NANOPARTÍCULAS DE METAIS NOBRES NA SUPERFÍCIE DE FLOCOS DE GRAFENO

NANOPARTICLES OF NOBLE METALS ON THE SURFACE OF GRAPHENE FLAKES

НАНОЧАСТИЦЫ БЛАГОРОДНЫХ МЕТАЛЛОВ НА ПОВЕРХНОСТИ ЧЕШУЕК ГРАФЕНА

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RESUMO

O carbono é um elemento comum que possui muitas combinações diferentes de reações. A preparação de novos materiais compósitos à base de nanopartículas é um tema muito urgente e promissor, uma vez que as nanopartículas possuem propriedades únicas. Essas propriedades são mantidas e até mesmo aumentadas quando as nanopartículas estão localizadas em matrizes diferentes. Além disso, atualmente a criação de compósitos à base de grafeno e estruturas a partir dele é uma direção promissora na síntese de nanomateriais compósitos. Pesquisas anteriores mostraram que o grafeno tem um conjunto único de propriedades eletrofísicas, térmicas, ópticas e mecânicas. O objetivo principal deste trabalho é a síntese de nanocompósitos, que são nanopartículas de metais nobres (Au, Pd, Rh) na superfície de flocos de grafeno; estudo da sua composição, estrutura, propriedades físico-químicas e possíveis aplicações em catálise. Neste trabalho, foi realizada a síntese de nanocompósitos, que são nanopartículas de metais nobres (Au, Pd, Rh) na superfície de flocos de grafeno, bem como o estudo de sua composição, estrutura, propriedades físicas e químicas e possíveis aplicações em catálise. Um método para imobilizar nanopartículas na superfície de óxido de grafeno e grafeno foi desenvolvido e foi criado um método original para a síntese de nanopartículas nanocompósitos de metais nobres na superfície de flocos de grafeno usando isopropanol supercrítico como um agente redutor para a conversão de óxido de grafeno em grafeno. Os resultados do estudo das propriedades físico-químicas dos nanocompósitos obtidos e os resultados do estudo dos nanocompósitos obtidos como catalisadores para modelos de reações orgânicas de acoplamento cruzado e hidroformilação têm mostrado a possibilidade de criar nanoestruturas à base de grafeno como nanomateriais funcionais eficazes. Os trabalhos dedicados à síntese de compostos de grafeno e no estudo de suas propriedades físicas únicas formam uma das áreas promissoras da química e física de novos materiais funcionais inorgânicos. Os nanocompósitos resultantes podem ser usados em aplicações como eletrodos para LEDs e células solares, transistores de efeito de campo, supercapacitores, sensores, células de combustível.

Palavras-chave: grafeno, óxido de grafeno, nanopartículas, metais nobres, nanocompósitos.

ABSTRACT

Carbon is a spread element that has many different reaction combinations. Obtaining new composite materials based on nanoparticles is a very actual and perspective topic because nanoparticles possess unique properties. These properties are retained and even amplified when nanoparticles are located in various matrixes. Furthermore, nowadays, the creation of graphene-based composites and graphene-related structures is a promising area of synthesis of composite nanomaterials. Previous research has determined that graphene has a unique set of electrophysical, thermal, optical, and mechanical properties. In this study, the synthesis of nanocomposites representing nanoparticles of noble metals (Au, Pd, Rh) on the surface of graphene flakes

were carried out, and the study of their composition, structure, physical and chemical properties, and possible applications in catalysis. The immobilization of nanoparticles on the surface of graphene oxide and graphene was developed, and the original method of synthesis of nanocomposite noble metal nanoparticles on the graphene flakes surface using supercritical isopropanol as a reduction agent for the transformation of graphene oxide into graphene was created. The study of physical and chemical properties of the obtained nanocomposites and results of the study of obtained nanocomposites as catalysts for model organic reactions of cross-coupling and hydroformylation showed that it is possible to create the graphene-based nanostructures as effective functional nanomaterials. Research on the synthesis of graphene compounds and its unique physical properties form a promising direction in the chemistry and physics of new inorganic functional materials. The resulting nanocomposites can be used in such branches as electrodes for LEDs and solar cells, field-effect transistors, supercapacitors, sensors, fuel cells.

