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PREPARATION AND CHARACTERIZATION OF ZnO NANOPARTICLES BY SOLVENT FREE METHOD

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Abstract: ZnO nanoparticles have numerous applications as photo catalysts, gas sensors, UV lasers, as optoelectronic and microelectronic devices or in cosmetic field. ZnO nanoparticles were synthesized by solvent free method using zinc nitrate hexahydrate as precursor and glycerol as dispersant, without solvent present. This method proved to be very simple, economic and ecofriendly. Zinc nitrate and glycerol were mixed in different ratio in order to avoid and overcome a possibility of agglomeration. Characterization of samples was performed by UV/VIS and FTIR spectrophotometry. The strongest absorption appeared at wavelength 206 nm. Using combination of UV/VIS spectrophotometry and hyperbolic band model (HBM) particles size of ZnO particles were evaluated to 2.06 nm. Additionally, using Tauc plot, a band gap energy was determined. Band gap energy of ZnO nanoparticles amounted to 5.00 eV. IR spectrum showed existence of ZnO in interval 600-400 cm^{-1}.
Keywords: ZnO, nanoparticles, solvent free method, band gap.

1. INTRODUCTION

Nanotechnology has witnessed tremendous advancement over the last several decades putting emphasis on the unique physicochemical properties of various nanomaterials in order to create new structures or devices with potential applications in a wide variety of disciplines. The special attention is given to the semiconductor materials and zinc oxide is one of the best representatives, belonging to the group of the semiconductor materials type II^b –VI. There are numerous literature data [7,12−14] on zinc oxide promoting it for a wide implementation in many areas of high technology, industry and medicine [1]. The wide implementation is based on good characteristics of zinc oxide such as the high index of refraction, thermal conductivity, non-toxicity, antibacterial activity and protection of UV radiation [2]. Thanks to all these characteristics, zinc oxide is used for making the emitters of ultraviolet radiation, the varistor, the piezoelectric converters, the aeriform sensors, the surface of acoustic wavelike devices, then in transparency of high energetic electronics and in many electronic devices. One of the most important characteristics of zinc oxide is a wide spectrum of energy band gap that allows zinc oxide to be used in optoelectronic devices, the surface of acoustic-wavelike devices, the emitters of field, light emitter (LED diode), the piezoelectric transformers, chemical, gas and bio-sensors, the transparency conducting materials, the varistors, the solar cells, etc. [3]. Further, zinc oxide because of its non-toxic, antibacterial properties and protection of UV light is in ingredients in many pharmaceutical and cosmetic products [4]. There are lots of different methods which can be used for a synthesis nanoparticles of zinc oxide such as sol-gel, microwave thermal evaporation, hydrothermal, vapor phase transport, electrochemical deposition, pulsed laser deposition, thermal oxidation, „solid state" method, etc. [2]. Using these methods, nanoparticles differ by their uniformity, size of the particles and physical-chemical characteristics. Furthermore, nanomaterials can be modified by doping process of different other elements so their characteristics and application potential becomes improved. *„Solvent free"* or method without solvent is newer method for the synthesis of nanoparticles. It is quite effective, simple and economic and it is used as the method of synthesis in this research paper. The aim of this paper is to ascertain the efficiency of the method

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without solvent by using the minimal amount of glycerol as a dispersant.

2. EXPERIMENTAL

2.1. Synthesis of ZnO nanoparticles

Analytical grade *Sigma Aldrich* $Zn(NO_3)_2 6H_2O$ was used as a precursor for synthesis of ZnO particles in solvent free method. Glycerol (85%) purchased from Merck, was added as an dispersant agent. One of the characteristics of nanoparticles is the aspiration for agglomeration. To avoid this phenomenon, except being a dispersant agent, glycerol had a role to overcome the agglomeration process of nanoparticles and to obtain a fine nanodust powder. The proper amount of zinc hexahydrate and glycerol were mixed by the scheme presented in the table 1.

