Vibrational, X-ray diffraction and Microscopic Studies of Andrographis paniculate generated Metal oxide nanoparticles

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ABSTRACT

ZrO2 nanoparticles can be produced in an economical and environmentally friendly way by employing the leaf extract of Andrographis paniculata. For the biosynthesized nanoparticles, the phyto compounds in the extract function as reducing, stabilising, and capping agents. The characterisation studies were carried out using UV-VIS, FTIR, SEM, EDX, and XRD techniques.

KEY WORDS: Nanoparticles (NPs), *Andrographis paniculate*, Spectroscopic and microscopic studies .

1. INTRODUCTION

The synthesis of nanomaterials and the fabrication of nanostructures can broadly bedivided into two approaches top-down [1] and bottom-up [2-4]. Simple attrition (abrasion) or milling (which roughly speaking is grinding between hard balls) are the most typical and common top-down methods of making nanoparticles. On the other hand, the colloidal dispersion technique is a good example of a bottom-up approach for synthesizing nano-sized particles. Lithography may be considered a hybrid approach, since the growth of thin films is bottom-up, whereas etching is top-down, while nanolithography and nanomanipulation are commonly bottom-up approaches. It is well-known that top-down techniques such as lithography can cause significant crystallographic damage to the processed patterns [5]and additional defects may be introduced even during the etching steps [6]. For instance, nanowires usually made by lithography do not have a perfectly smooth surface for the reason that the method introduces a lot of impurities and structural defects on it.

A growing need for green strategies that do not include the consumption of hazardous chemicals as byproducts is the demand for environmentally acceptable non-hazardous technologies for the production of nanomaterials. For the synthesis of metal nanoparticles, a range of natural sources are available, including plants, algae, actinomyces, yeast, bacteria, and fungi, among others. The use of fungi, bacteria, algae, and various plant parts such as roots, leaves, flowers, stems, etc. in the bio-mediated production of noble nanometals has grown in importance as a safe alternative that is better than physical methods and chemical procedures.

EXPERIMENTAL

2.1.Materials: Andrographis paniculata leaves were collected within areas of Lakshmipuram village, Jeelugumilli Mandal, Eluru district, Andhra Pradesh. Chemicals such as Zirconium oxy chloride octa hydrate [ZrO Cl_2 $8H_2O$] were purchased from Merck, India Pvt. Ltd., and Sigma Aldrich. Deionized water was used to clean glassware, to prepare chemical solutions and for experimental procedure. Fresh leaves of *Andrographis paniculata* was collected from the barren lands in and around Lakshmipuram village in Jeelugumelli Mandal of West Godavari district in the Andhra Pradesh state of India,where it was found naturally.

2.2. Preparation of leaf extract:

To prepare the extract, Andrographis paniculata leaves were washed with double distilled water, dried at room temperature for three days, and powdered. It was sieved to a 100 mm size. At 120 ^{0}C, 20 g of leaf powder was boiled with 100 ml of distilled water. Before running the plant extract through Whatman No. 1 filter paper, it was cooled. The resultant extract was employed to create nanoparticles as a solvent. Figure:1

