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## **Sol-gel Synthesis and Characterization of Zinc Oxide Nanoparticles Using Black Tea Extract**

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### **Abstract**

The use of plant extract is generating the interest of researchers toward cost effective, nontoxic, economic viability and eco-friendly green synthesis of nanoparticles. In the present work, zinc oxide (ZnO) nanoparticles were synthesized using black tea extract and zinc nitrate as the zinc source by the sol-gel method. The synthesized ZnO nanoparticles were characterized by powder X-ray diffraction (XRD), UV-visible spectroscopy and Fourier Transform Infrared Spectroscopy (FTIR). The average crystallite size of ZnO nanoparticles was calculated using Scherrer formula. The X-ray powder diffraction (XRD) analysis revealed the formation of wurtzite hexagonal phase ZnO with average particle size of 32 nm.

**Keywords:** *ZnO, Nanoparticles, Biosynthesis, Nanobiotechnology, Sol-gel.*

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## Introduction

In the last few years, synthesis of metal oxide nanostructures with desired architecture has received considerable attention due to their unique properties and potential for many applications [1-4]. Among all of the metal oxides, ZnO is of a great interest due to its wide band gap (3.37 eV) and large excitation binding energy (60 meV). Zinc oxide (ZnO) is an inorganic semiconductor with a hexagonal wurtzite crystal structure [5]. The ZnO-NPs have numerous applications such as catalysis [6], piezoelectric devices [7], pigment [8], chemical sensors [9], and cosmetic material especially for transparent UV protection [10].

ZnO-NPs have been prepared with different sizes via several methods such as solvothermal and hydrothermal synthesis [11,12], precipitation [13,14], polymerization method [15], laser ablation [16], sonochemical [17,18], chemical vapor deposition [19], thermal decomposition [20] and sol-gel [21-23]. The sol-gel method has gained much interest among researchers as it offers controlled consolidation, shape modulation, patterning of the nanostructures [24] and low processing temperature [25]. Recently, green synthesis of ZnO-NPs by plants such as aloe vera leaf extract [26], Citrus aurantifolia extract [27], milky latex of Calotropis procera [28] and Plectranthus amboinicus [29] have been reported.

In this work, for the first time, we have synthesized zinc oxide nanoparticles using black tea powder extract, zinc nitrate as the zinc source and water as solvent by sol-gel process, as a cheap and friendly approach to the nature. The obtained samples were characterized by Fourier Transform Infrared spectroscopy (FTIR), UV-Visible spectroscopy and X-Ray Diffraction Pattern (XRD).

## Experimental

### *Material and methods*

Black tea powder was obtained at a local health food store. Zinc nitrate hexahydrate  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ , was purchased from daijung (Darmstadt, Korea) used without further purification. The IR spectra were measured on a Jasco 6300 FT-IR spectrometer (KBr disks). UV-Vis absorption spectra were prepared on a Metrohm (Analytical Jena-Specord 205) double beam instrument. The UV-Visible measurements were carried out from 200 nm to 700 nm wavelength for all of the samples. The structural properties of synthesized nanoparticles were investigated by X-ray powder diffraction (XRD) pattern on a X'Pert-PRO advanced diffractometer using Cu ( $\text{K}\alpha$ ) radiation (wavelength: 1.5406 Å) at 40 kV and 40 mA at room temperature in the range of  $2\theta$  from 20 to 80°.

