ANNOTATION

of the dissertation for the Philosophy Doctor (PhD) degree of in the educational program "8D07112 - Nanomaterials and Nanotechnologies" by

ZHUMADILOV RAKHYMZHAN

INVESTIGATION OF CARBON NANOWALL PROPERTIES FOR ELECTRONIC DEVICE DEVELOPMENT

Characterization of the work. The work is devoted to the complex study of the properties of carbon nanowalls (CNWs) and the development of electronic devices based on them.

The relevance of the work. CNWs are vertically oriented and interconnected graphene sheets. Due to free bonds at the edges of vertically oriented small graphene sheets, high electrical and thermal conductivity, nano- and/or microporous structure, large surface area, CNWs are used to fabricate pressure sensors, capacitors, temperature sensors, gas sensors, electrochemical devices, photodiodes, etc.

Nowadays, various gas-sensitive devices based on CNWs have been developed. For example, gas sensors based on CNWs/SiO_2/Si with resistive changes have been fabricated for the detection of toxic gases such as ammonia (NH_3) and nitrogen dioxide (NO_2) at room temperature. In addition, CNWs/SiC/Si based gas sensors showed excellent performance (sensitivity - 82 μA/ppm/cm^2; response time - 500 ms) for the detection of O_2 and H_2 gases has been demonstrated. These exceptional results were attributed to the unique structural nature of CNWs, specifically their ability to facilitate rapid electron transfer at the edges of vertically oriented multi-wall graphene nanosheets, but it has a slow response of the sensing devices. Furthermore, despite these achievements, there is no information in the literature regarding the application of CNWs for CO_2 gas detection. Thus, to fabricate CNWs-based gas sensors with improved performance, requires additional investigations.

CNWs have found applications in the field of photoelectric detectors, demonstrating promising development potential. Photodetectors have been fabricated, particularly based on Schottky transition CNWs/Si, CNWs/Au/Si, CNWs/PDMS, etc. The sensitivity of photodetectors based on CNWs/DLC/Si has been demonstrated to increase by a factor of 1.4 (responsivity - 2×10^3 A/W; detectivity - 7.2×10^{10} Jones) compared to detectors based on CNWs/Si. At this stage of development, optoelectronic devices are widely used in space technology, where they may encounter various forms of ionizing radiation. Therefore, there is a rising demand for new radiation-resistant functional materials and optoelectronic devices. Currently, radiation-resistant carbon nanotube (CNFETs) based field-effect transistors have been fabricated, using both the external advantages of CNFETs due to the geometry of the devices. There is also an experimental study of the radiation resistance of Q-carbon by irradiation with heavy ions with an accumulated dose of 10 dpa. In summary, considering the wide range of practical applications for CNWs and the increasing demand for nanostructured radiation-resistant electronic materials, there is a need for a systematic understanding of the influence of various ionizing radiations on the properties of CNWs and the optoelectronic devices based on them.

The large surface area, highly active graphene edges, and catalyst-free fabrication have contributed to the extensive application of CNWs as electrode material for electrochemical sensors. In recent years, the electrochemical properties of CNWs for detection of various analytes such as lactate, paracetamol, glucose, hydrogen peroxide, ascorbic acid, and uric acid have been studied in detail. To improve the electrochemical properties of CNWs, electrochemical sensors were fabricated by incorporating Pt nanoparticles, manganese oxide, etc. The obtained nanocomposite electrode showed excellent electrochemical activity for H_2O_2 detection exhibiting high sensitivity (698.6 μA mM^{-1} cm^{-2}). However, the effectiveness of the sensors relies on the use of composite structure, expensive noble metal Pt and specific enzymes, which complicates the sensor fabrication technology. One of the simple methods to improve the electrochemical

properties of the material is nitrogen doping. N-doped graphene has been found to exhibit higher electrocatalytic activity than the most other electrocatalysts. Research on the application of nitrogen-doped CNWs as non-metallic/enzymatic electrodes in electrochemical systems has not been conducted, which in fact makes the study of the electrochemical properties of N-doped CNWs a relevant topic.

Therefore, considering the aforementioned factors, a complex study of the properties of CNWs for the development of highly sensitive gas and electrochemical sensors, the study of the influence of ionizing irradiation on the properties of CNWs and photodiodes based on them, is a relevant topic.

