Microwave assisted green synthesis of ZnO nanotubes using *Amorphophallus paeoniifolius* tuber extract.

P Naresh Kumar¹, B Vijayakumar¹ and R Ranjith²

¹ Department of Physics, SNS College of Technology, Coimbatore, Tamil Nadu, India.
² Department of Mechatronics Engineering, SNS College of Technology, Coimbatore, Tamil Nadu, India.

**Abstract.** Green nanoparticle synthesis is gaining significant interest and is the perfect alternative to the chemical and physical synthesis process. This paper introduces a novel plant-mediated microwave-assisted green synthesis of Zinc Oxide (ZnO) nanotubes using *Amorphophallus paeoniifolius* tuber extract. In the nanoparticle synthesis process, the tubers phytochemicals serve as a reducing agent and a bio template. The synthesized nanoparticles are exposed to microwave radiation for 15 minutes and are then annealed at 400°C for 1 hour. The green synthesized nanoparticles are analyzed with XRD, UV-Vis spectroscopy, HRTEM, EDX, and FTIR spectroscopy. Subsequently, TEM images depict the tube-shaped ZnO NPs with d-spacing of 2.3Å. The XRD confirms the wurtzite phase with 14 nm as mean particle size.

**Keywords:** Nanoparticles; Semiconductors; green synthesis; *Amorphophallus paeoniifolius*; ZnO

1. Introduction

In recent years, the usage of nanoparticles is widely increasing in various fields. Among different metal oxide nanoparticles, ZnO NPs have been a matter of interest due to their attractive optical [1], semiconducting [2], and good catalytic properties [3]. These remarkable properties make the ZnO NPs used in several industrial and medicinal sectors like solar panels, transducers, piezoelectric devices, antimicrobial drugs, and cosmetics [4-8]. It is necessary to progress a simple, environmentally friendly, and cost-effective process to synthesis ZnO NPs. These ZnO NPs presently synthesized in bulk quantities by hydrothermal method, sol-gel method, Electro-chemical method, and sonochemical process [9-13]. These methods involve time-consuming, complicated procedures and toxic chemicals. Green synthesis involving bio-extracts could be the best alternative synthesis method to conventional methods and overcome their drawbacks. The bio-extracts act as a template and reduces the precursors to yield ZnO NPs. Extracts from *Citrus aurantifolia* fruit [14], *Azadirachta indica* leaves [15], *Eichhornia crassipes* leaves [16] reported in the literature to synthesis ZnO NPs.

In this article, a unique method is reported to synthesis ZnO nanotubes employing water based extracts of *Amorphophallus paeoniifolius* tubers. The biomolecules present in the tuber's reduces the precursor to form metal ions. Also these biomolecules structure provide a base template over which the metal ions gets anchored. *Amorphophallus paeoniifolius* have its place in the Araceae family, commonly known as "elephant foot yam." It is most commonly cultivated and taken as food in many
south-eastern regions of the world. The tuber contains 11-28% of starch, 0.7-1.7% of sugar and 0.8-2.6% of protein [17]. The tuber extract contains proteins, flavonoids, tannins, and carbohydrates [18], reducing agents. After synthesizing, the ZnO NPs are primarily subjected to microwave irradiation, for rapid and homogenous drying.[19].

2. Materials and methods
2.1. Materials
Precursor Zinc acetate dihydrate (99%) bought from Sigma-Aldrich. The Amorphophallus paeoniifolius tubers were collected from near by farm house located at Coimbatore, Tamilnadu.

2.2 Amorphophallus paeoniifolius tuber extract preparation process
Tubers are cleansed with normal water and then by de-ionized water to eliminate the impurities like mud particles present over its surface. The outer layer is removed from the tubers and the inner edible corn part alone is taken for extract preparation. 20 gm of the sliced corn is boiled in 500 ml of deionised water. Then the extract is decanted and kept in a closed container.

2.3 Green synthesis of ZnO NPs
0.2M of zinc acetate dihydrate solution is taken for the synthesis process. 25 ml of aqueous tuber concentrate is added to the precursor solution and was stirred at 80°C for 30 min the formation of the pale yellow color precipitate. The end mixture is decanted and the microwave dried for 5 min, A pale white powder obtained as an end product and it is annealed at a temperature of 400°C in muffle funace for 1 hr in a silica crucible.

2.4 Characterization of ZnO NPs
Zinc oxide nanoparticles were characterized and analysed for crystallinity, chemical composition, structure of the prepared ZnO NPs were analyzed using an X-ray diffractometer with Rigaku Rint 200 model, Energy Dispersive X-ray analysis with SIGMA HV – Carl Zeiss with Bruker Quantax 200 – Z10 EDS model , HR-TEM with JEOL, JEM-2100 make equipments respectively. The UV-Vis absorbance spectrum of the prepared ZnO NPs recorded with a UV-Vis spectrophotometer of Jasco V-570 make. FTIR spectroscopy usages to analyze and detect the functional group present in the prepared ZnO NPs (Bruker, Alpha-E).

