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Coating of Carbon Black (CB) and Graphene Oxides (GOs) with Magnetite (Fe_3O_4)

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Abstract

Composites containing iron oxides are obtained by the co-precipitation of iron(II) and iron(III) compounds in the presence of different substrates in an alkaline environment. Newly synthesized graphene oxide (GO), reduced graphene oxide (rGO) and carbon black (CB) are used as substrates. Methods of obtaining GO–amorphous iron compound, rGO–Fe_3O_4, and CB–Fe_3O_4 composites are developed. It is determined that rGO–Fe_3O_4 and CB–Fe_3O_4 magnetic composites can be obtained at 70°C to 75°C, while in the presence of GO, a non-magnetic composite containing an amorphous iron compound is formed under the same conditions. This composite, when heated in vacuum at 170°C to 175°C, undergoes exfoliation, in result of which a powder composite rGO–amorphous iron compound is formed, the volume of which is 2.7 times greater than that of initial powder. Partial reduction of the formed composite takes place at 550°C and rGO–Fe_3O_4 is obtained. Formation of the magnetite phase is determined by XRD (X-Ray Diffraction) analysis. The structural-morphological study of the synthesized composites is carried out by the SEM (Scanning Electron Microscopy) method. Their magnetic characteristics are studied using VSM (Vibrating Sample Magnetometry) method.

Key Words: *Graphene oxide; Reduced graphene oxide; Activated carbon; Magnetite; Magnetic composite*

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Introduction

The unique structure of graphene (G) and graphene oxides (GOs) attracts a lot of attention from researchers of various fields. Many promising materials are obtained from G, which are used in the fields of energy storage, composite materials engineering, electronics, sensorings, catalysis, medicine and for solving environmental problems as well. GOs are constructed from different types of oxygen-containing functional groups, through which many organic substances can be immobilized and composites with completely new properties can be formed [1-3].

Recently a room-temperature ferromagnetic amorphous GO was synthesized [4] by introducing abundant oxygen-containing functional groups and C-defects into single-layered graphene, followed by a self-assembly process under supercritical CO_2. It is mentioned that GO obtained by this method exhibits the highest saturation and remnant magnetizations, 1.710 emu/g and 0.251 emu/g, compared to the rest of metal-free graphene-based materials. Material is promising for use in spintronics devices.

Let's consider the methods of obtaining graphene–magnetite (G–Fe_3O_4), graphene oxide–magnetite (GO–Fe_3O_4) and reduced graphene oxide–magnetite (rGO–Fe_3O_4) composites, and their properties and fields of application. In [5], GO–Fe_3O_4 composites were obtained with the $FeCl_3$ and $FeCl_2$ co-precipitation at presence of GO up to 25%. According to their content, two structurally different composites were obtained. They were used in heterogeneous Fenton-like reaction for Acid Orange-7 degradation. GO–Fe_3O_4 magnetic composites for medical use as drag targeting transport obtained by co-precipitation method [6] are characterized by superparamagnetism. GO was synthesized using Hummers method by adding $KMnO_4$ to graphite–$NaNO_3$–H_2SO_4 suspension at 5°C. The GO–Fe_3O_4 composite itself was obtained by adding monodisperse Fe_3O_4 to GO dilute solution. G–Fe_3O_4 composite was formed from the obtained composite by heating it to 700°C. In fact, GO–Fe_3O_4 composite properties did not study, but that of G–Fe_3O_4 because the XRD (X-Ray Diffraction) reflex at $2\theta = 10°$ to $12°$ characteristic of GO is not visible in presented diffractograms.

There are known many methods of obtaining nanostructured iron oxides: hematite (α-Fe_2O_3), maghemite (γ-Fe_2O_3) and magnetite (Fe_3O_4), which then can be combined for coating different matrices. In the review [7], there are described the methods of receiving such composites, where G and its oxides are used as substrates. Magnetite composites are obtained by co-precipitation, hydrothermal, sol–gel and microemulsification methods. They are widely used in the production of electrochemical sensors of different substances, as anode materials, in lithium cells, as catalysts, for the removal of organic and inorganic pollutants, in electronic devices, etc.

In this work, we focused only on the coating of certain substrates such as CB (Carbon Black), GO and rGO with magnetite phase. Further studies of the obtained materials should include HRTEM (High-Resolution Transmission Electron Microscopy) to determine the nature of the GO an rGO-flakes, as well as Raman studies to observe their vibrational modes.

In [8], rGO–Fe_3O_4 compositions were obtained by the co-precipitation method with the difference from standard one that $FeCl_3$ and $FeSO_4$ were added to the rGO dispersion under sonication and precipitation of Fe_3O_4 was carried out by adding NH_4OH. It is confirmed that the Fe_3O_4 species deposited on rGO have size of 20 nm. These composites are used to remove toxic metal ions from polluted waters.

The rGO–Fe_3O_4 composite used for enzyme immobilization was obtained [9] by the interaction of GO and Fe^{II}, when Fe^{II} oxidized to Fe^{III} by the GO-matrix and the Fe_3O_4 phase was formed. The process is carried out by 650-well ultrasonication of GO in NH_4OH and rapid adding of $FeCl_2$ solution at 80°C. Composite separated magnetically. Treatment of GO-suspension was carried out [10] by ultrasonication at 85°C for 2 h, after which $FeCl_3$, $FeCl_2$ and NH_4OH solutions were gradually added. Claimed that Fe^{II} ions are oxidized by GO and GO–Fe_3O_4 composite is formed. However, according to the presented XRD analysis results, no GO reflex is observed in the $2\theta = 10°$ to $12°$ region, which indicates that the rGO–Fe_3O_4 composite, not GO–Fe_3O_4, is formed in this process. Composite rGO–Fe_3O_4 was obtained by ultrasonication of GO–$FeCl_3$–urea mixture and subsequent autoclave treatment. Fe_3O_4 deposited on G was formed by a similar method. For this purpose, hollow G, the $FeCl_3$–PEG-4000–CH_3COONa system containing PEG (PolyEthylene Glycol), was used. It was processed at 200°C for 18 h [11].

