ANNOTATION

dissertation work

«ELECTROCHEMICAL AND STRUCTURAL PROPERTIES OF NANOSTRUCTURED SEMICONDUCTOR OXIDES»

submitted for the degree Doctor of Philosophy (PhD)

specialty «8D07101 – Nanotechnology in engineering»

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The goal of the dissertation work is to develop low-cost methods for the controlled synthesis of nanostructured oxide semiconductors and study their electrochemical and structural properties with the prospect of application in sensor electronics.

Research objectives and their place in carrying out research work

1. To analyze methods for producing nanostructured zinc oxide and determine further prospects for the use of synthesized nanostructured semiconductor oxide materials in sensor electronics devices . The solution to this problem is reflected in Chapter 1. The physicochemical characteristics of oxide semiconductors, known methods for obtaining ZnO nanostructures , and the use of oxide semiconductor nanomaterials in sensor electronics devices are presented .
2. Develop effective, cost-effective methods for the synthesis of nanostructured semiconductor oxides: low-temperature hydrothermal method, chemical deposition method, thermal decomposition method. The solution to this problem is reflected in Chapter 2. The low-temperature hydrothermal method for the synthesis of zinc oxide, chemical precipitation and thermal decomposition is presented.
3. Determine the optimal parameters for controlled synthesis. The solution to this problem is reflected in Chapter 2. This chapter reflects the main parameters of low-temperature hydrothermal synthesis, chemical precipitation and thermal decomposition. The necessary equipment for carrying out research work is provided.
4. Investigate the electrochemical and structural properties of the obtained samples. The solution to this problem is reflected in Chapter 3. The results of scanning electron microscopy, X-ray structural analysis, optical spectroscopy, photoluminescence, and electrochemical characteristics of the obtained modified electrodes based on nanorods and zinc oxide nanofilms are presented.
5. Determining the prospects for the use of synthesized nanostructured semiconductor oxide materials in sensor electronics devices. The solution to this problem is reflected in Chapter 3. The considered methods for the synthesis of ZnO with the specified parameters make it possible to obtain electrodes for the non-enzymatic determination of ascorbic acid and highly active photocatalysts for the decomposition of organic dyes under the influence of UV radiation. These methods are economical, easy to implement, do not require complex expensive equipment and are suitable for large-scale production.

Research methods

As part of the dissertation work, the following methods were used:

- critical analysis of literary sources and patent research,
- planning and conducting experiments on the development of biosensors based

on nanostructured semiconductor oxide materials.

To achieve the objectives, the following chemical methods for the synthesis of nanostructured zinc oxide were used: hydrothermal method, chemical precipitation method, thermal decomposition method.

To interpret the research results, such modern methods of analyzing nanostructured materials as optical spectroscopy, scanning electron microscopy, X-ray diffraction, Raman spectroscopy, photoluminescence, cyclic voltammetry, and X-ray photoelectron spectroscopy were used .

Basic provisions (proven scientific hypotheses and other conclusions that are new knowledge) submitted for defense

1. Treatment of arrays of zinc oxide nanorods obtained by the hydrothermal method in an atmosphere at a temperature of 450°C for an hour followed by short-term treatment in hydrogen plasma entails the passivation of surface states created by oxygen adsorbed at grain boundaries during preliminary annealing in air, which contributes to an increase in number of free electron carriers, which accelerate charge transfer and reduce the resistance of ZnO samples.

2. The sensitivity of the electrochemical enzyme-free sensor depends on the technological processing. The sensitivity values of ascorbic acid (AA), measured in the neutral electrolyte PBS, were 73, 44 and 92 μAmM-1 cm-2 for sensors based on ZnO nanorods, initial, annealed in air (AT), and annealed in air with subsequent treatment in hydrogen plasma (AT +RT) respectively. It has been shown that thermal treatment followed by hydrogen plasma treatment of arrays of ZnO nanorods synthesized by chemical deposition is an effective technological step for creating a highly sensitive enzyme-free sensor for detecting ascorbic acid molecules in a neutral electrolyte.

3. ZnO samples treated in hydrogen plasma have the lowest absorption coefficient, and the initial samples have the highest. The optical band gap of the initial samples was 3.125 eV, 3.15 eV for samples subjected to thermal annealing, 3.2 eV for samples annealed in air followed by treatment in hydrogen plasma, 3.25 eV for samples treated only with hydrogen plasma. It was noted that the synthesized ZnO samples subjected to thermal annealing followed by treatment in hydrogen plasma had the highest photoluminescence intensity.

