

DOI: 10.17725/rensit.2021.13.039

## Synthesis and study of composite based on porous anodic alumina modified by silver nanowires

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Received February 20, 2021, peer-reviewed February 26, 2021, Accepted February 28, 2021

**Abstract:** The paper presents the results of an experimental study of the deposition of modified silver into the pores of ceramic  $\text{Ag}\&\text{Al}_2\text{O}_3$  membranes, laboratory samples of thin nanocomposite membranes were obtained based on the developed technological methods of silver deposition, and their composition and surface morphology were studied.

**Keywords:** nanopores, aluminium oxide, silver, electrochemical synthesis

UDC 544.66

**Acknowledgments:** The work was performed within the framework of the state assignment "Sensor".

**For citation:** Mikhail Yu., Ilya N. Mikhailov., Alexander E. Isaev, David Z. Safoshkin, Igor D. Kosobudskii, Nikolai M. Ushakov. Synthesis and study of composite based on porous anodic alumina modified by silver nanowires. *RENSIT*, 2021, 13(1)39-44. DOI: 10.17725/rensit.2021.13.039.

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### 1. INTRODUCTION

To identify active sites and surface intermediates in catalytic reactions [1,2], many methods are used, such as signal enhancement Raman spectroscopy on the surface of samples (SERS) [3], X-ray photoelectron spectroscopy (XPS) [4], infrared (IR) spectroscopy [5,6]. Among them, SERS, which uses optically excited coherent oscillations of conduction electrons on a developed (rough or porous) metal surface to dramatically amplify the Raman signals of absorbed molecules, is a unique spectroscopic detection method that offers information on both surface-sensitive and chemical bonding,

and it is ideal for direct detection of surface chemical intermediates. For direct detection of intermediate products of surface reactions during photocatalysis, nanocrystalline SERS substrates with a large area with a uniform and strong amplification of the electromagnetic field are required. In [7], it was demonstrated that using the Langmuir-Blodgett method, it is possible to collect faceted Ag nanocrystals with sharp corners into a close-packed substrate of a large area with gaps between particles less than a nanometer in size, which have a gain of up to  $10^8$  and are optically homogeneous for performing quantitative ultrasensitive determination arsenic with a detection limit of  $\sim 1$ ppb. In [8], it is reported that membranes with a surface cubic morphology of silver, in which silver nanocubes with sharp edges and corners serve as "hot spots", made it possible to increase the sensitivity of the spectral method by amplifying the signal by 5 orders of magnitude.

To obtain optically transparent membranes with a developed metallized surface, the method of electrochemical anodic oxidation of metal surfaces is known as one of the simple and effective technological methods. The manufacture of porous membranes based on anodic alumina (PAOA) is based on simple and inexpensive electrochemical anodization, combined with the self-ordering process of nanopores that does not require lithography or templates, with the ability to control the process of obtaining ideally ordered and size-controlled nanopores with the required geometry [9].

