ABSTRACT
of dissertation for the Philosophy Doctor (PhD) degree on «6D071000 – Materials science and technology of new materials» specialty

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Researching the properties of functionalized few-layer graphene nanostructures

The general characteristics of the study

From the general point of view, this work studied the properties of functionalized few-layer graphene nanostructures.

The first section was devoted to literature review of graphene, functionalized few-layer graphene nanostructures (FFLGN), methods for the synthesis of graphene, FFLGN, FFLGN membrane, reduction of FFLGN, basics of computer simulation, classification of computer simulation methods, computer simulation of FFLGN, Ga-doped graphene, application of FFLGN membrane as a humidity sensor and comparison of the its performance.

The second section of the thesis was presented to the main research methods in the study of FFLGN. The main characteristics of the used research instruments are considered. In the process of research, the following methods were used: SEM and EDS; Raman spectroscopy; AFM; TGA; XRD; Optical microscope; Spectrophotometer Lambda 35.

The third section present results of computer simulation of some possible stable structures of graphene and few-layer graphene, functionalized Ga, FFLGN, reduced FFLGN; synthesis of FFLGN, preparation of FFLGN films and FFLGN membranes, thermal reduction of FFLGN films and membranes at various temperatures and investigation of their optical, electrical properties, creation of a humidity sensor based on FFLGN membrane. The most detailed results are presented on the influence of temperature on the composition and structure of the FFLGN membrane, as well as the changes in the thickness of the FFLGN films and membranes, also changes in the interplanar distance, intensities and the ratio of the Raman spectroscopy bands of the membrane after thermal reduction. In addition, the results of the electro-physical characteristics of the humidity sensor based on the FFLGN membrane and performance comparison with other similar sensors are presented.

The relevance of the study

As is known, graphene is a two-dimensional hexagonal structure of carbon atoms, connected by the sp^2 electron configuration. Graphene, functionalized graphene, and its related structures remain to this day an object of increased interest in various fields of science and technology due to its unique mechanical, electrical and optical characteristics. In addition, graphene and its related structures are considered as promising materials in the production of various gas sensors, humidity sensors, electronic devices, electrical sources, in particular, lithium-ion batteries, which can be used in various fields of production, such as nanoelectronics, aviation, military technology, and medicine.

One of the main directions of graphene related research is the study of its modifications, for example, GO, which may be referred to functionalized few-layer graphene (FFLGN). Graphene oxide (FFLGN) is an oxide form of graphene, which is an atomic-thin sheet-like material dispersed in water, which has numerous oxygen-containing groups, where oxygen is introduced into graphene by chemical oxidation.

Functionalization of graphene can be carried out by various methods, in particular, the creation of radiation defects, hydrogenation, oxidation, etc. During the functionalization with strong acids such as H_2SO_4, HNO_3, $KMnO_4$, bulk graphite will have hydroxyl and epoxy groups on their plane, as well as carbonyl and carboxyl groups at the edges. As a result, the functionalized graphene becomes a semiconductor, unlike graphene, therefore its field of practical application will expand significantly. In this regard, functionalized graphene is a relevant material and has a wide range of applications in semiconductor electronics for creating biosensors, supercapacitors, various gas sensors, humidity sensors, organic electrodes, LEDs, etc.

On the other hand, the most urgent task is to reduce such sheets of functionalized graphene by removing oxygen-containing groups. Reduced sheets of functionalized graphene are usually considered as one of the types of chemically produced graphene and have a number of other names such as functionalized few-layer graphene (FFLGN), chemically modified graphene, transformed graphene, or reduced GO.

The most attractive property of FFLGN is the change in its electrical and optical characteristics, which is realized by removing functional oxygen-containing groups using thermal reduction of FFLGN films and membranes in air and hydrogen atmosphere at optimum temperature conditions. Also, thermal reduction contributes to the production of graphene and graphene-like materials in a large-scale quantity, which is still an actual problem and to this day researchers are trying to achieve a large-scale and more affordable production technology.

The past few years demonstrate an increase in attention to the functionalization of graphene using radiation methods, for example, the formation of radiation defects and doping them with atoms of various elements such as Ga, As, N, B, S.

