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ZnO–Au NANOCOMPOSITE: SYNTHESIS, COMPOSITION, STRUCTURE, PROPERTIES

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Abstract

In this work, a method of obtaining*ZnO–Au* nanocomposite has been developed.The developed synthesis method is based on the sol-gel method of obtaining nanoscale zinc oxide, and on the method of chemical recovery for obtaining gold nanoparticles. The structure and the phase composition of the obtained composite were studied with the use of the methods of x-ray phase analysis and IR spectroscopy. The morphology of nanoparticles of the obtained*ZnO-Au*composite was studied by scanning electron microscopy. It has been shown that the developed method of synthesis allows obtaining a nanocomposite material that consists of *ZnO*nanoparticles with the shape of columns covered with gold nanoparticles. The acid-base properties of the surface of particles of the*ZnO-Au*nanocomposite in the obtained samples were studied using the indicator method for determining defects and surface composition.

Keywords:*ZnO-Au*nanocomposite, scanning electron microscopy, infrared spectroscopy, x-ray phase analysis, acid-base properties of the surface.

Introduction

One of the priorities of the modern areas of materials science development is synthesis of inorganic nanocomposite materials. Among these nanocomposite materials, nanoparticles of noble metals enclosed in the volume of matrices of various nature [1-3] have recently become particularly important.*ZnO-Au*nanocomposites are widely used in the interdisciplinary fields of science and technology, from plasmonics to biomedicine, due to the possibility of varying the spectral position and the amplitude of the plasmon resonance of metal nanoparticles by changing their size, shape and structure [1-3, 4, 5].Possible technical variants of application of highly dispersed *ZnO*forms are the "metal – oxide" composite materials and particularly *ZnO-Au*, which are of interest as functional electric contact materials [6]. The functional properties of such composites tend to improve with increasing dispersion and homogeneity of metal

distribution in the oxide matrix. Several methods of obtaining zinc oxide are known, including performing the reaction by the hydrothermal method, photochemical synthesis. However, the most common method is the sol-gel process. Such methods provide the opportunity of obtaining dispersed forms of *ZnO*with controlled size and morphology by adjusting the deposition conditions [7].

This paper is devoted to the problems of obtaining nanocomposite *ZnO-Au*material, and to studying its structure and composition.

The methods of forming structures

The developed method of synthesizing the nanocomposite *ZnO-Au*material consists of the following steps:

1. Preparation of the initial solutions of a zinc-containing precursor and a solution of the chloraurate acid;
2. Synthesis of the *ZnO*sol;
3. Recovery of*Au* nanoparticles on the surface of*ZnO;*
4. Converting sol into gel;
5. Centrifugal separation of the obtained gel and washing it with distilled water;
6. Drying the gel at the temperature of 150 ℃.

The choice of the drying temperature was due to the fact that this temperature (150 ℃) was sufficient for decomposition of $Zn(OH)_2$crystallites, zinc acetates, and for formation of the *ZnO* phase.

Results and discussion

The phase composition and the structure of *ZnO-Au*nanocomposites were determined by x-ray phase analysis. The diffraction pattern of a *ZnO-Au*sample dried at 150 ℃is shown in Figure 1.