G and GOs coated with Fe_3O_4 nanoparticles have been widely used to create Li-ion batteries and capacitors. For example, rGO–Fe_3O_4 composite was synthesized [12] by a facile one-step solvothermal method. Fe_3O_4-embedded rGO composites were obtained by evaporation of the rGO–$FeCl_3$ suspension and heating the solid mass in an inert atmosphere at 550°C to 800°C [13].

The influence of the of G-matrix structure and methods of coating with iron oxides on morphology and properties of the materials is discussed in [14]. Co-precipitation method was used and GO–Fe_3O_4, GO–Fe_2O_3 and GO–Fe composites were obtained. By the XRD method it was established the formation of γ-Fe_2O_3, γ-FeO(OH) and α-FeO(OH) phases on GO-plate, particles size of which are in the range of 10 nm to 100 nm. The co-precipitation method is often used to obtain materials with improved operational properties that will be used in fields of energy storage devices, Li-ion batteries and supercapacitors [15-21].

The room temperature magnetic properties of GO decorated with magnetite nanoparticles GO·Fe_3O_4 were discussed in [22]. The ultrasonication method was used, because of which Fe^{II} ions in an alkaline medium form the Fe_3O_4 phase deposited on GO. The reaction scheme is as $3Fe^{II} + 8OH \rightarrow Fe_3O_4 + 4H_2O$. From the XRD analysis results, it is clear that when the wt.% ratio GO:$FeCl_2$ is 1 or 2, the GO reflex is observed on the diffractogram, and when the amount of $FeCl_2$ increases, this reflex disappears, probably is transferred to rGO, although its reflex is not highlighted.

From the above short literature review, we can conclude that the deposition of magnetite phase on materials with G-like structure can be done by a relatively simple and inexpensive method. We have used it in previous, as well as present, works. Previously, we synthesized 2D-materials based magnetic systems and studied their properties. We suggested several methods of deposition and intercalation of magnetic clusters on 2D-materials, such as G, GO, rGO and hexagonal boron nitride h-BN, based on different chemical processes, among them, the obtaining of 2D-material–Fe_3O_4 composites by co-precipitation of iron(II) and iron(III) compounds in the presence of h-BN.

Due to the structural-morphological features of G, GOs and h-BN, it is possible to intercalate them with magnetic clusters or coating their surface by the same chemical processes. These methods were used in works [23-26].

Experimental

Starting materials, equipment, and chemical synthesis methods described here, in the most part, were used in our earlier studies as well and, therefore, in details are given elsewhere [23-26]. Below they are presented in short, but added with recent modifications.

Starting materials

The degree of purity of chemical reagents and solvents used for synthesis reaches 99.00% to 99.99%. Reagents $FeSO_4·7H_2O$, $FeCl_3·6H_2O$, $Fe(NO_3)_3·9H_2O$, $Fe(CO)_5$, $KMnO_4$, $NaNO_3$, 98%H_2SO_4 and 37%HCl purchased from Sigma Aldrich and are used without prior purification. Graphite flake, natural, 325-mesh, 99.98% purity (metals basis) purchased from Alfa Aesar is used to obtain G, GO and rGO. An inert environment is created in the reaction area using nitrogen and argon.

Equipment

A 45 kHz Ultrasonic Cleaner and JY92–IIDN Touch Screen Ultrasonic Homogenizer (20 kHz to 25 kHz and 900 W) are used for the suspensions ultrasound treatment and homogenization. Thermal treatments (<1500°C) of GO and rGO are conducted in high-temperature Kejia vacuum furnace.

XRD patterns are obtained with DRON–3M diffractometer (Cu–Kα, Ni-filter, $\lambda = 1.5418$ Å, 2°/min) and the powder particles size is determined by Scherer method. GO and rGO particles size also are measured by Winner 802DLS photon correlation nanoparticles size analyzer.

The morphology and microstructure of the powders are studied with SEM (Scanning Electron Microscope) JEOL–JSM 6510 LV equipped with energy-dispersive micro-X-ray spectral analyzer X-MaxN (Oxford Instruments), through which the elemental composition of obtained magnetic composites are determined.

VSM (Vibrating Sample Magnetometer) Lake Shore 7300 is used for the general characterization of the magnetic state of the received materials by measuring its magnetic characteristics such as: saturation and remnant magnetizations, Curie and Neel temperatures, coercivity, some superparamagnetic properties, etc.

Chemical synthesis

Synthesizing GO. 40 ml of 98% sulfuric acid is added to 1 g of pGFW (<140 μm) in a glass reactor. The mixture is stirred at 35°C to 40°C for 0.5 h and 3 g of $KMnO_4$ is added at 40°C to 50°C during 1 h. After the mixture is stirred for 3 h, a gray viscous mass is obtained, which is cooled to 10°C and 100 ml of ice water is added to the glass reactor. The mixture is diluted to 500 ml, and 2 ml of 30% H_2O_2 solution is added. And a yellowish suspension of GO is obtained. During the washing of the sediment, its color gradually changes to dark brown. 20 min later solution is removed by decantation. This process is repeated twice. For the rapid precipitation of GO from the suspension, a 5% solution of hydrochloric acid (500 ml) is added. Decantation is repeated 3 times in 10 min intervals. An aqueous gel-like mass is obtained. Washing of this precipitate is continued until the pH of the solution reached 5–6. GO is separated from the obtained suspension by centrifugation and dried in a vacuum at 60°C for 4 h. The suspension without separation of GO is used to obtain composites containing iron oxides.

