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Research Article
Green Synthesis of Nickel Oxide (NiO) Nanoparticles Using *Spirostachys africana* Bark Extract

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Abstract

Background and Objectives: Applications of nanoparticles in the biomedical field are diverse. Metal-based nanoparticles are attracting many researchers in biomedicine. Whilst various methods of nanoparticle synthesis are being explored, green synthesis is considered an environmentally friendly, safer and cost-effective method. The objectives of the study encompass the green synthesis of nickel oxide nanoparticles (NiO NPs) using bark extract of *Spirostachys africana* and their characterization using various techniques. **Materials and Methods:** Distilled water, *S. africana* bark and nickel nitrate hexahydrate ($Ni(NO_3)_2.6H_2O$) were some of the materials used. The methodologies employed were extraction, phytochemical analysis, green synthesis, oven drying, annealing and characterization of the synthesized nanoparticles using different techniques. **Results:** In the phytochemical analysis test, seven phytochemical constituents tested positive. In X-ray photoelectron spectroscopy (XPS), nickel and oxygen spectra were observed. X-ray diffraction (XRD) confirmed the presence of nickel and oxygen elements. Fourier transform Infrared spectroscopy (FTIR) showed peaks that are associated with the presence of C-O and C=C. Scanning Electron Microscopy (SEM) revealed agglomerated and amorphous morphology. Ultraviolet-visible spectroscopy (UV-VIS) showed a maximum peak of 240 nm. **Conclusion:** NiO NPs were successfully synthesized using the green chemistry route (green synthesis). Physical properties of NiO NPs were investigated and *S. africana* bark extract showed the presence of secondary metabolites.

Key words: Characterization techniques, green synthesis, nickel oxide nanoparticles, *Spirostachys africana*, physical properties, X-ray diffraction

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Competing Interest: The authors have declared that no competing interest exists.

Data Availability: All relevant data are within the paper and its supporting information files.

INTRODUCTION

Metal-based nanoparticles are attracting many researchers in biomedicine, as they are easily synthesized, manipulated and have distinct functional groups that allow them an easy association with drugs of interest, ligands and anti-bodies[1]. Nanoparticles are exceptionally small in size. Their surface area to volume ratio, resulting in the significant differences in their properties; biological, catalytic activity, mechanical properties, melting point, optical absorption, thermal and electrical conductivity and properties that are lacking in the same material at a larger scale[2]. These properties put metal nanoparticles on the spectra of a broad range of potential applications in targeted drug delivery and diagnostic imaging[3]. NiO NPs evince particular catalytic, anomalous electronic and magnetic properties. NiO is a p-type semiconductor transition metal oxide that has a cubic lattice structure and a bandgap ranging from 3.6-4.0 eV[4]. Moreover, NiO NPs have electron transfer capability, high chemical stability, electro-catalysis and super capacitance properties, which make their application-wide[5].

The standard synthesis of nanoparticles employs expensive chemical and physical processes that utilize toxic materials with potential hazards, which include environmental toxicity, cytotoxicity and carcinogenicity[6]. Green synthesis method, however, uses less harmful and eco-friendly nanoparticles synthesis procedures. Ideal solvents and biological materials (bacteria, fungi, algae and plant extracts) are often employed in green synthesis. However, the utilization of plant extracts is a much simple process that allows bulk production of nanoparticles and also, plants are readily available[7]. *Spirostachys africana sond*, a member of the family of *Euphorbiacciae*is found distributed all over Southern and Central Africa[8]. The plant is known for its toxic milky latex that exudes from all its parts. In South Africa, the stem bark is used to treat stomach pains, stomach ulcers, kidney complaints, cough and eye complaints[9-13]. This study aimed to synthesize NiO NPs using the bark water extract of *S. africana sond* and characterize the resultant nanoparticles using various techniques. Future studies will explore the effectiveness of NiO NPs in the anti-proliferation of breast cancer cells.

MATERIALS AND METHODS

Study location: The study was carried out at iThemba labs in July, 2018 and completed in 2019 at the unit of drug discovery laboratory of the Central University of Technology. The plant was collected from its natural habitat in Kruger National Park, Limpopo Province, South Africa.

Plant preparation and extraction: Plants were washed thoroughly with distilled water and dried at room temperature, then ground to a fine powder. The powdered bark material was extracted with distilled water; material (30 g) was mixed with 250 mL boiling water and left to stir for 12 hrs. The mixture was cooled for 12 hrs and then filtered.

