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# Development of electroforming method for coating of polymer membranes by graphene oxide

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The current research is focused on development of electroforming method for coating of porous membranes by graphene oxide. A mixture based on polymethylmetacrylate dissolved in acetone and graphene oxide was pumped through the syringe pump onto the needle and high voltage was applied to both electrodes, one of which was on a glass plate, and the second was a needle thereby forming fibers, which coated the surface of membrane uniformly. The main parameters and concentrations of used polymer for uniform and complete coating of the surface of membrane are studied. Surface morphology of coated membranes was studied by SEM.

**Keywords:** electroforming method; graphene oxide; membranes; polymethylmetacrylate; desalination; water.

## Introduction

The process of electroforming is the formation of fibers under the action of electrostatic forces and gravity. In the course of liquefaction of the jet, the surface density of charge changes, which in turn affects the electric field. After the jet passes from the Taylor cone into an almost straight line, the motion of the liquid jet is subjected to various forces, such as the Coulomb force of the electric field applied by the external electric field, surface tension forces, gravitational forces, and air resistance [1]. Based on D. A. Savill's work on electrohydrodynamic processes that occur in the Taylor cone, the state of the jet can be represented in the form of four stationary equations: the laws of conservation of mass and electric charge, the equation of moments of forces, the Coulomb law for an electric field. Thus, the jet of electrospinning can be represented by the following equations [2]: the law of conservation of masses is written as follows

$$\pi r^2 \vartheta = Q, \tag{1}$$

where $Q$ is a constant volume flow, $R$ is the radius of the jet and $\vartheta$ is the axial velocity of the liquid inside the jet [3]. The law of conservation of charge can be expressed by the formula:

$$\frac{d}{dz}(2\pi R\sigma v + \pi R^2 KE) = 0, \tag{2}$$

where $\sigma$ is the surface density of charge, $K$ is the conductivity of the jet, $E$ is the electric field strength; the moment equation has the form

$$\frac{d(\pi R^2 \rho v^2)}{dz} = \pi R^2 +$$

$$+\frac{d}{dz}\left(\pi R^2(-P+\tau_{zz}) + \frac{Y}{R}\left(2\pi R(\frac{dR}{dz})\right) + 2\pi R(t_z^e - t_z^e(\frac{dR}{dz}))\right), \quad (3)$$

where $\rho$ is the density of the liquid, $\tau$ and $t$ are the characteristics of viscosity in the axial direction and the tangential component, respectively, $\gamma$ is the surface tension. The Coulomb integral for tangential electric forces inside the jet is given by the following expression

$$E - ln\frac{1}{x}\left[\frac{\beta}{2}\frac{d^2(R^2E)}{dz^2} - \frac{1}{\varepsilon_{air}}\frac{d(\sigma R)}{dz}\right] = E_\alpha. \quad (4)$$

As can be seen from the equations, the electric field strength is one of the main parameters of formation of jet, but in our experiments a pulsed electric field generator is used, which, in turn, makes quantitative calculations more difficult [4].

In its turn, the importance of water supply in people's livelihoods increases simultaneously with population growth. The major amount of water is concentrated in the seas and oceans (more than 98%).The salinity of the sea water reaches 35g/kg, while the content of fresh water (with salinity less than 1 g/kg) is about 1.7% of the world's reserves, from which only 0.001% of all fresh water is accounted on river water [5].

Desalination of water can be carried out in various ways, such as reverse osmosis, membrane, ion exchange, electrodialysis and thermal methods. Currently, the first three methods of desalination of water are the most often used [6].

Membrane technologies include reverse osmosis, nanofiltration and ultrafiltration. In recent years, a great interest in these methods has increased due to the high quality of membranes, commercial availability, as well as the simplicity of design of membrane technology [7]. Nanofiltration (NF) and the reverse osmosis (RO) are the methods, which are widely used for the production of clean water, since they can deflect pollutants efficiently [8]. NF and RO membranes are composite thin-film polyamide-based membranes, which still have some limitations, such as low water permeability and susceptibility to pollutions [9-12].

