ABSTRACT

of the dissertation for degree of Doctor of Philosophy (PhD) in the specialty "6D074000 - Nanomaterials and Nanotechnology"

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Obtaining nanostructured materials based on zinc, tungsten oxides and study of their properties

General characteristics of the study

The experimental preparation of effective nanopowders based on zinc tungstate and tungsten oxide to solve the problems of water purification from organic compounds, tungsten oxide nanoparticles and reduced tungsten for the development of electrochemical energy storage electrodes and the study of the optical and electrical properties of nanostructured polycrystalline zinc oxide films treated in hydrogen plasma promising for use in phosphors and gas sensors are presented in this thesis.

The first chapter is devoted to a literature review of the basic materials of photocatalysts, electrodes for supercapacitors and their requirements. The principle and mechanism of water purification from pollution using solar radiation and photocatalysts are described using modern literature. The main types of electrochemical devices and energy storage mechanisms using metal oxides capable of redox reactions are considered. A review of the literature on the study of the optical and electrical properties of nanomaterials based on zinc oxides and the effect of technological treatments on their properties is presented. Moreover, the application prospect of ZnO films are considered.

The synthesis and analysis methods are presented in the second chapter of the dissertation. In the work, such methods for the synthesis of nanopowders, films based on zinc oxide and tungsten such as the hydrothermal method, the template method using a fibrous matrix and the method of pyrolysis of aerosol particles were used. The technology for producing electrodes based on tungsten metal coated with a tungsten oxide film for capacitors are proposed. Modern analysis methods were used: scanning and transmission electron microscopy to study the morphology of the obtained nanostructured samples, optical transmission, absorption and diffuse reflection spectra, photoluminescence and Raman spectra to study the energy and phonon spectra, X-ray diffraction analysis to determine the phase composition, cyclic voltammetric methodology, galvanostatic charge and discharge, spectroscopy of electrochemical impedance.

The third chapter presents the results of a study of the functional properties of the obtained photocatalytic active nanopowders of tungsten oxides, zinc tungstate and the relationship of the main characteristics with the catalytic properties of materials.

The study of the electrochemical characteristics of electrodes from samples of synthesized tungsten oxide and reduced tungsten oxide using methods of cyclic voltammetry, impedance spectroscopy, and galvanostatic charge-discharge is devoted in the fourth chapter.

The fifth chapter presents the results of a study of the effects of technological treatments on the properties of nanostructured zinc oxide films.

The relevance of research

Currently, the pollution of water with organic compounds and dyes from various sources (for example, the textile industry, paper and pulp industry, dye industry, pharmaceutical industry, etc.) is an important ecological problem. Some substances are very toxic and dangerous to living organisms, and the development of effective methods for the removal of these organic pollutants to preserve the environment has attracted much attention from researchers around the world. One of the promising methods for purifying water from pollution is photocatalysis using solar radiation and catalysts. Despite the fact that photocatalysis has recently appeared, the use of the method for commercial and industrial purposes has increased rapidly. The number of studies on searching effective photocatalysts which satisfied main requirements such as stability in the aquatic environment, stability to photocorrosion and a high absorption coefficient of solar radiation in this area is growing every year. Methods of synthesizing nanomaterials with controlled properties and establishing the relationship of the catalytic properties of materials with functional properties are a key aspect of modern photocatalysis.

Despite the existence of various technologies of energy storage and conversion, such as batteries, which are well suited for storing and releasing energy, electrodes leading to improved energy density and power are still relevant. A new trend in the creation of modern energy storage devices is aimed at the development of devices that include the properties of capacitors and batteries. Supercapacitors are also considered as an important class of energy storage technology, which is currently being developed rapidly. This technology plays a central role in energy storage and delivery technology and differs from batteries in its ability to store and release energy very quickly during short charging/discharging periods. It ensures the quality of power supply, as well as the safety and performance of other energy storage technologies by regulating peak voltage and bias load in case of power fluctuations and application of pulsed power.

Zinc oxide and nanoscale structures based on its are promising for use in many fields, such as light-emitting diodes (LEDs), gas sensors, biosensors, piezoelectric structures, thin-film transistors. Highly conductive ZnO films are also promising as TCO (transparent conductive oxide) layers for the manufacture of thin-film solar cells and transparent electronic components. The properties of zinc oxide films can be adjusted using various technological treatments to obtain the required characteristics.

The objects of study are photocatalytic $ZnWO_4$, WO_3 nanopowders, electrodes for capacitors from WO_3 and metallic W, nanostructured polycrystalline ZnO films.

The subject of the study is the development of methods for producing nanomaterials based on ZnO, WO_3 and $ZnWO_4$ and the study of their structure, photocatalytic, electrochemical, electrical and optical properties.

The purpose of the thesis is the development of experimental methods for the directed ynthesis of nanoparticles based on zinc and tungsten oxides suitable for the photocatalytic decomposition of organic compounds and the creation of electrodes for electrochemical energy storage, moreover, the development of methods for improving the electrical and photoluminescent properties of ZnO nanostructured films.

Research objectives

1. To develop regimes for the synthesis of nanoparticles based on zinc and tungsten oxides with the necessary properties;
2. To study the effect of the properties of the obtained materials on the photocatalytic activity of the samples and, based on this, select the optimal technological conditions for the synthesis;
3. Develop methods for producing tungsten oxide nanopowders for the manufacture of supercapacitor electrodes, study their characteristics and develop methods for achieving high electrochemical parameters of electrodes;
4. To study the effect of various technological treatments on the optical and electrical properties of nanostructured polycrystalline ZnO films.