Synthesis of NiO NPs using bark extract of *S. africana*: A 100 mL of the water bark extract filtrate was mixed with 5 g of the precursor salt, Nickel nitrate hexahydrate $(NiNO_3)_2.6H_2O$ (Sigma, South Africa). An immediate color change to dark brown was observed. The mixture was left to stir for 4 h, centrifuged and dried in the oven (60°C) for 6 hrs. Some of the dried material was further annealed for 2 hrs at 500°C[14].

Phytochemical analysis: Phytochemical studies of the powdered plant parts were carried out using colorimetric assays to determine the presence of phytosterols, pentose, tannins, glycosides, triterpenoids, anthraquinones, saponins, flavonoids and alkaloids using a Method by Jeyaseelan, E.C. and Jashothan, P.J.[15].

Characterization: The infrared spectrum of the solid NiO NPs was recorded by Shimadzu FTIR spectrometer to identify organic (and in some cases) inorganic materials. The wavelengths that are absorbed by the sample are characteristic of its molecular structures. The particle shape of NiO NPs was determined by SEM. The model used is EDAX Boron using on accelerating voltage at 200 KV. XRD (X-ray diffraction model Bruker AXS D8 advance) with radiation λCuka1 = 1.5406 was used to determine the crystallographic structures of the nanoparticles[16] and XPS was used for chemical analysis of the nanoparticles.

Statistical analysis: The statistical analysis was relevant in the characterization techniques only. Origin software was used to plot and analyze the data collected by synchrotron XRD and UV-VIS. Spin orbital splitting and peak area ratios assist in element identification which is plotted on graphs in

the XPS technique. In FTIR, the detector is used to measure the special interferogram signal, then the computer stores the digitalized signals and the final interpretation is done by peaks. The morphology analysis was carried out using SEM.

RESULTS

Phytochemical analysis: The bark plant material tested positive (+) for all secondary metabolites except for flavonoids as shown in Table 1.

Characterization: The functional groups present in secondary metabolites found in the bark extract of *S. africana* were analyzed using FTIR by observing the different peaks of both the un-annealed (room temperature) and annealed (exposed to 500°C) (Fig. 1). Peaks were observed at ~2000, ~1500 and ~1000 for samples, whilst the intensity was higher for the annealed NiO NPs than the un-annealed NiO NPs. The peak at ~2000 could denote the presence of C-O and C=C bond which normally ranges at peaks 2260-2100.

SEM images of NiO NPs with a magnification of X1000, X5000 and X7000 are shown in Fig. 2a-c. At the highest magnification, an agglomeration of NiO NPs with a distribution size of (10.0 mm) is observed. The agglomerated nanoparticles formed an amorphous shape.

Synthesized NiO NPs (annealed at 500°C and un-annealed (23°C)) were investigated by XRD. The XRD profile of both annealed and un-annealed NPs is shown in Fig. 3a and b, respectively. In Fig. 3a, seven sharp peaks were observed and their maxima is observed at 2θ = 37.12, 43.16, 44.36, 51.70, 62.71, 75.37 and 79.31. Their respective correspondence is 3000, 4900, 2100, 900, 2100, 800, 400 and 500. Investigation of NiO NPs at room temperature (Fig. 3b) revealed five sharp peaks and their maxima was observed at 2θ = 37.22, 43.16, 44.25, 51.56, 62.79 and 76.12 whilst their corresponding values are 900, 1500, 2400, 900, 500 and 200.

Table 1: Phytochemical analysis of the bark and leaf plant material of *S. africana*

Phytochemical group	Leaves	Bark
Phytosterols	-	+
Pentose	-	+
Tannins	+	+
Glycosides	+	+
Triterpenoids	-	+
Anthraquinones	-	+
saponins	+	+
Flavonoids	-	-
Alkaloids	+	+