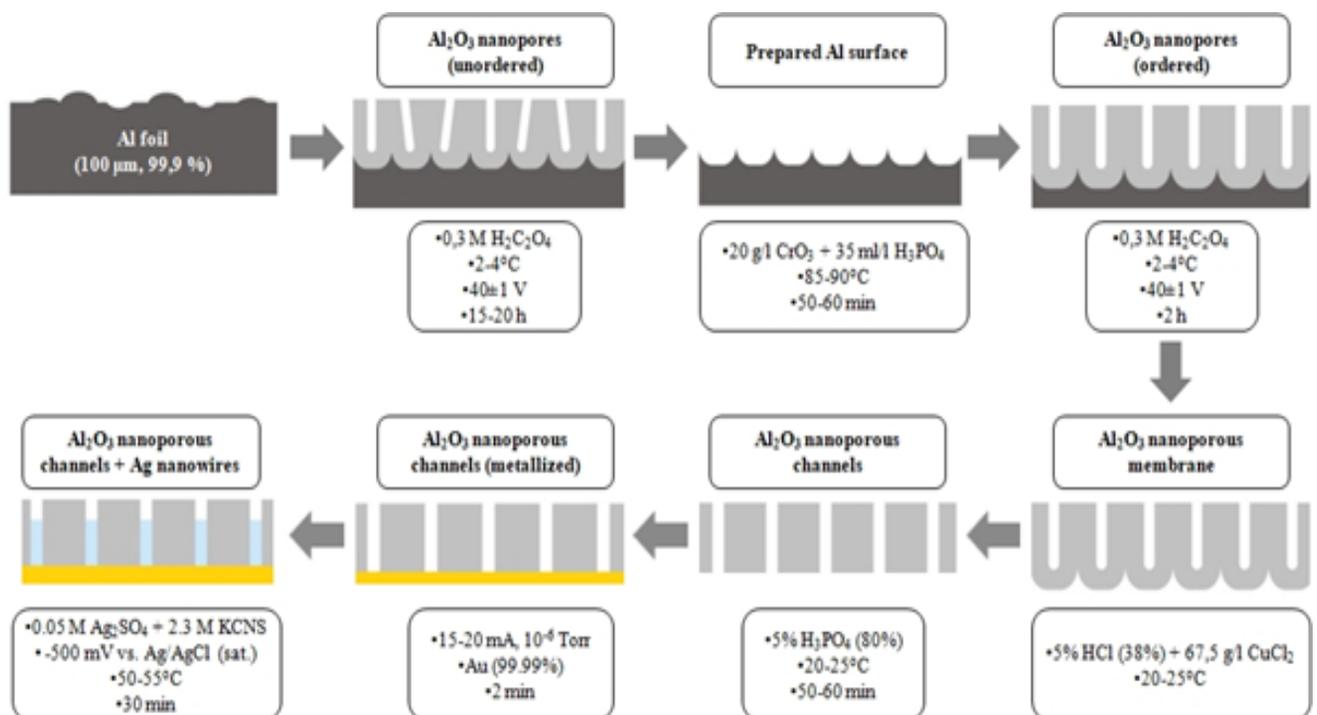
The electronic structure of aluminum oxide ( $\text{Al}_2\text{O}_3$ ) is of increasing interest due to its various applications in optical, electronic, and structural devices. Thus, thin optically transparent ceramic metallized membranes based on porous anodic alumina can serve as a platform for various optical and electronic applications.

The aim of this work was to experimentally study the process of modified deposition of silver into the nanopores of ceramic membranes, to manufacture thin nanocomposite membranes based on the developed technological methods

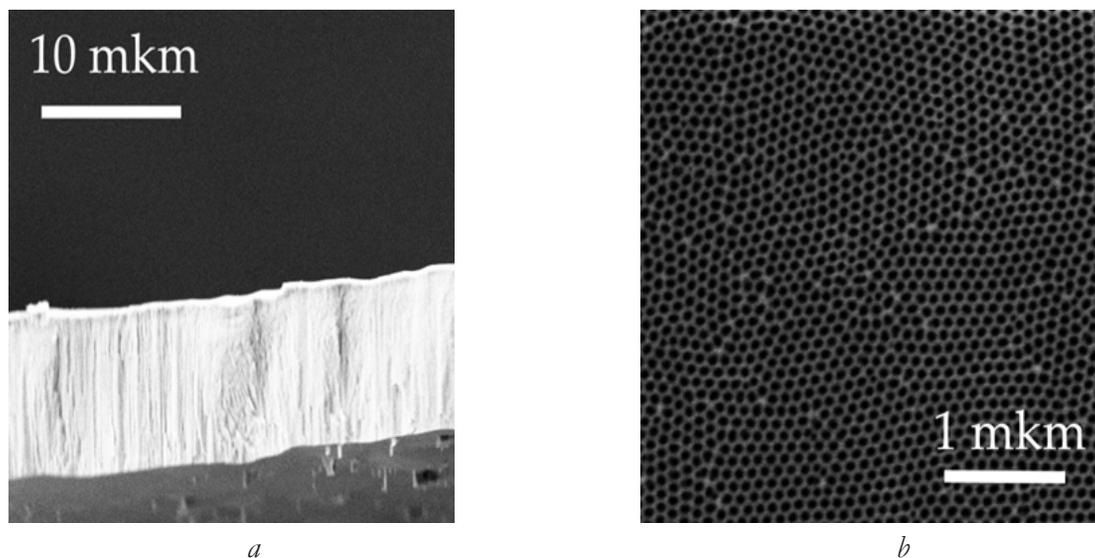
for silver deposition, and to study their composition and surface morphology.