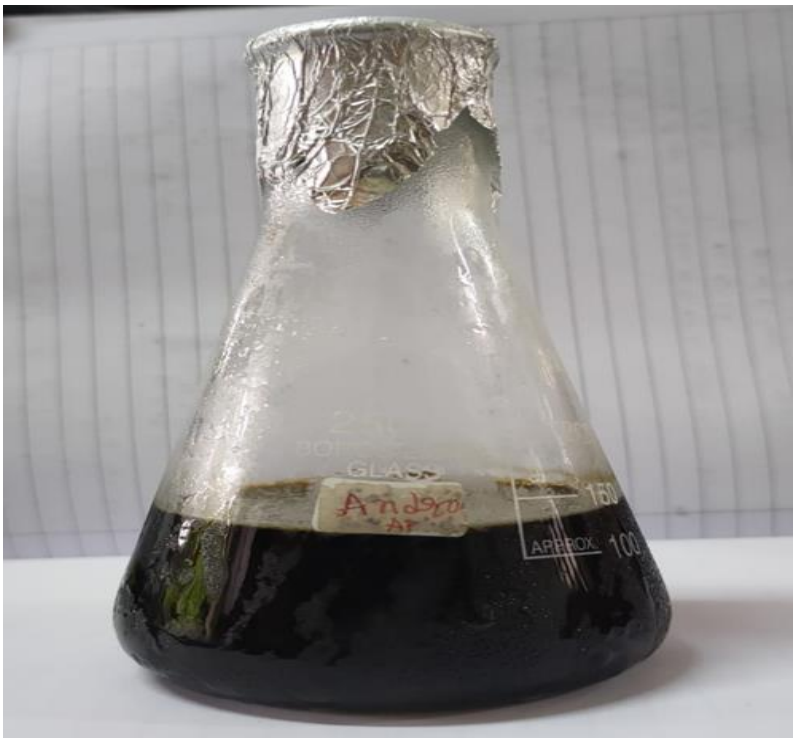

Figure.1. Leaf Extract Andrographis paniculata

2.3. Synthesis of ZrO_2 nanoparticles:

Using the green method technique and Andrographis paniculata leaf extract, zirconium oxide nanoparticles were created. Under vigorous stirring at 60 ^{0}C for 2–3 hours, 50 ml of Andrographis paniculata leaf extract was added to 50 ml of a 0.01M ZrO Cl2 8H_2O solution. After then, it was left to stand for a day before being centrifuged. The nanoparticles were obtained by centrifugation at 4000 rpm for 10-15 minutes, and the contaminants were then removed by washing with distilled water. The drying of created nanoparticles took place at 50 ^{0}C in the oven. To produce pure ZrO2 nanoparticles, the dried material was subsequently heated to 600–700 ^{0}C in a furnace.

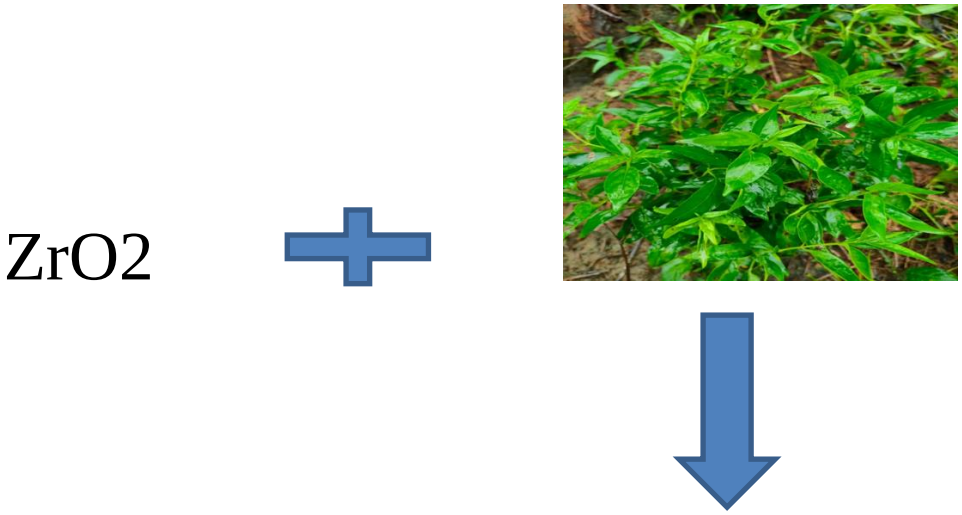

Figure.2. Preparation of ZrO_2 MNPs from precursor solutions

2.4. Characterization

Utilizing a UV-Visible spectrophotometer, the absorption spectra of produced NPs were assessed. Between 100 and 500 nm in wavelength, there was an intensity of absorption. The nano zirconia's functional moieties were examined using an FTIR spectrophotometer (Perkin Elmer), and M-O bond operations were discovered in the transmittance range of 4000- 400 cm^{-1}. The XRD pattern recordings on the Power XRD employing CuKa radiation (k=1.5406 A^0) were used to determine the material's atoms crystallinity. SEM and Energy-dispersive X-ray spectroscopy were used to determine the size, surface shape, and elementary composition of the ZrO_2 NPS (EDX).

