JOURNAL OF OPTOELECTRONICS AND ADVANCED MATERIALS Vol. 17, No. 7-8, July – August 2015, p. 952 - 957

Study of the influence of capping agents on the structural and optical properties of ZnO nanostructures

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In recent years, a lot of techniques for obtaining ZnO nanostructures were developed together with different methods for nanoparticles surface modification. Hence, the changing of particles chemical and physical properties improves their compatibility with different polymeric matrices leading to interesting, new practical applications of ZnO in various domains.
In this study, the structural and optical properties of new types of ZnO nanoparticles surface modified with oleic acid and elaidic acid as capping agents are reported, that were used to control the size and the morphology of ZnO NPs. The suitable capping agents were chosen on the base of their ability to attach on the nanoparticles surface further improving their features. The structure and morphology of modified ZnO nanoparticles (ZnO-oleic acid and ZnO-elaidic acid) were analyzed in detail using X-ray diffraction (XRD), field emission scanning electron microscopy (FESEM) and Fourier transform infrared spectrometry (FT-IR). The optical properties of the as-prepared samples also were investigated using photoluminescence (PL) and absorption spectroscopy. Results showed the particles size was in the range of 30-50 nm and the morphology of the synthesized NPs to be dependent on the capping agent. FTIR spectra indicated the types of functional groups present on the surface of ZnO nanoparticles.

(Received April 9, 2015; accepted June 24, 2015)

Keywords: Zinc oxide, Nanoparticles, Surface modification, Oleic acid, Elaidic acid

1. Introduction

Over the years, zinc oxide played an important role in many areas of science and technology due to its broad spectrum of properties and outstanding performances [7, 33, 34]. Zinc oxide is a promising material and has attracted a remarkable attention for potential applications in different industries, including optoelectronic devices, pigment, coatings, pharmaceutical and cosmetics, biomedical, photocatalytic sensors, solar cells, textile and agriculture etc. [9, 12, 16, 22, 25].

ZnO nanostructures appear in various types of morphologies including nanorods, nanobelts, nanowires, nanoflowers, nanoparticles, etc. [13, 28, 32, 35]. Nanostructures can be easily accomplished by chemical or physical techniques such as hydrothermal method, precipitation method, sol–gel method, spray pyrolysis, chemical vapor deposition, electrochemical deposition, combustion method, decomposition of organometallic precursors, etc [17, 19 - 21, 27].

At present, a variety of methods for obtaining nanoparticles are developed, but in all cases it is observed that the inorganic nanoparticles tend to easily agglomerate, due to their specific surface area and volume effects. Nanoparticles aggregation has significant effect by changing their size, shape and influences the properties [6, 26].

In order to solve this problem different capping agents were used to change the nanoparticles chemical and physical properties, as well as to improve the compatibility with various organic matrices [8, 11, 15].

Furthermore, the capping agents were often used to prevent the growth of larger size particles and modifying their morphology, but also to stabilize them from aggregation by controlling the structural characteristics and to achieve biocompatibility [2, 18].

The choice of the suitable capping agent is extremely important, because it should have a good capacity and high affinity to attach to the surface of nanoparticles. The capping agents contain some functional groups which can bind to the surface of particles and improve their features, but also it is necessary to take in consideration and the desired application domain [1, 5].

Many researchers have demonstrated that oleic acid (cis-9-octadecenoic acid, OA) is the most used capping agent due to carboxyl group, long alkyl chain and unsaturated bond, allowing to chemically modify the surface of nanoparticles by the esterification reaction between the carboxyl group present in the acids molecules and the hydroxyl groups of the nanoparticle surface [23, 24, 30].

Fatty acids (such as oleic acid) are considered to be strong carboxylate ligands, often used for modifying the nanoparticles by bonding the functional groups on their surface. On the other hand, the presence of the long-alkyl chain and unsaturated bond provides a significant hydrophobicity to the nanoparticles and is beneficial for a good interfacial bonding between the nanoparticles and the different matrix [3, 4, 10, 14].

In the present study, we have investigated the effect of the oleic acid (cis-9-octadecenoic acid, OA) and elaidic acid (trans-9-octadecenoic, EA) on the nanoparticles surface, and also established the optimal parameters.

The influence of capping agents on morphology, particle size, shape and structure has been investigated with X-ray diffraction (XRD), field emission scanning electron microscopy (FESEM) and Fourier transform infrared spectrometry (FT-IR). The optical properties of the samples have been analyzed using photoluminescence (PL) and absorption spectroscopy.