Table 1. Samples for the synthesis of ZnO nanoparticles

Sample	m ($Zn(NO_3)_2 . 6H_2O$) /g	V(Glycerol) /mL
1	6,5	0.033
2	6,5	0.066
3	6,5	0.099
4	6,5	0.132
5	6,5	0.165

A proper weight of chemicals was transferred in a 50 mL silica crucible and constantly stirred for 30 minutes until the sample got a consistency of pasta. Such prepared samples were transferred into muffle furnace. The initial temperature was set to 50 ^oC and then temperature was slowly raised to 300 ^oC (approximately 3 ^oC per minute) in order to avoid overheating and eventual mass losses. Degradation path of zinc nitrate is proposed as follows: on lower temperatures, zinc nitrate is firstly transformed to zinc peroxide and then with constant heating at higher temperatures zinc peroxide transforms into zinc oxide [2].

$$Zn(NO_3)_2 \rightarrow ZnO_2 + 2NO_2$$

$$2ZnO_2 \rightarrow 2ZnO + O_2$$

The product of this reaction is the crystalline zinc oxide powder the color of which depends on the amount of glycerol added. Samples were changing from light yellow (sample 1) to pure white (samples 4 and 5). Such obtained zinc oxide powders were submitted to further characterization.

2.2 Characterization of ZnO nanoparticles

Characterization of obtained ZnO samples was performed by UV/VIS spectrophotometry (Perkin Elmer Lambda 25 UV/VIS) and IC spectroscopy (Bruker Tensor FTIR spectrophotometer).

The size of zinc oxide was defined by using the hyperbolic range (HBR) and by Tauc plot function the size of energy band gap was defined.

3. RESULTS AND DISCUSSION

3.1. FTIR spectroscopy

Figure 1. shows the FTIR spectra of zinc oxide synthesized by the solvent free method. The spectra are displayed according to the content of glycerol used for synthesis of zinc oxide nanoparticles. The spectrum is placed in the middle area of infrared spectra, in the range from 400 to 4000 cm^{-1}. Vibration peaks of organic groups are mainly manifested in this area. Metal oxide generally gives absorption bands under 1000 cm^{-1} [5]. According to literature, characteristic vibration bands of ZnO are in the range of 400-700 cm^{-1}[1,6,7]. As one can see, at IC spectra, samples designated as 3, 4 and 5 showed one well deformed stretched vibration band on 530.41 cm^{-1} that comes from zinc oxide. Sample 1 and sample 2 did not show any peaks in this area which leads us to conclusion that zinc oxide particles were not synthesized in these samples.

Besides this characteristic peaks belonging to the formation of zinc oxide nanoparticles, three different vibration peaks are also pronounced. The vibration peak, on 814 cm^{-1} originates from carbonate group, while vibration stretched band on 1323 cm^{-1} belongs to nitrate. Also, the wide stretched peak in the range from 1600 to 1800 cm^{-1} is attributed to bending OH-group [8].

By spectroscopic analysis, we came to the conclusion that the synthesis of zinc oxide nanoparticles by using 0,132 mL glycerol as a dispersant gave the best results in synthesis method. Therefore the sample 4 was submitted for further characterization.

3.1.2 UV/VIS spectroscopy

In order to specify and to determine the optical characteristics of ZnO nanoparticles, a proper amount of zinc oxide (0.01 g) was dispersed in 10 mL of 96% ethanol and UV/VIS spectrum was recorded. The ZnO oxide spectrum is presented in Figure 2 with designated maximum value of absorption (λ_{max}) at 206.01 nm.