Membranes based on carbon nanomaterial-graphene oxide (GO), act as an ideal molecular filter, blocking all molecules or hydrated ions larger than 9 angstroms in water. Evidence of this fact, obtained by scientists from the UK [13], promises the use of such nanostructures in filtration and desalination of seawater (Figure 1).

As known, graphene is a carbon layer with thickness of one atom with a hexagonal crystal lattice. GO in many ways resembles "clean" sheets. GO sheets can be easily stacked on each other, resulting in very thin, but mechanically strong membranes. These membranes consist of millions of small flakes of GO with nano-sized channels (or capillaries) between them [14].

The goal of this study is to the develop the method for uniform coating polymeric membranes by GO using electrospinning techniques. Porous membranes

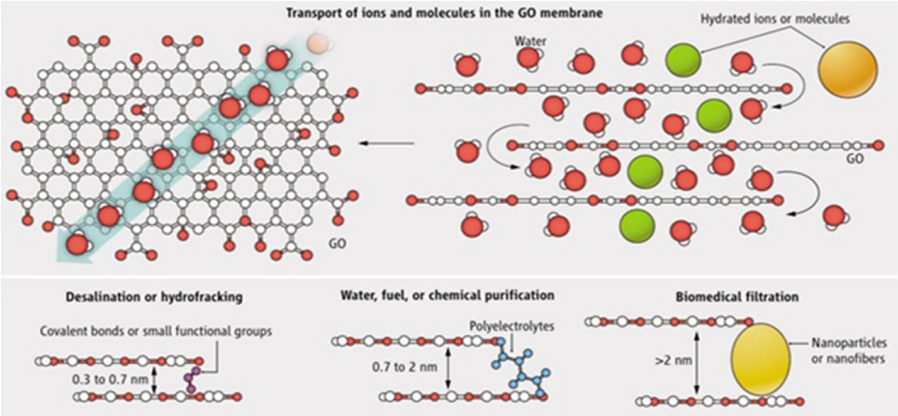



Figure 1. Scheme of principle of filtration of water using a membrane coated by GO.

based on cellulose acetate were used as substrate for coating by GO. We propose that use of electroforming method will allow obtaining the uniform coating for porous membranes with a large amount of connected capillaries that, in perspective, will impact on improvement of the techniques used in process of water desalination.

## Experimental

Natural graphite with purity of 98% was purchased in Nanostructured & Amorphous Materials [15], Inc. (Houston, USA). Polymethylmetacrylate (PMMA), ethanol and acetone were purchased in Sigma Aldrich. The purchased chemicals were used without further purification.

Graphene oxide was obtained from natural graphite by modified Hummer's method [16].

GO in amount of 0.01 g was added to 10 ml of ethanol and subjected to ultrasound at a frequency of 37 kHz. A certain amount of PMMA was dissolved in acetone at 50 °C under stirring for 20 minutes. After complete dissolution of the polymer a dispersion of GO in ethanol was added to the mixture and stirred. The resulting mixture was pumped through the syringe pump onto the needle. In turn, a high voltage was applied to the needle and collector.

Figure 2 shows a schematic representation of the installation for conduction of coating of membrane by electroforming method. High voltage was applied to two electrodes, one of which was on a glass plate, and the second was a needle.