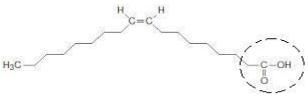
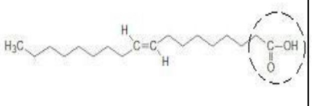
2. Experimental details

2.1 Materials

Zinc oxide powder with the average particle size of about 50 nm was supplied by IMT- Bucharest (obtained by sol-gel method). The oleic acid (OA, 90 %) and elaidic acid (EA, 95%) were purchased from Aldrich. Deionized water and ethanol (99 %) were also used throughout the experiments. All reagents were used as received.

In Table 1 are presented the characteristics of capping agents.

Table 1. Characteristics of capping agents

Molecular formula Synonyms	Molecular weight (g/mol	Chemical structure and anchoring groups
$C_{18}H_{34}O_2$ Oleic acid; C18-cis cis-9-Octadecenoic acid	282.47	
$C_{18}H_{34}O_2$ Elaidic acid; C-18 trans trans-9-otadecenoic acid		

2.2 Synthesis of capping agents modified ZnO nanoparticles

In our experiments two types of capping agents (oleic acid and elaidic acid) were used. The detailed steps for the samples preparation are described as follows.

An established amount of ZnO powder, ethanol and oleic acid were charged into a bottle and the mixture was stirred vigorously for three hours at 60 ºC and then sonicated with ultrasonic frequencies for 30 min.

Then, the white colloidal precipitate was allowed to stand for 24 hours. After that, the modified ZnO nanoparticles were washed three times with a solution of deionized water and ethanol to remove oleic acid residue. The resulting precipitated ZnO nanoparticles modified with oleic acid (ZnO-OA) were dried at low temperature to get a white powder.

The experiment was repeated under same conditions to obtain ZnO nanoparticles modified with elaidic acid (ZnO-EA). Finally, the obtained samples were analyzed in details using different techniques.

2.3 Characterization

X-ray powder diffraction patterns were obtained with a Rigaku Smartlab X-ray Diffraction System using CuKα = 1. 540593Å radiation generated at a voltage of 45 kV and a current of 200 mA. Data were collected with a scan rate of 2 °/min. in the range of 20°- 80°.

The emission electron scanning images were obtained on powdered samples using Nova NanoSEM 630, a Field Emission Scanning Electron Microscope (FE-SEM) (FEI Company, USA), with Ultra-high resolution characterization at high and low voltage in high vacuum of 1.6 nm @ 1 kV.

The Fourier Transform Infrared (FTIR) spectra were performed by Bruker Tensor 27 spectrometer in the range of 4000 – 400 cm^{-1} by averaging 64 scans with a resolution of 4 cm^{-1}. The samples were mixed with KBr and compressed into pellets with a hydraulic press at pressure of 10 tons for 5 min.

Photoluminiscence spectra were measured at the room temperature with fluorescence spectrometer (FLSP 920) using a Xe lamp as excitation source. An excitation wavelength of 320nm was used.

The optical spectra were carried out using U-0080D UV-Vis spectrophotometer from Hitachi High Technologies, in the wavelength range 300-800nm.

3. Results and discussion

3.1 Structural characterization

3.1.1 Morphological analysis

The size, shape and morphology of the powders samples after modified with capping agents were studied using a scanning electron microscope.

SEM images of ZnO modified with oleic acid (ZnO-OA) and ZnO modified with elaidic acid (ZnO-EA) samples are shown in Figs. 1 (a) and 1(b).

Fig. 1 (a) presents a flower-like structure with random orientations. The results demonstrated the role played by oleic acid in the formation of hierarchical nanostructures.

Fig. 1 (b) shows that the particles are spherical in shape and the size is in the range of 20- 60 nm.

By comparing the samples (ZnO-OA and ZnO-EA), it can be concluded that the size and morphology of zinc oxide powders is influenced by the capping agents that had been used.

