National Research University Higher School of Economics

as a manuscript

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Obtaining of metal-polymer composites and metal nanowires of various configurations, study of their structure and physicochemical properties

Dissertation summary

for the purpose of obtaining academic degree

Doctor of Philosophy in Engineering

Academic Supervisor:

Honored Scientist of the Russian

Federation, Doctor of Physical and

Mathematical Sciences, Professor

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Moscow - 2024

Relevance of the research topic

Currently, the demand for the creation of various nanomaterials and structures based on them continues unabated. Work in the field of creation, research and application of nanostructures is becoming more and more relevant and in demand, due to the enormous possibilities for their use in various fields of micro- and nanoelectronics, radio electronics, chemical industry, medicine, etc. The wide range of resulting nanostructures provides a variety of possibilities for their application.

One of the types of resulting nanostructures is metal nanowires (NWs). It is expected that metal NWs may have improved electrical properties and mechanical strength under repeated mechanical stress compared to bulk metal materials, making them a promising material for practical flexible/wearable devices. In addition, these objects may be of practical interest from the point of view of improved chemical properties, in particular for use as sensors and catalysts. A distinctive feature of NWs arrays is that they have a developed surface area with a relatively low total amount of material used, which can provide their increased catalytic activity. At the same time, a promising method for producing catalysts from NWs is the use of relatively inexpensive materials (for example, copper, cobalt), compared to the widely used platinum group metals.

Of particular interest from both scientific and applied points of view are hybrid metal-polymer composites, consisting of a polymer matrix with metal nanoparticles embedded in them. This interest is due to the possibility of combining the elasticity properties of a polymer material with the electrical conductivity of a metal nanoobject.

Thus, the described areas of research are quite relevant, and therefore this dissertation is devoted to the development of methods for obtaining effective nano-sized metal structures and metal-polymer composites, experimental identification of the features of their formation, morphology and structure, as well as the influence of various factors on their physicochemical properties and finding technical solutions for implementing improved properties of nano-sized materials and composites based on them in various technical applications for practical use.

Degree of development of the research topic

There are several methods for obtaining nanostructures, for example, electronic and photolithography, epitaxy, etc. [1-4]. Among them, the matrix synthesis method stands out due to its simplicity and variability of the resulting structures. The essence of the method is to fill the pores of the matrix with the necessary material. This method has been described in the literature [4-6], but its capabilities have not yet been fully realized, in particular, when used in such industries as electronics, chemistry, medicine, etc. At the same time, a significant number of works are devoted to obtaining and studying the properties of nanostructures, rather than creating a product based on them.

Basically, porous aluminum oxide (AAO) and track membranes (TM) made of polymeric materials are used as a matrix for synthesis. Polymer TMs are characterized by a chaotic arrangement of pores with the possibility of overlapping each other, which makes it possible to create a conductive chain inside the membrane itself. They are distinguished by their flexibility and the ability to purposefully change the shape and diameter of the pores. In addition, in TM it is possible to vary the pore density over a wide range, regardless of their diameter. A significant difference between TM is the ability to change the angle of pore inclination when irradiated with heavy ions [7]. When using TMs irradiated at a certain, indirect angle, it is possible to increase the number of intersections of grown NWs by increasing the ion irradiation flux density. The number of intersections in the volume of a track membrane can be estimated both by calculation and experimentally [8].

The pores of track membranes can be filled chemically and electrochemically. The electrochemical process is preferred due to its faster filling rate. Metals of the iron group, copper, silver and gold are widely used as materials for deposition.

It becomes possible by changing the structural and dimensional parameters (the geometric dimensions of films and nanowires, the structure of interfaces, etc.) to change the physical and chemical characteristics of the created nanomaterials within a wide range, and therefore obtain the necessary combination of various properties (mechanical, electrophysical, chemical, etc.). There is a real opportunity to change the properties of a material, giving it characteristics that are unattainable for bulk materials. Conical NWs can be used, for example, as electron emitters. The sandwich-type structure can be used as a source of terahertz radiation and flexible skin [9-13].

One of the promising applications is catalysis due to its importance, for example, in the after-treatment of contaminated exhausts or in the chemical industry [14-17]. It is of interest to study the catalytic properties of conical nanowires and sandwich-type nanostructures. Currently, the key catalyst materials for various types of reactions are platinum group metals. The creation of cheap, but not inferior in efficiency, catalysts is an important task for the development of the chemical industry.

