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THE FORMATION MECHANISM OF COLLOIDAL SPHERES OF ZnO IN ETHYLENE GLYCOL

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Zinc oxide is currently one of the world most studied materials, because of its specific properties. In addition, this material can be obtained in the form of various nanostructures with unique properties, which can be widely used in electronics, optoelectronics, and chemistry as well as in medicine. The article analyzed the formation mechanism of nanoballs of zinc oxide in ethylene glycol, and the effect of water on their size. These spheres were synthesized for use in the formation of three-dimensional photonic crystals. Tests were carried out using a scanning electron microscope (SEM) and a transmission electron microscope (TEM) and showed that the average size of the ZnO nanoballs immediately after synthesis was 100 to 200 nm. However, as demonstrated by research done using dynamic light scattering method (DLS) average particle size changes very rapidly under the influence of water added to a solution containing nanoballs.

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Keywords: Zinc oxide; Nanoballs; Ethylene glycol; Effect of water

1. Introduction

One field in intense research of new materials is optoelectronics, in particular one of its branches engaged in the generation and testing of photonic crystals. For a simple and low-cost production of three-dimensional photonic crystals techniques are being sought of manufacturing perfectly spherical nanoballs with a well-defined diameter. A very good material suitable for this purpose is zinc oxide due to the large value of its refractive index being n = 2.00-2.10 in the visible range [1].

Of interest would be a synthesis method of zinc oxide nanoballs allowing control of their diameter by changing the process parameters such as temperature, substrate concentration or the duration of the process. Furthermore, the spherical nanostructures can be doped by either closing in their interior other material or depositing it on their surface to obtain nanomaterials with desired properties [2-4]. ZnO nanoballs with metal clusters deposited on their surface could be applied not only in optoelectronics and sensor technology but also in heterogeneous catalysis and as modern piezoelectric material with gigantic electro-mechanic coupling coefficients [5].

Spherical ZnO nanoparticles were synthesised for the first time by Jezeguel and others [6]. Nanoballs were formed in the reaction of hydrolysis of zinc acetate dissolved in diethylene glycol. Hydrolysis occurred at elevated temperature. However, as is clear from the test results, the authors received a colloid of spherical nano and microparticles of zinc oxide with a diameter varying in a wide range from 100 to 1500 nm. Modification of the Jezeguel method performed and described Seelig [7]. According to the authors, the modified method can be used to receive stable, spherical particles of zinc oxide monodisperse size, and such therefore may be used for the constitution of

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three-dimensional photonic crystals. Seelig was receiving nanospheres of zinc oxide in a two-step hydrolysis process of zinc acetate. In the first step of hydrolysis of zinc acetate in diethylene glycol he was receiving a supernatant consisting of glycol, dissolved synthesis products, water and unreacted ZnAc (zinc acetate). The supernatant, the product of the first stage of synthesis, was added to a heated solution of zinc acetate dissolved in diethylene glycol. Adding to the solution of the supernatant showed a decrease of its temperature and a precipitation of monodisperse nanoballs of zinc oxide. According to Seelig, after the precipitation of the nanoballs of ZnO, the reaction mixture should be heated and stirred for one hour and then cooled down to room temperature. The dimension of the obtained nanoballs depends on the amount of added supernatant. This two-step method can be used to obtain the monodisperse solution of colloidal spheres.

Despite the fact that method presented by Seeling is simple and does not require complex equipment, it is low reproducible and the mechanism of forming colloidal ZnO spheres is not well understood. Moreover, effect of the water present in the solution is significantly. In order to clarify the mechanism of forming balls in ethylene glycol detailed studies were performed, the results of which are presented in this article.

2. Experimental

For the synthesis of nanoballs of ZnO ethylene glycol pure for analysis and zinc acetate dihydrate p.a. were used, produced by POCH (Poland). In the synthesis deionized water with conductivity of 0.075 μS was used. Reagents were not purified or dried prior to the process. Colloidal nanospheres of ZnO were synthesized by a two-step method described by Seelig [7] modified by authors.

In the synthesis diethylene glycol was not used as a solvent, but ethylene glycol. In the first stage supernatant liquid was obtained. For this purpose, zinc acetate dihydrate was dissolved in ethylene glycol. The resulting solution was heated in a reflux condenser until a white precipitate was deposited. The resulting precipitate was centrifuged and the supernatant solution was used in the next step of the synthesis. In the second stage of the process, like in the first stage, a solution of glycol and zinc acetate was heated and the supernatant was added at an appropriate temperature.

