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Synthesis of functional nanocomposites based on aluminum oxide

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A universal method has been developed for producing nanomaterials based on the use of solid-phase matrices with ordered porosity; these are called solid-phase nanoreactors, in this case, porous aluminum oxide. It allows you to create nanomaterials with a unique complex of functional properties that are characteristic only for highly organized arrays of ordered nanoparticles with a pore size narrow distribution. Perspective matrices for the synthesis of the nano-composites are films of porous anodic aluminum oxide having an ordered structure. They are thermally stable and chemically inert with respect to most materials. The purpose of this work was to study the features of preparing nano-structured anodic aluminum oxide as a matrix to create a composite Al_2O_3–WO_3 system with specified functional properties. Influence of the nature of sulfuric acid and oxalic acid electrolytes and their concentration on the porosity of anodic aluminum oxide was established. The synthesis parameters for obtaining oxide films on an aluminum substrate with a given pore geometry and nanostructures in the bulk of the aluminum oxide matrix were determined. A method for immobilizing by introduction of WO_3 in a film of porous aluminum oxide is proposed which makes it possible to obtain an electrode suitable for use in gas semiconductor sensors for detecting nitric oxides NO_x.

Keywords: porous aluminum oxide, nanomaterials, nanocomposites, orderliness, oxide film, formation modes.

Разработан универсальный метод получения наноматериалов, основанный на использовании твердофазных матриц с упорядоченной пористостью — твердофазных нанореакторов, в данном случае пористого оксида алюминия. Это позволяет создавать наноматериалы, обладающие уникальным комплексом функциональных свойств, характерных только для высокоорганизованных массивов упорядоченных наночастиц с узким распределением пор по размеру. Перспективной матрицей для синтеза нанокомпозитов являются пленки пористого анодного оксида алюминия, имеющие упорядоченную структуру, они термически устойчивы и химически инертны по отношению к большинству материалов. Цель работы – исследование особенностей получения наноструктурированного анодного оксида алюминия как матрицы для создания композитной системы Al_2O_3–WO_3 с заданными функциональными свойствами. Установлено влияние природы электролитов (1 М H_2SO_4 и 0,5 М $C_2H_2O_4$), их концентрации на пористость анодного оксида алюминия. Определены параметры синтеза, которые позволяют получать оксидные пленки на алюминии с заданной геометрией пор и наноструктуры в объеме матрицы Al_2O_3. Предложена методика иммобилизации WO_3 в пленку пористого оксида алюминия, позволяющая получить чувствительный элемент для использования в газовых полупроводниковых сенсорах для детектирования NO_x.

Синтез функціональних нанокомпозитів на основі оксидів алюмінію.
Г.Г.Тульський, Л.В.Ляшок, Г.С.Шевченко, О.В.Васильченко, О.А.Стельмах.

Розроблено універсальний метод отримання наноматеріалів, заснований на використанні твердофазних матриць з упорядкованою поруватістю і твердофазних нанореакторів, у данному випадку поруватого оксиду алюмінію. Це дозволяє створювати наноматеріали, що володіють унікальним комплексом функціональних властивостей, характерних тільки для високоорганізованих масивів впорядкованих наночастинок з вузьким розподілом пор за розміром. Перспективною матрицею для синтезу нанокомпозитів є плівки поруватого анодного оксиду алюмінію, що мають впорядковану структуру, вони термічно стійкі і хімічно інертні по відношенню до більшості матеріалів. Метою роботи є дослідження особливостей отримання наноструктурованого анодного оксиду алюмінію як матриці для створення композитної системи Al_2O_3–WO_3 із заданими функціональними властивостями. Встановлено вплив природи електролітів (1 М H_2SO_4 і 0.5 М $C_2H_2O_4$), їх концентрації на поруватість анодного оксиду алюмінію. Визначено параметри синтезу, які дозволяють отримувати оксидні плівки на алюмінії із заданою геометрією пор та наноструктури в об'ємі матриці алюмінієвого оксиду. Запропоновано методику іммобілізації WO_3 у плівку пористого оксиду алюмінію, яка дозволяє отримати електрод, придатний для використання у газових напівпровідникових сенсорах для детектування NO_x.