Thanks to the development of methods for the synthesis of nanomaterials, it becomes possible to manufacture composite materials based on nanostructures. Among composite conductors, one can distinguish thin-film multilayer conductors [20, 21, 23] and composite conductors with nanoparticles located both on the surface of films [18, 22-24] and integrated into their volume [19, 20].

Thin film multilayer conductors can be used for all types of optoelectronic interface devices, such as touch screens [18, 20, 22, 23], solar cells [20, 23], light emitting devices [18, 20]. These objects can be obtained in various ways, for example, by chemical vapor deposition, vacuum thermal spray, etc.

In our opinion, the most promising methods for producing composite conductors include methods based on the integration of metal nanowires into the bulk of polymer films. Metal nanowires made from materials such as Ag [25], Au [25] and Pt [26] have good electrical properties [27, 28] and increased mechanical strength compared to bulk samples from the corresponding material under conditions of repeated mechanical stress [29, 30], therefore, one-dimensional conducting nanostructures can be considered, for example, as materials for flexible electronic devices and conducting electrodes, as indicated in [24]. The experimental obtaining and study of the physical properties of the “silver NW-polyethylene terephthalate (PET)” structure was one of the objectives of this work.

Purpose and objectives of the study

The purpose of this work is to develop methods for producing nano-sized metal structures of various configurations and metal-polymer composites based on them, to experimentally identify the features of formation, morphology and structure, as well as the influence of various factors on the physico-chemical properties of synthesized nano-sized structures and composites, to find technical solutions for implementation properties of the studied nano-sized materials and composites in various technical applications and development of recommendations for their practical use.

To achieve the set goal, it was necessary to solve the following tasks:

- Development of methods and testing of modes for obtaining NWs of various configurations and sandwich-type structures consisting of NWs located between two layers of metal;
- Identification of features of the morphology and structure of metal nanoparticles of various configurations associated with the methods of their production;
- Development of methods for producing catalysts based on copper and cobalt NWs;
- Experimental acquisition of new scientific data on the catalytic properties of NWs from cobalt and copper, the influence of various factors on them;
- Development of a synthesis method and testing of production modes for metal-polymer composites based on a polymer film (PET, polycarbonate, polyimide) and metal nanowires embedded in it (silver and cobalt);
- Experimental acquisition of new scientific data on the physical properties of the synthesized silver-PET composite and the influence of various factors on them;
- Development of a method for manufacturing a film heating element based on “silver-PET” with an array of intersecting current-carrying nanowires;
- Finding technical solutions for realizing the properties of synthesized NWs and metal-polymer composites in various technical applications and developing recommendations for their practical use.

Scientific novelty of the dissertation work

- Methods for producing nanowires (NWs) of various configurations have been proposed and practically implemented: cylindrical NWs, conical NWs, sandwich-type structures (NWs located between two layers of substrates), modes for obtaining NWs and metallization of the matrix surface have been developed;
- Features of the morphology and structure of metal nanopowders of various configurations related to the methods of their obtaining have been identified;
- New scientific data were obtained on the catalytic properties of copper NWs and the influence of various electrodeposition modes on these properties; in particular, it was found that the use of copper films with copper NWs located on them significantly enhances the catalytic effect in the oxidation of carbon monoxide, with the greatest effect (an increase in the degree of oxidation by 60–70%) being achieved in the case of using cylindrical NWs; it has been shown that the effect is observed at fairly low temperatures of 200–350°;
- A method for manufacturing a catalyst for the oxidation of CO into CO_2 based on copper NWs was proposed and practically implemented; it was shown that the maximum efficiency of CO oxidation into CO_2 is achieved in the temperature range from 300°C to 350°C for nanowires with a diameter of 100 nm; this method is protected by a Russian patent;
- New scientific data on the catalytic properties of cobalt NWs were obtained for the first time; the effect of increasing the catalytic activity of cobalt in the reaction of ethylene hydrogenation was discovered with an increase (tens of times) in the surface area of the cobalt sample by creating an NW array. It has been shown that the use of cobalt NWs as a catalyst makes it possible to carry out the hydrogenation reaction of ethylene at 200°C with a conversion of 20%;
- A new method for the synthesis of metal-polymer composites based on a polymer film (PET, polycarbonate, polyimide) and metal nanowires embedded in it (silver and cobalt) has been proposed and practically implemented;

