e-ISSN: 2687-6698 **Research Article**

Turkish Journal of Analytical Chemistry
www.turkjac.org
2019

Green synthesis and structural characterization of ZnO nanoparticles and ZnO@TiO_2 nanocomposites by *Cinnamomum verum* bark extract

Gökçenur Selva Keleşoğlu[1], Mesut Özdinçer[2], Aslıhan Dalmaz[3], Kübra Zenkin[1], Sefa Durmuş[3]*

[1] Düzce University, Graduate Education Institute, Department of Chemistry, 81620, Düzce, Türkiye
[2] Düzce University, Graduate Education Institute, Faculty of Technology, Department of Composite - Materials, 81620, Düzce, Türkiye
[3] Düzce University, Faculty of Art and Science, Department of Chemistry, 81620, Düzce, Türkiye

Abstract

In this work, a facile and efficient approach for the green synthesis of ZnO@TiO_2 bimetallic oxide nanoparticles by exploiting the potential of *Cinnamomum verum* bark extract as a biogenic reducing agent is presented. The synthesized nanoparticles were subjected to an extensive characterization process involving various spectroscopic techniques. These techniques include X-ray diffraction analysis, Fourier transform infrared spectroscopy, Scanning electron microscopy and Energy dispersive X-ray spectroscopy. Based on the obtained results, it highlights the potential of green synthesized ZnO@TiO_2 nanocomposites as a promising material for many applications.

Keywords: *Cinnamomum verum*, ZnO@TiO_2 nanocomposites, ZnO NPs, green synthesis

1. Introduction

In recent years, the application of biosynthesis to the production of nanoparticles (NPs) has attracted attention as a more environmentally sustainable, safer and cost-effective alternative to traditional chemical and physical methods [1]. Plant extracts in particular hold great promise for 'green' production due to their widespread availability, affordability, ease of use and scalability [2,3]. These extracts contain a potent combination of antioxidants, including polyphenols, reducing sugars, nitrogenous bases and amino acids, which have the ability to reduce metal ions in a metal salt solution. The reduction of metal ions initiates the formation of nucleation centers which attract additional metal ions and incorporate neighboring nucleation sites, ultimately leading to the formation of nanoparticles. These particles are associated with organic substances from plant extracts which help to increase the stability of the particles. It has also been reported that these nanoparticles have no toxicity compared to those produced by traditional chemical methods [4]. Due to their unique properties compared to their bulk materials, there has been considerable interest in the synthesis and characterization of these nanoparticles particularly metal oxide nanoparticles, in the last decades. The high surface to volume ratio of these nanoparticles is a major factor contributing to their distinctive properties [5–7]. Among metal oxide nanoparticles zinc oxide (ZnO), titanium dioxide (TiO_2) show particularly promising physical and chemical properties [8,19]. Their unique properties make them very important in a wide range of applications [10,11] and research endeavors. Various methods, including chemical [1], sonochemical [12,13], electrochemical, photochemical and microemulsion techniques, are used to produce them. However, many of these methods involve complex reaction conditions and the use of toxic chemicals, leading to environmental pollution problems. As a result, researchers have sought to develop environmentally friendly methods for the synthesis of nanoparticles

Cinnamomum verum (*C. verum*), commonly known as cinnamon, is a very abundant, economical and easily available plant. It is known to be rich in phytochemicals such as alkaloids, polyphenolic compounds, terpenoids and flavonoids, which act as stabilizing and capping

Citation: G.S. Keleşoğlu, M. Özdinçer, A. Dalmaz, K. Zenkin, S. Durmuş, Green Synthesis and Structural Characterization of ZnO Nanoparticles and ZnO@TiO_2 Nanocomposites by *Cinnamomum verum* Bark Extract Turk J Anal Chem, 5(2), 2023, 118–123.
https://doi.org/10.51435/turkjac.1395817

Author of correspondence: sefadurmus@duzce.edu.tr
Tel: +90 (380) 541 24 04
Fax: +90 (380) 541 24 03

Received: November 25, 2023
Accepted: December 06, 2023

agents during the synthesis process [14]. Moreover, the bark of *C. verum* contains a notable concentration of carboxylic and phenolic functional groups, such as bisabolol, cinnamic acid, heptanoic acid, hexadecenoic acid, linalool, and phytol [15]. However, it is of great importance to identify accurately the specific phytochemicals responsible for the formation of nanoparticles with controlled properties. This understanding can significantly contribute to the utilization of cinnamon in various applications, especially in the field of nanotechnology [16,17].