Obtaining of GO–amorphous iron compound composite by co-precipitation of iron(II) and iron(III) compounds in presence of GO. 100 ml suspension containing 1 g of GO is pre-sonicated for 1 h and placed in a 250 ml three-necked flask equipped with a gas tube, thermometer and dropping funnel. Argon is pumped into the flask for 1 h. After that, the suspension is heated to 50°C and 0.82 g of

$FeCl_3 \cdot 6H_2O$ solution is added dropwise. After 30 min, 0.42 g of $FeSO_4 \cdot 7H_2O$ is added dropwise to the acidified solution. The suspension is heated to 70°C and after 30 min, 15 ml of 25% ammonium hydroxide (NH_4OH) solution is added dropwise. The resulting black suspension is stirred for 3 h at 75°C. The reaction mixture is cooled to room temperature. The obtained black precipitate is filtered and washed 3 times with water and ethanol. The wet mass is dried in vacuum at 60°C (for 6 h and under 2 mmHg to 4 mmHg). In this way, the black powder of a non-magnetic composite of GO–amorphous iron compound is obtained. It is kept in a desiccator. The rGO–Fe_3O_4 and CB–Fe_3O_4 composites are obtained by a similar procedure.

Vacuum-thermal exfoliation of GO–amorphous iron compound composite. 0.5 g of composite powder is placed in a quartz ampoule. After vacuuming the flask, it is heated at rate of 5°C/min to 170°C to 175°C. In this temperature range, the volumetric exfoliation of the composite powder takes place. The powder volume increases by 2.5 to 2.7 times. Obtained black non-magnetic powder is cooled in argon.

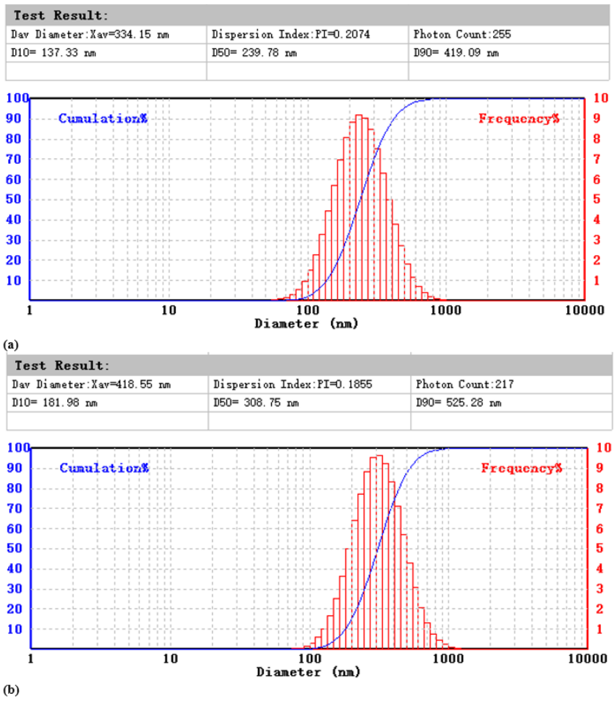
Obtaining of rGO–Fe_3O_4 composite. In order to fully form the Fe_3O_4 phase, 0.5 g of the composite obtained at 170°C to 175°C by vacuum-thermal exfoliation process is placed in a quartz tube (diameter 12 mm), which, in turn, is placed in a tube furnace in an argon flow (25 ml/min). The sample is heated at a rate of 5°C/min for 30 min. At 550°C, heat treatment of the sample lasts for 1 h. Then the furnace is turned off and cooled to room temperature in the argon atmosphere. As a result of such heat treatment of the initial amorphous powder, a black magnetic rGO–Fe_3O_4 composite powder is obtained. It is stored in a desiccator. Here the amorphous phase crystallizes into Fe_3O_4. At lower temperatures, the magnetite phase is not well formed. That is, 550°C is the optimal temperature for obtaining magnetite. The mechanism of the process is as follows: high temperature promotes the interaction and dehydration of Fe^{+2} and Fe^{+3} ions in GO–amorphous iron compound composite, or more precisely, their amorphous oxohydroxides forming the magnetite phase. Since the appropriate molar ratio Fe^{+2}:Fe^{+3} = 1:2 is preserved in the amorphous mass, $FeO.Fe_2O_3$ or Fe_3O_4 is obtained.

Vacuum exfoliation of GO and obtaining of rGO. 0.5 g GO plates are cut into small pieces (2 mm to 4 mm) and placed in a 1 l glass flask. After vacuuming the flask, it is heated at a rate of 5°C/min to 220°C to 250°C. In this temperature range, there is possible a volumetric exfoliation of the GO plates and the formation of a fluffy black powder. Vacuuming is continued for 1 h, and then the flask is cooled under vacuum. The bulk density of the obtained powder reaches 20 mg/ml to 30 mg/ml.

Obtaining of G from rGO. rGO contains 15 wt.% to 17wt.% oxygen because it consists of various types of oxygen-containing functional groups. Their removal is performed by heating the rGO to high temperatures (>1000°C) in vacuum under inert gas or hydrogen. G is obtained by us through heating the sample at 1000°C to 1200°C for 5 h in vacuum. G obtained by this method contains only 2wt.% to 5wt.% of oxygen. G with a defective structure is obtained by chemical method.

Results and Discussion

As GO consisting of many oxygen-containing functional groups obtained by different methods, it has been used to obtain iron oxides containing composites as well. The oxygen content in GO depends on the method of its preparation. In laboratory practice, GO is obtained in forms of suspension, powder or elastic plates. By adjusting the ultrasonication mode and the pH value for the suspension, it is possible to obtain the GO particles in the size range of 50 nm to 1000 nm. Our experiments mainly used suspensions, in which the particles average size reached 200 nm to 500 nm (Figure 1).



