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RESEARCH PAPER

# Green Synthesis of Zinc Oxide Nanoparticles Using Garlic Skin Extract and Its Characterization

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ABSTRACT

Plant-mediated synthesis of metal oxide nanoparticles is a promising alternative to the traditional method of physical and chemical synthesis. In this paper, we report the synthesis of Zinc Oxide nanoparticles (ZnO NPs) by a biological method. During the study, ZnO nanoparticles were synthesized by Allium sativum skin (garlic skin) extract. Formation of ZnO nanoparticles has been confirmed by UV-visible spectroscopy, UV diffuse reflectance spectroscopy (UV-DRS), X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), Scanning Electron Microscope (SEM) with Energy dispersive X-ray studies (EDX) and transmission electron microscope (TEM), Atomic Force Microscopy (AFM), Brunauer-Emmet-Teller (BET), Thermogravimetric analysis (TGA). UV-vis spectroscopy confirms the synthesis of ZnO nanoparticles and showed the characteristic of the absorption peak at 370 nm. The scanning electron microscope (SEM) and Transmission electron microscope (TEM) confirms the formation of the rod and hexagonal shaped nanoparticles having an average size of 7.77 nm. Use of waste garlic peel extract for the reduction of zinc chloride to Zinc oxide is the novelty of work. Energy dispersive X-ray analysis (EDX) states the formation of highly pure ZnO nanoparticles. The ZnO nanoparticles synthesized using garlic skin are expected to have applications in biotechnology, biomedical, catalysis, coatings, sensors, and water remediation. Therefore, the study reveals an efficient, cheap, simple, novel, eco-friendly, safe and convenient method for the green synthesis of multifunctional ZnO NPs.

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## INTRODUCTION

Nanotechnology is the most innovative emerging field which can lead to a new revolution in every field of science for the purpose of manufacturing new materials at the nanoscale level [1, 2]. Nanotechnology is an important branch in the major fields of biology, chemistry, physics and material sciences [3]. The synthesis of metal and metal oxide nanoparticles have gained much interest due to their fascinating physical, electrical, chemical, mechanical, catalytic and optical properties compared to the bulk of the same chemical composition [4,5]. Several physical and chemical procedures have been reported for the synthesis of metal oxide nanoparticles but now a day there is a growing need to develop eco-friendly nanoparticles synthesis methods which do not use any toxic materials and high energy consumption during the synthesis process [6-8]. Nanoparticles have been integrated into various industrial, health, food, feed, space, chemical and cosmetic industry of consumers which calls for a green and environment-friendly approach for their synthesis [9].

Zinc Oxide (ZnO) is an inorganic compound,

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appears as a white powder and insoluble in water. In material science, ZnO is called II-IV semiconductor [10]. Due to increased surface area and activity of nanoscale ZnO compound, it shows the potential to improve the efficiency of both aqueous and organic solvents, allowing them for incorporation into material processes. Apart from these, ZnO nanoparticles synthesized by biological approach are nontoxic and compatible with the skin, which makes them very much suitable for to be applied as an additive that comes in contact with the human body [11].

Based on the review of literature, the biosynthesis of ZnO nanoparticles (ZnO NPs) has been carried out using various plants such as *Aloe barbadensis* miller leaf extract [12], *Pyrus Pyrifolia* leaf extract [13], *Spathodeacam panulata* leaf extract [14], *Pongamia pinnata* leaf extract [4], *Cassia fistula plant* extract [15].

The present study focuses on the synthesis of ZnO nanoparticles by garlic skin extract as a reducing agent and Zinc chloride as a precursor for zinc. As the garlic skin is a waste product, most of the people throw it out after collecting garlic clove. We have collected garlic skin from the thrown waste and used as a reducing agent to synthesize ZnO NPs. After collecting the extract, garlic skin biomass can also be used to separate cellulose, lignin, etc. The synthesized ZnO NPs were characterized using different characterizing techniques.

## MATERIALS AND METHODS

All the chemicals such as zinc chloride, sodium hydroxide were purchased from Sigma Aldrich. Garlic skin was collected from the vegetable market, Gandhinagar, Gujarat.