As a result, it has become essential to investigate synthesis routes for ZnO NPs and TiO_2 nanocomposites and to explore their properties and applications through extensive research. In this context, our study aims to investigate the synthesis of ZnO@TiO_2 nanocomposites using *C. verum* bark extract, which is a sustainable and environmentally friendly approach

2. Materials and methods

2.1. Reagents and chemicals

Cinnamomum verum, used as a stabilizing and reducing agent in the study (Fig. 1), was obtained from local markets in Düzce province. In addition, all of the chemical materials used in the study are of analytical purity. Sodium hydroxide, zinc nitrate hexahydrate and titanium(IV)isopropoxide chemicals used in the synthesis stage of metal oxide nanoparticles were obtained from Merck company.

Figure 1. Image of *Cinnamomum verum* bark

2.2. Apparatus

Heidolph brand magnetic stirrer was used to ensure homogeneous mixing of the solutions throughout the experimental studies. An Isolab brand pH meter was used to ensure that the nanoparticles precipitated appropriately. Elektromag M5040P brand oven was used to dry the synthesized products. Radwag brand electronic balance was used throughout the experimental studies. Separation of the products was carried out using a VWR brand centrifuge. Filtration of *C. verum* extract and nanoparticles obtained through the extract was carried out using an Isolab brand vacuum pump. The elemental composition of the nanoparticles obtained as a result of the studies was determined by energy dispersive X-ray analysis (EDX), and their morphology and size were determined by scanning electron microscopy (SEM) (FEI Quanta FEG 250).

The functional groups present in the structure of the nanoparticles were recorded using a Perkin Elmer Spectra Two UATR Fourier transform infrared spectroscopy (FT-IR) spectrophotometer. X-ray diffraction (XRD) patterns of ZnO NPs and ZnO@TiO_2 nanocomposites were obtained using a Smart Lab instrument with Cu-Kα radiation (1.5406 Å).

2.3. Preparation of *Cinnamomum verum* bark extract

Cinnamomum verum was first obtained from local markets and ground into powder. The powdered cinnamon was washed several times with deionized water to remove impurities. Following this step, to prepare extract, 2.5 g *C. verum* bark was heated in 100 mL deionized water for one hour in a magnetic stirrer. After this time, the extract (Fig. 2) was allowed to cool at room temperature and filtered with Whatman filter paper. It was stored in the refrigerator at 4 °Cto be used for the synthesis of ZnO NPs and ZnO@TiO_2 nanocomposites.

Figure 2. Schematic representation of the preparation steps of *C. verum* bark extract

2.4. Green synthesis of ZnO NPSs

In order to synthesize ZnO NPs, 25 mL *C. verum* bark extract was heated to 60 °Cand 2.08 g $Zn(NO_3)_2.6H_2O$ was dissolved in 25 mL deionized water and added. The resulting solution was stirred with a magnetic stirrer at 60 °C for one hour color change were observed. Following this step, 0.1 M NaOH was added to adjust the pH of the solution to 8. The mixture was centrifuged at 5000 rpm for 7 min. and then washed several times with deionized water. The resulting product was then dried in an oven at 60 °C for 24 hours. After the drying step was completed, it was subjected to calcination at 450 °C for 2.5 hours. The white-colored ZnO NPs formed as a result of calcination was stored in a desiccator at room temperature (Fig. 3).