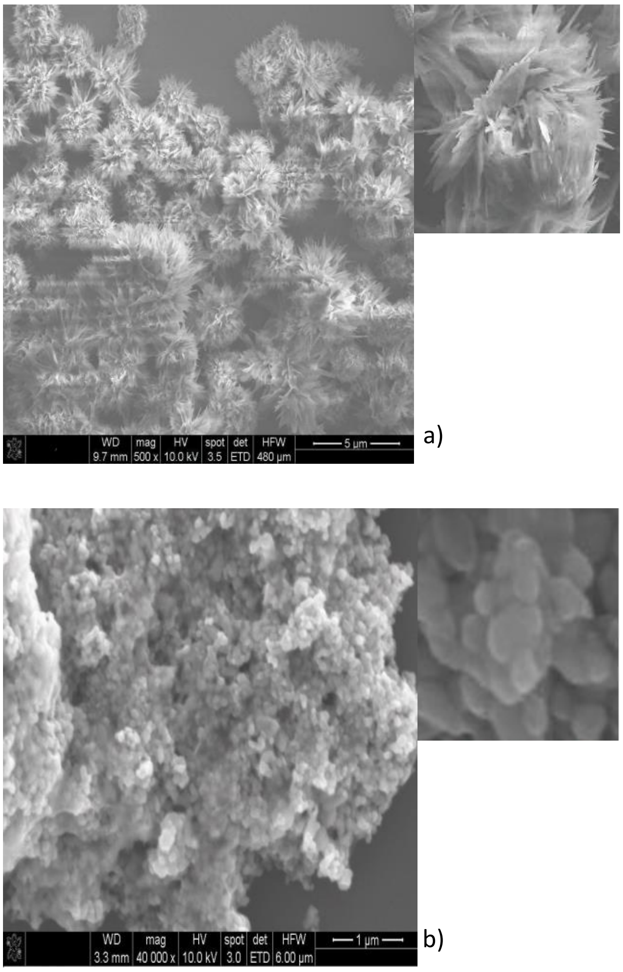


Fig. 1. SEM images of a) ZnO-OA and b) ZnO-EA powders

3.1.2 X-Ray diffraction analysis

The crystalline structure, crystallite size and lattice parameters of the powders were characterized by X-ray powder diffraction (XRD).

Figs. 2 (a) and 2(b) show the XRD pattern of ZnO-OA and ZnO-EA powders.

A lot of characteristic peaks were observed at 2θ of 31.4°, 34.1°, 35.9°, 47.2°, 56.2°, 62.5°, 66.1 67.7° and 68.7° correspond to the plans with Miller indices (100), (002), (101), (102), (110), (102), (110), (103), (200), (112), (201). These diffraction peaks confirm the existence to wurtzite structure of ZnO showing that the capping agent did not influence the crystalline structure of the ZnO nanoparticles.

The diffraction peaks have lattice constants of a = b = 3.26A and c = 5.22A, respectively. The difference between two patterns was observed in the peak intensities.

Thus, for sample ZnO-EA (Fig. 2 (b)) the peaks are much higher and narrow shaped than for Zn-OA (Fig.2 (a)) indicating a good crystalline structure.

According to Scherrer's equation, the average crystallite size of ZnO powder in Fig. 2 (b) was calculated to be 30 and 50 nm and is basically in accordance with the SEM images.

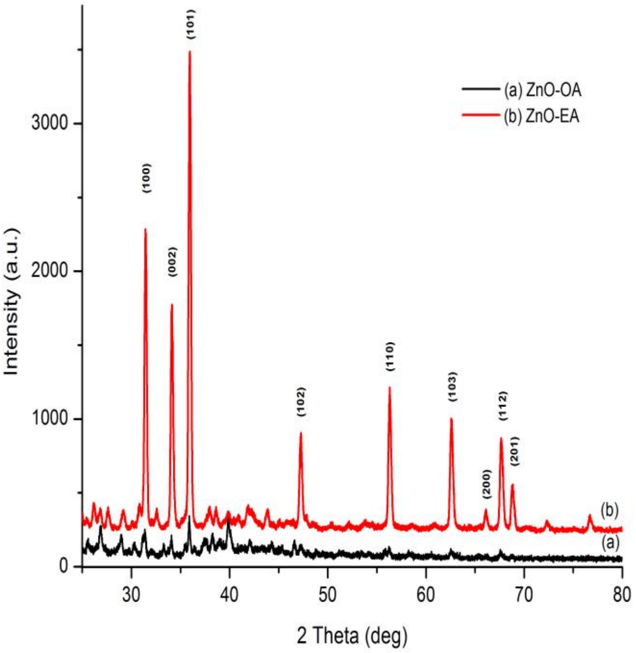


Fig.2. XRD pattern of a) ZnO-OA and b) ZnO-EA powders

3.1.3 FTIR analysis

Fig. 3 shows the FTIR spectra of pure oleic acid (a) and ZnO modified with oleic acid (ZnO-OA) (b), pure elaidic acid (c) and ZnO modified with elaidic acid (ZnO-EA) (d).

Typical FTIR spectra of the pure oleic acid (a) and elaidic acid (c) are characterized by peaks that can be attributed to the stretching vibration mode of C=O bond (in the range 1720 - 1710 cm^{-1}), C-O bond (1285 cm^{-1} and 1090 cm^{-1}) and to the vibration mode of C-H bonds (2960 - 2820 cm^{-1} asymmetric and symmetric stretching of CH$_2$ groups, 1380 cm^{-1} bending vibration mode of CH$_3$ groups and 1250 cm^{-1} for CH$_2$ groups and at 3020-3005 cm^{-1} for = C-H).

