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Preparation of titanium oxide nanoparticles on the surface of reduced graphene oxide in supercritical isopropanol

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Abstract: **Sequential synthesis of anatase modification titanium oxide nanoparticles 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 titanium oxide nanoparticles on reduced graphene oxide, where supercritical isopropanol was the graphene oxide reducing agent and the reaction medium. The resulting nanocomposites were studied using X-ray phase analysis, transmission electron microscopy, and atomic force spectroscopy methods.**

Keywords: **nanoparticles, titanium oxides, anatase, graphene oxide, reduced graphene oxide**

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Contents

1. INTRODUCTION

A variety of carbon nanomaterials have long been widely used in various areas of industrial practice, and a large number of studies have been devoted to their study. In recent years, special attention has been drawn to graphene, which is a two-dimensional single layer of carbon, only one sp^2-carbon atom thick. Works on the synthesis of graphene compounds 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].

The design of nanomaterials from nanoparticles is promising due to the fact that nanoparticles can be obtained in a wide range of sizes, various shapes, compositions, and crystal structures. They can interact with the environment in different ways. Among numerous functional nanomaterials, researchers are currently attracting the attention of composite compounds based on graphene and nanoparticles on its surface, due to the promise of such composites for use in catalysis, fuel cells, and other areas [4,5]. Nanocomposites based on reduced graphene oxide (rGO) and titanium oxide (TiO_2) turned out to be especially attractive for use. A number of these nanomaterials are already being successfully used.

The literature has already described methods for the preparation of TiO_2–rGO composites, mainly the reduction of graphene oxide and titanium compounds by various synthesis methods [6–8]. 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]. The work is aimed at obtaining a practical result as soon as possible.

In the present work, two universal, easy methods for the synthesis of TiO_2 nanoparticles (anatase polymorph) on rGO using a nontoxic reagent, supercritical isopropanol, have been developed.

2. EXPERIMENTAL PART

Natural graphite (purity 99.9%, China), titanium isopropoxide Ti $(OCH(CH_3)_2)_4$ (Titan (IV)-isopropylat, 98%), isopropyl alcohol C_3H_7OH high purity grade, hexane Analytical analysis, ethanol C_2H_5OH high purity, acetone C_3H_6O high purity.

2.1. Preparation of TiO_2 nanoparticles (anatase)

Titanium oxide nanoparticles were obtained by hydrolysis of titanium isopropoxide [10], where 5 ml of $Ti(OCH(CH_3)_2)_4$ was mixed with 15 ml of C_3H_7OH and 250 ml of deionized water. Thoroughly stirred for 30 min, then dried in an oven at 65°C for 19 hours, washed with ethanol C_2H_5OH and dried to constant weight at 80°C. The resulting powder was repeatedly washed with C_2H_5OH and dried in a vacuum oven at 100°C for 3 hours, followed by annealing at 250°C for 2 hours.

2.2. Preparation of graphene oxide and reduced graphene oxide

Graphene oxide (GO) was obtained by the modified Hummers method [11], by successively oxidizing natural graphite with acids, followed by washing to neutral pH and ultrasonic treatment (frequency, 20.4 kHz, specific power, 0.1–1 W/cm^3), for 30 min until obtaining a stable dispersion of dark brown color with a concentration *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 TiO_2 nanoparticles on the surface of reduced graphene oxide (I method)

To 0.1 g of GO and 5.8 ml of C_3H_7OH were added to 0.01 g of TiO_2, and the mixture was sonicated for 20 min. The solution was poured into a quartz container and placed in an autoclave, which is in an air thermostat at 285°C for 24 hours for recovery 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 obtained samples were investigated by physicochemical methods of analysis.

2.4. Preparation of TiO_2 nanoparticles on the surface of reduced graphene oxide (II method 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 oven at 100°C for 3 hours, followed by annealing at 250°C to obtain anatase 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. The obtained samples were investigated by physicochemical methods of analysis.