Keywords: *graphene, graphene oxide, nanoparticles, noble metals, nanocomposites.*

АННОТАЦИЯ

Углерод – распространенный элемент, который имеет множество различных комбинаций реакций. Получение новых композиционных материалов на основе наночастиц является очень актуальной и перспективной темой, поскольку наночастицы обладают уникальными свойствами. Эти свойства сохраняются и даже усиливаются, когда наночастицы расположены в различных матрицах. Кроме того, в настоящее время создание композитов на основе графена и структур на его основе является перспективным направлением синтеза композитных наноматериалов. Предыдущие исследования показали, что графен обладает уникальным набором электрофизических, тепловых, оптических и механических свойств. Основная цель данной работы – синтез нанокомпозитов, представляющих собой наночастицы благородных металлов (Au, Pd, Rh) на поверхности чешуек графена; изучение их состава, структуры, физико-химических свойств и возможных применений в катализе. В данной работе был проведен синтез нанокомпозитов, представляющих собой наночастицы благородных металлов (Au, Pd, Rh) на поверхности чешуек графена, а также изучение их состава, структуры, физических и химических свойств и возможных применений в катализе. Разработан метод иммобилизации наночастиц на поверхности оксида графена и графена и создан оригинальный метод синтеза нанокомпозитных наночастиц благородных металлов на поверхности чешуек графена с использованием сверхкритического изопропанола в качестве восстановителя для превращения оксида графена в графен. Результаты исследования физико-химических свойств полученных нанокомпозитов и результаты исследования полученных нанокомпозитов в качестве катализаторов модельных органических реакций кросс-сочетания и гидроформилирования показали возможность создания наноструктур на основе графена как эффективных функциональных наноматериалов. Работы по синтезу соединений графена и исследованию его уникальных физических свойств образуют одно из перспективных направлений химии и физики новых неорганических функциональных материалов. Полученные нанокомпозиты могут быть использованы в таких областях применения, как электроды для светодиодов и солнечных батарей, полевые транзисторы, суперконденсаторы, сенсоры, топливные элементы.

Ключевые слова: *графен, оксид графена, наночастицы, благородные металлы, нанокомпозиты*

1. INTRODUCTION:

A topical research topic is producing new composite materials based on nanoparticles (Bulychev, 2019; Bulychev and Ivanov, 2019; Kirichenko *et al.*, 2019; Wani *et al.*, 2020). These properties are retained and even amplified when nanoparticles are located in various matrixes (Kretinin *et al.*, 2014; Erokhin *et al.*, 2018; Bulychev *et al.*, 2019). The creation of graphene-based composites and graphene-related structures is a promising area of synthesis of composite nanomaterials. Graphene is a unique two-dimensional material; the thickness of graphene is only one sp^2 - carbon atom. Despite

this, graphene has a wide range of unusual peculiar properties. Besides, there are substances similar to graphene structures such as fullerenes, nanotubes, nanographite, graphene oxide, and modified graphene (Tan *et al.*, 2013; Xu *et al.*, 2013).

Graphene has high mechanical, thermal, and chemical resistance. It is a simple element with one carbon atom tightly packed into a crystal lattice of a cellular structure. Graphene nanoribbons (GNRs) and nanoflakes (GNFs) that are finite in both dimensions can be considered as fragments or molecular subunits of graphene. Since their initial successful fabrication, GNRs and GNFs have rapidly reduced from the

microscale down to nanometer sizes either by top-down or bottom-up approaches. Based on size and shape, GNFs can form ordered columnar mesophases. It is important to understand the properties of HNF and its saturated analogs, polycyclic aromatic hydrocarbons (PAHs), since the main functional components of future electronic and spiroelectronic devices should be nanoscale.

Graphite and graphene are uninterrupted semiconductors. Large deviations in energy can occur when the size of the carbon particles is reduced to a level where the quantum effect becomes noticeable. For clusters with a small number of carbon atoms, the energy gaps are approximately 8.5 eV, and for carbon frameworks consisting of 80 carbon atoms, gaps below 2 eV have been found. Research on sized carbon particles will make them interesting candidates for nanotechnology applications (Neri *et al.*, 2019).