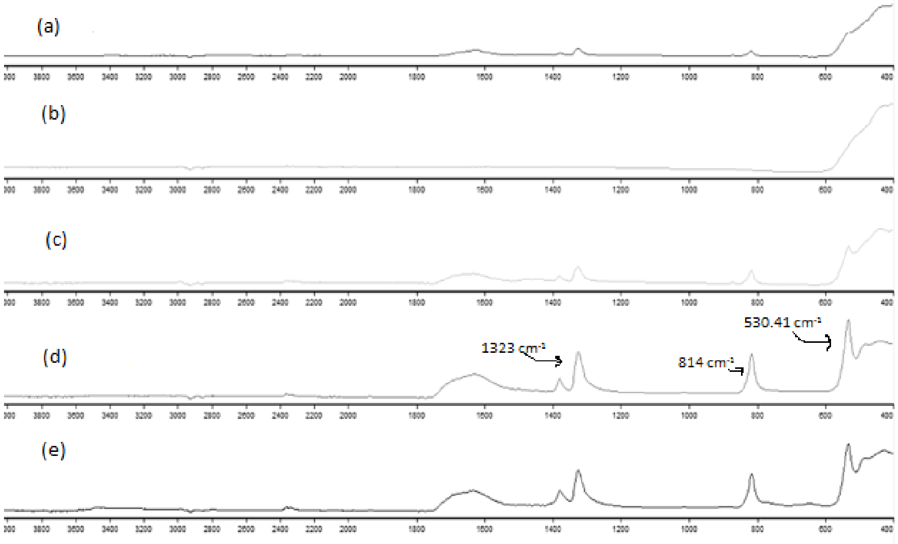

Figure 1. FTIR spectra of ZnO nanoparticles synthesized using different amount of glycerol as a dispersant, designated with following order (sample 1 - a, sample 2 – b, sample 3 – c, sample 4 – d and sample 5 – e)

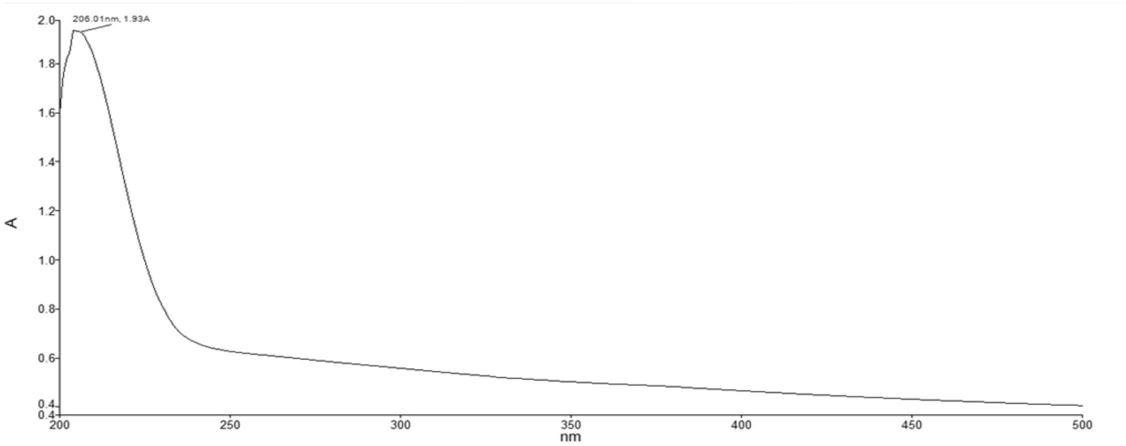

Figure 2. UV–Vis spectra of Zinc oxide nanoparticle in the range 200 – 500 nm

Using the value of λ_{max} an energy band gap for ZnO was determined. The simplest way to specify the size of energy band gap was by using the following equation (1):

$$E = \frac{h \times c}{\lambda_{max}} \ (eV) \quad (1)$$

The calculated size of energy band gap amounted to 6.01 eV which is quite high value comparing to literature data [1,2,5,10] where energy band gap is in range of 3 to 5 eV. In order to confirm the value of band gap energy, we used more accurate method to determine the energy band gap called Tauc plot function. Tauc plot function is mostly used for semiconductors materials such as ZnO. By using the Tauc plot function, coefficient of absorption for permitted transitions is counted according to equation (2):

$$(\alpha h\nu)^{\frac{1}{n}} = A(h\nu - Eg) \quad (2)$$

Where E_g is energy band gap, $h\nu$ is energy of photon, A is constant and the n is the size that depends on the type of transition. For ZnO n = ½ which matches to the direct and allow transitions while the α is an absorption coefficient that is counted according to the relation (3):

$$\alpha = \frac{4\pi\kappa}{\lambda_{max}} \quad (3)$$

By construction of graph, energy of band gap was determined by extrapolation on the x axis [11].

