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SYNTHESIS OF THE COMPOSITES OF GRAPHENE NANOPLATELETS/(Ni-Co) AND THEIR PROPERTIES

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On the base of graphene/metal type systems there are high-content capacitors, electrodic and magnetic materials of different applications are created with use of nickel, cobalt, and iron. The catalytic activity of systems with bimetal inclusions was studied, moreover the special synergies of the properties of bimetallic particles and fundamental difference between systems containing individual metals were highlighted. The system GNP/(Ni-Co) was synthesized by co-precipitation from a solution of hydrazine-hydrate. The presence of phase GNP, nickel, cobalt was shown by method of X-ray diffraction analysis of crystallites of the size of 15÷20 nm. The image of transmission electron microscope shows that the size of metal particles is 20 nm, and that of their agglomerates in composite is 200 nm.

The nanocomposites are sensitive to vapors of acetone, ammonia, ethyl alcohol. The process of adsorption in acetone and ammonia vapors happens with the irreversible loss of properties, which is due to the oxidation of metals on the GNP surface. Sensory properties of composites GNP/(Ni-Co) are stable over many cycles using ethanol vapors.

The electrophysical studies indicate a significant difference between the properties at low frequencies of Ni-Co and GNP/(Ni-Co). In the area of ultra-high frequency the characteristics have similar values, which are due to the relaxation phenomena.

The resulting nanocomposites can be promising for use in energy conversion devices, catalysis, gas sensor, screening, and magnetic devices.

Keywords: *graphene nanoplates, nanostructure composites, metal nanoparticles, gas analyzers, electrical and magnetic properties*

INTRODUCTION

Graphene structures are rising in practical use and research due to the complex of unique properties, high operational performance, low cost, manufacturability. Cost-effective technology for high-quality graphene composite materials is one of the prerogatives of a current research.

Graphene is a two-dimensional carbon allotropy and due to its low resistance and developed surface is a promising sounding material. In recent years graphene, graphene oxide, and reduced graphene were used as a working substance for the analysis of various gases: H_2O, NO_2, CO, NH_3, and others [1, 2]. The sensitivity of the devices and easiness of processing devices of graphene materials makes them attractive targets for research and future use. It is shown [3, 4] that the actual development of hybrid composites is based on graphene or graphene oxide, comprised Fe_2O_3, ZnO, WO_3, SnO_2 and others.

On the base of graphene/metal type systems there are high-content capacitors, electrodic and magnetic materials of different applications created with the use of nickel, cobalt, iron and so on [5, 6].

Graphene and hybrid materials are acquiring a widespread use for catalysis needs. The catalytic activity of systems with bimetal inclusions was studied, moreover the special synergies of the properties of bimetallic particles and fundamental difference between systems containing individual metals were highlighted [7].

Methods of obtaining such systems are very diverse [8], but the particle size is difficult to adjust and to reproduce during each experiment. The particle size is mainly determined by the method of preparation. Thus, plasma chemical synthesis [9] provides a high productivity, but

this method has a broad particle size distribution, and a significant amount of impurities. Bimetallic and trimetallic particles used for systems such as core-shell are received by the method of radiolysis. Thermal metal particles are obtained from the thermal decomposition of appropriate salts or hydroxides. Positive signs of such method include low concentration of impurities in the final product synthesis and a distribution of the particle size, however the particles have a significant size of 100–300 nm. The disadvantages of cryochemical synthesis are low temperature and large size of the particles obtained [9].

Chemical deposition of a salt solution is the simplest and most common method because it does not require special equipment and special conditions of synthesis. For additional control of the size of the particles obtained, there are stabilizing solutions introduced. The process is also regulated by changing the conditions (temperature, pH, nature of precursors, concentration of reactants, *etc*.) in order to obtain the final product with desired characteristics [10].

The aim is to develop a method of synthesis of nanostructured composites of graphene nanoplates/(Ni-Co) by restoring the crystalline carbonates of nickel and cobalt by the aqueous hydrazine hydrate solution, to obtain test samples in the form of powders and suspensions and to investigate their physical and chemical properties.

METHODS AND MATERIALS

Graphene nanoplates (GNP) are obtained by the electrochemical deposition in an electrolyte (KOH) of low concentration by passing a current to 60 mA/cm^2 in a mode of stabilization of current at voltage up to 30 V. With the aim of separation of large particles of nanoscale graphite, electrodes were placed between polypropylene filter fabric. GNP were kept in suspension of a graphene mass with the concentration of 2 % and pH = 12. Ni-Co particles were obtained by a chemical vapor deposition from a solution of hydrazine hydrate carbonates of nickel and cobalt [11] at the temperature of 350 K. For the synthesis of the GNP/(Ni-Co) composites, the method was modified: coprecipitation of carbonate solution and suspensions was conducted at the temperature of boiling point of graphene-hydrazine hydrate at a weight ratio of components of 9:1. The presence of KOH created favorable conditions for the formation of metal particles, GNP acted as crystallization centers and helped to stabilize the size and chemical composition of nanoparticles.

