Synthesis and electrochemical characterization of zinc oxide nanoparticles using green method

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Abstract

In recent years for synthesis of metal nanoparticles researchers give attention to develop efficient green chemistry method. In this article cost effective and eco-friendly method for the synthesis of zinc oxide nanoparticles using leaf extract of guava plant. Reduction of metal ions through leaf extracts leading to the formation of zinc oxide nanoparticles. The size, structure, morphology and electrochemical behavior of synthesized nanoparticles were characterized by UV-Visible spectroscopy, FTIR, X-ray diffraction, SEM-EDS, and Cyclic voltammetry.

Keywords: Zinc oxide nanoparticles, guava leaf extract, SEM-EDS, Cyclic voltammetry

1. Introduction

Unique size dependent properties of nanoparticles have received an increasing amount of research interest since last three decade [1]. Nanoparticles have higher surface to volume ratio with their small size have many potential applications. Metal nanoparticles play an important role in many key technologies. It is gaining importance of areas such as mechanics, optics, biomedical sciences, chemical industry, electronics, space industries, drug-gene delivery,
energy science, catalysis, optoelectronic devices, photoelectrochemical applications, and nonlinear optical devices [3-9]. Nanoparticles of zinc oxide are considered for humans and they reflect UV light better than micro-particles [10]. They have been widely used as ingredients in cosmetics and sunscreen and also widely used as nanosensors [11], zinc oxide have extensive application in water purification [12], also used in solar cells [13] etc.

For metal nanoparticles there are various chemical and physical methods are used for synthesis which include sol-gel [14], sonochemical method [15], electrochemical deposition [16], chemical vapour deposition method [17], radiation assisted [18], etc. The development of safe eco-friendly methods for biogenetic production is now of more interest due to simplicity of the procedures and versatility [19-20]. One more alternative and environmentally friendly green method is used. In our work leaf extract of guava plant have been used for zinc oxide nanoparticles synthesis.

2. Experimental and Methods

Fresh leaf of *psidium guajava* (guava) were collected from Dr. Babasaheb Ambedkar Marathwada university campus and zinc acetate (99%) NaOH by sigma Aldrich.

2.1 Preparation of leaf extract of guava plant

The fresh leaf of guava leaf extract solution was prepared by taking 10 gm of thoroughly washed and finally cut leaves in 250 ml Erlenmeyer flask along with 100ml double distilled water and then boiling the mixture for 15min before finally decanting it. The extract of leaf was filtered through whatman filter paper no. 1 and stored.

Zinc oxide nanoparticles was synthesized by taking 50ml 0.02M zinc acetate solution after 10min stirring 2ml of leaf extract of guava plant was added drop wise to the same. 1M NaOH was added drop wise to make ph 12 resulted in pale white aqueous solution. This was stirred for 2hr. after that pale white precipitate was taken out and washed by distilled water 2-3 times followed by ethanol. Then pale white powder of zinc oxide nanoparticles was obtained after drying at 50 ^{0}C in oven overnight. For X-ray diffraction analysis dried zinc oxide nanoparticles powder was Calcinated at 500 ^{0}C in muffle furnance for 2hr.

2.2 Characterization of synthesized nanoparticles

The synthesized zinc oxide nanoparticles were characterized by UV-visible, FT-IR, XRD, SEM-EDS, Cyclic voltammetry techniques

The wavelength of absorbance were determined by UV Visible spectrophotometer (JASCO 503). The FT-IR spectra were recorded on [JASCOFTIR/4100] Japan. The X-Ray powder diffraction patterns of the zinc oxide nanoparticles were recorded on mini flex goniometer under 30kv/15Ma, Xray scanning mode is continuous, scan axis- 2θ/θdata was taken for the 2θ range 20 to 80. The elemental composition and morphology were examined using SEM-EDS, electrochemical study of synthesized nanoparticles by cyclic voltammetry PGSTAT128N with NOVA software.