- New scientific data on the physical properties of the PET-silver nano/micro-wire composite were obtained; the probabilities of intersections of silver nano- and microwires located in PET pores were calculated for a system of intersecting pores; using the calculations and experiments performed, it was established that the mechanical properties of the metal-polymer composite are significantly influenced by the number of mutual intersections of the wires and their diameter; in particular, it has been experimentally shown that by changing the wire diameter from 400 to 600 nm, the ductility of the composite can be doubled. A linear dependence was also obtained linking the difference in electrical potentials with the heating temperature of the composite;
- A method has been developed for manufacturing a film heating element from a polymer material with an array of through intersecting cylindrical channels in which conductive elements - silver NWs - are located; it has been shown that filling the pores of the track matrix membranes with silver makes it possible to raise the heating temperature to 78°C without deformation or damage to the heating element; This heating element is intended for the manufacture of flexible electronics elements; the method of its manufacture is protected by a Russian patent.

Theoretical and practical significance of the work

The results presented in the dissertation work expand the range of knowledge about the patterns of formation, morphology, structural features, as well as the physicochemical properties of one-dimensional nanostructures and metal-polymer composites, make a significant contribution to the understanding of various processes occurring in the studied materials under the influence of various factors - geometric dimensions and TM pore shapes, electrodeposition modes, temperature, oxidizing environment, etc. The method proposed in the dissertation for creating a flexible film heating element based on a composite film of a polymer material with an array of contacting conductive silver NWs inside it can be used in elements of flexible electronics, when creating a heating film for human skin, thermal control of electronic devices, etc. The method proposed in the dissertation to increase the catalytic activity of cobalt in the hydrogenation reaction of ethylene allows the use of cobalt, which is effective for catalysis and relatively cheap (compared to platinum group metals). It is also important and convenient for practical use that the catalytic activity manifests itself at a fairly low temperature - about 200 °C. The thesis also developed a new method for producing a catalyst for the oxidation of CO into CO_2 and substantiated the possibility of using one-dimensional copper nanostructures in the catalytic oxidation of carbon monoxide, which is important for the after-treatment of exhaust gases from internal combustion engines.

The technical solutions found - the creation of methods for producing a film heating element based on a composite film of polymer material with an array of contacting conductive silver NWs inside it and a catalyst based on copper nanowires - were patented, and Russian patents for inventions were received.

Research methods

To obtain arrays of nanowires (NWs), the work used a matrix synthesis method based on galvanic filling of the pores of a pre-obtained matrix. The chosen technique allows one to widely vary both the geometric and structural parameters of the resulting nanoparticles. To obtain the structures, industrial track membranes made of polyethylene terephthalate with a thickness of 12 microns with pores with a diameter of 100 nm and a pore density of 1.2×10^9 cm^{-2}, produced by JINR (Dubna, Russia), were used. The orientation of the pores was up to ±30° along the film rolling direction (vertical) during ion irradiation and ±0.5° perpendicular to the film rolling direction (horizontal). In particular, films with pore diameters of 30, 65, 100, 200, 300, 400, 600 nm were used in the work.

To create a contact surface, copper was sprayed using vacuum thermal spraying onto one of the polymer surfaces using a VUP-4 installation. The copper substrate was deposited onto the contact layer in potentiostatic mode at 0.4 V. A P-2X potentiostat-galvanostat (Elins, Russia) was used as a current source.

Galvanic deposition of silver into membrane pores was carried out in a vertical cell made of polyethylene terephthalate glycol (PET-G) with a working area of 15 cm2. The silver electrolyte with the composition $AgNO_3$ – 0.177 mol/l was used; $K_4[Fe(CN)_6]$ – 0.136 mol/l; K_2CO_3 – 0.289 mol/l; KSCN – 1.029 mol/l, while galvanic deposition was carried out at an electrolyte temperature from 20 to 25 °C, cathodic and anodic current densities from 1 to 10 mA/cm^2.

