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Obtaining of titanium dioxide (rutile) particles on the surface of reduced graphene oxide in supercritical isopropanol

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Abstract: **Sequential synthesis of rutile modification titanium dioxide particles on reduced graphene oxide in supercritical isopropanol is described. In this case, only graphene oxide was reduced to reduced graphene oxide. A one-stage method (one-pot) was also developed for the preparation of rutile particles on reduced graphene oxide, where supercritical isopropanol was the graphene oxide reducing agent and the reaction medium. The resulting composites were studied using X-ray phase analysis, transmission electron microscopy, and atomic force spectroscopy methods.**

Keywords: **titanium oxides, rutile, graphene oxide, reduced graphene oxide**

UDC 546.2+546.7+546.05

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Contents

1. INTRODUCTION

Works on the graphene compounds synthesis and the study of its unique physical properties in the world form one of the most promising areas in the chemistry and physics of new inorganic functional materials [1–3]. One of the important consequences of the graphene discovery is the interest in obtaining composites of metal and metal oxides on the graphene surface [4,5].

Particularly attractive for use were composites based on RGO and titanium oxides. And a number of these composites are already being successfully used [6-8]. The works are aimed at obtaining a practical result as soon as possible. However, the choice of methods for the synthesis of both titanium dioxide nanoparticles and RGO is quite random. Often used for the synthesis of titanium oxide, as well as for the production of RGO, multistage methods, toxic substances [9]. However, there are practically no works on the synthesis of rutile composites on RGO. In our work, we have developed 2 universal, easy methods for the synthesis of TiO_2 (rutile) particles on RGO using a non-toxic reagent – supercritical isopropanol.

2. EXPERIMENTAL PART

As initial reagents we used: natural graphite (99.9% purity, China), titanium isopropoxide $Ti(OCH(CH_3)_2)_4$ (Titan(IV)-isopropylat, 98%, CAS: 546-68-9), isopropanol C_3H_7OH puriss. spec. TC 2632-011-29483781-09, hexane, analytical grade.

2.1. Production of TiO_2 particles (rutil)

Rutile particles were obtained by hydrolysis of titanium isopropoxide [10]. A solution was prepared from 5 ml of titanium isopropoxide and 15 ml of isopropanol. Distilled water (250 ml) was added to this solution. The solution was stirred at room temperature for 30 minutes. Then the resulting solution was poured into Petri dishes and placed in an oven at 95°C for 19 hours.

The volume of the solution was reduced by half and the resulting solution was dispersed using powerful ultrasound (parameters: frequency – 20.4 kHz, specific power – 0.1-1 W/cm^3) for 25 min. After cooling, they were centrifuged with hexane at 8000 rpm for 25 min. It was dried for several hours at 80°C, and then the resulting powder was washed with ethanol (3 times). The powder was calcined at 800°C for 2 h to get rutile.

2.2. Preparation of graphene oxide and reduced graphene oxide

Graphene oxide (GO) was obtained by the modified Hummers method [11], by sequentially oxidizing natural graphite acids with acids, followed by washing to neutral pH and ultrasonic treatment (parameters: frequency – 20.4 kHz, specific power – 0.1-1 W/cm^3), for 30 minutes until stable dark brown dispersion with c = 1 mg/ml. Part of the GO dispersion was dried to a constant weight, and the resulting dark gray powder was reduced in supercritical isopropyl alcohol using a small-volume autoclave made of EP-943 nickel alloys [12].