X-ray analysis was performed by powder diffraction on a DRON-4.7 diffractometer with CuK_α radiation nickel anode line filter in the reflected beam geometry when shooting on-shore Brittany. The morphology of samples was examined with the use of transmission of an electronic microscope JEOL JEM-1230 (Japan). Thermogravimetric measurements such as weight loss (TG) and differentially thermal analysis (DTA) were performed using a device Derivatograf Q-1500 D (Hungary) in static air. A sample weighing 100 mg was heated in a ceramic crucible from room temperature to 1250 K at 10 K/min.

The suspension of nanoparticles was mixed with a small amount of adhesive (acrylic suspension) in order to assess the sensitivity of the obtained composite to the gas. Measuring cell, a fiberglass plate with two parallel gold electrodes coated with a small brush of thin film material in the form of paste, was dried under atmospheric conditions. Measurements were carried out on individual samples in saturated ethanol, ammonia, and acetone vapors. Resistance measurements were carried out using a device UT 70B.

Investigation of the real (ε') and the imaginary (ε") components of the complex dielectric permittivity of composites was made in ultra-high frequency (UHF) ranging 8–12 GHz and using an interferometer RFK-18 which was based on measuring the phase difference. Standing wave ratio and the weakening of R2-60 by the no-electrode method. And the conductivity was made at low frequencies of 0.1, 1 and 10 kHz were made with two-contact method using an immittance meter E7-14 [12]. The relative error of ε', ε″, σ″, μ′, μ″ did not exceed ± 5% .

EXPERIMENTAL RESULTS AND DISCUSSION

With the use of the electron microscopic studies there were GNP metal particles sizing 40–200 nm (Fig. 1) found on the surface. However, more detailed images on the film of graphene contain particles of the size of less than

20 nm. Perhaps the larger particles are agglomerates composed of the smaller ones [11].

The results of the X-ray diffraction (Fig. 2) indicate the presence of GNP, nickel, and cobalt phases as well as the absence of reflexes of incoming carbonates. Thus, we associate the peaks of 22.4 and 31.3° with the presence of graphene samples in the structure, while the low-intensity peak corresponds to 27.1° graphite crystal lattice [14]. Nickel can meet peaks of 44.9° – octahedral (111), 52.2 and 91.8° – cubic systems. Cobalt crystal lattice of a cubic system correspond to peaks of 52.2° (111) 61.2° (200), 91.8° (220); hexagonal – 55.9° (101). So the peaks of 52.2 and 91.8° may indicate the presence of bimetallic Ni-Co particles with cubic crystal lattice (200) [13]. The crystallite dimensions, calculated by Scherrer equation, are 15÷20 nm for GNP/(Ni-Co) composite and 20÷26 nm for Ni-Co.

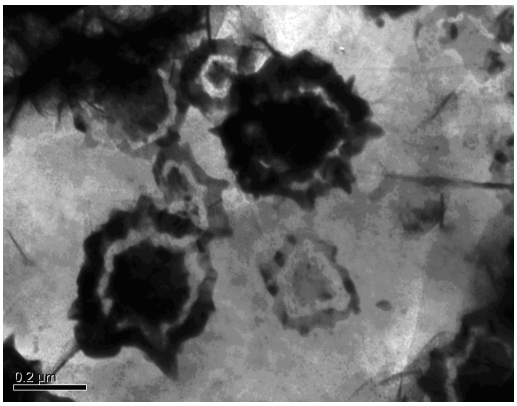

Fig. 1. TEM image of the composite GNP/(Ni-Co)

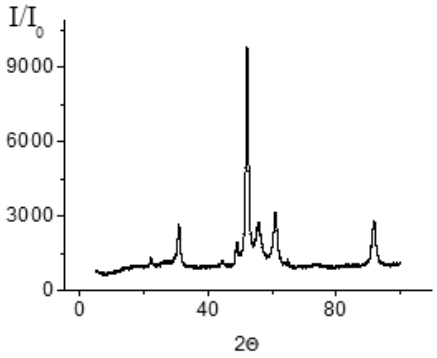

Fig. 2. The composite GNP/(Ni-Co) diffraction

The method of thermogravimetry found that the weight loss of components in the graphene composites began at the temperature of 295 K, run with the loss of mass due to the elimination of sorbed water. Oxidation of metal nanoparticles begins at 400 K and is accompanied by a weight gain (Fig. 3). Further destruction of the sample (600–730 K) is associated with the oxidation of polycrystalline graphite, the negligible share of which (3 wt. %) is a part of the composite.

