REVIEW
of official reviewer for a doctoral thesis of
Kuanyshbekov Tilek Kuanyshbekuly
on the topic «Researching the properties of functionalized few-layer graphene nanostructures», submitted for the degree of Doctoral of Philosophy (PhD) in specialty 6D071000 – «Materials science and technology of new materials»

1. The relevance of the topic and its connection with general scientific and national programs (the requirements of practice and the development of science and technology).

One of the main directions in the study of graphene is the study of its modifications, for example, GO, which may be referred to as 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.

Thesis work of Kuanyshbekov T.K. on the topic "Researching the properties of functionalized few-layer graphene nanostructures" is devoted to the synthesis and computer simulation of FFLGN, obtaining of FFLGN films and membranes and investigation of their physicochemical properties after thermal reduction at various temperatures as well as the creation of a humidity sensor based on a FFLGN membrane, and the study of its electrophysical characteristics.

The first section 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 its performance.

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

The third section presented the 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 to 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.

In conclusion, the main results obtained in the dissertation work are formulated.

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.

2. Scientific results in the framework of the requirements for dissertations (paragraphs 2, 5, 6 of the "Rules for the award of scientific degrees")

In the thesis of Kuanyshbekov T.K. the following scientific results were obtained:

1. Computer simulations of some possible stable structures of graphene and few-layer graphene functionalized by Ga, FFLGN, reduced FFLGN and calculating their energy and structural characteristics were performed;

2. The technology of obtaining FFLGN and the FFLGN membrane using the modified Hammers method was optimized, which leads to the large-scale production of graphene and also several filtration and washing with a 5% HCl solution using a centrifuge contributes to obtaining a pure FFLGN solution;

3. The process of temperature influence on FFLGN films led to a decrease in sheet resistance from 5 to 2.5 MΩ/square at temperatures of 200 °C - 280 °C and sheet resistance of the pure FFLGN at 280 °C is more than 5 times lower than the sheet resistance of the impure FFLGN and is equal to 13 MΩ/square, and percentage of transmission decreases approximately by 30 % from initial position, also according the AFM results average thickness decreased by 50 % from the initial sample thickness at 280 °C, which is explained by the removal of unstable and stable oxygen-containing groups and partial combustion of the carbon skeleton;

4. Determined that, in the temperature reduction process of FFLGN with increasing annealing temperature occurs a loss of mass and the removal of chemical functional groups and as a result of which TGA showed that the main mass loses are at temperatures of 150-300 °C, and at temperatures of 300-900 °C, the allotment of functional groups are much weaker due decomposition of unstable

and stable oxygen-containing functional groups. The elemental analysis by the EDS method demonstrates a changing in the C/O ratio from 4.18 to 45.08;

5. It was experimentally shown that heat treatment of the FFLGN membrane influence to the decreasing the interplanar distance between the layers from 1,07 to 0,37 nm and the thickness by ~37% (from 22 to 14 μm). The elemental analysis confirmed the decrease in the amount of oxygen, and TGA revealed the removal of unstable and stable oxygen-containing functional groups.

6. A simple and low-cost method was developed for creating of a humidity sensor based on FFLGN membrane, operating in a wide range of relative humidity (5-100%), with a symmetric signal response and recovery time (360 seconds), with high stability (+/- 2%).

3. Degree of validity and reliability of each scientific result (scientific provision) and conclusion of the applicant, formulated in the thesis.

The validity and reliability of scientific results are confirmed by a large amount of own research performed using a complex of physicochemical methods of analysis, the logical interrelation of the experimental results obtained and their consistency with generally accepted scientific principles.

In the studies, the author uses Quantum-mechanical methods of molecular dynamics and density functional theory (DFT) calculations within Dmol3 software-package using the software tools of Chem Office Materials Studio for creating computer models of FFLGN; technology for producing graphene nanostructures using chemical vapor deposition; 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 (UV-Vis) absorption spectroscopy).

The reliability of the results to be defended is confirmed by publications in journals recommended by the Committee for Control in Education and Science of the Ministry of Education and science of the Republic of Kazakhstan and foreign peer-reviewed journals with impact factor which is included in the Web of Science and Scopus databases. The main scientific results were presented in a number of international and foreign conferences.

4. The degree of novelty of each scientific result (scientific provision), conclusions of the applicant, formulated in the thesis.

The results of theoretical and experimental research presented in the dissertation are new.

1. On the basis of computer simulation of graphene nanostructures configuration with functional groups -O and -OH, the length and energies of chemical bonds are calculated using the density functional theory (DFT) considering the surface (C – O = 1.45 Å) and edge (C – O = 1.2 Å) of carbon atoms, and also to determine 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 with retention of 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-layer functionalized graphene is achieved by purifying the residual impurity chlorine atoms (Cl) and sulfur (S) at a concentration not exceeding 0.5 at.%.

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

5. The practical and theoretical significance of the obtained results.

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 optimized 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 of FFLGN can be potentially used in optoelectronics and as a conductive coating for a wide range of applications;

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 enable to use it as a humidity sensitive sensor. Dependences of the sensor's electrophysical characteristics (resistance, capacitance) on the relative humidity in a wide range were experimentally demonstrated. The results of study demonstrated the same response and recovery times, as well as stability at various levels of relative humidity.

6. Confirmation of sufficient completeness of publications of the main provisions, results and the conclusion of the dissertation

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 field 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.

7. Remarks, suggestions on the content and design of the dissertation.

The thesis is well written and documented. But there are typing errors in some words. The figures, schemes, and tables are shown properly as well. The conclusions confirm that the formed objective of the work was successfully finished.

However, there are some remarks which need to be explained in details.

- The work does not indicate what was the FFLGN deposited on to form a membrane by the method vacuum filtration?
- The work does not describe in detail the installation with which the humidity was created to measure the moisture sensitivity of the sensor.
- Author left the non-informative region on the TGA figures in section 3.2.6.

8. Compliance of the dissertation with the requirements of section 2 of the "Rules for the award of scientific degrees".

The above comments are not of fundamental importance and do not reduce the scientific significance of the work. Thesis of Kuanyshbekov T.K. on the topic "Researching the properties of functionalized few-layer graphene nanostructures" represents a complete research work and in its relevance, scientific novelty, importance for theory and practice, the volume of experimental studies, the passport of specified specialty fully meets the requirements of the "Rules for the award of scientific degrees" to dissertations.

The combination of new scientifically based theoretical and experimental results is an important achievement in the development of materials science and technology of new materials.

Based on the above, I believe that the applicant, Kuanyshbekov T.K., deserves to be awarded the degree of Doctor of Philosophy in the specialty 6D071000 – «Materials science and technology of new materials».

Official reviewer
Candidate of physical-mathematical
Sciences, Head lab Applied and
Theoretical materials science of the
Institute of Nuclear Physics _____ Kislitsin S.B.

Scientific Secretary of the
Institute of Nuclear Physics _____ Koztaeva U.P.