In a typical synthesis of 2.18 g (0.01 mol) of zinc acetate was dissolved in 100 ml glycol and heated. When the solution temperature was over 140°C, ZnO nanospheres were precipitated. After cooling the reaction mixture the precipitate was centrifuged, leaving the supernatant. In the second stage of the synthesis at a temperature ranging from 30°C to 120°C, between 5 ml and 20 ml of the supernatant was added to the reaction mixture.

Particle size distribution of the obtained ZnO was determined by dynamic light scattering (DLS). 380ZLS Nicomp apparatus was used (Particle Sizing Systems, USA) containing a laser with 532 nm wavelength and power 50 mW. Counting frequency of photons by autocorrelator was fixed at about 200 kHz, and a single measurement time was 3 min. The measurement was made using a polymethyl methacrylate PMMA cell with dimensions 40 × 10 × 10 mm. The calculations on the hydrodynamic diameter were performed based on the Stokes-Einstein equation, taking the measurements temperature of 298 K, a viscosity of the continuous phase (water) equal to 0.891 mPa·s and a viscosity of ethylene glycol of 16.1 mPa·s

The study of the microstructure of the obtained zinc oxide particles was carried out using a transmission electron microscope (TEM) EM900 (Zeiss, Germany) at a magnification of 81 000×. Samples were prepared by applying a drop of the suspension of the nanoballs onto a 200 mesh copper grid covered with a layer of carbon and coated with Formvar film. The measurement data processing was performed using AxioVision 4.8 (Zeiss) and ImageJ 1.42q software. The microstructure of nanoballs of zinc oxide was also examined using a scanning electron microscope JSM 5800 LV made by Jeol company, which is equipped with X-ray microanalysis system ISIS 300 made by Oxford company and semiconductor detector, analysing the characteristic X-ray energy. The X-ray microanalysis system (MAR) allows qualitative EDX (Energy Dispersive X-Ray Analysis) of elements from lithium (Li) to uranium (U).

The crystallographic structure of the structures of zinc oxide was determined by a High Resolution Materials Research Diffractometer Philips Materials Research Diffractometer (MRD) using CuKα radiation. A conventional scan for powdered materials was used, i.e. Θ/2Θ. The average size of crystallites was determined using the Sherrer equation. A spectroscopic analysis of solutions of zinc acetate dihydrate in ethylene glycol was performed by using a spectrophotometer Ocean Optics QE65000. Absorption spectra were measured in the wavelength range from 200 to 1000 nm.

3. Results and discussion

When synthesizing the nanospheres in the two-step method it was found that the supernatant obtained in the first step contains nanoparticles which are the centres of crystallisation in the next stage of the synthesis. DLS measurements of the average size of the resulting particles showed that the average size of the nanoparticles formed in the first step of the synthesis is 20, 40 and 940 nm. In the process of centrifugation the largest diameter particles are removed, and only particles of small diameter are left in the supernatant (Fig. 1).

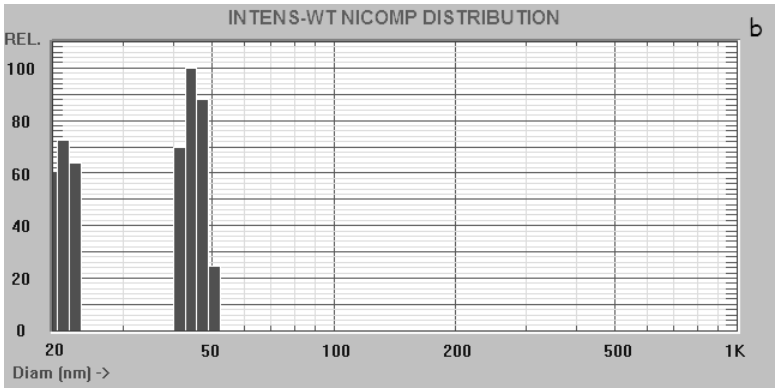


Fig. 1 The size distribution of nanoparticles obtained in the reaction mixture in the first stage of hydrolysis in supernatant after centrifugation.

A scanning electron microscope study of the microstructure of the particles in the supernatant and the nanoparticles resulting from the second step of the synthesis, in part confirmed tests made using the DLS. They showed that in the first stage particles are formed having a diameter of about 1 μm as well as particles of different sizes (Fig. 2), the presence of which the DLS studies did not reveal. In addition, the resulting nanoparticles do not always have a spherical shape.