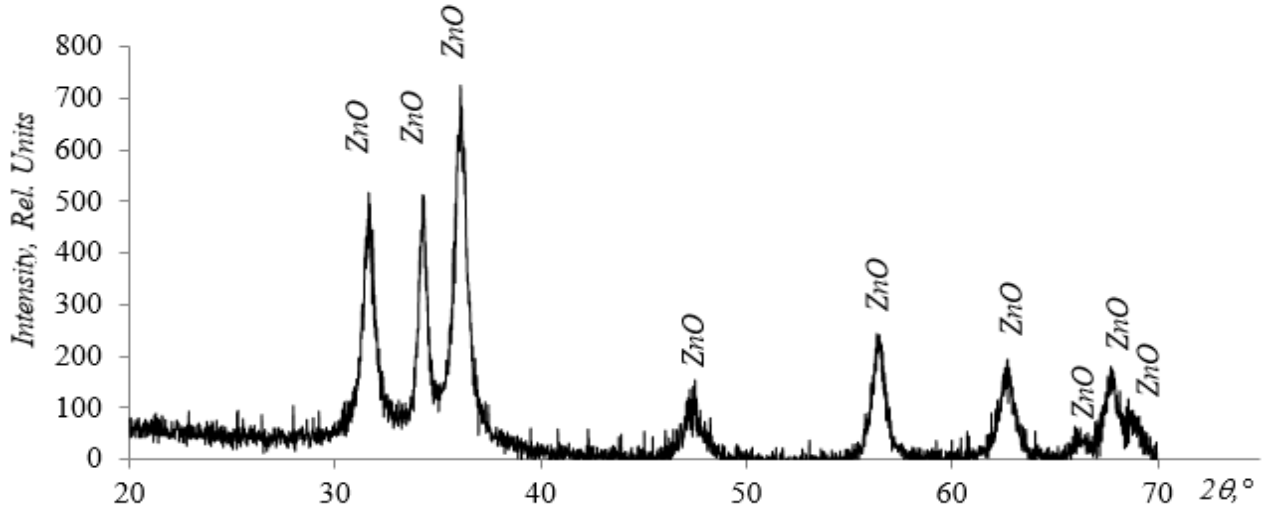


Figure 1 – The diffraction pattern of a *ZnO-Au*sample dried at 150 ℃.

Figure 1 shows that the position of peaks in the *ZnO-Au*nanocomposite x-ray reflection indicates the presence of wurtzite-like zinc oxide in the obtained samples. In the presented diffraction pattern, peaks of gold are absent, due to low concentrationsof *Au* in the *ZnO-Au*composite, in accordance with the conditions of synthesis (~ 1 %).

In order to determine the composition of the samples more accurately, the IR spectroscopy method was used. Figure 2 shows the IR spectrum of a sample of the *ZnO-Au*nanocomposite dried at 150 ℃.

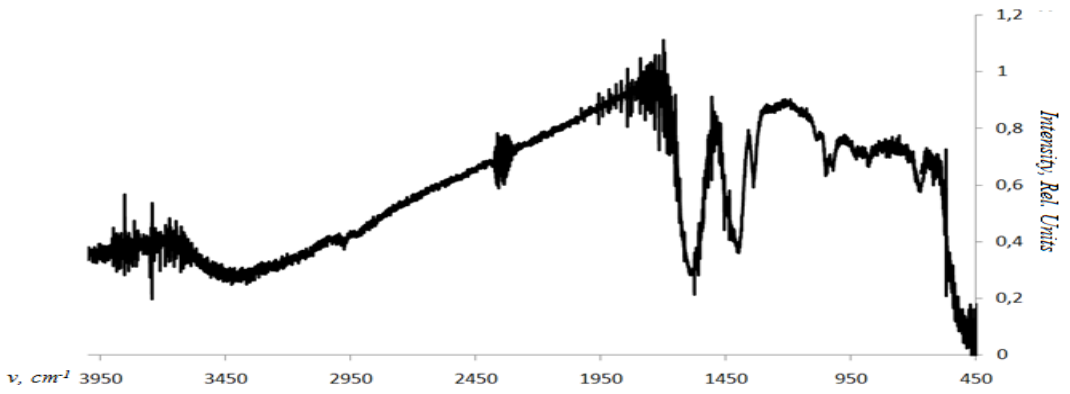
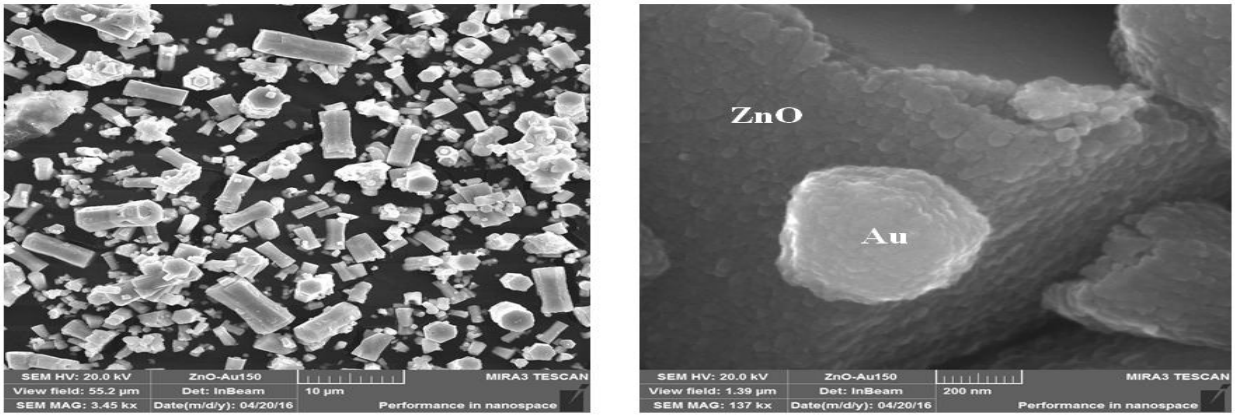


Figure 2 – IR spectrum of a sample of the *ZnO-Au*nanocomposite dried at 150 ℃.