#### *Preparation of black tea powder extract*

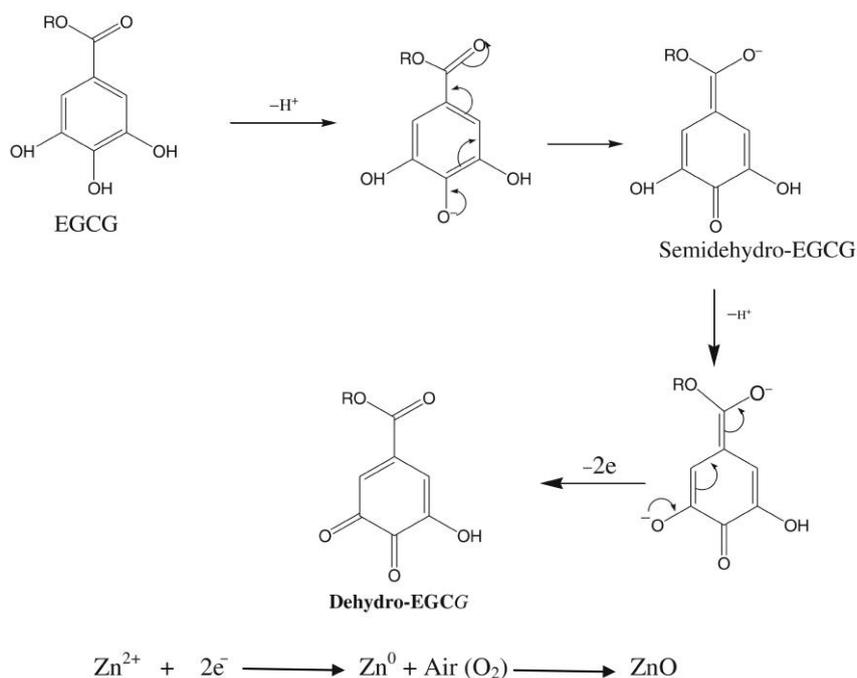
To prepare the black tea extract, 2 g of tea powder was dissolved in 100 ml of water and boiled for around 30 min. After cooling at room temperature, these were centrifuged for 20 min and filtered. The filtrates were stored at 5-10 °C for further experiments.

#### *Synthesis of ZnO nanoparticles using black tea extract*

To prepare ZnO-NPs, 2 g of  $Zn(NO_3)_2 \cdot 6H_2O$  was dissolved in 10 ml of distilled water and then stirred for 10 min. After that, 30 ml of tea powder extract was added to the zinc nitrate solution and the container was moved to a sand bath. The temperature of the sand bath was fixed at 75 °C. Stirring was continued for 12 h to obtain a brown color powder. The final product was calcined at 400 °C temperatures in air for 4h to obtain a white powder of ZnO-NPs.

### **Results and discussion**

The black tea extract was used as reducing as well as stabilizing agent for ZnO nanoparticles. The possible mechanism is shown in the Scheme 1. This gives strong evidence for the involvement of polyphenols in the rapid biosynthesis and for the stability of metallic nanoparticles in the aqueous medium [30, 31]. It suggests that well dispersed Zinc nanoparticles may have obtained through the reduction of  $Zn^{+2}$  using tea extracts that contains epigallocatechin gallate (EGCG), which acts as both the reducing and capping agent. EGCG is a highly water-soluble compound with strong polarity. As illustrated in Scheme 1, EGCG served as a stable (electron + proton) donor during interactions. It was first converted into the radical ion “semihydro-EGCG” and then into dehydro-EGCG through oxidation. DehydroEGCG and EGCG together constituted the redox system which was sufficient to reduce  $Zn^{2+}$  to Zn [32]. The lone pair electrons in the polar groups of EGCG can occupy two sp orbitals of the zinc ion to form a complex compound. The EGCG was capped with zinc ions, then synthesized Zn(0) nanoparticles through reduction of  $Zn^{2+}$  inside the nanoscopic templates. In the presence of nanoscopic templates, small zinc nanoparticles were easily formed. The other explanation may be attributed to the dispersion effect of the oxidation product of EGCG on the zinc nanoparticles after the completion of the reduction reaction. EGCG was converted into dehydro-EGCG through oxidation.



**Scheme 1.** A proposed mechanism for the formation of ZnO nanoparticles.

#### *Preparation of ZnO-NPs nanoparticles.*

The variety of methods for ZnO production, such as solvothermal, microwave, precipitation in an aqueous solution, hydrothermal synthesis, the sol-gel process, precipitation from microemulsions and mechanochemical processes, makes it possible to obtain products with particles differing in shape, size and spatial structure [33]. In this study, we demonstrate a new method of sol-gel to synthesizing ZnO-NPs using black tea without using any organic chemicals. In The major advantages of this research is the synthesis of ZnO-NPs in eco-friendly, very cost effective and green conditions. Precursors and particle sizes of the synthesized ZnO-NPs by various methods are listed in Table 1. The presented results show that using of black tea-based sol-gel method leads to the formation of fairly smaller particle sizes and more desirable phase purity and the crystallinity for the prepared ZnO-NPs in comparison with other methods (Table 1).

Table 1. Precursors and particle sizes of the synthesized ZnO-NPs by various methods.