Test Result:		
Dav Diameter:Xav=334.15 nm	Dispersion Index:PI=0.2074	Photon Count:255
D10= 137.33 nm	D50= 239.78 nm	D90= 419.09 nm

Test Result:		
Dav Diameter:Xav=418.55 nm	Dispersion Index:PI=0.1855	Photon Count:217
D10= 181.98 nm	D50= 308.75 nm	D90= 525.28 nm

Figure 1) *Histogram of particles size distribution in suspension of (a) GO at pH=2.3 and (b) CB at pH = 6.2.*

To obtain composites containing iron compounds from G and its products, a simple co-precipitation method is mainly used, which is based on the formation of the magnetite phase in the alkaline environment. The method is based on the chemical reaction: $FeSO_4 + 2FeCl_3 + 8NH_4OH \rightarrow Fe_3O_4 + (NH_4)_2SO_4 + 6NH_4Cl + 4H_2O$.

Many reports describe the preparation of GO–Fe_3O_4 composite using this reaction. Above we have showed that in some cases not GO–Fe_3O_4, but rGO–Fe_3O_4 was obtained. This conclusion is drawn by the absence of GO corresponding reflex in the diffractograms given. It is established that GO is a thermally unstable substance and easily changes its chemical composition, when the temperature increases. Accordingly, its composites are unstable as well. Obviously, this limits the application area of GO–Fe_3O_4. Therefore, there is a need to select optimal methods for obtaining magnetic composites. We discuss two possible methods of obtaining magnetic composites using GO, which is determined by its properties.

Method 1 includes the following steps: GO + Fe^{II} + Fe^{III} + OH co-precipitation → GO–iron compounds composite → GO–iron compounds composite exfoliation at 170°C to 175°C in vacuum → thermal treatment of obtained powders at 550°C for 1 h → ferromagnetic rGO–Fe_3O_4 powder → studying the magnetic characteristics. By further heating of ferromagnetic rGO–Fe_3O_4 powder, at 800°C G–Fe_3O_4 ferromagnetic composite is obtained – a similar method is described in the literature review.

Method 2 includes the following steps: GO vacuum-thermal exfoliation at 230°C to 250°C → rGO bulk powder → rGO + Fe^{II} + Fe^{III} + OH co-precipitation at 70°C to 75°C for 3 h → ferromagnetic rGO–Fe_3O_4 powder → studying the magnetic characteristics.

In both methods, newly synthesized GO suspensions are used, which are pre-sonicated. During the implementation of the Method 1, a black diamagnetic substance is formed in the co-precipitation process. The GO peak is visible on the XRD pattern, while compounds (oxides or oxohydroxides) diffraction peaks are not observed, i.e. GO has formed composite with an amorphous iron compound. Its exfoliation at 170°C to 175°C in vacuum produces a powder with a weak ability to be magnetized, although the magnetite or maghemite phases are not observed on the diffractogram, and the peak of GO is not observed as well. The powder becomes ferromagnetic if heated to 550°C in argon for 1 h in result of the magnetite phase formation. When the temperature increases, there is also a transition of GO into the rGO with peak at $2\theta = 26.88°$. The Method 1 steps XRD-monitoring results are summarized in Figure 2.

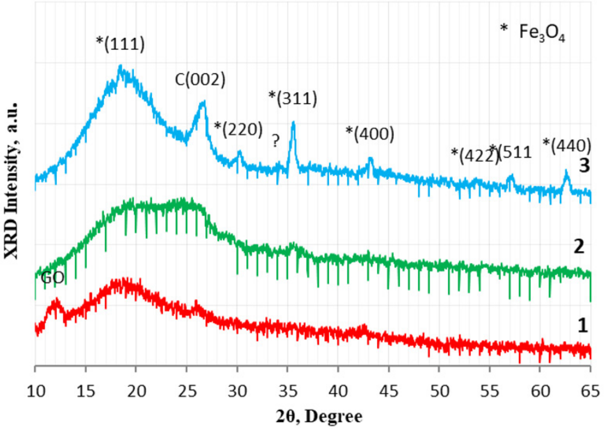


Figure 2) *XRD pattern of powders obtained by Method 1: (1) GO–iron compounds composite, (2) Its exfoliation at 170–175°C in vacuum, and (3) Ferromagnetic rGO–*Fe_3O_4 *powder obtained at 550°C.*

The forming of a non-magnetic amorphous iron compound instead of a magnetic iron oxide by the GO-based composite seems to involve specific interactions between GO and the iron species that inhibit crystallization or magnetic phase formation. To explain this, let's observe the co-precipitation processes on GO, rGO and CB. We find that the magnetite phase is directly obtained on rGO and CB, and in the case of GO – an amorphous mass instead.

Matrix must be responsible for such behavior. The difference between these matrices is that GO contains a large amount of oxygen-containing groups (carboxyl, hydroxyl, carbonyl and others), which form complexes with iron ions. The content of such groups is significantly smaller in rGO, while CB practically does not contain them. Under the conditions when the matrix does not contain complex-forming groups, Fe^{+2} and Fe^{+3} move freely in the suspension. For such a system, upon addition of ammonium solution, the magnetite phase separates as it does in the matrix-free solution. The same is proved by the fact that in the case of boron nitride matrix, which does not contain complex-forming groups, the magnetite phase is also obtained directly. The results are similar for aluminum oxide, silicon oxide, asbestos, zeolite and other matrices.

We come to the conclusion that the ability of GO to form complexes is the reason for the formation of an amorphous iron compound, which, in turn, inhibits the formation of the magnetite phase. The ability to form complexes with metal ions is used in the manufacture of GO-based water purification membranes and filters. In addition, GO is an amphoteric compound (anionite and also cationite) forming the complexes with both cations and anions and, therefore, working in both alkaline and acidic environments.