2.3. Deposition of rutile particles on the surface of graphene oxide (I metod)

0.1 g of GO and 5.8 ml of C_3H_7OH were added to 0.01 g of TiO_2-rutile, and the mixture was sonicated for 20 min. The solution was poured into a quartz container and placed in an autoclave, which was in an air thermostat at 285°C for 24 hours to restore in supercritical isopropanol. The resulting black precipitate was washed with C_3H_7OH and C_3H_6O in a ratio of 1:1 several times with a centrifuge at 6000 rpm for 10 min, after which the material

was dried at room temperature to constant weight. The composition and structure of rutile composites on the surface of RGO flakes were studied by a complex of physicochemical methods of analysis - X-ray phase analysis, atomic force spectroscopy and transmission electron microscopy

2.4. Obtaining of rutile particles on the surface of reduced graphene oxide (method II or one-pot method)

To 5 ml of $Ti(OCH(CH_3)_2)_4$ (in 15 ml of C_3H_7OH) was added in portions the earlier prepared dispersion of graphene oxide, sonicated for 20 min, with vigorous stirring on a magnetic stirrer. After that, 250 ml of deionized water was added, stirring for 30 minutes and dried at 65°C for 19 hours. The resulting powder was placed in a vacuum furnace at 100°C for 3 hours, followed by annealing at 800°C to obtain rutile on the RGO surface for 4 hours. The resulting powder was washed with C_3H_7OH and C_3H_6O in a ratio of 1:1 using a centrifuge at 6000 rpm for 10 min, after which the material was dried at room temperature to constant weight. Further, the obtained samples were investigated by physico-chemical methods of analysis.

3. RESULTS AND DISCUSSION

3.1. Research methods

To characterize rutile particles as well as composites of GO-rutile particles and RGO-rutile particles, a set of methods was used: *X*-ray phase analysis (XPA), transmission electron microscopy (TEM), atomic force microscopy (AFM).

The sizes and shapes of nanoparticles in a dispersion in an organic solvent and in nanocomposites were determined by analytical processing of TEM images obtained by TEM on a JEOL JEM-2100 setup at an accelerating voltage of 100 kV and 150 kV, respectively.

Before recording, the samples were placed on copper grids 3.05 mm in diameter covered with a polymer film. Transmission images were taken at magnifications up to 500,000 x, and a 0.4 μm diameter limiting diagram was used for electron diffraction imaging.

The ratio $\lambda L = Rd$ was used to determine the interplanar spacing using the reflections of the diffraction pattern in an electron microscope. The length of the chamber in an electron microscope was determined by passing electrons through all lenses.

AFM measurements were made in air using a Nanoscope III microscope (Digital Instruments) equipped with a 150 μm scanner in tapping and contact modes. We used commercial non-contact silicon cantilevers with a hardness of 11.5 N/m and a resonant frequency in the range of 193-325 kHz. The stiffness of the used contact cantilevers was 0.01 or 0.3 N/m. The scanning frequency is about 2 Hz. All AFM images were recorded simultaneously in two channels: height and deviation (for the contact mode) or height and amplitude (for the tapping mode). Image processing was performed using the FemtoScan program (Filonov AS et al., 2001).

Powder particles prepared at IGIC were diluted with distilled water. The resulting suspension was shaken, and 20 μl was taken from it to be applied to a fresh chip of mica, which was used as a substrate. The obtained samples were dried in a stream of nitrogen.

3.1.2. Study of the obtained GO and RGO

Fig. 1 shows the radiograph of the GO. The results of X-ray phase analysis showed the presence of one phase of GO, which is characterized by the presence of two peaks: the peak at 130 has a high intensity, and the peak at 430 is much less pronounced. The peak at 280 corresponds to the graphite peak.

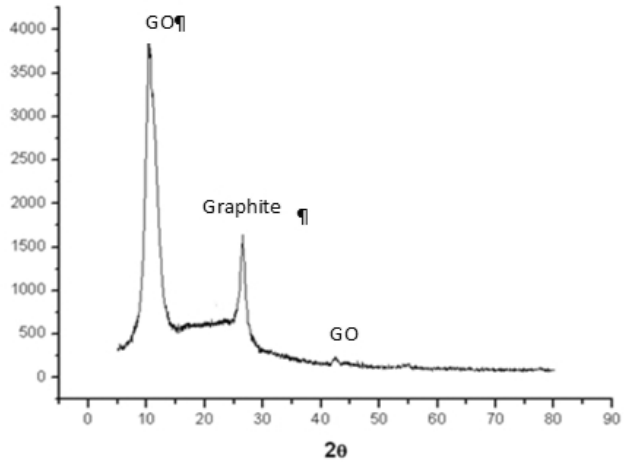


Fig. 1. *X-ray diffraction pattern of GO oxide.*

The presented TEM micrograph (**Fig. 2**) refers to GO.