4. The fabricated ITO/ZnO/GOx/Nafion electrodes with arrays of ordered thin ZnO nanorods showed high sensitivity of ~50 μA/mM cm ^{2} when detecting glucose in a buffer solution, which allows them to be considered as a basis for creating biosensors for detecting glucose.

Description of the main results of the study

During the scientific research, the following scientific results were obtained:

1. It has been shown that nanostructured arrays of zinc oxide nanorods grown by low-temperature hydrothermal method can be used as a basis for creating an effective, economical, stable, highly sensitive non-enzymatic electrochemical biosensor for detecting ascorbic acid.

2. It is noted that thermal annealing in air followed by short-term treatment in hydrogen plasma cleanses ZnO samples from moisture and OH– ions, affects various channels of optical recombination and increases the concentration of

passivated states, which leads to surface activation and an increase in the role of surface reactions with the analyte , that is, to increase the sensitivity of the biosensor.

3. The results of studying the elemental composition of the surface and the chemical state of the considered ZnO samples using X-ray photoelectron spectroscopy showed that thermal and plasma treatments lead to a shift of the Auger peak to lower energies, while at the same time the Zn2p3/2 and Zn2p1/2 peaks shift towards higher energies , which indicates that for ZnO NW AT+PT samples, the surface valence electron cloud densities of Zn and O decrease, and the binding energies of the valence electron and core level electron increase. The increase in the intensity of the O_2 oxygen band , corresponding to non-lattice O^{2-} ions or O^{2-} ions in oxygen vacancies, is consistent with an increase in the concentration of free carrier carriers in ZnO AT+PT samples; therefore, in ZnO AT+PT samples the concentration of recombination centers after H - processing.

4. It is noted that H-treatment of ZnO samples with preliminary annealing in the atmosphere helps to stabilize the surface, as a result of which these samples do not exhibit a noticeable aging effect. The ZnO NW/ITO electrode retained 98.7% of its initial response after 10 days, 97.8% after 20 days, and 96.8% after 30 days, indicating the high stability of these ZnO layers.

5. Highly oriented layers of zinc oxide in the form of thin films and arrays of nanorods on ITO substrates were synthesized using an economical method of chemical deposition from solution. The optical, structural and biochemical properties of these samples were studied. It was shown that samples with separately growing ZnO nanorods demonstrated greater sensitivity than samples with rods forming a thin film.

6. ZnO nanorods demonstrated a suitable matrix for GOx immobilization due to good enzyme retention. Direct electron transfer between GOx and ZnO nanorods was achieved, resulting in catalytic properties toward glucose. The fabricated ITO/ZnO/GOx/Nafion electrodes can be used as a basis for glucose biosensors.

7. A comparison was made of the structural, photoluminescent and optical properties of samples consisting of zinc oxide nanorods vertically oriented relative to the substrate, synthesized by chemical deposition from solution, the original ones subjected to thermal annealing in a muffle furnace at a temperature of 450 °C for 1 hour, and also processed in hydrogen plasma with preliminary annealing in air. It was shown that the samples treated in hydrogen plasma had the lowest absorption coefficient, and the highest - the original ZnO samples. It was noted that the synthesized ZnO samples subjected to thermal annealing followed by treatment in hydrogen plasma had the highest photoluminescence intensity.

Justification of the novelty and importance of the results obtained

The justification for the need for this research work is the relevance of research in the creation of biosensors based on semiconductor nanomaterials.

Novelty of the work

1. It has been shown that arrays of zinc oxide nanorods grown by low-temperature hydrothermal method are effective, economical and reliable enzyme-free biosensors of ascorbic acid with stable parameters.

2. For the first time, a simple method has been developed to increase the sensitivity of a ZnO sensor by heat treatment followed by treatment in hydrogen

plasma. Stable and efficient ZnO NW/ITO electrodes were obtained, demonstrating a high sensitivity of 92 μAmM-1cm-2.

3. It was found that the main difference between the Raman spectra of samples synthesized by the hydrothermal method is that thermal treatment in the atmosphere at a temperature of 450 °C and subsequent treatment in hydrogen plasma contribute to an increase in the intensities of vibrational modes, the peaks of which occur at 100 cm^{-1}, 333 cm^{-1}, 437 cm^{-1} and 1152 cm^{-1}. An increase in the intensities of these modes and the absence of new peaks after thermal and H-treatments indicates an increase in the degree of crystallinity of ZnO samples after treatments.