Note that the XRD pattern of maghemite Fe_2O_3 is almost similar to that of magnetite Fe_3O_4. In the future, it would be worthwhile to perform additional Raman spectroscopy to unambiguously determine the ratio of iron oxide phases in the resulting composite. In this regard, see optical studies [27,28], which showed that composites containing a nanoscale phase of Fe_2O_3 nanocrystals (with some additional hydrolyzed oxide component, e.g. FeOOH) exhibit exceptional UV (UltraViolet) filtration and significant IR (InfraRed) reflectivity.

SEM and X-ray EDS (Energy Dispersive Spectrometry) methods (Figures 3 and 4) studied the obtained composite. It is determined that iron content in the composite reaches 11w/w% and it is evenly distributed on the rGO surface (Table 1). The powder particles size is in the range of 1 µm to 5 µm and they forms weakly sintered agglomerates.

One of the important steps in using the methods developed by us is the preparation of magnetic composites in the form of powders, because it makes possible to obtain various functional materials and their products by available technologies. For this purpose, the property of GO to undergo rGO by vacuum-thermal exfoliation at 230°C to 250°C is used. Complexes of GO with metal salts, oxides, and acids have the same property.

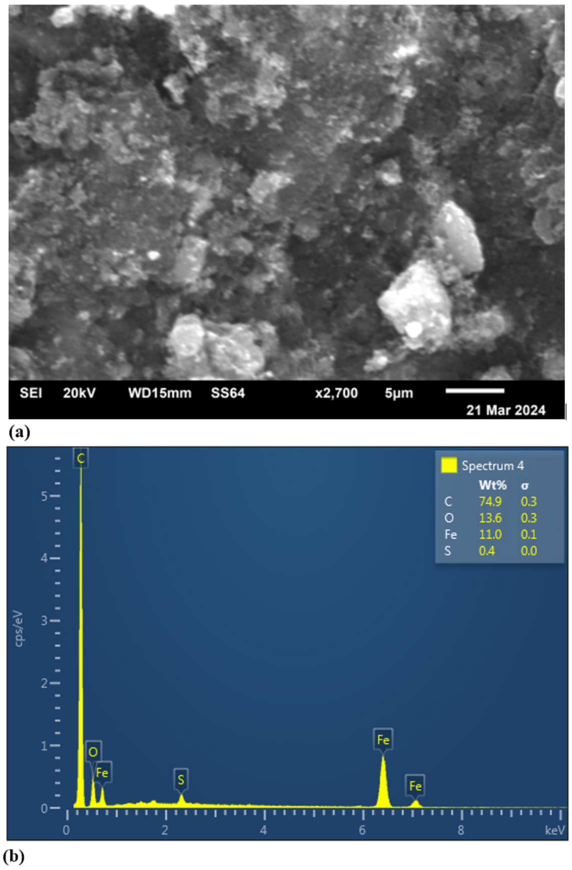


Figure 3) *Composite rGO–Fe_3O_4 obtained at 550°C: (a) SEM image and (b) X-ray EDS spectrum.*

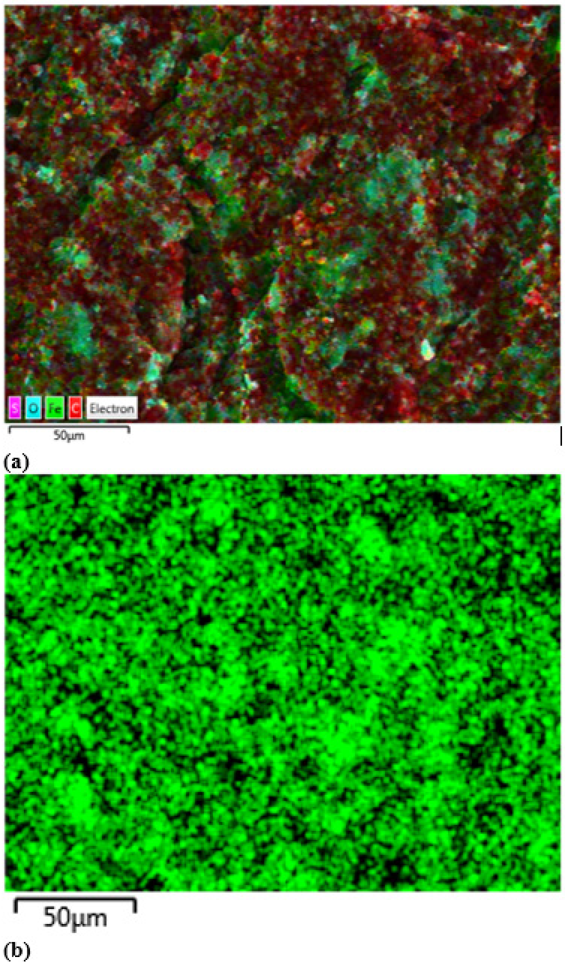


Figure 4) *EDS mapping of chemical elements distribution in rGO–Fe_3O_4 composite obtained at 550°C: (a) general and (b) Fe.*

TABLE 1

Statistics (wt.%) of chemical composition of rGO–Fe_3O_4 composites obtained at 550°C

Chemical element	C	O	Fe	S
Max	74.89	13.8	11.27	0.46
Min	74.88	13.39	10.87	0.45
Average	74.88	13.62	11.05	0.45
Standard Deviation	0	0.21	0.2	0

The exfoliation process is particularly vigorous in GO–metal nitrates systems, which were used to obtain rGO–metal and rGO–metal oxide composites, which were found to have high biocidal activity against bacteria [29]. For nitrate complexes, thermal decomposition temperature decreases to 120°C to 130°C. Obtained by us GO–iron compound composite also undergoes thermal decomposition in vacuum at 170°C to 175°C, resulting in a powder, the volume of which is 2.3 to 2.7 times greater, than that of initial powder. Figure 5 compares the volumes of 0.15 g GO plates and exfoliated rGO volumes obtained from them.