The purpose of the research. Complex study of the properties of CNWs and development of gas sensors, self-adaptive photodiodes and electrochemical sensors based on them.

The objects of the research are CNWs and electronic devices developed based on them, such as gas sensors, self-adaptive photodiodes and electrochemical sensors.

The subject of the research. Investigation of the electrochemical properties of CNWs, their gas sensitivity and photosensitivity, as well as characterization of the devices developed on their basis.

To achieve this purpose, the following tasks were set:

1. Development and fabrication of gas sensors based on CNWs and investigation of gas-sensing properties for various concentrations of CO_2 gas and device temperatures;
2. Complex study of the influence of ionizing irradiation on the properties of CNWs and fabrication of self-adaptive photodiodes;
3. Development and fabrication of electrochemical sensors based on nitrogen-doped CNWs for the detection of hydrogen peroxide (H_2O_2);

The methods of the research. Synthesis of CNWs by chemical vapor deposition using inductively coupled plasma (ICP-PECVD) and radical injection (RI-PECVD). To achieve the objectives of the study and fulfill the assigned tasks, the following research methods were employed for investigating the properties of CNWs: morphological analysis using scanning electron microscopy (SU8200 FE SEM Hitachi High-Technologies Corporation, SEM, ZEISS Crossbeam 540), transmission electron microscopy (TEM, JEOL JEM - 1400 Plus), optical microscopy DM 6000M (Leica); structural characterization methods: X-ray photoelectron spectrometer (XPS) (NEXSA, Thermo Scientific) and Raman spectroscopy (inVia Reflex Raman microscope, Ntegra Spectra, Renishaw with a laser wavelength of 473 nm, LabRAM Horiba Evolution & Omega Scope with a laser wavelength of 514.5 nm); investigation of optical properties using UV-Vis spectrophotometer (Lambda1050, PerkinElmer Ltd); methods for studying electrical properties - Hall effect measurement system Van der Pauw (HMS-5500, Ecopia), and analysis of electronic properties based on ultraviolet photoelectron spectrometer (UPS, NEXSA, Thermo Scientific); investigation of gas-sensing properties involves using a gas measurement system with continuous registration of sensor film current using a source meter (Keithley 2400); study of photosensitive characteristics (voltammetric characteristics) (B1500A, Keysight) using a solar simulator (Ossila Solar Simulator) and external quantum efficiency measurement system (ORIEL IQE200, Newport); irradiation method using electronic (ILU-10) and proton (UKP 2-1) irradiation; electrochemical investigation of CNWs based on a standard three-electrode setup with a potentiostat (Elins, MetrOhm DropSens i 400).

The main provision for the defense:

– Carbon nanowalls with maze-like morphology, with height of 150 nm and thickness of 28 nm, synthesized by the ICP-PECVD method, provide sensitivity of 1.03% for carbon dioxide sensors and response time of 57 s at CO_2 concentration of 400 ppm and temperature of 100°C.

– The structure based on carbon nanowalls with maze-like morphology, with height of 200 nm and thickness of 40 nm synthesized by the ICP-PECVD method, along with monocrystalline CdZnTe, provides the development of self-adaptive photodiode with responsivity of 0.11 A/W and specific detectivity of 5.2×10^{10} Jones, under proton irradiation with energy of 1.5 MeV and a total fluence of 10^{12} p/cm².

– Efficient electrochemical sensors for hydrogen peroxide can be fabricated based on nitrogen-doped CNWs with height of 640 nm and thickness of 25 nm synthesized by the RI-PECVD method with flow rate parameters (N2: 20 cm^3/min), demonstrating wide linear response range for H_2O_2 concentrations ranging from 1 μM to 250 μM, low detection limit of 14 μM, and high sensitivity of 679.6 μA mM^{-1} cm^{-2}.