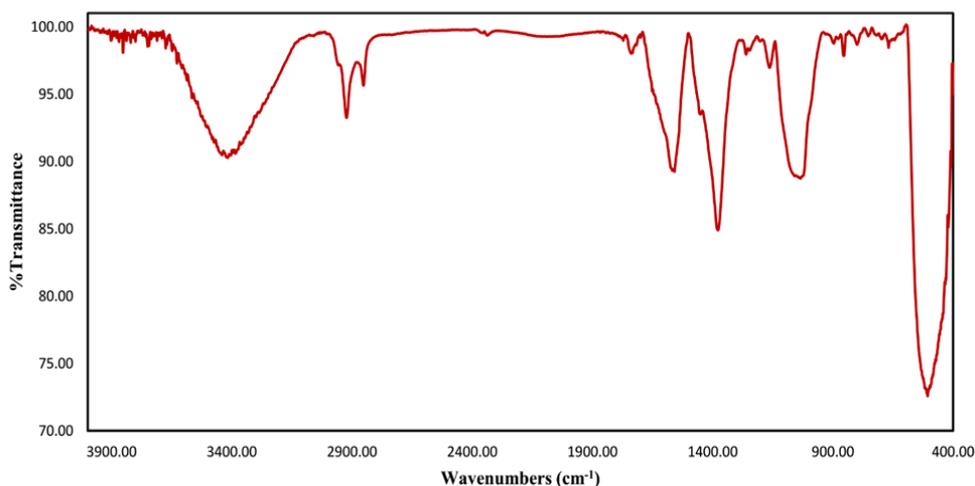
Entry	method	Precursors	Size of nanoparticles*	Ref.
1	Mechanochemical	ZnCl <sub>2</sub> , Na <sub>2</sub> CO <sub>3</sub> , NaCl	27-56	34
2	Precipitation	Zn(NO <sub>3</sub> ) <sub>2</sub> , NaOH	50	35
3	Precipitation	Zn(NO <sub>3</sub> ) <sub>2</sub> , NaOH	40	36
4	Precipitation	Zn(SO <sub>4</sub> ) <sub>2</sub> .7H <sub>2</sub> O, NaOH	74	37
5	Precipitation	ZnCl <sub>2</sub> , NH <sub>4</sub> OH, CTAB	54-60	38
6	Sol-gel	Zn(CH <sub>3</sub> COO) <sub>2</sub> , diethanolamine, ethanol	70	39
7	Sol-gel	Zn(NO <sub>3</sub> ) <sub>2</sub> .6H <sub>2</sub> O, gum tragacanth	50	40
8	hydrothermal	Zn(CH <sub>3</sub> COO) <sub>2</sub> , Zn(NO <sub>3</sub> ) <sub>2</sub> , LiOH, KOH, NH <sub>4</sub> OH	100	41
9	hydrothermal	Zn(CH <sub>3</sub> COO) <sub>2</sub> , NaOH, HMTA (hexamethylenetetraamine)	55-110	42
10	microwave	Zn(CH <sub>3</sub> COO) <sub>2</sub> .2H <sub>2</sub> O, hydrazine hydrate (N <sub>2</sub> H <sub>4</sub> ), ammonia (NH <sub>3</sub> )	50-150	43
11	Emulsion	Zn(NO <sub>3</sub> ) <sub>2</sub> , surfactant (ABS, Tween-80 and 40, C <sub>21</sub> H <sub>38</sub> BrN)	40-50	44
12	Green synthesis method	Zn(CH <sub>3</sub> COO) <sub>2</sub> , NaOH, leaf of Corriandrum sativum	66	45
13	solvothormal	Zn(CH <sub>3</sub> COO) <sub>2</sub> , ethanol, TEA	33	46
14	Sonochemical	Zn(CH <sub>3</sub> COO) <sub>2</sub> , NH <sub>3</sub> , NaOH	30-36	47
15	Biosynthesis	Zn, Trifolium Pratense flower	60-70	48
16	Precipitation	Zinc acetate dehydrate, NaOH, black tea	20 <sup>1</sup>	49
17	Sol-gel	Zn(NO <sub>3</sub> ) <sub>2</sub> .6H <sub>2</sub> O, black tea	32	This work