*Preparation of garlic skin extract*

Collected garlic skins were washed with tap water several times followed by distilled water. After that garlic skins were dried at 40 °C in the oven till 7 days and then the powder was prepared. 10 gram of garlic skin powder was taken soaked in a 250 ml Erlenmeyer flask containing 100 ml 80 % ethanol. The solution was heated at 60 °C for 20 min and stirred using magnetic stirrer for 24 hours. The extract was filtered by Whatmann filter paper No.1 at room temperature. 50 ml of filtrate was taken for the synthesis of nanoparticles while the rest of the filtrate was evaporated in a rotary evaporator at 45 °C until the extracts became completely dry. After evaporation, the extract was stored at 4°C until use [16]. Qualitative and quantitative analysis of garlic skin extract was done using standard methods.

*Synthesis of ZnO NPs*

200 ml of 2 mM zinc chloride solution was prepared and kept in stirrer for 20 hours. During the study, pH was optimized and best synthesis was occurred at pH 8. Due to this, the pH of the solution was adjusted to 8 using 1 M NaOH solution. Then the 30 ml of garlic skin extract solution was added drop wise to the above solution under constant stirring condition. The color of the reaction mixture was changed after 30 min of incubation time. The solution was left in stirred for 4 h after the incubation time confirmed the synthesis of ZnO NPs. The resulted precipitate was separated from the reaction solution by centrifugation at 7000 rpm for 15 min by washing several times with distilled water followed by ethanol to remove organic impurities and the pellet was collected [3]. Pellet was dried using hot air oven operating at 80 °C for overnight and preserved in airtight bottles for further characterization studies [17]. Graphical representation of the procedure for ZnO NPs synthesis is represented in Fig. 1.

*Characterization of ZnO nanoparticles*

The synthesized ZnO nanoparticles were measured for its maximum absorbance using UV-Vis spectrophotometry (Model number –Halo DB 20) in the range of 250-600 nm. The UV-vis reflection absorption of ZnO NPs was also recorded in the wavelength of 200 to 800 nm using UV-vis-NIR spectrometer (in diffuse reflectance mode using barium sulfate as a reference [18]. Crystallite structure of ZnO nanoparticles was characterized by X-Ray Diffraction (XRD) analysis. SEM EDX analysis was also done to characterize the surface of nanoparticles. The surface area of samples was also determined by the Brunauer-Emmett-Teller (BET) and pore size and pore volume analysis was also done by the Barrett-Joyner-Halenda (BJH) method [19]

## RESULT AND DISCUSSION

*UV Visible analysis*

The formation of ZnO NPs was initially confirmed by the visual assessment. The color of the mixture was changed from light yellow to white color during the reaction, which indicates the formation of ZnO NPs. The optical absorption

