ABSTRACT
of the thesis for the degree of Doctor of Philosophy (Ph.D.) in specialty
«6D074000 – Nanomaterials and nanotechnologies»

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SYNTHESIS OF CARBON NANOWALLS AND STUDY OF THEIR PROPERTIES

Characterization of the work. The work is devoted to the synthesis of carbon nanowalls (CNWs) by plasma chemical vapor deposition (PECVD) using various types of gas-discharge sources and substrates, as well as the study of the physicochemical properties of CNWs.

The relevance of the work. With the development of nanotechnology, nanomaterials, in particular carbon nanostructured materials, are increasingly finding various practical applications and are being actively introduced into various industries, in particular, in medicine, electronics, energy, oil and gas industry, construction, aerospace, mechanical engineering, and other areas.

Carbon nanowalls (CNWs) are one of the allotropic modifications of carbon, which consist of self-organized sheets of nanographene standing vertically on substrates and forming a labyrinthine structure. Although CNWs were discovered as recently as 2002, over the past two decades they have attracted enormous attention from most scientists around the world, as evidenced by the sharp increase in the number of publications and patents dedicated to CNWs.

Recently, significant attention has been focused on the functionality of CNWs for future devices due to their unique morphology. Due to its large surface area of about 1000 m^2/g, highly porous microstructure, and high current conductivity, CNWs are a promising material for applications in fuel cells, lithium-ion batteries, photovoltaic devices, solar cells, thin film transistors, gas sensors, field emission devices, light absorbers, improved biosensors, supercapacitors, and tissue engineering scaffolds.

However, at this stage of development of the nano industry, one of the most important conditions is the production of nanomaterials, including nanostructured nanomaterials, by the most efficient and less energy-consuming methods, which will lead to cost savings in the synthesis of nanostructured material. In addition, controlling the synthesis process and the final morphology of CNW films remains a difficult task, in particular, obtaining CNW with the required morphology and physicochemical properties. In this regard, plasma technologies are actively developing, which are widely used to obtain various nanostructured materials. The possibilities of plasma-chemical technologies in the field of materials science and the production of nanomaterials with desired properties are very promising and require further research.

In many experimental studies, gas discharge plasma of various types (high-frequency capacitive discharge, glow discharge plasma, microwave plasma, atmospheric pressure plasma, combined discharge) is used for the synthesis of CNWs as a universal medium, where, with the help of variations in discharge parameters, several possibilities arise for controlling the synthesis process in for precision control of morphology and properties, as well as studying the growth mechanism of the resulting material.

In connection with the above, we can conclude that the study of the synthesis process, the mechanism of growth and formation of CNWs, the control of morphology, and the study of their properties is a very urgent task for solving both fundamental and applied problems in nanotechnology and materials science.

The aim of the study. synthesis of CNWs by PECVD using various types of gas-discharge sources and substrates and study of their physicochemical properties.

Objects of the study. CNWs and PECVD synthesis technologies.

The subjects of the research. Synthesis of CNWs by PECVD using various plasma sources, in particular radio-frequency capacitive discharge plasma (CCP), induction discharge plasma (ICP), microwave plasma with the radicals injection (RI), the study of the properties of CNWs, and obtaining CNWs with a given morphology.

To achieve this goal, the following tasks are set:

1. Development of an experimental setup for the synthesis of CNWs using the CCP-PECVD method, determination of optimal synthesis conditions, and study of the morphological and structural properties of the resulting CNWs;
2. Study of the synthesis process of CNWs using the ICP-PECVD method and characterization of the physicochemical properties of the resulting samples;
3. Synthesis of CNWs on the surface of a nanoporous aluminum oxide membrane based on the RI-PECVD method and analysis of the resulting samples;

Obtaining of CNWs with a given morphology using CCP-PECVD and RI-PECVD methods.

