

# Green synthesis, characterization and optical properties of zinc oxide nanosheets using *Olea europea* leaf extract

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## ABSTRACT

In this paper, a green method is reported for synthesis and characterization of zinc oxide nanosheets using *Olea europea* leaf extract. ZnO nanosheets were characterized by UV-vis absorption spectroscopy, Fourier transform infrared spectroscopy (FT-IR), X-ray diffraction (XRD), and scanning electron microscopy (SEM). The UV-vis absorption spectrum shows an absorption band at 374 nm due to ZnO nanosheets. XRD characterizes the final product as highly crystalline ZnO with sizes in the range 18-30 nm. The SEM results reveal a presence of network of randomly oriented ZnO nanosheets or nanoplatelets with an average size of 500 nm and thicknesses of about 20 nm. This facile and green approach may provide a useful tool to large scale synthesis other nanoparticles that have potential biotechnology. Copyright © 2014 VBRI press

**Keywords:** Zinc oxide nanoparticles; *Olea europea* leaf extract; characterization; optical properties.



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## Introduction

Zinc oxide particles have versatile applications in semiconductors, piezoelectric devices, solar cells, catalysts, pigments, and electric devices, and cosmetic materials. Synthesis of zinc oxide nanoparticles (ZnONPs) have been achieved using various routes including precipitation method [1-4], hydrothermal synthesis [5-10], sonochemical [11, 12], sol-gel method [13, 14], polyol method [15], vapor-phase transport method [16], microemulsion method [17, 18], laser ablation [19-21], microwave technique [22, 23], aerosol process [24], electrochemical method [25], mechanochemical method [26, 27]. However, these routes have many disadvantages due to the difficulty of scale up the process of synthesis, separation and purification of nanoparticles from the surfactants, co-surfactants, organic solvents, and toxic materials. Developing facile and green methods for synthesizing zinc oxide nanoparticles are of importance and still a challenge for materials researchers. Recently biological methods for synthesis zinc oxide nanoparticle using microorganisms, enzymes, and plant extracts have been suggested as possible eco-friendly alternatives to chemical and physical methods. Few papers reported the biosynthesis of zinc oxide nanoparticles using plant extracts such as *Aloe barbadensis* miller [28], *Parthenium hysterophorus* [29], and *Poncirus trifoliata* plant dried fruits [30], and milky latex of *Calotropisprocera* [31].

In this study, we report for the first time a novel, rapid, cost-effective and environmentally biosynthesis of zinc oxide nanosheets using *Olea europea* leaf extract as capping and stabilizing agent.

## Experimental

### Materials

Zinc sulfate heptahydrate,  $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$  and sodium hydroxide, NaOH were analytical grade purchased from Merck and used without further purification. Distilled and deionized water was used in all experimental work.

### Preparation of plant leaf extract

*Olea europea* leaves (OeL) were collected from olive trees planted at the campus of Royal Scientific Society, El Hassan Science City, Amman, Jordan. Leaves were washed several times with distilled water to remove dust particles and then sun dried to remove the residual moisture. *Olea europea* leaf extract (OeLE) was prepared by placing 10 g of dried fine cut in 500 ml glass beaker along with 400 ml of sterile distilled water. The mixture was then boiled for 5 minutes until the color of aqueous solution changed from watery to yellow. Then the mixture was cooled to room temperature and filtered with Whatman No. 1 filter paper before centrifuging at 1200 rpm for 2 minutes to remove biomaterials. The extract was stored at room temperature in order to be used for further experiments.

### Synthesis of zinc oxide nanosheets

In a typical reaction mixture, 5-10 ml of the aqueous yellow leaf extract of *Olea europea* was added to 300 ml of 4 mM of aqueous zinc sulfate heptahydrate solution and stirred at room temperature for 5 min to achieve pale yellow solution. After that, 1M sodium hydroxide solution is added to the mixture drop by drop, with continuous stirring at room temperature, the yellow color of the above mixture started changing to yellowish-white suspension at pH 12. The suspended particles were purified by dispersing in sterile distilled water and centrifugation three times. Afterwards, the white particles were washed with ethanol to remove the impurities for the final product. Then a white powder was obtained after drying at 60 °C in vacuum oven for 6 h. The above procedure was repeated by using different amounts of *Olea europea* leaf extract and zinc sulfate heptahydrate concentration at room temperature.