Nanoparticles of noble metals (Au, Pd, Rh) existing both in the dispersions and surrounded by various matrixes are among the most studied classes of nano-objects. Nanoparticles of noble metals have outstanding optical and catalytic properties. Gold nanoparticles act as a uniform model objects for studying various properties of noble metals nanoparticles (Heinsalu *et al.*, 2019). The palladium black or colloidal palladium is known for a long time, but the structure and properties of the palladium particles have been studied only recently. Furthermore, palladium and rhodium are catalytically active metals (Jastrzebska *et al.*, 2017). So, palladium and rhodium nanoparticles are promising candidates for application as catalysts in various organic reactions to synthesize new substances. Materials based on graphene with noble metals nanoparticles attached to its surface can find their application in catalysis, manufacturing of fuel cells, chemical sensors, and other applications (Duan *et al.*, 2015; Zhang *et al.*, 2015; Ioni *et al.*, 2016). The main objective of this work was the synthesis of nanocomposites representing nanoparticles of noble metals (Au, Pd, Rh) on the surface of graphene flakes; study of their composition, structure, physical and chemical properties, and possible applications in catalysis.

2. MATERIALS AND METHODS:

Graphene oxide used in this work was obtained by the modified Hammer's method (Ioni *et al.*, 2016). Synthesis of graphene was carried

out by the original method of reduction of graphene oxide by supercritical isopropanol (SCI) (Figure 1). The developed method for obtaining graphene by reducing supercritical isopropanol is distinguished by the reproducibility of results and manufacturability (it uses off-the-shelf equipment). Isopropanol in the supercritical state can reduce oxygen-containing functional groups on graphene oxide surface, leading to graphene production in gram quantities. The method does not use explosive and toxic reagents. Obtaining graphene in appreciable quantities made it possible to start creating composites based on graphene with high mechanical properties. Obtained graphene oxide and graphene have been characterized by physical and chemical methods of analysis (elemental analysis, XRD, TEM, IR- and Raman spectroscopy). Elemental analysis of the samples was carried out on a EA1108 C/H/N analyzer by CarloEbraInstruments (Italy). A sample weighing up to 1 mg was burned automatically in the reaction tube of the analyzer at $T = 980\text{ }^{\circ}\text{C}$ with a pulsed oxygen supply. A complete analysis of combustion products was carried out using a thermal conductivity detector with processing of the obtained chromatographic data on a computer. The phase composition of the samples was determined by X-ray phase analysis on a Bruker D8 Advance spectrometer operating in the reflection mode on $\text{CuK}\alpha$ radiation (35 kV, 30 mA, $\lambda = 1.54056\text{ \AA}$) with a scanning step of 4 deg/min^{-1} .

Raman spectra of graphene and graphene oxide samples were recorded on a RenishawInVia Raman spectrometer. The laser wavelength was 514 nm (Ar, 20 mW), the power was varied in the range 0.00005–100% using ND filters. The study of the samples was carried out at room temperature in air in the backscattering geometry using a Leica DMLM confocal microscope (100' objective), focal length 250 mm, the laser beam size was changed from 1 to 300 μm .

Nanocomposites based on graphene oxide with noble metal nanoparticles on its surface were reduced using supercritical isopropanol. According to the original method, the powder of nanocomposite NM NPs/GO (100 mg) was dispersed in isopropanol by ultrasound and was placed in a quartz container at the autoclave and kept at $\sim 300\text{ }^{\circ}\text{C}$ for 24 hours. Ultrasonic treatment was carried out using a 500 W generator and a 20.4 kHz transducer. Ultrasonic exposure parameters: specific power - 0.1–1 W/cm^3 , exposure time - 20 min until a stable dispersion of graphene oxide is obtained ($\text{pH} =$

7). The transition into a supercritical state was performed by simultaneous increasing the temperature and the inner pressure of the autoclave. After cooling the autoclave to room temperature, the resulting solid product was washed with isopropanol, acetone, and water, centrifuged (6000 rpm, 10 min.), and dried at room temperature. Series of experiments (on the reduction in supercritical isopropanol of nanocomposites Au/graphene oxide, NPs/graphene oxide and Rh/graphene oxide, and study of samples of initial and obtained nanocomposites) shown that graphene oxide was reduced to graphene, but the nanoparticles are retained on the graphene surface after reduction (Averyushkin *et al.*, 2017; Baskakov *et al.*, 2017).