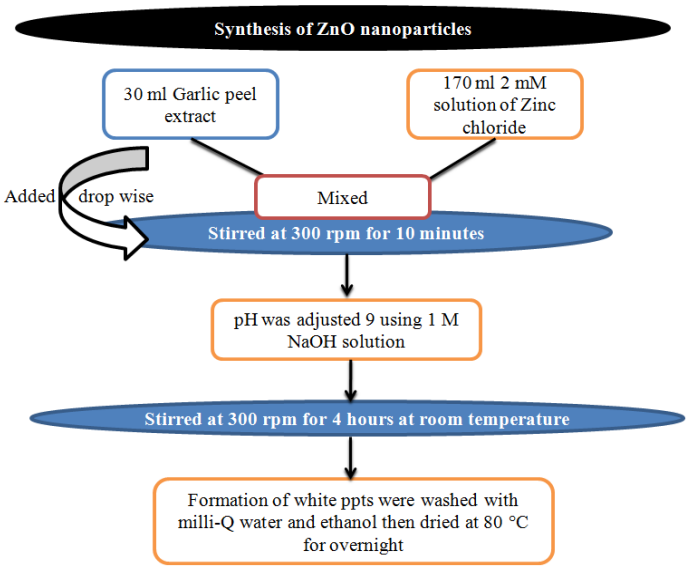



Fig. 1. Graphical representation of procedure for ZnO NPs synthesis

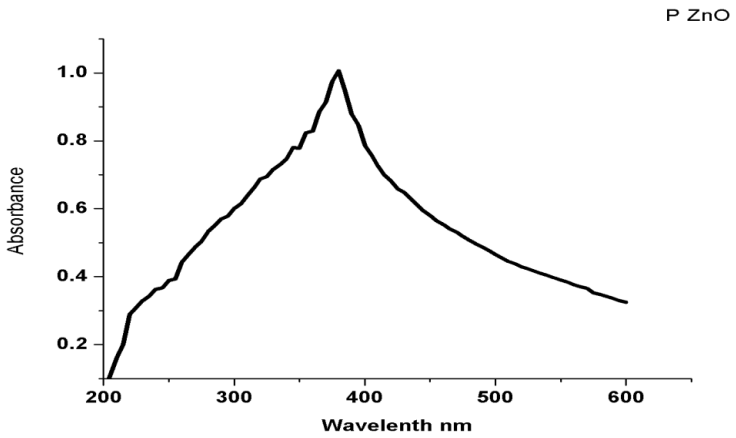



Fig. 2. UV visible spectrum of synthesized ZnO NPs

spectra of ZnO NPs were recorded using UV Vis spectrophotometer. Fig. 2 shows the UV-Vis absorption spectrum of ZnO NPs. The spectrum was recorded in the range of 250-600 nm for the sample. The spectrum showed the absorption peak at 375 nm corresponding to the characteristic band of ZnO nanoparticles.

The band gap value was determined using following formula:

$$E_g = \frac{1240}{\lambda_{edge}}$$

Where Eg is the band gap energy in electron volts (eV) and λ is the wavelength (nm) corresponding to maximum absorption. The band gap energy values of ZnO nanoparticles are calculated as 3.26eV.

*XRDanalysis*

XRD peak profile analysis is a very simple and efficient method to evaluate the peak broadening with crystallite size and lattice strain due to dislocation. The XRD pattern of synthesized ZnO nanoparticles was taken to characterize the crystal structure.3 depicts XRD patterns of the ZnO NPs synthesized by garlic skin extract. XRD analysis data reveals that the nanoparticles synthesized were pure and crystalline in nature.

The peaks at 2θ = 31.57°, 34.25°, 36.075°, 47.38°, 56.44°, 62.72°, and 67.82° were assigned to (100), (002), (101), (102), (110), (103) and (112) of ZnO NPs, confirming that the samples were