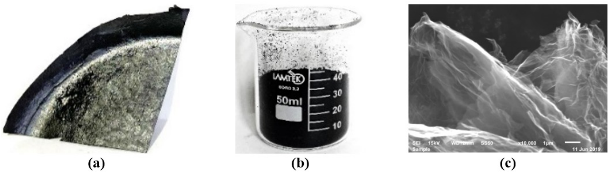


Figure 5) *Images of (a) GO plate and (b) powder of rGO exfoliated from it, and (c) typical SEM image of rGO obtained from GO by vacuum-thermal exfoliation at 230–250°C.*

In the literature, the mechanism of vacuum exfoliation of GO is explained as follows: during heating, water vapor (which it always contains) accumulates between the GO layers, as well as its gaseous decomposition products (the same water vapor, CO_2, CO and vapors of other organic compounds), which develop rather high pressure between the layers and separate them from each other.

The GO samples used in our experiments lose

45% to 55% of their mass during vacuum exfoliation, which means that gases are generated in large quantities between the layers. If the GO composite contains oxidizing components (nitrate ions, metal nitrates, etc.), then the separation occurs by explosion, because the gaseous products of oxidation are also added to the matrix gases. And if the GO composite contains such compounds as silicic or titanic acids or metal hydroxides, then chemical bonds are formed between the GO layers and they slow down the process of exfoliation. As a result, slightly exfoliated powders are obtained.

Thus, different composites experience different degrees of exfoliation. That is, it is possible to adjust the mixing process: this process depends on the method of obtaining GO, the sample aging, degree of its drying, composition of the composite, etc.

We have deposited iron and magnetite phases on exfoliated rGO, as well as G, CB and h-BN, both by co-precipitation and CVD (Chemical Vapor Deposition) methods, which are described in the experimental section. If the co-precipitation method uses matrices not containing large amounts of functional groups (rGO and CB) or are inert (G and h-BN), they are coated with magnetite crystalline phase already at 70°C to 75°C (Figure 6). Based on the results of XRD analysis, we can conclude that the diffractograms of magnetite phases in CB–Fe_3O_4, rGO–Fe_3O_4 and rGO–Fe_3O_4 (obtained at 550°C) composites are almost identical. These results are sharply different from the case of using a newly synthesized GO suspension for a matrix, when a diamagnetic amorphous composite is obtained.

SEM and EDS analysis results for CB–Fe_3O_4 composite are shown in Figure 7. Iron content reaches 13% and is evenly distributed on the matrix surface (Figure 8 and Table 2).

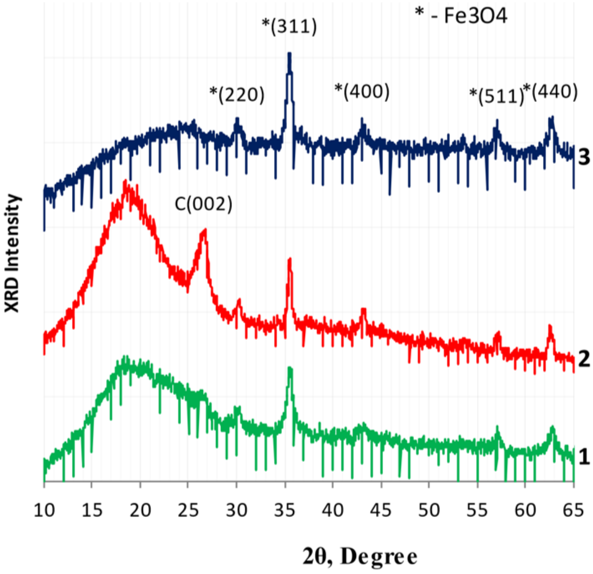
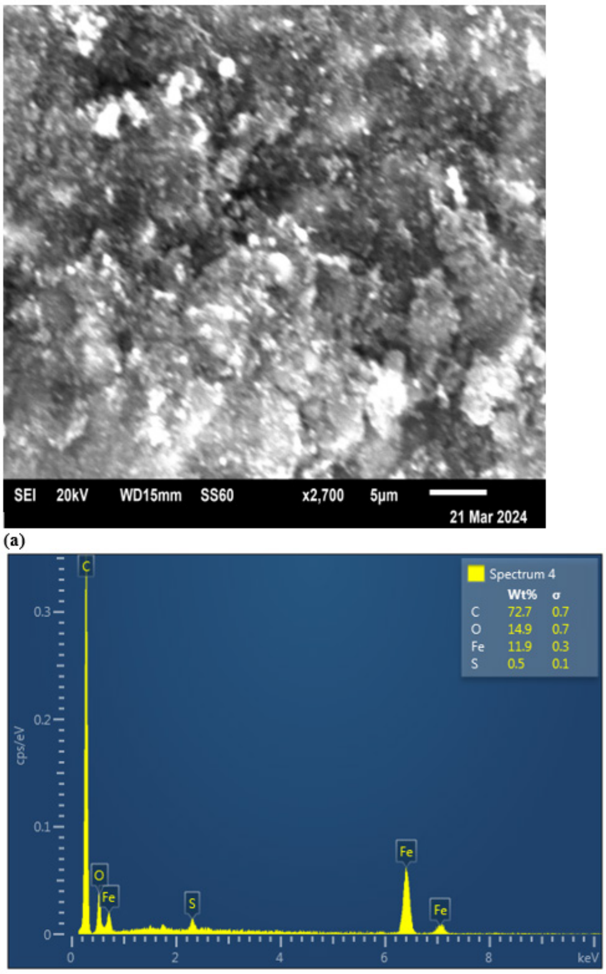