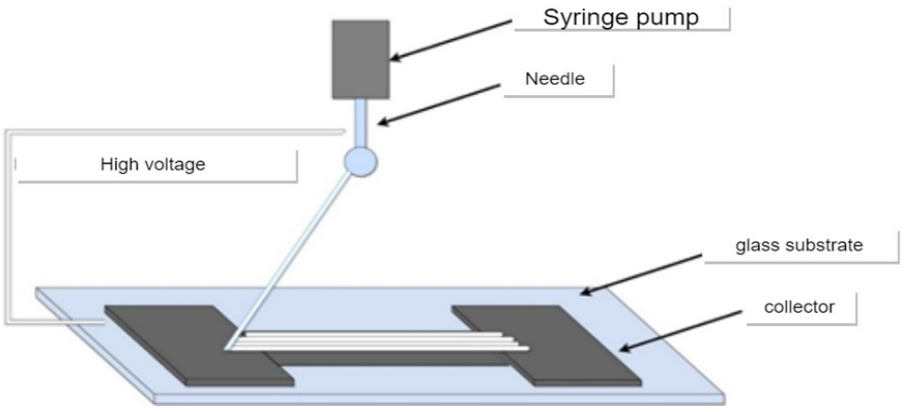
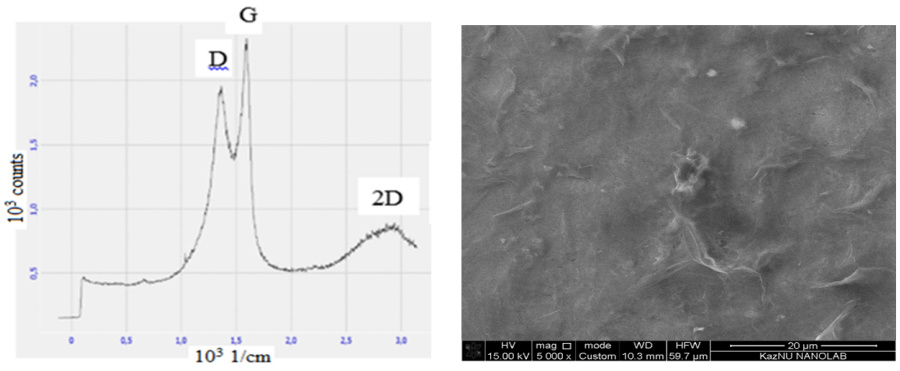



Figure 2. Scheme of experimental installation for coating of polymer membranes by electroforming method.

**Results and discussion**

GO that has been synthesized from graphite by its chemical oxidation is a powder in the form of brown agglomerates. Raman spectroscopy was used to identify of the presence of graphene layers in the obtained product (Figure 3).




a b

Figure 3. Raman spectrum (a) and SEM (b) of obtained GO.

Figure 3 (a) shows the peaks in the area of the G-band, which characterizes the oscillations of $sp^2$ carbon bonds system ($\approx$1580) - graphite like zone and 2D band ($\approx$2700), which is an overtone of the D-band ($\approx$1350). The presence of the D-band for samples of GO indicates formation of defect structure, and "blurring" 2D-band characterizes a small number of layers of graphene structure.

Figure 3 (b) shows that the resulting GO obtained from graphite by modified Hummer's method is represented by a layered structure. In some places there is a certain lightness of the structure, which indicates a low content of graphene layers in the structure.

For production of polymer fibers in all experiments similar conditions were used. The high voltage applied to the needle and collector was 1.5 kV per centimeter. The rate of the syringe pump was 1.5 ml/h. Membrane, based on cellulose acetate, was attached to the collector, which allowed the deposition of layers of graphene oxide and polymer fibers on its surface.

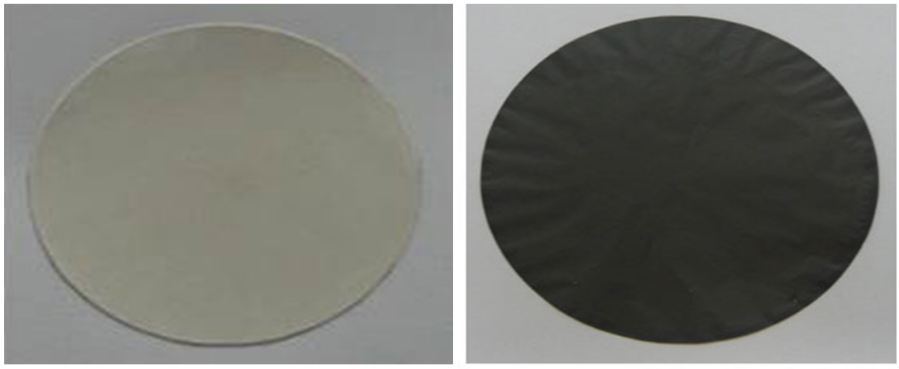
Compositions with different ratios of starting materials presented in Table 1 were prepared to carry out the process of coating membranes using electroforming method.