Chloroauric acid was used as a precursor for obtaining gold nanoparticles on the surface of graphene oxide. 100 μL of a 0.05 M $\text{HAuCl}_4/\text{HCl}$ solution was added to 10 mL of an aqueous dispersion of graphene oxide (1 mg/mL) with stirring. One hour after decolorization of the solution, 300 μL of a 0.05 M freshly prepared $\text{NaBH}_4/\text{NaOH}$ solution in water was added to the system, and the mixture was stirred for 10 minutes. To isolate a solid precipitate, the system was centrifuged (6000 rpm, 15 min.), washed with water, and dried in air at a temperature of 60 $^\circ\text{C}$. H_2PdCl_4 and RhCl_3 were used for a similar synthesis of nanocomposites containing Pd and Rh nanoparticles, respectively. HAuCl_4 was added to the dispersion of graphene oxide in water, then the reducing agent sodium tetrahydroborate was added to the brown solution. The resulting dispersion was cooled, centrifuged (6000 rot./min., 15 min.) for precipitation of the solid phase, washed several times with water, and dried in air. So, nanocomposite Au NPs/GO was obtained. In the second stage, the reduction of the resulting nanocomposite Au NPs/GO was carried out using isopropanol in supercritical conditions. The synthesis was carried out in a steel autoclave, the volume of isopropanol was 5.2 mL, $T \sim 270^\circ\text{C}$ for 24 hours, the working pressure of the autoclave was 54 atm. The transition to the supercritical state was carried out by increasing the temperature of the reactor and, at the same time, the internal pressure in the autoclave. The final product was nanocomposite Au NPs/Graphene. Both nanocomposites Au NPs/GO and Au NPs/Graphene were studied by complex analytical methods. Samples of nanocomposites were characterized by elemental and X-ray structural analysis, IR and Raman spectroscopy, and transmission electron microscopy. The method of X-ray diffraction analysis was used to

study the phase content of nanocomposite (Baskakov *et al.*, 2017; Bravo *et al.*, 2018; Parnianchi *et al.*, 2018 Yang *et al.*, 2019; Wu *et al.*, 2020; Gao *et al.*, 2020).

The purpose of the further study was to propose a fairly simple, convenient, and one-step method for producing nanographite, subsequently, graphene, without its preliminary chemical activation. Natural graphite was used to accomplish this task. It is known that the crystal structure of graphite has defects of various types (vacancies, bulges, and fine structure defects) (Lee *et al.*, 2019). Under the action of intense ultrasound, the splitting of the crystal structure presumably occurs, mainly along the defects of the crystal matrix. Various dispersed systems "graphite-solvent" and "graphite-solvent-surfactant" have been studied. Ultrasonic treatment is a very convenient way to obtain dispersed systems. The method is universal and does not require significant economic costs (Proa-Coronado *et al.*, 2018). In order to increase the stability of dispersed systems, various types of surfactants were used (sodium salt of dodecylbenzene sodium sulfonate (DBSS), sodium bis (2-ethylhexyl) sulfosuccinate (AOT), octadodecylamine (ODA), ethylhexadecyldimethylammonium bromide (EHDAB)), which were directly added to the initial graphite-solvent system (Beniwal *et al.*, 2017; Zhang *et al.*, 2019). To study the morphology and particle size of the nanographite dispersion, various types of microscopic studies were used: interference, transmission, scanning, and atomic force (Araújo *et al.*, 2018). The morphology of the samples was studied using transmission electron microscopy on a JEOL JEM 1011 setup at an accelerating voltage of 80–100 kV. Before recording, the sample was deposited on a copper mesh with a diameter of ~ 3.5 mm covered with a polymer film. Images in transmission mode were acquired at magnifications of up to 500000.

3. RESULTS AND DISCUSSION:

Figure 2 shows XRD data of initial graphite, graphene oxide, and reduced graphene oxide (graphene). Graphite has a sharp peak at $2\theta = 26.5^\circ$. The graphene oxide phase corresponds to a distinct peak at $2\theta = 12^\circ$, which disappears after a reduction towards graphene. The synthesized graphene oxide and graphene were examined using transmission electron microscopy (Figure 3). IR-spectroscopy analysis has been applied for the investigation of surfaces of graphene oxide and graphene flakes as well.

The process of immobilization of noble metals nanoparticles was performed in several stages. In the first step, the graphene oxide was dispersed by ultrasonification in water. Then, the precursor of the corresponding metal was added to graphene dispersion (Figure 4). As precursors for nanoparticles synthesis, $\text{HAuCl}\cdot 3\text{H}_2\text{O}$, $\text{H}_2[\text{PdCl}_4]$, and $\text{RhCl}_3\cdot 3\text{H}_2\text{O}$ were used.