For spectra of ZnO modified with oleic acid (b), and ZnO modified with elaidic acid (d) a slight shift of spectral bands to lower wave numbers was observed, confirming that the hydrocarbon chain around ZnO is in a "closed-packed" crystalline state. At the same time, the peak from 1720-1710 cm^{-1} disappear and two bands appear at about of 1545 cm^{-1} and 1525 cm^{-1} characteristics of vibration stretching mode of COO- group, suggesting the formation of an organic monolayer on the ZnO surface [8,15].

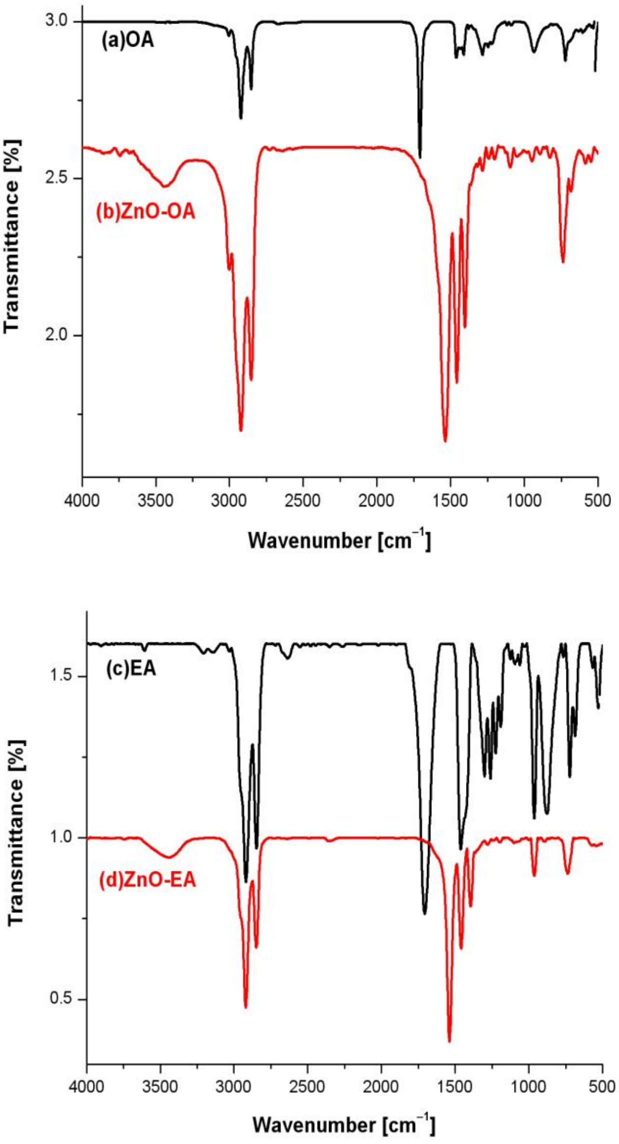


Fig.3. FTIR spectra of a) ZnO-OA and b) ZnO-EA powders

3.2 Optical study

3.2.1 Photoluminiscence analysis

The photoluminescence spectra analysis is an effective way for investigating the defects of structures.

The PL spectra of ZnO modified with oleic acid (a) and ZnO modified with elaidic acid (b) were investigated at room temperature, in the wavelength range of 350 to 800 nm, under 320 nm xenon lamp excitation. The results are shown in Fig. 4.

Comparing both samples, it can be seen that the intensity of the emission in the case of elaidic acid modified ZnO (b) is higher than in the case of oleic acid modified ZnO (a) but having almost the same shape.

Photoluminescence spectra possess two luminescence bands that consist of ultraviolet emission (UV) peak and a visible emission band. The first peak with a weak UV emission at 376 nm originates from the near band edge emission (NBE) resulted from recombination of the electrons from the conduction band with the hole from the valence band [29].

The results show that the reduction visible emission compared with ultraviolet emission suggests the decrease of surface defects and the possibility of electron-hole recombination. So, we can say that luminescent properties are significantly influenced by the type of capping agents.

We find that the intensity ratio between UV emission and the visible region is usually used to evaluate the quality of the samples obtained. For sample ZnO-EA (b) the intensity of the emission peak in the visible region is better defined than ZnO-OA (a), suggesting a decrease of defects density in nanoparticles [31].