The methods of the research. To achieve the goal of the work and complete the assigned tasks, the following methods were used to study both the properties of the plasma and the resulting material: the method of optical diagnostics of plasma, in particular optical emission spectrometry, methods of analyzing the morphological characteristics of CNS using analytical equipment, such as a scanning electron microscope (Quanta 3D 200i SEM FEI, SU8200 FE SEM Hitachi High-Technologies Corporation, SEM, ZEISS Crossbeam 540), probe scanning microscope (NTegra Therma), optical microscope DM 6000M (Leica), transmission electron microscope (TEM, JEOL JEM - 1400 Plus), structural characterization methods: Raman spectrometer (Solver Spectrum, NT-MDT, Russia with a laser wavelength of 473 nm and LabRAM Horiba Evolution & Omega Scope with a laser wavelength of 514.5 nm), X-ray photoelectron spectrometer (XPS) (NEXSA, Thermo Scientific) and an ultraviolet photoelectron spectrometer (UPS, NEXSA, Thermo Scientific), a method for studying optical properties - a UV-Vis spectrophotometer (Lambda1050, PerkinElmer Ltd), methods for studying electrical properties - a Van der Pauw Hall effect measurement system (HMS-5500, Ecopia), four-probe measurement system (RM3000, Jandel) and thermoelectric measurements, SEM-based energy dispersive X-ray spectroscopy, ZEISS Crossbeam 540 for elemental composition determination, morphology characterization methods based on fractal analysis and Minkowski functionals using Gwyddion software.

Provisions submitted for defense:

– the optimal parameters for the synthesis of CNWs based on the developed energy-efficient CCP-PECVD method, without the use of additional plasma sources, are at a temperature of 500 °C, the gas flow for the reaction gas Ar is 7-8 sccm and carbon-containing gas CH4 is 0.7-1 sccm, with a time limit synthesis 20-25 min and discharge power 8-15 W, and a further increase in high-frequency discharge power (up to 100 W) leads to the formation of multilayer graphene;

– increasing the synthesis time of CNWs from 30 to 60 min with a step of 10 min on quartz substrates using the ICP-PECVD method at a temperature of 800 °C and a discharge power of 140 W with a mixture consumption of Ar:CH4 (89.1:9.9%) and H2 20 sccm and 5 sccm changes the morphology of the CNW from labyrinthine with a height of 60 nm (with a synthesis time of 30-40 min) to petal with a height of 190 nm (with a synthesis time of 50-60 min), which leads to an increase in the crystallinity of the CNW, in particular, to a narrowing of the FWHM Raman peak G from 37.84 to 33.27 cm^{-1}, an increase in the IG/ID ratio from 0.92 to 1.59 and the degree of graphitization from 41% to 52%, as well as a decrease in surface resistance from 2000 to 600 Ω/□ and a change in semiconductor properties from p-type (30-40 min) to n-type (50-60 min);

– changing the thickness of the nanoporous aluminum oxide membrane from 3 μm to 18 μm and the pore diameter from 75 nm to 200 nm during the synthesis of CNWs using the RI-PECVD method leads to a decrease in the CNW height from 907 nm to 85 nm and the average wall length from 443 to 314 nm, as well as an increase in the pore density of CNS from 17 to 32 μm^{-2};

the morphology of the CNWs repeats the morphology of a nanoporous aluminum oxide membrane with a pore diameter of 150-200 nm and a thickness of 10 μm when synthesized by the CCP-PECVD method at a power of 11 W, a temperature of 460 °C, in a flow of a gas mixture Ar:CH4 – 7:0.8 sccm and synthesis time 25 min and by the RI-PECVD method at a power of 400 W, temperature 460 ^{o}C, in a flow of CH4:H2 – 50:100 sccm with a synthesis time of 10 min using a nanoporous membrane as a substrate.

The main results of the study obtained and established during the dissertation work:

1. An energy-efficient CCP-PECVD method for synthesizing CNWs with optimal plasma parameters has been developed, within the range of discharge power 8-15 W, gas flow for reaction gas Ar 7-8 sccm, and carbon-containing gas CH4 0.7-1 sccm, temperature 500°C, synthesis time 10-25 min, without the use of additional plasma sources, which makes it possible to obtain high-quality CNWs. Based on the results of SEM, Raman spectroscopy, and AFM, a map of the synthesis process was developed.