3. Results and Discussion

3.1. UV – Visible spectroscopy studies

The most popular technique for the initial characterization of nanoparticles is UV-visible spectroscopy. In this study, the development of a milky white precipitate was the first indication that zirconium oxide nanoparticles had formed. This resulted from ZrO Cl_2 $8H_2O$ being converted to ZrO_2NPS [7]. The produced nanoparticles' UV-visible spectrum is shown in Fig. 1 in the 100–500 nm scanning range. [8]. Tetragonal ZrO_2 nanoparticle production is confirmed by an absorption peak at 229 nm in Fig.3. A peak is created when the electrons are stimulated from the VB to the CB [9]. ZrO_2 is created when different forms of zirconium, ions, atoms, or clusters, for example , interact with H_2O molecules. ZrO_2 is easily fragmented into nanoparticles in a liquid solution. Due to its high UV absorption, this green ZrO_2-NP can be used in medicinal applications like antibacterial and antifungal activities. [10].

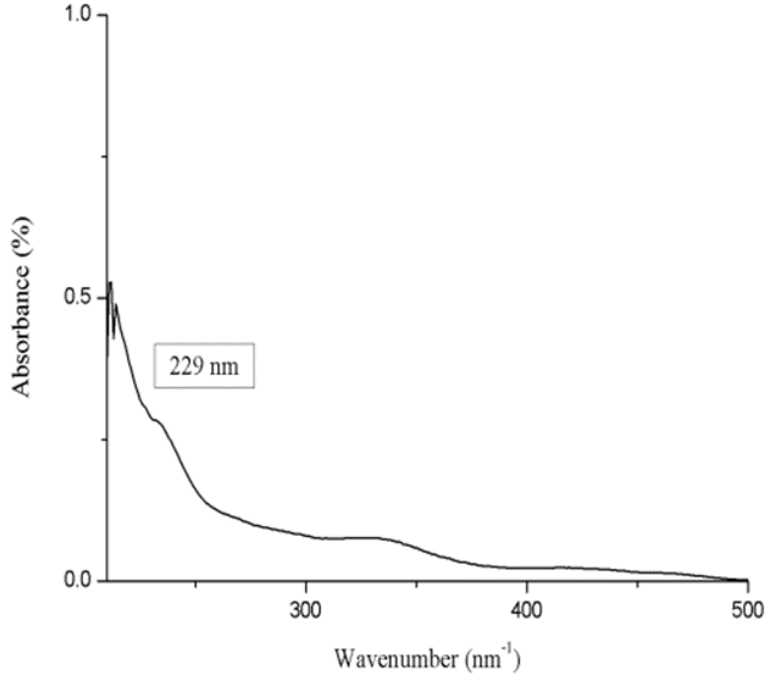

Figure:3. UV-visible spectrum of the green ZrO_2 NPs that were created

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3.2.Fourier transform infrared spectroscopic investigation

The Fourier Transform infrared spectrum of the ZrO2 NPS produced by calcining Andrographis paniculata leaf extract. The Zr-O-Zr vibrational band symmetric stretching, the OH stretching and bending vibrations of absorbing water, and the OH stretching of alkanes were all linked to the peaks between 400 cm and 800 cm. Zirconia NPs that were created using the chemical co-precipitation technique had similar outcomes [11]. In Fig. 3 No peaks of the typical organic functional groups were observed, suggesting that organic moieties had been eliminated by annealing at a high temperature, from the surface . This is because pure ZrO_2 NPS was produced when high-temperature annealing broke down polyphenols, which served as capping agents.