To obtain a film conductor, it is necessary to remove the auxiliary layer of copper. Selective removal of copper was carried out using a peroxide solution with the addition of $C_6H_8O_7$ – 1.561 mol/l; NaCl – 0.856 mol/l.

Galvanic deposition of copper into membrane pores was carried out using $CuSO_4 \cdot 5H_2O$ electrolyte – 200 g/l; H_2SO_4 – 16 g/l. Deposition was carried out in potentiostatic mode at a potential from 0.2 V to 0.6 V.

Galvanic deposition of cobalt into the membrane pores was carried out using $CoSO_4$ electrolyte – 320 g/l; H_3BO_3 – 40 g/l. Deposition was carried out in potentiostatic mode at a potential of 0.9 V.

The length of the resulting NWs was monitored using a JCM 6000 Plus scanning electron microscope (SEM) (Jeol, Japan) with a built-in energy-dispersive spectroscopy (EDS) attachment. The studies were carried out in the secondary electron mode at an accelerating voltage of 15 kV. It should be noted that for the SEM study, the matrix was removed in a NaOH solution.

X-ray phase analysis and calculation of crystallite size were carried out using an X'pert Pro MPD powder X-ray diffractometer (PANalytical, the Netherlands) at an accelerating voltage of 40 kV at a current of 40 mA with copper radiation (Cu Kα = 1.54 nm). The survey was carried out in Bragg-Brentano geometry. The High Score Plus program was used to interpret the radiographs using the ICSD PDF-4 database.

The mechanical properties of the samples were studied experimentally in the uniaxial tensile mode on a universal testing machine Autograph AGS - 5kN (Shimadzu, Japan) at a tensile speed of 2 mm/min. The data was processed using built-in software.

The study of catalytic properties was carried out by measuring the concentration of ethylene in the gas mixture after the reaction. The installation contains a tubular quartz reactor with a diameter of 6 mm, a gas supply and exhaust system, a gas flow regulator, and a programmable furnace. The composition of the initial gas mixture is $CO(2\%)–O_2(5\%)–He$ in the case of a copper catalyst and $C_2H_4(2\%)–H_2(10\%)–N_2$ in the case of a cobalt catalyst. The flow rate was 20 ml/min. Samples were loaded into the reactor: copper films (flat pieces) with cobalt nanowires measuring 9 × 6 mm. These samples were placed vertically into the reactor tube without deforming the film. The width of the film sample, 6 mm, corresponds to the inner diameter of the tube; therefore, the film was located along the central axis, and the gas mixture flowed around it on both sides. Two control samples were also obtained: a cobalt film with a size of 9 × 6 mm and a copper film (without nanowires) of the same size. After the reaction, part of the gas mixture was selected using a loop for chromatographic analysis on a Khromatek-2000 chromatograph. The samples were heated stepwise in the temperature range 150–300°C. The gas composition was determined 5 minutes after the temperature was established.

Provisions for defense:

- methods for producing copper nanowires (NWs) of various configurations;
- patterns of formation of NWs of various configurations and changes in their morphology and structure depending on the method of their obtaining;
- a new method for the synthesis of metal-polymer composites based on a polymer film (PET, polycarbonate, polyimide) and metal nanowires embedded in it (silver and cobalt);
- a new method for creating a film heating element based on a composite film of polymer material (PET) with an array of contacting conductive silver NWs inside it, intended for use in flexible electronics elements;
- experimental data on the physical properties of the PET-silver nano/micro-wire composite and the influence of various factors on them;
- a new method for producing a catalyst based on cobalt nanowires: experimental data on the catalytic properties of cobalt nanowires and the influence of various factors (sample geometry, temperature) on these properties.

Reliability of the results obtained

The reliability of the results obtained in the dissertation work is due to a fairly good agreement between the data obtained on the basis of experimental studies and numerical calculations. their reproducibility, the use of certified analytical modern research equipment, complementary experimental research methods: scanning electron microscopy, energy dispersive analysis, X-ray phase analysis. Developed technical solutions - the creation of methods for producing metal-polymer composites based on a polymer film (PET, polycarbonate, polyimide) and metal nanowires embedded in it (silver and cobalt), as well as manufacturing a film heating element from these composites with an array of contacting conductive conductors metal NWs and a catalyst based on copper nanowires were patented: Russian Federation patents for the invention were obtained.