Graphene oxide was found to have oxygen-containing functional groups on its surface (Figure 4A). It is assumed that metal ions coordinate with various functional groups on the surface of the oxide graphene (Figure 4B). Further on, in the second stage, the reduction agent was introduced for nanoparticles formation (Figure 4C). As a reduction agent, NaBH_4 was used. Since metal ions coordinate with the functional groups of the graphene oxide, these functional groups could act as the centers of crystallization of the new phase to form and grow nanoparticles. The third stage is the reduction of graphene oxide with nanoparticles of noble metals located on its surface to graphene by supercritical isopropanol (Figure 4C). The final result of this reaction is nanocomposite NM NP/Graphene.

The resulting graphene oxide and graphene have a transparent, flake-like structure; the number of graphene layers does not exceed 10. The content of the graphene oxide elements before and after reduction by supercritical isopropanol has been determined by elemental C, H, N – analysis (Table 1). Figure 5 shows the Raman spectra of the initial graphite, graphene oxide, and graphene after the reduction of graphene oxide by supercritical isopropanol. It was found that the spectra of graphite oxide, graphene, and graphene are consisting of two peaks: G – line, which is related to sp^2 - carbon bonds ($\sim 1580\text{ cm}^{-1}$), and 2D – line ($\sim 2700\text{ cm}^{-1}$), which is an overtone of D – lines ($\sim 1330\text{ cm}^{-1}$). The presence of D – lines for graphene and graphene oxide samples indicates the formation of defect structure compared to the original structure of graphite, and the changing of 2D-peak shape is related to a small number of layers in the graphene structure. There are different oxygen-containing functional groups in the graphene oxide spectrum: hydroxyl, epoxy- and carbonyl groups. After reduction by SCI, the content of these functional groups in samples is decreased, as shown in the IR-spectra (Figure 6).

The novel method for synthesizing nanocomposite of Noble Metal Nanoparticles on the graphene surface (NM NP/Graphene) has been developed. In contrast to graphene oxide,

graphene has only a monolayer of carbon atoms in the sp^2 - hybridized state and has no functional oxygen groups, which could act as nucleation sites for nanoparticles formation. That is why, in this work, it was necessary to develop an original method of immobilization of nanoparticles of noble metals (Au, Pd, Rh) on the graphene surface through the formation of an intermediate nanocomposite of Noble Metal Nanoparticles on the graphene oxide surface (NM NP/GO).

The transmission electron microscope was used for studying the size distribution and morphology of gold nanoparticles on the surface of graphene and graphene oxide (Figure 7). Also, for comparison, the dispersion of gold nanoparticles in water was obtained. In the picture of Au NPs in water dispersion (Figure 7a) and the sample of nanocomposite Au NPs/GO (Figure 7b), it is shown that gold nanoparticles have a shape close to spherical. The distribution of the size of the nanoparticles of both samples was 6-10 nm. The average size is near 8 nm. After reducing the nanocomposite Au NPs/GO by SCI, gold nanoparticles on the graphene surface becomes larger due to the disappearance of oxygen-containing functional groups, and distribution of the size of the nanoparticles became 6-19 nm, and the average size is 13.5 nm (Figure 7c).

Figure 8a shows the XRD pattern of the synthesized nanocomposite Au NPs/GO indicating that Au nanoparticles were formed at the graphene oxide surface. The peak at $2\theta=12^\circ$ is related to the graphene oxide phase. Figure 8b shows the XRD pattern of nanocomposite Au NPs/Graphene after reduction by SCI of nanocomposite Au NPs/GO. Diffraction peak $2\theta=12^\circ$ related to graphene oxide has disappeared, which means the reduction of graphene oxide to graphene occurs. However, in Figure 8b, it is obvious that Au nanoparticles are retained on the graphene surface after reduction by SCI.

Gold nanoparticles have a strong band of surface plasmon resonance in the range 500 to 580 nm; its position and intensity depend on the size and shape of the particles. Figure 9A shows the absorption spectra of Au NPs dispersion, graphene oxide dispersion, and Au NPs/GO dispersion in water. Au NPs, both “naked” and in the graphene oxide surface, have a pronounced sharp surface plasmon absorption at 520 nm, corresponding to 10 nm size. Figure 9B shows the absorption spectra of graphene dispersion in water and Au NPs/Graphene in water. It should be noted that the band of surface plasmon

resonance of the gold nanoparticles disappeared in the resulting nanocomposite Au NPs/Graphene.