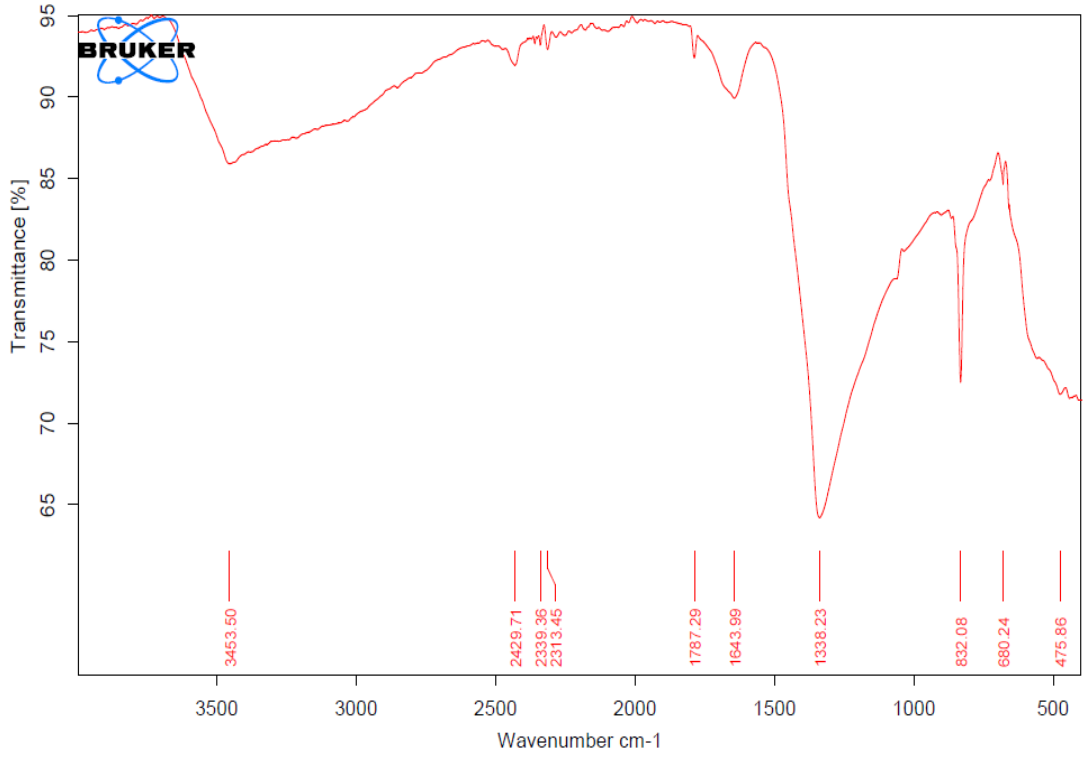

Figure: 4. Fourier transform infrared spectrum of Zr NPs(Andrographis paniculata).

3.4. X-ray diffraction analysis :

A quick analytical method known as X-ray powder diffraction (XRD) can reveal information on the dimensions of individual unit cells and is mostly used to identify the faces of crystalline materials. The average bulk composition of the sample under analysis is established after it has been finely ground and homogenized. Using samples of crystalline powder, the temperature was calcined for two hours between 20^0 and 60^0 C. The diffraction peaks were brought on by the wider temperature range during calcination. (Fig. 4) to become sharper, narrower, and substantially more intense (500-600 ^{0} C). This is a sign of a significant improvement in the crystallinity of zirconium oxide nanocrystals, which results from an increase in crystalline planes brought on by the particle size enlargement [12]. The tetragonal phase of the nanoparticle is implied by the distinctive diffraction peaks distinctive diffraction peaks for ZrO_2 particles (2 theta = 26.60, 29.58, 36.45, 43.34, 43.45, 61.38, 73.54, whose Miller indices were (111),(111), (200),(102),(220),(311), and (400) correspondingly). Fig:5. When these peaks were matched to the card number on the Joint Committee on Powder Diffraction Standard (JCPDS) database. It was discovered that they were 00-050-1089 as stated [13]. The following Debye Scherer equation was calculated using origin $8.D^{1/4}\ 0{:}89k = \eth bcoshþ$

Where k – Cu Ka radiation (1.5406 A^O), b-full –width half maximum of (200) plane, theta is the diffraction angle.