1. Introduction

One of the most important areas of chemical design of modern materials is connected with solution of the problem of producing nanostructures with specified characteristics and creating functional nanomaterials based on them. An additional problem is the metastability of phases in the nanocrystalline state [1]. It is connected with a significant increase in the specific surface of particles as their linear dimensions decrease; this results in increase in the chemical activity of the compound. The main method for synthesis of nanocomposites includes reception of free nanoparticles and their subsequent incorporation into an inert matrix. To obtain nanoparticles of the desired morphology with a narrow size distribution, as a rule, the method of synthesis in colloidal nanoreactors is used [2–4]. This approach is rather simple, but it imposes serious restrictions on the choice of the matrix, since organic polymeric compounds are usually used as matrices, and they do not always have the necessary physical properties. In addition, this approach does not completely eliminate processes of aggregation of nanoparticles. An essential significant drawback of the method is also the impossibility to obtain nanocomposites with an ordered arrangement of nanoparticles in the matrix; that significantly limits the production of materials with such unique properties. This aim is possible to reach only in the case of highly ordered systems (for example, systems with specified magnetic, electrical and optical properties) [5]. In this regard, of particular interest is the development of methods for the formation of nanocomposites using spatially-ordered nanostructures. As a rule, such structures are necessary for the creation of various classes of functional materials where metals, their oxides, semiconductors, dielectrics, etc. can act as the nanophase. One of solutions to this problem is proposed in this work; it is the method of nanocomposite synthesis, based on formation of nanostructures in the bulk of the aluminum oxide (Al_2O_3) matrix during a chemical reaction. In this case, the matrix should contain structural voids (pores) that can be filled with compounds; their subsequent modification leads to the formation of nanoparticles in these voids. In other words, the pore walls should limit the zone of reaction with the participation of the compounds introduced in them, i.e. pores act as solid-phase nanoreactors [6]. Obviously, choosing compounds with different geometry of structural voids, one can synthesize nanostructures with different morphology and in various solid phase reactors [6] (for example, in nanoporous oxides of niobium, tantalum, and aluminum with amorphous or crystalline structures). If such voids are ordered, then it becomes possible to obtain spatially-ordered nanocomposites. The proposed approach allows us to avoid the drawbacks of the methods for obtaining free nanoparticles in colloidal nanoreactors with subsequent immobilization in an inert matrix. Also we can directly control the parameters of nanoparticles in the matrix at the stage of their formation and change these parameters during the operation of the material and sub-

stantially facilitate practical application of some unique materials [7].

From the physicochemical point of view, anodic aluminum oxide (AAO) is an X-ray amorphous mixture of aluminum hydroxide $Al(OH)_3$, aluminum oxyhydroxide AlOOH, hydrated aluminum oxide $Al_2O_3 \cdot (H_2O)_{0.3}$ and anions integrated from an electrolyte solution [8]. The nature of anions in the structure of AAO strongly depends on the type of electrolyte and can range from 2 % for $C_2H_2O_4$ to 13 % for Hb_2SO_4 [9].

The structure of the AAO can be represented in the form of hexagonal dense packed cylindrical pores perpendicular to the surface of the barrier film. In the AAO film, porous and barrier layers are distinguished. The porous layer constitutes the most part of the anodic Al_2O_3 volume. The barrier layer is a rather thin and dense film located at the base of the pore. Usually, the structure of AAO can be characterized by such parameters as the degree of porosity, pore diameter, distance between pores, wall thickness, thicknesses of the porous film and barrier layer. Porous aluminum oxide is characterized by the following properties: regular porosity close to a perfectly ordered structure; relative simplicity of managing the pore sizes in a wide range; high homogeneity of the porous structure; good reproducibility of the production process. It should be noted that the porous structure has a low dispersion of the distribution of pores in diameter; this parameter can be controlled by changing the anodizing conditions ranging from a few units to hundreds of nanometers. In addition, to obtain pores of a certain size, an appropriate electrolyte should be used. Pores of the smallest diameter are obtained when the anodization is carried out in sulfuric acid [10].

Despite intensive ongoing researches and developments of effective methods for the synthesis of porous anodic metal oxides, a uniform approach to explaining mechanisms and kinetics of formation of ordered pore arrays during anode oxidation has not yet been developed. This fact significantly hinders implementation of the method in industrial technologies of ordered nanostructures.

The aim of this work was to study the peculiarities of producing anode nanostructural aluminum oxide as a matrix to create a composite Al_2O_3–WO_3 system with specified functional properties.

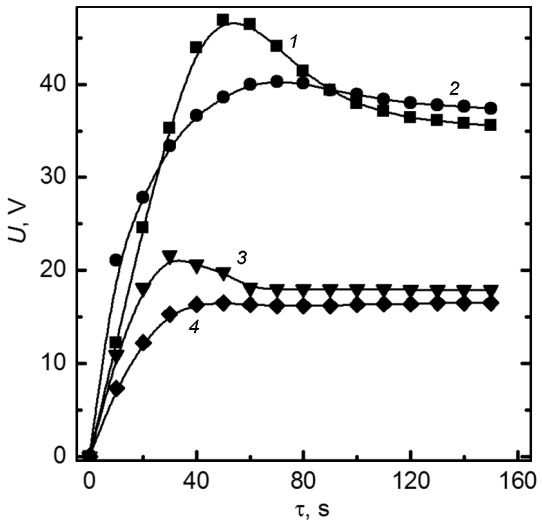

Fig. 1. Voltage versus anodizing time dependences for oxalic acid and sulfuric acid solutions of different concentrations: *1* — 1 M $C_2H_2O_4$; *2* — 0.5 M $C_2H_2O_4$; *3* — 1 M H_2SO_4; *4* — 0.5 M H_2SO_4.