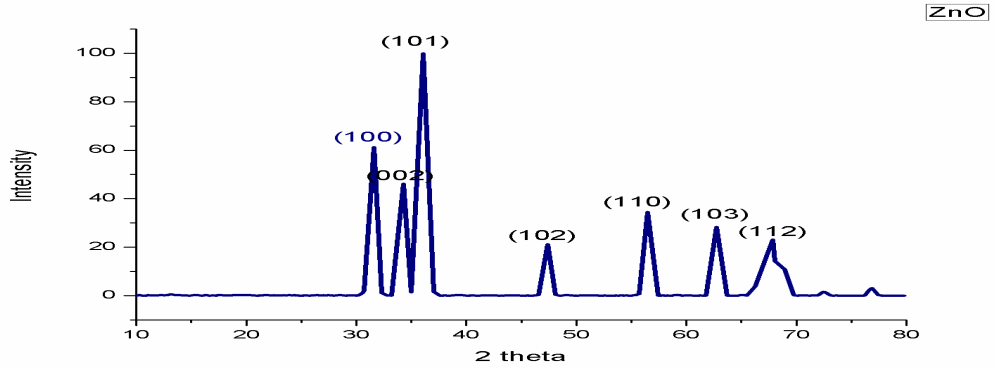



Fig. 3. XRD plot for ZnO NPs

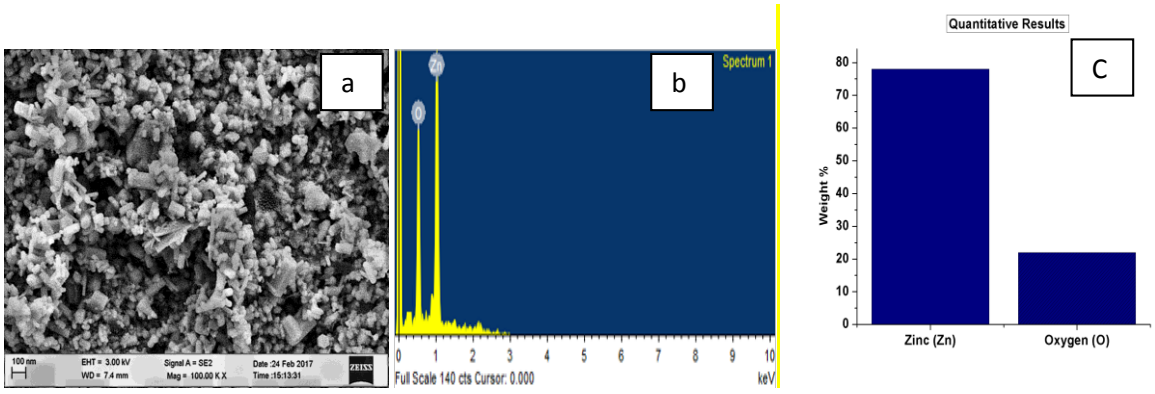



Fig. 4. (a) SEM , (b) EDAX (c) Percentage composition of synthesized ZnO NPs

polycrystalline wurtzite structure. By comparing these data with known standard data published by the Joint Committee on Powder Diffraction Standard (Zincite, file no. JCPDS 5-0664). No characteristic peaks of any impurities were detected, which illustrates that all the precursors have been completely decomposed and high-quality ZnO NPs were synthesized by garlic skin extract [6]. The peak broadening in the XRD pattern clearly indicates the presence of small nanocrystals in the sample. The average crystallite size was estimated by Debye-Scherrer equation nanocrystals in sample. The average crystallite size was estimated by Debye-Scherrer equation [20].

$$D = \frac{K\lambda}{\beta hkl Cos\theta}$$

Where $\beta_{hkl}$ is the integral half width, K ia a constant equal to 0.90, $\lambda$ is the wave length of the incident X-ray ($\lambda$= 0.154 nm was taken), D is the crystallite size, and θ is the Bragg angle. The average crystallite size calculates for synthesized ZnP NPs was 12.61 nm.

*SEM and EDX analysis*

The morphology of the synthesized NPs was examined by scanning electron microscopy. Fig. 4 (a) shows the surface morphology of the ZnO NPs. EDAX analysis confirms the presence of Zinc (78%) and oxygen (22 %) signals that the produced NPs are in their highest purified form, which is shown in no 4 (a) and (b)

*TEM*

The TEM images of ZnO NPs are shown in Figs. 5 (a), (b), (c). TEM images suggest that the size of synthesized nanoparticles is in nanometer range. The TEM images of ZnO NPs confirm that the nanoparticles are rod and hexagonal shape with slight variation in thickness. The average size of ZnO NPs was found to be 7.77 nm in diameter. The extent of agglomeration is very less which can be clearly seen from Fig..

*AFM analysis*

The size of the NPs is obtained from tip-corrected AFM measurements, and the shape of the NPs is estimated on the basis of AFM images