Table 1.
PMMA/GO ratio in solutions used for electroforming

| Type | PMMA/GO ratio | Amount of solvent for PMMA, % |
|---|---|---|
| PMMA/GO | 100:1 | 20 |
| PMMA/GO | 300:1 | 12 |
| PMMA/GO | 500:1 | 20 |
| PMMA/GO | 700:1 | 20 |

As a result of the studies, it was found that at ratio of 100:1 and 300:1 of PMMA and GO, the membrane was not coated with the formed fibers because of the low density of used composition. However, as the polymer concentration was

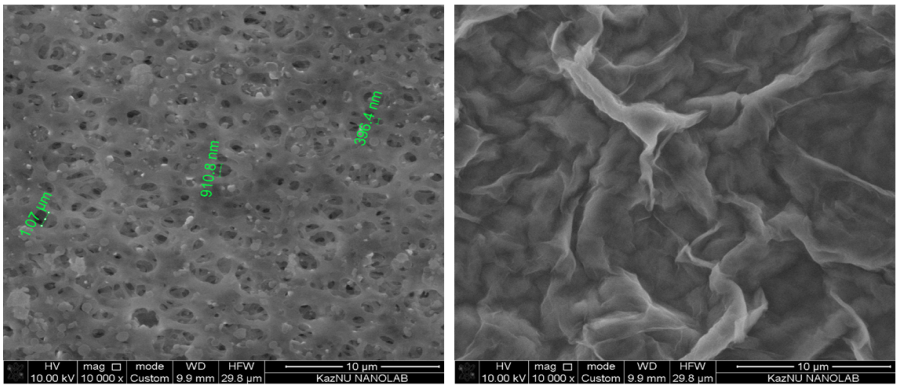
increased to a ratio of PMMA/GO as 500:1, the cellulose acetate membrane was uniformly and completely coated. A further increase in the concentration of the polymer resulted in plugging of the needle.



a b

Figure 4. Pictures of non-coated cellulose acetate based membrane (a) and coated with PMMA/GO (ratio 500:1) (b).

Pictures of non-coated and coated with PMMA/GO membranes are presented in Figure 4. The coating of cellulose acetate based membrane by PMMA/GO solution at ratio 500:1 is uniform and along the whole surface of membrane (Figure 4b).




a b

Figure 5. SEM images of non-coated cellulose acetate based membrane (a) and coated with PMMA/GO (ratio 500:1) (b).

Surface morphology of non-coated and coated with PMMA/GO (ratio 500:1) membranes was studied by SEM. Cellulose acetate based membrane is presented by porous structure with pore diameter in wide range starting from 300 nm up to microns (Figure 5 a). After coating cellulose acetate based membrane with PMMA/GO (ratio 500:1) using electroforming method it is evident that GO-layers are located on the surface of membrane overlapping each other thereby forming a film with a number of wrinkles. GO-layers clog the pores of membranes forming reaction layer with nanocappilaries [17], which is responsive for desalination of water.

## Conclusion

A simple and effective method for uniform and complete coating of a porous surface by GO using electroforming effect has been developed. This method combines three techniques: using of polymer - PMMA, carbon nanomaterial - GO and

electroforming effect. The effect of concentration of polymer on electroforming method is studied. It is found that at ratio of PMMA and GO as 500:1 the coating of a porous cellulose acetate based membrane is uniform and complete. GO layers clog the existing pores of membrane thereby forming reactive layer on its surface under electroforming effect, which is responsive for desalination of water. As has been reported elsewhere, the described GO-based membranes, obtained by electroforming method, are excellent candidates for water desalination.

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