Figure 3. Schematic representation of the preparation steps of ZnO NPs

2.5. Green synthesis of ZnO@TiO$_2$ nanocomposites

Cinnamomum verum bark extract was heated to 60 °C, then a solution of 2.97 g Zn $(NO_3)_2.6H_2O$ in 10 mL deionized water was added slowly. To this solution 0.1 M NaOH was added until pH = 8, then 3 mL of titanium(IV) isopropoxide was added slowly and stirring was continued at 60 °C for one hour on a magnetic stirrer. The resulting mixture was centrifuged at 5000 rpm for 7 min. and the product was washed several times with deionized water to remove impurities. It was then placed in an oven to dry at 60 °C for 24 hours. The dried product was then subjected to calcination in a muffle furnace at 450 °C for 2.5 hours (Fig. 4) and the off-white-colored product was stored in a desiccator for analysis.

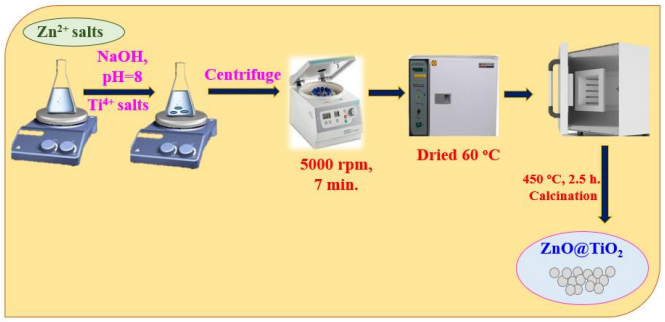


Figure 4. Schematic representation of the preparation steps of ZnO@TiO$_2$ nanocomposites

3. Results and discussion

3.1. FT-IR spectra

FT-IR spectroscopy analysis was carried out to determine the presence of functional biomolecular groups in *C. verum* extract and synthesized ZnO NPs and ZnO@TiO$_2$ nanocomposites. When the FT-IR spectrum of *C. verum* shown in Fig. 5 is examined, the bands at 3271 and 2928 cm^{-1} are due to O-H stretching vibrations in the structure of polyphenols and asymmetric C-H stretching vibrations of -CH_3 groups in the structure of biomolecules. The presence of the O-H group in the structure of water is indicated by the peak at 1586 cm^{-1} in the FT-IR spectrum. Also observed at 1408 cm^{-1} and 1386 cm^{-1} are peaks belonging to aliphatic C-H stretching and CH_3 symmetric bending vibrations. The C-O stretch vibration of hydroxy flavonoids in the biostructure of *C. verum* is seen at 1260 cm^{-1}, while the band at 1043 cm^{-1} is related to the C-O stretch of primary alcohols. The peak corresponding to the C=C vibrations in the structure of the benzene ring was observed at 614 cm^{-1} [18-20]. In the FT-IR spectrum of ZnO NPs, only the peak at 402 cm^{-1} belonging to Zn-O bond was observed. Moreover, in the FT-IR spectrum of ZnO@TiO$_2$ nanocomposites, vibrations at 402 cm^{-1} are attributed to Zn-O bond [21,22] and vibrations at 388 cm^{-1} to Ti-O bond. When the FT-IR spectra of ZnO NPs and ZnO@TiO$_2$ nanocomposites were analyzed, no vibrations belonging to organic compounds in the structure of cinnamon extract were observed.

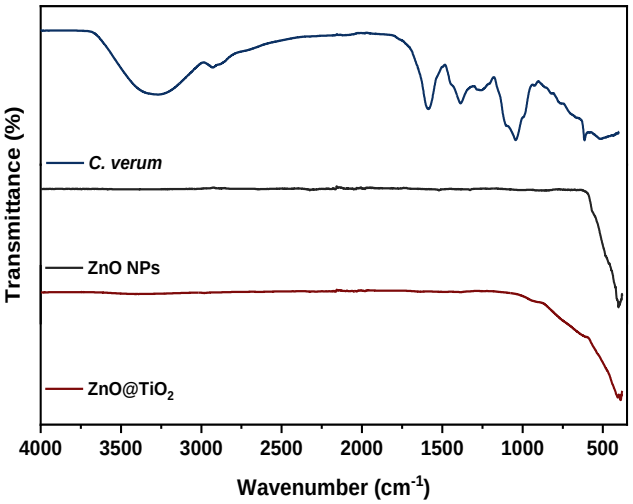


Figure 5. FT-IR spectra of dry C. verum extract, ZnO NPs and ZnO@TiO$_2$ nanocomposites

