ABSTRACT

for the thesis on the topic

«STRUCTURAL FEATURES OF MULTIFUNCTIONAL NANOPOROUS MEMBRANES OF METAL OXIDES AND NANOFIBERS BASED ON THEM»

submitted for the degree of Doctor of Philosophy (PhD) in the educational program 8D07112 – «Nanomaterials and Nanotechnologies»

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General characterization of the work. The thesis presents the results of investigation of nanostructured multifunctional porous and fibrous materials based on TiO_2 and Al_2O_3 with controlled morphology. The structural features and properties as well as the potential applications of metal oxide nanoporous/nanofibrous layers have been studied.

Relevance of the study. Recently, aluminum oxide and titanium dioxide nanostructures obtained by electrochemical anodization have attracted increasing interest due to the diversity of their structural features and functional properties. The possibility to control various parameters and conditions of the anodization process paves the way to obtain the structures with desired morphology (nanotubes, nanopores, nanofibers), including pore size, tube length, pore geometry and spacing.

Nanostructures based on TiO_2 exhibit a wide range of unique properties, including chemical stability, photocatalytic activity, biocompatibility, availability, corrosion resistance which allow their application as photocatalysts, in solar cells, in gas sensors, in supercapacitors, as well as for creating self-cleaning surfaces and as substrates bases for surface-enhanced Raman scattering (SERS) used to detect small concentrations of various substances.

To date, commercial SERS substrates are based on various periodic nanoscale structures of gold (Au) or silver (Ag), which exhibit efficient plasmon resonance absorption of electromagnetic radiation. However, such substrates are rather expensive, disposable and are produced using high-tech techniques. In order to solve this problem, combinations of Ag and Au with nanostructured titanium dioxide surfaces (TiO_2/Ag, TiO_2/Au) are actively investigated. An important advantage of using such composites as SERS substrates is the possibility of creating a rough morphology in the form of nanotubes and nanograss from TiO_2, providing a high specific surface area for efficient adsorption and effective plasmonic signal enhancement, as well as the possibility of reusability of such substrates due to the self-cleaning ability of TiO_2.

In this work, silver was chosen as the plasmonic metal for the creation of SERS substrates based on TiO_2 nanotubes and nanograss, because in this metal the surface plasmon resonance is more pronounced compared to other plasmonic metals such as gold or copper.

Similar to titanium dioxide nanostructures, research on nanostructured Al_2O_3 remains relevant due to its attractive physicochemical properties, high adsorption

capacity, controllable structural features and morphology, providing a wide range of applications, particularly as sensors and filters. In addition, nanoporous through membranes based on aluminum oxide are actively used for water purification from organic pollutants and separation of biological molecules (DNA, proteins) for biomedical purposes.

To date, despite the successful application of aluminum oxide membranes for water purification, there are problems associated with the hydrophobicity of the nanoporous surface and low efficiency, which are solved by deposition of additional layers, chemical functionalization and plasma treatment, which complicates the process of creating filters. This work proposes to solve this problem by structural modification of porous Al_2O_3 membranes. The formation of nanofibers on the surface of porous structures by varying the parameters in a single anodization process can significantly increase the specific surface area and the degree of hydrophilicity, while maintaining the simplicity of filter fabrication. Thus, the combination of nanoporous and nanofiber structures due to increased hydrophilicity promotes rapid and uniform distribution of liquid over the entire surface of the membrane, and the increased specific surface area of nanofibers increases the contact between the filtered solution and the membrane, which increases the efficiency of the filtration process, allowing to retain smaller particles of pollutant.

Considering the above-mentioned, the synthesis of metal oxide materials with a given morphology (nanopores, nanotubes, nanofibers) and the study of their structural features that expand the areas of their application and increase their efficiency in already applied areas is an urgent topic of research.

Objects of study. Nanostructured porous/fibrous layers based on Al_2O_3 as well as TiO_2 nanotubes and nanograss modified with silver nanoparticles and nanofilms, respectively.

Study subject. Technological conditions of anodization process to obtain porous/tubular/fibrous layers based on TiO_2 and Al_2O_3 with specified morphology and properties.

The aim of the thesis research. Synthesis and study of structural features of metal oxide nanoporous and nanofibrous layers to reveal their functional properties.

In order to achieve the mentioned aim, the following tasks were set:

- refinement of the method for obtaining nanoporous and nanofibrous structures based on titanium and aluminum oxides, as well as study of the influence of the main parameters of the electrochemical anodization process on their morphology;
- study of TiO_2 nanotubes and nanofibers modified with silver in the form of nanoparticles and nanofilms for use as SERS substrates;
- preparation of through nanofiber membranes based on porous aluminum oxide and study of their hydrophilic properties and filtering ability.

Methodological basis of the study - electrochemical anodizing process, chemical etching, thermal treatment, vacuum thermal evaporation, electrochemical deposition from solution.