**2. MATERIALS AND METHODS**

The technological scheme for obtaining a composite material based on a matrix of porous anodic aluminum oxide (PAOA) filled with silver nanowires is shown in **Fig. 1**. The starting material for obtaining the composite was Al (99.9%) in the form of a foil ~100 μm thick. To prepare the metal and structure its surface for the further formation of an ordered system of porous channels, the primary anodic oxidation of aluminum was carried out. The process was carried out in a 0.3 M solution of  $\text{H}_2\text{C}_2\text{O}_4$  in an electrochemical cell made of an inert material at a temperature of 2-4°C in a two-electrode mode. A working sample made of aluminum was connected to the positive pole of the current source (anode), and a steel perforated electrode of equal area was connected to the negative pole (cathode). A constant voltage in the range of  $40 \pm 1$  V was applied to the electrodes, the distance between which was 10-15 mm, and held for 15-20 hours. The thin layer of  $\text{Al}_2\text{O}_3$  obtained after primary anodizing on the metal surface had a disordered porous structure ("sacrificial



**Fig. 1.** Technological scheme for obtaining a composite based on a matrix of PAOA filled with Ag nanowires.



**Fig. 2.** Micrographs of scanning electron microscopy of the PAOA membrane: a) - side view (inset - external view of the working sample), b) - top view (porous layer).

layer") and was removed at 85-90°C by chemical etching in a solution of CrO<sub>3</sub> and H<sub>3</sub>PO<sub>4</sub> (80%) with a concentration of 20 g/L and 35 ml/L, respectively. The metal thus prepared underwent a second anodization for 2 h under conditions similar to the primary anodic oxidation, as a result of which an ordered porous structure of Al<sub>2</sub>O<sub>3</sub> was formed on the Al surface.

To make the PAOA sample optical transparency, the metal sublayer at room temperature was dissolved in a mixture of 5 wt% HCl (38%) with the addition of 67.5 g/L CuCl<sub>2</sub>. The result was thin PAOA membranes (Fig. 2a), one side of which was covered with a continuous layer of Al<sub>2</sub>O<sub>3</sub> (barrier layer), while the other had an "open" porous structure (porous layer, Fig. 2b). To form a matrix of hollow channels, a continuous oxide layer was dissolved in 5% H<sub>3</sub>PO<sub>4</sub> (80%), after which a thin Au layer with a thickness of less than 10 nm was deposited on one side of the membrane by plasma spraying, which served as a conductive contact at the bottom of the pores. At the final stage of the technological scheme, the PAOA membrane was functionalized with silver by electrochemical deposition. Ag electrodeposition was carried out at 50 ± 5°C in a potentiostatic mode at a potential of -450 mV (rel. Ag/AgCl (sat.)) (With a graphite auxiliary

electrode, S ~5 cm<sup>2</sup>) from a mixture of 0.05M Ag<sub>2</sub>SO<sub>4</sub> + 2.3M KCNS for different times. Upon completion of the technological scheme, the obtained samples were washed with distilled water and dried in air at room temperature. Ag electrodeposition was carried out at 50 ± 5°C in a potentiostatic mode at a potential of -450 mV with a graphite auxiliary electrode, S ~5 cm<sup>2</sup> from a mixture of 0.05M Ag<sub>2</sub>SO<sub>4</sub> + 2.3M KCNS for different times. Upon completion of the technological scheme, the obtained samples were washed with distilled water and dried in air at room temperature.