3. RESULTS AND DISCUSSION

In this work, TiO_2 nanoparticles were obtained on the surface of reduced graphene oxide using supercritical isopropanol as a medium. The choice of solvent is due to the fact that the synthesis of titanium oxide nanoparticles in it is easily controlled, reproduced, and makes it possible to obtain particles of certain sizes. In addition, it prevents particle agglomeration due to the interaction of –OH functional groups with the surface of TiO_2 nanoparticles. To implement the idea, it was decided to deposit TiO_2 nanoparticles on the surface of graphene oxide and also reduce the resulting sample to rGO in supercritical isopropanol.

3.1. Research methods

The resulting nanocomposites were studied by powder *X*-ray diffraction (Bruker D8 Advance; reflection mode, CuKα radiation, 35 kV, 30 mA, λ = 1.54056 Å), transmission electron microscopy (TEM) (JEOL JEM-2100; at an accelerating voltage of 100 kV and 150 kV, respectively) and atomic force microscopy (AFM) (Nanoscope III, Digital Instruments; equipped with a 150 μm scanner in tapping and contact modes, scanning frequency 1–3 Hz).

3.2. Results of the obtained nanoparticles

According to the obtained XRD data, the analysis of *X*-ray diffraction patterns proved that there are reflections corresponding to the TiO_2–anatase phase (JCPDS No. 84-1280). According to the Debye-Scherrer formula, the average particle size was calculated, which is 5-6 nm (**Fig. 1**).

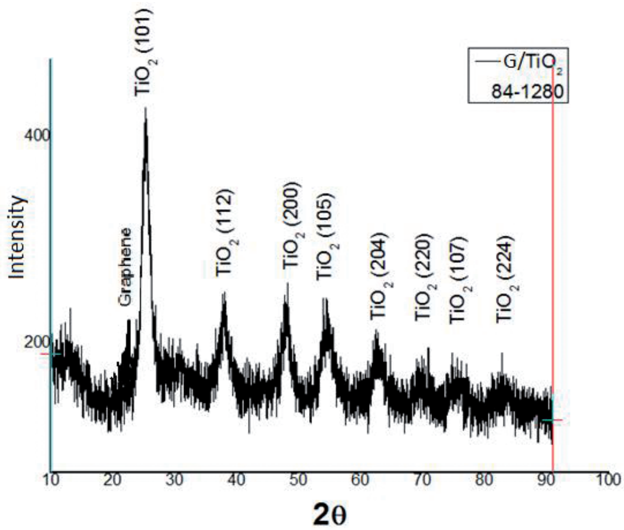


Fig. 1. *X-ray pattern of TiO_2 (anatase) nanoparticles.*

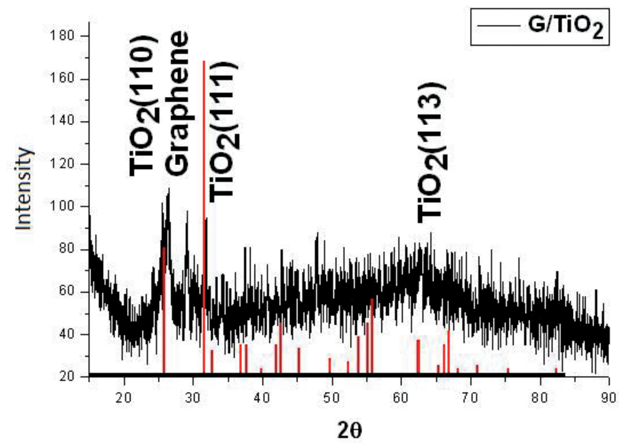


Fig. 3. *X-ray pattern of TiO_2 (anatase) nanoparticles on the surface of rGO flakes.*

The micrograph of a sample of TiO_2 (anatase) nanoparticles shown in **Fig. 2**, it is clearly seen that the particles have a shape close to spherical, the crystal structure is quite homogeneous, and according to the size distribution histogram they have an average size of ~5 nm, at the same time, the distribution, in general, is quite narrow.