+: Present,-: Absent

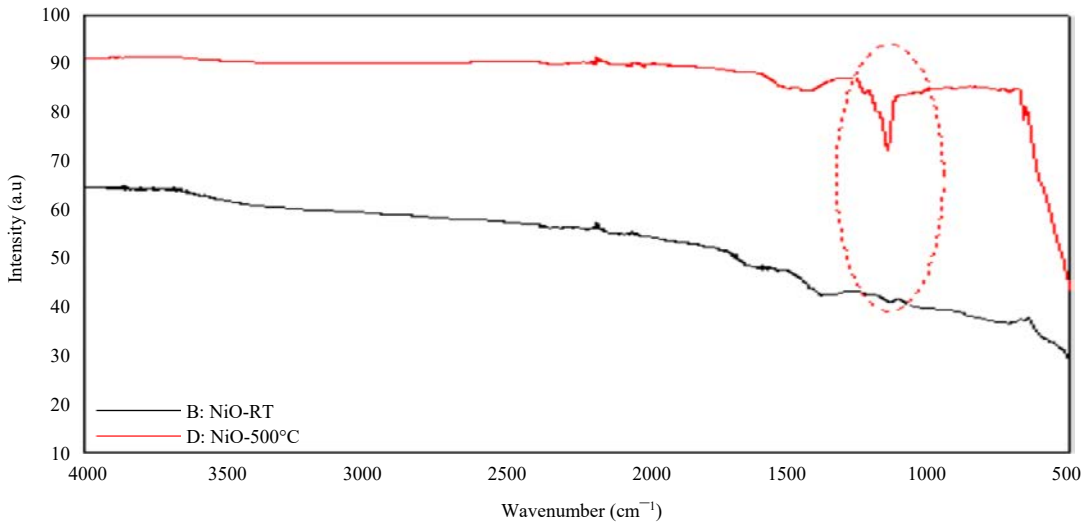

Fig. 1: FTIR spectra of annealed (red line graph) (black line graph) NiO NPs

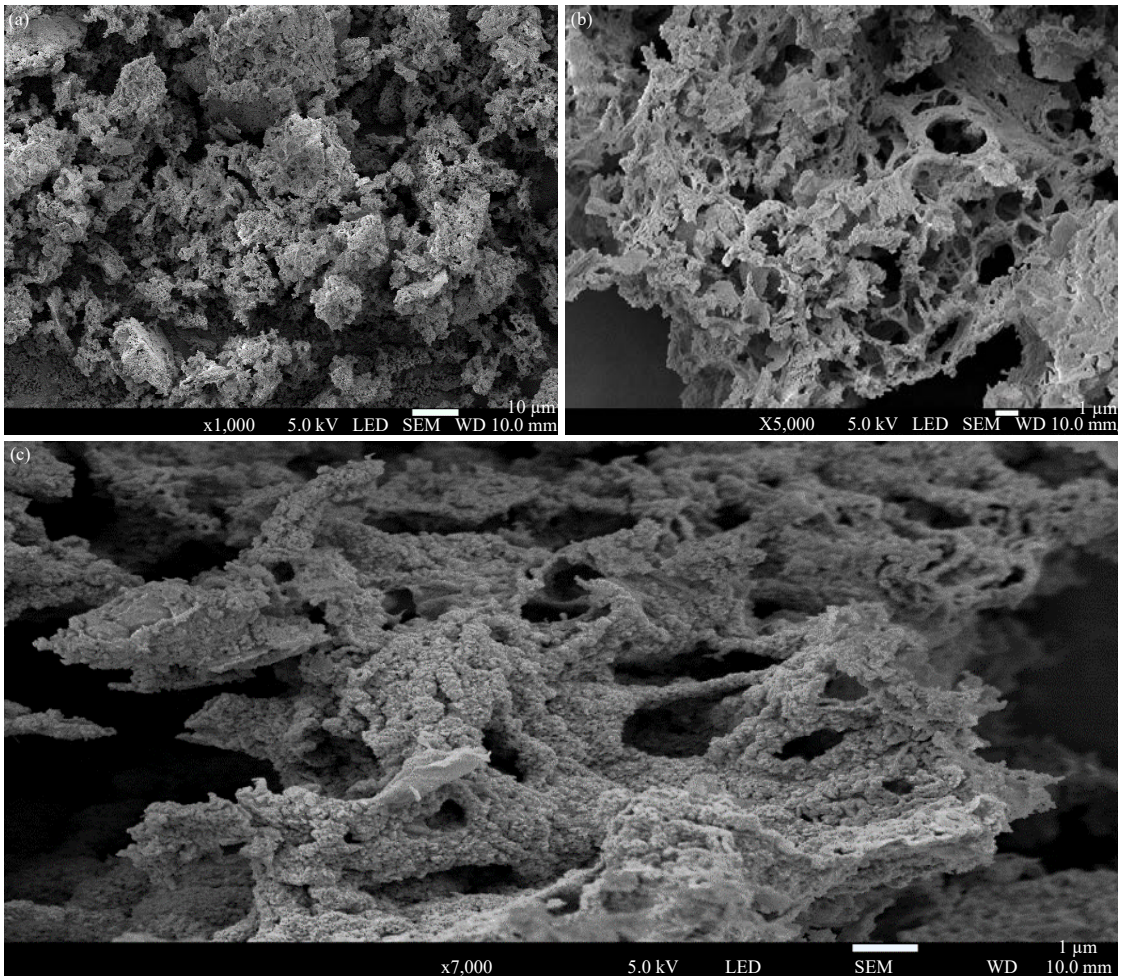

Fig. 2(a-c): SEM image of NiO NPs at (a) ×1000 magnification and 1 µm scale, (b) ×5000 magnification and 10 µm scale and (c) ×7000 magnification at a scale of 1 µm

The XPS spectra taken from Ni and O region of NiO NPS are shown in Fig. 4a and b, whilst Fig. 4c shows a spectra of NiO NPs. The data confirms the presence of Nickel and oxygen in the sample. The peaks in NiO NPs spectra are observed at 1000, 860, 700, 640, 540, 280 corresponding to OKLL, Ni2p1, Ni2p3, Ni LMM, Ni LMM.

In Fig. 5, the sharpness of the maximum absorption peak is at approximately 240 nm making the synthesised NiO NPs stable.

DISCUSSION

The bark extract of *S. africana* showed the presence of all metabolic constituents tested except flavonoids (Table 1). The chemical structures of the metabolic constituents consist of C-C, C=C and C-O bonds, as revealed by FTIR.

Metallic nanoparticles are synthesized by metal ion reduction using chemical molecules found in plants. Terpenoids and some other metabolites found in plants are free radical scavenging molecules that are used in synthesizing nanoparticles. Hydroxyl and carboxyl groups may act as reducing agents[17]. The reduced nanoparticles are capped and stabilized by functional groups such as alkaloids. Therefore the presence of alkaloids, saponins, anthraquinones, triterpenoids, glycosides and tannins in the bark extract suggests a high concentration of reducing agents[18]. According to literature, phytochemical studies of the latex from *S. africana* have shown the presence of beyerene derivatives, diosphenols, ketols, starchy ones and acid metabolites[19]. The phytochemical analysis of *S. africana* is not recorded in literature.