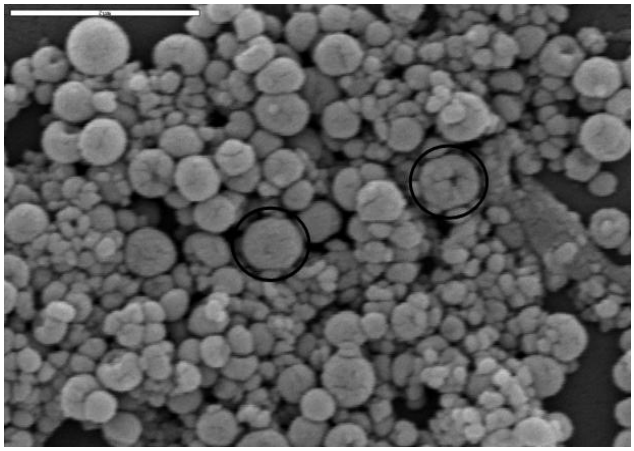
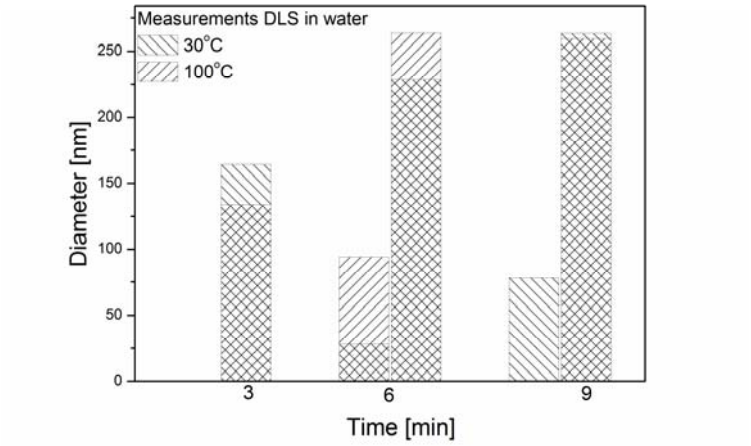


Fig. 2 The microstructure of ZnO balls produced in the first stage of the synthesis (SEM image).

The average particle size produced in the second stage was determined using the DLS method. In these studies, distilled water and a few drops of the resulting suspension were poured into the measuring cell with dimensions 40×10×10 mm. By measuring the average size of the resulting particles it was found that the average dimension changes over time. Examples of changes in the diameter and the percentage particle size distribution of the nanoparticles over time are shown in Fig. 3.



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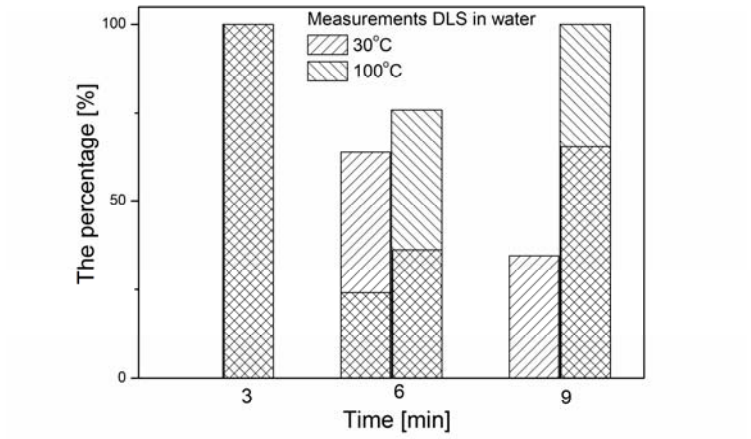
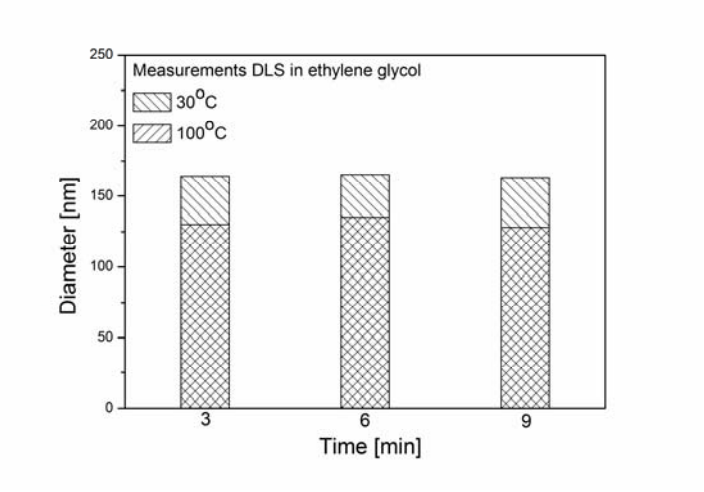


b)

Fig. 3 Changes: a) the average size of the nanoparticles, b) the percentage of particles of a given size measured in DLS method. The nanoparticles were obtained in the second stage in the reaction mixture hydrolysis after the addition of 10 ml of the supernatant into the simple solution at the temperature of 30ºC and 100ºC.