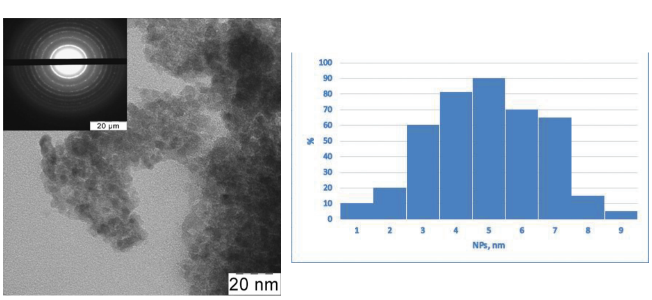
Thus, titanium oxide nanoparticles with anatase polymorphic modification with an average particle size of ~5 nm were obtained, which coincides with the data obtained by XRD and TEM.

I method

After processing in the SKI, *X*-ray phase analysis showed that the resulting samples retain reflections corresponding to the TiO_2 phase (No. 84-1750) and a reflection appears in the region $2\theta = 26°$, corresponding to the graphene phase, which indicates the complete reduction of graphene oxide to graphene (**Fig. 3**). The reflections related to anatase are strongly narrowed in the diffraction pattern, which indicates small particle sizes in the nanocomposite. The size of anatase particles calculated by the Debye-Scherrer formula was ~8 nm.

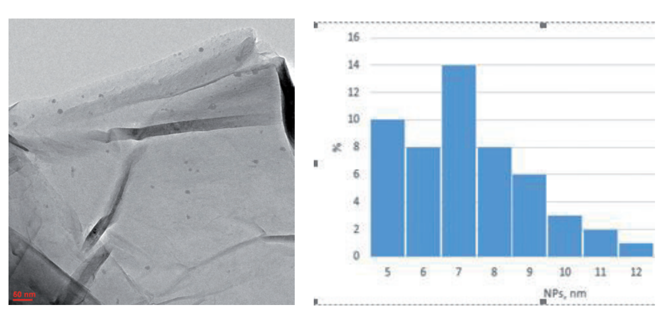
A micrograph of a sample of the TiO2 nanocomposite obtained on the surface of reduced graphene oxide is shown in **Fig.4**.

The study of titanium oxide nanoparticles by the TEM method



a *b*

Fig. 2. *Micrograph of TiO_2 (anatase) nanoparticles (a); size distribution histogram of nanoparticles (b) (more than 100 flakes counted).*



a *b*

Fig. 4. *Micrograph of TiO_2 (anatase) nanoparticles on the surface of rGO flakes (a); size distribution histogram of nanoparticles (b) (more than 50 flakes counted).*

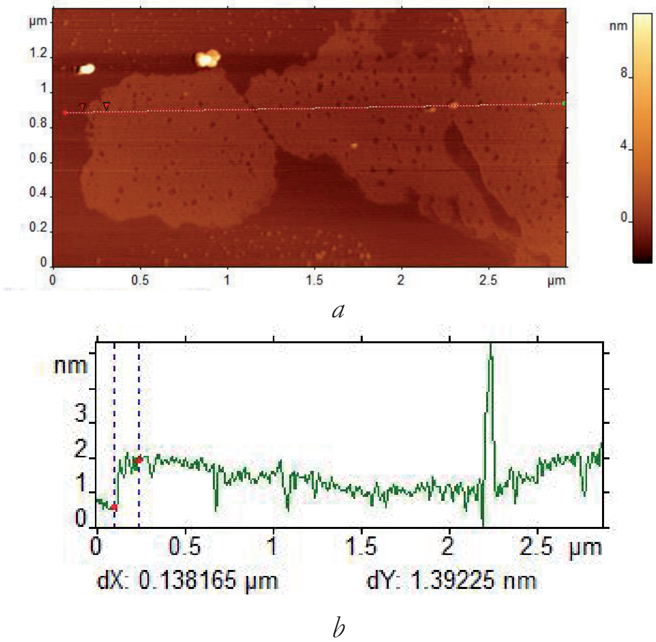


Fig. 5. *AFM image of* TiO_2 *(anatase) nanoparticles on the surface of rGO flakes (a); longitudinal section along the cut line (b).*

showed that their crystal structure is quite homogeneous, and the shape is close to spherical. It is also clearly seen that the nanoparticles are immobilized on the surface of the reduced graphene oxide and are not in a separate phase. From the size distribution histogram, which is quite narrow, the TiO_2 nanoparticles have an average size of ~7 nm.