A study of composites as gas sensors was conducted (Fig. 4 *a, b*). The composites are sensitive to vapors of acetone, ammonia, ethyl alcohol. The electrical resistance of samples sharply increases in 1.2–2.5 times as gas enters the atmosphere, indicating the adsorption of molecules adsorbent on nanoparticles surface, and the blocking the conduction channel.

An intense oxidation of samples with the irreversible loss of properties happens in the vapors of acetone and ammonia (Fig. 4 *a*). For comparison, similar research of the initial GNP (preparation for the experiment was conducted under the same conditions) was carried out. GNP are less sensitive compared to composites and do not lose their properties over many cycles. Relative resistance of Independent Trade Union shall not be returned to their original values, increasing every cycle for average of 10 %.

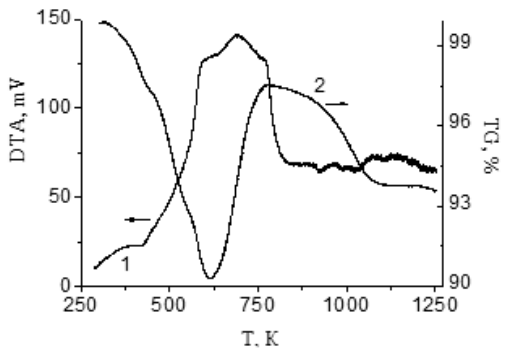

Fig. 3. DTA (*1*) i TG (*2*) composite GNP/(Ni-Co) as function of temperature

Obviously, the desorption for a given recovery time and temperature does not proceed entirely, part of the sorbed gas remains on the surface of the sample. So the destruction of the composite GNP/(Ni-Co) in vapors of acetone and ammonia is associated with the oxidation of the metal component, which at the same time creates additional sites of adsorption, accelerates surface reactions of adsorbate.

Composites of the GNP/(Ni-Co) are susceptible to ethanol vapor, the relative electrical resistance in the presence of alcohol

increases by almost a quarter (Fig. 4 *b*). Time of adsorption is approximately equal to desorption time. The relative values of electrical GNP do not acquire the previous results, keeping the difference at the beginning and the end of the process of adsorption constant. Unlike the Independent Trade Union Composites GNP/(Ni-Co) exhibit stable properties of ethanol in vapors for many cycles.

The electrophysical studies conducted indicate a difference in electrical properties of initial components Ni-Co, GNP and those of composite GNP/(Ni-Co) (Table 1).

The electrical conductivity Ni-Co greatly exceeds the corresponding value of nanocomposite GNP/(Ni-Co) at low frequencies, which apparently is caused by a decrease in the number of metal-metal contacts. In the area of ultrahigh frequency, the difference of the components of the complex permittivity becomes less important by reducing the role of contacts between the particles.

Composites of the GNP/(Ni-Co) have expressed the magnetic properties (Table 2).

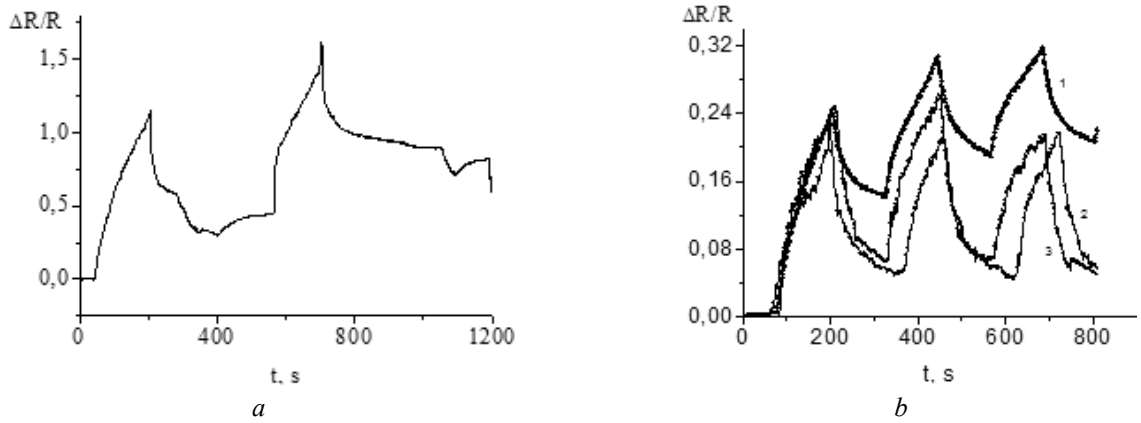

Fig. 4. (*a*) Dependence of the relative resistance of composites GNP/(Ni-Co) on time in the saturated acetone vapor at $T = 293$ K, (*b*) dependence of the relative resistance of composites GNP/(Ni-Co) (*1* and *2*) and GNP (*3*) on time in saturated ethanol vapor at $T = 293$ K

