ABSTRACT

PhD dissertation submitted for the degree of Doctor of Philosophy (PhD) in the educational program "8D07110 – Materials Science and Technology of New Materials"

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CARBON NANOWALLS AND THEIR HYBRID COMPOSITES AS ELECTROCATALYTIC MATERIALS FOR HYDROGEN ENERGY

General characteristics of the work. This dissertation presents the results of research on carbon nanowalls (CNWs) and their hybrid composites as promising electrocatalytic materials for the hydrogen evolution reaction (HER).

Relevance of the topic. The growth in global energy consumption and the increasing severity of environmental problems necessitate a transition toward low-carbon energy systems. Hydrogen energy is considered one of the promising directions, as hydrogen has a high specific energy, while its utilization in fuel cells produces water as the only by-product. An environmentally friendly method for hydrogen production is the electrochemical splitting of water, the efficiency of which is largely determined by the performance of electrocatalysts. The most active catalysts for the HER are platinum-based materials. However, their high cost and limited natural abundance stimulate the search for affordable alternatives with high catalytic activity and stability.

CNWs are promising platforms for the development of such catalysts due to their high electrical conductivity, chemical stability, and developed surface area. Their three-dimensional morphology provides efficient charge transport and a large number of accessible active sites. Modification of CNWs with transition-metal compounds, particularly WO_3 and sulfur-containing molybdenum compounds, makes it possible to combine the conductive properties of the carbon matrix with the catalytic activity of the functional components. Of particular interest is ammonium thiomolybdate ($(NH_4)_2Mo_3S_{13}$), which contains active Mo-S sites. Its immobilization on nitrogen-doped CNWs may enhance the accessibility of active sites and improve electron-transfer efficiency.

Thus, the development of hybrid composites based on CNWs and transition-metal compounds is a relevant research direction for the fabrication of efficient, stable, and economically viable HER electrocatalysts and for advancing hydrogen energy technologies.

The aim of the dissertation was to investigate CNWs and their hybrid composite structures as efficient electrocatalytic materials for the HER.

The objects of the study are CNWs and their hybrid composites with oxide and sulfide compounds of transition metals, intended for application in electrocatalysis of the HER.

The subject of the study is the morphological, structural, and electrocatalytic properties of CNWs and their hybrid composites modified with oxide and sulfide compounds of transition metals in the HER.

Research objectives:

1. To investigate the influence of substrate type and synthesis time on the morphology, structure, and electrochemical properties of CNWs obtained by the capacitively coupled plasma plasma-enhanced chemical vapor deposition CCP-PECVD method.
2. To fabricate composite electrodes based on CNWs modified with tungsten oxide (WO_3), and to study their electrocatalytic activity in the HER.
3. To synthesize coatings of ammonium thiomolybdate ($(NH_4)_2Mo_3S_{13}$) anchored on nitrogen-doped CNWs, and investigate their catalytic properties and durability.

Research methods. The morphology and microstructure of the samples were investigated using scanning electron microscopy (SEM) and transmission electron microscopy (TEM), while surface topography and roughness parameters were analyzed by atomic force microscopy (AFM). The elemental composition of the materials was determined by energy-dispersive X-ray spectroscopy (EDS), whereas the chemical composition and electronic states of the elements were studied using X-ray photoelectron spectroscopy (XPS). Structural and vibrational properties were examined by Raman spectroscopy, while the crystalline structure and phase composition were analyzed using X-ray diffraction (XRD). The work function was determined by ultraviolet photoelectron spectroscopy (UPS). The electrocatalytic properties of the electrodes toward the hydrogen evolution reaction (HER) were studied in a standard three-electrode electrochemical cell using linear sweep voltammetry, cyclic voltammetry, and electrochemical impedance spectroscopy (EIS).