3 Result and Discussion

3.1 UV-Visible spectroscopy

As the phenomenon of surface Plasmon resonance occur only in the case of nanoparticles and not in the case of bulk metallic particles hence unique optical properties of nanoparticles can be studied using UV-visible spectroscopy**.** Absorption band can be attributed to the surface Plasmon resonance (SPR) peak of zinc oxide nanoparticles. The UV-visible absorption spectrum recorded for zinc oxide nanoparticles shows in Figure 1 exhibits maximum absorption at 355 nm. A broad peak around 355 nm can be attributed to wide size distribution of particles form in the solution. The particles showed hardly any change in the absorption spectra even after a month of ageing time, with are consistent with highly stable nature of particles the broadening of SPR peak is due to the agglomeration of the nanoparticles in the sample and high width of these particles distribution.

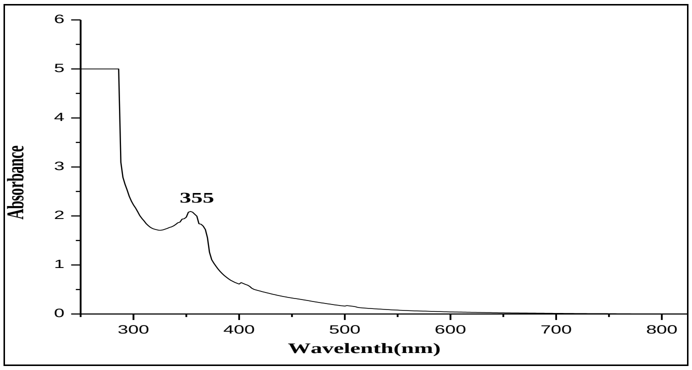


Fig. 1 UV spectra of zinc oxide nanoparticles.

3.2 FT-IR spectroscopy

FTIR measurement of both the guava (*psidium guajava)* leaf extract and the synthesized nanoparticles of zinc oxide were carried out to identify the possible biomolecules responsible for the reduction and efficient stabilization of the bio-reduced zinc oxide nanoparticles. The FTIR of plant extract and synthesized nanoparticles are shown in fig.2 (a) and (b). flavonoid and terpenoids are abundant in the plant extract of *psidium guajava* due to this it display a number of strong and intense adsorption peaks, as broad band at 3400cm^{-1} indicates O-H stretching, 3000cm^{-1} and 1480cm^{-1} attributable to aliphatic C-H stretching and bending modes. Peaks at 2390-2380cm^{-1} indicates C-O stretching, 1600cm^{-1} absorption peak correspond to C=C, peaks at 1240cm^{-1} for C-N linkage, primary and secondary alcohols functionalities bands at 1160-1080cm^{-1}, By comparing the spectrum of zinc oxide nanoparticles (b) with that of leaf extract, we can conclude that the two spectra are similar in their spectral features, the absorption peaks at 3400, 2390,1600,1480,1160,1080 corresponding to O-H,C-O,C=C,C-H observed in plant extract get narrower in the spectra of zinc oxide nanoparticles, the intensity of such peak changed confirm that the reduction and stabilization of zinc oxide nanoparticles synthesized by eco-friendly method.

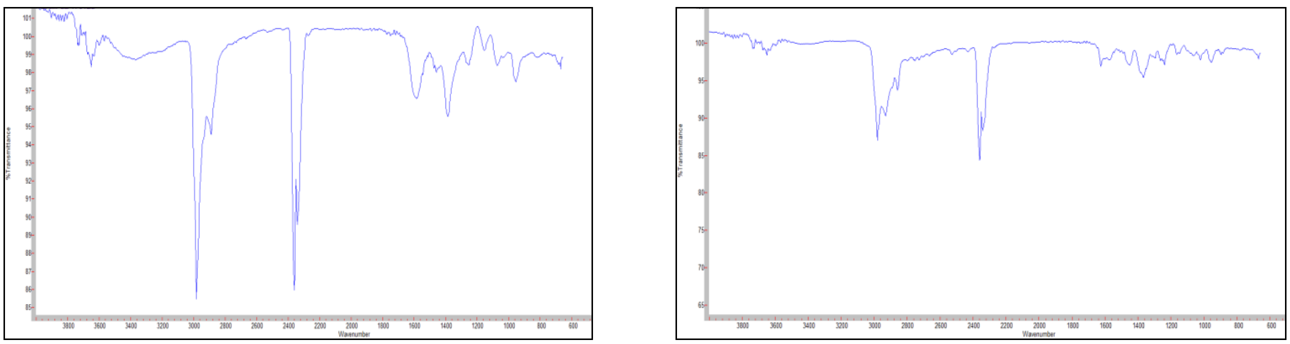


Fig 2: (a) FTIR of leaf extract of Guava plant and (b) FTIR of synthesized nanoparticles of zinc oxide.