Author's personal contribution

The author's personal contribution to the dissertation work is the obtaining of matrices for electrochemical filling; development of modes for filling matrices - creation of nanowires; obtaining samples for research; conducting research using scanning electron microscopy and X-ray phase analysis, participating in the preparation of publications and conducting research on the physicochemical properties of arrays of resulting nanowires, creating methods for producing a number of metal-polymer composites and a film heating element made of polymer material with an array of intersecting conductive metal nanowires inside it, as well as a catalyst based on cobalt nanowires, carrying out the analysis of the results obtained personally (in work without co-authors) or with fellow co-authors; formulation of conclusions on the dissertation work.

Approbation of results

The main results of the dissertation were presented at the following all-Russian and international conferences:

1. International Scientific Youth Forum «Lomonosov-2023». Russian Federation, Moscow, 8-12 April 2019. Development of methods for obtaining an array of cone-shaped nanostructures.
2. XXIX International Conference «Radiation Physics of Solid State». Russian Federation, Sevastopol, 8-13 July 2019. Track matrices for obtaining an array of cone-shaped nanostructures.
3. XXVIII Russian Conference of Electron Microscopy «Modern methods of electron, probe microscopy and complementary methods in the study of nanostructures and nanomaterials». Russian Federation, Chernogolovka, 5-10 September 2020 г. Studies of nanostructures of various geometries using scanning electron microscopy.
4. XXX International Conference «Radiation Physics of Solid State». Russian Federation, Sevastopol, 24-29 August 2020 г. Track membranes in the synthesis of nanowires of various geometries for use in catalysis.
5. XXX International Conference «Radiation Physics of Solid State». Russian Federation, Sevastopol, 24-29 August 2020 г. Features of galvanic filling of track membrane pores to obtain nanowires of various types.
6. International Scientific Youth Forum «Lomonosov -2021». Russian Federation, Moscow, 12-23 April 2021 г. Obtaining of nanowires from cobalt and their magnetic properties.
7. Second International Conference «Physics of Condensed Matter». Russian Federation, Chernogolovka, 31.05-04.06 2021. Film heater with silver nanowires.
8. Second International Conference «Physics of Condensed Matter». Russian Federation, Chernogolovka, 31.05-04.06 2021. Copper nanowires as a catalyst for CO oxidation.
9. Second International Conference «Physics of Condensed Matter». Russian Federation, Chernogolovka, 31.05-04.06 2021. Preparation of nanowires from cobalt with different types of crystal lattices.
10. XXXI International Conference «Radiation Physics of Solid State». Russian Federation, Sevastopol, 2-9 July 2021 г. Preparation of nanowires from cobalt and their magnetic properties.

List of published articles on the topic of the dissertation

The main provisions on the topic of the dissertation are presented in 4 publications indexed in the international Scopus system:

1) Panov D.V. Studying the Mechanical Properties and Structure of the Silver-Polyethylene Terephthalate» Composite / Inorganic Materials: Applied Research 2023.Vol. 14, No. 5, pp.1245-1250.
2) Kozhina E., Panov D., Kovalets N, Apel P., Bedin S. A thin-film polymer heating element with a continuous silver nanowires network embedded inside / Nanotechnology, 2024, Vol. 35, Issue 3, No. 035601, pp.1-8.
3) Panov D. V., Bichkov V. Yu., Tulenin Yu. P., Zagorskiy D. L. Cobalt Nanowires as a Catalyst for Ethylene Hydrogenation / Journal of Surface Investigation: X-ray, Synchrotron and Neutron Techniques, 2023. Vol. 17, No. 6, pp.1496-1501.
4) Panov D. V., Bichkov V. Yu., Tulenin Yu. P., Zagorskiy D. L., Kanevskiy V. M., Volchkov I. S. Copper Nanowires as Catalysts for CO Oxidation. // Journal of Surface Investigation: X-ray, Synchrotron and Neutron Techniques, 2021, Vol. 15, No. 6, pp. 1264–1269. DOI: 10.1134/S1027451021060380

Intellectual property objects

1) Panov D.V., Bychkov V.Yu., Tyulenin Yu.P., Zagorsky D.L., Muslimov A.E. A method for producing a catalyst for CO oxidation based on copper nanowires. Patent for invention No. 2787291, 09.01.2023;
2) Bedin S.A., Kozhina E.P., Panov D.V., Apel P.Yu. A method for manufacturing a film heating element and a film heating element produced by this method. Patent for invention No. 2809786, 18.12.2023.