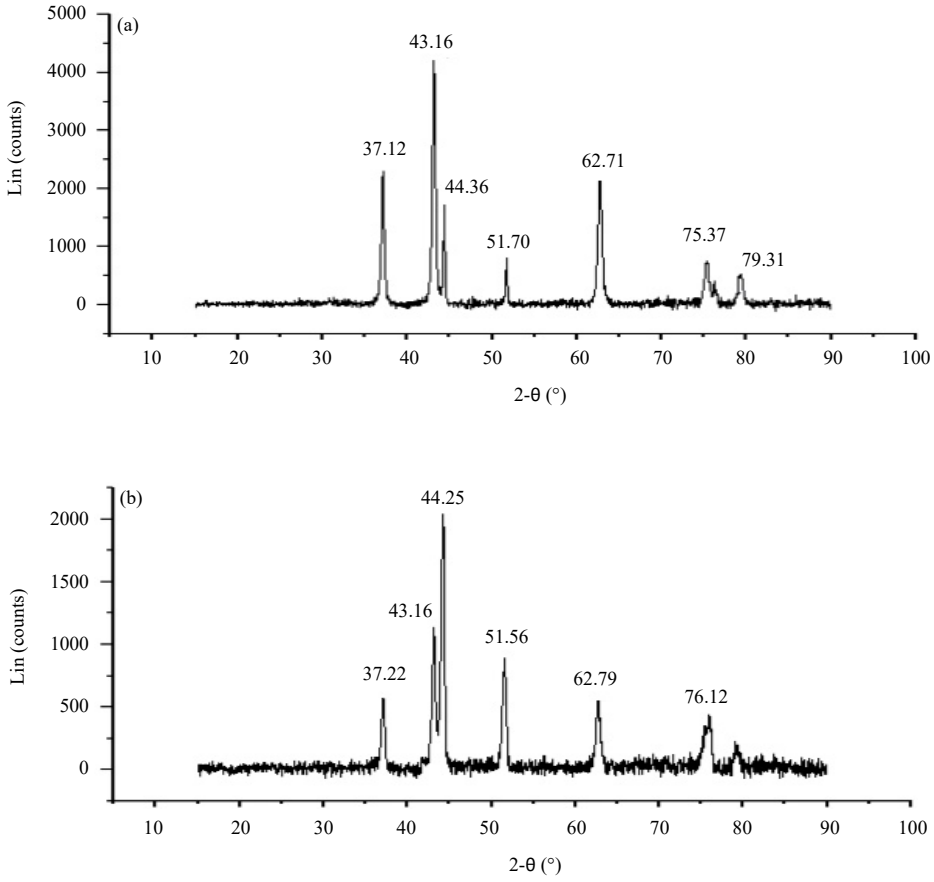

Fig. 3(a-b): (a) x-ray diffraction spectroscopy of NiO NPs at 500°C and (b) XRD spectra of NiO NPs at room temperature

In FTIR, the peak at ~1500 could be associated with the presence of C-Stretch in the aromatic ring[20]. The peak at ~1000 depicts C-O which is a carbonyl stretch of ethers which is mostly found in alkaloids, glycosides and triterpenoids. The chemical structures of tannins, saponins, phytosterols, anthraquinones, triterpenoids, glycosides and phytosterols all show the presence of C-C, C=C and C-O bonds, which were all present in the bark extract of *S. africana*.

The agglomerated NiO NPS revealed an amorphous shape. The agglomeration of NiO NPs revealed by SEM is due to van der Waals forces that pull the particles together. This occurs mostly in nanoparticles of smaller sizes[21]. Literature shows that agglomeration can be attributed to the fact that NiO NPs have high surface energy and high surface tension of the ultrafine nanoparticles[22]. The secondary metabolites found in plant extract, which reduce the nitrate precursor into NPs, can also affect the size of the synthesized NiO NPs. The NiO NPs that were synthesized using *Arabic gum*, on the contrary, revealed spherical surface morphology[23]. The contrast can be a result of the different plant extracts which probably contain varying phytochemical constituents.

XRD and XPS results showed peaks at the varying intensity with those depicted in the literature[24]. The varying size, shape and reagent used during synthesis can affect the crystallinity of the metal nanoparticles hence the different peaks. UV-VIS on the contrary, showed the maximum absorbance peak at approximately 240 nm as is depicted in the literature. The sharpness of the maximum absorption peak suggested that the synthesized NiO NPs were stable and the additional broad peak suggests the presence of some impurities[25].

For future studies, a comparative study on the morphology, size and parameters (PH) during synthesis should be done. In addition, NiO NPs will be screened for enhanced cytotoxicity to assess their effectiveness in inhibiting growth of breast cancer cells, thereby exploring their potential for use in chemotherapy.