### Characterization techniques

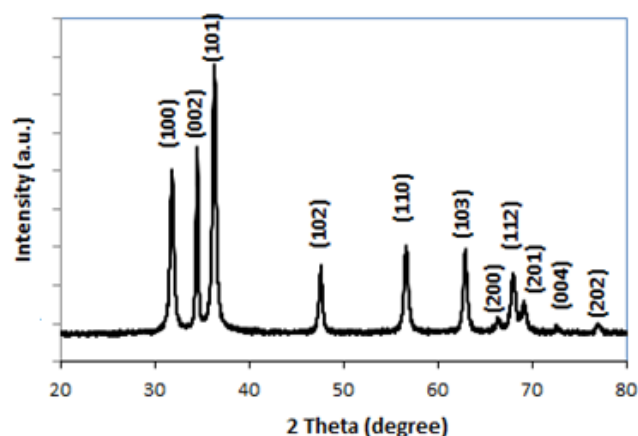
Scanning electron microscopy (SEM) analysis of synthesized zinc oxide nanoparticles was done using a Quanta FEI 450 SEM machine. Powder X-ray diffraction was performed using a X-ray diffractometer, Shimadzu, XRD-6000 with  $\text{CuK}\alpha$  radiation  $\lambda = 1.5405 \text{ \AA}$  over a wide range of Bragg angles ( $20^\circ \leq 2\theta \leq 80^\circ$ ). Fourier transform infrared spectroscopic measurements were done using Shimadzu, IR-Prestige-21 spectrophotometer. UV-vis spectrum of zinc oxide nanoparticles was recorded, by taking 0.1 ml of the sample and diluting it with 2 ml deionized water, as a function of time of reaction using a Shimadzu, 1601 spectrophotometer in the wavelength region 300 to 700 nm operated at a resolution of 1 nm.

## Results and discussion

**Fig. 1** shows the X-ray diffraction (XRD) pattern of ZnO nanopowder synthesized from zinc sulfate and sodium hydroxide in the presence of *Olea europea* leaf extract at room temperature. The XRD pattern revealed the orientation and crystalline nature of zinc oxide nanoparticles. The peak position with  $2\theta$  values of  $31.841^\circ$ ,  $34.507^\circ$ ,  $36.324^\circ$ ,  $47.592^\circ$ ,  $56.634^\circ$ ,  $62.895^\circ$ ,  $66.426^\circ$ ,  $67.983^\circ$ ,  $69.091^\circ$ , and  $76.987^\circ$  are indexed as (100), (002), (101), (102), (110), (103), (002), (112), (201), and (202) planes, which are in good agreement with those of powder ZnO obtained from the International Center of Diffraction Data card (JCPDS-36-1451) confirming the formation of a crystalline monoclinic structure. No extra diffraction peaks of other phases are detected, indicating the phase purity of ZnO nanopowder. The average crystallite size of the synthesized zinc oxide nanosheets was calculated to be 20 nm using Debye-Scherrer equation [32]:

$$D = K\lambda/\beta\cos\theta$$

where D is the crystallite size of zinc oxide nanosheets,  $\lambda$  represents wavelength of x-ray source 0.1541 nm used in XRD,  $\beta$  is the full width at half maximum of the diffraction peak, K is the Scherrer constant with value from 0.9 to 1 and  $\theta$  is the Bragg angle.