Figure 6) *XRD patterns of (1) CB–Fe_3O_4, (2) rGO–Fe_3O_4 and (3) rGO–Fe_3O_4 (obtained at 550°C) composites.*



(a)

(b)

Figure 7) *(a) SEM image and (b) EDX spectrum of obtained CB–Fe_3O_4 composite.*

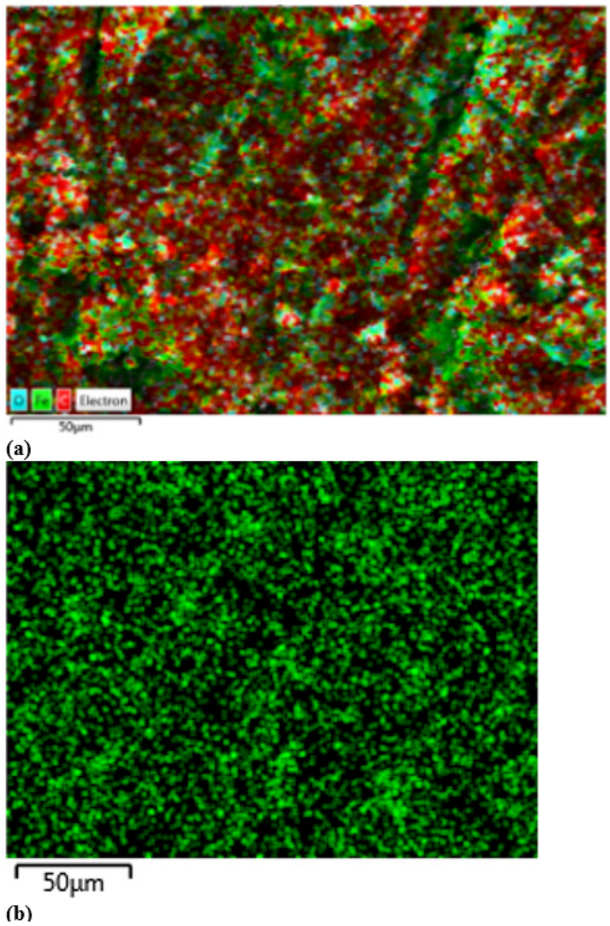


Figure 8) *EDS mapping of chemical elements distribution in CB–Fe_3O_4 composite: (a) general and (b) Fe.*

TABLE 2

Statistics (wt.%) of chemical composition of CB–Fe_3O_4 composite obtained at 550°C

Chemical element	C	O	Fe	S
Max	77.02	14.88	13.88	0.54
Min	72.71	8.55	11.95	0.46
Average	74.79	11.71	12.99	0.51
Standard Deviation	2.16	3.16	0.98	0.04

Composites CB–Fe_3O_4 and rGO–Fe_3O_4 obtained by co-precipitation method (at 550°C) contain about 0.5wt.% sulfur, the main source of which should be the used reagent $FeSO_4.7H_2O$ forming the complexes with GO's oxygen-containing functional groups. Since CB is obtained by pyrolysis of methane, which does not contain any sulfur at all, its source in the CB–Fe_3O_4 composite can only be iron sulfate $FeSO_4$. But there is another source of sulfur. The point is that GO was synthesized using an oxidation system containing 98% sulfuric acid. An acid of such concentration easily intercalates between the graphite layers and reacts both with the graphite itself and with its oxidation products, such as graphite oxide and GO. Anyway, sediment washing should be carried thoroughly.

Practice shows that sulfur compounds are mostly removed from GO in the process of its purification, but a small amount still remains. This is due to the fact that sulfur is covalently bound to GO. In general, removing sulfur from carbon composites is quite difficult and requires the use of high temperatures and chemical reagents that partially decompose them. Since iron forms compounds with carbon already at 700°C, these composites can be transformed into iron carbides or (in a reducing atmosphere) reduced to metallic iron. Another reason why these methods cannot be used in our case is that we will not obtain GO's composites because it will transform into defective G.

When the source of sulfur is iron sulfate reagent, sulfur exists in the composite as sulfate-ion, which, in principle, can be removed by washing the GO suspension multiple, 10 to 15, times with a 5% hydrochloric acid solution, since it favors the sulfate-ions desorption from carbon-materials of various origin. But we washed the suspension only 3 to 4 times and therefore traces of sulfur remained in the composite. Alternatively, one can replace the iron sulfate with another iron salt, such as iron chloride.

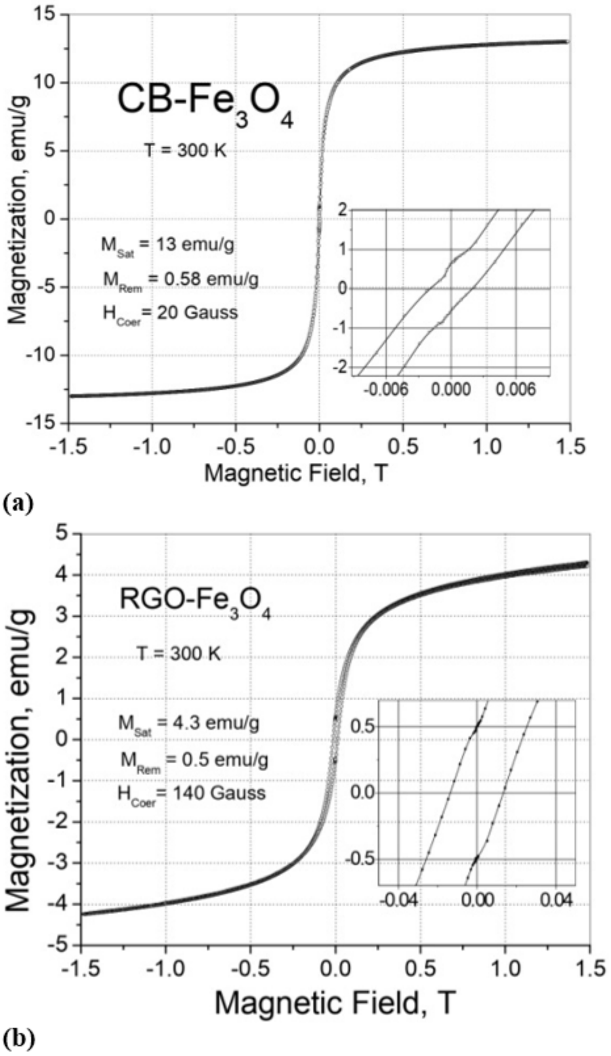
As for the issue of whether the detected amount of sulfur will affect the magnetic properties of the obtained materials, it requires additional experiments comparing sulfur-containing and sulfur-free composites.