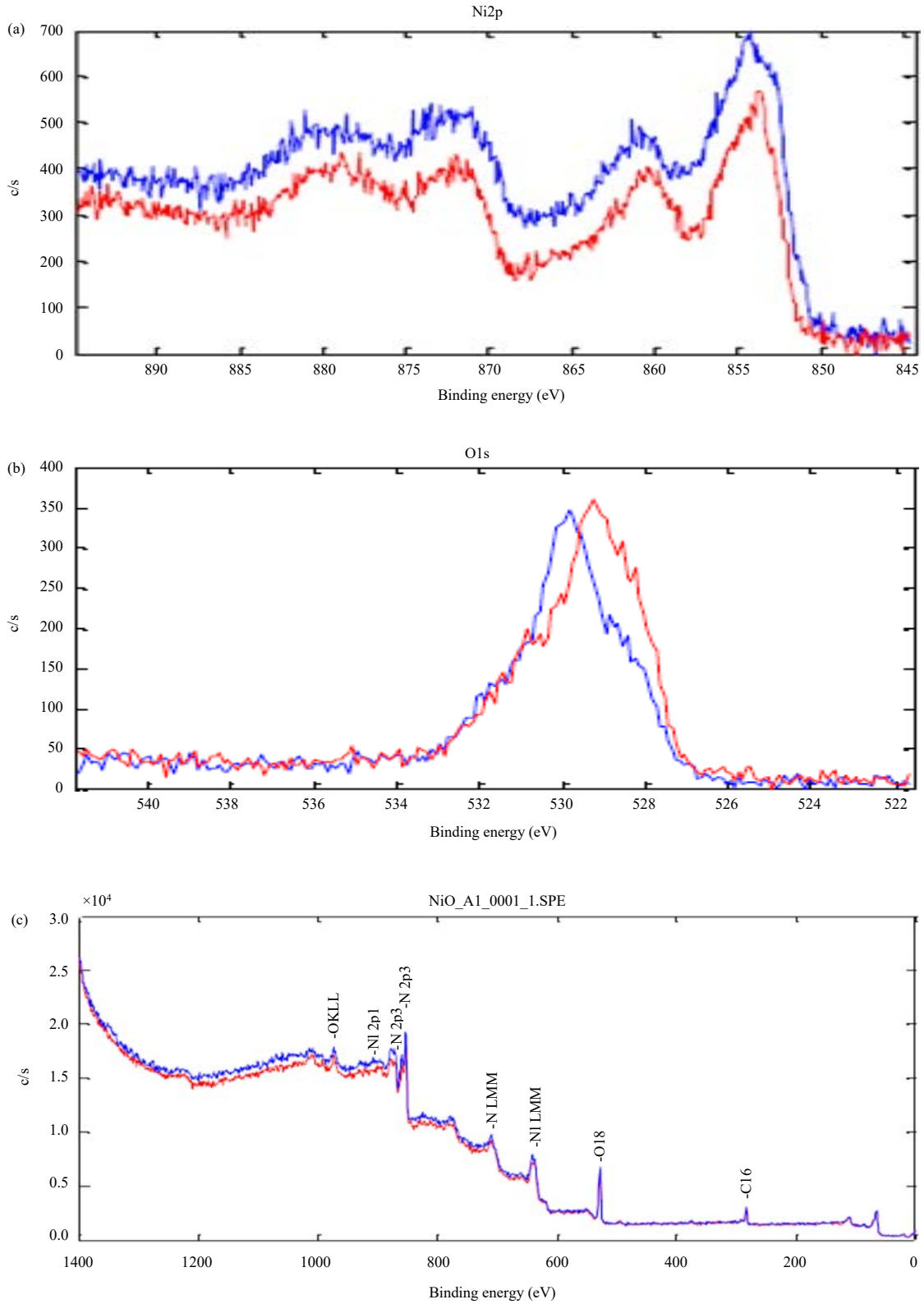

Fig. 4(a-c): XPS spectra of (a) Nickel spectra, (b) Oxygen spectra from NiO NPs region and (c) NiO NPs spectra showing peaks at 1000, 860, 700, 640, 540 and 280 corresponding to OKLL, NiO2p1, Ni@p3, NiLMM, O1s and c1s

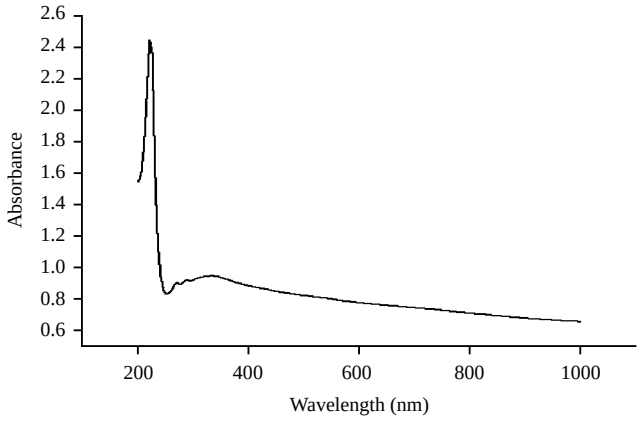

Fig. 5: UV-VIS spectrum of NiO NPs (peak at around 240 nm)

CONCLUSION

NiO NPs were successfully synthesized by green chemistry route using *S. africana* bark extract as a reducing agent. The characterization techniques revealed the physical properties of NiO NPs, while phytochemical analysis revealed the secondary metabolites present in *S. africana*.

SIGNIFICANCE STATEMENT

This study discovers the effectiveness of the green chemistry route (green synthesis) to synthesize metal nanoparticles using a medicinal plant as a reducing agent. The green synthesis that can be beneficial for bulk production of nanoparticles and is also environmentally friendly. The study further highlights characterization parameters which can be used to confirm the successful synthesis of nickel oxide nanoparticles.

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