**Fig. 1.** XRD pattern of the synthesized zinc oxide nanosheets

In order to determine the functional groups on *Olea europea* leaf extract and identify their role in the synthesis of zinc oxide nanoparticles, FT-IR analysis was performed. FT-IR spectrum of *Olea europea* leaf extract and synthesized ZnONPs are shown in **Figs. 2** and **3**. The *Olea europea* leaf extract spectra showed a number of peaks thus reflecting a complex nature of the *Olea europea* leaf extract powder. The FT-IR spectrum of OeLE (**Fig.2**) showed strong absorption bands at  $3336 \text{ cm}^{-1}$ ,  $2920 \text{ cm}^{-1}$ , and  $2353 \text{ cm}^{-1}$  which is characteristic of the  $-\text{OH}$  stretching vibration,  $-\text{CH}$  stretching,  $\text{N-H}$  stretching or the  $\text{C}=\text{O}$  stretching vibrations, respectively and shifted to higher frequency region  $3421 \text{ cm}^{-1}$ , and lower region  $2864 \text{ cm}^{-1}$ , and  $2282 \text{ cm}^{-1}$  in the spectrum of synthesized ZnONPs (**Fig. 3**). The absorption band at  $2920 \text{ cm}^{-1}$  can be ascribed to the stretching mode of C-H bonds and its shift to  $2846 \text{ cm}^{-1}$  in synthesized ZnONPs (**Fig. 3**), confirming that diamine

molecules are adsorbed on ZnO nanoparticles crystal surface. The peaks shift from 3336 to 2353  $\text{cm}^{-1}$  implicated that these groups may be involved in the process of zinc oxide nanoparticles synthesis. There was a shift in the following peaks: 1612  $\rightarrow$  1620  $\text{cm}^{-1}$ , 1435  $\rightarrow$  1458  $\text{cm}^{-1}$ , 1315  $\rightarrow$  1361  $\text{cm}^{-1}$ , and 1018  $\rightarrow$  1095  $\text{cm}^{-1}$ . The peak located at 1612  $\text{cm}^{-1}$  could be assigned to the C=O stretching in the carboxyl or C=N bending in the amide group of OeLE. The sharp band at 1018  $\text{cm}^{-1}$  indicated the stretching vibration of (NH)-C-O group, which is shifted to 1107  $\text{cm}^{-1}$ , and the band at 1435  $\text{cm}^{-1}$  is due to aromatic -CH stretching vibrations. After reduction of Zn ions the decrease in intensity of 1516  $\text{cm}^{-1}$  indicated the involvement of the secondary amines in the reduction process. The band at 856  $\text{cm}^{-1}$  is due to asymmetrical and symmetrical stretching of zinc carboxylates resulting from the involvement of carboxylic groups in protein of OeLE. Strong bands at 420  $\text{cm}^{-1}$  and 570  $\text{cm}^{-1}$  are attributed to the vibrations of elongation and of deformation of vibratory Zn-O. The structural changes in FT-IR spectra indicated that the capping and stabilization of zinc oxide nanoparticles via the coordination with OH, -NH, C=O, C=N. The physicochemical properties of *Olea europea* leaf extract act as capping agent and prevents the nanoparticles formed from aggregation.

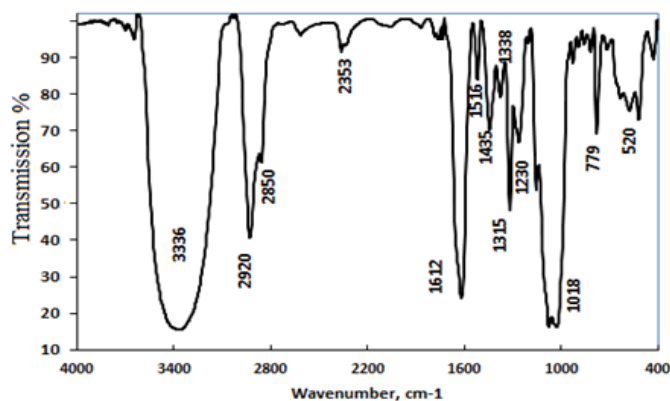


Fig. 2. FT-IR of *Olea europea* leaf extract.

