STUDY OF THE INFLUENCE OF THE TYPE OF THE ALCOHOL ENVIRONMENT ON THE STRUCTURE OF NANOSCALE ZINC OXIDE

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Abstract

This paper is devoted to studying the influence of the reaction medium on the morphology and the structure of nanoscale zinc oxide. In this work, nanoscale ZnO was obtained by the sol-gel method in alcohol environments. Ethanol, propanol, butanol and isopropanol were used as solvents. Phase composition of the obtained samples of nanoscale zinc oxide was studied by the method of x-ray-phase analysis. To define the morphology of the obtained ZnO particles, samples were examined with the use of scanning electron microscopy. Next, the obtained samples were studies by the method of IR spectroscopy for determining their composition. By the results of the research, a conclusion was made that the solvent has significant influence on the shape of the obtained ZnO nanoparticles and on their phase composition.

Keywords: nanoscale zinc oxide, x-ray phase analysis, infrared spectroscopy, scanning electronic microscopy, alcohol environment

Introduction

Today, there are many papers devoted to the issues of synthesizing and studying properties of nanoscale zinc oxide [1–8]. The interest in this material is due to the possibility of using ZnO nanoparticles in various fields: electronics, solar energy, medicine, etc. [1–3].

Nanoparticles of zinc oxide can be obtained with the use of various physical and chemical methods, the most promising of which are the methods of deposition from solutions, especially chemical deposition, the sol-gel method and hydrothermal synthesis. Depending on the chosen method of synthesis, various properties of nanoparticles, such as structure, phase composition, morphology, size, defects, etc., may vary. The sol-gel method makes it possible to
adjust properties of the obtained nanoparticles in a wide range by changing synthesis parameters: by choosing various precursors, solvents, temperature, active acidity of the medium, etc.

Some papers report that in various alcohol mediums, smaller monodisperse ZnO particles can be obtained, as compared to the particles obtained in aqueous solutions [5 – 8]. In this regard, the urgent task is the development of a technology for synthesizing nanoscale zinc oxide in various aqueous media and studying their properties.

Methods of formation

Zinc oxide was synthesized by deposition from alcohol solutions of zinc acetate with the use of potassium hydroxide. 0.1 n. alcohol solution of potassium hydroxide was added drop by drop to an alcohol solution of 0.1 n. zinc acetate with vigorous stirring. Ethanol, propanol, butanol and isopropanol were used as solvents. The alcohols were not additionally purified before synthesis; the purity level was consistent with the chemically pure qualification. The synthesis performed at \( t = 50 \, ^{\circ}C \). The obtained sols were centrifuged, washed and dried at \( t = 50 \, ^{\circ}C \).

Results and discussion

In the first stage, all the samples of nanoscale zinc oxide were studied using the x-ray phase analysis. The phase composition was studied with an x-ray diffractometer “PANalytical Empyrean” (manufacturer “PANalytical B. V.”, the Netherlands). The obtained diffraction patterns are shown in Figure 1.
Figure 1 shows that during synthesis in all alcohols, a phase of zinc with wurtzite-like structure was detected. The analysis of the data obtained by decoding the diffraction patterns shows that the samples synthesized in ethanol and butanol-1, in addition to the ZnO phase, have the phase of hydroxacetate complexes of zinc. The sample obtained in isopropanol also has 2 phases – zinc oxide ZnO and zinc hydroxide Zn(OH)\(_2\). It should be noted that the intensity of the reflection peaks that are responsible for the presence of hydroxide and hydroxacetate complexes is low, as compared to the reflexes of the zinc oxide phase. The best results, i.e. nanoparticles of zinc oxide with the most homogenous phase structure, containing only one phase - zinc oxide crystallized in a hexagonal wurtzite-like structure - were obtained in propyl alcohol. In the next stage, the obtained samples of nanoscale zinc oxide were studied with a scanning electronic microscope MIRA-LMH made by Tescan. Electronic microphotographs of samples of nanoscale zinc oxide synthesized in various alcohols (ethanol, isopropanol, propanol, and butanol) are shown in Figure 2.
As shown by the analysis of the data obtained with the use of scanning electron microscopy, the morphology of nanoparticles of zinc oxide significantly depends on the nature of the alcohol medium in which synthesis was performed. For example, ZnO nanoparticles obtained in ethanol and n-butanol have the shape of plates with the thickness of tens of nanometers and the length of hundreds of nanometers, and feature high polydispersity. However, ZnO nanoparticles synthesized in isopropanol and propanol have almost spherical shape with the average size of about 30 nm. In all samples, regardless of the nature of the solvent, particles are in the aggregated state, which is a feature of the materials obtained by the sol-gel method in alcohol medium. It is important to note that nanoscale zinc oxide synthesized in propanol is more homogeneous and monodisperse. In the next phase of studies, samples of nanoscale ZnO were studied by infrared spectroscopy at an IR spectrometer FSM 1201 with Fourier transformation in order to determine their chemical composition. The obtained IR spectra are shown in Figure 3.
Figure 3: IR spectra of samples of nanoscale zinc oxide synthesized in the medium of:

a) ethanol  b) butanol-1,  c) propanol,  d) isopropanol
After analyzing data from the literature [1-2, 9-14], IR spectra of nanoscale zinc oxide were decoded, and the characteristic bands inherent to fluctuations of ties between certain groups of atoms were detected. In the IR spectrum of nanoscale ZnO, some absorption bands are quite broad due to overlapping of the fluctuation frequencies of ties between certain groups of atoms and the fluctuation frequencies of ties with other groups of atoms.

Analysis of the data from the literature [1-2, 9-14] showed that the IR spectra of samples of the nanoscale zinc oxide synthesized in various alcohols contain the absorption bands resulting from the presence of ZnO nanoparticles of the hydroxyl (1020 – 1067 cm\(^{-1}\)) and the acetate groups (725, 1332, 1400, 1550, 2880 – 2970 cm\(^{-1}\)), chemically and physically adsorbed water (677, 877, 918, 1550, 3145 – 3435 cm\(^{-1}\)), and aquatic complexes (677, 877, 918 cm\(^{-1}\)) of zinc Zn(H\(_2\)O)\(_{2}\)\(^{2+}\) on the surface.

**Conclusion**

As a result of the research, it can be said that the synthesizing of zinc oxide in an alcohol medium forms nanoparticles that contain, in addition to ZnO, hydroxyl and acetate complexes of zinc. Thus, the nature of the solvent greatly influences the formation of zinc oxide nanoparticles with homogeneous phase structure. According to the results of the research, the best solvent for obtaining homogeneous ZnO nanoparticles is propanol.

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**References**