The aforementioned equation revealed that the prepared nano zirconia's average diameter was 8.5 nm.

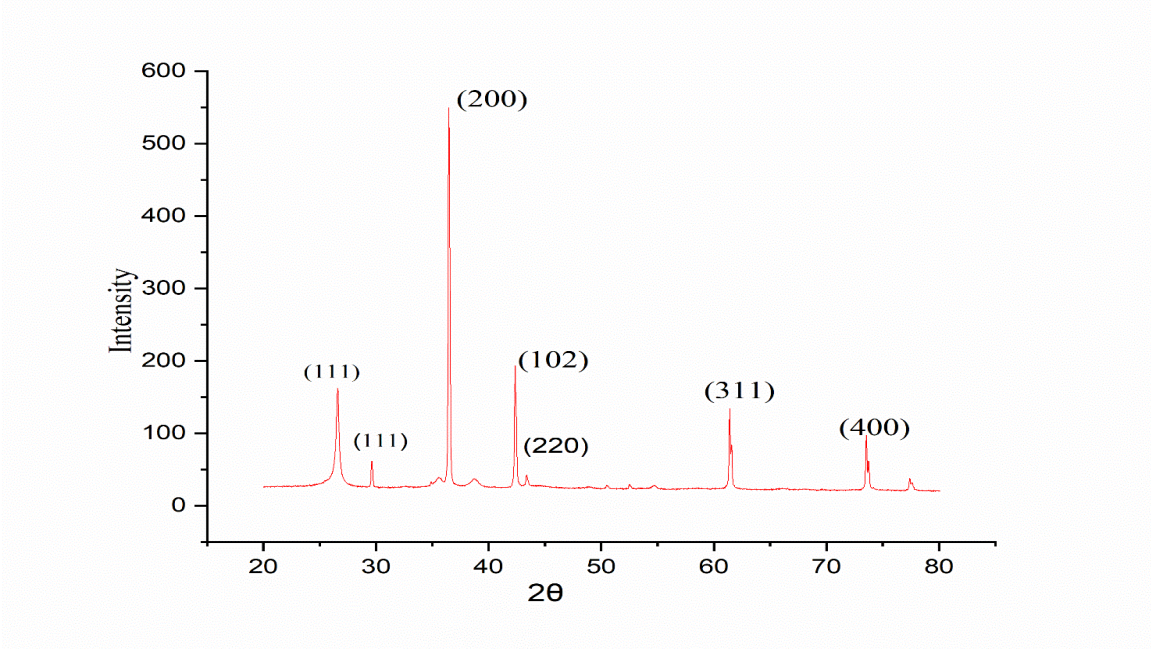

Figure:5. XRD analysis of ZrO_2 nanoparticles (Andrographis paniculata).

3.5. SEM – EDAX analysis

- The calcinated ZrO2 nanoparticles' size and form were examined using a scanning electron microscope. Zirconium dioxide nanoparticles were created using Andrographis paniculata as shown in Table 1 and Fig. 6(a) It was found that the majority of the shape of particles were in spherical, and have smooth and fused surfaces, are heavily aggregated, and are dispersed unevenly. Similar outcomes were attained in research

with ZrO2 nanoparticles made using the sol-gel technique [14]. The primary cause of this is the calcination process, which promotes nanoparticle development by encouraging agglomerate along their borders. This agglomeration is regulated by an organic component found in plant matter, such as polysaccharides, proteins, and other Phytochemicals that were found in the center and along the particles' surface function somewhat as a protective sheet, preventing the nanoparticles from growing for an extended period [15]. Crystal size was determined to be less than 10 nm, which is in agreement with the result obtained using the Debye-Scherer equation.[16] The signal properties of zirconium and oxygen were further validated by EDX analysis of the ZrO2 nanoparticles in Fig. 6 (b) Without any unexplained signals, all of the reported peaks are attributed to Zirconium and Oxygen, demonstrating the purity and calcination-derived production of ZrO_2.