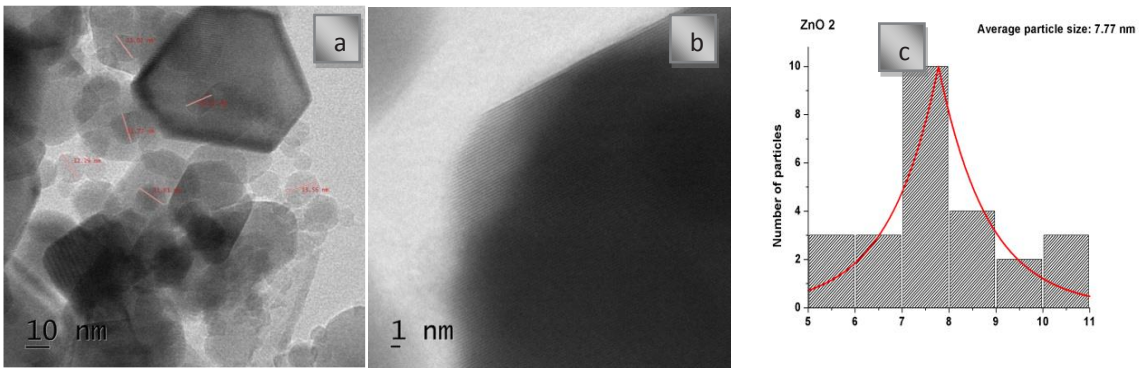
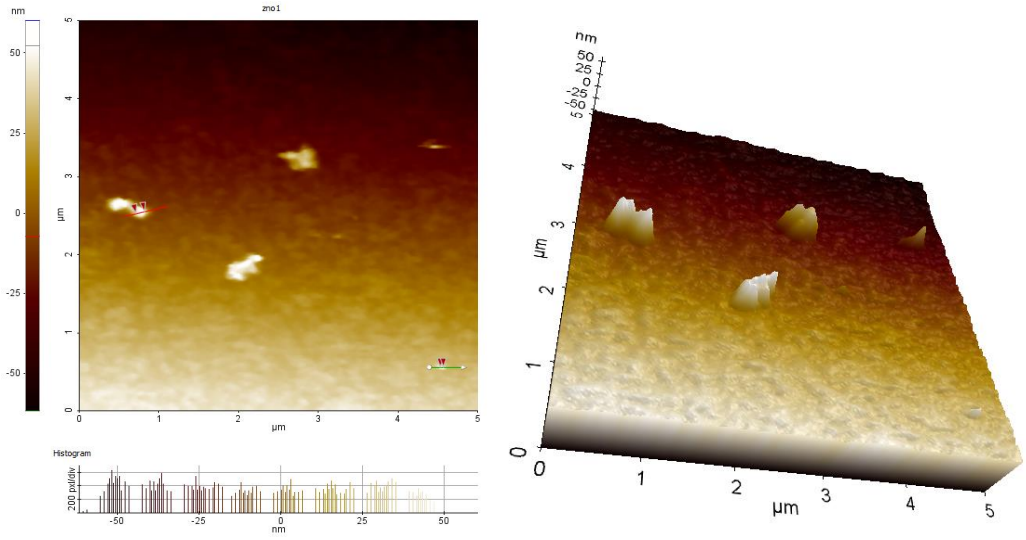



Fig. 5. (a), (b) TEM micrograph (c) Particle size distribution graph for ZnO NPs




Statistics

| Line | Min(nm) | Max(nm) | Mid(nm) | Mean(nm) | Rpv(nm) | Rq(nm) | Ra(nm) | Rz(nm) | Rsk | Rku |
|---|---|---|---|---|---|---|---|---|---|---|
| Red | -10.301 | 58.599 | 24.149 | 12.705 | 68.900 | 23.762 | 21.014 | N/A | -0.724 | 1.951 |
| **Green** | **27.456** | **51.342** | **39.399** | **33.992** | **23.886** | **7.427** | **6.114** | **N/A** | **-1.151** | **2.832** |

Fig. 6. (a) 2D image and (b) 3D image for ZnO NPs

and line scans [21]. fig 6 (a), (b) represent the 2D and 3D images of synthesized ZnO nanoparticles. The atomic force microscopy was executed to identify the topological appearance and the size range was found out around 25 nm rendering 3D profile. However maximum surface particle size of the ZnO NPs affirmed within 23.34 nm. The AFM images were also used for the evaluation of roughness, porosity and fractal dimension.

*FT-IR analysis*

Fig. 7 shows the FTIR spectra of ZnO NPs taken in the range of 400-4500 $cm^{-1}$ .the FTIR peak at 441 $cm^{-1}$ corresponds to ZnO bonding which confirms the presence of ZnO particles. The broad peak at 3471 $cm^{-1}$ illustrated O-H group stretching of O-H, bonded single bridge. The peak at 1614 $cm^{-1}$ may be due to the absorption of atmospheric moisture. The peak at 1018 $cm^{-1}$ indicates C-O stretching in amino acid. The peak at 590 $cm^{-1}$ indicates the presence of alkyl halide. The absorbance bands at 1424 $cm^{-1}$ belong to stretching and bending vibrations of $–CH_2$.