Dispersed systems of nanographite in various solvents were obtained by the action of ultrasonic cavitation. It was found that graphite powder is dispersed by ultrasound to graphite plates, which are stable as a suspension in a number of solvents. The output of the dispersed phase, depending on the process conditions, is 2-5% (for 7-10 minutes of ultrasonic treatment). The time of graphite dispersion in various solvents was selected using a qualitative assessment of the time of 50% sedimentation of suspensions in a capillary. From the dependences of the sedimentation of nanographite suspension in various solvents on the time of ultrasonic treatment, it follows that nanographite particles precipitate in organic solvents faster than in water, that is, nanographite dispersions in organic solvents are characterized by a shorter stability time than dispersions in water. It has been shown that an increase in the dispersion time (over 7 – 10 min.) does not affect the stability of suspensions.

It was found that ortho-xylene nanographite suspensions are stable for 1-2 days, in acetonitrile and toluene – for 203 days. After the indicated time, there was no absorption in the UV spectra of the suspensions. After centrifugation, the nanoparticles aggregate, and according to X-ray phase analysis, the residue phase corresponds to the phase of graphite. The aqueous dispersion of nanographite is stable for 12-14 days, the particles do not agglomerate with each other. It was shown that in the systems "graphite–organic solvent–surfactant" in comparison with the system "graphite–organic solvent," there is no increase in the stability of dispersions and a decrease in the time of sedimentation of particles, which is associated with the hydrophobicity of solvents. However, when using water as a hydrophilic solvent, the opposite result is observed. It was shown that the greatest stability of nanographite dispersed systems is achieved when using anion-active stabilizers as surfactants. It is likely that stabilization by surfactant molecules occurs along the boundaries of defects in the graphite crystal matrix. Because of the highest stability of dispersions, the systems "graphite–water" and "graphite–water–anion-active stabilizers" were selected for further research.

In the size distribution diagrams of a nanographite dispersion in water (with and without a surfactant), two peaks of the size

distribution are visible. Presumably, the first refers to the thickness of the nanographite plates, and the second is their lateral size. In the case of an aqueous dispersion of nanographite without surfactants, these dimensions were found to be 30 ± 10 nm and 350 ± 50 nm, respectively; in the second case – in the presence of anionic stabilizers – 35 ± 15 nm and 400 ± 75 nm. Microscopic data also confirm this assumption.

The product isolated from the aqueous dispersion without and with the addition of surfactants was identified by XRF. Graphite has two characteristic reflections – at 26.5° and 54.5° . After its dispersion in water under powerful ultrasound action, nanographite with a phase identical to that of graphite was obtained. The X-ray diffraction pattern of a nanographite sample obtained by dispersing the initial graphite under the action of high-power ultrasound in water in the presence of anion-active stabilizers shows that the structure of the crystal lattice is preserved, a slight broadening of the peaks and a significant decrease in their intensity are observed, which indicates a decrease in the particle size. Also, another low-intensity reflex appears, corresponding to the formation of a graphite oxide phase. To compare the changes in the structure of the graphite dispersion product with the initial graphite, the method of Raman spectroscopy was used. However, it is not possible to determine the exact number of graphene layers based on Raman spectra. However, the number of layers is significantly reduced compared to the initial structure of graphite (by 1.5–2 orders of magnitude).

The image obtained by interference microscopy shows and confirms that when graphite is dispersed using powerful ultrasound, the graphite structure is thinned by several orders of magnitude – the resulting nanographite flakes deposited on a silicon oxide substrate are combined into film structures. Such film structures are rather thin, which allows them to be viewed through an optical microscope using the interference contrast method.

It is not possible to see the structure of graphite with a transmission electron microscope. However, samples of nanographite dispersion in water with the addition of anion-active stabilizers deposited on a carbon grid give a clear image. It shows a layered structure of nanographite, which is rather thin in contrast to graphite. According to the data of scanning electron microscopy, the structure of graphite nanoparticles is practically the same for both samples. Nanographite is a layered structure with transparent plates. The

particle size of nanographite in some layers can reach 400-500 nm. However, on the surface of the nanographite plates, smaller structures are visible, the length of which is much less than 100 nm. Such plates can then be fractionally separated by centrifugation.

The atomic force microscopy analysis showed that nanographite plates obtained from an aqueous dispersed system without the addition of surfactants with a surface profile along the scanning line have a lateral plate size of 200-300 nm, the surface height is 20-30 nm. The surface of the nanographite plate is inhomogeneous – the difference in surface heights is about 10 nm. Nanographite plates obtained from an aqueous dispersion with the addition of anionic surfactants and their surface profile along the scanning line have a lateral plate size of 200-300 nm and a surface height of 20-35 nm. The difference in surface heights is about 15 nm.