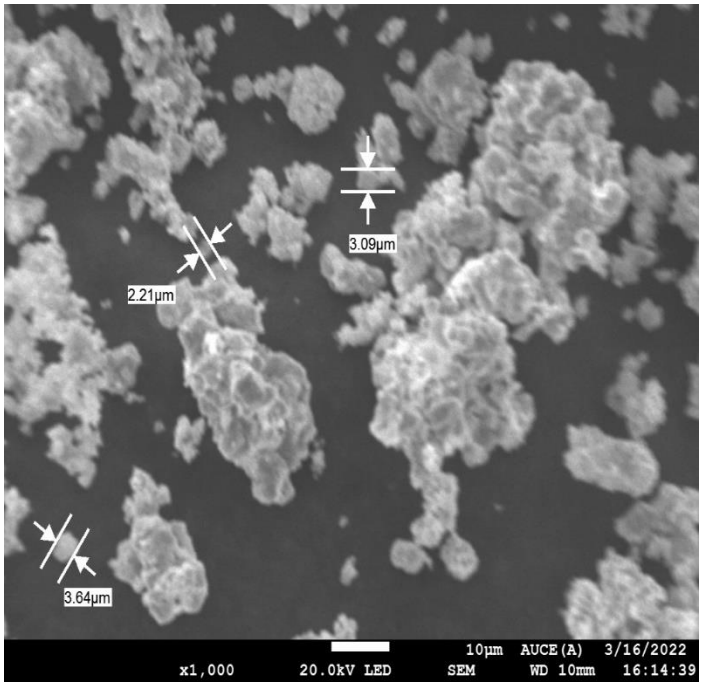

Figure:6. (a) SEM analysis of ZrO_2NPs

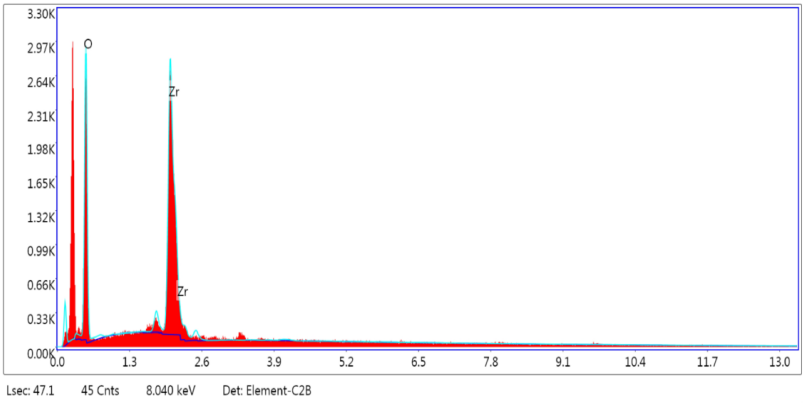

Figure:6. (b) EDX spectrum of ZrO_2NPs

Element	Weight %	Atomic %
O K	57.4	88.5
Zr L	42.6	11.5

3.6. CONCLUSION

In this study, a method for producing Zro2 nanoparticles from Andrographis paniculata leaf extract that is ecologically secure is proposed. It has been established by UV-VIS spectral analysis that the particles are nanoscale based on the locations of the Surface Plasmon Resonance (SPR) bands. The existence of secondary metabolites of Phyto molecules, which serve as the bio reducing and capping agents of the created nanoparticles, is confirmed by FTIR data. Results of XRD and SEM investigations demonstrated that ZrO_2 NPs have a cubic crystalline structure and a spherical shape, with sizes ranging from 20 to 100 nm.

Conflicts of interest: There are no conflicts of interest that we can disclose.

2. 7. ACKNOWLEDGEMENT

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