Fig. 3 shows the result of X-ray phase analysis of the RGO. It is known that the RGO peak is similar to the graphite peak, but is shifted by 20, i.e. the peak related to RGO is 260, as shown in the image.

First, graphene oxide was obtained, after placing GO in the SCI, successful reduction occurred, and fully reduced graphene (RGO) was obtained with one peak at 260. This can be seen in the X-ray pattern (Fig. 3).

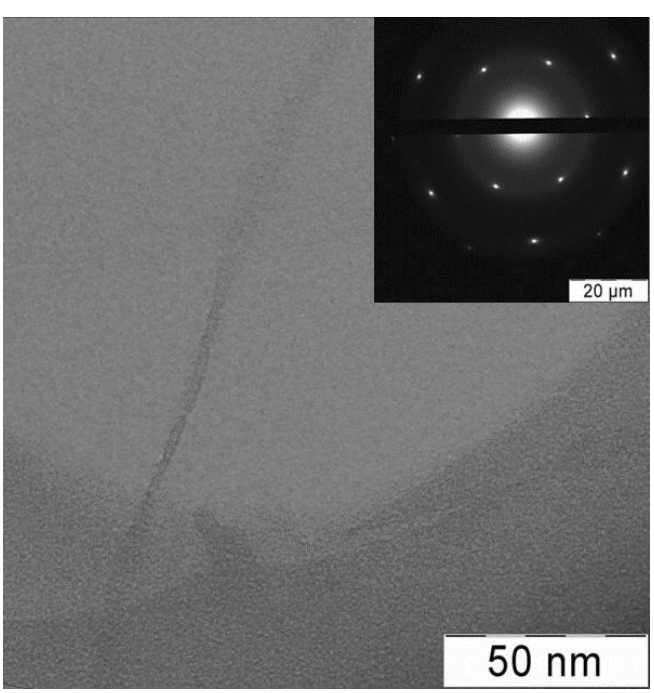


Fig. 2. *Micrograph of GO oxide.*

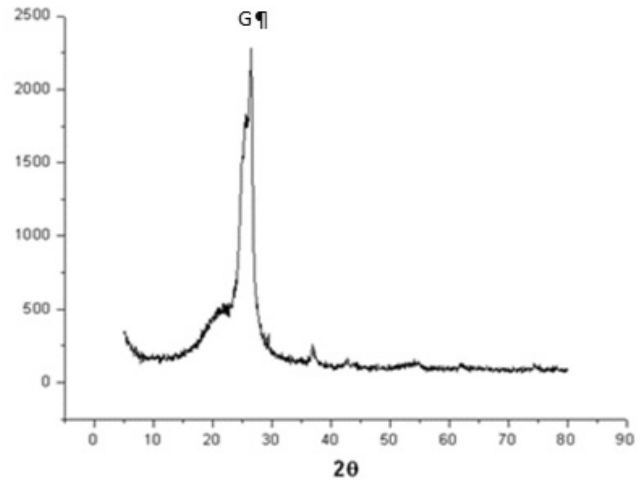


Fig. 3. *X-ray of the RGO.*

Fig. 4 shows a TEM micrograph of the RGO after SCI.

3.2. Deposition of rutile particles on the surface of graphene oxide

GO (0.1 g) and isopropanol C_3H_7OH (5.8 ml) were added to 0.01 g of titanium oxide (rutile), the mixture was treated with ultrasound (frequency – 20.4 kHz, specific power – 0.1-1 W/cm^3) within 20 min. The resulting crystalline rutile (0.069 g) was mixed with graphene oxide (0.135 g) and isopropanol (5.8 ml). The resulting solution was poured into a quartz container and placed in a small-volume autoclave for recovery in the SCI.