The results showed that by adding 10 ml of the supernatant to the solution at the temperature of 100°C nanoparticles are formed with an average size of about 134 nm, and when the solution temperature is 30°C nanoparticles are formed with an average size of at 164 nm. It was also found that the change in the average particle size is faster when their diameter is smaller (nanoparticles of smaller diameter were formed after the addition of the supernatant to the solution at the temperature of 100°C) (Fig. 3).

Analyzing the test results the authors concluded that the only factor that can cause a change in the average particle size measured by DLS is water, because the resulting reaction mixture did not undergo sedimentation over time. Thus tests were done for the average size of the obtained nanoparticles, whereby ethylene glycol was used as a solvent. Studies have shown that the average size of the particles does not change (Fig. 4).



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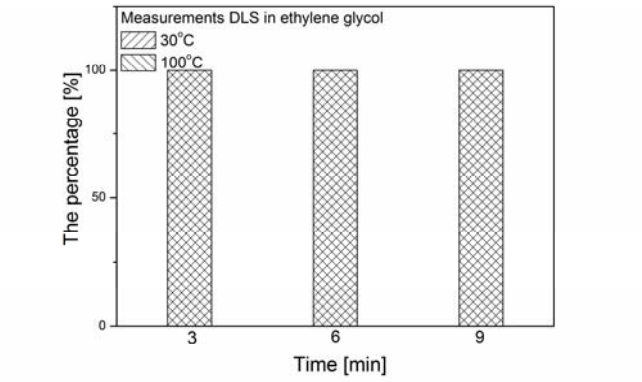


b)

Fig. 4 a) the average size of the nanoparticles, b) the percentage of particles of a given size when measured by DLS. The nanoparticles were obtained by hydrolysis of the reaction mixture at a temperature of 30°C or 100°C after addition of 10 ml of the supernatant.

Thus, analysing the measurement results of DLS, it was found that the diameter of the nanoparticles of zinc oxide is changed under the influence of the liquid dispersant. If ethylene glycol was used as a dispersing liquid, the average particle size when measured by DLS did not undergo changes (Fig. 4).

In order to explain the observed phenomenon tests were performed analysing the microstructure of the obtained nanoballs of zinc oxide using a transmission electron microscope. Studies have shown that the nanospheres are composed of nanocrystallites (Fig. 5).

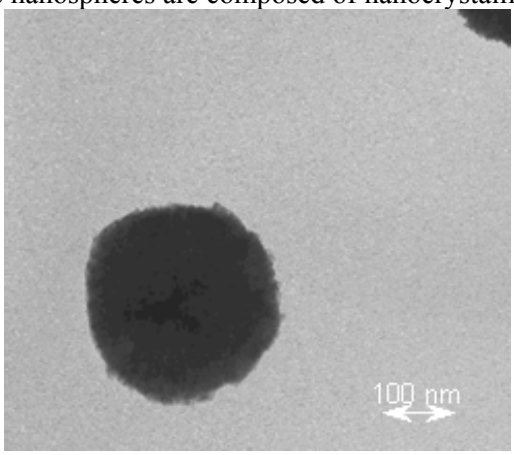


Fig. 5 TEM image of nanospheres of zinc oxide formed after addition of 10 ml of the supernatant to a solution at the temperature of 30°C.

Also the crystal structure of the obtained nanoballs were studied using the XRD method. The studies have shown that the resulting spherical zinc oxide structures are composed of nanocrystallites of wurtzite type structure (Fig. 6) with an average size of 5.8 nm to 10.3 nm.

