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FABRICATION OF NANOSTRUCTURED MATERIALS BY SIMPLE ANODIZATION AND ELECTROCHEMICAL DEPOSITION

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Мембрани з наскрізними порами в анодному оксиді алюмінію (АОА) з різним розміром пор та відстанню між порами були успішно отримані методом двох-стадійного само-організованого анодування Al фольги в електролітах на основі сірчаної, оксалатної та фосфорної кислоти. Обговорюється вплив параметрів процесу анодування, таких як прикладена напруга, тривалість процесу, склад електроліту та ін. на структурні особливості АОА мембран. Такі мембрани використовувались для виготовлення металевих (Ag, Cu і Sn) та полімерних (поліпірол) матриц з нано – волокнами.

Отримання само-організованого пористого титану досягалося методом трьох-стадійного само-організованого електрохімічного анодування Ti в електроліті на основі етилен – гликолю в потенціостатичному режимі. Вивчався вплив анодного потенціалу на структурні параметри пористого анодного титану, такі як діаметр пор та відстань між ними. Була показана лінійна залежність між діаметром пор, відстанню між ними та анодним потенціалом. Обговорюються також перспективи застосування синтезованих нано – матеріалів

1.   Introduction

During the last decade nanomaterials have received significant attention due to many unique chemical and physical properties. Nanotechnology is now one of the most popular sciences which have opened a lot of new and modern perspectives in almost all scientific disciplines [1].

Therefore, nanostructured materials have found a great variety of promising applications and considerable attention has been paid on developing new, simple and non-expensive methods of nanofabrication. Many promising strategies have been already reported. Among them, simple anodization process has been successfully employed to fabrication of nanoporous oxide layers on the surface of different metals [2]. Nanoporous anodic alumina (AAO) membranes, with a thickness up to 60 microns, pore diameters from several to several hundreds of nanometers and different interpore distances can be easily synthesized by a simple self-organized two-step electrochemical anodization of aluminum carried out in acidic electrolytes including sulfuric acid [3], oxalic acid [4] and phosphoric acid [5].

All structural futures of AAO membranes can be easily controlled by adjusting of anodizing conditions such as anodizing potential, time and electrolyte composition [2]. After suitable preparation, AAO membranes can serve as templates for fabrication of great variety of nanomaterials such as: nanowires, nanotubes and nanodots which offers a lot of modern technological applications e.g., in magnetic, photonic, electronic, and sensing devices and structures [6]. On the other hand, porous anodic titanium oxide (ATO) obtained by anodization of Ti substrates proved to be very efficient catalysts used for water photolysis, hydrogen generation and decomposition of unwanted organic compounds. Other technological applications of porous titania includes

dye-sensitized solar cells, structural ceramics, humidity, gas and biochemical sensors as well as biocompatible materials for bone implants [7].

Here, we discuss the procedures for fabrication of AAO and ATO layers by simple electrochemical anodizing. In addition, some results from the synthesis of metallic and polymer nanowire arrays by electrodeposition are also presented.

2. Experimental

2.1. Preparation of through–hole AAO membranes

The annealed aluminum foil (99.999%, Good Fellow), 0.5 mm thick was used as a starting material. After degreasing in ethanol, substrates with dimensions of 25 mm × 5 mm × 0.5 mm were electropolished in a mixture of perchloric acid (60 wt.%) and ethanol (1:4 vol.) at the constant current density of 0.5 $A \cdot cm^{-2}$ for 1 min at 10 °C. A two-step anodizing procedure was employed for fabricating nanoporous films. Alumina layers obtained during first anodization were chemically removed in a mixture of 6 wt.% H_3PO_4 and 1.8 wt.% $H_2Cr_2O_4$ at 45 °C for 12 h. Subsequently, the second anodization was carried out in the same experimental conditions as were used in the first step.

