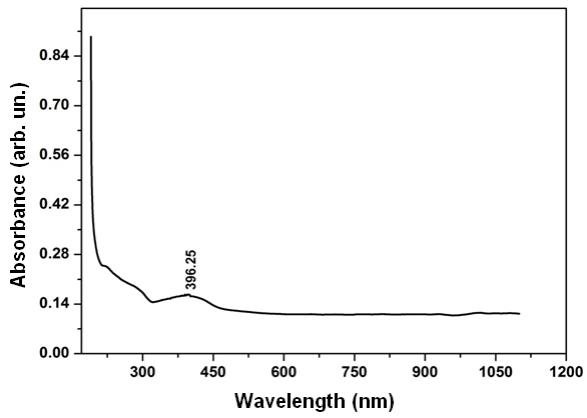

Fig. 3. UV-vis spectum of ZnO NPs.

3.3. UV-vis spectra analysis

UV-vis spectroscopy is one of the most important methods in the studies of biosynthesized metal oxide NPs. The UV-vis spectrum presented in Fig. 3 shows absorption in the range of 323 to 440 nm [23] with a peak at 396 nm, which evidences high efficiency of the ZnO NP preparation process. In this process, hydroxyl groups present in the *Moringa* gum reduce zinc.

3.4. SEM analysis

ZnO NPs were investigated by SEM to reveal their structure and morphology. The SEM images of the biosynthesized ZnO NPs using zinc acetate are shown in Fig. 4 [24]. It can be seen from this figure

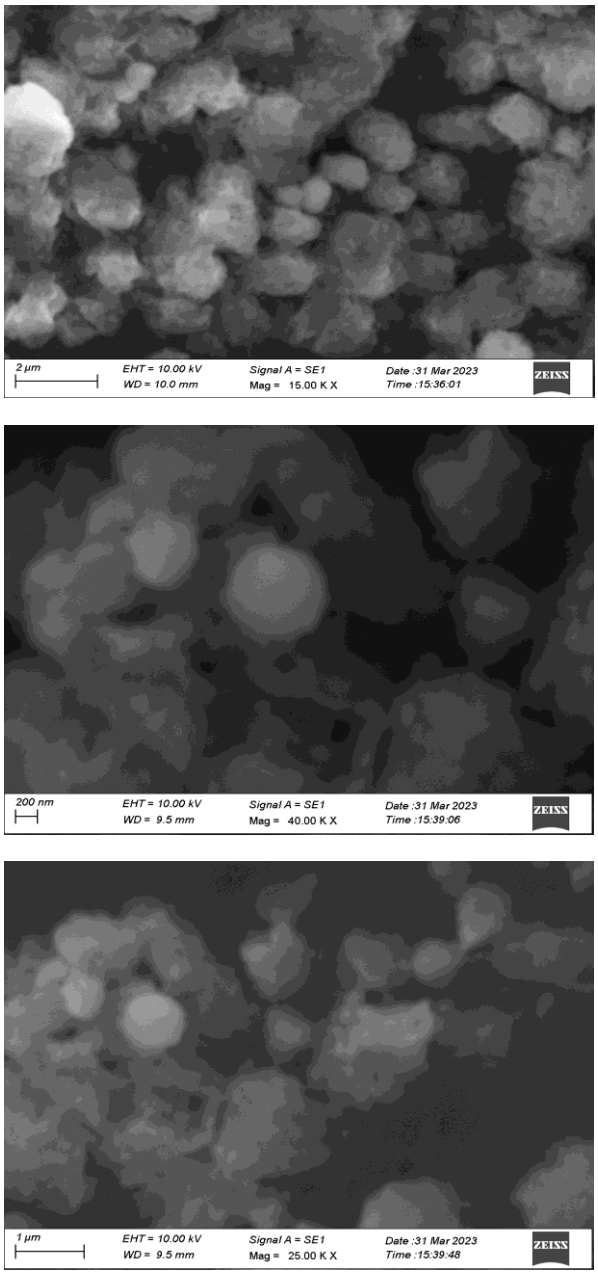

Fig. 4. SEM images of ZnO NPs.

that the NPs are spherical and collected in agglomerates. The SEM investigations also confirm the crystallinity of the NPs, which agrees with the XRD results discussed above.

3.5. Impedance analysis

ZnO NPs were analyzed using impedance spectroscopy. The obtained impedance spectrum, also called Cole–Cole plot, is shown in Fig. 5. The Cole–Cole plot depicts the real (*Z′*) *versus* imaginary (*Z″*) part of impedance. When the frequency is continuously swept, the Cole–Cole plot of the sample provides a single semicircle. From the impedance spectroscopic data, we could study the electrical properties of our materials. The complex impedance of the material is given by $Z^* = Z' - jZ''$ and $Z^* = Dj/\omega^2C^{2.}$ Here, ω is the angular frequency, *C* is the capacitance of the sample, *j* is the square root of −1, and *D* is the loss tangent, respectively. As can be seen from Fig. 5, when the real part of impedance increases, the imaginary part also increases up to –655 Ohm and then above –655 Ohm, *Z″* gradually falls to lower values and then it provides a semicircular arc. This semicircular behaviour is is due to the grain boundaries and indicates semiconducting nature of the prepared ZnO NPs [25].

