

# ELECTROPHORETIC SEDIMENTATION OF GRAPHENE OXIDE ON CYLINDRICAL SURFACE OF MICROWIRES

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*Abstract.* Electrophoretic sedimentation of graphene oxide on both the flat surface of copper foils and on the cylindrical surface of copper wires was investigated. It is shown that during an electrophoresis of the order of minutes, it is possible to obtain graphene oxide (GO) films of micron thicknesses on copper wires, metal foils and anodes of complex shape. It has also been established that self-deposition occurs (without applying voltage) GO from dispersion on Cu, Ni, Al metals. This process is much slower than electrophoresis.

*Keywords:* graphene, graphene oxide, electrophoresis, films, wires

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## 1. INTRODUCTION

Graphene oxide (GO) films, easily converted into graphene films on the surface of substrates, have recently been extensively studied in the design of both supercapacitors, sensors, and other devices. [1]. As the authors of a number of publications note, graphene oxide electrophoresis (GO) can prove to be a promising method of obtaining new materials for new technologies that require materials with unique properties. For practical purposes, it is desirable to increase the adhesion to the substrate and to monitor the continuity of the GO film.

This applies both to the flat surface of the substrate, and to the cylindrical surface of wires, filaments, fibers [2]. In some works, the method used to apply such coatings is the electrophoresis of aqueous dispersions of graphene oxide

using deionized water, alternating current electrophoresis or pulsed electrophoresis. However, for practical purposes, more detailed studies of this non-standard process are needed.

In this paper, the electrophoretic sedimentation of graphene oxide on both the flat surface of copper foils and on the cylindrical surface of copper wires was investigated. It is shown that during an electrophoresis of the order of minutes, it is possible to obtain GO films of micron thicknesses on copper wires, metal foils and anodes of complex shape.

It has also been established that self-deposition occurs (without superimposing the potential) GO from the dispersion onto Cu, Ni, and Al metals. This process is much slower than electrophoresis.

## 2. EXPERIMENTAL PART

### 2.1. Materials and methods

As the microfibers used copper wire with a diameter of 120  $\mu\text{m}$ -200  $\mu\text{m}$ ; quartz filaments (both individual fiber and fiber bundle) with a diameter of 10  $\mu\text{m}$ -12  $\mu\text{m}$ . Wire made of Cu with a diameter  $d = 200 \mu\text{m}$  was electropolished. Anodic polishing of the wires was carried out in a worked (pre-electropolished foil from Cu) acid  $\text{H}_3\text{PO}_4$  (15M) at a voltage of +1.2V; polishing lasted about 50 minutes.

The polishing quality was assessed visually when observing the surface of the wires in an optical microscope Neophot 32 Carl Zeiss JENA with an increase of x500. The polished surface of the wires did not have grooves of dragging and protrusions more than 1  $\mu\text{m}$ .

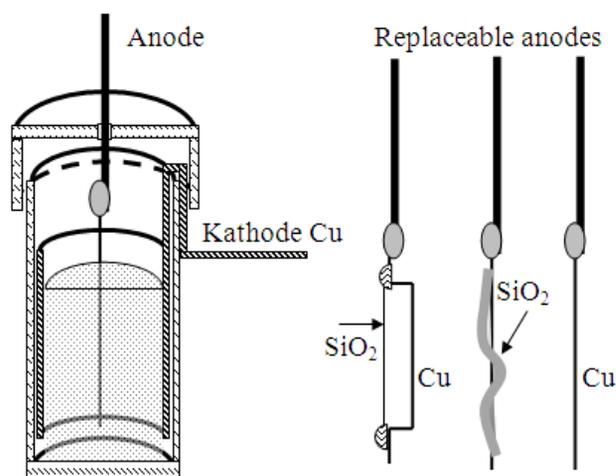
A standard dispersion with a concentration of 1.2-2.3 mg/ml graphene oxide (GO) was prepared by ultrasonic treatment of

the GO sample, followed by centrifugation and separation of the precipitate. For electrophoretic studies, an electrochemical cell was used, as in **Fig. 1**. The internal resistance of the cell with different batches of distilled water varied in the range of 13 k $\Omega$  to 17 k $\Omega$ .

The cell consists of a cylindrical vessel with a diameter of 25 mm and a height of 100 mm. On the inner wall of the cylinder is a cathode of copper foil. The anodes were of several types:

1. for fibers that conduct current, the fiber itself was used as an anode;
2. for conductive fibers, a conductive anode was inserted into the cell, in the surface layer of which the fiber was fixed in one way or another. The anode was copper wire.

For electrophoresis, the potentiostat P-30J from Elins was used. All studies were performed at room temperature. The voltage from 0.4 V to 1.2 V was used, currents from a few mc to dozens of mA.



**Fig. 1.** Scheme of the electrochemical cell for electrophoretic deposition of graphene oxide on the fibers. On the left - electrochemical cell, on the right - ways of fastening fibers to the anode, depending on their nature.