All anodizations were performed in a simple electrochemical cell with vigorous magnetic stirring, thermostated by a powerful circulating system (Thermo Haake, DC10-K14). A Pb plate was used as the cathode and the distance between both electrodes was about 3 cm. After anodization, nanoporous films were separated from the remaining aluminum substrate by immersing in a saturated $HgCl_2$ solution. Then a chemical etching of continuous alumina layer at the pore bottoms was performed in 5 wt.% H_3PO_4 solution. All anodizing conditions together with structural features of as-prepared membranes are collected in Table 1.

Table 1. **Anodizing conditions together with structural features of AAO membranes obtained by two-step anodization in different electrolytes**

Electrolyte	Anodizing voltage [V]	Temperature [°C]	Duration of the first/second anodization [h]	Pore diameter* [nm]	Interpore distante [nm]	Oxide layer thickness [μm]
0.3 M H_2SO_4	25	1	8/10	23	~60	~40
0.3 M $H_2C_2O_4$	45	25	1/4	34	~108	~36
2 % H_3PO_4 in CH_3OH – water system (1:4 vol.)	175	0	8/30	180	~390	~50

* before pore opening/widening procedure

2.2. Fabrication of ATO layers

A titanium foil (99.5% purity) 0.25 mm thick (Alfa Aesar) was used as a starting material. Ti samples (0.5 cm × 2.5 cm) were electrochemically polished in a mixed solution of acetic acid (99.5%), sulfuric acid (98%), and hydrofluoric acid (40%) (60:15:25 in volume) at constant current density of 70 $mA \cdot cm^{-2}$ and 20 °C for 1 min, followed by chemical polishing in a mixture of HF (40%) and nitric acid (65%) (1:3 in volume) for 10

s until a mirror finish was exposed. The anodic oxide layer was formed by a three-step procedure under a constant cell voltage ranging between 30 and 70 V an ethylene glycol solution containing NH_4F (0.38 wt%) and H_2O (1.79 wt%) at 20 °C. The duration of the first and second anodizing steps was 3 h. After both anodizing steps, the oxide layer was removed by an adhesive tape. After the oxide removal, the titanium sample was re-anodized under the same conditions as in previous steps. The duration of the third anodization was 10 min.

2.3. Synthesis of nanowire arrays

Through–hole AAO membranes were used as templates. Before electrodeposition, an Au conducting layer was sputtered at the bottom side of the membrane. The DC galvanostatic electrodeposition of metallic nanowire arrays and potentiostatic electropolymerization of pyrrole was performed in a three-electrode cell. AAO membrane serves as a working electrode, and Pt plates as counter and reference electrodes. In case when electropolymerization was performed, the SCE reference electrode was used. An EG&G potentiostat (model 273A, Princeton Applied Research) was used during electrochemical deposition. The experiment conditions for different materials deposition are collected in Table 2. After electrodeposition, samples were immersed in a 1 M NaOH solution for 45 min in order to dissolve the alumina membrane. The morphology of as-fabricated structures was analyzed with a field–emission scanning electron microscope (FE-SEM/EDS, Hitachi S-4700 with a Noran System 7) and compositions of nanowire arrays were confirmed by EDS analyses.

Table 2. Experimental conditions for fabrication of nanowire arrays

Type of nanowires	Electrolyte	Experimental conditions
Ag	Commercial plating solution (Alfa Aesar, Ag content 28.7 g · dm^{-3})	Galvanostatic electrodeposition $j = 0.5 \, mA \cdot cm^{-2}$ $t = 120 \, min$
Sn	$7 \, g \cdot dm^{-3} \, SnCl_2 + 25 \, g \cdot dm^{-3}$ sodium citrate	Galvanostatic electrodeposition $j = 2 \, mA \cdot cm^{-2}$ $t = 10 \, min$
Cu	$0.5 \, M \, CuSO_4 + 0.5 \, M \, H_2SO_4$	Galvanostatic electrodeposition $j = 2 \, mA \cdot cm^{-2}$ $t = 60 \, min$
polypyrrole	$0.1M \, NaClO_4 + 0.05M \, Py$	Potentiostatic electropolymeryzation $E = 1.5 \, V \, vs. \, SCE$ $t = 100 \, s$