### 3. RESULTS AND DISCUSSION

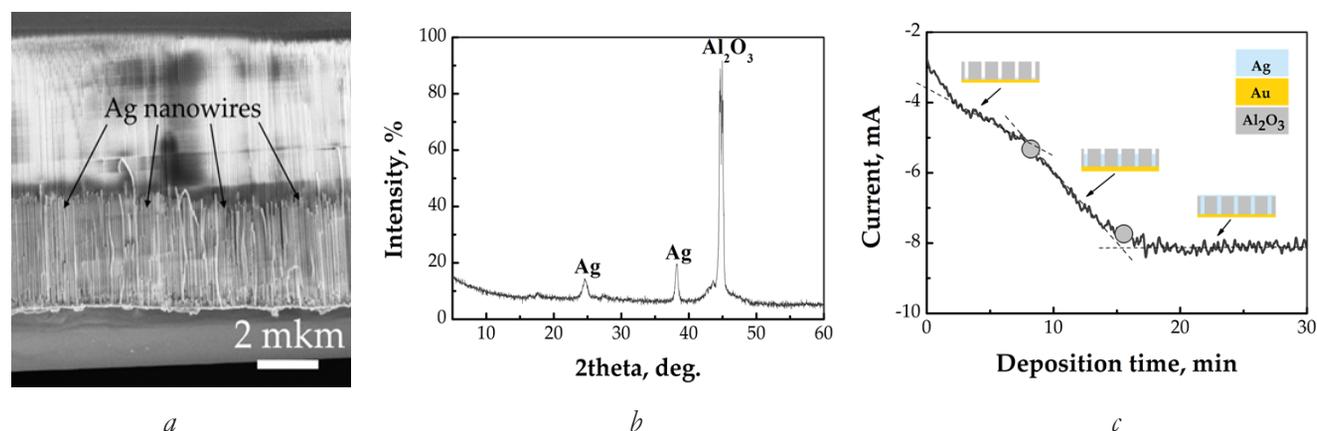
The surface morphology and structure of the obtained composites based on porous anodic Al<sub>2</sub>O<sub>3</sub> modified with Ag were studied by scanning electron microscopy (SEM) at the AURIGA Crossbeam 350 workstation (Carl Zeiss Gr., Germany). As mentioned above, the surface of PAOA membranes had a highly ordered two-dimensional structure in the form of hexagonally located pores with a diameter of (52.9 ± 2.7) nm (Fig. 2b), a height of ~10 μm with a packing density of 1.1 · 10<sup>10</sup> cm<sup>-2</sup>. There were practically no artifacts and defective areas on the surface. The porous channels were oriented mutually parallel in a direction perpendicular to the original substrate (Fig. 2a).

After the deposition of silver on the surface of the composite, there was observed the appearance of spherical agglomerates ranging in size from 0.1 to 1.0  $\mu\text{m}$ , which were "caps" of silver, obtained as a result of the release of metal from the porous channel to the surface of the membrane (Fig. 3a). It should be noted that the "caps" were formed rather scattered and with a low surface density. This can be explained by the high filling rate of single pores due to a kind of electrical "breakdown", which leads to the rapid deposition of silver in these channels. Most of the pores do not have metal "caps", since their filling with metal occurs evenly, and it takes a longer time to completely fill. As an example, Fig. 3a shows a cross section for a PAOA-based composite modified by Ag deposition for 30 min. It can be seen that for a given deposition time interval, the length of the Ag filaments is about half the length of the porous channel ( $\sim 5 \mu\text{m}$ ). The filaments have a dense, continuous structure, almost equal in length and a diameter corresponding to the pore diameter. The complete filling of the nanopores occurred with the periodic removal of a compact metal Ag layer from the surface of the PAOA membrane and the process time was about 60 min.

The qualitative composition of the obtained PAOA/Ag composites was studied by X-ray phase analysis (XPA) using an ARL X'TRA X-ray diffractometer (0.154 nm,  $\text{CuK}\alpha$ , Thermo Scientific, Switzerland). The diffraction pattern