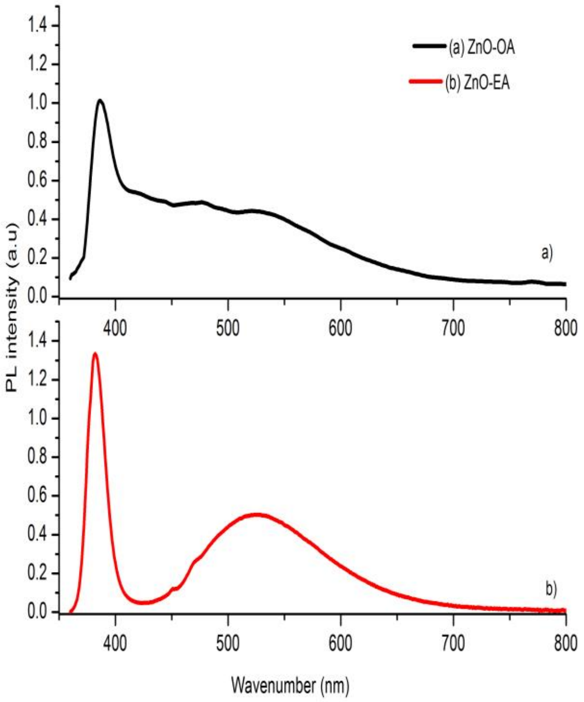


Fig.4. PL spectra of a) ZnO-OA and b) ZnO-EA powders

3.2.2 UV-VIS analysis

The effect of capping agents on the optical analyses is required to evaluate the optical quality of the samples.

Figs. 5 (a) and 5(b) shows UV-Vis absorption spectra of the samples ZnO-OA together with ZnO-EA for comparison as a function of wavelength.

The optical characteristics of the samples were investigated using absorption measurements in the wavelength range of 300-800 nm.

Although the general features of the both spectra are the same, it can be observed a well defined sharp absorption peak centered at ~ 375nm for ZnO-EA sample, corresponding to a bandgap of 3.3 eV. The comparison of the UV-Vis absorption spectra of the samples shows that the spectrum for ZnO-OA is lower, indicating the nanoparticles morphology changed.

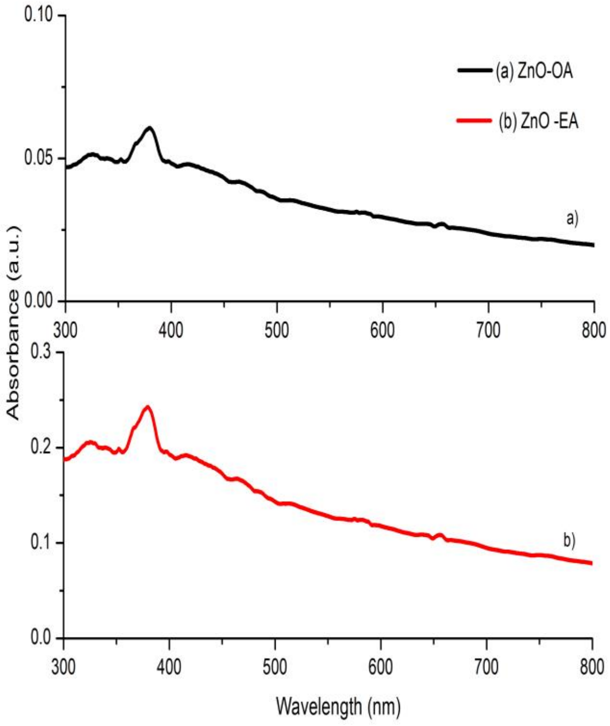


Fig.5. UV-VIS spectra of a) ZnO-OA and b) ZnO-EA powders

4. Conclusions

In summary, surface modified ZnO nanoparticles were synthesized using two types of capping agents (oleic acid and elaidic acid). These agents were used for the surface modification of ZnO nanoparticles by introducing the long aliphatic chain and also the carbon-carbon double bonds.

The effect of capping agents on the ZnO samples structural and optical properties was investigated by various characterization methods.

From the XRD measurements, it was observed that the powders were indexed with wurtzite structure without any other phases and the diffraction peaks ere slightly different. SEM images of the samples show that the morphology was clearly changed depending on the capping agent used.

FTIR analysis confirms the presence of capping agent on the surface of ZnO nanoparticles. Also, the optical properties of the ZnO-EA compared to ZnO-OA samples show an appreciable increase in intensity.

To improve the quality of the nanoparticles modified with various capping agents, able to be compatible with various polymeric matrices, is another trend of future research.

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