3.   Results

3.1. Fabrication of AAO templates

The two–step self–organized anodization of aluminum results in the formation of porous alumina layer that consists of hexagonal cells with nanopores at their centers (Figure 1A). At the bottom of pores, continuous and dielectric oxide layer, called "barrier layer" is built (Figure 1B).

All structural features of porous anodic alumina layers, such as: oxide layer thickness, pore diameter, interpore distance, "barrier layer" thickness as well as the regularity of pore arrangement strongly depend on anodizing condutions, especially chosen electrolyte, anodizing voltage and duration of the process.

A self-organized process of aluminum anodization is usually performed in a sulfuric, oxalic or phosphoricacid solutions.

The nanostructures with the smallest pores (from tens to about 35 nm) and highest pore density can be obtained by anodizing in sulfuric acid solutions (Figure 2A). Using oxalic acid as electrolyte, oxide layers with pore diameters between 40 and 100 nm (Figure 2B) can be formed. On the contrary, anodizations carried out in electrolytes containing phosphoric acid (Figure 2C) results in formation of AAO membranes with the highest pore diameters (up to 300 nm) and interpore distances (up to 500 nm).
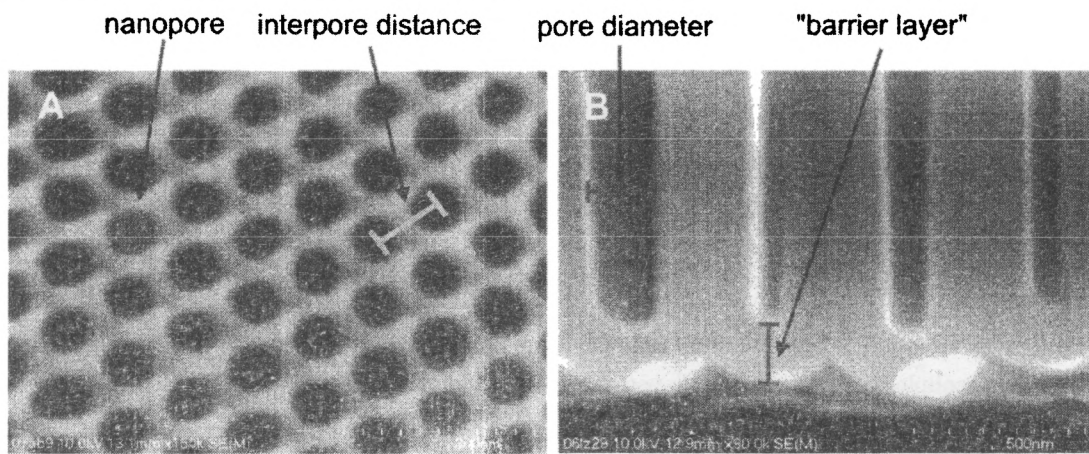

Figure 1. **FE-SEM images of nanoporous AAO membranes. Top-view (A) and cross-sectional view (B)**
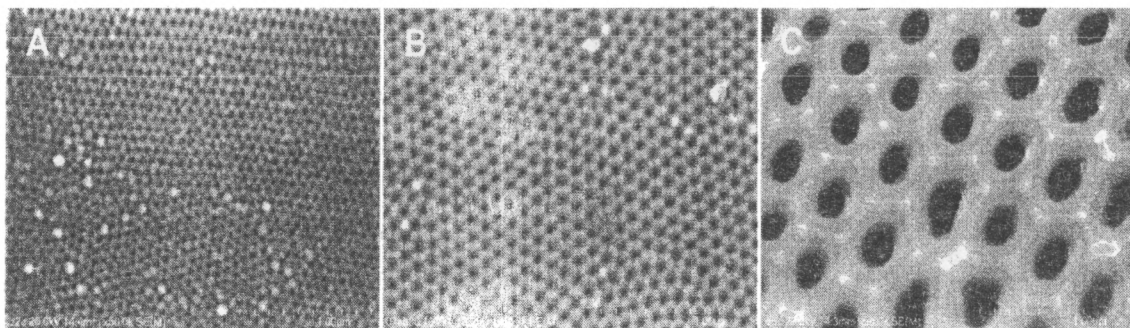