Key scientific statements submitted for defense:

1. The substrate type and synthesis time in the CCP-PECVD process are determining factors in the formation of the structure and electrochemical properties of CNWs. The transition from dielectric to metallic substrates leads to accelerated growth and increased density of nanowalls, while increasing the synthesis time contributes to a decrease in charge transfer resistance (for Ti: from ~7789 Ω to ~2664 Ω). This behavior is attributed to differences in the thermal conductivity and surface energy of the substrates, which affect the kinetics of gas mixture decomposition as well as the nucleation and growth processes of CNWs.
2. The fabricated Ti/CNWs/WO_3 electrode demonstrates high catalytic activity in the HER, where the conductive three-dimensional CNWs matrix ensures efficient charge transfer, while WO_3 forms catalytically active sites. Furthermore, the CNWs/WO_3 interfacial junction reduces the charge transfer resistance R_{ct} (from ~7839 Ω to ~702 Ω) and increases the electrochemically active surface area (by ~2.5 times), resulting in a reduction of the overpotential to $\eta_{10} \approx 40.9$ mV and an acceleration of the HER kinetics (Tafel slope ≈ 76 mV·dec^{-1}).
3. The Ti/N-CNWs/ATM electrode exhibits high HER activity, with an overpotential of 45 mV and a Tafel slope of 82 mV dec^{-1}. This activity is attributed to the synergistic interaction between molecular Mo-S clusters and the conductive N-CNWs matrix. During HER, $(NH_4)_2Mo_3S_{13}$ undergoes reconstruction into amorphous MoS_x, accompanied by an increase in terminal S^{2-} sites, thereby providing optimal hydrogen adsorption and efficient charge transfer. After 20 h of

operation, 98% of the initial activity is retained.

Main results of the study obtained and established in the course of the dissertation work:

The dissertation presents a comprehensive study of the synthesis, structure, and electrochemical properties of CNWs and hybrid electrocatalytic systems based on them, aimed at improving the efficiency of the HER. The relevance of the study is determined by the need to develop efficient, stable, and cost-effective electrocatalysts capable of replacing noble-metal-based materials.

1. It was demonstrated that CNWs synthesized by the CCP-PECVD method on quartz, SS304, Ta, and Ti substrates exhibit different morphologies and structural characteristics, which are associated with the nature of the substrates. Metallic substrates, particularly Ti, promote more intensive CNW growth, resulting in higher wall density and thickness. It was established that CNW morphology significantly affects their electrochemical properties: Ti/CNWs electrodes demonstrate an increase in cathodic current with increasing deposition time, which is attributed to the formation of an efficient conductive framework and strong interfacial interaction.
2. A Ti/CNWs/WO_3 electrode was developed, in which the CNWs provide a conductive three-dimensional architecture, while WO_3 serves as the catalytic component. XRD and Raman spectroscopy confirmed the formation of the monoclinic WO_3 phase, while XPS analysis demonstrated the predominance of W^{6+}. In 0.5 M H_2SO_4, the electrode exhibited high HER activity, with an overpotential of η_{10} = 40.9 mV and a Tafel slope of 76 mV dec^{-1}. Electrochemical testing and post-operando analysis confirmed low charge-transfer resistance, preservation of the electrode structure, and high long-term durability.
3. An electrocatalyst based on nitrogen-doped CNWs, Ti/N-CNWs/ATM, containing molecular Mo-S clusters, was developed. Aerosol deposition enabled controlled ATM loading and regulation of the density of active sites. The configuration with nine deposition cycles demonstrated the optimal performance. The electrode exhibited an overpotential of 45 mV at 10 mA cm^{-2} and a Tafel slope of 82 mV dec^{-1}. After 20 h of continuous operation, approximately 98% of the initial activity was retained, confirming the high stability of the system.

Thus, it was demonstrated that the use of CNWs as a conductive, high-surface-area framework in combination with oxide and molecular catalytic components is an effective approach for the development of highly active and stable HER electrocatalysts. The developed systems can be fabricated using relatively simple and scalable methods.

Novelty of the work.

– For the first time, a comprehensive study was conducted on the influence of substrate type (dielectric and metallic) and synthesis time in the CCP-PECVD method on the formation of the morphology, degree of graphitization, and electrochemical properties of CNWs.

– A novel composite Ti/CNWs/WO_3 electrode was developed and experimentally validated using a combined CCP-PECVD and magnetron sputtering approach, providing an increase in the electrochemically active surface area, a

reduction in charge transfer resistance, and an acceleration of HER kinetics.

– For the first time, $(NH_4)_2Mo_3S_{13}$ based coatings on nitrogen-doped CNWs (Ti/CNWs/ATM) were fabricated and investigated, demonstrating enhanced activity and long-term stability toward the HER.

