Synthesis and modification of nanofibrous carbon materials and graphite-like materials for functional applications

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Relevance of work. Today, the synthesis of new carbon materials that would have a set of certain characteristics useful for their application is a key area in chemistry and chemical engineering. For example, developed porous structure and electrical conductivity for supercapacitors; high content of surface functional groups and specific surface area for catalysts and sorbents; low level of defectiveness combined with specific surface chemistry for polymer composites, etc. One of the leading places in the scientific literature is occupied by two classes of carbon materials: nanofibrous carbon materials (carbon nanofibers, multi-walled carbon nanotubes, single-walled carbon nanotubes) and graphite-like materials (graphite nanoplatelets, graphite oxide, reduced graphite oxide, and others). If the first class has been studied since the 90s' of last century, the receipt of the Nobel Prize for achievements in the study of graphene in 2010 gave impetus to the study of new graphite-like and graphene-like materials. However, the most acute issue is the application of the results of numerous studies for the large-scale production of these materials for specific requirements of consumers (industrial enterprises). In this case, there are many problems associated with the inability to scale certain methods of synthesis and modification, insufficient information about the optimal parameters of the processes, which prevents their successful implementation in large-scale production. Most of the data published in the modern scientific literature are fragmentary and require generalization and detailed elaboration. For the most part, there is no real information on the parameters of the synthesis and modification of nanofiber carbon materials and graphite-like materials, although manufacturers are trying to gradually increase their production. It is rather difficult to single out the scale of production of the above materials due to incomplete information about the real productivity, but nevertheless the following large companies should be distinguished: OCSIAL (single-walled carbon nanotubes and products based on them); Zeon Co. (single-walled carbon nanotubes); Arkema (multi-walled carbon nanotubes); Carbonics (single wall carbon nanotubes); Sigma Aldrich (graphene oxide); Thomas Swan (graphene nanoplates); XG Sciences (graphene nanoplatelets and graphite nanoplates); First Graphene (graphene nanoplates) and many others. In this regard, studies aimed at creating the highly efficient nanofibrous carbon materials and graphite-like materials, studying the basic relations "synthesis–properties" with the aim of forming the certain textural, morphological, structural characteristics, defectiveness, qualitative and quantitative composition of surface functional groups and achieving the maximum high performance in their practical applications.

The **aim of the work** was to establish the general relations and a number of dependences of the effect of synthesis and modification of nanofibrous carbon materials (carbon nanofibers, multi-walled carbon nanotubes) and graphite-like materials (graphite oxide, reduced graphite oxide, thermally

expanded graphite, graphite nanoplates) on the structure, morphology, chemical composition, textural characteristics, as well as characteristics of materials in promising applications (epoxy composites, supercapacitors, gas sensors).

The following **tasks** have been stated: • To determine the effect of high-energy grinding and heat treatment of carbon nanofibers on their physicochemical characteristics and electrophysical properties of epoxy composites; • To develop the refined ratios for calculating the electrical properties of epoxy composites based on nanofibrous carbon material in a wide range of filler concentrations; • To establish the effect of thermal treatment of MCNTs on the properties of electreted epoxy compositions; • To develop a modified method for the synthesis of graphite oxide, which makes it possible to avoid the use of water in the system and to analyze the role of preliminary holding of graphite in a $NaNO_3$–H_2SO_4 mixture, the ratio of the reagents taken to porosity, degree of oxidation, content of functional groups; • To develop the regression equations "synthesis parameters–properties" linking the parameters of obtaining reduced graphite oxide and its characteristics (yield, bulk density, specific capacity); • To establish the effect of the concentration of nitric acid solutions on the physicochemical characteristics of graphite nanoplatelets and their specific capacity in supercapacitors; • To determine the optimal parameters for the synthesis of MCNTs directly on the Si/SiO_2 substrate to ensure the highest possible performance of ammonia gas sensors operating at room temperature. • To study the regularities of changes in the characteristics of gas sensors of ammonia based on MWCNTs treated in oxygen plasma with subsequent plasma copolymerization of maleic anhydride and C_2H_2; • To develop a gas sensor for the determination of ammonia based on graphite oxide and to determine the relationship between its sensor characteristics and the relative humidity of the air.

Scientific novelty of the work is as follows: • Dependences of the electrical conductivity and dielectric constant of epoxy composites on the frequency of an alternating field in the range of 0.1 - 106 Hz, with the addition of a wide range of carbon nanofiber fillers, differing in different structural, surface and textural characteristics have been established; • Peculiarities of changes in structure, morphology, chemical composition, texture characteristics, defectiveness of graphite nanoplates obtained by dispersing artificial graphite in organic solvents of different polarity have been studied; • For the first time, a number of regression equations describing the influence of the parameters of obtaining reduced graphite oxide by the programmed heating of graphite oxide at relatively low temperatures (250–350°C) on the bulk density, yield, structural and textural characteristics, and the specific capacity of supercapacitors were obtained; • For the first time, the principal possibility of obtaining four different types of graphite oxides in the process of synthesis by the modified Hammers method with C: O ratios (at., according to XPS data) 0.52–2.33 and reduction temperatures 154–188°C was shown only by using different synthesis times; • For the first time, carbon materials of the "core-shell" type for the determination of ammonia in air, which have an extremely high response (22.5%,

27.9% and 31.4% in relation to 100 ppm, 250 ppm and 500 ppm NH3, respectively), were obtained by the method of joint plasma processing.

Practical significance of the work. Based on the experimental studies on the production of epoxy resin/nanofiber carbon materials composites, new approaches to the modification of carbon nanomaterials are proposed to change the frequency dependences of the electrical properties as applied to the areas of shielding of electromagnetic radiation and protection from electrostatic discharge. The regression relationships "synthesis parameters–properties" of thermally reduced graphite materials obtained from graphite oxide have been developed. A modification of the Hummers method is proposed, which makes it possible to obtain graphite oxides with a high content of functional groups. A method for plasma modification of carbon nanomaterials is proposed to increase the sorption characteristics and create highly sensitive ammonia gas sensors operating at room temperature. Based on the results of the work, recommendations were formulated for the technology of obtaining nanofiber carbon materials and graphite-like materials for functional purposes for polymer composites, supercapacitors and gas sensors.

Scientific provisions for the defense:

• Dependences of the electrical conductivity and permittivity of epoxy composites on the frequency of an alternating field in the range of 0.1–10^6 Hz with the addition of a wide range of carbon nanofiber fillers differing in different structural, surface and textural characteristics;

• Ultrasonic dispersion of artificial graphite in organic solvents of different polarity leads to significant changes in the structure, morphology, chemical composition, texture characteristics and defectiveness of graphite nanoplatelets;

• A number of regression equations describing the influence of the parameters of obtaining reduced graphite oxide by the programmed heating of graphite oxide at comparatively low temperatures (250–350°C) on the bulk density, yield, structural and textural characteristics, and the specific capacity of supercapacitors were obtained;

• When using the modified Hammers method, the beginning of the formation of graphite oxide in the synthesis time range of 10-60 min is shown;

• The fundamental possibility of obtaining four different types of graphite oxides in the process of synthesis by the modified Hammers method with C: O ratios (at., According to XPS data) 0.52–2.33 and reduction temperatures 154–188°C was shown only through the use of different durations;

• Obtained active carbon materials "core-shell" for the determination of ammonia in the gas phase, with an extremely high response (22.5%, 27.9% and 31.4% in relation to 100 ppm, 250 ppm and 500 ppm NH_3, respectively).