Structural characterization of ZnO nanoparticles synthesized by co-precipitation and sol-gel method

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ZnO nanoparticles were synthesized by two routes: co-precipitation and sol-gel method. The ZnO nanoparticles were investigated by means of X-ray diffraction, scanning electron microscopy, Fourier transform infrared spectroscopy and UV-VIS spectroscopy. XRD analysis showed that the ZnO nanoparticles have a hexagonal crystalline structure. The average crystallite size was around 64 nm for the sample synthesized by co-preciptation method and 43 nm for the one synthesized by sol-gel method. Optical properties of synthesized ZnO nanoparticles revealed that the sample obtained by co-precipitation method has a band gap value around 3.30 eV and the sample obtained by sol-gel method around 3.27 eV.

1. Introduction

Nanostructured materials present a high interest due to their unique properties and possible application in electronics, optics and photonics [1]. Among nanostructured materials, zinc oxide (ZnO) materials presented a high interest because of their optical, electrical and magnetical properties [2].

Zinc oxide is a semiconductor material (II-VI compound) [3] with a wide range of applications in optics, sensors, electronics, etc. [1,3,4]. Also, the optical properties of ZnO materials, with a wide direct band-gap of about 3.37 eV and a large exciton binding energy of 60 meV, present a great interest for applications in optoelectronics, photovoltaics and biological sensing [5,6]. ZnO material is one of the potential semiconductors in solar energy conversion because of its stability against photocorrosion and photo-chemical properties [7,8]. In normal conditions, ZnO semiconductor crystallizes in a hexagonal wurtzite structure with a = b = 3.2427 Å, c = 5.1948 Å, $\alpha = \beta = 90°$ and $\gamma = 120°$ (JCPDS no. 75-0576) [9]. This tetrahedral coordination is typical for P63mc space group.

In the literature have been reported a large number of investigations regarding the synthesis method of ZnO materials, such as: hydrothermal method [10], sol-gel method [11], co-precipitation method [12], combustion method [13], etc..

In the present work we report the synthesis of ZnO nanoparticles by two different methods: co-precipitation method and sol-gel method using NH4OH solution like a precipitating agent. The structural, morphological and optical properties of the prepared samples were instigated by X-ray diffraction (XRD), scanning electron microscopy (SEM), Fourier transform infrared spectroscopy (FT-IR) and UV-VIS spectroscopy.

2. Experimental procedure

ZnO nanoparticles were synthesized by co-precipitation and sol-gel method.

In co-precipitation method $Zn(NO_3)_2 \cdot 6H_2O$ (Merck, $\geq 99.0\%$) was used as precursor and NH_4OH (25%) solution was used as precipitating agent. The precursor was dissolved in distilled water and stirred continuosly on a magnetic stirrer at room temperature. Then, the NH_4OH (25%) solution was added drop by drop till the final pH of the solution was 10.5. The mixture was stirred for 2 hours at 65°C. The precipitate was washed with distilled water and ethyl alcohol and dried at 80°C for 4 hours. The obtained powders was then thermally treated at 500°C for 4 hours.

In sol-gel method $Zn(NO_3)_2 \cdot 6H_2O$ was dissolved in isopropyl alcohol at room temperature. In this solution (0.1M), the NH_4OH (25%) solution was added drop by drop till the final pH of the solution was 10.5. Then, the mixture was continuously stirred for 2 hours at 95°C. The formed gel was dried at 80°C for 4 hours. The white powder was also thermally treated at 500°C for 4 hours.

Characterization of the structure and composition of both samples was carried out. The structural characterization was made by X-ray diffraction (XRD) obtained using a PANalytical X'Pert Pro diffractometer having CuK_α incident beam ($\lambda = 1.5418$ Å). The morphology of the samples was obtained using a INSPECT S scanning electron microscope (SEM). Also, the elemental analysis of the samples was investigated by

energy dispersive X-ray analysis (EDX). FT-IR analysis was performed using a Bruker Vertex 70 spectrophotometer. Optical properties of the samples were investigated using a Lambda 950 Model UV-VIS NIR spectrophotometer.