Depending on the nature of the fiber and the deposition time, the color of the coating varied from greenish brown to black.

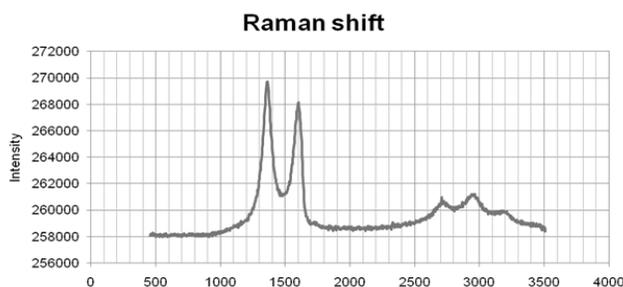
The product was analyzed as follows:

1. visual observation of the presence of coating (deposition) of the fiber after electrophoresis with an increase in the microscope x500;
2. the presence of GO or reduced graphene oxide (rGO) in the coating was established by the method of Raman spectroscopy (Raman spectroscopy);
3. the elemental composition of the coating was established by X-ray photoelectron spectroscopy (XPS);
4. the morphology of the coating was studied by the scanning electron microscope (SEM) method.

**2.2. Removal of coating from the surface of the fiber**

A sample of the coated copper fiber was lowered into a solution of FeCl<sub>3</sub> at a concentration of 2.5 M and kept at room temperature for several days. In this case, complete dissolution of the copper fiber occurred and a GO tubule with an outer diameter of 2-3 microns greater than the diameter of the fiber was obtained.

When removed from solution, washed in water and dried GO, the tubule retained the shape of a hollow cylinder with an internal diameter corresponding to the diameter of the original fiber. A typical Raman spectrum is shown in Fig. 2.

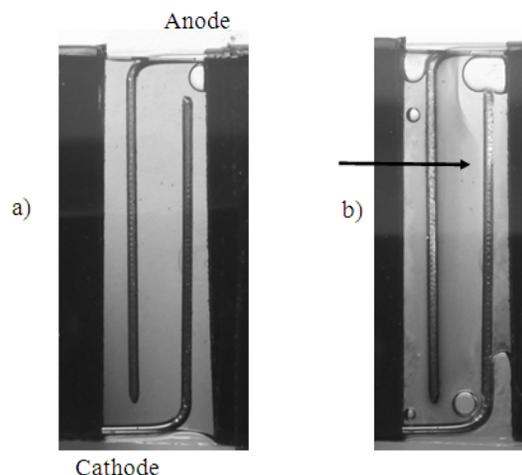


**Fig. 2.** RAMAN spectrum for one point on a graphene tube. There are D and G peaks characteristic of GO. The D-peak is located at 1330-1360 cm<sup>-1</sup> and corresponds to the A<sub>1g</sub> mode, which arises mainly due to defects and edges of GO flakes. G-peak is located at 1590-1600 cm<sup>-1</sup>, corresponds to the symmetric E<sub>2g</sub> mode arising from the stretching of the double bonds C=C in the sp<sup>2</sup> plane.

**3. RESULTS AND DISCUSSION**

**3.1. Electrophoretic study of graphene oxide**

It is generally accepted that the water dispersion of GO consists of individual flakes, which are negatively charged as a result of the carboxyl groups contained in their structure, capable of dissociation. Dispersions of GO, as a rule, acidic with pH 5-5.5. Movement of negatively charged GO flakes to the electrode can be observed visually in Fig. 3. The figure shows an experiment with a flat cell consisting of



**Fig. 3.** a) A photograph of an improvised cell where there is a GO dispersion and two open-circuit wire electrodes between the two cover glasses, at a distance of 4mm and a length of 20mm; b) The same cell after the current is switched on: initial value ~40 μA, final value ~10 μA (after 60 minutes).

two cover glasses and two wire electrodes with a diameter of 0.7 mm located 4 mm apart. The cell was filled with an aqueous dispersion of GO.

The figure shows the cell before and after electrophoresis. It is seen that after the current was turned on, the uniform color of the dispersion changed. In the space near the cathode, the color has weakened (the solution became more transparent), and in the space around the anode the solution noticeably darkened, compared with the original color, which indicates the concentration of the dispersion components in the near-electrode space.

The arrow indicates the position of a lighter layer of "clean" water depleted of GO particles and located next to the cathode. On the left is the area where GO particles are concentrated, next to the anode. It is thus shown that the flakes of the GO aqueous dispersion can be moved and concentrated near one electrode.

### 3.2. Spontaneous deposition of GO on a smooth surface

In our experiments it was shown that the copper wire (or foil), purified by the method given in the experimental part, being lowered into the aqueous dispersion of GO, is slowly covered with a GO film for several hours at room temperature. A similar picture is observed in the case of nickel and tin. On aluminum, the process takes place even more slowly and only in places.

