ABSTRACT

of the dissertation work

«SYNTHESIS AND STUDY OF THE PROPERTIES OF NANOSTRUCTURED SEMICONDUCTOR MATERIALS FOR APPLICATION IN SENSOR DEVICES», submitted for the degree of Doctor of Philosophy (PhD) in the specialty "8D07103 - Materials Science and Engineering"

by **PALTUSHEVA ZHANIA URAZGALIEVNA**

The goal of the dissertation work is the synthesis of nanostructured semiconductor materials used as the basis for effective highly sensitive sensor devices, determining their sensitivity and detection limit in relation to selected analytes.

Research objectives and their place in the implementation of scientific research work

1. Study the physicochemical properties of semiconductor nanostructures (ZnO and ZnO/GO) and methods of their synthesis to create highly efficient sensors. The solution to this problem is reflected in Chapter 1. The physicochemical properties of oxide semiconductors and composites based on them, the main methods of synthesizing ZnO and ZnO/GO nanostructures are described.

2. Study the operating principles of biosensors and the role of nanomaterials in increasing their sensitivity and selectivity. The solution to this problem is reflected in Chapter 2. This chapter describes the methods of using semiconductor nanomaterials and composites based on them in sensor devices, the classification and operating principle of biosensors.

3. Develop a ZnO-based fiber optic biosensor for detecting the CD44 glycoprotein with a highly sensitive response, calibrate it and analyze its characteristics. The solution to this problem is reflected in Chapter 3. The fiber optic sensor was calibrated and prepared. The selection of suitable components for activation and functionalization of the surface of a fiber optic sensor with a thin layer of zinc oxide was carried out. The results of detection and processing of the signals obtained from a fiber optic sensor with a spherical resonator are presented.

4. Develop an electrochemical biosensor based on ZnO/GO for detecting ascorbic acid with optimization of sensitivity and operating parameters. The solution to this problem is reflected in Chapter 4. In this chapter, optimal conditions and parameters for the synthesis of ZnO/GO are selected and the results of studying the electrochemical sensor for determining ascorbic acid using ZnO, ZnO-GO nanostructures deposited on a glassy carbon electrode (GCE) are presented.

Research methods

The dissertation work used methods of critical analysis of patent research and literature sources to study the state of the field and prospects for the development of biosensors based on nanostructured semiconductor materials, as well as methods for planning and conducting experimental work, including synthesis, manufacture of sensors and their functionalization, using modern analytical tools such as an optical reflectometer, a scanning electron microscope with energy dispersive X-ray spectroscopy, transmission electron microscope, infrared absorption spectrophotometer with Fourier transform, X-ray diffractometer, electron scanning microscope, spectrometer and single-channel potentiostat galvanostat.

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

1. The first fiber optic biosensor with a spherical tip coated with a thin layer of zinc oxide (ZnO) 100 nm thick, deposited by the inexpensive sol-gel method, for measuring the CD44 protein in the range from 100 aM to 100 nM is presented. This sensor is easy to manufacture, has a good response to protein changes with a detection limit of 0.8 fM and high sensitivity to changes in the refractive index of the environment.

2. The possibility of regenerating the interaction between the main analyte (CD44 protein) and ligand is demonstrated, which allows double use of the functionalized sensor surface for repeated measurements. The sensitivity of the resulting sensor was tested with respect to the concentration of the control protein PSA, as well as without antibodies - CD44. These characteristics of the biosensor represent a promising new method for detecting an important biomarker CD44 in cancer diagnostics.

3. A modified ZnO-GO/GCE electrode with high sensitivity of 0.386 $mAM^{-1}cm^{-2}$ to ascorbic acid was obtained by chemical precipitation from a solution followed by heat treatment in air at a temperature of 375°C, the detection limit corresponded to 7.3 nM, promising for use as a basis for a biosensor for determining the level of vitamin C in the blood, in food products and medicines.

4. Heat treatment of the ZnO-GO composite in air at a temperature of 375°C allows increasing the sensitivity of the ZnO-GO/GCE electrode, as well as controlling the luminescent and structural properties of ZnO-GO samples, which makes these materials promising for use in the production of white light-emitting diodes, display devices, biological labeling and other optical devices of nanoelectronics.