The resulting functionalized graphene nanostructures are promising for use in nanoelectronics, supersensitive sensors, electrical power sources, flexible electronic and power devices. However, by the moment the stable atomic configurations of graphene, functionalized with individual atoms of different elements not well understood and not clear determined the way of their production in graphene nanostructures and of obtaining the required characteristics. In some cases, solving these issues is a difficult task for experimental research and correct interpretation of data; therefore, computer modeling becomes a very effective research tool for better understanding the physical and chemical properties of functionalized graphene nanostructures and predicting their characteristics. In this regard, the presentation of the results of computer simulation of some possible stable structures of Ga-doped graphene, and few-layer graphene, as well as the study of the basic principles of their energy and structural characteristics are one of the issues of this dissertation work.

One of the important tasks of this work is the creation of a sensitive humidity sensor based on the FFLGN membrane due to its absorption properties and the study of its electrophysical characteristics, which are the great importance in measuring and controlling the humidity of the environment for industrial, agricultural and human activities. Compared to existing present-day sensors, our humidity sensor has a wide operating range of humidity measurements, the equal response and recovery times, as well as stability at various levels of surrounding humidity, and it also has the most important properties, such as low cost, not requiring high technology and stability of works in an aggressive environment.

Thus, the development of technology for producing FFLGN, films and membranes based on them, the study of the optical, electrical properties of FFLGN films with optimal thermal annealing, the study of the influence of temperature on the structure and composition of the FFLGN membrane after thermal reduction, and the use of the FFLGN membrane as a humidity sensor are an actual task in the field of materials science.

The purposes of the thesis

Synthesis and computer simulation of FFLGN, obtaining of FFLGN films and membranes and investigation of their physicochemical properties after thermal reduction at various temperatures.

The tasks of the thesis:

1. Creation of computer models of FFLGN, some possible stable structures of graphene and few-layer graphene, functionalized by Ga atoms, various bonding types between graphene and oxygen and calculation of their binding energy and structural characteristics;
2. Synthesis of the FFLGN and obtaining FFLGN films and thermal reduction of these films in the air at temperatures: 80 °C, 120 °C, 160 °C, 200 °C, 240 °C, 280 °C and investigation of the optical and electrical properties of FFLGN films after thermal reduction;
3. Preparation of the FFLGN membrane and thermal reduction in a hydrogen atmosphere at temperatures: 150 °C, 300 °C, 500 °C, 900 °C and investigation of temperature influence on the structure and composition of these samples;
4. Creation of a humidity sensor based on the FFLGN membrane and the study of its electrophysical characteristics.

Objectives of the thesis

Functionalized few-layer graphene nanostructures obtained by a modified Hammers method.

Subject of the research

Structure and properties of functionalized few-layer graphene nanostructures.

Methodological framework of the research

Quantum-mechanical methods; technology of obtaining FFLGN; separation of solids from liquid in a centrifuge; obtaining separate layers of material using exposure to ultrasound; obtaining free-standing films using vacuum-assisted filtration; analytical methods: SEM and EDS, Raman spectroscopy, TGA, XRD, optical microscopy, ultraviolet and visible spectroscopy.

The scientific novelty of the thesis

1. For the first time, typical configurations of graphene doped by Ga and various arrangements of their atoms, types of oxygen bonds with graphene and the binding energies of the functionalizing C-O and C-O-H groups, the model of the possible reduction process of FFLGN were calculated.

2. The simultaneous analysis of elemental composition and electrophysical characteristics of the synthesized samples demonstrates that residual impurities in the solution of FFLGN, obtained by acid exfoliation, have a critical negative effect on the properties and reduction process of FFLGN.

3. The features of the relationship between the interplanar distances in FFLGN and their dynamics during thermal reduction, with the thickness of the films, with the thermograviometric parameters of the films and their electrical and optical properties are investigated.

4. A simple and low-cost method was developed for creating of humidity sensor based on FFLGN membrane, operating in a wide range of relative humidity (5-100%), with a symmetric signal response and recovery time, with high stability (+/-2%).