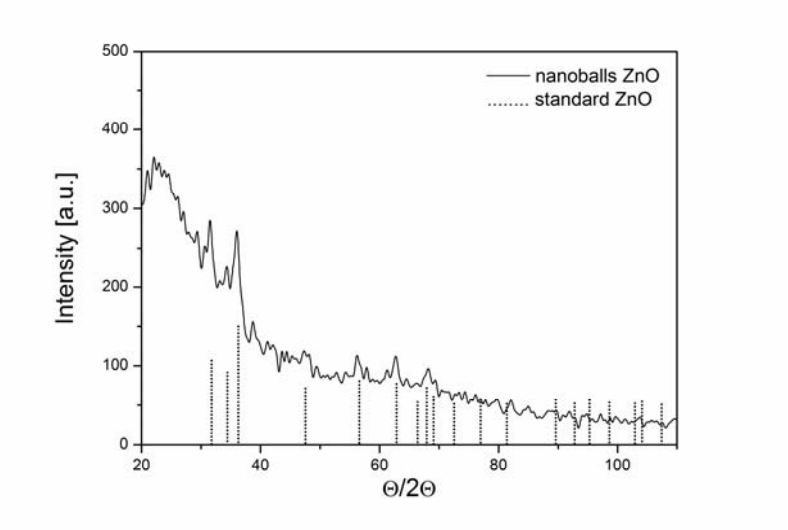


Fig. 6 X-ray diffraction pattern of zinc oxide nanoballs.

Characteristic peaks appearing in the X-ray diffraction of spherical ZnO nanoparticles are slightly shifted relative to the characteristic peaks occurring for the volume of zinc oxide (Fig. 6). This shift is the result of a specific construction of the nanoparticles [8].

Tests carried out with a scanning electron microscope (Fig. 7) showed that the ZnO nanoparticles formed during the process (the second stage) have a spherical shape. However, the size determined on the basis of these observations, did not agree with the results of the measurements made by the DLS method (Figure 4). In each sample, there were particles both small and large in diameter and the effect of agglomeration of smaller spherical particles and formation of spherical particles is particularly well visible in Figure 7.

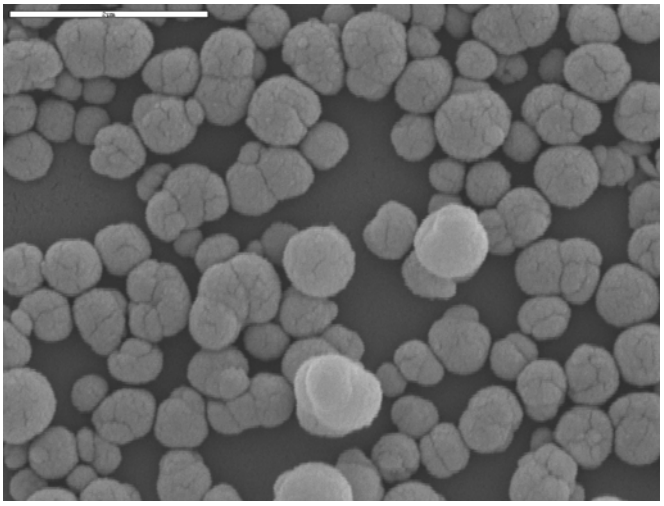
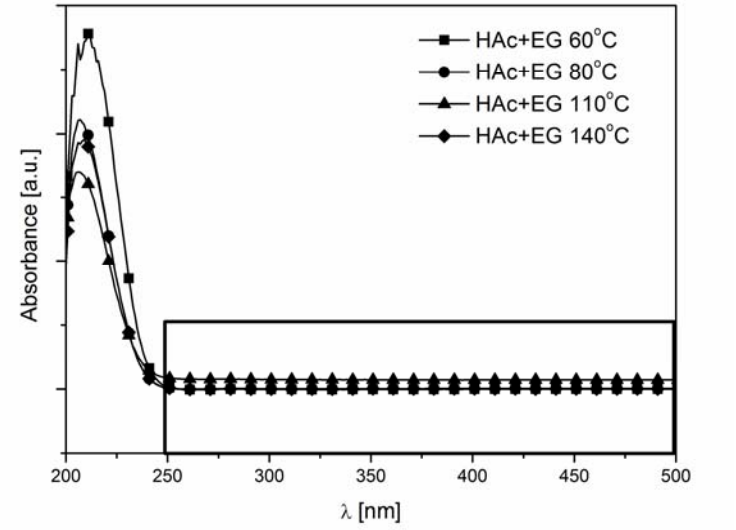


Fig. 7 Microstructure of ZnO balls obtained in the reaction mixture, to which was added 10 ml of supernatant at the temperature of 30°C. SEM observations, 20.000x magnification.

Analysing the obtained results of the research and the literature data [9], the authors believe that during the first stage of the process of obtaining the nanoballs of zinc oxide, a multilayer complex forms in the reaction of glycol with zinc ions and acetate residue [10] as

evidenced by the results of the spectroscopic studies (Fig. 8). Used in these studies were ethylene glycol (EG) and acetic acid (HAc) solutions as well as solutions of zinc acetate $Zn(Ac)_2$ in ethylene glycol. Solutions of acetic acid in ethylene glycol were tested by using them as a reference solution to determine the effect of acetic acid residues on the spectrum of zinc acetate solution in ethylene glycol.