Description of the main research results

The following research results were obtained during the research:

1. A literature review has shown that nanostructured semiconductor materials are poorly understood as a basis for sensor devices, highlighting the need for further research to improve the sensitivity, selectivity, and stability of sensors for detecting analytes such as CD44 and ascorbic acid.

2. The first fiber optic biosensor with a spherical tip coated with a thin 100 nm zinc oxide (ZnO) layer deposited using a low-cost sol-gel method has been developed to measure CD44 protein in the range from 100 aM to 100 nM. The advantages of this biosensor include ease of fabrication on standard, low-cost telecommunication fibers in a single step and ease of deposition of a thin ZnO layer using a sol-gel method without the use of expensive equipment. 3. The obtained fiber optic ball resonator showed a good response to the change of CD44 glycoprotein with a detection limit of 0.8 fM and high sensitivity to the changes in the refractive index of the environment and excellent reproducibility demonstrated on three sensors, which makes it promising as a biosensor platform after functionalization.

4. The possibility of achieving sensor regeneration without damaging the functionalized surface was demonstrated. The sensitivity of the obtained sensor was tested with respect to the concentration of the control protein, as well as without antibodies - CD44. These characteristics of the biosensor represent a promising new way to detect an important biomarker CD44 in cancer diagnostics.

5. Nanostructured ZnO samples and ZnO-GO composites were synthesized by a simple, inexpensive chemical precipitation method from solution. The morphology, as well as the electrochemical and structural characteristics of the synthesized ZnO and ZnO-GO samples were studied. The results of the SEM study of the synthesized

samples showed that the synthesized samples grow as two-dimensional thin plates with a length and height of several hundred nanometers and a thickness of several tens of nanometers.

6. It is shown that heat treatment of the synthesized ZnO-GO nanoparticles in air at 375 °C can affect various types of optical recombination. It is noted that the intensity of the UV band decreased after heat treatment, which may be due to partial dissociation of the exciton associated with the donor. The proposed method for the synthesis of ZnO-GO and ZnO nanoparticles with subsequent heat treatment allows one to control their luminescent and structural properties, which makes these materials promising for use in the production of white LEDs, information display devices, biological labeling and other optical devices in nanoelectronics.

7. The cyclic voltammetry method was used to evaluate the electrochemical properties of ZnO/GCE and ZnO-GO/GCE electrodes in detecting ascorbic acid. It was shown that heat treatment of ZnO-GO in air at a temperature of 375 °C allows increasing the sensitivity of the ZnO-GO/GCE electrode, which can be explained by both a decrease in defects in the sample and an increase in the interplanar distance of graphene oxide after annealing, which entails an increase in the specific surface area of the samples. The designed electrochemical sensor based on ZnO-GO/GCE showed a high sensitivity of 0.386 mA M^{-1} cm^{-2} and a detection limit of 7.3 nM, which makes it an effective tool for quantitative analysis and monitoring of vitamin C content in various samples, including pharmaceuticals and food products.

Justification of the novelty and importance of the obtained results

The justification for the need to conduct this research work is the relevance of research in the creation of biosensors based on nanostructured semiconductor materials.

Novelty of the work

1. The first fiber optic sensor based on a spherical resonator uniformly coated with a thin layer of zinc oxide (ZnO) ~100 nm thick by the environmentally friendly sol-gel dip-coating method was developed to detect the integral cellular glycoprotein CD44, expressed in many types of cancer, which is an adhesion receptor that regulates the process of metastasis on the cell surface.

2. For the first time, the regeneration of the interaction of the main analyte (CD44 protein) with the ligand was carried out, which allowed the functionalized surface of the sensor to be used twice for measurements

3. The effect of thermal treatment of ZnO-GO nanocomposites at 375 °C in air on their optical properties was revealed: the intensity of the UV band decreases, which is due to partial dissociation of the exciton associated with the donor. It is shown that control of temperature processing conditions allows targeted modification of the photoluminescent characteristics of the material, which makes it promising for use in sensor and optoelectronic systems.