Figure 2. **Porous alumina layers obtained by anodization of aluminum in sulfuric acid at 25 V (A), oxalic acid at 45 V (B) and phosphoric acid at 175 V (C)**

The characteristic parameters of AAO layers shown in Figure 2 obtained by anodizing in different electrolytes under specific conditions are collected in Table 1. It is generally accepted that the pore diameter and interpore distance of the AAO lattice are linearly proportional to the anodizing potential with a proportionality constants of about 1.1 nm/V and 2.5 nm/V, respectively. It is worth noting that in many cases these constants can vary depending upon the particular type and geometry of the electrochemical cell. This indicates that all anodizing procedures need to be optimized in each laboratory to achieve reliable data. For the certain applied

voltage and temperature, the depth of nanoporous channels in AAO films can be easily adjusted between a few and hundreds of microns by varying anodizing time. It is widely recognized that anodization of aluminum in acidic electrolytes results in porous structures but, the best pore arrangement is formed only under a specific anodizing potential equals to 195 V for phosphoric acid, 40 V for oxalic acid and 25 V for sulfuric acid [2]. By applying different voltages, structures with poorly arranged pores and defects in a hexagonal lattice are formed. Unfortunately, in some cases the anodic dissolution of metal occurs instead of stable porous oxide growth and applying potentials close to the self-ordering regime is impossible. The problem often appears in phosphoric acid solutions. This is a reason why the potential of 175 V is used instead of 195 V. Fortunately, the addition of methanol to the electrolyte improved significantly the pore arrangement [5].

In order to obtain through-hole membranes, the pore opening/widening process has been carried out in 5 wt.% phosphoric acid. Figure 2 presents undersides of AAO membranes formed by anodizing in oxalic (Figures 3A and 3B) and phosphoric acid (Figures 3C and 3D) before and after the opening of the pore bottoms. Pore diameter after the opening procedure was estimated to be about 80 nm and 380 nm for membranes synthesized by anodization in oxalic and phosphoric acid, respectively. The rate of oxide etching strongly depends on temperature and phosphoric acid concentration and also should be optimized for each laboratory.
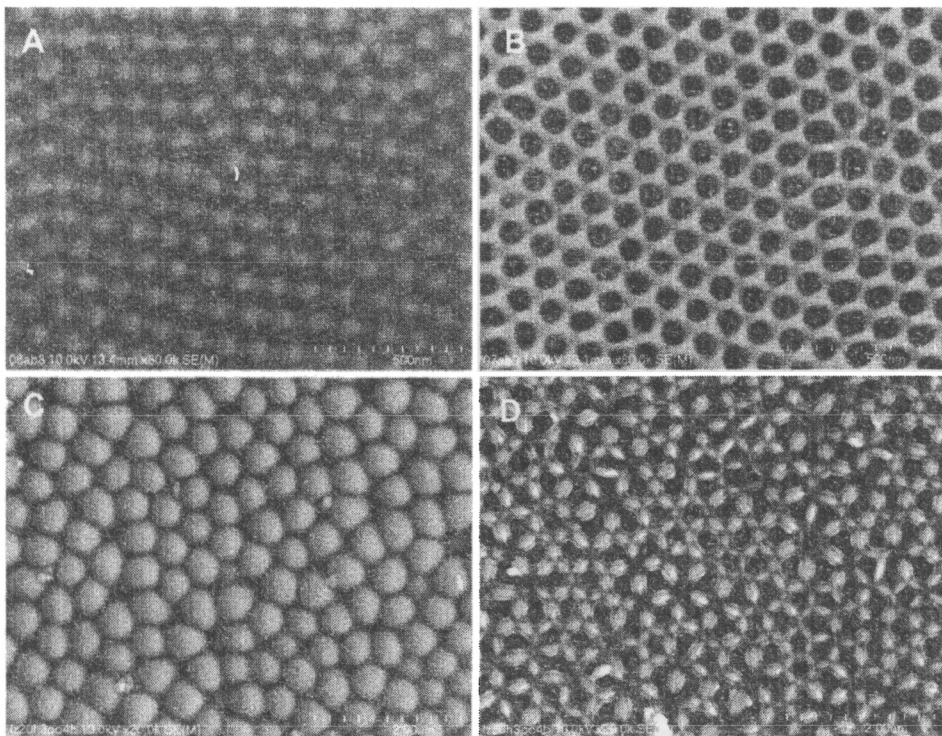