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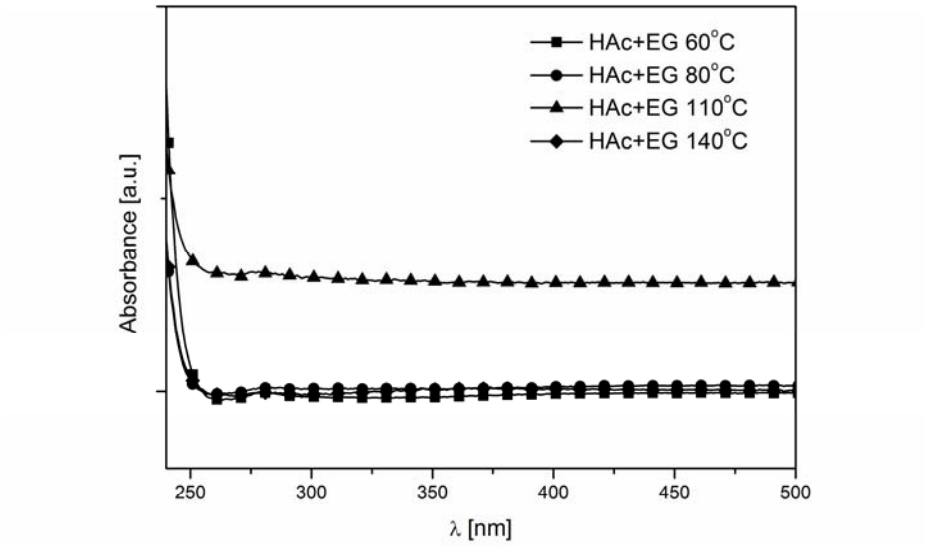
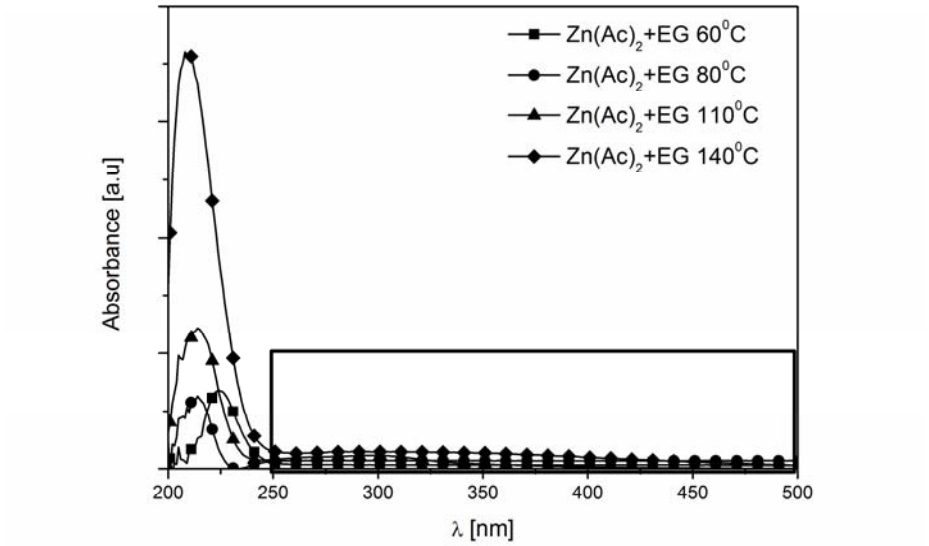


b)

Fig. 8 The relationship of absorbance versus wavelength in solution ethylene glycol and acetic acid heated to different temperatures a) λ=200-500nm, b) zoom to range λ=250-500nm.

The peak observed at a wavelength of approximately 210 nm occurs during both test solutions of ethylene glycol and acetic acid as well as ethylene glycol solution containing zinc acetate. However, in the optical studies of ethylene glycol solution containing zinc acetate at a temperature above 80°C there is a clear second peak at a wavelength of about 290 nm (Fig. 9).