Small-volume autoclaves made of EP-

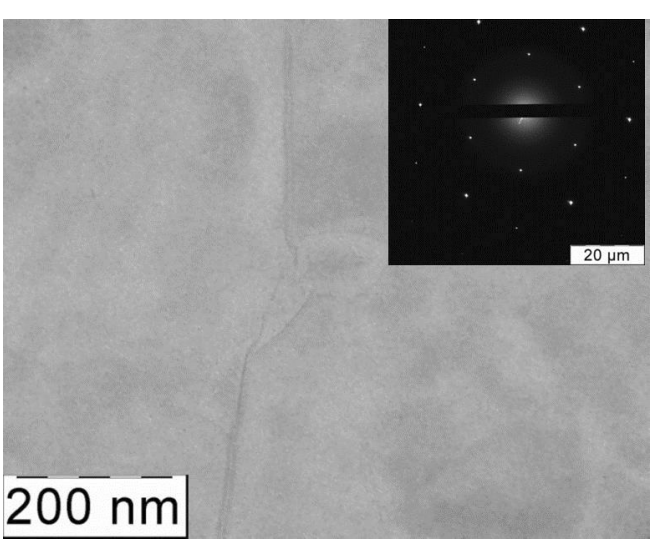


Fig. 4. *Micrograph of RGO.*

943 nickel alloys [13] were used for the experiment. A quartz container containing a dispersion of titanium dioxide, GO, and isopropanol was placed in the autoclave. The autoclave, in turn, is placed in an air thermostat, and kept at a given temperature for the required time (time in supercritical 18 hours, temperatures 280-285°C).The resulting black precipitates were redispersed in isopropanol using a centrifuge at 6000 rpm 3 times. After that, the powders were dried at room temperature to constant weight. Further, the resulting black precipitates were washed with isopropanol and acetone in a ratio of 1:1 several times, centrifuged at 6000 rpm for 10 minutes, after which the material was dried at room temperature to constant weight. The composition and structure of rutile composites on the surface of RGO flakes were studied using a complex of XRD, AFM, and TEM methods.

Rutile particles on the GO surface were obtained using isoropanol as a medium. The choice of isopropanol as a solvent was due to the fact that the synthesis of nanoparticles in it is relatively easy to control, reproducible and allows obtaining particles of a certain size. In addition, this solvent prevents particle agglomeration due to the interaction of functional –OH – groups with the particle surface.TiO_2.

3.3. Methods for the obtained samples studying

To characterize particles of titanium oxides, as well as composites of GO-rutile and RGO-rutile particles, a set of methods was used: X-ray phase analysis (XPA), transmission electron microscopy (TEM), and atomic force microscopy (AFM).

The analysis of the X-ray diffraction pattern of rutile presented in **Fig. 5** showed the presence of one TiO_2 phase (JCPDS # 86-0147, tetragonal, primitive space group $P4_2/$

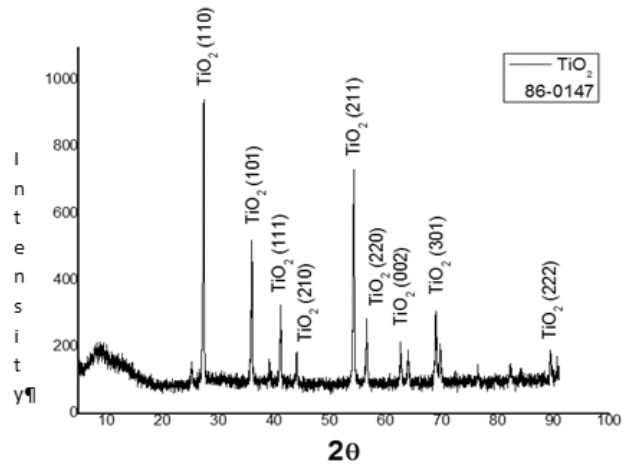
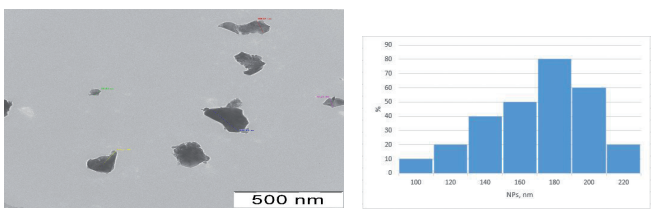