Table 1. The electrical characteristics of the GNP, Ni-Co and GNP/(Ni-Co)

Sample	Relative specific conductivity, σ at frequency 1 kHz, $Ohm^{-1} \cdot cm^{-1}$	Components of the complex dielectric constant ε at the frequency 9 GHz	
		Real ε′	Imaginary ε″
GNP	0.13	–	–
Ni-Co	8.0	4.9	3.0
GNP/(Ni-Co)	1.0	4.0	2.4

Table 2. The magnetic characteristics of Ni-Co and GNP/(Ni-Co)

Sample	Magnetic permeability in the range 0.1-10 kHz	Specific magnetization $G \cdot cm^3/g$	Components of the complex magnetic permeability μ on the frequency 8 GHz	
			Real μ′	Imaginary μ″
Ni-Co	96	73	3.6	5.1
GNP /(Ni-Co)	98	14	1.7	0.7

The difference in the properties of nanocomposites Ni-Co and GNP/(Ni-Co) is caused by a difference in size of the particles obtained in the synthesis process. The presence of GNP promotes the stabilization of the particle size, which affects electrical conductivity, the value of the real and imaginary components of the complex magnetic permeability, as well as the specific magnetization. The coercive force, as a rule, has higher values for larger nanoparticles, which is confirmed by the data of X-ray analysis for these systems. The presence of a suspension of graphene increases the number of crystallization centers, thus limiting the size of the crystallites.

CONCLUSIONS

The composites of GNP/(Ni-Co) were derived by the method of co-precipitation from the solution of hydrazine hydrate. The method of X-ray diffraction analysis showed the presence of phases of GNP, nickel, cobalt crystallite with size of 15–20 nm, the absence of reflexes of incoming carbonates. It has been shown that composites contain 20 nm particles as well as their agglomerates of the size up to 200 nm.

Composites are sensitive to acetone, ammonia, ethyl alcohol vapors. The electrical resistance sharply increases up to 1.2–2.5 times as the gas enters the atmosphere, indicating the blocking of conduction channels. The process of adsorption in acetone and ammonia vapors proceeds with the irreversible loss of properties, which happens due to the oxidation of the metal surface. The sensoric properties of composites GNP/(Ni-Co) using ethanol vapors are stable over many cycles.

The electrophysical studies indicate a significant difference between the properties at low frequencies of Ni-Co and GNP/(Ni-Co). In the area of ultra-high frequency, the characteristics have similar values, due to the relaxation phenomena.

The resulting nanocomposites can be promising for use in energy conversion devices, catalysis, gas sensor, screening and magnetic devices.

Синтез композитів графенові нанопластини/(Ni-Co) та їхні властивості

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Синтезовано нанокомпозити системи ГНП/(Ni-Co) методом співосадження з розчину гідразин-гідрату. Методом рентгенофазового аналізу показано присутність фаз ГНП, нікелю, кобальту з розміром кристалітів 15÷20 нм. Зображення трансмісійного електронного мікроскопа вказують, що розмір металевих частинок досягає 20 нм, а їхніх агломератів до 200 нм.

Нанокомпозити є чутливими до парів ацетону, амоніаку, етилового спирту. Процеси адсорбції в парах ацетону та амоніаку відбуваються з незворотною втратою властивостей за рахунок окиснення металів на поверхні ГНП. Сенсорні властивості композитів ГНП/(Ni-Co) при використанні парів етилового спирту стабільні протягом багатьох циклів. Досліджено електрофізичні та магнітні властивості металевих наночастинок і композиту.

Ключові слова: *нанопластини графену, наноструктурні композити, металеві наночастинки, газоаналізатори, електрофізичні та магнітні властивості*

Синтез композитов графеновые нанопластины/(Ni-Co) и их свойства

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Синтезированы нанокомпозиты системы ГНП/(Ni-Co) методом соосаждения из раствора гидразин-гидрата. Методом рентгенофазового анализа показано присутствие фаз ГНП, никеля, кобальта с размером кристаллитов 15÷20 нм. Изображения трансмиссионного электронного микроскопа указывают, что размер металлических частиц достигает 20 нм, а их агломератов до 200 нм.

Нанокомпозиты чувствительны к парам ацетона, аммиака, этилового спирта. Процессы адсорбции в парах ацетона и аммиака протекают с необратимой потерей свойств, за счет окисления металлов на поверхности ГНП. Сенсорные свойства композитов ГНП/(Ni-Co) при использовании паров этилового спирта стабильны в течение многих циклов. Исследованы электрофизические и магнитные свойства металлических наночастиц и композита.

Ключевые слова: *нанопластины графена, наноструктурные композиты, металлические наночастицы, газоанализаторы, электрофизические и магнитные свойства*

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