Figure 1. (a) & (b) XRD & EDAX images of synthesized ZnO NPs
3. Results and discussion

Figure 1(a) shows the synthesized ZnO NPs’ X-ray diffraction patterns. The high spikes were noted at angles \( (2\theta) \) 32.57\(^\circ\), 35.13\(^\circ\), 37.02\(^\circ\), 47.92\(^\circ\), 57.02\(^\circ\), 63.32\(^\circ\), 68.28\(^\circ\), 69.52\(^\circ\), 77.42\(^\circ\) corresponding to miller indices (100), (002), (101), (102), (110), (103), (201), (112), (202) positions indicate the prepared ZnO NPs are exhibiting wurtzite structure. The average grain size has been calculated to be 14 nm using the below formula
\[
d = \frac{0.89\lambda}{\beta \cos \theta}
\]

Figure 1(b) indicates the EDAX spectrum of prepared ZnO NPs. The high spike indicates the existence of Zinc and oxygen with weight % of 74.67\% and 25.33\% respectively.

The TEM and HRTEM analysis helps to investigate further the crystalline structure with the morphology of prepared ZnO NPs. As seen in Figure. 3(a) & 3(b), the ZnO NPs have tube-like morphology with diameter 29.12 nm and 32.76 nm. The selected area electron diffraction image of synthesized ZnO NPs shown in Figure. 2(c). The picture indicates a ring pattern with some scattered diffraction spots, indicating the crystallinity of ZnO NPs. Figure. 2(d) shows the HRTEM images taken at 5 nm resolution, which depicts d-spacing of 2.3 Å.

**Figure. 2** (a) & (b)TEM images of green synthesized ZnO nanotubes at different magnifications, (c) SAED pattern, and (d) HRTEM image of synthesized ZnO NPs at 5nm magnification.
Figure 3 (a) & (b) The UV-Vis spectroscopy & FTIR spectrum of prepared ZnO NPs respectively.

Figure 3(a) shows the UV-Vis absorption spectra graph of prepared ZnO NPs. An absorption peak at the wavelength of 373 nm indicates ZnO NPs intrinsic energy bandgap of 3.32 eV. Using the formula

$$E = \frac{hc}{\lambda}$$  \hspace{1cm} (2)

Where

h is Planck's constant,

c is the velocity of light,

\(\lambda\) is the wavelength, which is in agreement with the previous studies.

Figure 3(b) indicates the graph of FT-IR spectroscopy analysis of prepared ZnO NPs. The absorption peaks were found in the between wavenumbers 4000 cm\(^{-1}\) to 500 cm\(^{-1}\), corresponding to the vibration modes of compounds namely alkane, carboxylate, carboxyl & hydroxyl members present in the nanoparticles. Also, spectral graph show the absorption band at wavenumber 3330 cm\(^{-1}\) represents the O-H stretching vibration of H\(_2\)O and in 2937 cm\(^{-1}\) represents the C-H stretching mode vibrations of alkane groups present in the prepared ZnO NPs. Absorption peak at 2340 cm\(^{-1}\) arises due to the presence of carbon-di-oxide molecule on the ZnO nanoparticle during the drying process. Peaks observed at 1592 cm\(^{-1}\), 1484 cm\(^{-1}\) and 1376 cm\(^{-1}\) are mainly due to the Carbon monoxide and, carboxylate group (COO\(^{-}\)), and bending vibration of –CH\(_2\) respectively. The peaks at 1035 cm\(^{-1}\) indicate the stretching vibration C-O. The peak at 824 cm\(^{-1}\) represents the bending mode of carbonate group. The prominent Zn-O stretching mode vibrations was seen at the infrared region at the wave number 563 cm\(^{-1}\).

4. Conclusion

In this paper, a microwave-assisted simple, cheaper, and eco-friendly method to synthesis ZnO NPs using *Amorphophallus paeoniifolius* tuber was reported for the first time. The *Amorphophallus paeoniifolius* tuber extract acts as a reducing agent and as a bio-template of the synthesis process. The green synthesized ZnO nanotubes have an average particle size of 14 nm with
an energy band gap of 3.32 eV. Therefore this method adopts for bulk synthesis of ZnO nanotubes to prepare transducers, photoelectrodes, etc.

References

[1] Akermi M, Jaballah N, Alarifi IM, Rahimi-Gorji M, Chaabane RB, Ouada HB, Majdoub M. Synthesis and characterization of a novel hydride polymer P-DSBT/ZnO nano-composite for optoelectronic applications. *Journal of Molecular Liquids*. 2019 Aug 1;287:110963.

[2] Isai KA, Shrivastava VS. Photocatalytic degradation of methylene blue using ZnO and 2% Fe–ZnO semiconductor nanomaterials synthesized by sol–gel method: a comparative study. *SN Applied Sciences*. 2019 Oct 1;1(10):1247.

[3] Ganesh M, Lee SG, Jayaprakash J, Mohankumar M, Jang HT. Hydnocarpus alpina Wt extract mediated green synthesis of ZnO nanoparticle and screening of its anti-microbial, free radical scavenging, and photocatalytic activity. *Biocatalysis and agricultural biotechnology*. 2019 May 1;19:101129.