In the IR spectra of composite *ZnO–Au* samples, there are valence and deformation oscillations -*OH*(3390-3840 cm^{-1}, 1340-1390 cm^{-1}), deformational fluctuations of ties - CH_3(1020cm^{-1}), fluctuations of *Me-CO* (1390-1450 cm^{-1}), which indicates the presence of physically and chemically bound water in the samples,as well as traces of zinc hydroxide,CH_3COO^-,apparently adsorbed on the surface of nanocomposite crystals [8 – 14].

Next, the morphology of particles of the obtained samples of *ZnO-Au*nanocomposites was studied by scanning electron microscopy. Figure 3 shows SEM images of the *ZnO-Au*nanocomposite dried at 150 °C.



a b

Figure 3 – SEM images of the *ZnO-Au*nanocomposite dried at 150 °C.

Scanning electron microscopy showed that zinc oxide in the obtained samples had the shape of columns with the characteristic dimensions of 1 – 5 µm (length) and 0.5 – 2 µm (diameter) (Figure 3 (a). Elemental analysis of various areas of the nanocomposite showed that the surface of *ZnO*particles was covered with smaller spherical particles of

Au (figure 3 (b)). A particle of gold shown in Figure 3 (b) is an aggregate of small (with the dimensions of ~ 20 nm) nanoparticles. The acid-base properties of the surface of *ZnO-Au*nanocomposites were studied with the use of the indicator method [15]. This method is based on selective adsorption of indicators with various *pKa*values in various active centers of the material. The intensity of the acid-base centers on the surface characterizes *pKa*of the indicator that is adsorbed in conjugated form, and the amount of the adsorbed indicator shows the number of centers of this intensity. The indicator method makes it possible to get an idea about defects on the surface of the material.

At the temperature of 150 °*C* zinc hydroxide is present in the samples, which is an amphoteric compound, and can have both acidic and basic properties. Various shapes of active centers on the surface of *ZnO-Au*before the decomposition temperature is reached are shown in Figure 4.

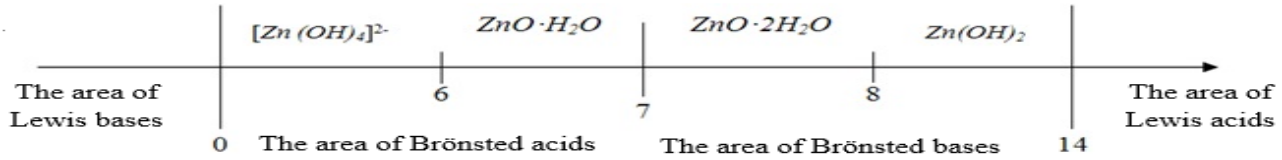


Figure 4– Possible shapes of active centers on the surface of *ZnO-Au*at the drying temperatures that are insufficient to remove the adsorbed water.

Figures 5 and 6 show the results of studying indicators adsorption on the surface of pure nanoscale *ZnO*, and the *ZnO-Au*nanocomposite, respectively.

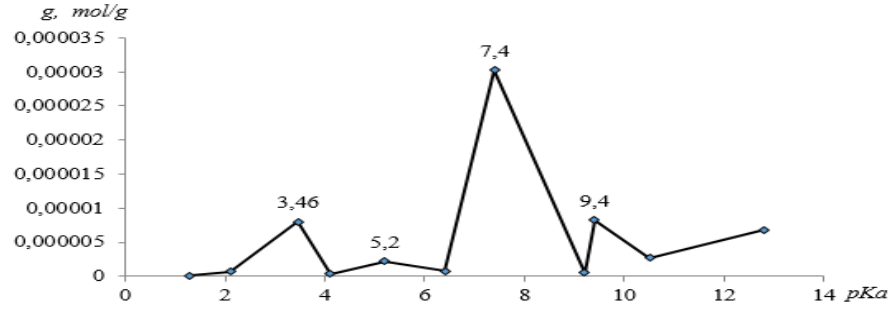


Figure 5 – The curve of indicators adsorption on the surface of *ZnO* dried at the temperature of 150 ℃

