

# Conductivity of graphene oxide films: Dependence from solvents and photoreduction



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## ABSTRACT

The moisture effect on conductivity of graphene oxide (GO) films was studied. GO films of 200–500 nm thickness become conductive ( $\Omega$  ranges from  $10^{-6}$  to  $10^{-2}$  S/cm) upon the moisture increase from 30% to 100%. Waters diffusion changes the films morphology. The UV reduction of GO reduces the film sensitivity toward moisture until the complete disappearance. Proton character conductivity is concluded for GO, the isotopic effect for the conductivity being  $\sigma_H/\sigma_D = 1.4 \pm 0.1$ . The GO film conductivity increases in polar solvents vapors (alcohols, acetone, pyridine, etc.), however, nonpolar (toluene and hexane) and chlorine containing ( $\text{CCl}_4$ ,  $\text{CHCl}_3$ ) solvents vapors do not affect the conductivity.

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## 1. Introduction

After isolation of individual graphene nanoleaves in 2004, the world-wide interest to graphenes was drastically increased. Presently, it is considered [1] that graphene (or graphene-like materials having graphene properties) in large amounts can be obtained from graphene oxide (GO) that is easily synthesized from graphite upon 'mild' conditions. Graphite/graphene oxide contains on its surface oxygen-containing groups, such as hydroxyl, epoxide, carbonyl, and carboxyl ones. GO thermal and chemical reduction results in the complete graphite oxide 'purification' from oxygen-containing groups and respective reduction to graphite/graphene (r-GO) [2,3]. On the other hand, GO can serve itself as an important material for many different applications, for instance: (a) possibility to use GO, as well as graphenes, in composition materials [4]; (b) GO paper possesses excellent mechanical properties [5]; (c) possibility to integrate GO in graphene electronic devices [6,7], e.g. as the electrolyte in graphene supercapacitors [7]; (d) possibility to obtain blue luminescence in GO [8]; (e) GO application for hydrogen-accumulating materials [9], etc. Compounds, incorporating graphene oxide with transition-metal ions, are promising for magnetic resonance tomography [10]. Respectively, GO and processes connected with GO reduction become important and principle for GO material science as well as for the reduction mechanism resolving.

One of the GO reduction methods (besides thermal and chemical) is the photochemical one (applying UV-light). In our previous works [11,12], GO reduction was studied in water suspension and in films, deposited on a quartz layer, upon the irradiation with UV-light at room temperature (without heating). It was revealed

that: (1) upon the UV-light irradiation, absorption increases in visible and near-IR spectral region; (2) the cut-off light energy, leading to the photolysis products, is 3.2 eV; (3) the quantum efficiency for oxygen-containing groups elimination grows up with the increase of excitation-light energy above the cut-off value; (4) the GO layer conductivity grows up in the course of UV-light irradiation; (5) upon UV-light irradiation of GO films in vacuum, molecules  $\text{H}_2\text{O}$ ,  $\text{O}_2$ ,  $\text{CO}$ ,  $\text{CO}_2$  are revealed with the use of mass-spectroscopy to release. Further, in Letter [13] it was demonstrated that photochemical reduction can occur even at 77 K. Based on these data, in reports [11–13], it was concluded that the GO reduction with UV-light possesses the photochemical dissociation character and a domain model for GO reduction, assuming that at the initial stage molecular dissociation of the starting GO fragments and formation of small-size  $\text{sp}^2$  domains take place, was suggested. At further UV-light irradiation, the domains were shown to grow up until the formation of a conductive nanographite layer.

Electric properties of GO thin films were studied in works [14,15]. In contribution [14], voltage-current characteristics of GO thin films were elucidated and it was revealed that these characteristics have nonlinear forms. Upon chemical GO reduction, the current was shown to increase for more than three orders of magnitude. In contribution [15], GO thin films, chemically reduced, were applied as chemical sensors since r-GO films conductivity is drastically increased in vapors of polar solvents, such as acetone, HCN, and dinitrotoluene. In works [6,16], effect of moisture on GO electroconductive properties was reported. Thus, the voltage-current characteristics resolved at stationary conditions [16] suggest significant increase in GO films conductivity upon the environment moisture increase. In [17] intercalated water in graphite oxide (GO) was investigated by using different techniques: broadband dielectric spectroscopy, differential scanning calorimetry, X-ray diffraction, and Fourier infrared spectroscopy

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(ATR-FTIR). It was shown that the interlayer distance during hydration increases from 5.67 to 8 Å when changing the water concentration in the layer from 0 wt% up to 25 wt%. The activation energy of the relaxation process varies from 0.41 eV (5 wt%) to 0.52 eV (25 wt%). In [18] it was shown that there is a negative coefficient of thermal expansion, coupled with the loss of water layer of GO.

In the present report, results of our experiments on moisture effects on the GO films conductivity before and after photochemical reduction are revealed.