On **Fig. 5** shows an AFM image showing anatase nanoparticles on the surface of rGO flakes. The micrograph confirms that the nanoparticles are immobilized on the surface of reduced graphene oxide, the thickness of which is ~1.5 nm, and the height of the titanium oxide particles is ~7 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].

II method or one-pot method

The analysis of X-ray diffraction patterns of the obtained nanocomposites by the one-pot method confirms the presence of two phases: anatase modification titanium oxide (No. 84-1750) and graphene (**Fig. 6**). Reflexes of anatase, strongly behind the ears, which indicates the small size of titanium oxide particles. The reflection in the region $2\theta = 26°$ proves the complete reduction of graphene oxide to graphene. According to the Debye-Scherrer formula, the average size of nanoparticles was calculated from the half-width of the peaks, which was ~6 nm.

AFM results (**Fig. 7**) show that titanium oxide nanoparticles are immobilized on the surface of rGO flakes and are located at a certain distance from each other. The average height of TiO_2 nanoparticles is ~8 nm. The thickness of the reduced graphene oxide flakes is ~0.6 nm, while the lateral size of the flakes is ~500 nm.

The micrograph (**Fig. 8**) clearly shows that titanium oxide nanoparticles are located at a certain distance from

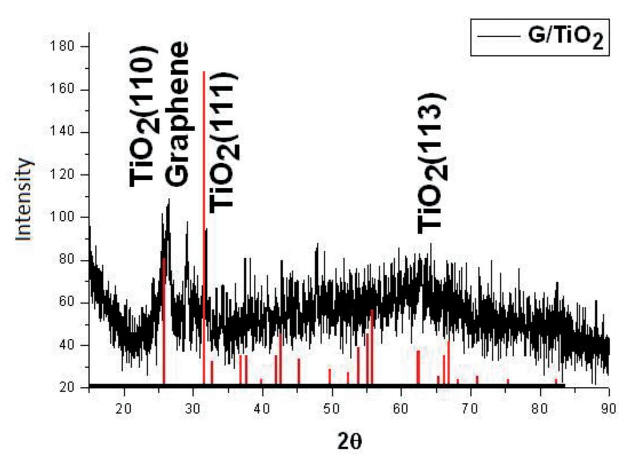


Fig. 6. *X-ray pattern of* TiO_2 *(anatase) nanoparticles on the surface of rGO flakes (one-pot method).*