The main research findings obtained and established during the dissertation work

1. Two different gas sensors were fabricated using direct synthesis of CNWs films on Au microelectrodes on quartz (CNWs-1) and by transferring CNWs films on Au microelectrodes on glass (CNWs-2). CNWs were synthesized using the ICP-PECVD method. The morphology of the CNWs film in CNWs-1 exhibits a petal-like structure, whereas the film in CNWs-2 has a maze-like structure. Analysis of Raman spectra demonstrated that the intensity ratio of the D and G peaks, as well as D′ and G in the CNWs film of the CNWs-2 device (0.88 and 0.47, respectively) is higher than that in the CNWs film of the CNWs-1 device (0.51 and 0.27, respectively). This indicates that the CNWs film in CNWs-1 has lower defect density. It was found that depending on the method of fabricating of gas sensors, the sp^2 hybridization component changes in the CNWs films in the CNWs-1 and CNWs-2 devices, 65.1% and 66.0%, respectively. It was found that the sensitivity of CNWs-2 was 1.18% with a response time of 57 sec, whereas for CNWs-1, these parameters were 0.44% and 92 sec, respectively. It was determined that CNWs-2 can adsorb more CO_2 molecules in its volume due to the higher density of graphene sheets and defects (free bonds) in the CNWs film. Additionally, the sensitivity of the gas sensors linearly increases with the increase in CO_2 gas concentration. The fabricated gas sensors demonstrated an acceptable level of stability and excellent repeatability and reproducibility. The obtained results demonstrate the applicability of CNWs for CO_2 gas detection and the potential for manufacturing effective and easy-to-manufacture gas sensors using CNWs.

2. Experimental studies of the influence of ionizing radiation of electrons and protons on the properties of CNWs using various modern methods of material characterization have been carried out. CNWs films on quartz substrates were irradiated with 5 MeV electrons and 1.8 MeV protons with accumulated fluence of 7×10^{13} e/cm^2 and 10^{12} p/cm^2, respectively. It was found that depending on the type of irradiation (electron or proton), the morphology and structural properties of CNWs changes. In particular, the wall density decreases and the sp^2 hybridization component increases after electron and proton irradiation, from 66.4% to 68.6% and 70.4%, respectively. The morphological and structural changes, in turn, lead to changes in the electronic, optical, and electrical characteristics of the material, in particular, a change in the work function to 4.76 eV and 4.28 eV, an improvement in the optical transmittance, an increase in the sheet resistance, and a decrease in the specific conductivity of the CNWs films.

A self-adaptive photodiode with a sensitivity of 0.11 A/W and a specific detectivity of 5.2×10^{10} Jones at a wavelength of 730 nm has been developed using CNWs with maze-like morphology, with a height of 200 nm and a thickness of 40 nm synthesized by the ICP-PECVD method and CdZnTe. The CNWs/CdZnTe photodiode structure unexpectedly demonstrated improved responsivity and detectivity after proton irradiation (1.5 MeV, 10^{12} p/cm^2), attributed to enhanced optical transmission. The outstanding stability of the key photodiode parameters (R, D*, and LDR) is achieved due to a unique self-adaptation mechanism of the CNWs/CdZnTe photodiode structure induced by proton radiation, which relies on the synergy of increased responsivity and reduced electrical noise at − 1.5 V. As a result, the proposed self-adaptive CNWs/CdZnTe photodiodes can reliably operate in complex radiation environments, such as space or radioactively contaminated regions.

3. Electrochemical sensors for hydrogen peroxide have been developed, demonstrating a wide linear response range at H_2O_2 concentrations ranging from 1 μM to 250 μM, a low detection limit of 14 μM, and high sensitivity of 679.6 μA mM^{-1} cm^{-2}, using nitrogen-doped CNWs with a height of 640 nm and a thickness of 25 nm synthesized by the RI-PECVD method at a flow rate parameter (N2: 20 cm^3/min). It was found that the intensity ratio of the G and D peaks (I_G/I_D) in CNWs synthesized at a flow rate of 20 cm^3/min is greater than that at 10 cm^3/min, 0.75 and 0.66,

respectively, indicating that CNWs synthesized at a high nitrogen gas flow rate are less defective. It has been observed that the current response of CNWs increases with the increase in nitrogen content. A high content of graphitic N bonds in CNWs promotes the adsorption of H_2O_2 and enhances electron transfer kinetics, leading to an increase in the reduction current.

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

– The sensitivity and response/recovery time of fabricated sensors based on CNWs at CO_2 gas concentrations of 10-500 ppm and device temperatures of 27 °C - 100 °C were investigated. It is shown that the CNWs is able to adsorb more CO_2 molecules in its volume due to its maze-like morphology and defects (free bonds).