What is the nature of interaction between rGO and the iron oxide? Is it of a physical or chemical nature? In attempting to answer these questions, it is useful to take into account the available reports on the mechanisms of interaction of G and GO with metal and oxide nanoparticles.

The synthesis of a nanocomposites, namely, nanofluid based on silver [30] and gold [31] nanopartecles decorated with G-nanosheets dispersed with ethylene glycol, was performed utilizing LLSI (Laser Liquid Solid Interaction) method dedicated to the synthesis of nanostructures and materials in the form of thin film coatings. It is a hybrid chemical–physical approach for the synthesis of metallic and oxide nanoparticles in form of colloidal nanosuspensions. This technique is based on laser–solid interaction with the target immersed in a liquid or covered by a protective liquid layer. In [32], GO was incorporated in the hydrothermally synthesized Co and Mn oxides based electrodes for supercapacitors. GO was amalgamated in these nanocomposites due its great surface area and electrical conductivity.

As for GO and metal oxides, both chemical and physical interactions should take place between them. It is known that insoluble oxides of any metal, and especially hydroxides, contain hydroxide groups that easily react with carboxyl or other oxygen-containing functional groups of GO and form C–O–Me type bonds. Therefore, as long as there exist such groups, C–O–Fe chemical bonds will be realized in any of the composites obtained by us. It should also be taken into account that GO is a macroligand, and therefore in both acidic and alkaline environments forms complexes with metal ions, which are stable chemical compounds and dissociate only when the temperature increases significantly to crystallize their inorganic part into separate phases. In this case, the main form of the composite will be the matrix coated with magnetic phase, in which the physical forces will dominate.

At the next stage, the room temperature magnetization curve – magnetization M as a function M(H) of the applied magnetic field H – of CB–Fe_3O_4 and rGO–Fe_3O_4 (550°C) composites were studied: see the Figure 9. Their key magnetic parameters are: saturation magnetization M_S = 13.0 and 4.3 emu/g, remnant magnetization M_R = 0.58 and 0.50 emu/g, and coercive force H_C = 20 and 140 G, respectively [33-37].



(a)

(b)

Figure 9) *Room temperature magnetization curves for (a) CB–Fe3O4 and (b) rGO–Fe3O4 composites.*

Conclusion

In the presence of newly synthesized GO suspension, co-precipitation of iron(II) and iron(III) compounds is carried out in inert atmosphere at 70°C to 75°C. Magnetic composites rGO–Fe_3O_4 and CB–Fe_3O_4 are obtained at 70°C to 75°C, while in the presence of GO, a non-magnetic composite containing an amorphous iron compound is formed. GO–amorphous iron compound composite undergoes exfoliation, when heated in a vacuum at 170°C to 175°C. Other synthesized composites do not have similar properties. At 550°C, the amorphous composite transforms into the ferromagnetic composite rGO–Fe_3O_4. Some magnetic properties of GO–amorphous iron compound and CB–Fe_3O_4 composites are determined.

Finally, we list some of the latest reports on possible spintronics and electronics applications of the 2D-materials related to the developed ones.

A study of curved graphene in the presence and absence of a real magnetic field conducted to determine its free energy, magnetization and magnetic susceptibility shows that curvature induces effective pseudomagnetic fields associated with oscillating electronic forces opposing deformations. These forces, divergent in flat graphene, suggest that free standing (without a substrate) graphene attains mechanical equilibrium through local corrugations preventing the expected pristine graphene's diamagnetic divergence and producing a finite magnetic susceptibility. In general, electronic structure of graphene-based materials with room-temperature ferromagnetism favors their effective potential application as spintronics.

Composites of segregated conductive polymers (e.g., ultra-high molecular weight polyethylene) with Fe_3O_4-decorated graphite nanoparticles were developed for microwave shielding. Because of abundant surface functional groups and lattice defects, the graphite nanoparticles modified with Fe_3O_4 lead to an essential improvement in the electromagnetic interference shielding due to enhanced microwave absorption in the frequency range of tens of GHz. The possibility of tailoring the graphene electronic properties by its dielectric substrate materials was demonstrated by fabricating the samples of CVD-grown graphene transferred onto silicon wafers covered with alumina, titanium dioxide, and silicon dioxide and measuring the THz transmission spectra of these samples to extract the frequency-dependent conductivity. The sheet resistance of graphene is strongly affected by the underlying dielectric material, while the carrier scattering time remains almost the same. These results show that the carrier concentration in graphene can be efficiently tuned by the material of the dielectric substrate. The systematic review shows that the evolution of EDLC (Electric Double-Layer Capacitors) has significantly benefited from advancements in graphene-based materials, in particular, GO and rGO. The incorporation of GO and rGO in EDLCs leads to significant improvements in their specific capacitance, energy density, and cycling stability.

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