The scientific and practical significance of the study

1. Computer simulation of possible stable structures of FFLGN has been created, which can be used to better understanding the unforeseen physical and chemical properties of FFLGN. A technology has been optimtized for the production of films and membranes of FFLGN;

2. The possibility of changing the electrical and optical properties of FFLGN films by removal functional oxygen-containing groups at various temperatures of thermal reduction in air and hydrogen is shown. Thermally reduced thin films FFLGN can potentially be used in optoelectronics and as a conductive coating for a wide range of uses;

3. Thermally reduced FFLGN membranes have a developed surface, which allows them to be considered as promising materials in the manufacture of electronic devices, electrical sources, and also in gas sensors;

4. Obtaining free-standing FFLGN membranes by the vacuum filtration method enables to use it as a sensitive humidity sensor. Experimentally demonstrated dependences of the sensor's electrophysical characteristics (resistance, capacitance) on the relative humidity in a wide range. The same response and recovery times, as well as stability at various levels of relative humidity.

The main provisions for the defense of the thesis

1. On the basis of computer simulation of the configuration of graphene nanostructures with functional groups -O and -OH, the length and energies of chemical bonds are calculated using the density functional theory (DFT) taking into account the surface (C – O = 1.45 Å) and edge (C – O = 1.2 Å) carbon atoms, and also to establish the energetically favorable position of the Ga atom between the graphene layers.

2. The interplanar distance of functionalized graphene nanostructures can be efficiently controlled from 1.07 to 0.37 nm while preserving the highly oriented structure by thermal reduction in a hydrogen atmosphere in the temperature range from 150 to 900 ^{O}C.

3. A low sheet resistivity value of thermally reduced graphene from few-layered functionalized graphene is achieved by purifying the residual impurity chlorine atoms (Cl) and sulfur (S) with a concentration not exceeding 0.5 at.%.

4. Functionalized graphene nanostructures with a low concentration of residual chlorine (Cl) and sulfur (S) impurities are a sensitive material for sorption of water molecules and allow recording relative humidity with a symmetric time response in a wide range (from 5-100%).

Experimental and theoretical methods.

The composition and structure of FFLGN were studied by SEM and EDS, Raman spectroscopy, TGA, X-ray diffraction(XRD), ultraviolet and visible (UV-Vis) spectroscopy, AFM.

The personal contribution of the author

The author participated in the process of density functional theory (DFT) calculations within Dmol3 software-package using the software tools of Chem Office Materials Studio for creating computer models of FFLGN. He has worked out technology for producing FFLGN using the modified Hammers method and FFLGN films, and membranes using the vacuum filtration method. FFLGN films were thermally reduced in air and their optical and electrical properties were investigated, and the effects of temperature on the structure and composition of the FFLGN membrane after thermal reduction in a hydrogen atmosphere at different temperatures were studied. The TGA of FFLGN was performed and the optimal modes of heat treatment of films and membranes of FFLGN were determined at which the functional oxygen-containing groups were removed, as a result of which the optical and electrical characteristics changed. A humidity sensor based on an FFLGN membrane was created, and its electrophysical characteristics were studied.

Publications

Based on the materials of the thesis 9 articles were published, including 4 articles published in journals recommended by the Committee for Control in the fileld of Education and Science of the Ministry of Education and science of the Republic of Kazakhstan. Two articles were published in journals with impact factor

Sensors & Transducers, 2019 (IF 0.3); Journal of Computational and Theoretical Nanoscience, 2019 (IF 0.45) and 3 abstracts are published in national and international conferences. All of these publications were made during the Ph.D. program.

Relation of the dissertation topic with the plans of scientific works

This dissertational work was carried out in the framework of the scientific project named “Development of technology in creation of protective coatings based on functionalized graphene nanostructures and investigation of their properties”, funded under the financing grant of project, № AP05130413 of the Science Committee of the Ministry of Education and Science of the Republic of Kazakhstan.

Volume and structure of the thesis

The thesis work contains a list of symbols and abbreviations, an introduction, the main part of 3 sections, a conclusion and a list of references. The work is presented on 100 pages, contains 52 Figures, 5 tables and 206 bibliographical references.