These experiments showed that the GO film is formed on the metal surface even before the appearance of the electric potential. According to preliminary

experiments, GO from an aqueous dispersion can be sorbed on a quartz fiber: after exposing the fiber to an aqueous dispersion of GO for several hours and subsequent high-temperature treatment (30 minutes at 220°C), KR spectra revealed the presence of rGO on the surface.

### 3.3. Electrophoresis deposition of GO on metal foils and wires

The main objective of the study was to identify the features of precipitation of graphene oxide flakes during electrophoresis on cylindrical surfaces of fibers, metal and dielectric.

Preliminary experiments were carried out on the electrophoretic deposition of GO on a flat surface - copper or nickel foil. The experiments were carried out using an electrophoretic cell, the general form of which is shown in Fig. 1, where a plate of the corresponding metal was used instead of the wire. It has been established that during the electrophoresis from 3 min to 10 min, with a constant potential on the cell from 0.45V to 0.8V, a dark film is deposited on the smooth surface of the electrode (anode). The intensity of the color could vary from brownish-green to black and depended on the time of electrophoresis.

It has been found that replacing the foil in an electrolytic cell with a copper wire cleaned by the above method and applying a potential in the same ranges as above results in the deposition of GO on the cylindrical surface of the wire. Comparative observation in an optical microscope showed that the color and morphology of the coating on the fiber does not differ from that observed on copper foil.

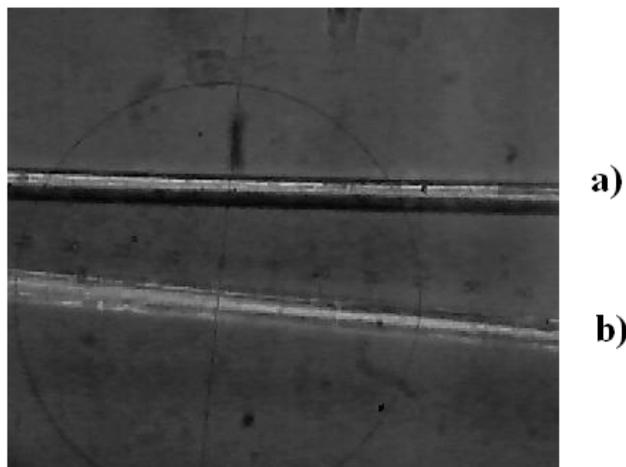
### 3.4. Electrophoresis deposition of GO on a bundle of quartz fibers

A series of experiments on the deposition of GO from dispersion to dielectric fiber was carried out with a beam of quartz fibers 10  $\mu\text{m}$  in diameter each. For this purpose, the following method was used: a bundle of dielectric fibers was placed (adhered) in direct contact with a flat electrode (copper foil). When voltage was applied to the foil, the process described in the previous section occurred; at sufficiently long (several minutes) the process on copper foil a thick enough (up to 1 mm) film, covering the dielectric fiber pressed to the surface, was growing. After separation, a bundle of quartz fibers is obtained, each of which is uniformly coated with a layer of precipitated GO.

The obtained samples of the composite fiber-film GO were characterized by a complex of methods listed in the experimental part.

### 3.5. GO electrophoresis on a separate quartz fiber

Experiments were carried out on the deposition of GO on a separate quartz fiber with a diameter  $d = 10 \mu\text{m}$  and a length of 6 cm. The small fiber diameter required the development of new techniques for conducting the experiment. In previous experiments, the fibers were placed in a cell in a free suspension; in connection with the small diameter of the fiber, it became necessary to fix it in the near-electrode layer at two points—the upper and the lower—in a stretched state (Fig. 1a). When performing electrophoresis under standard conditions, GO precipitates on the copper anode as described above. When the process is carried out for a long time, a coating thickness is



**Fig. 4.** a) Photograph of quartz fiber  $d = 10 \mu\text{m}$  coated with rGO (GO thermally reduced at  $220^\circ\text{C}$  for 30 minutes). The increase in the optical microscope is  $\times 500$ . The characteristic black color of rGO is seen. b) For comparison, the next row is the original pure quartz fiber  $d = 10 \mu\text{m}$ .

achieved that includes quartz fiber. When the process is carried out for a long time, a coating thickness is achieved that includes quartz fiber.

After the end of the process, the fiber is removed, dried and examined by the complex of methods described above. In Fig. 4, obtained with the use of an optical microscope, one can clearly see the difference in color and morphology of the fiber that has undergone electrophoresis from the initial fiber. Confirmation of the presence of GO film on a dark-colored fiber is obtained using a set of methods, indicated above.

## 4. CONCLUSION

Thus, as a result of the experiments, it was shown that the method of GO dispersion electrophoresis makes it possible to obtain a coating of fibers of a different nature with a GO film. Depending on the nature of the fiber, its composition and diameter, techniques have been developed that can effectively precipitate graphene oxide layers and, in certain areas, regulate this process. It

can be assumed that coatings of quartz fiber with GO or rGO film will later be used in high power optical fibers, to protect them from optical breakdown.

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