Figure 3. **FE-SEM bottom views of AAO membranes before (A, C) and after (B, D) pore widening process. The procedure was carried out in 5 % H_3PO_4 for 80 min at 25 °C for membranes obtained by anodizing in oxalic acid (A, B) and in 10 % H_3PO_4 for 40 min at 45 °C for membranes obained by anodizing in phosphoric acid solution (C, D)**

3.2. Fabrication of ATO layers

Similarly to anodic alumina, the ideal structure of the highly ordered TiO_2 layer is represented by a closed-packed array of hexagonally arranged cells containing pores in each cell center. Typical FE-SEM top-,

bottom- and side-view images of anodic titania layer obtained by the three-step anodization performed in an ethylene glycol solution containing NH_4F (0.38 wt%) and H_2O (1.79 wt%) at 40V and 20 ° C are shown in Figure 4. The duration of the third step was 10 min. As can be seen, anodizing of titanium in an ethylene glycol-based electrolyte can give a periodic lattice of nanopores (Figure 4A). The dimensions of pores and distances between them are quite uniform but, the pore arrangement is far from the ideal hexagonal arrangement. During the porous oxide growth, a thin and compact barrier layer at the pore bottom is also formed (Figure 4B). A cross-sectional view (Figure 4C) shows that the oxide coating is a relatively thick (about 2 μm) as for 10 min of anodization.