– The influence of electron and proton irradiation on morphological, structural, electrical, and optical properties of CNWs has been investigated. It is shown that the use of CNWs as a buffer layer in the CNWs/CdZnTe photodiode structure results in enhanced sensitivity and detectivity following radiation exposure, attributed to the improvement in optical transmittance.

– The influence of nitrogen content on the electrochemical properties of devices based on CNWs for hydrogen peroxide (H_2O_2) detection has been investigated. It is shown that a high content of graphite N bonding in CNWs promotes adsorption of H_2O_2 and enhances the kinetics of electron transfer, which leads to an increase in the reduction current.

Scientific and practical significance of the research

Carbon dioxide gas sensor based on CNWs with maze-like morphology, with a height of 150 nm and a thickness of 28 nm synthesized by the ICP-PECVD method, has been developed.

Self-adaptive photodiode with a sensitivity of 0.11 A/W and a specific detectivity of 5.2×10^{10} Jones at a wavelength of 730 nm has been developed using CNWs with maze-like morphology, with a height of 200 nm and a thickness of 40 nm synthesized by the ICP-PECVD method under proton irradiation with an energy of 1.5 MeV and a total fluence of 10^{12} p/cm^2.

Electrochemical hydrogen peroxide sensors based on nitrogen-doped CNWs synthesized by RI-PECVD method at nitrogen flow rate parameters (N2: 10,15,20 cm^3/min) were developed.

The reliability and validity of the obtained results were confirmed using accurate and modern methods of analysis as well as scientific approach. To ensure reliability and reproducibility, all experiments were conducted in several parallel cases, and their results were confirmed by publications in journals with a high impact factor, publications recommended by the CQAFSHE MSHE RK, as well as scientific conferences of both national and international level, and the filed patent for a utility model of the Republic of Kazakhstan.

Publications.

The research results have been published in 4 articles in high-impact factor journals included in the international databases Web of Knowledge (Web of Science, USA) and Scopus (Elsevier, Netherlands), in 1 article in journals recommended by the Committee for Quality Assurance in the Field of Science and Higher Education of the Ministry of Science and Higher Education of the Republic of Kazakhstan, as well as in the form of 1 utility model patent application in the Republic of Kazakhstan, and in 6 presentations at international scientific conferences.

Approbation of work. The results obtained were reported and discussed at the following international conferences: The 10th International Conference on Nanomaterials and Advanced Energy Storage Systems (INESS-2022) Astana, Kazakhstan, August 4-6, 2022; Third Annual Meeting of Kazakh Physical Society, Kurchatov, Kazakhstan, 07-11, June 2023; International Conference of Students and Young Scientists “Farabi Alemi”, Almaty, Kazakhstan, April 08-11, 2023; 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. Also, experimental results were discussed at weekly scientific seminars of the School of Plasma Physics, 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 PhD, S.A. Orazbayev (Al-Farabi Kazakh National University, Kazakhstan),

PhD, Ye. Yerlanuly (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), prof. V.V. Brus (Nazarbayev University, Kazakhstan) and prof. M.T. Gabdullin (Kazakh-British Technical University, Kazakhstan).

Author's personal contribution. The presented research results, including the development of a carbon dioxide gas sensor based on CNWs, investigation of device sensitivity at various concentrations of CO_2 and device temperatures, study of the influence of electron and proton irradiation on the properties of CNWs, fabrication of a photodiode with stable characteristics, and study of the effect of nitrogen content on the electrochemical properties of CNWs-based devices, were carried out by the author. The formulation of problems and discussion of the obtained experimental results were carried out jointly with scientific advisors. Zhumadilov R. participated in all experimental works, thus making the main contribution to 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: Scientific Committee of the Ministry of Education and Science of the Republic of Kazakhstan AP08856684 "Synthesis of carbon nanowalls in a plasma environment, investigation of their properties, and practical application" 2020-2022; Scientific Committee of the Ministry of Education and Science of the Republic of Kazakhstan AP19676443 "Development of bio-, photo-, and gas-sensitive sensors based on carbon nanowalls" 2023-2025; Scientific Committee of the Ministry of Education and Science of the Republic of Kazakhstan BR21882187 "Development of new nanomaterials and technologies for chemical and electrochemical energy conversion and storage devices" 2023-2025.