OPTIMIZATION OF THE CONDITIONS FOR THE SYNTHESIS OF ZINC OXIDE NANOPARTICLES BY PLASMA CHEMICAL METHOD

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Abstract. Zinc oxide nanoparticles (ZnO) have a lot of useful properties, thanks to which they are used in various fields of science, technology and medicine. The properties of such nanoparticles largely depend on the method of their synthesis. This paper presents the results of optimization the conditions for the synthesis of zinc oxide nanoparticles by the plasma chemical method, as well as, clarifying the structure of the obtained samples. It is shown that the lack of air and the duration of the discharge affect the size and structure of the resulting particles. Analysis of the data obtained shows that synthesis in a vacuum chamber on graphite electrodes located inside a galvanised pipe at a pressure of 66, 7 kPa, a voltage of 20 V, DC power of 75 A is optimal for obtaining zinc oxide nanorods by the plasma chemical method.

1. Introduction

The development of technological bases, simple and powerful methods for obtaining nanoscale ordered structures of zinc oxide with reproducible properties is of great interest in order to create effective materials with specified properties as a functional material [1-3].

Hollow objects in which the size of one of the measurements falls into the nanometer range are of particular interest [4]. A high degree of anisotropy of properties, the effects of quantum localization, a large specific surface area and selective adsorption on the inner walls allows them to be attributed to promising materials. There is also an increased interest in quasi-one-dimensional filamentous crystal, thin and thick zinc oxide films, which are seen as promising in the field of creating miniature optoelectronic systems, physical-chemical sensors.

Zinc oxide (ZnO) nanoparticles, which have useful semiconductor, optical, piezoelectric and catalytic properties, are used in various areas of science, technology and medicine: in displays, gas sensors, piezoelectric devices, as well as catalysts [5].

The photocatalytic properties of zinc oxide are particular interesting in the area of reducing the technogenic negative impact on the environment. When cleaning industrial effluents from organic toxicants, the method of heterogeneous photocatalysis can be applied [6]. A photocatalyst based on an oxide semiconductor material, including zinc oxide, increases the cleaning efficiency under the influence of electromagnetic radiation [7]. Non-toxicity, chemical resistance (including at high temperatures), high reactivity of zinc oxide in the photocatalytic oxidation of organic pollutants, the possibility of modifications of structural, morphological surface and optical properties allows us to consider it as a promising catalyst that retains its photocatalytic activity after several cycles of reuse [8, 9].
2. Literature Review
The useful properties of such nanoparticles largely depend on the method of their synthesis, which differ from each other, in relative ease of implementation, the ability to control the size, morphology, composition and structure of the product, environmental safety and economic feasibility. Currently, solid-phase, liquid-phase, gas-phase methods of synthesis of nano- and microparticles of zinc oxide have been made regarding the relative arrangement of atoms and their electronic structure.

Liquid-phase methods (method of precipitation from aqueous solutions of Zn salts hydrothermal method, microemulsion method) [10] make it possible to obtain homogeneous rod-shaped zinc oxide particles with a narrow size distribution.

For example, during the synthesis by the hydrothermal method at a reaction temperature 120 °C and a duration of 24 hours, ZnO nanoparticles with a rod diameter of 450±50 nm and a length of over 10 microns were obtained [11].

Gas-phase methods make it possible to obtain a wide nomenclature of ZnO structures: nanotubes, nanorods, nanocircles, nanofilms, nanolegs etc. Depending on the goal setting, it is possible to vary the geometry of the synthesis chambers, preionization methods, etc. [12].

Pure, structurally homogeneous, monocrystalline nanofilms of Zn, Sn, In, Cd, and Ga oxides with a rectangular cross section and constant dimensions were synthesized by the method of thermal sublimation [13]. The authors describe the structure of ZnO, as a series of alternating planes consisting of tetrahedral ions O and Zn arranged alternately along one axis. They form polar surfaces, leading to spontaneous polarization along the axis and the appearance of a dipole moment and a divergence in surface energy. The authors note that the process of thermal evaporation is very sensitive to the concentration of oxygen in the system, which affects not only the volatility of the starting material, but also the stoichiometric composition of the gas phase, as well as the formation of the product.

In the paper [14], the authors demonstrated the formation of the heterostructure of coaxial Zn-ZnO nanorods by the pyrolysis of zinc acetylacetone and suggested that the single-crystal structure of ZnO is a shell of a core of pure zinc, which can be considered as the basis for the subsequent spontaneous formation of single-crystal nanotubes of ZnO.

At the same time, a number of authors claim that although low-valent zinc compounds Zn are extremely rare, compounds containing the Zn-Zn bond can be obtained and are quite stable under the conditions studied [15, 16].

