Features of carbon layers synthesis on the porous anodic alumina

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Abstract. Carbon nanotubes and graphene are two of the most important forms of nanoscale carbon materials. Both materials can be synthesized by CVD method with the use of various "catalysts". The term "catalyst" is conditional; it refers to a surface, on which graphite islands are formed at a relatively low temperature. Either carbon nanotubes or graphene layers can grow on the surface depending on its shape and physical-chemical properties. As a rule, the materials of such surfaces are the most common metals of auxiliary groups [1], in which the carbon is dissolved after chemical deposition from the gas phase. Then, as a result of supersaturation of carbon solution in metal, the carbon precipitates on the surface in the form of graphite islands, which combine into graphene or nanotubes. However, the ordered carbon structures can be obtained not only by dissolving carbon in metals, but also by using special surfaces, where the surface diffusion of carbon can occur. Aluminum oxide provides an example of such material.

1. Introduction
Among the existing technologies for separating substances, a special place from the point of view of economic prospects is occupied by semipermeable membranes with nanoscale pores (nanomembranes). A number of such membranes include track membranes, porous anodic alumina (PAA), cellulose acetate, and others. This direction has received considerable attention from researchers. In particular, relatively recently, a number of studies have been carried out aimed at studying nanomembranes, the selectivity of which can be varied by a certain external influence. The specified effect, which allows to control the transport properties of the membrane, are such parameters of the external environment as pH [1-8], temperature [9-10], light exposure [11-12], electric field [13-16], ionic strength of the solution [17-18]. According to [16], nanomembranes sensitive to the pH of the medium are of interest, primarily due to the relevance of the problems of bioseparation of amino acids or components of organic medicinal substances. In [16], the synthesis of a film of hydrogenated amorphous carbon (diamond-like film - DLC) was demonstrated using plasma-induced vapor deposition in the presence of nitrogen. In this way, the effect of doping the DLC film with nitrogen was achieved, giving it n-type semiconductor conductivity. This coating provided a low sorption of anions, as well as record high oxygen and hydrogen reduction potentials and, accordingly, a wide operating potential window. Membranes of this type had sufficient thickness (10 μm) and demonstrated the possibility of electrical switching of
transport properties for both anions and cations, as well as the possibility of functioning at high modulus potentials (from −1.5 V to +2.0 V), without the influence of the reduction factor of hydrogen and oxygen.

2. Synthesis

The synthesis of PAA was carried out by electrochemical treatment of aluminum foil in an aqueous solution of oxalic acid (40 g/l). The anodizing process was carried out at room temperature. The time needed to obtain a 15 µm thick PAOA layer with a pore diameter of 50 nm was 80 min at a current density of 10 mA/cm² in a galvanostatic mode (figure 1).

Nanostructured alumina obtained by anodizing method contains functional groups of the acid residue from the electrolyte. The aluminum oxide surface actively interacts with water to form AlOOH. Both factors affect the pore structure, and there is always a large amount of physical adsorbed water in the pores. To place the catalyst for the growth of carbon nanotubes in the pores, it is necessary to free them from the water adsorbate and functional groups on the surface of the PAA. For this, the material is subjected to an hour-long vacuum annealing at a temperature of 300 °C, heating to a predetermined temperature is performed at a rate of 20 °C/min or lower at the choice of the operator. Cooling after annealing is natural in vacuum up to 99-140 °C.

Carbon can be deposited on PAA by itself, but its quality and quantity is greatly increased in the presence of a catalyst. For this, either nickel was introduced into the pores by the method of pulsed deposition [19] or a precursor based on an ammonia complex of nickel chloride, after which carbon nanotubulenes were synthesized at a temperature of 600 °C by pyrolysis of ethanol vapors [20] supplied to the reactor. With the growth of carbon nanotubes at temperatures above 600 °C, the aluminum support should be removed from PAA due to the fact that aluminum becomes fluid and surface tension will significantly distort the structure of PAA and dissolve the catalyst in itself by passivating it. The standard process for the growth of nanotubes in PAA is the regime at a temperature of 600 °C and an ethanol vapor pressure of 20 kPa. The heating rate should be no more than 20 °C/min. Annealing time before filling is 5 minutes. The time of filling the steam-gas mixture is 15 ± 2 minutes. Natural cooling to 150 °C or less. The same mode of carbon deposition in PAA was realized without a catalyst.