2. Experimental

Anodic behavior of aluminum was studied in solutions of 1 M sulfuric acid (H_2SO_4) and 0.5 M oxalic acid ($C_2H_2O_4$) at different temperatures (5°C and 15°C). Aluminum foil samples (99.99 %) were subjected to anodization. For the study, the method of voltammetry was used. Gravimetric measurements were used to calculate the porosity of the anodic oxide films. The surface area of the samples was 2 cm^2. The counter electrode was made of lead. Morphology of the produced coatings was studied using the scanning electron microscopy method (SEM) using a microscope JSM-7001F.

3. Results

Study of the growth kinetics of a porous aluminum oxide layer was carried out in a galvanostatic mode with a variation of anodizing parameters (voltage and current). The dependences obtained as a result of the research are shown in Fig. 1.

The character of the dependences in Fig. 1 shows that a higher voltage and, presumably, pore size is achieved when using 0.5 M oxalic acid. Due to the more stable nature of the curves, solutions of 0.5 M oxalic acid and 1 M sulfuric acid were chosen for the further research.

The results of the study of electrolyte temperature effect on the growth of AOF are shown in Fig. 2.

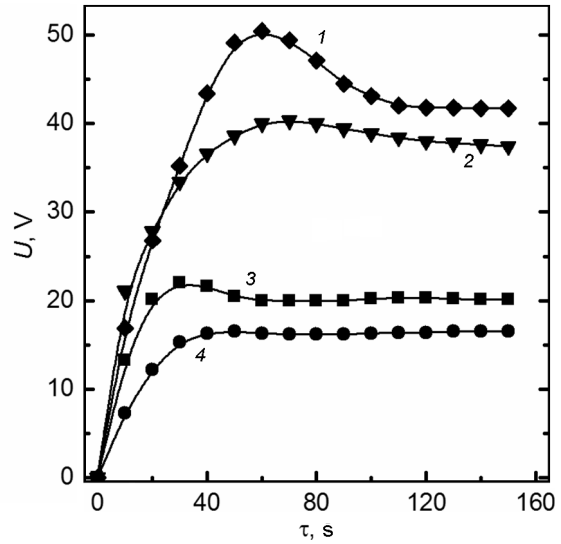

Fig. 2. Voltage versus anodizing time dependences at different electrolyte temperatures: *1* — 0.5 M $C_2H_2O_4$, 5°C; *2* — 0.5 M $C_2H_2O_4$ 15°C; *3* — 1 M H_2SO_4, 5°C; *4* — 1 M H_2SO_4, 15°C.

Regardless of the electrolyte composition, a change in temperature from 5 to 15°C with a current density of 5 mA·cm^{-2} resulted in different voltage values. As the temperature raises, the aggressiveness of electrolyte increases; thus, the processes of AOF dissolution and decrease in film thickness are accelerated. Therefore, temperatures above 15°C can lead to the destruction of a porous anodic film on aluminum.

The structural characteristics of AOF which were formed in solutions of 1 M sulfuric acid and 0.5 M oxalic acid under various synthesis conditions are given in Table 1.

As can be seen from the obtained indicators, the porosity of AOF on aluminum depends on the nature of electrolyte and anodizing conditions. Study of the structure of the obtained films confirms that pores with a larger diameter are formed in oxalic acid (Fig. 3); this result is in accordance with the results given in [10].

It can be seen from the above figures that the synthesized films have an ordered porous structure with a uniform pore size distribution.

As it is known, nitric oxides NO_x are one of the most toxic components of industrial emissions and exhaust gases of vehicles. In solving the problem of monitoring their concentration in atmosphere, semiconductor metal oxide sensors with tungsten oxide WO_3 as a sensing element are relevant [2].

The method of the nanocomposite synthesis is based on the formation of nanostructures in the bulk of the Al_2O_3 matrix during a chemical reaction.

Immobilization with WO_3 was carried out by impregnation from a saturated solution of ammonium tungstate prepared by the reaction:

$$H_2WO_4 + 2NH_4OH \rightarrow (NH_4)_2WO_4 + H_20.$$

Then, the samples impregnated in the ammonia solution were dried at temperature of 100 to 110°C, while ammonium paratungstate (APT) crystallized:

$$12(NH_4)_2WO_4 \rightarrow (NH_4)_{10}H_2W_{12}O_{42} \cdot 4H_2O + 14NH_3 + 2H_2O.$$

In the next stage the thermal decomposition of APT was carried out in air atmosphere in a muffle furnace at temperature of 600 to 700°C:

$$(NH_4)_{10}H_2W_{12}O_{42} \cdot 4H_2O \rightarrow 12WO_3 + 10NH_3 + 10H_2O.$$

Thus, the method described above has allowed us to synthesize a semiconductor composite $Al_2O_3{\cdot}WO_3$ based on nanostructured aluminium oxide.