Conclusion

The dissertation research obtained the following results:

• Using matrix synthesis, methods have been developed for producing copper nanowires of various configurations on a metal substrate - cylindrical nanowires, conical nanowires, sandwich-type structures (nanowires located between two copper layers).

• Features of the morphology and structure of metal nanowires of various configurations related to the methods of their obtaining were revealed;

• New scientific data were obtained on the catalytic properties of copper nanowires and the influence of various electrodeposition modes on these properties; a comparison of NWs of various types was carried out - cylindrical, conical, arrays between two surfaces; It has been established that the use of copper films with copper NWs located on them significantly enhances the catalytic effect in the oxidation of carbon monoxide, with the greatest effect (an increase in the degree of oxidation by 60–70%) being achieved in the case of using cylindrical NWs; It was shown that the effect is observed at fairly low temperatures of 200–350°C.

• A method has been developed for producing a catalyst for the oxidation of CO into CO_2 based on copper NWs, this method is protected by a Russian patent; it was shown that the maximum efficiency of CO oxidation into CO_2 is achieved in the temperature range from 300°C to 350°C for nanowires with a diameter of 100 nm; the possibility of using one-dimensional copper nanostructures in the catalytic oxidation of carbon monoxide, which is important for the post-treatment of exhaust gases of internal combustion engines, has been substantiated.

• New scientific data were obtained on the catalytic properties of cobalt nanowires and the influence of various electrodeposition modes on these properties; The effect of increasing the catalytic activity of cobalt in the reaction of ethylene hydrogenation was experimentally demonstrated. A way to increase activity was to increase (tens of times) the surface area of the cobalt sample by creating an array of NWs; the magnitude of the effect depends on the geometric parameters of the nanowires; the greatest effect was observed for nanowires with a diameter of 100 nm. It has been shown that the use of cobalt NWs as a catalyst makes it possible to carry out the hydrogenation reaction of ethylene at 200°C with a conversion of 20%. The proposed method allows the use of relatively cheap (compared to platinum group metals) cobalt for catalysis; It is also important and convenient for practical use that the catalytic activity manifests itself at a fairly low temperature - about 200°C.

• A new method for the synthesis of metal-polymer composites based on a polymer film (PET, polycarbonate, polyimide) and metal nanowires embedded in it (silver and cobalt) has been proposed and practically implemented; a method has been developed for manufacturing a film heating element from these composites with an array of contacting conductive metal NWs;

• New scientific data on the physical properties of the PET-silver nano/microwire composite were obtained; the probabilities of intersections of silver nano- and microwires located in the pores of TM PET were calculated for a system of intersecting pores; Using the calculations and experiments performed, it was established that, in particular, it was experimentally shown that by changing the wire diameter from 400 to 600 nm, the ductility of the composite can be doubled. The work also obtained a linear dependence relating the difference in electrical potentials with the heating temperature of the composite;

• An experimental study of a film heating element made of PET polymer material with an array of intersecting current-conducting silver nanowires inside it showed that filling the pores of track membranes (TM) with silver makes it possible to raise the heating temperature, measured by electrical characteristics, to 78°C without deformation or damage to the heating element. The manufacturing method of this heating element is protected by a Russian patent;

Recommendations, prospects for further development of the topic

• The metal-polymer composites based on silver-containing NWs obtained in the work and the created composite film flexible heater can be recommended for use in the creation of elements of flexible electronics, as well as for thermal regulation of electronic devices;

• The resulting cobalt and copper NWs can be recommended for use as catalytically active materials in the chemical industry and in the automotive industry for the purification of exhaust gases from internal combustion engines.

• Further research is expected to obtain new scientific data on the emission properties of aluminum and copper nanowires with different geometries, as well as the magnetic properties of cobalt nanostructures. In addition, it is planned to conduct experiments on the introduction of a heating element based on silver-polyethylene terephthalate into electronic devices and instruments.

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