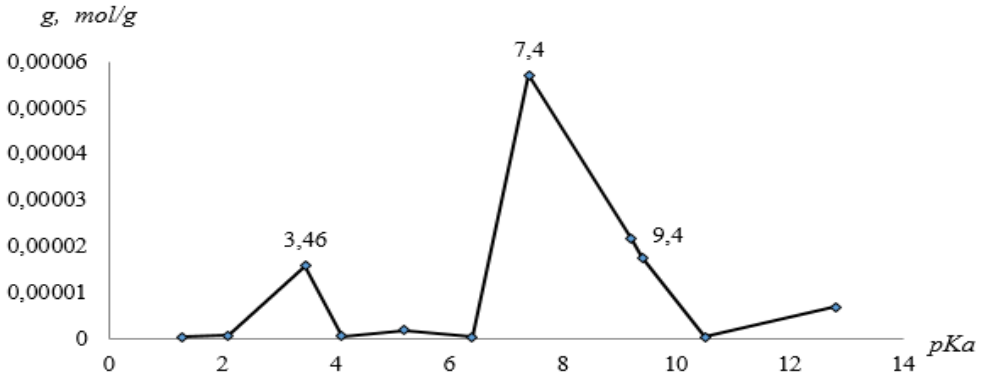


Figure 6 – Adsorption of indicators on the surface of *ZnO-Au* dried at the temperature of 150 ℃.

Analysis of Figures 5 and 6 shows that both on the surface of nanoscale *ZnO*and the *ZnO-Au*composite there are active centers with acid properties (*pKa* = 3.46, *pKa*= 5.2), which corresponds to $[Zn(OH)_4]^{2-}$, *ZnO*aqua-complexes (*pKa*= 7,4) and base centers with *pKa*= 9.4.

Let us consider the possible mechanism of gold nanoparticles formation on the surface of zinc oxide.

In obtaining composite material *ZnO-Au,* the precursor for *Au* is $HAuCl_4$, which can dissociate in aqueous solutions as follows:

$$HAuCl_4 \xrightarrow{H_2O} H^+ + [AuCl_4]^-$$

The complex cation $[AuCl_4]^-$ can interact with the basic centers on the surface of *ZnO.*

Table 1 shows the results of comparing the concentration of the active centers on the surface of *ZnO-Au*dried at 150 °C and the concentration of the active centers on the surface of *ZnO* dried at the same temperature.

Table 1 –Changes in concentration of the active centers on the surface of *ZnO-Au*dried at the temperature of 150 °C, as compared to the concentration of the active centers on the surface of *ZnO* dried at the same temperature.

pKa	*g (ZnO),* mol/g	*g (ZnO-Au),* mol/g	Change in the concentration	Active centers
pKa = 3.46	0.000008	0.000016	increased 2 times	$[Zn(OH)_4]^{2-}$
pKa = 5.2	0.000002	0.000002	unchanged	-
pKa = 7.4	0.00003	0.000057	increased 2 times	$ZnO\ 2H_2O$
pKa = 9.4	0.000008	0.000017	increased 2 times	$Zn[AuCl_4]_2$

Primary adsorption of the $[AuCl_4]^-$anions occurs in the base centers with *pKa*= 9.4, which is evidenced by their increased concentration, as compared to pure *ZnO*. Using the solution of $HAuCl_4$as a precursor promotes formation of *ZnO*aqua-complexes (*pKa*= 7.4).

Formation of active centers on the surface of $ZnO \cdot nH_2O$ before the temperature of 250 °Cis reached can be expressed by the following equation:

$$[-Zn\begin{matrix}O-H\\O-H\end{matrix}] \xrightarrow{H_2O} [-Zn<]^{2+} + 2\,OH^-,$$

Brönsted's base Lewis' conjugate acid

The following equation describes the possible process of $[AuCl_4]^-$ adsorption in the active centers:

$$[-Zn <]^{2+} + 2[AuCl_4]^- \rightarrow -Zn \genfrac{}{}{0pt}{}{AuCl_4}{AuCl_4}$$

Further growth of the *Au* nanoparticles allegedly occurs on the adsorbed ions of gold.

Conclusion

The developed method allows obtaining the *ZnO-Au*nanocomposite with the use of the sol-gel method. Studying the phase composition with the use of the XFA method showed that the main phase of the obtained composite was*ZnO*in a crystal wurtzite-like lattice. Further study of the composite with the use of the IR spectroscopy method showed the presence of physically and chemically bound water, and acetate groups. Therefore, calcination at the temperature above 150 °C is required for complete desorption of water and decomposition of the acetate complexes of zinc. Studying the morphology of the particles of the obtained *ZnO-Au*composite showed that zinc oxide particles had the shape of columns. Gold particles occur as spherical aggregates, and are present on the surface of *ZnO*particles. Studying the acid-base surface properties of the obtained samples showed the predominance of neutral active centers on the surface of the composite. Besides, total concentration of active centers on the surface of the obtained *ZnO-Au*nanocomposite is about two times higher than the concentration of active centers on the surface of*ZnO* dried at the same temperature.

Acknowledgments

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