2. Experimental work was carried out on the deposition of CNWs on the surface of a quartz substrate using the ICP-PECVD method depending on the synthesis time. The resulting CNW films consist of vertically oriented multilayer graphene sheets with a height of 60 to 190 nm. Depending on the synthesis time, the morphology of CNW films changes from labyrinthine (30-40 min) to petal-like (50-60 min). Analysis of the Raman spectra of the samples showed that the resulting materials are CNs. The IG/ID peak ratio increases, FWHM analysis of the G peak of the Raman spectrum shows a narrowing of the G peak from 37.84 cm-1 to 33.27 cm^{-1}, which indicates an improvement in the quality of the structure of the resulting CNWs with increasing growth time. The influence of the CNW morphology on various optical, structural and electrical properties of the material was revealed. In particular, Hall and Seebeck effect measurements of the samples show that CNW films with a labyrinthine morphology (synthesis time 30 and 40 min) exhibit p-type semiconductor properties, whereas CNW films with a petal morphology (synthesis time 50 and 60 min) exhibit n-type semiconductor properties. type of conductivity.

3. Experimental work was carried out on the synthesis of CNWs on the surface of a nanoporous aluminum oxide membrane based on the RI-PECVD method. It has been established that an increase in the thickness of the aluminum oxide membrane leads to a decrease in the height of the CNS. The calculated ratio of peaks D and G (ID/IG), which indicates the degree of imperfection of the structure, showed the same values for all samples, except for the sample where the thickness of nanoporous aluminum is 10 μm and the height of the CNW is 334 nm;

Experimental results are presented on the synthesis of CNWs with a specified morphology on the surface of a nanoporous alumina membrane using two different methods, namely CCP-PECVD and RI-PECVD. The dependence of the reproducibility of membrane morphology of CNWs structures on the time of synthesis by the CCP-PECVD method has been established. In the case of CNWs grown using RI-PECVD, nanowalls grow predominantly vertically, which is explained by the intense injection of hydrogen radicals, which prevent the secondary growth of CNWs. The influence of pore diameter and membrane thickness on the growth of CNWs using the RI-PECVD method was revealed.

The novelty of the work. The novelty and originality of the work lies in the fact that for the first time, it contains:

– An energy-efficient method for synthesizing CNWs based on CCP-PECVD without the use of additional plasma sources has been developed.

– The influence of the time of synthesis of CNWs using the ICP-PECVD method on the change in the morphology of the resulting material from labyrinthine to petal-shaped was studied.

– The influence of the thickness of the nanoporous aluminum oxide membrane and the pore diameter during the synthesis of CNWs using the RI-PECVD method on the height, average length of the walls, and pore density was established.

The synthesis parameters of the CCP-PECVD and RI-PECVD methods were determined for which the synthesized CNWs repeat the morphology of a nanoporous aluminum oxide membrane.

The scientific and practical significance of the work is confirmed by the high interest of the international scientific community, both in plasma physics, chemistry, materials science, electronics, and in the field of nanotechnology. The results obtained are valuable for the development of nanotechnology, in particular, the development of a cheap technology for the synthesis of CNWs, which will lead to the production of a cheaper product, and the production of a material with a given morphology makes it possible to solve applied problems, in particular for the practical use of CNWs as electrodes for supercapacitors and in solar elements for creating gas sensors, photodetectors, biosensors and radiation-resistant optoelectronic devices. The study of the influence of plasma parameters and properties on the synthesized CNWs, the growth mechanism and formation of CNWs, and the analysis of the physicochemical properties of the nanomaterial are important for further practical applications.

The need for such research at the national level is associated with the wide applied application of the results of the work in such areas as energy, electronics, plasma technologies, nanotechnologies, and nanomaterials (carbon nanomaterials), which are priority areas of scientific, technological and industrial-innovative development of Kazakhstan.