3.2. XRD analysis

In the XRD pattern of ZnO NPs and ZnO@TiO$_2$ nanocomposites are shown in Fig. 6. Different peaks were observed in the XRD pattern of ZnO NPs at 2θ=31.82°, 34.45°, 36.29°, 47.60°, 56.63°, 62.91°, 66.46°, 67.98°, 69.06°, 72.63° and 77.06°. These peaks were interrelated to (100), (002), (101), (102), (110), (103), (200), (112), (201), (004) and (202) hkl planes. All these diffraction peaks are consisted to wurtzite (hexagonal) structure compatible with JCPDS Card No. 036-1451 [23] and space group: $P6_3mc$ [24]. Moreover, the cell parameters of the ZnO NPs a= b= 3.24 Å, and c= 5.20 Å. The absence of distinct peaks in the XRD pattern indicates that the nanoparticles do not contain impurities. In the XRD pattern of ZnO@TiO$_2$ nanocomposites, in addition to the peak belonging to ZnO NPs, 25.41° and the associated (101) hkl planes of the anatase phase (space group: $I4_1/amd$) of TiO$_2$ with JCPDS card no. 21-1272 are shown [25].

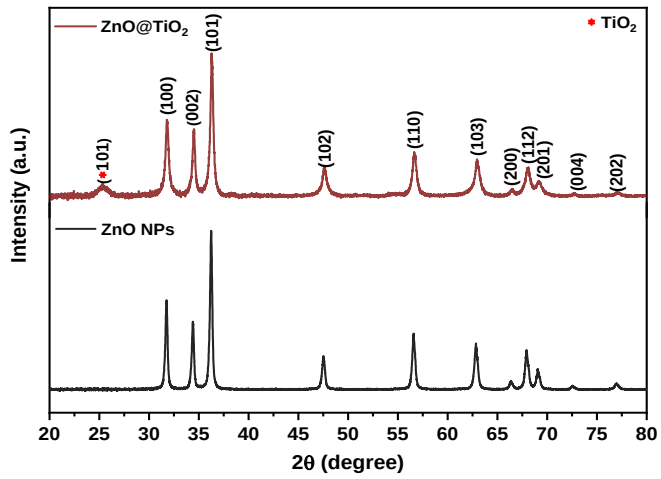
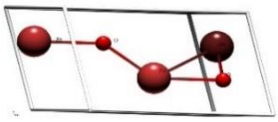
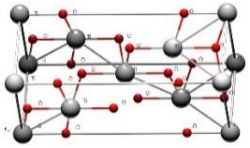


Figure 6. XRD pattern of ZnO NPs and ZnO@TiO$_2$ nanocomposites

Table 1. The structural parameters of ZnO and TiO_2 NPs.

Sample	JCPDS Card no:	Crystal Structure	Space Group	Lattice Parameters (Å)	Cell Volume (Å^3)	Unit Cell
ZnO	036-1451	Hexagonal	$P6_3mc$	a= b= 3.24 c= 5.20	54.58	
TiO_2	21-1272	Anatase	$I4_1/amd$	a= b= 3.80 c= 9.61	138.76	

The cell parameters of the TiO_2 NPs a= b= 3.80 Å, and c= 9.61 Å as shown in Table 1. In addition, the weight fraction of ZnO@TiO_2 nanocomposites was determined using the Whole Powder Pattern Fitting (WPPF) method, which approximates the components and fraction of the sample based on the measured XRD pattern and the materials [26]. According to WPPF weight fraction analysis, ZnO@TiO_2 nanocomposites consists of 89% ZnO and 11% TiO_2 NPs.

3.3. SEM-EDX analysis

The SEM images in Fig. 7(a-c) depict the surface morphology of green-synthesized ZnO NPs and ZnO@TiO_2 nanocomposites using *C. verum* extract. The ZnO NPs exhibit hexagonal and near-spherical shapes, with some irregularities indicating non-homogeneity [27,28]. The particle size of ZnO NPs falls within the range of 30 - 50 nm, and there is a noticeable tendency for slight agglomeration (Fig. 7(a)).