3.3 X-Ray diffraction

XRD give regularity in atomic arrangement. In fig. (c) shows X-ray diffractogram of zinc oxide nanoparticles, Calcinated at 500^{0}c in muffle furnance for 2hr. The Sharpe peaks at (100), (002), (101), (102), (110), (103), (112), (201), (202) with lattice parameter a=3.249, b=3.249, c=5.206, α=90^0, β=90^0, γ=120^0 with hexagonal phase shows good agreement with JCPDS card No. 36-1451. Obtained Zinc oxide nanoparticles are in pure phase because there are no other characteristic impurities peaks were present. This result is in agreement with that of UV–visible absorption spectroscopy

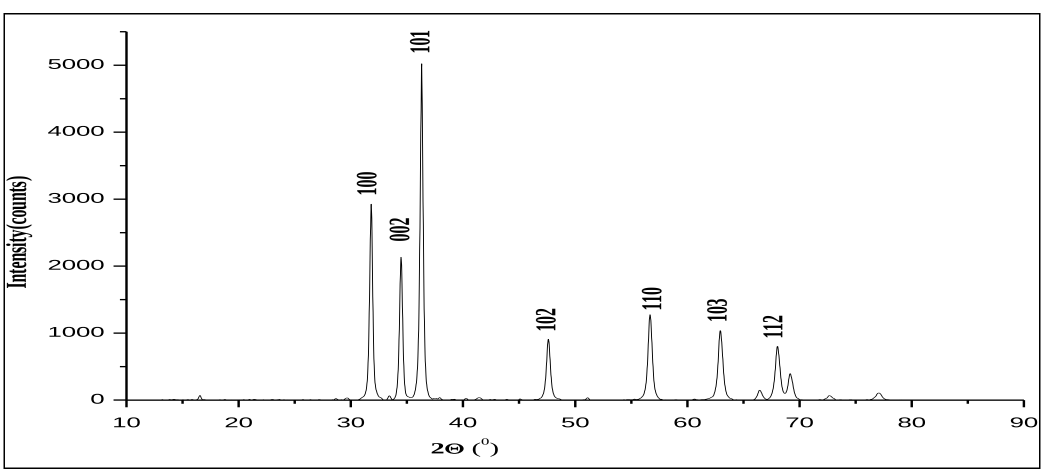


Fig 3: XRD pattern of zinc oxide nanoparticles.

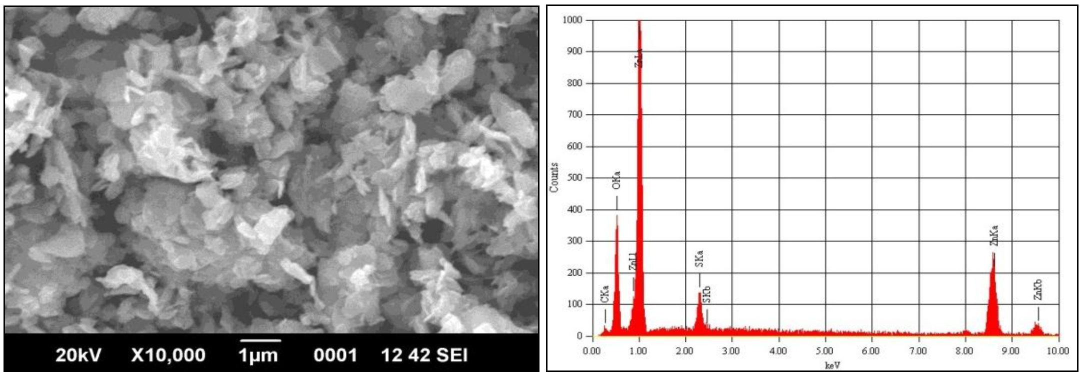
The average crystallite size of zinc oxide nanoparticles is 21.9nm has been computed by the equation of scherrer's [1]

$$D = \frac{0.9}{\beta cos\theta}\lambda$$

1) Where, D-average crystalline size
λ- X-ray wavelength 1.5405A^0
Θ- Diffraction angle
β- full width at half maximum