[4] Neupane GR, Kaphle A, Hari P. Microwave-assisted Fe-doped ZnO nanoparticles for enhancement of silicon solar cell efficiency. *Solar Energy Materials and Solar Cells*. 2019 Oct 1;201:110073.

[5] Rahamanian R, Mozaffari SA, Amoli HS, Abedi M. Development of sensitive impedimetric urea biosensor using DC sputtered Nano-ZnO on TiO2 thin film as a novel hierarchical nanostructure transducer. *Sensors and Actuators B: Chemical*. 2018 Mar 1;256:760-74.

[6] Yadav H, Sinha N, Goel S, Kumar B. Eu-doped ZnO nanoparticles for dielectric, ferroelectric and piezoelectric applications. *Journal of Alloys and Compounds*. 2016 Dec 25;689:333-41.

[7] Suresh J, Pradheesh G, Alexramani V, Sundrarajan M, Hong SI. Green synthesis and characterization of zinc oxide nanoparticle using insulin plant (Costus pictus D. Don) and investigation of its antimicrobial as well as anticancer activities. *Advances in Natural Sciences: Nanoscience and Nanotechnology*. 2018 Feb 2;9(1):015008.

[8] Awan F, Islam MS, Ma Y, Yang C, Shi Z, Berry RM, Tam KC. Cellulose nanocrystal–ZnO nanohybrids for controlling photocatalytic activity and UV protection in cosmetic formulation. *ACS omega*. 2018 Oct 1;3(10):12403-11.

[9] Hessien M, Da'na E, Taha A. Phytoextract assisted hydrothermal synthesis of ZnO–NiO nanocomposites using neem leaves extract. *Ceramics International*. 2021 Jan;47(1):811-6.

[10] Ismail AM, Menazea AA, Kabary HA, El-Sherbiny AE, Samy A. The influence of calcination temperature on structural and antimicrobial characteristics of zinc oxide nanoparticles synthesized by Sol–Gel method. *Journal of Molecular Structure*. 2019 Nov 15;1196:332-7.

[11] Chattopadhyay S, Misra KP, Agarwala A, Shahee A, Jain S, Halder N, Rao A, Babu PD, Saran M, Mukhopadhyay AK. Dislocations and particle size governed band gap and ferromagnetic ordering in Ni doped ZnO nanoparticles synthesized via co-precipitation. *Ceramics International*. 2019 Dec 1;45(17):23341-54.

[12] Mika K, Socha RP, Nyga P, Wiercigroch E, Malek K, Jarosz M, Uchacz T, Sulka GD, Zaraska L. Electrochemical synthesis and characterization of dark nanoporous zinc oxide films. *Electrochimica Acta*. 2019 May 10;305:349-59.

[13] Alothman AA, Albaqami MD. Nano-sized Cu (II) and Zn (II) complexes and their use as a precursor for synthesis of CuO and ZnO nanoparticles: A study on their sonochemical synthesis, characterization, and DNA-binding/elevage, anticancer, and antimicrobial activities. *Applied Organometallic Chemistry*. 2020 Oct;34(10):e5827.

[14] Durmuş A, Çolak H, Karaköse E. Production and examination of ZnO thin film for first time using green synthesized method from aqueous Citrus reticulata peel extract. *Journal of Alloys and Compounds*. 2019 Nov 15;809:151813.
[15] Saravanan P, SenthilKannan K, Divya R, Vimalan M, Tamilselvan S, Sankar D. A perspective approach towards appreciable size and cost-effective solar cell fabrication by synthesizing ZnO nanoparticles from Azadirachta indica leaves extract using domestic microwave oven. *Journal of Materials Science: Materials in Electronics*. 2020 Mar;31(5):4301-9.

[16] Ramanathan S, Selvin SP, Obadijah A, Durairaj A, Santhoshkumar P, Lydia S, Ramasundaram S, Vasanthkumar S. Synthesis of reduced graphene oxide/ZnO nanocomposites using grape fruit extract and Eichhornia crassipes leaf extract and a comparative study of their photocatalytic property in degrading Rhodamine B dye. *Journal of Environmental Health Science and Engineering*. 2019 Jun 1;17(1):195-207.

[17] Rahman SS, Muhsin MM, Karim MR, Zubaer M, Rahman MH, Rouf SM. Proximate composition, phytochemical screening and anti-hyperglycemic effect of elephant foot yam (Amorphophallus paeoniifolius) tuber on alloxan induced diabetic rats.

[18] De S, Dey YN, Ghosh AK. Phytochemical investigation and chromatographic evaluation of the different extracts of tuber of Amorphophallus paeoniifolius (Araceae). *Int J Pharm Biol Res*. 2010;1(5):150-7.

[19] Henam SD, Ahmad F, Shah MA, Parveen S, Wani AH. Microwave synthesis of nanoparticles and their antifungal activities. *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*. 2019 Apr 15;213:337-41.