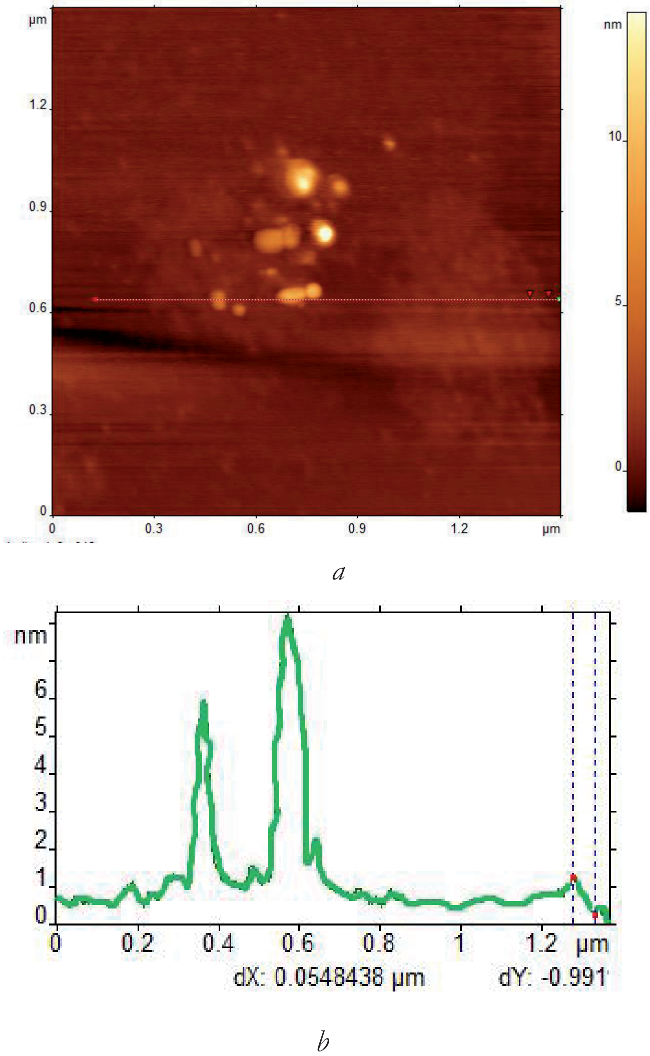


Fig. 7. *AFM image of TiO_2 (anatase) nanoparticles on the surface of rGO flakes (one-pot method) (a); longitudinal section along the cut line (b).*

each other and are immobilized on the surface of rGO flakes. According to the size distribution histogram, titanium oxide particles have an average size of ~7 nm

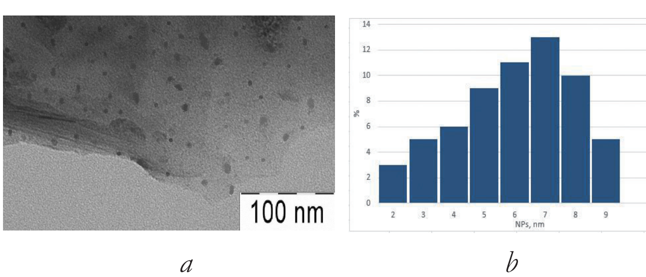


Fig. 8. *Micrograph of TiO_2 (anatase) nanoparticles on the surface of rGO flakes (a); size distribution histogram of nanoparticles (b) (more than 50 flakes counted).*

Using the one-pot method, a TiO_2 nanocomposite in the anatase polymorph with an average particle size of ~8 nm was obtained on the surface of reduced graphene oxide flakes.

4. CONCLUSION

According to the results of XRD, TEM and AFM, the size of TiO_2 (anatase) nanoparticles is about ~5-6 nm. After their deposition on the surface of graphene flakes, the size slightly increased to 7 nm. According to the one-pot method, the size of titanium oxide (anatase) nanoparticles was 8 nm. If we compare the thickness of graphene flakes, then in the first method it was 1.5 nm (4-5 layers). This is more than in the one-stage method, which was 0.6 nm (1-2 layers). According to the results of the study, both methods show close results, but in the one-pot method, the thickness of the flakes is 1-2 layers. Also, this method has a time advantage.

Thus:

1. Easy and convenient methods have been developed for the preparation of anatase nanoparticles on rGO in a non-toxic reagent, supercritical isopropanol.
2. As a result of the work done, rGO–TiO_2 (anatase) nanocomposites were obtained and studied using two methods. The methods used are based on the reduction of graphene oxide in supercritical isopropanol.
3. It has been shown that when using pre-prepared anatase and graphene oxide nanoparticles, composites are formed containing nanoparticles on the surface of rGO-TiO_2 (anatase) 7 nm flakes.

4. rGO flakes of 3-5 layers with a lateral size of up to 500 nm were obtained.
5. It has been shown that the same composites can be obtained in one stage (one-pot method) by introducing a metal salt and graphene oxide into the reaction mixture, followed by reduction with supercritical isopropanol.
6. Supercritical isopropanol is used in all processes as a reaction medium and as a reducing agent.
7. The resulting nanocomposites were studied by XRD, AFM, and TEM methods.

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