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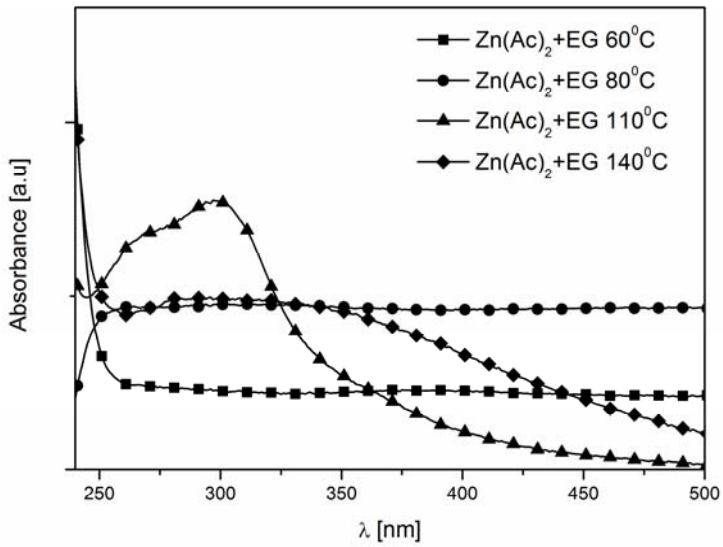

b)

Fig. 9 The relationship of absorbance as a function of wavelength of ethylene glycol and zinc acetate solution heated to different temperatures a) λ=200-500nm, b) zoom to range λ= 250-500nm.

According to literature reports [11], the presence of this peak indicates the appearance in the solution of hexagonal ZnO nanocrystallites (with a diameter of a few nm), the diameter of which is equal to their height. Thus, on the basis of spectroscopic tests made it can be concluded that above the temperature of 80°C in a glycol solution of zinc acetate hexagonal nanocrystallites form, the diameter of which is equal to their height. With the increase in temperature of the reaction solution to a temperature above 110°C, the resulting nanoparticles collide with one another to form nanocrystallites (Fig. 9-10), whose average size is smaller than 10 nm, as shown by XRD studies.

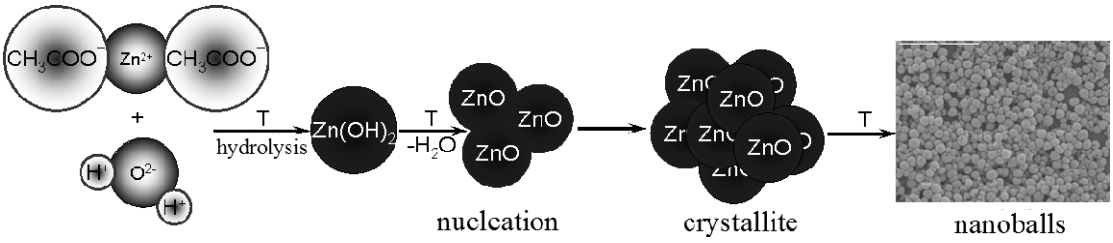

Fig. 10 Stages of nucleation and growth of nanoballs during the hydrolysis of zinc acetate.

Nanocrystallites of zinc oxide, according to research carried out by the means of TEM, form spherical agglomerates (nanoballs) only at temperatures above 140ºC.

Typically, the increase of nanoparticles occurs after exceeding their critical size and can occur under one of the three basic mechanisms [12]:

- Consecutive atoms attaching to an existing crystal;
- Ostwald recrystallization;
- Coalescence.

In the solutions of colloidal nanoparticles a generally dominant process in the increase in their size is the process of attaching the metal oxide molecules to the surface of an existing embryo or crystallite. The second process, recrystallization Oswald [13] lies in the fact that smaller colloid particles undergo the process of dissolution and re-precipitate resulting in an increase of nanoparticles. The third process - the coalescence is a fusion or else adherence of nanocrystals to create a larger one (with full matching crystalline network), and then their growth continues as a whole. This growth mechanism of nanocrystals is quite common. It occurs most extensively immediately after the completion of nucleation, when the energy of the Brownian motion of the nanocrystallites is not large enough to fully counterbalance the van der Waals interaction between the nanoparticles located at a sufficiently small distance from each other.

Based on the research carried out authors believe that at the beginning of the hydrolysis process the dominant process is the one leading to the formation of nanocrystallites which occurs due to the joining of next ions and molecules. Due to the physico-chemical properties of the used solvent ie. ethylene glycol, the growth process of the crystallites takes place very slowly. At a temperature of 293 K the dynamic viscosity (absolute viscosity) of ethylene glycol is 21 mPa·s, and is therefore far greater than that of water (1.004 mPa·s). Since the mobility of the ions depends on the viscosity according to the following formula (1), the rate of diffusion of zinc ions and the ZnO nanoparticles in ethylene glycol is small. For this reason, in the glycol solution, nanoparticles form and in the same conditions in aqueous solutions microstructures [9].

$$u_i = \frac{|q_i|}{6 \cdot \pi \cdot \eta \cdot r_i} \tag{1}$$

where: u_i - ion or molecule mobility, q_i - ion or molecule charge, η - viscosity of the solvent, r_i - radius of an ion or molecule.