Fig. 5. *X-ray diffraction pattern of TiO2 particles (rutile).*

mmm, $a = 4.594$ Å, $c = 2.958$ Å). The reflections in the diffraction pattern are narrowed, which indicates the large sizes of the studied particles. The calculation using the Debye-Scherer formula showed that the average particle size of rutile is about 170-180 nm.

Fig. 6 shows an electron microscopic image of TiO_2 (rutile) particles, from which it can be seen that the studied sample has a shape close to spherical, and also has a narrow size distribution for an aggregate of more than 100 particles. The size distribution histogram showed that the average NP size is 180 nm.

The results of the study of the rutile/RGO X-ray pattern (**Fig. 7**) showed the presence of two phases: TiO_2 (JCPDS # 86-0147, tetragonal, space group $P4_2/mmm$, $a = 4.594$ Å, $c = 2.958$ Å) and graphene. The reflections of titanium oxide (rutile) on the diffraction pattern are narrowed, which indicates a significant size of the particles under study.



a *b*

Fig. 6. *a) micrograph of rutile particles, b) size distribution histogram.*

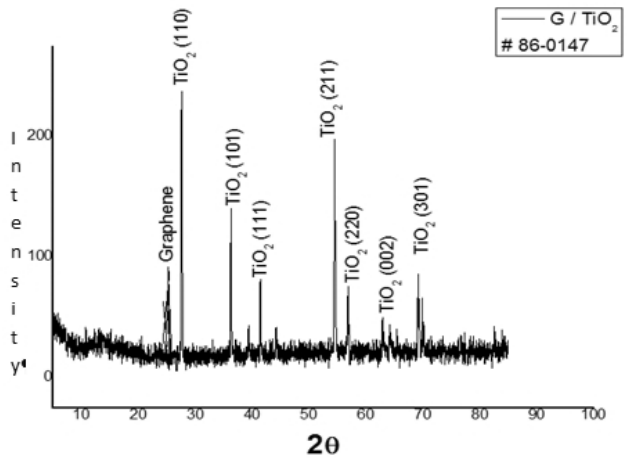


Fig. 7. *Rutile/RGO radiograph.*

According to the Debye-Scherer formula, it was calculated that the average particle size of TiO_2 (rutile) is about 170-180 nm.

According to the AFM images (**Fig. 8**) of rutile/RGO particles, it can be said that rutile particles are located only on the surface of graphene flakes, their average height is 180 nm. The thickness of graphene flakes is 5 nm, and the lateral size of graphene flakes is 1 μm.