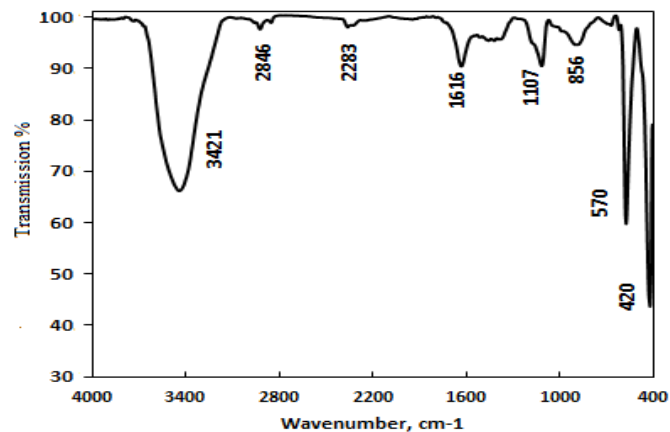


Fig. 3. FT-IR of synthesized zinc oxide nanosheets in the presence of *Olea europea* leaf extract.

UV-vis of the synthesized zinc oxide nanoparticles is shown in Fig. 4. An absorption peak was observed in each

spectrum at 374 nm which is characteristic band for the pure zinc oxide. No other peaks were observed in the spectrum, indicating the high purity of the synthesized zinc oxide nanoparticles by this green method.

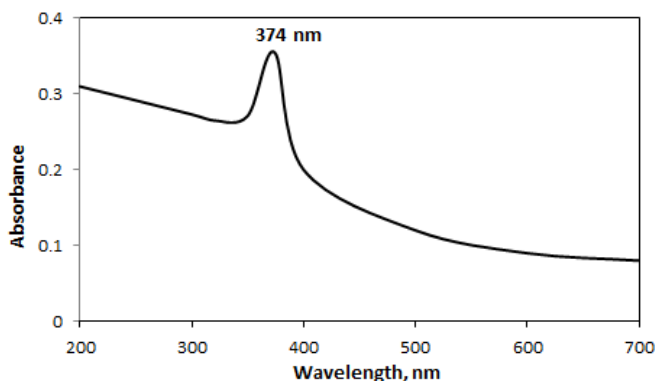


Fig. 4. UV-Vis spectra of synthesized ZnO NPs

The band gap can be calculated by the intercept of the tangent to the  $(ah\nu)^2$  versus photon energy ( $h\nu$ ) plot. As shown in Fig. 5,  $E_g$  can be calculated by plotting  $(ah\nu)^2$  as a function of photon energy and extrapolating the linear portion of the curve to the photon energy axis. From the plot, the direct energy band gap was found to be 3.32 eV.

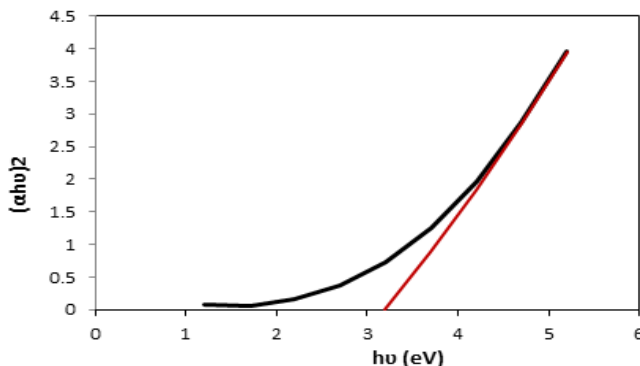


Fig. 5. Plot of  $(ah\nu)^2$ - $h\nu$  of zinc oxide nanoparticles

SEM images, Fig. 6 (a,b,c and d) of synthesized zinc oxide nanosheets by this green method, we found that the *Olea europea* leaf extract strongly influences the morphologies of the resultant zinc oxide nanosheets. As-synthesized zinc oxide were mainly composed of nanosheets and nanoflowers sizes ranges with the average size in the range of 500 nm and primary particles coalesced together to form larger-sized secondary particles. While using larger quantities of *Olea europea* leaf extract zinc oxide nanosheets (Fig.6c and Fig.6d) with quite surface were synthesized with an average size of ca. 500 nm and average thickness of 8 nm. The figures show a quite dense morphology comprised of randomly oriented overlapping, thin sheets of ZnO where the individual sheets appear to have a lateral dimension of less than one micrometer. A good estimate of the nanosheets thickness is in the range of 10 to 30 nm. However, it is possible that the thicker sheets may consist of several thinner sheets aggregated to form a nanosheet networks. Such ZnO nanosheets or platelet format form a useful baseline in the

sense of demonstrating that ZnO of very high crystallinity and near-perfect stoichiometry which agrees well with the XRD results.