3. Results and discussions

The X-ray diffraction patterns of ZnO nanoparticles synthesized by co-precipitation and sol-gel method are presented in Fig. 1.
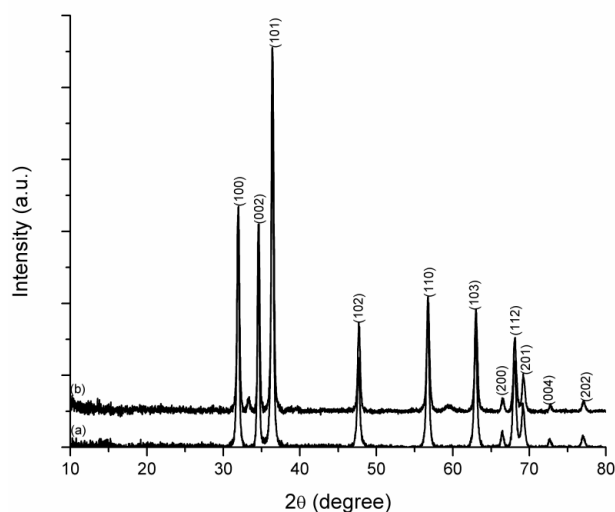

Fig. 1. X-ray diffraction pattern of ZnO nanoparticles obtained by (a) co-precipitation method and (b) sol-gel method

It can be seen, that both samples presents diffraction peaks which can be indexed to hexagonal ZnO phase (JCPDS no. 75-0576) [9]. The position of diffraction peaks and the distances between crystal planes (d) for ZnO nanoparticles synthesized by co-precipitation and sol-gel method are presented in Table 1.

Table 1

No.	hkl	ZnO (co-precipitation)		ZnO (sol-gel)	
		2 Theta (deg)	d-spacing (Å)	2 Theta (deg)	d-spacing (Å)
1	100	31.9002	2.80	31.9798	2.79
2	002	34.5771	2.59	34.6097	2.59
3	101	36.4006	2.46	36.4271	2.46
4	102	47.6700	1.90	47.7420	1.90
5	110	56.6314	1.62	56.7592	1.62
6	103	62.9119	1.47	63.0092	1.47
7	200	66.4279	1.40	66.6211	1.40
8	112	67.9941	1.37	68.0507	1.37
9	201	69.1410	1.35	69.1763	1.35
10	004	72.6284	1.30	72.6913	1.30
11	202	77.0012	1.23	77.1256	1.23

The results obtained by X-ray diffraction analysis for the ZnO nanoparticles synthesized by co-precipitation and sol-gel method are in accordance with that of standard pattern (JCPDS no. 75-0576) [9].

The average crystallite size (D) was calculated using Schererr's equation [14]. The average crystallite size (D) was calculated for each X-ray diffraction line and an average of the values was made. The volume (V) and the parameters of the unit cell were calculated using the program X'Pert HighScore. The values of the average crystallite size, the parameters and the volume of the unit cell are presented in Table 2.

Table 2

Sample	a=b (Å)	c (Å)	V (Å^3)	D (nm)
ZnO (co-precipitation)	3.312	5.202	49.16	64
ZnO (sol-gel)	3.302	5.192	48.95	43

It can be observed that the average crystallite size has a smaller value for the ZnO nanoparticles synthesized by sol-gel method (43 nm) in comparison for the sample synthesized by co-precipitation method (64 nm).

The elemental analysis of ZnO nanoparticles was determined by energy dispersive X-ray analysis (EDX). The EDX spectra of ZnO nanoparticles synthesized by co-precipitation and sol-gel method are presented in Fig. 2.
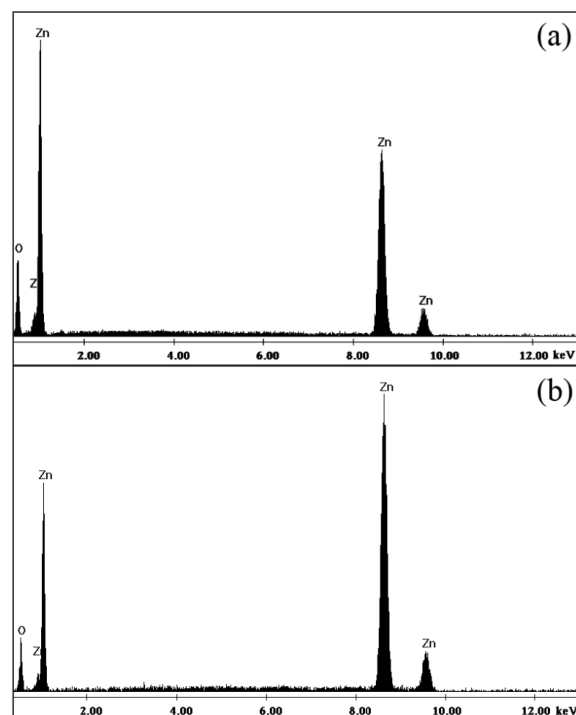

Fig. 2. EDX spectra for ZnO nanoparticles obtained by (a) co-precipitation method and (b) sol-gel method

It can be observed that, in both, ZnO nanoparticles synthesized by co-precipitation method (Fig. 2 a)) and ZnO nanoparticles synthesized by sol-gel method (Fig. 2 b)), Zn and O elements are present. Moreover, Fig. 2 proves that no other impurities are present in the obtained ZnO nanoparticles.