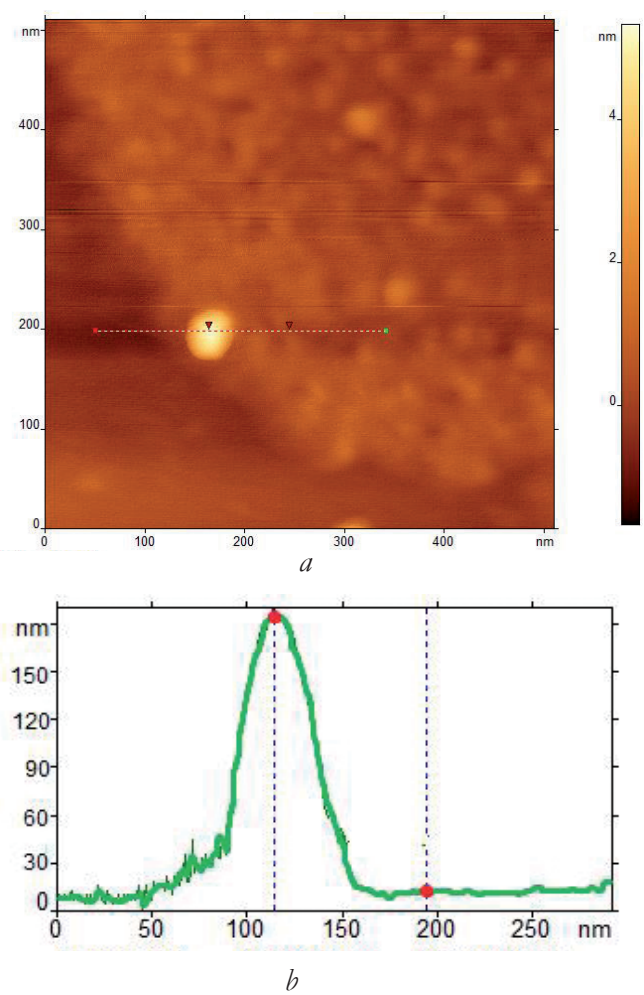


Fig. 8. *a) AFM/RGO image), b) longitudinal section along the cut line.*

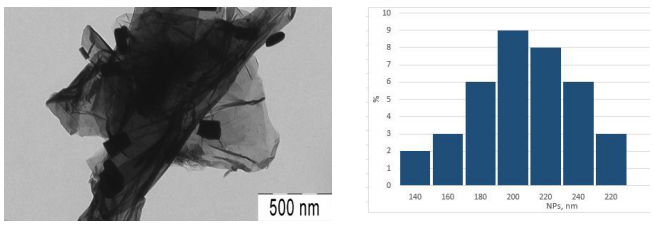


Fig. 9. *a) micrograph of rutile/RGO), b) size distribution histogram.*

The micrograph of the rutile/RGO sample (**Fig. 9**) under study clearly shows that the particles are immobilized on the graphene surface. Also, according to the size distribution histogram, the average size of TiO_2 nanoparticles was 200 nm

The XRF analysis is shown in **Fig. 10**. The image shows the presence of two phases: TiO_2 (# 78-1510, tetragonal, space group $P4_2/mmm$) and graphene. The reflections of the studied titanium oxide sample on the X-ray diffraction pattern are expanded, which indicates the large size of the nanoparticles. The peak at 260 corresponds to the graphene peak. The average size was calculated using

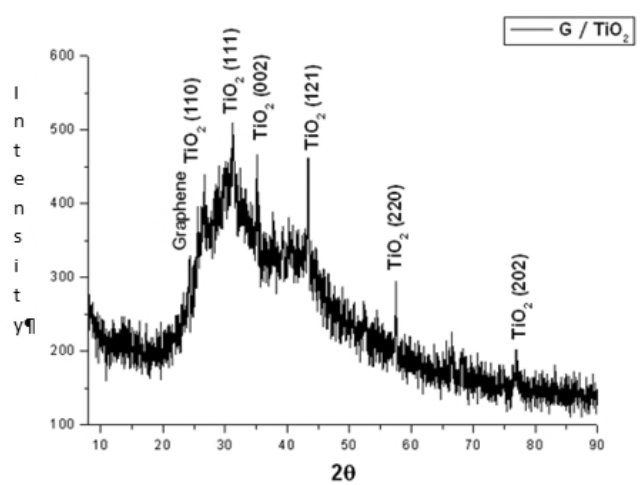
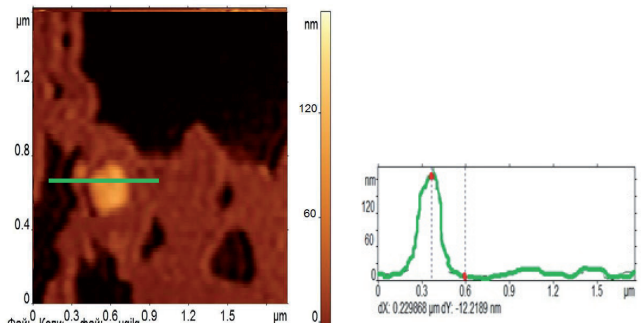