Recent studies have shown that there is an optimum amount of TiO_2 that is effective in inhibiting growth and phase transformation of ZnO NPs, leading to production of smaller ZnO NPs [29]. This method resulted in obtaining ZnO@TiO_2 nanocomposites with an average size of 20 nm, as shown in Fig. 7 (b, c). The surface morphology of the ZnO@TiO_2 nanocomposites shows the presence of both spherical and hexagonal shapes. In addition, TiO_2 NPs are widely dispersed on the surface of the ZnO@TiO_2 nanocomposites.

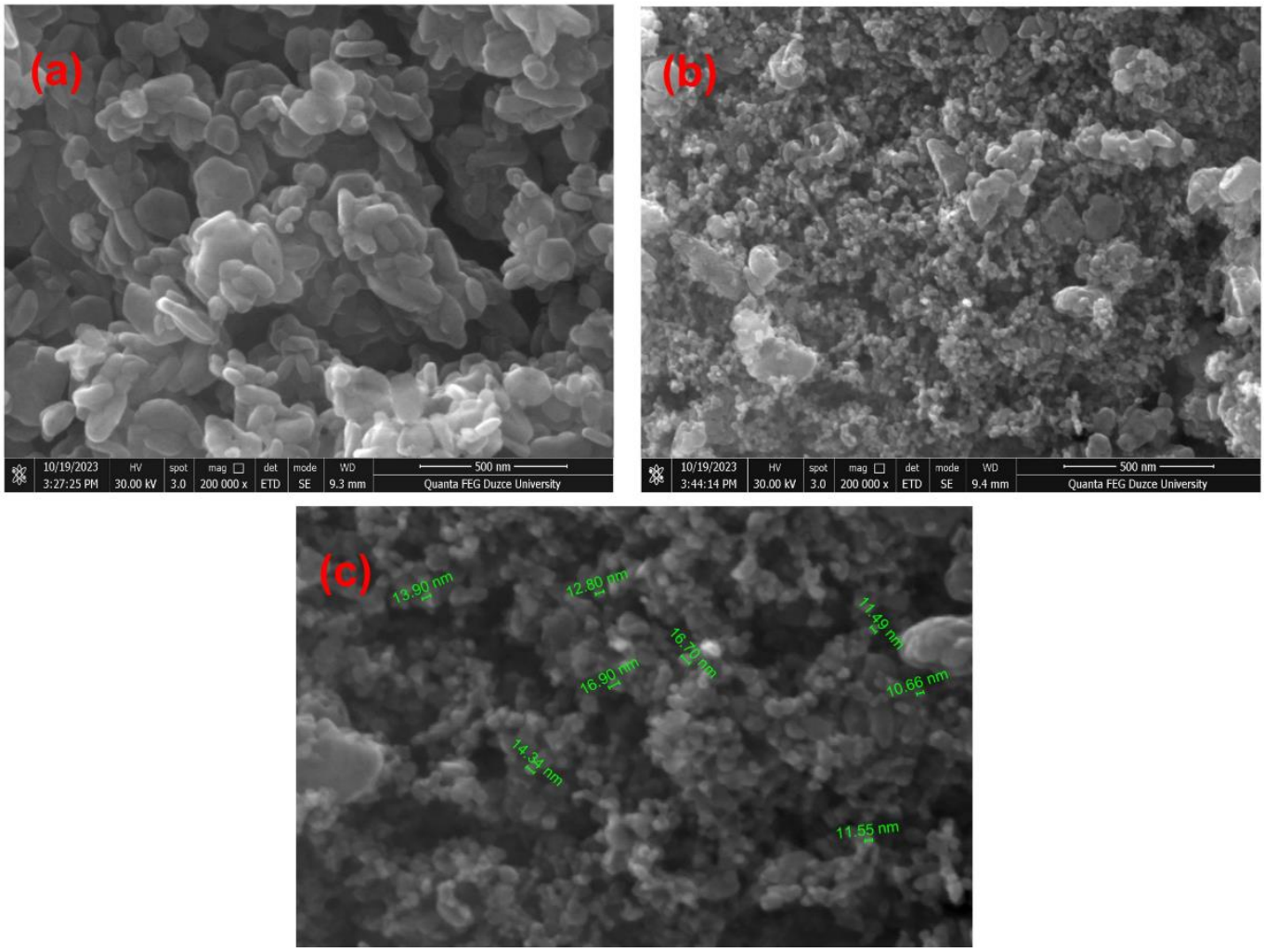


Figure 7. SEM images of the synthesized (a) ZnO NPs (b, c) ZnO@TiO_2 nanocomposites