4. The dependence of the charge transfer resistance of nanostructured ZnO samples, which affects their electrochemical properties, on the post-growth treatments used was determined.

Practical significance of the work

Samples obtained as a result of low-temperature synthesis have a larger specific surface area, since they are presented in the nanoscale range. Due to their electrochemical and structural properties, the resulting nanostructured semiconductor materials are promising for use as the basis for sensor electronics devices.

In the dissertation work, using modern research methods, experiments were carried out as close as possible to production conditions, which determines a sufficient degree of reliability of the results of scientific work.

Compliance with areas of scientific development or government programs

According to the State Program for Industrial and Innovative Development of the Republic of Kazakhstan for 2020–2025, it is necessary to create a competitive manufacturing industry of the Republic of Kazakhstan in the domestic and foreign markets. Therefore, the study of the electrochemical and structural properties of nanostructured semiconductor oxides for use in sensor electronics will expand the range of processed goods that are in demand in the domestic and foreign markets.

The research was carried out within the framework of the project AP08856173 “Synthesis and study of the properties of low-dimensional semiconductor materials for the creation of highly sensitive biosensors.”

Contribution to the preparation of each publication

The doctoral student’s personal participation in obtaining scientific results consists of planning and conducting experiments, performing theoretical and experimental studies, discussing and summarizing the results.

7 scientific papers have been published on the topic of the dissertation work, including: 1 (one) article in a peer-reviewed scientific publication on the scientific direction of the dissertation topic, indexed in the Science Citation Index Expanded database of the Web of Science (Clarivate Analytics) and according to CiteScore in the Scopus database (Elsevier) IF = 5.4 Quartile (Web of Science) – Q1, Percentile SCOPUS-78%, 3 (three) articles in domestic publications in the field of physics, nanomaterials and nanotechnologies, recommended by COXON MES RK, 3 (three) works in collections of International conferences.

Information about the main publications indexed in the Science Citation Index Expanded of the Web of Science database (Clarivate Analytics), in a peer-reviewed scientific publication that has a CiteScore percentile in the Scopus (Elsevier) database on the topic of the dissertation:

1. Tolubayeva, D.B.; Gritsenko, L.V.; Kedruk, YY; Aitzhanov, M.B.; Nemkayeva, R.R.; Abdullin, K. A. Effect of Hydrogen Plasma Treatment on the Sensitivity of ZnO Based Electrochemical Non-Enzymatic Biosensor. Biosensors 2023, 13, 793. IF = 5.4 Quartile (Web of Science) – Q1, SCOPUS-78% percentile, https://doi.org/10.3390/bios13080793

Information on publications in publications recommended by the Committee for Quality Assurance in the Sphere of Science and Higher Education of the Ministry of Science and Higher Education of the Republic of Kazakhstan for the publication of the main results of scientific activity:

1. D.B. Tolubaeva, L.V. Gritsenko, Dependence of the electrochemical properties of biosensors on the morphology of zinc oxide layers // Bulletin of KazNU, Physical Series. – 2022. – No. 4 (83). - With. 29-37.

2. DB Tolubayeva, YY Kedruk and LV Gritsenko, Influence of plasma and heat treatments on the properties of ZnO nanorods // Physical Sciences and Technology. – 2022. – Vol. 9 (No. 3-4). – p. 11-17.

3. DB Tolubayeva, LV Gritsenko, YY Kedruk, KK Mustafina, MB Aitzhanov, Kh.A. Abdullin, Influence of zinc oxide morphology on its photocatalytic properties // Bulletin KarSU , Series physical _ – 2023. – Vol. 110, No. 2. - With . 34-45.

Information about reports presented and discussed based on the results of dissertation work at International and Republican scientific and practical conferences:

1. Tolubaeva D.B., Gritsenko L.V. The influence of glucose oxidase on the electrochemical properties of biosensors // Proceedings of the XLVII international scientific and practical conference “ Advances” in Science and Technology ", Moscow . – 2022. – p. 33-35.

2. Tolubaeva D.B., Paltusheva Zh.U., Zhaidary A., Gritsenko L.V. Electrochemical properties of zinc oxide nanorods // Proceedings of the International Conference of Students and Young Scientists “ Farabi Alemi ”, Almaty. – 2023. – P. 96.

3. Tolubaeva D.B., Gritsenko L.V. Electrochemical Biosensor Based On ZnO Nanorods // Proceedings of the International Conference of Students and Young Scientists “ Farabi Alemi ”, Almaty. – 2023. – P. 95.