3. Results and discussion

After the ethanol pyrolysis process, the oxide darkened, indicating the deposition of carbon in the pores. To study the sample, the aluminum part was completely vented from it in hydrochloric acid buffer of copper chloride. The remaining membrane was dispersed in ultrasound for 15 min, and the resulting
colloid was applied to a porous carbon grid. The sample was examined by transmission electron microscopy (figure 2).

![TEM image of PAA with carbon fibers](image1.png)  
**Figure 2.** TEM image of PAA with carbon fibers (indicated by an arrow).

The sample consists mostly of fragments of PAA, for a more efficient TEM study, these samples were processed in a chromium etchant PAA (20 g/l CrO₃, 35 ml/l H₃PO₄) for a more efficient TEM study before dispersion, in this regard, very thin PAA fragments were found in some fragments carbon nanofibers ~50 nm in diameter, which corresponds to the initial pore diameter of PAA. Carbon in PAA is not identified either in the dark-field image, which has an amorphous halo, or in the form of graphite planes in the fiber walls. Nevertheless, indirect data on the darkening and the presence of nanofibers on TEM allow us to interpret them as carbon.

For the electrochemical deposition of metals in a pulsed mode, PAA was obtained with the final stage of thinning the barrier oxide. The barrier oxide was thinned at the last stage in a stepwise potentiostatic mode with a sequential decrease in voltage. Immediately after obtaining PAA, the sample was subjected to ion bombardment with argon, after which nickel was deposited into the pores in a pulsed mode, which also led to the darkening of the oxide. After synthesis in the sample of carbon nanofibers, the aluminum part in the copper chloride hydrochloric buffer was completely etched from it. The remaining membrane was dispersed in ultrasound for 15 min, and the resulting colloid was applied onto a porous carbon grid. The sample was examined by transmission electron microscopy (figure 3).
Figure 3. TEM image of PAA carbon nanofibers.

The TEM clearly shows carbon nanofibers connected to nickel as shown in figure 3. Nickel is identified by reflexes in the dark-field image. Nanofibers are uniquely hollow, their walls have pronounced graphite planes; thus, the resulting nanofibers are characterized as carbon nanotubes with a diameter of ~50 nm, which corresponds to the pore diameter of PAA.

The catalyst was introduced by impregnation with a catalyst precursor in a desiccator at 60 °C. After carbon deposition in PAA, the area of aluminum with PAA darkened. To study the sample, the aluminum part was completely vented from it in hydrochloric acid buffer of copper chloride. The remaining membrane was dispersed in ultrasound for 15 min, and the resulting colloid was applied to a porous carbon grid. As a result, frames of the type shown in figure 4.

Figure 4. Carbon nanofibers from PAA (a) TEM image (b) SEM image.
From the studies carried out, it can be seen that carbon nanofibers exactly repeat the structure of the pores of PAA. The investigated nanofibers are coated with catalyst nanoparticles, which themselves did not give rise to CNT growth, but served as a carbon source for the formation of carbon nanofibers. The carbon nanofibers themselves have well-ordered walls and are clearly filled with amorphous carbon inside.

4. Conclusion
The synthesis of carbon nanofibers in the pores of anodic aluminum oxide makes it possible not only to fabricate arrays of free-standing carbon nanotubes, but also to obtain membranes based on PAOA with carbon walls. Thus, the carbon coating of the PAA walls can impart conductive properties to them, and hence control the flow of ions through the pore. Conductivity, in turn, is determined by the structure of the carbon coating.

As a result of the study, it became clear that the carbon coating of PAA can be determined by the presence of a catalyst. If the technology requires hollow carbon fiber, then the catalyst can seed the entire pore surface. If the catalyst needs to be localized, then it makes sense to deposit it by pulse electrochemical methods.

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