**ABSTRACT**
**to the doctoral dissertation (PhD) with majors in 6D074000 – "Nanomaterials and Nanotechnologies" of Yevgeniya Yuryevna Kedruk**
**"Low-temperature synthesis methods and functional properties of wide-gap semiconductive materials"**

**General description of the paper**

Nanostructural samples (materials) of ZnO and ZnO/CuO composites were obtained and investigated in the presented thesis research. These researches allowed completing work on the low-cost synthesis technology of ZnO nanoparticles and ZnO/CuO composites by annealing of zinc acetate in the atmosphere, during low-temperature hydrothermal synthesis, using method of chemical precipitation from a solution. According to the researches, such methods are based on the controlled synthesis of nanostructures of semiconducting materials with the given morphology and properties. Photocatalytic activity, morphology, electrical and structural properties of the synthesized samples have been studied.

**Relevance of the research**

Development issues of low-cost synthesis technologies of multifunctional materials attract a large focus of the research workers. Broad options of the materials' structure and properties management are discovered during the synthesis of nanostructured materials due to dimensional effects manifested in nanometric areas, and surface substantial contribution to the material properties. Such nanostructured materials as zinc oxide and copper oxide have high application potential in electronic, optical, magnetic and thermoelectric devices for solar and hydrogen energetics, in fuel elements and accumulators.

Discharge of organic wastes of various manufacturing sectors such as manufacture of leather, paper, pharmacy services, iron and steel enterprises, afflicts damage not only to human health but to the environmental conditions. Due to its high effectiveness and low cost, photocatalysis is actively used for organic dyes degradation. Zinc oxide (ZnO) with the high band gap and high exciton binding energy is widely adopted as photocatalyst, as well as in UV lasers, solar cells on dyes, gas sensors, UV-sensors, film solar cells, biosensors, etc.

Nowadays development of semiconductive photocatalysts with unusual morphology and characteristics is one of the most important tasks due to their unique chemical and physical properties.

Consequently, there is a task on development of the cost-efficient and highly active photocatalyst for decomposition of harmful organic compounds.

Photocatalysis has variety of advantages compared to other treatment methods, such as total dissolved solids, absence of waste-disposal problem, low cost, no need for mild conditions for temperature and pressure.

Relevance of development of the effective low-cost synthesis methods of oxide semi-conductors and their composites are stipulated by their unique properties making these materials promising for wide range of practical

implementation.

Thus, **justification of this scientific and research thesis is** the development of methods for obtaining highly efficient photocatalytically active nanomaterials based on zinc oxide and its composites for wastewater treatment from harmful organic compounds.

**Subjects of the research –** photocatalytic active nanostructured samples of zinc oxide (ZnO) and composite materials of ZnO/CuO.

**Scope of the research.** Low-cost controlled synthesis methods of nanostructured oxide semi-conductors and their composites, as well as research of their photocatalytic activity, morphology, electric and structural properties.

**Purpose of the thesis research** – to develop low-temperature controlled synthesis methods of nanostructured wide-band semiconductive materials allowing obtaining the materials with the given morphology, optical, structural and photocatalytic properties. To select optimal modes for each synthesis method. To explore physical and chemical (optical, structural, photoluminescent and photocatalytic) properties of the synthesized materials using the wide range of experimental procedures, to analyze properties of the obtained materials depending on the technological parameters of the synthesis.

The following **tasks** were resolved to achieve the assigned purpose:

1. to develop controlled synthesis methods of nanostructured zinc oxide and its composites, to determine optimal parameters for the synthesis of materials with the given properties (morphology, optical and structural characteristics);

2. to synthesize nanoparticles of zinc oxide using low-cost method of chemical precipitation and thermal decomposition, to determine the optimal growth parameters of nanoparticles;

3. to synthesize composite materials of ZnO/CuO using low-temperature synthesis methods, to explore morphology, optical and structural properties of the obtained composite materials depending on the synthesis parameters and concentration of the solution components;

4. to explore dependence of photocatalytic activity of the synthesized nanostructured materials on their geometric, optical and structural characteristics to select optimal technological parameters of the synthesis.

**Methodological framework of the research** is such synthesis methods of nanostructured samples as zinc acetate annealing in the atmosphere, low temperature hydrothermal synthesis and chemical precipitation from a solution.

**Scientific novelty of this research.**

1. It has been shown that during the synthesis of zinc oxide by chemical precipitation, the alkali concentration in the growth solution determines the morphology and size of ZnO particles, while the photocatalytic activity of ZnO nanoparticles nonmonotonically depends on the alkali content in the growth solution and reaches a maximum degradation rate of 0.0337 $min^{-1}$ (2.022 $h^{-1}$) at a concentration of 0.4 M.

2. The effect of temperature and duration of thermal action during the synthesis of ZnO nanoparticles has been detected and explored by the thermal decomposition method on the optical band gap of the synthesized ZnO samples

and their photocatalytic activity for decomposition of organic compounds, optimal technological conditions for achievement of the highest photocatalytic activity were determined; activity 98.48% and the average degradation rate of RhB dye 0.027 $min^{-1}$ (1.595 $hour^{-1}$) were obtained during the synthesis at 400°C within 10 hours, and decomposition of broad-spectrum organophosphate insecticide was also demonstrated against harmful insects of all groups and mites “BI-58 New”.