Energy dispersive X-ray spectroscopy, a mode of operation of SEM, is used to determine the elemental composition of nanomaterials and provides information on the percentage of each element in the materials (Fig. 8). The presence of oxygen, titanium and zinc elements were observed in the EDX spectra of ZnO NPs and ZnO@TiO_2 nanocomposites. The stoichiometric ratios seen in the spectra are compatible with the proposed structure and it is seen from these ratios that the amount of TiO_2 doped corresponds to 10.8% [30].

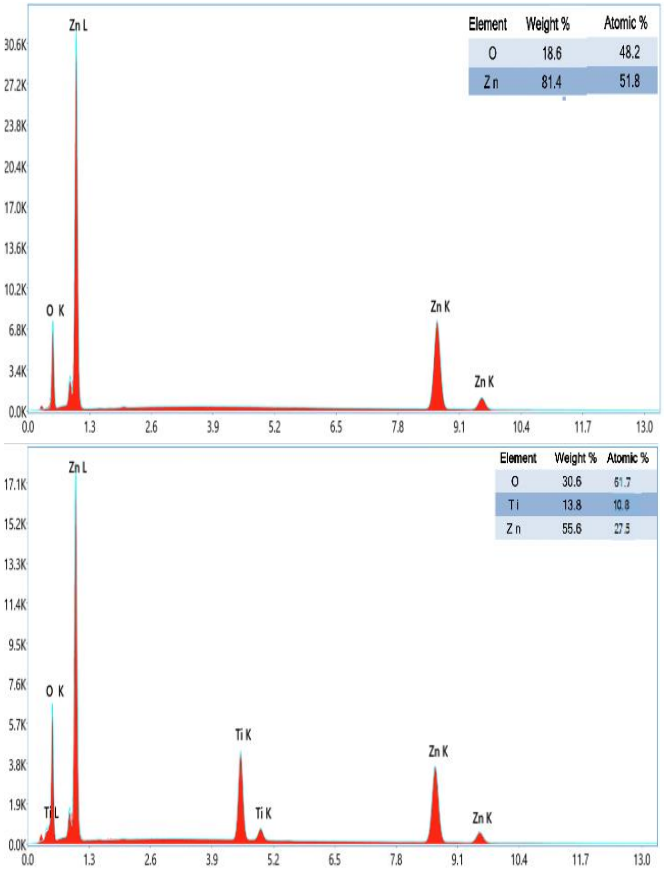


Figure 8. EDX analysis of the synthesized (a) ZnO NPs (b) ZnO@TiO_2 nanocomposites

4. Conclusion

In this study, ZnO NPs and ZnO@TiO_2 nanocomposites were synthesized using aqueous extract of *C. verum* as natural chelating agent that stabilizes and aid in the bioreduction of the nanoparticles without using any harmful surfactant. FT-IR and XRD results show that ZnO NPs and ZnO@TiO_2 nanocomposites are free from any organic compounds and impurities. According to SEM results, ZnO NPs and ZnO@TiO_2 nanocomposites have hexagonal, spherical particles with an average shape of 40 nm and 20 nm respectively. The EDX results indicated that, the amount of TiO_2 addition was found to be 10.8%, which is in agreement with the XRD analysis value calculated by the WPPF method. Furthermore, the EDX spectrum exhibited no impurities in the compound's structure. ZnO NPs and ZnO@TiO_2 nanocomposites have more extensive application in biotechnology, optical device, medical, sensors, coatings, catalysis and drug delivery. This green synthesis is a highly efficient approach, using fewer chemicals and controlling costs. This has led to additional research to investigate the further implementation of environmentally friendly nanoparticles.