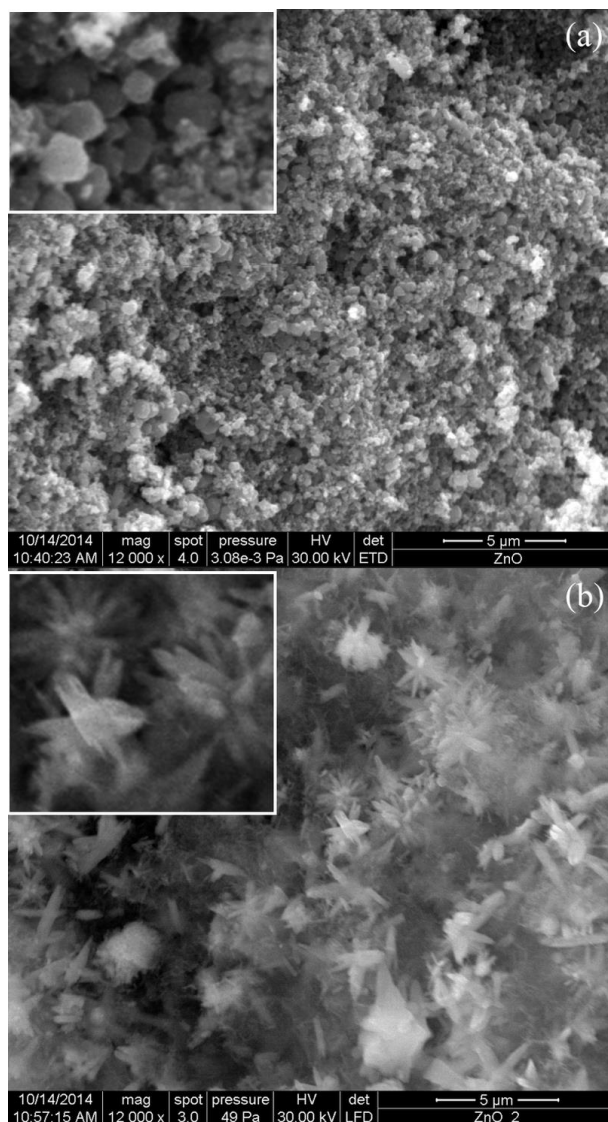In Fig. 3 the SEM images of ZnO nanoparticles are presented.

Fig. 3. SEM image for ZnO nanoparticles obtained by (a) co-precipitation method and (b) sol-gel method

In case of ZnO nanoparticles synthesized by co-precipitation method (Fig. 3 a)), it can be observed that the sample presents agglomerations with different sizes. In the inset of Fig. 3 a) one can see that the agglomeration consists of particles with hexagonal shape. Also, in this area was determined that a diameter of agglomerations is different, between 1 and 2 μm, which is clearly much higher that the results obtained by X-ray diffraction analysis. This means that the agglomeration may consist of a large number of nanoparticles.

In case of ZnO nanoparticles synthesized by sol-gel method (Fig. 3 b)), it can be observed that the particles have a nanorods shape and different orientations.

In Fig. 4 the FT-IR spectra of ZnO nanoparticles prepared by co-precipitation and sol-gel method are presented.
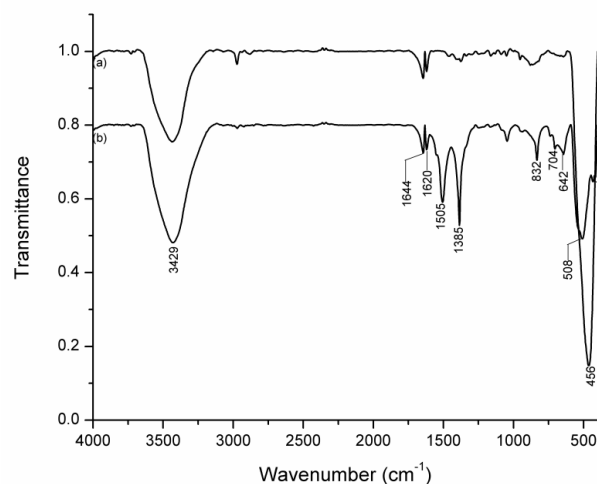