*BET analysis*

The BET surface area of samples was measured

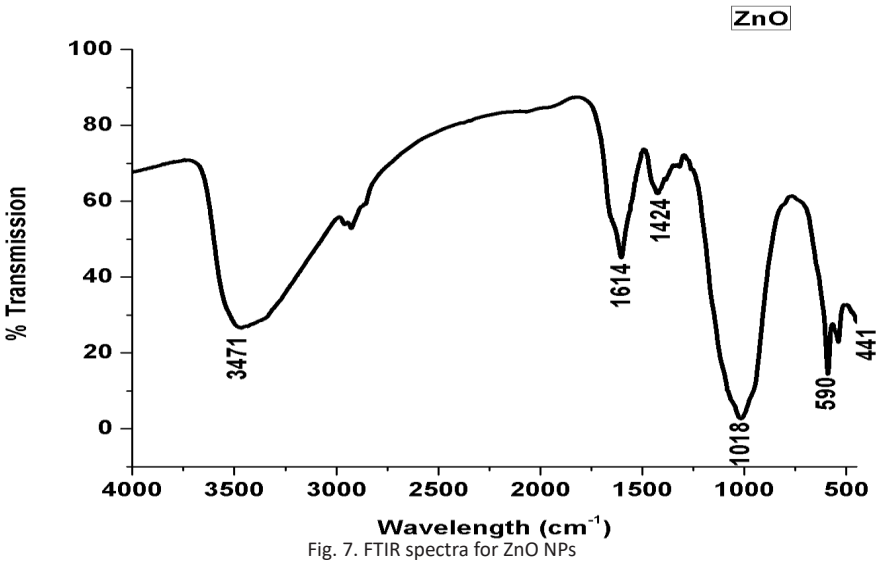



Fig. 7. FTIR spectra for ZnO NPs

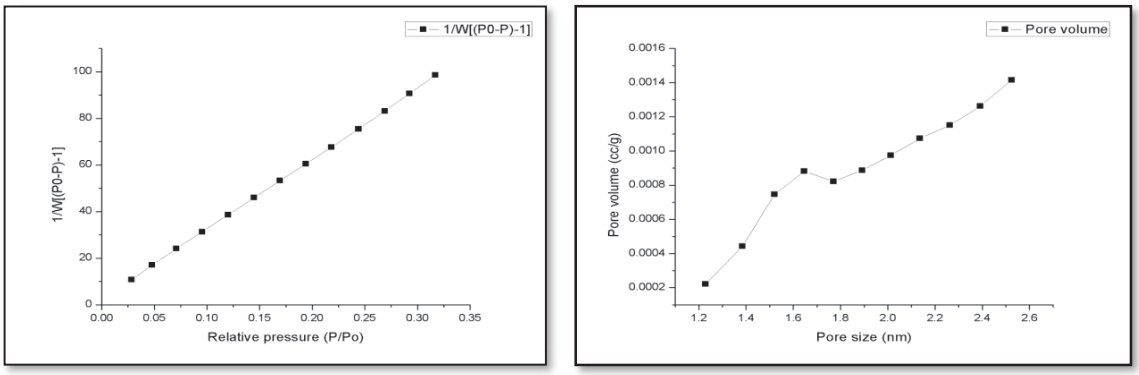



Fig. 8. (a), (b) BET plot for ZnO NPs

by nitrogen adsorption isotherms. The specific surface area of metal oxides was determined by BET method. The BET method involved physical adsorption of $N_2$ at its boiling temperature. The following basic equation is used to find out surface area by BET method [22].

$$\frac{P}{Va\left(Po-P\right)}=\frac{1}{VmC}+C-\frac{1}{VmC}\times\frac{P}{P0}$$

Where P= Adsorption equilibrium pressure, P0= Saturated vapor pressure of adsorbate, Va= Volume of adsorbate corresponding to pressure Vm = Volume of adsorbate required for a monolayer coverage, C= A constant relating to the head of adsorption

As per the BET method a plot of P/Va(Po-P) against P/Po yields a straight line when P/Po <0.3. From the slope and intercept of the straight line Vm can be calculated by following equation.

$$SurfaceArea\left(\frac{m2}{g}\right)=Vm\times\frac{N}{22414\times W}\times Am$$

Where, Vm= Monolayer volume in ml at STP N= Avagardo number, W= Weight of the powdered sample (g), Am= Cross sectional area of adsorbate molecule (0.162 $nm^2$ for $N_2$).