Acknowledgement

This work is supported by Düzce University Scientific Project (Project no: 2022.05.03.1365).

References

[1] L. Krishnia, P. Thakur, A. Thakur, Synthesis of nanoparticles by physical route, in synthesis and applications of nanoparticles (1. Edition), 2022, Singapore: Springer Nature.

[2] L. Soltys, O. Olkhovyy, T. Tatarchuk, M. Naushad, Green synthesis of metal and metal oxide nanoparticles: principles of green chemistry and raw materials, Magnetochem, 7, 2021, 145.

[3] M. Jamzad, B. Mokhtari, P.S. Mirkhani, Green synthesis of metal nanoparticles mediated by a versatile medicinal plant extract, Chem Pap, 77, 2022, 1457–1467.

[4] D. Gnanasangeetha, M. Suresh, A review on green synthesis of metal and metal oxide nanoparticles, Nat Environ Pollut Technol, 19, 2020, 1789–1800.

[5] M.P. Nikolova, M.S. Chavali, Metal oxide nanoparticles as biomedical materials, Biomimetics, 5, 2020, 27.

[6] J.J. Xu, W.C. Zhang, Y.W. Guo, X.Y. Chen, Y.N. Zhang, Metal nanoparticles as a promising technology in targeted cancer treatment, Drug Deliv, 29, 2022, 664–678.

[7] P. Prasannalakshmi, N. Shanmugam, Fabrication of TiO_2/ZnO nanocomposites for solar energy driven photocatalysis, Mater Sci Semicond Process, 61, 2017, 114–124.

[8] N. Geetha, S. Sivaranjani, A. Ayeshamariam, M. Kavin Micheal, D. Saravankkumar, S. A. Fowziya, A.M Uduman Mohideen, M. Jayachandran, ZnO/TiO_2 nanocomposites semiconductor for bacterial applications and dye-sensitized solar cell applications, J Adv Microsc Res,13, 2018, 3–11.

[9] G.K. Upadhyay, J.K. Rajput, T.K. Pathak, V. Kumar, L.P. Purohit, Synthesis of ZnO:TiO_2 nanocomposites for photocatalyst application in visible light, Vacuum, 160, 2019, 154–163.

[10] M. Özdinçer, S. Durmuş, Fabrication, characterization and corrosion inhibition properties of SCW-based ZnO nanofluids, Chem Eng Commun, 2023, 1–16.

[11] K. Akshaya, A. Rajasekar, S. Rajeshkumar, Antioxidant activity of zinc oxide nanoparticles synthesized using grape seed extract: An in vitro study, Plant Cell Biotechnol. Mol Biol, 21, 2020, 21–29.

[12] A. Hassanjani-Roshan, M.R. Vaezi, A. Shokuhfar, Z. Rajabali, Synthesis of iron oxide nanoparticles via sonochemical method and their characterization, Particuology, 9, 2011, 95–99.

[13] M. Darroudi, A. Khorsand Zak, M.R. Muhamad, N.M. Huang, M. Hakimi, Green synthesis of colloidal silver nanoparticles by sonochemical method, Mater Lett, 66, 2012, 117–120.

[14] P.V. Rao, S.H. Gan, Cinnamon: A multifaceted medicinal plant, Evid Based Complement Alternat Med, 2014, 2014.

[15] H.H. Phu, K. Pham Van, T.H. Tran, D.T.N. Pham, Extraction, chemical compositions and biological activities of essential oils of *Cinnamomum verum* cultivated in Vietnam, Process, 10, 2022, 1713.

[16] M.A. Alghuthaymi, A.M. Diab, A.F. Elzahy, K.E. Mazrou, A.A. Tayel, S.H. Moussa, Green biosynthesized selenium

nanoparticles by cinnamon extract and their antimicrobial activity and application as edible coatings with nano-chitosan, J Food Qual, 2021, 2021,1–10.

[17] X. Zhu, K. Pathakoti, H.M. Hwang, Green synthesis of titanium dioxide and zinc oxide nanoparticles and their usage for antimicrobial applications and environmental remediation, Green Synthesis, Characterization and Applications of Nanoparticles, Editors: A.K Shukla, S. Iravani, 2018, Elsevier.