3. Dependence of photocatalytic activity, on the one side, and photoluminescence intensity of ZnO/CuO composite structures synthesized using low-cost chemical precipitation method, on the other side, on the synthesis temperature and growth solution composition has been determined; these technological conditions determine size and morphology of synthesized crystallites.

**Defended provisions:**

1. Maximum photocatalytic activity of zinc oxide nanoparticles obtained using chemical precipitation is achieved by the synthesis with concentration of the growth solution NaOH of 0.4 M and zinc acetate $(CH_3COO)_2Zn{\times}2H_2O$ 0.1 M due to the fact that these conditions of the synthesis are favorable for the rapid growth of nanorods, thereby crystallites with maximum size are synthesized along the direction 002 and low concentration of surface defects; this conclusion is confirmed by the minimum intensity of impurity photoluminescence of such ZnO samples, i.e., low concentration of surface defects.

2. A significant increase in the intensity of photoluminescence with simultaneous degradation of photocatalytic activity, observed after annealing of thin ZnO films, synthesized using chemical precipitation in oxidizing atmosphere followed by plasma treatment in hydrogen atmosphere, takes place due to passivation of charged oxygen acceptors on the surface of grain boundaries.

3. The photocatalytic activity of ZnO samples obtained by thermal decomposition depends both on the morphology of nanoparticles and on the concentration of surface defects; photocatalytic activity increases with an increase in the length to thickness ratio of nanoparticles (the highest photocatalytic activity is 98.48% at a length to thickness ratio of nanoparticles of 9.6).

4. The highest rate of photocatalytic degradation of the organic dye rhodamine-B in an aqueous solution under the action of UV radiation in the presence of ZnO/CuO nanocomposites obtained by chemical precipitation is achieved at the growth parameters: 20.0 mM zinc chloride, 1.0 mmol copper sulfate, 0.1 mM NaOH, and synthesis temperature 70°C. With an increase in the content of CuO with the composition of copper atoms in the ZnO/CuO samples to 29% and a decrease in the size of ZnO crystallites to 20–40 nm, the photocatalytic activity of the samples with respect to the degradation of the RhB dye increases to 95% at a decay rate of 1.164 $h^{-1}$.

**Scientific and practical significance of the research.** The samples obtained in the result of low-temperature synthesis have size within the nanorange and, accordingly, a larger specific surface area compared to their microanalogues, which makes the synthesized nanosamples more active. Due to their photocatalytic, electrical and gas-sensitive properties, these nanostructured

semiconductive materials and their composites are promising for the use in manufacture of gas sensors, transistors and for waste water treatment from organic pollutants.

**The author's individual contribution**. The results of the research presented in the dissertation were obtained by the author personally. Measurement of optical, photoluminescent and electrical characteristics has been performed by the author personally. The research of structural properties, surface morphology, elemental analysis of the obtained samples was performed with the assistance of the employees of the National open-type nanolaboratory of KazNU named after al-Farabi. The obtained results were discussed and analyzed in cooperation with the research supervisor, Doctor of Philosophy (PhD), professor L.V. Gritsenko and foreign consultant, Doctor of Philosophy (PhD), professor J. Chichero, as well as with Doctor of Physical and Mathematical Sciences, professor V. A. Moshnikov during the foreign internship at the St. Petersburg State Electrotechnical Institute LETI named after V. I. Ulyanov.

The defender of the thesis is the senior research assistant in the research and development project AP08856173 "Synthesis and research of the properties of low-dimensional semiconductive materials for creation of highly sensitive biosensors", research associate in the project AP09058501 "Development of background basics for creation of nanostructured materials promising for energy storage and photoelectrochemical devices".

**Approval of the conducted researches.** The results of the thesis research were presented at the following scientific international and foreign conferences: The X$^{th}$ Annual Conference of Nanotechnological Russian Community (Moscow, 2019), Satpayev Reading (Almaty, 2019, 2020, 2021), International Conference of Students and Young Scientists "Farabi alemi" (Almaty, 2019, 2020, 2022), Meeting of Kazakh Physical Society (Almaty, 2019, 2022), The 7$^{th}$ International Conference on Nanomaterials and Advanced Energy Storage Systems (Almaty, 2019), SCON 2$^{nd}$ International Conference on Nanotechnology (Netherlands, Amsterdam 2019), the X International Conference of FizikA.SPb (Russia, Saint Petersburg, 2020, 2021), The 8$^{th}$ International Conference on Nanomaterials and Advanced Energy Storage Systems (INESS-2019, Almaty), Amorphous and Microcrystalline Semiconductors (Russia, Saint Petersburg, 2021).

**Publications.** The results of the dissertation are published in 27 articles, among them 5 – in the international scientific magazines (1$^{st}$, 2$^{nd}$, 3$^{rd}$ and 4$^{th}$ quartile as reported by Journal Citation Reports of Clarivate Analytics and/or available in the database Scopus, percentile indicator according to CiteScore), 4 articles in the editions recommended by the Committee for Control of Education and Science (3 articles in the Bulletin of KazNITU and 1 in the Bulletin of ENU), 18 articles in the collections of international research and practical conferences. A patent for an invention of the Republic of Kazakhstan "Production process of photocatalytic active powder of zinc oxide" No. 35707 has been obtained, issued on 10.06.2022, application No. 2021/0249.

**Scope and structure of the dissertation**

The paper consists of Introduction, three sections, Conclusion and Bibliography, containing 293 titles. The total scope of the dissertation is 138 pages of the typewritten text, including 62 figures, 9 tables and 2 annexes.