On the basis of Tauc plot function, the value of energy band gap is 5.30 eV (Figure 3) and it is more accurate in comparison with the value obtained by equation 1. The direct energy band gap of zinc oxide on the room temperature is 3.37 eV (*E bulk*) [1, 3, 4, 10], and it is much lower than the value we got. It is a general statement that smaller particles give higher energy of band gap [15], so evaluation of the size of obtained zinc oxide nanoparticles seems to be very important. For evaluation of particles size, a hyperbolic band model (HBM) was used. According to this method, the diameter of molecule R can be counted using the formula (4):

$$R = \sqrt{\frac{2\pi^2 h^2 Ebulk}{m^e(E^2nano - E^2bulk)}} \qquad (4)$$

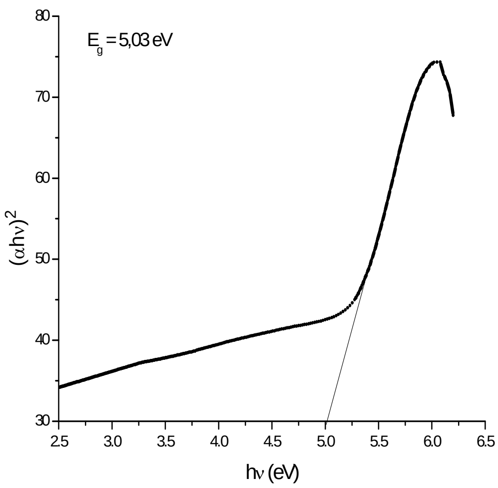

Figure 3. The Tauc plot of ZnO nanoparticles

Where the m^e is an effective mass of electrone [9, 10]. The dimension of ZnO nanoparticles counted by the proposed method of HBM was 2.06 nm. The particles of this size belong to the category of quantum dots. There are a lot of literature data concerning the size of ZnO particles synthesized by various methods. S. Dhivakar et al [2] reported the 78 nm for the size of zinc oxide nanoparticles which were synthesized by the same method as ours. Debanath et al [16], reported synthesis of zinc oxide (ZnO) nanoparticles *via* wet chemical method. Based on XRD results, the size of ZnO nanoparticles was 8.5 nm. They also use HBM model for determination size of nanoparticles and according to that results, the size was 8 nm. Kulkarni et al [17] used sol-gel method and the average size of zinc oxide nanoparticles, according to XRD analysis was 14.36 nm. Brintha et al [18] also in their research paper reported synthesis of ZnO nanoparticle *via* wet chemical, sol-gel and hydrothermal method and according to their results, the size was in range from 13 to18 nm, depending from the method used.

4. CONCLUSION

Solvent free method proved to be very efficient method for the synthesis of ZnO nanoparticles with size of quantum dots. The method of synthesis was performed by using the zinc nitrate hexahydrate with different volume of glycerol as a dispersant. The sample 4 gave the best results. Characterization of sample was performed using UV/VIS and FTIR spectroscopy. Using a Tauc plot function, the band gap energy was evaluated and amounts to 5.03 eV. According to the method of HBM, the size of zinc oxide nanoparticles were defined with value of 2.06 nm.

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СИНТЕЗА ZnO НАНОЧЕСТИЦА *SOLVENT FREE* МЕТОДОМ И ЊИХОВА КАРАКТЕРИЗАЦИЈА

Сажетак: ZnO наночестице користе се у различите сврхе и то као фотокатализатори, гасни сензори, UV ласери, у козметици, оптоелектричним и микроелектроничним уређајима. У овом раду ZnO наночестице су синтетисане *Solvent free* методом употребом цинк-нитрат-хексахидрата као полазног једињења и глицерола као дисперзионог средства. Овај метод се показао као веома једноставан, економичан и еколошки исправан метод синтезе. Цинк-нитрат и глицерол су помијешани у различитим односима како би се пронашла оптимална количина глицерола и при том спријечила агломерација. Карактеризација узорака је одрађена употребом UV/VIS и FTIR спектроскопије. Резултати показују максимум апсорпције при таласној дужини од 206 nm. На основу резултата добијених употребом UV/VIS спектроскопије и методе хиперболичног опсега (ХБМ), одређен је пречник ZnO честица који износи 2.06 nm. Поред тога, употребом Таук Плот функције одређена је и величина енергетског процјепа цинк-оксида, која износи 5 eV. IC спектри показују присуство карактеристичне траке ZnO у опсегу 600–400 cm^{-1}.

Кључне ријечи: ZnO, наночестице, метода без растварача, величина енергетског процјепа.