3.4 SEM-EDS analysis

Synthesized zinc oxide nanoparticles sample was analyzed at STIC-COCHIN by scanning electron microscope (SEM). SEM image shows external morphology of synthesized nanoparticles in the range of 1 μm because SEM shows lateral dimension of particles (including the reducing agent also may be agglomerated of the nanoparticles is of the order of few tens of nm.) synthesized zinc oxide nanoparticles are leaf like in appearance, fig. 4(a) and (b) For chemical composition Energy dispersive X-ray spectra also recorded for zinc oxide nanoparticles. EDS spectrum shows that the nanoparticles containing Zinc, oxygen, carbon and sulphur in table no.1 with mass and atom%. Presence of trace amount of Carbon and sulphur indicates that the leaf extract of guava plant acts as stabilizer.



(a) (b)

Fig 4: (a) SEM micrograph of ZnO nanoparticles, **(b)** EDS spectrum

Table 1: Elemental composition of nanoparticles.

Element	(keV)	Mass%	Atom%	K
C K	0.277	2.22	7.1	2.6284
O K	0.525	17.57	42.17	1
S K	2.307	5.96	7.14	0.9415
Zn K	8.63	74.25	43.6	4.4186
Total		100	100	

3.5 Cyclic Voltametry

Cyclic voltammetry was performed in an analytical system model PGSTAT128N with NOVA software. A three electrode cell assembly with Pt-wire electrode as counter electrode, Pt plate as a working electrode, and Ag/AgCl as reference electrode used for electrochemical study. All three electrode was ultrasonically cleaned and washed with double distilled water and dried at room temperature. Cyclic voltammetry is used to record the redox potential of species which are under experimental consideration. Cyclic voltammogram, fig. (5) is recorded for 0.1M KNO_3 solution containing 0.5 ml 0.02M zinc acetate solution with a scan rate 0.1 v/s. in potential range +1.0 to -1.0 after addition addition of leaf extract of guava plant cathodic peak shifted towards negative potential at -0.82V it indicate that the reduction of Zn $^{+2}$ ions and after addition of 1M NaOH solution, reoxidation of zinc as Zn^{+2} ions and it result in an anodic peak at -0.39V.

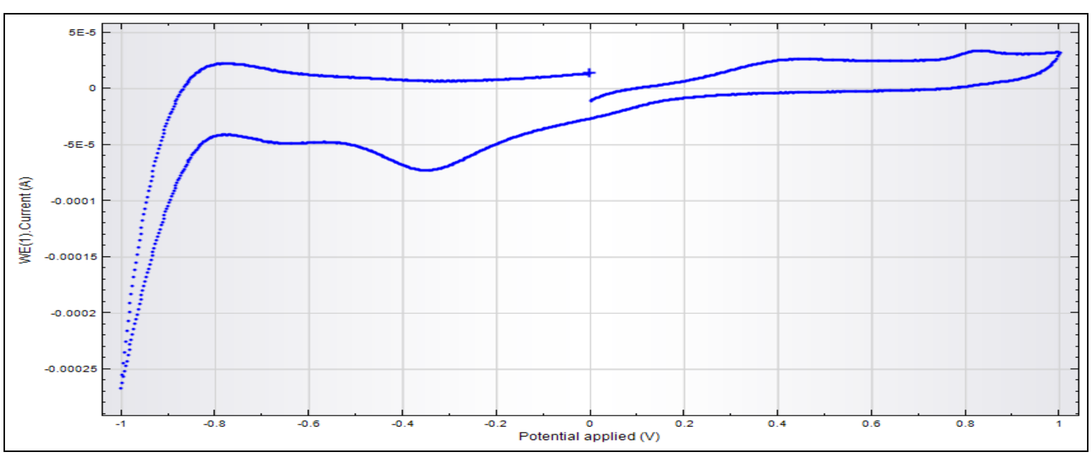


Fig 5: Cyclic voltammogram of zinc oxide nanoparticles.

4. Conclusion

Zinc oxide nanoparticles are biosafe, biocompatible and can be used for biomedical application. Green synthesis shows good result for the synthesis of crystalline, spherical, hexagonal nanoparticles of zinc oxide with 21.9nm size at atmospheric condition. The simplicity of this green method allows low cost fabrication of large amount of long lived zinc oxide nanoparticles without chemical stabilizing agent.

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