The measured BET plots are represented in Fig. 8 (a), (b). Table.1 summerizes the surface area and pore diameter for ZnO NPs.

*Thermal stability analysis*

The differential thermal analysis and thermo gravimetric analysis (TGA) have been carried out on the ZnO NPs synthesized by garlic skin extract to determine changes in weight in relation to

Table 1. Summarizes the BET surface area and BJH pore diameter of ZnO nanoparticles.

| Sample | BET surface area $m^3g^{-1}$ | BJH | |
|---|---|---|---|
| | | Pore radius (A°) | Pore volume (cc/g) |
| ZnO | 13.014 | 1.52 | 0.023 |

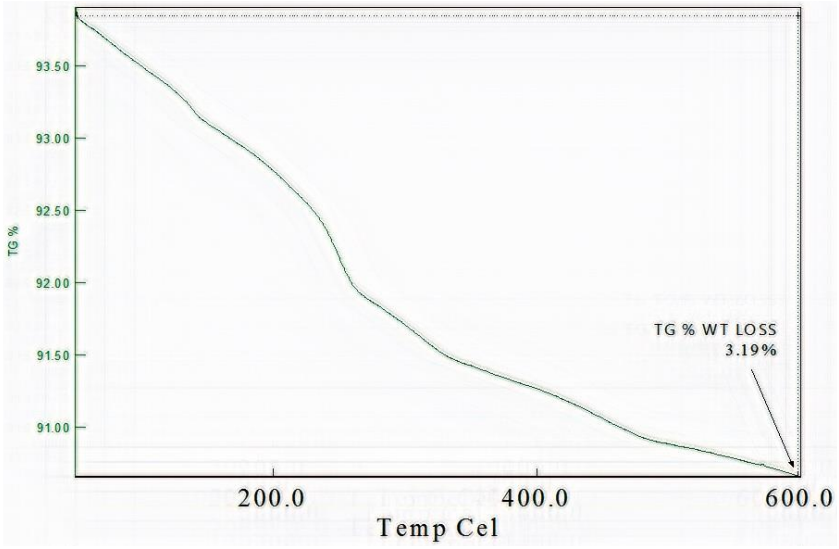



Fig. 9. TGA and DTA plot for ZnO NPs

change in temperature. TGA curve in Fig. 9 shows that the weight loss because of the evaporation of water and removal of bio-products due to heating. The total loss found to be around 3.19% of the original weight [23].

## CONCLUSION

The synthesis of nanoparticles by conventional physical and chemical methods has some adverse effects like critical conditions of temperature and pressure, use of expensive and toxic chemicals, long reflux time of reaction, toxic by-products, etc. The ZnO nanoparticles have been successfully synthesized using garlic skin extract as base source and stabilizing agent. The synthesized ZnO NPs were hexagonal in shape and were characterized using UV-Vis, UV-DRS, XRD, FTIR, SEM-EDX, TEM, AFM, BET and TGA techniques. The ZnO NPS exhibits the indirect band gap of 3.26 eV FTIR spectra revealed the functional groups of stretching bands of ZnO NPs around 600-450 $cm^{-1}$. XRD result showed the sample was well crystallized in a hexagonal wurtzite phase which is the most stable form of ZnO having crystallite size of 12.61 nm. SEM-EDS analysis showed the morphology of hexagonal nanoparticles with the composition of Zn and O elements. TGA analysis showed that about 3.19 % weight loss of ZnO NPs was occurred. ZnO NPs showed around 13.014 $m^3g^{-1}$ surface area according to BET analysis data. This process is an economical method for the synthesis of ZnO NPs with respect to energy, time and simplicity, cost effectiveness, eco-friendly.

## CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this manuscript.

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