## 2. Materials and methods

GO synthesis and films fabrication were described in previous reports [11–13]. Graphite oxide was prepared by Hammers [19], with some modification [20]. A typical procedure for preparing suspensions consisted of mixing the GO (100 mg) and water (100 ml) followed by sonication for 30 min. For removing large particles in the suspension was centrifuged for 20 min at 4000×g. Suspension after centrifugation was on clearance uniform brown color and can be stored for a long time without delamination. The elemental composition of the product corresponded to a formula  $C_8O_{4.6}H_{1.8}(H_2O)_{0.58}$ . According to X-ray diffraction study, the interplanar distance is 0.81 nm in our sample. The cell for electrochemical measurements was built by means of coating a fiberglass substrate bearing gold or copper electrodes. The film thickness was in the range of 200–500 nm depending on the GO concentration in a starting suspension and, additionally, was controlled by the interferential method. The use of such thicknesses excludes possible electrode phenomena, connected with partial coating of the electrode by GO film. Electroanalytical measurements were conducted with use of potentiostat P-30S N1EX3. The moisture dependences were obtained with the placement of the electrochemical cell in water vapors over saturated solutions of inorganic salts. UV-light irradiation was achieved with a high-pressure Hg lamp (1000 W power). The region of 260–390 nm was obtained with the use of a light filter made of glass; the applied light intensity was ca. 400 mW/cm<sup>2</sup>.

## 3. Results and discussion

GO films dried under Ar atmosphere are isolators with the conductivity less than 10<sup>-7</sup> S/cm. At room temperature, a GO film, exposed to air, becomes conductive and its conductivity depends on atmosphere conditions. The presence of hydroxyl and epoxy-groups on the surface of graphene leaves and also carbonyl and

carboxyl groups at the edges of the leaves or defects allows absorbing water molecules and thus the film becomes a conductor. On Figure 1, the dependence of the film conductivity ( $\sigma$ ) on moisture ( $H$ ) is demonstrated and the dependence is evident to appear a power character.

On Figure 2, the current–voltage characteristic of a GO film studied in the cyclic voltammetry regime is shown for the 99% humidity. Electrochemical reduction of GO occurs at voltage ( $U$ ) of 1.2 eV [21], therefore, in our case (the working potential ranging from –1 to +1 V) redox processes on the GO film are not observed. The cyclic curves character reveals that electric current is due to several processes, for instance, electric charges (electrons or holes) motion in electric field and diffusion of the charge carriers in a film.

When the cyclic electrochemical process is stopped at zero potential ( $U = 0$ , curve 6–6\*, Figure 2), the current dependence is seen to drop down and can be extrapolated with two curves: a fast decay, close to exponential, and further slow process originated by the diffusion of the charge carriers in a GO film:

$$i = A + ae^{-t/\alpha} + b(1 - k\sqrt{t}).$$

Since such a dependence is due to the diffusion of water molecules into a GO film, then at large thickness ca. 200–500 nm, this process can be compared with diffusion of a gas or water vapors into a polymer [22,23]. Upon water vapors supply into a cell under study, water molecules diffuse through a GO film and thus electric current appears. The transition process is shown on Figure 3.

The current decay depends on the both: film thickness and experimental conditions. On curve 1 (Figure 3), the conductivity kinetics is given for a freshly made GO film of the thickness ca. 200 nm after its placement into water vapor. At first, the current occurs that is due to the charging capacity of electrodes (the initial sector is shown on the insert). Further current increase is due to the diffusion of water molecules through a GO film. After drying the GO film in dry argon flow, the current kinetics changes (Figure 3, curve 2): charging current and diffusion current are drastically reduced as compared with the first experiment. Such a behavior can be explained by the fact that the GO film morphology changes in the course of the GO film saturation with water. Immediately after formation of a film from the water suspension, it has loose surface with many voids. After the GO film placement into water vapor and electric current passing, graphene layers start moving and the whole film compresses that are observed with the current decay (curve 1, Figure 3). This is also evidenced by the current reduction in the second and following experiments. A partial electrochemical reduction or chemical reorganization of some groups into others, e.g. hydroxyls into epoxy-groups or vice versa, cannot be excluded for graphene oxide.

For the thicker films (ca. 500 nm), the initial charging period is not clearly seen, meanwhile, after several measurements kinetic curve is only resulted from diffusion processes (Figure 4).

After water vapor feeding into an electroanalytical cell (distinguished with symbol  $\uparrow$  on Figure), water molecules reach electrodes with effective diffusion coefficient  $D$  after the characteristic time  $\tau_1$  [22,23]:

$$\tau_1 = d^2/\pi^2D$$

The true diffusion coefficient depends on many factors, such as mass, volume, size, and shape of the diffusive molecules and also on their chemical nature (e.g., polarity). However, the basic contribution to the diffusion processes is most likely brought by the GO film structure that is made of graphene nanoleaves linked with water molecules by means of hydrogen bonds. The effective diffusion coefficient  $D$  can be estimated with the use of induction time  $\tau_D$  (see: the insert on Figure 4) applying the method suggested for polymers in report [24]:

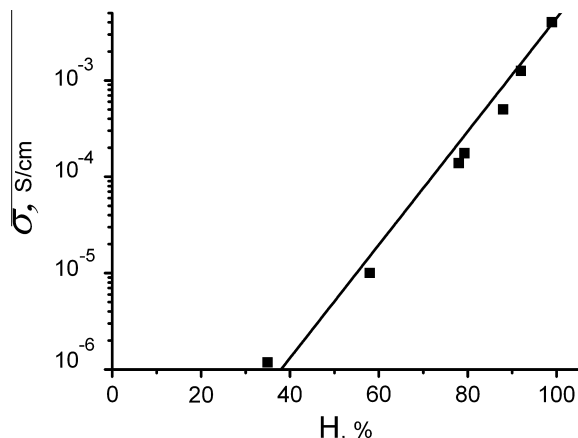


Figure 1. The dependence of the film conductivity ( $\sigma$ ) on moisture ( $H$ ) at 20 °C.

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