Practical significance of the work

The practical significance of the study lies in the fact that the samples obtained during low-temperature synthesis have an increased specific surface area due to their nanostructured state. Due to their unique electrochemical and structural properties, these materials represent a promising basis for the development of sensors, including devices for detecting biomarkers such as CD44 and ascorbic acid. An important achievement of the work is the demonstration of the repeatability of the results on three sensors, which confirms the stability of their characteristics in real-world operating

conditions.In the dissertation research, experiments were conducted using modern methods of analysis that were as close as possible to real production conditions, which guarantees the reliability and reliability of the results obtained.

Compliance with scientific development directions or state programs

Obtaining and studying the properties of nanostructured semiconductor materials for use in sensor devices for detecting biomarkers such as CD44 and ascorbic acid corresponds to modern directions of scientific development and state programs of the Republic of Kazakhstan aimed at supporting innovative technologies in the field of medicine, ecology and information technology. An important element of the Digital Kazakhstan state program is the introduction of high technologies into medical and diagnostic devices, which contributes to improving the quality of diagnosis and treatment.

Contribution of the doctoral student to the preparation of each publication

The personal participation of the doctoral student in obtaining scientific results consists of developing a plan and conducting experiments, performing theoretical and experimental studies, as well as discussing and summarizing the obtained data.

On the topic of the dissertation, 19 scientific papers have been published, 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 of the Web of Science (Clarivate Analytics) and by CiteScore in the Scopus (Elsevier) IF = 5.4 Quartile (Web of Science) - Q1, SCOPUS Percentile - 89%, 4 (four) articles in domestic publications in the field of physics, nanomaterials and nanotechnology recommended by the Committee on Comprehensive Scientific Research of the Ministry of Education and Science of the Republic of Kazakhstan, 14 (fourteen) works in collections of international conferences and 1 (one) patent for an invention was received.

Based on the materials of the dissertation, 19 printed works were published, including 1 article in an international peer-reviewed scientific journal included in the Scopus and Web of Science databases:

1. **Paltusheva Zh.U**., Ashikbayeva Zh., Tosi D., Gritsenko L.V. Highly Sensitive Zinc Oxide Fiber-Optic Biosensor foe the Detection of CD44 protein// Biosensors. – 2022. - V.12. - Issue11. - P.1015. (Q1, процентиль 89%)

4 articles in publications recommended by the Committee for Quality Assurance in Education and Science of the Ministry of Education and Science of the Republic of Kazakhstan, included in the Scopus/Web of Science database:

2. **Paltusheva Zh.U.**, Alpysbaiuly N., Kedruk Y.Y., Zhaidary A.D., Aitzhanov M.B., Gritsenko L.V., Abdullin Kh.A. Photocatalytic activity of zinc oxide – graphene oxide composites// Bulletin of the university of Karaganda-physics. - 2022. - V.2. -P.102-110. ***Web of science***.

3. Gritsenko L.V., Kedruk Y.Y, **Paltusheva Zh.U.**, Syritski V. Structural properties of ZnO nanopowders synthesized by thermal decomposition// Physical sciences and technology. - 2023. - V. 10. - P.3-4. ***Scopus.***

4. **Paltusheva Zh.U.**, Gritsenko L.V., Kedruk Y.Y., Abdullin Kh. A., Aitzhanov M.B., Kalkozova Zh.K. Электрохимический сенсор аскорбиновой кислоты на основе наноструктур оксида цинка// Recent Contributions to Physics - 2023. - V.86.-№3. - P.49-56. ***Web of science***.

5. **Paltusheva Zh.U.**, Kedruk Y.Y., Gritsenko L.V., Tulegenova, Syritski V., Abdullin Kh.A. The influence of synthesis parameters and thermal treatment on the optical and structural properties of zinc oxide- based nanomaterials// Physical Sciences and Technology. – 2024. – V.11, №1-2. – P. 49-57. ***Scopus.***

14 proceedings of international scientific and practical conferences:

6. Кедрук Е.Ю., Айтжанов М.Б., **Палтушева Ж.У.**, Гриценко Л.В., Абдуллин Х.А. Влияние термической обработки на фотокаталитические свойства наностержней оксида цинка //Труды Сатпаевских чтений. – Алматы, 2021. - С. 1094–1097.