Fig. 4. FT-IR spectrum of ZnO nanoparticles obtained by (a) co-precipitation method and (b) sol-gel method

The absorption bands that appear at 433, 456, 508 and 642 cm^{-1} are related to Zn-O stretching vibration [15]. The other absorption bands that appear at 1385, 1620 and 3429 cm^{-1} are related to the deformation vibration of -OH groups [16]. Also, the absorption band that appear at 1644 cm^{-1} is related to the C=O bond which may appear due to the atmospheric moisture and CO_2 [17]. The CO_2 from atmosphere can be absorbed on the surface of the material and due to this, the peak observed at 1644 cm^{-1} appears.

In Fig. 5 the absorption spectra of ZnO nanoparticles synthesized by co-precipitation and sol-gel method are presented. The absorption spectra were recorded between 300 and 500 nm and it can be seen that the maximum absorption is around 350 nm.
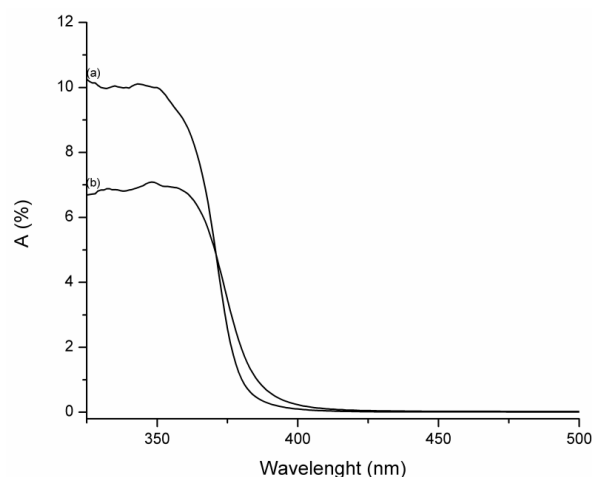

Fig. 5. Absorption spectra of ZnO nanoparticles obtained by (a) co-precipitation method and (b) sol-gel method

Also, from Fig. 5 it can be observed that the intensity of absorption is higher for the sample synthesized by co-precipitation method (Fig. 5 a)).

From absorption spectra, using Kubelka-Munk equation [18,19], the values of the band gap were determined (Fig. 6). It was found that the band gap of the ZnO nanoparticles synthesized by co-precipitation method (Fig. 6 a)) is around 3.30 eV and of the ZnO nanoparticles synthesized by sol-gel method (Fig. 6 b)) is around 3.27 eV. These values are in agreement with the literature data [20].

Also, it can be observed that the band gap value presents a small increase when the crystallite size increases.
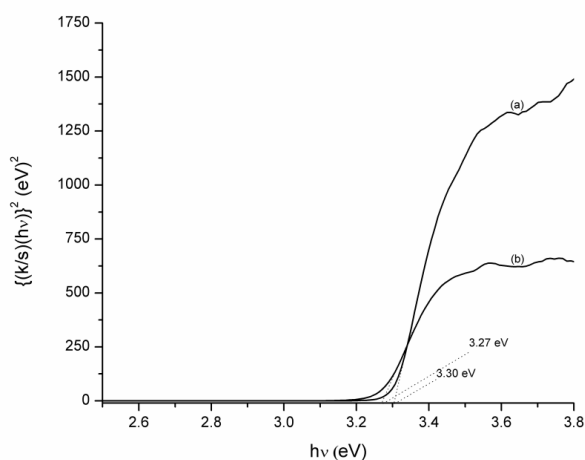

Fig. 6. Plot of $\{(k/s)(h\nu)\}^2$ $(eV)^2$ vs. hv (energy) for ZnO nanoparticles obtained by (a) co-precipitation method and (b) sol-gel method

4. Conclusions

ZnO nanoparticles were synthesized successfully by co-precipitation and sol-gel method. X-ray diffraction analysis revealed the nanocrystalline structure of the obtained materials, the average crystallite size being around 64 and 43 nm. SEM analysis showed that the ZnO nanoparticles synthesized by co-precipitation method have hexagonal shape and tend to agglomerate and that the ZnO nanoparticles synthesized by sol-gel method have a nanorods shape. The band gap value of the obtained ZnO nanoparticles was about 3.27 eV for sol-gel synthesis and 3.30 eV for co-precipitation synthesis. These results suggest that the obtained ZnO nanoparticles have good optical properties being appropriate candidates for optoelectronics and solar cells applications.

Acknowledgement

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