In the previous work [17], the authors of this article reviewed the results of plasma chemical synthesis of zinc oxide nanoparticles in an argon arc on a graphite electrode under conditions of oxygen deficiency. The obtained samples were examined by electron microscopy. The analysis of elements showed that the samples contain 70 wt.% Zn, 23 wt.% O, 5.6 wt.% C. It was assumed that under these conditions carbon nanotubes coated with zinc oxide in the form of a "pipe in a pipe" or "Russian matryoshka" were obtained.

3. Experimental part
The aim of these research was to optimize the conditions for the synthesis of zinc oxide nanoparticles by the plasma chemical method, as well as to refine the structure of the obtained samples.

The experiment was carried out in a vacuum chamber for plasma chemical synthesis of nanostructures, the scheme of which is shown in Fig.1.

As a source of Zn, a galvanized iron tube with a diameter of 19mm was used inside which an arc discharge took place. Graphite, molybdenum and zinc rods were used as electrodes, a copper plate or micron mesh made of stainless steel were used as a substrate, a power source was a DC generator.

An observation in the wall of the water-cooled vacuum chamber allowed to observe the experiment, a special device made it possible to adjust the distance between the electrodes.

During the experiments, the pressure inside the chamber, the gas surrounding, the current and voltage varied. Experimental data on the optimization of the conditions for the synthesis of zinc oxide
nanoparticles by plasma chemical method are given in Table 1. The obtained samples were examined by transmission electron microscopy method (TEM).

**Figure 1.** Vacuum chamber for plasmachemical synthesis of nanostructures. 1- front door; 2 - viewing window for observation in the front door; 3 - door lock; 4 - water supply pipe; 5- water outlet pipe; 6 - electrodes; 7 - upper regulator of the distance between the electrodes.

Table 1 shows that experiments N 5, 6, and 7 turned out to be effective.

**Table 1.** Conditions for the synthesis of ZnO nanoparticles by plasmachemical method.

| Experiment conditions | Experiment number | 1    | 2    | 3    | 4    | 5    | 6    | 7    |
|-----------------------|-------------------|------|------|------|------|------|------|------|
| Electrode material    |                   | graphite | graphite and Zn-galvanized pipe | graphite and molybden | graphite | graphite |
| Air surrounding       |                   | Air | Argon+ Air | Argon+ Air | Air |
| Source of zinc        | ZnO (s)           | Zn-galvanized pipe |
| Pressure, kPa         |                   | 38  | 100  | 100  | 100  | 66.7 | 66.7 | 66.7 |
| Current strength, A   |                   | 15-30 | 0.1 | 0.1 | 0.1 | 60 | 75 | 75 |
| Voltage, В            |                   | 30 | 5000 | 5000 | 5000 | 20 | 20 | 20 |
| Discharge duration, sec |                 | 50 | 30 | 30 | 30 | 90 | 40 | 60 |
| Result                |                   | Negative | Plates | Nanorods |
| Quantity              |                   | A few | Many | Many |
| Colour                |                   | Transparent | White | White |
| Linear dimensions     |                   | d= diametr | 120-150 nm | 70-300 nm |
|                       |                   | l= length/ width | 10-30 mkm/ 5-10 mkm | 10^6 nm | 1-2*10^4 nm |
|                       |                   | h= thickness | 0.75 mkm | - | - |

Figures 2 and 3 show electronic images of the nanostructures obtained in experiment N 7.
4. Conclusions
It can be seen that the lack of air and the duration of the discharged affect the size and structure of the resulting particles: in an argon-air environment depending on the duration of the discharge, the formation of both lamellar particles and nanorods with a very high length/meter ratio is possible. Nanorods with a wide range of particle size dispersion and a lower length/meter ratio are obtained in the air.

The data of the elemental analysis obtained during the experiment of №7 nanorods were also analyzed. Elemental composition 70 weight % Zn, 23 weight % O, 5,6 weight % assumes the general chemical formula of the obtained particles - Zn\textsubscript{2}O\textsubscript{3}C. The presence of carbon may indicate the formation of a carbon nanotube coated with zinc oxide. However, the developed specific surface area and high adsorption capacity of the obtained samples, as well as the low percentage of carbon atoms characteristics of all nanostructures, suggest that it may be carbon dioxide CO\textsubscript{2} adsorbed from the air. Deducting CO\textsubscript{2} from the general formula, we get the formula of the resulting substance Zn\textsubscript{2}O. This indicates two possible variants of the structure of the resulting substance: either it is the structure of a ZnO coaxial nanorode, in which a core of pure zinc is covered with a thin regular layer of zinc oxide, or it consists of Zn(I) oxide. Clarification and verification of the assumption made will be the subject of the further research.

Thus, the analysis of the data obtained showed that the synthesis in a vacuum chamber on graphite electrodes located inside a galvanized pipe at pressure of 66.7 kPa, a voltage of 20 V, a DC power of 75 A with a charge duration of 60 seconds is optimal for obtaining zinc oxide nanorods by the plasma chemical method.
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