The reliability and validity of the results obtained are confirmed using accurate and modern analytical methods, as well as the scientific method. To ensure reliability and reproducibility, all experiments were carried out in several parallels, and the results were confirmed by publications in journals with a high impact factor and in publications recommended by the Committee for Quality Assurance in Science and Higher Education of the Ministry of Science and Higher Education of the Republic of Kazakhstan (CQASHE MSHE RK), in the proceedings of international scientific conferences near and far abroad, as well as the received patent for a utility model of the Republic of Kazakhstan.

Publications. Based on the research results, 11 articles were published in journals with an impact factor included in the international information resource Web of Knowledge (Web of Science, USA) and Scopus (Elsevier, the Netherlands), 2 articles in journals recommended by CQASHE MSHE RK, 1 patent for a utility model RK, 2 works in the book “White Book on Nanotechnology”, 11 works in the materials of International scientific conferences.

Approbation of work. The results obtained were reported and discussed at the following international conferences: International conference on Advanced Energy materials (AEM-2018), Surrey, UK 10-12 September 2018; First Annual Meeting of Kazakh Physical Society, Astana, Kazakhstan, 10-13 October 2018; International Conference of Students and Young Scientists “Farabi Alemi”, Almaty, Kazakhstan, April 8-11, 2019; Second annual meeting of Kazakh Physical Society Almaty, Kazakhstan, June 6-8, 2019; International Conference on Applied Surface Science 2019 (ICASS), Pisa, Italy 17-20 June 2019; XXXIV International conference on Phenomena in ionized gases (XXXIV ICPIG) Sapporo, Hokkaido, Japan 14-19 July 2019; The 7th International Conference on Nanomaterials and Advanced Energy Storage Systems (INESS-2019) Almaty, Kazakhstan, August 7-9, 2019; International workshop “Recent Advanced in Plasma Physics and technology” dedicated to the memory of academician Fazylkhan Baimbetov, Almaty, Kazakhstan, December,19-21 2019; International scientific conference of students and young scientists, “FARABI ALEMI”, Almaty, April 8-11, 2020; Scientific-Coordination Session on "Non-Ideal Plasma Physics" Moscow, Russia, December 16-17, 2020; 7th Nano Today conference Guangzhou, China, November 16-18, 2021; 20th International Congress on Plasma Physics, Gyeongju, Korea from November 27 to December 2, 2022; 25th International Symposium on Plasma Chemistry (ISPC25), Kyoto, Japan, May 21-26, 2023; Third annual meeting of Kazakh Physical Society Kurchatov, Kazakhstan, June, 7-11, 2023. Also, experimental results were discussed at weekly scientific seminars of the Laboratory of Dust Plasma and Plasma Technologies, led by Academician of the National Academy of Sciences of the Republic of Kazakhstan, Doctor of Physical and Mathematical Sciences, prof. T.S. Ramazanov of the Faculty of Physics and Technology of Al-Farabi Kazakh National University and with scientific consultants prof. M.T. Gabdullin (Kazakh-British Technical University, Kazakhstan) and prof. M. Hori (Nagoya University, Japan), and collaborators: prof. Hiroki Kondo (Nagoya University, Japan), prof. A.N. Jumabekov (Nazarbayev University, Kazakhstan) and prof. V.V. Brus (Nazarbayev University, Kazakhstan).

Author's personal contribution. The presented research results, in particular the development of an experimental setup and a method for synthesizing CNWs based on CCP-PECVD, a study of the synthesis process of CNWs using various synthesis methods, and a study of the properties of the resulting materials were carried out by the author. The formulation of problems and discussion of the obtained experimental results were carried out jointly with scientific consultants. In all articles, Yerlanuly Ye. is the first author or corresponding author, thus making the main contribution in the preparation of all these scientific works.

Connection of the topic with the research plan and various State programs. The work was carried out in accordance with the plans of applied research work: grant of the Scientific Committee of the Ministry of Education and Science of the Republic of Kazakhstan AP08856684 “Synthesis of carbon nanowalls in a plasma environment, study of their properties and practical application” 2020-2022; grant from the Committee for Scientific Education of the Ministry of Education and Science of the Republic of Kazakhstan AP19676443 “Creation of bio-, photo- and gas-sensitive sensors based on carbon nanowalls” 2023-2025.