\*Calculated by Scherer formula

<sup>1</sup>Determined by Transmission electron microscopy*Characterization of ZnO nanoparticles.*

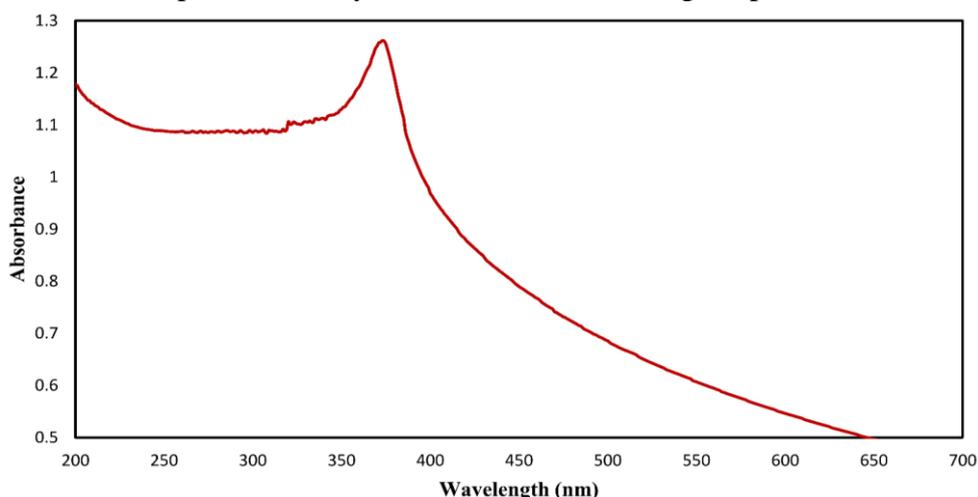
FTIR spectra were recorded in solid phase using the KBr pellet technique in the range of 400-4000 cm<sup>-1</sup>. Figure 1 shows the IR spectrum of the sample calcined at 400°C for 4 hours. According to Figure 1, it is observed that the bands are at 3416 cm<sup>-1</sup>, 2932 cm<sup>-1</sup>, 1559 cm<sup>-1</sup>, 1378 cm<sup>-1</sup>, 1034 cm<sup>-1</sup>, 874 cm<sup>-1</sup> and 506 cm<sup>-1</sup>. The peak in the region between 400 and 600 cm<sup>-1</sup> is allotted to Zn-O [50]. Also, the band at 506 cm<sup>-1</sup> corresponds to the E<sub>2</sub> mode of hexagonal ZnO (Raman active) [51]. The bands at 3416 cm<sup>-1</sup> and 1599 cm<sup>-1</sup> are characteristic

for hydroxyl group (O-H). The peaks at  $1378\text{ cm}^{-1}$  and  $1034\text{ cm}^{-1}$  may be ascribed to C-O and -C-O-C stretching modes. The band which appeared at  $2932\text{ cm}^{-1}$  is due to C-H stretching.