[18] H. Özcan, A. Dalmaz, M. Özdinçer, K. Zenkin, S. Durmuş, Biosynthesis and characterization of α-FeOOH nanoparticles using Isabella grape (*Vitis labrusca* L.) extract, Turk J Anal Chem, 5, 2023, 43–49.

[19] F. Mojarrad, A. Asadi, A. Abdolmaleki, S. Mirzaee, S. Zahri, Preparation of cinnamon-coated cerium oxide nanoparticles and evaluation of their anticonvulsant effect in rats, Pharm Chem J, 57, 2023, 648–655.

[20] A. Sameen, S. Fathima, S. Ramlal, S. Kumar, F. Khanum, Nanopackaging of silver using spice extract and their characterization, Sci Technol Arts Res J, 3, 2014, 52–56.

[21] R. Bekem, S. Durmuş, A. Dalmaz, G. Dülger, *Agaricus bisporus* Ekstraktı Kullanılarak ZnO Nanopartiküllerinin Yeşil Sentezi: Yapısal Karakterizasyonu ve Biyolojik Aktivitelerinin İncelenmesi, DÜBİTED, 11, 2023, 551–562.

[22] S.N. Gençay, S. Durmuş, A. Dalmaz, G. Dülger, Ticari Bal Kullanılarak ZnO Nanopartiküllerinin Yeşil Sentezi, Yapısal Karakterizasyonu ve Biyolojik Aktivitelerinin İncelenmesi, DÜBİTED, 11, 2023, 1437–1445.

[23] T. Bezrodna, G. Puchkovska, V. Shymanovska, J. Baran, H. Ratajczak, IR-analysis of H-bonded H_2O on the pure TiO_2 surface, J Mol Struct, 700, 2004, 175–181.

[24] F.A. Alharthi, A.A. Alghamdi, N. Al-Zaqri, H.S. Alanazi, A.A. Alsyahi, A.E. Marghany, N. Ahmad, Facile one-pot green synthesis of Ag–ZnO nanocomposites using potato peeland their Ag concentration dependent photocatalytic properties, Sci Rep, 10, 2020, 20229.

[25] S. Kumar, D. Arora, A. Dhupar, V. Sharma, J.K. Sharma, S.K. Sharma, A. Gaur, Structural and optical properties of polycrystalline ZnO nanopowder synthesized by direct precipitation technique, J Nano-Electron Phys, 12, 2020, 04027-1-04027–5.

[26] R. Nawaz, H. Ullah, A.A.J. Ghanim, M. Irfan, M. Anjum, S. Rahman, S. Ullah, Z.A. Baki, V. Kumar Oad, Green synthesis of ZnO and black TiO_2 materials and their application in photodegradation of organic pollutants, ACS Omega, 8, 2023, 36076–36087.

[27] D. Negrea, E. David, V. Malinovschi, S. Moga, C. Ducu, X-ray analysis of spent catalysts and recovered metals, Environ Eng Manag J, 9, 2010, 1235–1241.

[28] D. Ramírez-Ortega, A.M. Meléndez, P. Acevedo-Peña, I. González, R. Arroyo, Semiconducting properties of ZnO/TiO_2 composites by electrochemical measurements and their relationship with photocatalytic activity, Electrochim Acta, 140, 2014, 541–549.

[29] A. Hossain, Y. Abdallah, M.A. Ali, M.M.I. Masum, B. Li, G. Sun, Y. Meng, Y. Weng, Q. An, Lemon-fruit-based green synthesis of zinc oxide nanoparticles and titanium dioxide nanoparticles against soft rot bacterial pathogen *Dickeya dadantii*, Biomol, 9, 2019, 863.

[30] M. Zamani, M. Rostami, M. Aghajanzadeh, H. Kheiri Manjili, K. Rostamizadeh, H. Danafar, Mesoporous titanium dioxide@zinc oxide–graphene oxide nanocarriers for colon-specific drug delivery, J Mater Sci, 53, 2018, 1634–1645.