To calculate the theoretical amount of WO_3 introduced in the oxide matrix, we assume that the volume of WO_3 is equal to the pore volume of the matrix. Taking into consideration that the pores of anodic aluminum oxide have a cylindrical shape and are perpendicularly located to the surface, also, the thickness of the synthesized film is equal to the height of a pore, we can calculate the area and volume of one pore.

The number of pores per surface unit depends on the anodization current density j and is calculated using the formula

Table 1. Characteristics of porous structure of synthesized anodic oxide films

Electrolyte	Current density j, mA·cm^{-2}	Voltage U, V	Cell diameter D_c, nm	Pore diameter D_p, nm	Porosity P, %
1 M H_2SO_4	5	20	54.3	18.1	10.2
0.5 M $C_2H_2O_4$	5	60	166.3	55.4	7.1

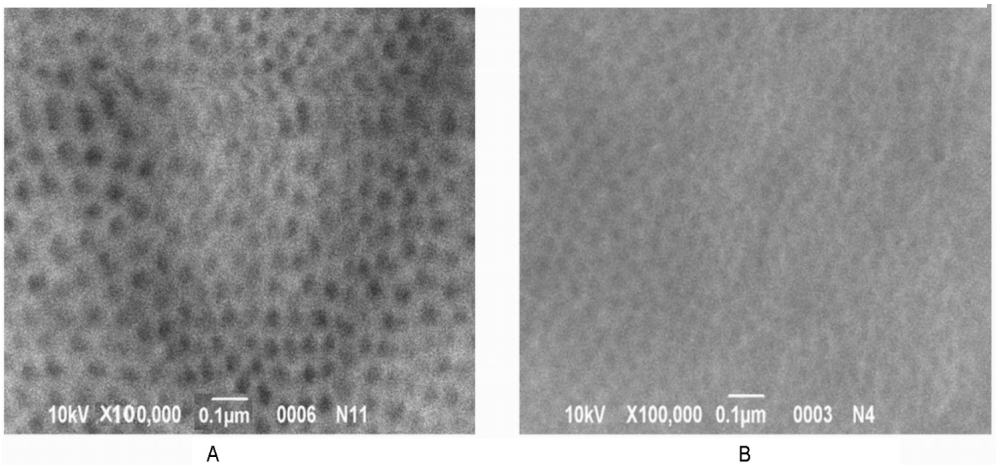

Fig. 3. Micrographs of porous AAO synthesized in: A — 0.5 M $C_2H_2O_4$; B — 1 M H_2SO_4.

Table 2. The main parameters of the synthesized composite

Electrolyte	Number of pores, n	Pore volume, cm^3	Theoretical mass of WO_3, mg	Practical mass of WO_3, mg
0.5 M $C_2H_2O_4$	$21 \cdot 10^9$	$0.5 \cdot 10^{-3}$	1.59	1.74

$$n = n_0 j^{-\alpha},$$

where n is the number of pores per cm^2; n_0 is a constant that equals $112 \cdot 10^9$ cm^{-2} for oxalic acid based electrolytes; α is a constant, which is 0.72 for oxalic acid based electrolytes.

Knowing the volume of one pore and the number of pores per surface unit, we can calculate the theoretical mass of WO_3 introduced in the oxide matrix. The practical mass was calculated gravimetrically by weighing the samples before and after filling. Parameters of the formed composite are given in Table 2.

Apparently from Table 2, the practical mass of implemented WO_3 is larger than theoretically calculated. This result suggests that in synthesized composites, WO_3 is not only in pores, but also on the surface of the samples.

To determine the gas-sensitive properties, the developed electrodes were saturated with NO_x gas for a certain time. The electrical conductivity of the composites was measured as a certain amount of gas was repeatedly added. The conductivity value was measured using an automated laboratory bench.

It can be concluded that the obtained electrode turned out to be sensitive to NO_x and can be proposed for use in gas semiconductor sensors for detecting NO_x [2]. Such sensors can also be used in industries, for example, nitric acid, oxide-semiconductor capacitors, etc., where there are emissions of NO_x.

4. Conclusions

Thus, the process of the single-stage production of AAO with the ordered structure of pores has been investigated in this work. Electrolysis parameters which allow obtaining oxide films with a given pore geometry on aluminum substrates were determined. Theoretical calculations are confirmed by scanning electron microscopy data. A method for immobilizing by introduction of WO_3 in a film of porous aluminum oxide is proposed. The performed tests confirmed that the synthesized composite can be used to detect NO_x.

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