Scientific novelty of the dissertation:

• a positive effect of hydrogen treatment on the photocatalytic activity of WO_3 samples was observed: the photocatalytic activity of the WO_3 after hydrogen calcinations at 450 °C doubly higher than initial oxide;

• W@WO_3 material with a “metal core-oxide shell” structure was synthesized, consisting of tungsten nanoparticles coated with a thin oxide layer, the resulting material exhibits high electrochemical characteristics: W@WO3 electrodes showed a capacity of 272 F g^{-1}, while the capacity of the electrodes from the initial WO_3 was 56.8 F g^{-1};

• it was found that the reduction of the monoclinic modification of WO_3 in hydrogen atmosphere leads to the formation of a stable phase of tungsten, while the reduction of hexagonal h-WO_3 leads to formation of metastable tungsten beta-W;

• reversible changes in the interband PL intensity were found that correlate with changes in the electronic conductivity in ZnO samples after a short-term (3 minutes) treatment in high-frequency hydrogen plasma: the PL intensity and electronic conductivity decrease synchronously when the samples are held in the dark and increase under ultraviolet illumination of the samples.

Scientific and practical relevance of the study

The results presented in this paper expand the understanding of photocatalytic processes using nanopowders from WO_3 and $ZnWO_4$. These materials can be used to purify water from industrial waste, such as various organic compounds, in particular dyes, the presence of which in waters is a significant environmental problem.

The development of electrode materials for supercapacitors is important for solving the problems of efficient storage and use of electrical energy during the operation of a wide range of devices and equipment.

The discovered effect of an increase in the PL intensity and an increase in the electrical conductivity of ZnO films as a result of short-term processing of ZnO films in hydrogen plasma, and the detection of the sensitivity of the photoluminescent and electrical properties of ZnO samples from ultraviolet light can be used to create various sensors.

Main provisions for defense:

• the photocatalytic activity of WO_3 samples can be significantly increased by heat treatment in a hydrogen atmosphere, which is associated with the formation of oxygen vacancies in the material;

• high specific capacitance of WO_3 electrodes is achieved by the formation of W@WO3 structures having a metal core coated by a thin natural layer of an oxide shell; W@WO3 structures are obtained by reducing tungsten oxide nanoparticles at temperatures > 450 °C in a hydrogen atmosphere, the capacitive characteristics of W@WO3 structures are 5-7 times higher than the characteristics of the initial oxide;

• the hexagonal phase of h-WO_3 can be synthesized by aerosol pyrolysis at temperatures <500 °C, pyrolysis at higher temperatures produces monoclinic WO_3, hydrogen reduction of hexagonal WO_3 allows the formation of a metastable beta-W phase, and hydrogen reduction of monoclinic WO_3 allows to obtain a stable phase of the metallic tungsten;

• a significant increasing of the intensity of interband photoluminescence and a simultaneous increasing of electrical conductivity in ZnO nanostructured films is achieved as a result of their short-term treatment in hydrogen plasma due to the formation of a high concentration of small donors in the films.

Conferences: The results of this work were discussed and reported at the following international and foreign conferences, seminars: 9th International Scientific Conference "Modern achievements of physics and fundamental physical education." Almaty, KazNU named after al-Farabi. 2016; 4th international conference "Modern Problems of Condensed Matter Physics, Nanotechnology and Nanomaterials (Sarsembin Readings)". Almaty, KazNU named after al-Farabi. 2016 International Satpayev readings “Competitiveness of technical science and education” of the Republic of Kazakhstan, Almaty, KazNTU named after K.I. Satpayev. 2016 8th International Conference of Students, Graduate Students and Young Scientists “Prospects for the Development of Basic Sciences”, Tomsk, Russia, 2016; Energy Fluxes and Radiation Effects (EFRE-2016): International Congress, October 2–7, 2016, Tomsk, Russia — Tomsk, 2016; International scientific-technical and scientific-methodical conference "Modern technologies in science and education" STNO-2017. Ryazan 2017; 18th International Conference on Radiation Physics and Chemistry of Condensed Matter. Tomsk. Russia. 2018; 11th International Scientific Conference "Modern Physics and Fundamental Physical Education". Almaty, KazNU

named after al-Farabi. 2018; Second Annual Meeting of Kazakh Physical Society, Kazakh British Technical University, Almaty, 6-8 June.

Publications

Based on the materials of the thesis, 20 published works were published, of which 2 articles included in the Scopus information resource (Elsevier, Netherlands), 1 article included in the Web of Science database (Clarivate Analytics, USA), 3 in scientific publications recommended by ESMC MES RK, 1 article in RSCI journals, 1 article in Kazakhstan publications in English and 12 abstracts and reports in the proceedings of international conferences.

The connection of the topic of the dissertation with the plans of scientific work

This dissertation was carried out as part of the scientific project 0118PK00202 "Development of technologies for producing nanostructured oxide semiconductors for a wide range of applications" (2018-2020) and 0115PK00520 "Synthesis and study of the properties of photocatalytic materials based on nanostructured semiconductors" (2015-2017).

Volume and structure of the dissertation

The dissertation consists of an introduction, five sections, a conclusion and a list of references containing 188 titles. The work is presented on 101 pages of typescript, including 61 figures, 3 tables and 1 appendix.