From the data obtained, it can be noticed that dispersed systems of nanographite in water (with and without the addition of surfactants) contain nanographite plates, the lateral size of which is 200-500 microns, and the thickness is 20-40 nm. Presumably, these plates contain from 30 to 50 graphene layers. Thus, an original one-stage method for dispersing graphite in various solvents using powerful ultrasound has been developed. A stable disperse system of nanographite was obtained in organic solvents (toluene, acetonitrile, ortho-xylene) and in water. The possibility of stabilization of dispersed systems of nanographite using various surfactants has been investigated. It has been shown that the most stable is the dispersed system of nanographite in water with the addition of the sodium salt of dodecyl sulfobenzoic acid. A complex of methods of physicochemical analysis (DLS, XRF, Raman spectroscopy, AFM, SEM, TEM) has established that the resulting disperse system consists of nanographite plates, the lateral size of which is 200-500 nm, the thickness is 20-50 nm.

Thus, direct (without any preliminary activation of the initial graphite) dispersion of graphite by means of ultrasound leads to the production of nanometer-sized plates. Using well-known techniques (spin-coating, Langmuir-Blodgett techniques, and others), dispersed systems of nanographite can be used to create thin films on various substrates, which opens up new possibilities for creating materials based on graphite nanoparticles.

It is known that carbon nanostructures can possess biological activity, which determines their application in various biomedical fields. In experiments with the osteoblasts cultivation, it was found that mono- and multilayer carbon nanostructures noticeably affect the size and other features of growing cells. The comparison was carried out with similar cultures grown on a borosilicate glass substrate. It has been shown that a decrease in the thickness of carbon nanolayers enhances the proliferation of osteoblasts and the synthesis of alkaline phosphatase, and also causes calcium deposition. When studying the dependence of the characteristics of cultured cells of different types (osteoblasts, fibroblasts, chondrocytes) on the size of carbon nanoparticles, an increase in osteoblast adhesion caused by a decrease in the size of the plates was noted. Microscopic studies have revealed cell shape modifications caused by the binding of carbon nanostructures to cell membranes.

The resulting nanocomposites can be used in numerous applications such as catalysis, supercapacitors, (bio)sensors.

4. CONCLUSIONS:

As a result of this study, the following problems were solved. Development of a method for fixation of nanoparticles of noble metals (NM) – gold, palladium, and rhodium on the graphene oxide surface (GO), exploration of the samples by the complex of physical and chemical analyses. Study of the interaction of nanocomposites – nanoparticles of noble metals/graphene oxide (NM NP / GO) with supercritical isopropanol (SCI) in order to reduce graphene oxide to graphene with nanoparticles of noble metals fixed on the graphene flakes surface. Development of procedures for the preparation of nanocomposites – nanoparticles of noble metals on the graphene surface (NM NP / Graphene) and explore physical and chemical properties of nanocomposites. An original method of synthesis of nanocomposite materials based on graphene has been developed.

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Table 1. Results of elemental analysis of graphene oxide and graphene

Sample	Elements content, %		
	C	H	O
Graphene oxide	58.0 ± 1.0	1.5 ± 0.5	39.0 ± 1.0
Graphene	91.0±1.0	1.5±0.5	6.0±1.0

Figure 1. Scheme of graphene synthesis

Figure 2. XRD of graphite, graphene oxide, and graphene

Figure 3. TEM image of graphene oxide and graphene

Figure 4. Scheme of the immobilization of noble metals nanoparticles on the surface of graphene: A – initial graphene oxide; B – coordination of metal ions with the functional groups on the surface of graphene oxide; C – formation of nanoparticles on the surface of graphene oxide; D – reduction of the nanocomposite NB NP/GO to nanocomposite NB NP/Graphene by the supercritical isopropanol

Figure 5. Raman-spectra of graphite, graphene oxide, and graphene

Figure 6. IR-spectra of graphene oxide and graphene

Figure 7. TEM images: a) Au NPs dispersion in water; b) Au NPs/GO; c) Au NPs/Graphene

Figure 8. XRD data: a) Au NPs/GO; b) Au NPs/Graphene

Figure 9. UV/vis-spectra: a) Au NPs/GO; b) Au NPs/Graphene