**Figure 1.** FT-IR spectrum of ZnO NPs.

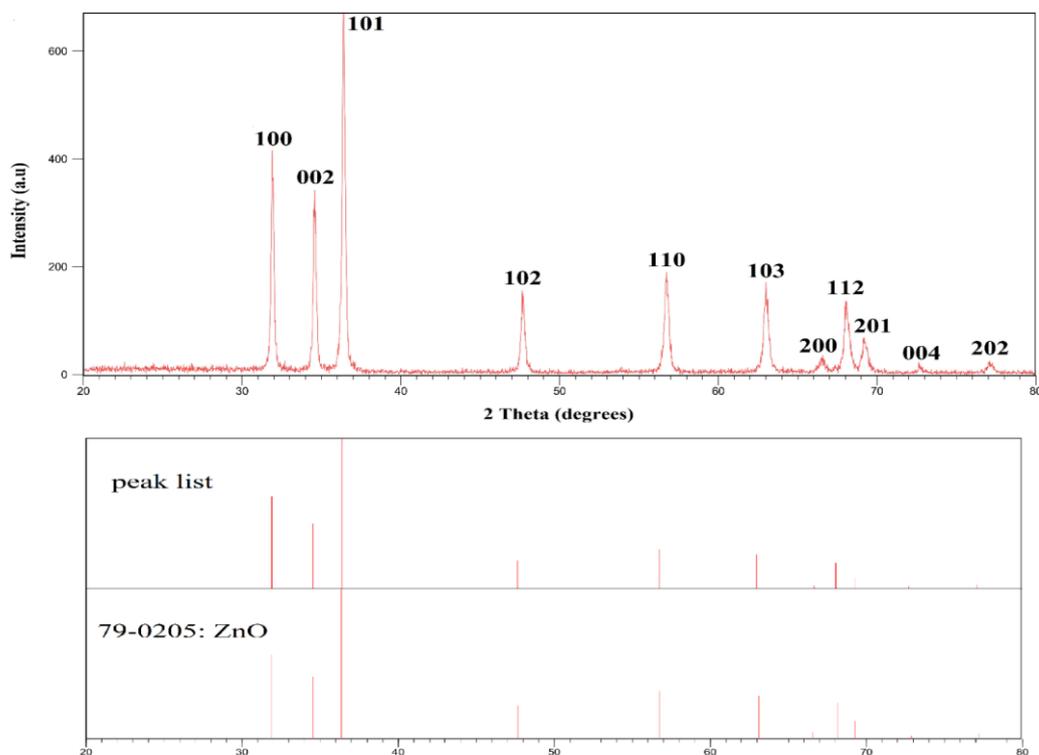
Figure 2. shows UV spectra of biosynthesized ZnO NPs using tea powder extract.



**Figure 2.** UV-Vis spectrum of ZnO NPs.

The ZnO-NPs were dispersed in water with concentration of 0.1 wt% and then the solution was used to perform the UV-Vis measurement. The spectrum reveals a characteristic absorption peak of ZnO at wavelength of 374 nm which can be assigned to the intrinsic band-gap absorption of ZnO due to the electron transitions from the valence band to the conduction band ( $O_{2p}-Zn_{3d}$ ) [52,53]. In addition, this sharp peak shows that the particles are in nano-size, and the particle size distribution is narrow.

The crystal structure confirmation analysis was carried out by the X-ray diffraction patterns. XRD patterns of the product obtained by calcination of precursor at 400 °C are shown in Figure 3.



**Figure 3.** XRD patterns of ZnO-NPs calcined at 400 °C.

The diffraction peaks of the nanoparticles are identified as zincite phase with hexagonal wurtzite crystal structure with lattice constants of  $a = b = 3.241 \text{ \AA}$  and  $c = 5.187 \text{ \AA}$ . The  $2\theta$  characteristic peaks of ZnO at  $31.90^\circ$ ,  $34.54^\circ$ ,  $36.38^\circ$ ,  $47.65^\circ$ ,  $56.71^\circ$ ,  $62.96^\circ$ ,  $66.63^\circ$ ,  $68.04^\circ$ ,  $69.24^\circ$ ,  $72.72^\circ$  and  $77.08^\circ$ , corresponding to the (100), (002), (101), (102), (110), (103), (200), (112), (201), (004) and (202) planes of the crystal lattice, respectively. These values agree well with those provided by the standard card JCPDS 79- 0205. The diffraction patterns are well matched with the literature [23] and no impurity peaks were observed. Furthermore, the strong and sharp diffraction peaks confirm the high crystallinity of the products. The average particle size of ZnO nanoparticles was determined from the full width at half maximum (FWHM) of the XRD patterns using the well- known Scherrer formula:  $D = 0.9\lambda/\beta\cos \theta$  Where  $D$  is the crystallite size (nm),  $\beta$  is the full width at half maximum of the peak,  $\lambda$  is the X-ray wavelength of Cu  $K\alpha = 0.154 \text{ nm}$  and  $\theta$  is the Bragg angle [54]. Using the above method we obtained an average size of 32 nm for ZnO nanoparticles.

## Conclusions

In summary, we have reported for the first time, the use of black tea powder extract for the synthesis of ZnO nanoparticles using water as solvent by the sol-gel method. A pure hexagonal (wurtzite) structure was formed after heat treatment at 400 °C for only 4 h. This method is interesting in applying and extending the green chemistry rules in the preparation of nanoparticles. The other advantages of the method are simple synthesis, in a normal atmosphere, and low cost, giving a potential avenue for further practical scale-up of the production process and applications. It is expected that these nanoparticles can find potential applications in different fields such as cosmetics and optical/electrical devices as well as medicinal applications.

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