Scientific and practical significance of the work.

The results of the dissertation research have fundamental and applied significance for materials science, nanotechnology, and hydrogen energy. The developed methods for functionalizing CNWs with WO_3 and molecular ATM clusters enable the fabrication of efficient electrocatalysts for the HER. The high electrocatalytic activity and stability of the developed materials toward HER confirm their potential as cost-effective alternatives to noble-metal-based catalysts. The technological simplicity of the applied synthesis methods provides the potential for scaling up the production of such electrodes.

Reliability and validity of the obtained results are confirmed by experimental data obtained during the dissertation work. In addition, the reliability of the results is supported by publications in international peer-reviewed journals with high impact factors.

Publications. Based on the results of the dissertation, 3 articles have been published in high-ranking journals indexed in Scopus and Web of Science (2 in Q1 and 1 in Q2), as well as 3 articles in journals recommended by the Committee for Quality Assurance in Science and Higher Education (CQASHE).

Articles published in journals with impact factor indexed in international scientific databases Scopus and Thomson Reuters:

– **Zhumadilov B. Y.**, Zhumadilov R. Y., Nemkayeva R. R., Markhabayeva A. A., Bozheyev F., Ramazanov T. S., Yerlanuly Y., Gabdullin M. T. Influence of Substrate Type and Synthesis Time on Morphological and Structural Properties of Carbon Nanowalls // Advanced Physics Research. – 2025. – 4(12). – e00156.

– **Zhumadilov B. Y.**, Zhumadilov R. Y., Nemkayeva R. R., Markhabayeva A. A., Ramazanov T. S., Yerlanuly Y., Gabdullin M. T. WO_3-modified carbon nanowall electrodes for efficient hydrogen evolution reaction // International Journal of Hydrogen Energy. – 2026. – 223. – 154356.

– Zhumadilov R. Y., Markhabayeva A. A., **Zhumadilov B. Y.**, Nemkayeva R. R., Bozheyev F., Akhtanova G., Xu F., Yerlanuly Y., Gabdullin M. T. Ammonium thiomolybdate ($(NH_4)_2Mo_3S_{13}$) coatings on N-doped carbon nanowalls as optimal and durable electrocatalysts for hydrogen evolution // Chemical Engineering Journal Advances. – 2026. – 101163.

Articles published in journals 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):

– **Zhumadilov B. Y.,** Zhumadilov R. Y., Nemkayeva R. R., Markhabayeva A. A., Gabdullin M. T., Yerlanuly Y. Role of synthesis time in shaping the morphology and structure of carbon nanowalls // Recent Contributions to Physics. – 2024. – 94(3), – P. 80-86.

– Zhumadilov R. Y., **Zhumadilov B. Y.,** Nemkayeva R. R., Kondo H., Markhabayeva A. A, Yerlanuly Y., Gabdullin M. T., Hori. M. In-situ Raman

analysis of carbon nanowalls during electrochemical measurement // Physical Sciences and Technology. – 2025. – 12(1-2), – P. 57-67.

– **Zhumadilov B. Y.** Effect of synthesis duration on the morphology and structure of carbon nanowalls on the surface of carbon paper // Recent Contributions to Physics. – 2026. – 96(1), – P. 39-47.

Approbation of the work. The results obtained in the course of the dissertation research were presented and discussed at seminars, as well as at the 18th International Conference on Plasma-Nano Technology & Science (March 3-7, 2025, Chubu University, Japan).

Author's personal contribution. The synthesis and investigation of the properties of hybrid composites based on CNWs were carried out by the author independently. The formulation of scientific objectives, as well as the analysis and interpretation of the obtained experimental data, were performed in collaboration with the scientific supervisors.

Relation of the research topic to the research plan and state programs. The dissertation work was carried out within the framework of the research project BR28712419 (2025-2027) "Carbon nanowalls: comprehensive study of synthesis, properties, and applications in modern electronic devices".

Structure and Volume of the Dissertation.

The dissertation includes a list of abbreviations and symbols, an introduction, a main body consisting of 4 sections, a conclusion, and a list of references. The total volume of the work is 142 pages, containing 99 figures, 6 formulas, 30 tables, and 213 bibliographic sources.