Fig. 10. *X-ray diffraction pattern of rutile/RGO composite.*



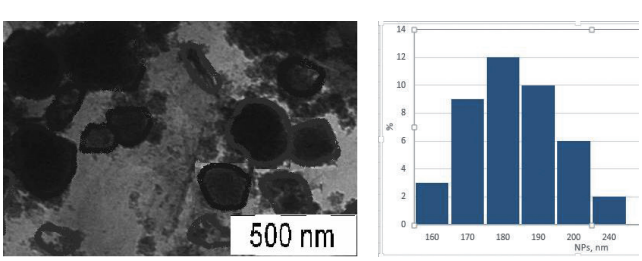
a *b*

Fig. 11. *a) AFM image of RGO rutile particles, b) longitudinal section along the cut line.*

the Debye-Scherer formula, which was 180 nm. According to the data obtained, it can be seen that, after reduction in supercritical isopropanol, titanium oxide nanoparticles were not reduced to Ti, which is typical for anatase powders, as was shown earlier [13].

The AFM micrograph (**Fig. 11**) shows that rutile particles are on the surface of graphene flakes. The particle size of rutile is 180 nm, which corresponds to the XRF data. Also, according to the longitudinal section along the cut line, it can be said that the thickness of the graphene flakes is 3 nm, and the lateral size of the graphene flakes is 1.5 μm.

According to the results of transmission electron microscopy in **Fig. 12**, it can be seen that the resulting rutile particles have a shape close to spherical, and they are also immobilized on the surface of graphene flakes. A histogram of the size distribution was plotted and the average particle size of rutile was shown to be 180 nm.



a *b*

Fig. 12. *a) micrograph of rutile/RGO, b) size distribution histogram.*

The resulting rutile particles on RGO were characterized by physico-chemical methods and their size was determined, which was 180 nm. When particles were fixed on the surface of graphene flakes, the particle size increased to 200 nm. Rutiles were also obtained on the RGO surface by the one-pot method, the size of which was also 180 nm. If we compare the thickness of graphene flakes in both cases, then in the one-stage method it was 3 nm (up to 8 layers), which is less than in the two-stage method.

Comparing the two-stage method and the one-pot method, we can say that in the case of the one-stage method, the particle size turned out to be somewhat smaller, and the thickness of the graphene flakes was less, it was 5 layers. In addition, the one-stage synthesis method takes 2 times less time compared to the two-stage one. However, the preparation of rutile nanoparticles (with a rutile particle size of less than 100 nm) on RGO requires further experiments.

4. CONCLUSION

1. As a result of the work done, graphene-TiO_2 (rutile) composites were obtained and characterized by two methods. The methods used are based on the reduction of SCI graphene oxide.

2. It has been shown that when using a dispersion of pre-prepared nanoparticles of metal oxides and graphene oxide, composites are formed containing rutile microparticles on the surface of graphene flakes.

Rutile microparticles are 180 nm in size, graphene flakes are 3-5 layers thick with a lateral size of up to 500 nm.

3. It is shown that it is possible to obtain the same composites in one stage (one pot method) by introducing a metal salt and graphene oxide into the reaction mixture, followed by SCI reduction.

4. SCI is used in all processes as a reaction medium and as a reducing agent for graphene oxide.

5. The obtained composites were characterized by the following methods: X-ray phase analysis, atomic force microscopy, transmission electron microscopy.