7. **Палтушева Ж.У.**, Гриценко Л.В. Применение наноструктурированного оксида цинка в биосенсорных устройствах// Труды Сатпаевских чтений. – Алматы, 2021. - С. 1101–1105.

8. Кедрук Е.Ю., **Палтушева Ж.У.**, Гриценко Л.В., Абдуллин Х.А. Разложение органических соединений под действием фотокаталитически активного ZnO//Аморфные и микрокристаллические полупроводники: сборник тезисов Международной конференции. – Санкт-Петербург, 2021 г. - С. 130–131.

9. Гриценко Л. В., **Палтушева Ж.У.**, Кедрук Е.Ю., Абдуллин Х.А. Исследование фотокаталитической активности наноструктурированного оксида цинка// ФизикА.СПб: тезисы докладов международной конференции. – Санкт-Петербург, 2021 г. - С. 120–121.

10. **Палтушева Ж.У.**, Кедрук Е.Ю., Жайдары А.Д., Гриценко Л. В. Структурные свойства композитов ZnO-GO// Международная конференция студентов и молодых ученых «Фараби әлемі», Алматы. – 2023. – С. 88.

11. Толубаева Д.Б., **Палтушева Ж.У.,** Жайдары А., Гриценко Л.В. Электрохимические свойства наностержней оксида цинка// Международная конференция студентов и молодых ученых «Фараби әлемі», Алматы. – 2023. – С. 96.

12. **Палтушева Ж.У.**, Гриценко Л. В., V. Syritski. Волоконно-оптический биосенсор на основе оксида цинка// Сборник докладов «65-й Всероссийской научной конференции МФТИ». – Москва, 2023 г. - С.74-76.

13. Кедрук Е.Ю., **Палтушева Ж.У.**, Гриценко Л. В., Абдулли Х.А. Влияние концентрации сульфата меди в растворе роста на морфологию композитов ZnO–CuO // Сборник докладов «65-й Всероссийской научной конференции МФТИ». – Москва, 2023 г. - С.70-72.

14. **Paltusheva Zh.U.**, Gritsenko L.V. Electrochemical sensor based on zinc oxide-graphene oxide composites // Международная конференция студентов и молодых ученых «Фараби әлемі», Алматы. – 2024. – С. 114.

15. **Палтушева Ж.У.**, Гриценко Л. В., Syritski V. Структурные свойства оксида цинка, синтезированного золь-гель методом// ICHEPMS: Сборник тезисов II Международной конференции по физике высоких энергий, материаловедению и нанотехнологиям. - Алматы, 2024г. - С.67-68.

16. **Палтушева Ж.У.**, Гриценко Л.В., Syritski V. Физико-химические свойства оксида цинка для сенсорных приложений// Труды международной научно-практической конференции: Ресурсосберегающие технологии в минерально-индустриальном мегакомплексе в условиях устойчивого развития экономики. - Алматы, 2024. - С. 416–418.

17. **Палтушева Ж.У.**, Гриценко Л. В. Сенсор на основе оксида цинка// Международная конференция студентов и молодых ученых «Фараби әлемі». – Алматы, 2024. - С.106.

18. Л. В. Гриценко, **Ж.У. Палтушева** Электрохимические свойства наноструктур ZnO/GO // Сборник докладов Международной конференции «Наноуглерод и Алмаз» (НиА’2024), Россия, Санкт-Петербург, 1 – 5 июля 2024г. – С. 221.

19. Гриценко Л.В., Толубаева Д.Б., **Палтушева Ж.У.,** Калкозова Ж.К. Структурные свойства наноструктурированных слоев оксида цинка, Материалы Международной конференции "ФизикА.СПб", Россия, Санкт-Петербург, 21–25 октября 2024 г., С. 121-122.

Patent for invention:

A patent for the invention of Abdullin Kh.A., Gritsenko L.V., Kedruk E.Yu., Paltusheva Zh.U. "Method for producing photocatalytically active zinc oxide powders" No. 35707, issued 10.06.2022, application No. 2021/0249 was received.