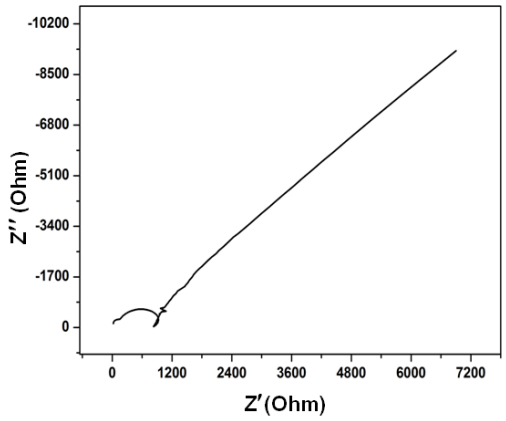

Fig. 5. Cole–Cole plot for ZnO NPs.

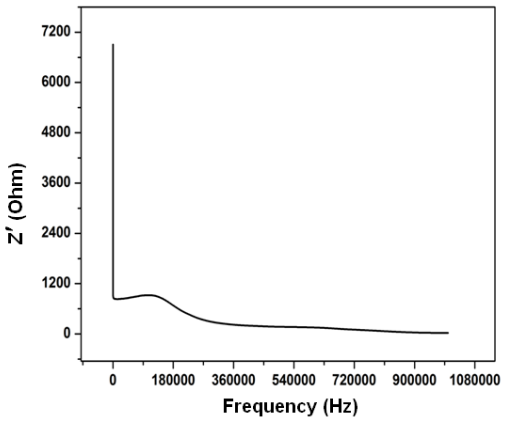

Fig. 6. Real part of impedance *vs* frequency for ZnO NPs.

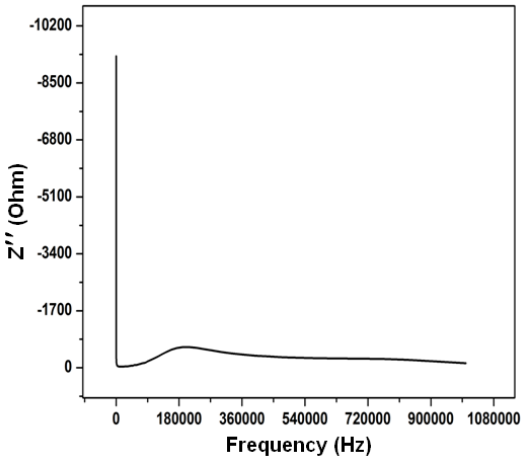

Fig. 7. Imaginary part of impedance *vs* frequency for ZnO NPs.

Figs 6 and 7 show variations of the real and the imaginary part of impedance with frequency. The sharp decrease in both the *Z′* and *Z″* values, when the frequency increases from 12 to 19 kHz, is caused by the space charge polarization effect. The values of *Z′* and *Z″* decrease very slowly when the frequency increases from 4 to 12 kHz and from 4 to 19 kHz. Since space charge polarization is reduced by increasing the frequency, no further decrease in the impedance at higher frequencies was observed.

4. Conclusion

Very low-cost, eco-friendly, surfactant-free biosynthesis method has been used to synthesize ZnO NPs. the crystallite size and structure have been obtained by powder XRD. FTIR studies have confirmed the formation of functional groups and ZnO NPs. Absorbance analysis has revealed that the NPs absorption took place in the UV and visible spectral regions. SEM analysis has confirmed the crystallinity of NPs. It has demonstrated as well that NPs had the sizes in the nanometer range and were collected in aggregates. The impedance analysis of samples rise trend with increasing frequency due to grain boundaries and Cole–Cole plot exhibit semiconductor nature in prepared NPs.

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Indira R.: writing – review & editing.

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Зелений метод отримання наночастинок оксиду цинку з використанням екстрактів листя *Moringa oleifera* та їх структурні, оптичні, та імпедансні спектральні властивості

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Анотація. У цій статті досліджено біосинтез наночастинок оксиду цинку (ZnO) з екстракту з листя *Moringa oleifera* за допомогою екологічного методу. Використовуючи імпедансну спектроскопію, рентгенівську дифракцію порошків, скануючу електронну мікроскопію, інфрачервону Фур'є-спектроскопію та спектроскопію в ультрафіолетовому діапазоні, було проаналізовано кристалічну структуру, оптичні властивості, морфологію та імпедансні характеристики наночастинок ZnO. Порошкові рентгенограми підтвердили кристалічність приготованих зразків, а також дали змогу визначити розмір кристалів і частку чистої фази у них. Дослідження за допомогою інфрачервоної Фур'є-спектроскопії підтвердили наявність функціональних груп, відповідальних за відновлення іонів металу у наночастинки ZnO. Спектри поглинання в ультрафіолетовому діапазоні містили пік поглинання, характерний для наночастинок ZnO. Дослідження з використанням імпедансної спектроскопії приготованих наночастинок ZnO дозволили виявити наявність границь зерен у них та підтвердили їхню напівпровідникову природу.

Ключові слова: частота, імпедансна спектроскопія, екстракт з листя, *Moringa oleifera*, біосинтез, спектри поглинання.