Scientific novelty of the research:

1. It is revealed that the change of morphology of formed titanium dioxide from nanotubes to nanofibers with given structural features is achieved by controlling the anodization parameters.

2. It is shown that the deposition of silver atoms on nanostructured TiO_2 substrates depends on the morphology of the substrates: nanoparticles are formed on TiO_2 nanotubes and nanofilms are formed on TiO_2 nanofibers. It is found that the structure based on silver-coated TiO_2 nanofibers provides more "hot spots" required for Raman signal enhancement compared to the structure of TiO_2 nanotube with Ag nanoparticles.

3. It was found that the presence of nanofibers on the surface of porous membranes based on Al_2O_3 leads to an increase in their hydrophilicity, which allows the use of the obtained porous-fiber membranes for efficient filtration due to a more rough surface.

Statements submitted for defense:

1. The change of titanium dioxide morphology from nanotubular to nanofibrous is achieved by decreasing the fluorine diffusion rate while increasing the viscosity of the electrolyte in the anodization process, while reducing the water fraction from 10 wt.% to 2 wt.% in the electrolyte based on ethylene glycol with 0.5 wt.% NH_4F. By varying the voltage and time of anodization it is possible to control such structural parameters of formed nanotubes and nanofibers as pore diameter, wall thickness, length of tubes and fibers.

2. Structural features of titanium dioxide determine the form of deposited silver: in the case of nanotubes silver is deposited in the form of nanoparticles, and in the case of nanofibers - in the form of nanocoating. The use of SERS substrate based on TiO_2/Ag nanofibers allows increasing the Raman signal intensity by 2 times compared to SERS substrates based on TiO_2/Ag nanotubes due to the increased density of Ag "hot spots" at a more rough TiO_2 surface. This allows detection of methylene blue molecules with a concentration of 10^{-12} mol.

3. Varying the voltage and anodization time, it is possible to form a combination of nanofibrous and porous aluminum oxide structures with controlled structural parameters. Nanofibrous through membranes based on porous aluminum oxide with a thickness of 10 μm allow reducing the concentration of organic dyes in water by ~10 times during double filtration due to nanofibers with a diameter of ~20 nm on the surface, which increase hydrophilicity and specific surface area.

Scientific and practical significance of the study:

1. Possibilities of application of nanofibers formed at anodizing of titanium and aluminum have been demonstrated for the first time.

2. For the first time effective SERS substrates based on Ag-modified TiO_2 nanograss allowing detection of organic molecules of extremely low concentrations (down to 10^{-12} mol) were obtained. The results of selection and comparison of different reference materials showed that the highest value of enhancement factor of the SERS substrate based on TiO_2 nanograss is $5.5x10^7$.

3. It is shown that the combination of nanoporous membrane with hydrophilic aluminum oxide nanofibrous structures allows efficient filtration of organic dyes dissolved in water.

The author's personal contribution. All the samples studied in this thesis were prepared personally by the author. Development of the methodology and selection of anodization parameters were carried out by the author independently. The study of morphology, elemental analysis, phase composition and Raman spectra of the synthesized samples were carried out jointly with the research group of the National Nanotechnology Laboratory of the Open Type of al-Farabi KazNU, as well as in the Jülich Research Center (Germany, Jülich). Evaluation of the filtering properties of membranes based on aluminum oxide, as well as modification of nanostructures based on titanium dioxide with nanoparticles and silver nanofilms were carried out by the dissertant independently. The results obtained in the dissertation work were discussed and analyzed together with the scientific supervisor PhD B.Ye. Alpysbayeva and foreign consultant PhD V.Y. Smirnov. The dissertant directly participated in writing scientific articles and presentation of the results of the research at seminars and conferences, she is also the corresponding author of the main scientific articles prepared based on the results of conducted research works.

Approbation of the conducted research. The results of this work were presented at the following international and foreign conferences: «The 7th International Conference on Nanomaterials and Advanced Energy Storage System INESS-2019», (Almaty, 2019) and INESS- 2020 (Astana, 2020); «IEEE Conference of Russian Young Researchers in Electrical and Electronic Engineering, ElConRus», (St. Petersburg, 2019 and Moscow, 2021); International Scientific Conference of Students and Young Scientists «Farabi alemi», (Almaty, 2020).

Publications. According to the results of the dissertation work 10 printed papers have been published, including 2 articles in international peer-reviewed scientific journals included in Q2 and Q3 quartiles, according to Journal Citation Reports of Clarivate Analytics company and/or having CiteScore percentile in Scopus database, 4 articles in journals recommended by the Committee for Control of Higher Education and Science, 4 papers in proceedings of scientific and practical international conferences, 2 of them are included in Scopus database.

Scope and structure of the dissertation. The dissertation contains a list of notations and abbreviations, an introduction, the main part of four sections, a conclusion, a list of used sources and an appendix. The total volume of the thesis is 100 pages of typewritten text, including 56 figures, 7 tables and a list of 198 references.