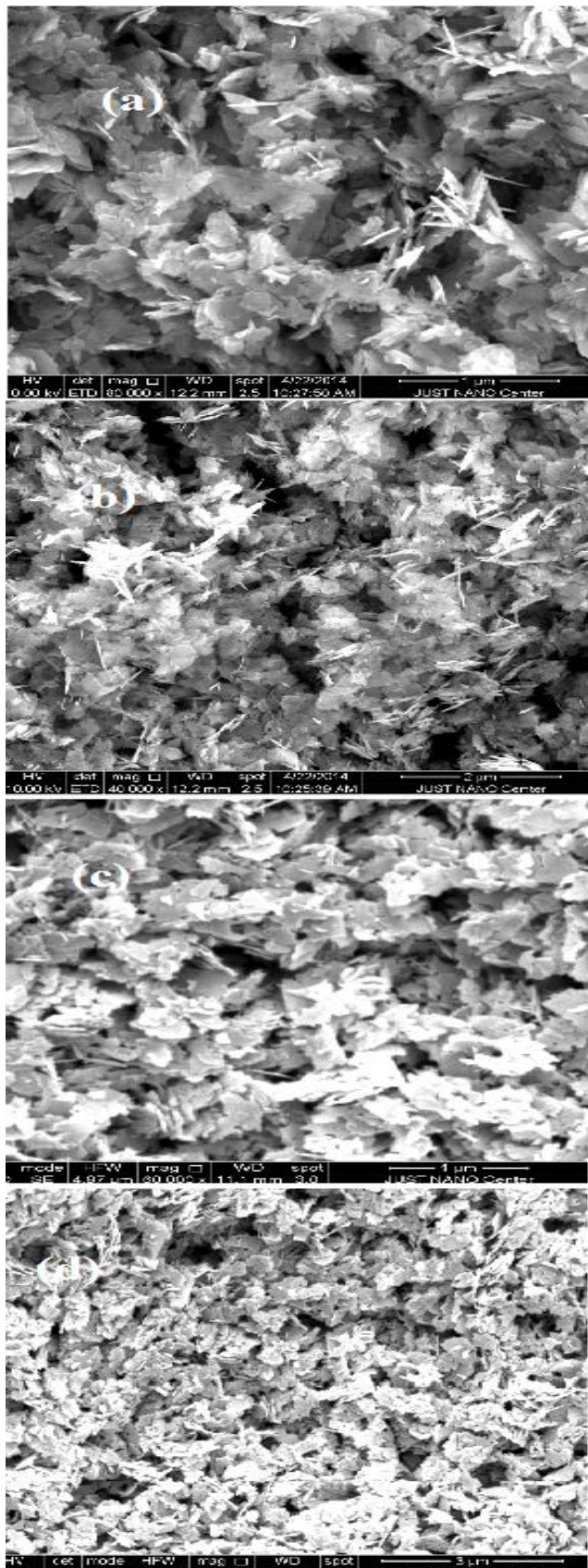


Fig. 6. SEM image of the synthesized ZnO nanosheets.

## Conclusion

In the present work, we first report an eco-friendly and simple method for the synthesis of zinc oxide nanosheets using *Olea europea* leaf extract. FT-IR analysis of aqueous *Olea europea* leaf extract indicates the presence of phytoconstituents such as amine, aldehyde, phenol, and alcohols which were the surface active molecules stabilized the zinc oxide nanosheets. XRD analysis reveals that the average size of the nanoparticles was found to be 20 nm which was calculated by Debye-Scherrer equation. FT-IR and XRD results corroborated the purity of the synthesized ZnO nanosheets. The method of the present study offers several important advantageous features. First, the synthesis route is economical and environmentally friendly, because it involves inexpensive and non-toxic materials for second, large scale synthesis.

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