of the composite synthesized at 30 min of Ag deposition (Fig. 3b) showed a diffraction doublet of high intensity ( $44.6^\circ$ ,  $44.9^\circ$ ), related to the  $\alpha$ -phase of  $\text{Al}_2\text{O}_3$ , and a diffuse halo ( $43.5^\circ$ ) for aluminum oxide with an amorphous structure, from which it follows that the synthesized PAOA membrane had various structural modifications. The characteristic reflections at  $24.7^\circ$  and  $38.2^\circ$  were attributed to the  $\alpha$ -phase of metallic Ag, while their low intensity indicated a low metal concentration. The average crystallite size, found according to P. Scherrer's formula ( $K \approx 1$ ), for  $\alpha$ - $\text{Al}_2\text{O}_3$  and  $\alpha$ -Ag was 15.9 nm and (11.3–23.4) nm, respectively. Thus, the synthesized composite material was an ordered porous matrix of mixed  $\text{Al}_2\text{O}_3$  with a predominance of the crystalline  $\alpha$ -phase, the inner cavity of which was filled with metallic  $\alpha$ -Ag.

When analyzing the current-time dependences of silver deposition, it was found that the deposition curves had characteristic regions corresponding to certain stages of the PAOA modification process (Fig. 3c). At the initial moment of time (0–8 min), a slight increase in the cathodic current was observed, which was associated with the occurrence of silver nucleation processes at the bottom of the pores. After the formation of Ag nuclei, the internal cavity of the nanoporous channel was gradually filled in the vertical direction, which manifested itself in the current – time dependence in an increase in the growth rate of the deposition



**Fig. 3.** Cross-sectional SEM micrograph (a) and X-ray diffractogram (b) of the composite based on Ag-modified PAOA (top view in the inset). Time dependence of the cathode current during the deposition of silver into the PAOA matrix (c).

current. After 16 min of the process, the cathodic current changed insignificantly, which indicated the formation and evolution of a continuous Ag layer on the membrane surface due to the unification of metal "caps". No further changes were recorded in the deposition curve. It can be concluded that by varying the time of the process and a qualitative analysis of the dependences of the deposition current on time, it is possible to obtain composites based on PAOA with different degrees of pore filling with metallic silver.

#### 4. CONCLUSION

Laboratory samples of thin ceramic composite PAOA nanomembranes on the basis of the developed technological procedure for the creation of composite nanomaterials from nanoporous anodic aluminum oxide filled with silver nanowires were prepared. The surface of the PAOA membranes had a highly ordered two-dimensional structure in the form of hexagonal pores with a diameter of  $(52.9 \pm 2.7)$  nm, a height of  $\sim 10$   $\mu\text{m}$  with a packing density of  $1.1 \cdot 10^{10}$   $\text{cm}^{-2}$ . At the same time, there were practically no defect areas on the surface.

It is shown that the process of modified deposition of silver into the pores of membranes has a two-stage character. At the first stage of silver deposition on the surface of the composite, the appearance of scattered spherical agglomerates with a size of 0.1 to 1.0  $\mu\text{m}$  with a low surface density, obtained as a result of the exit of metal from the porous channel to the membrane surface was observed. The appearance of silver agglomerates can be explained by the high rate of filling of single pores due to a kind of electrical "breakdown", which leads to a rapid deposition of silver in these channels. At the second, final stage, there is a uniform volumetric filling of the pores with PAOA. Within 30 min, the length of the Ag filaments is about half the length of the porous channel ( $\sim 5$   $\mu\text{m}$ ). The filaments have a dense, continuous structure, almost equal in length and a diameter corresponding to the pore diameter.

The complete filling of the nanopores occurred with the periodic removal of a compact metal Ag layer from the surface of the PAOA membrane and the process time was about 60 min.

X-ray diffraction analysis showed that the synthesized composite material was an ordered porous matrix of mixed  $\text{Al}_2\text{O}_3$  with a predominance of crystalline  $\alpha$ -phase, the inner cavity of which was filled with metallic  $\alpha$ -Ag. The average crystallite size for  $\alpha$ - $\text{Al}_2\text{O}_3$  and  $\alpha$ -Ag was 15.9 nm and (11.3-23.4) nm, respectively. It can be concluded that by varying the time of the process and a qualitative analysis of the dependences of the deposition current on time, it is possible to obtain composites based on PAOA with different degrees of pore filling with metallic silver.

The developed nanoceramic porous silver modified membranes can become the basic platform for the construction of various sensor devices.

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