The second mechanism of the nanoparticle growth (Oswald crystallization) in the tested case is a very slow process because ethylene glycol is a much weaker ionic solvent than water. The water molecule has a large polarity therefore its dielectric constant at a temperature of 25°C has a value of 78.4, and ethylene glycol at 25°C is 37.7.

Because of the high viscosity of ethylene glycol there is a third process of crystal growth – the coalescence, as is apparent from the study it occurs in this case, but does not lead to nanocrystals sticking together into one larger nanocrystal with full matching crystal network. As the temperature increases the viscosity of ethylene glycol decreases exponentially (2):

$$\eta = A \cdot \exp(B/RT) \tag{2}$$

where: A, B - solid characteristic of the solvent.

Therefore, the energy of the Brownian motion of the generated zinc oxide nanocrystallites increases and agglomerates get created taking the form of nanoballs. Due to the properties of the used solvent (ethylene glycol) nanocrystallites forming spherical agglomerates of zinc oxide do

not undergo rapid recrystallization.

The addition of water which can be treated as an electrolyte, to the solution of glycol-containing ZnO nanoballs, which can be regarded as a non-polar dispersion, reduces the electrostatic energy barrier [14]. In consequence, coalescence takes place, i.e. spherical agglomerates of nanocrystallites join together to form larger balls, which is well visible both in Figure 2 and Figure 7. This process is associated with the decrease of the free enthalpy of the system. In the researched system the Oswald recrystallization process cannot be completely ruled out. However, as shown by microscopic examination performed using a transmission electron microscope, nanoballs stored in the reaction mixture undergo very slow recrystallization (Fig. 11).

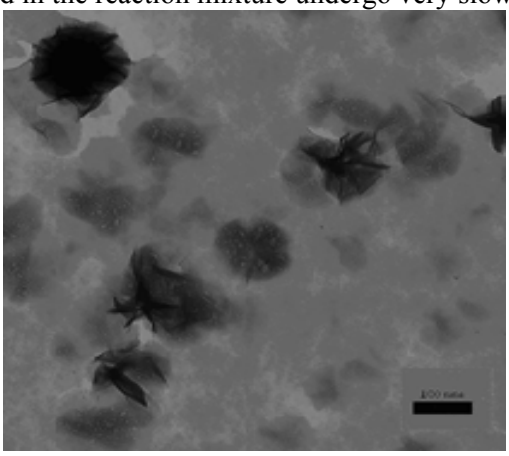

Fig. 11 TEM image of zinc oxide nanoballs formed by the addition of 10 ml of the supernatant to the solution at the temperature of 30°C. The study was performed six months after the date of the completion of the synthesis.

4. Conclusions

In this study the mechanism forming zinc oxide nanoballs was analysed in anhydrous ethylene glycol. Nanoballs of ZnO were obtained using a two-step method described by Seelig modified by authors. The analysis of the obtained results and the literature data shows that at temperatures below 80°C in the ethylene glycol solution containing zinc acetate a multilayer complex forms. This complex is the product of reaction of glycol with zinc ions and acetate residue. Above 80°C the complex is decomposed and hexagonal nanoparticles form whose diameter is equal to their height. This result confirmed the results of the modeling studies carried out by Al-Hilli and M. Willander [11]. Further increase in temperature causes a decrease in viscosity of the reaction mixture, the increase in energy of Brownian motion, leading to a process of nanocrystals agglomeration and formation of nanoballs at a diameter above 100 nm.

The resulting zinc oxide nanospheres very quickly change their dimensions in an aqueous medium, as a result of coalescence. The addition of the electrolyte solution (water) to the non-polar disperse system of ethylene glycol colloid containing nanoballs of zinc oxide lowers the free enthalpy of the system. For this reason, zinc oxide nanoballs formed in the glycol in the presence of water are combined in balls of larger diameter.

In the case considered, it is difficult to identify a typical coalescence due to the solvent used. Hexagonal nanostructures form nanoballs initially touching one another through contact spots. As a result of slowly running recrystallization processes full recrystallization of nanoparticles takes place and a lamellar nanostructure gets formed.

Acknowledgements

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