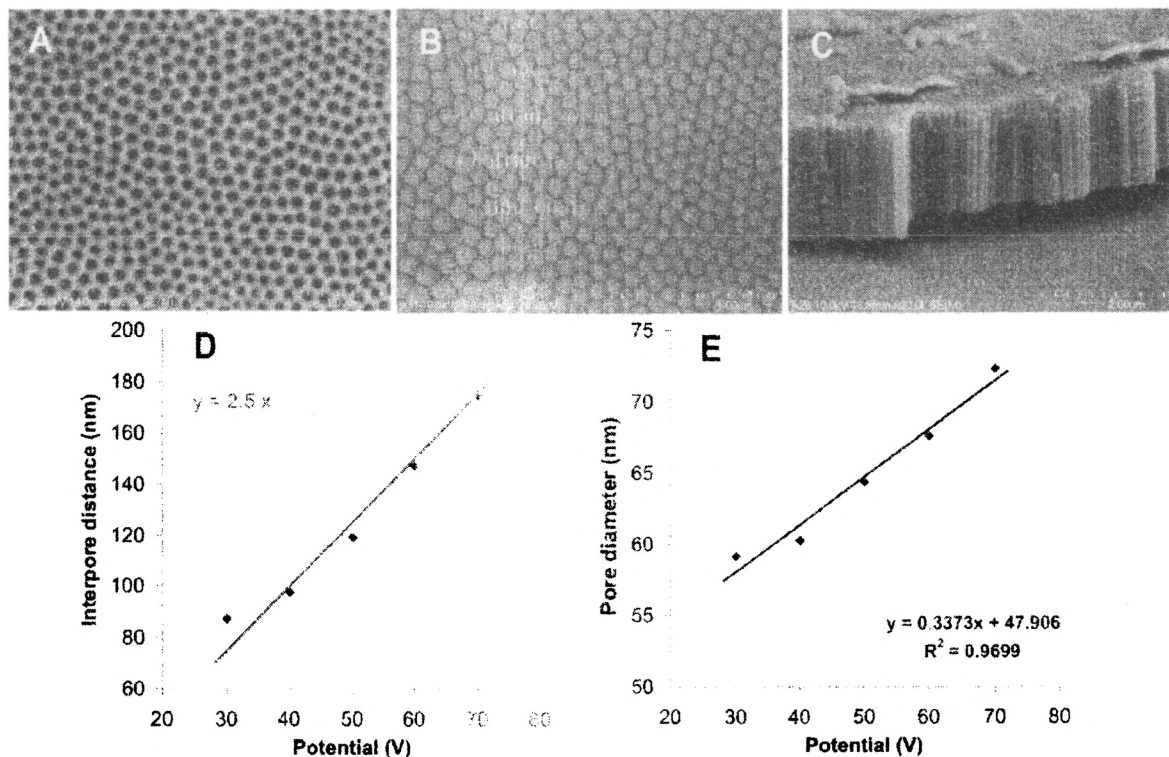Figure 4. **Top- (A), bottom- (B) and side-view images of nanoporous titania layers obtained by a simple three-step anodization in an ethylene glycol-based electrolyte at 40 V and 20 °C together with the illustration of anodic potential influence on interpore distance (D) and pore diameter (E)**

Structural features of titania layers also depend on anodizing conditions. The potential influence on interpore distance and pore diameter of ATO layers is shown in Figure 4D and 4E, respectively. The experimental data points show that the interpore distance is linearly dependent upon the anodization voltages and varies from about 90 to 175 nm in the range of anodizing potential from 30 to 70 V. Also linear relationship between pore diameter and anodizing potential is observed. As can be seen, the pore diameter increases from about 59 to 72 nm when anodizing potential increases from 30 to 70 V. The anodizing potential also influences considerably the nanopore arrangement. The best hexagonal arrangement of nanopores is observed for the anodizing potential of 40 V. On the other hand, the structure of anodic TiO_2 depends on the duration of the third anodizing step. For the ethylene glycol-based electrolyte, the porous structure is formed only for a short period of anodizing time, not exceeding 45 min. Consequently, further increase in anodizing time up to 3 h results in a

fibrous-like structure with nanotubes underneath. This is attributed to the chemical dissolution of the newly formed anodic oxide by F^- ions present in the electrolyte. Our current research is focused on investigation of the influence of other parameters, such as: temperature, electrolyte composition *etc.*, on the structural features of anodic titania films. Additionally, some experiments on electrodeposition of metals into the pores of ATO are performed.

3.2. Synthesis of nanowire arrays

Through–hole AAO membranes obtained by two–step anodizing in a 0.3 M oxalic acid solution at 45 V and 20 °C were employed as templates for fabrication of metallic and polymeric nanowire arrays. After 90 min of pore opening process, carried out in 5 % H_3PO_4 the pores have diameter of about 80 nm and depth of about 40 μm. The composition of the plating solutions and conditions used in the electrochemical deposition of nanowires were collected in Table 2.

FE-SEM images of free–standing Ag, Cu and Sn nanowire arrays after dissolution of porous templates are shown in Figures 5A, 5B and 5C respectively. Metallic nanowires are continues, homogeneous in shape and arranged parallel to each other.
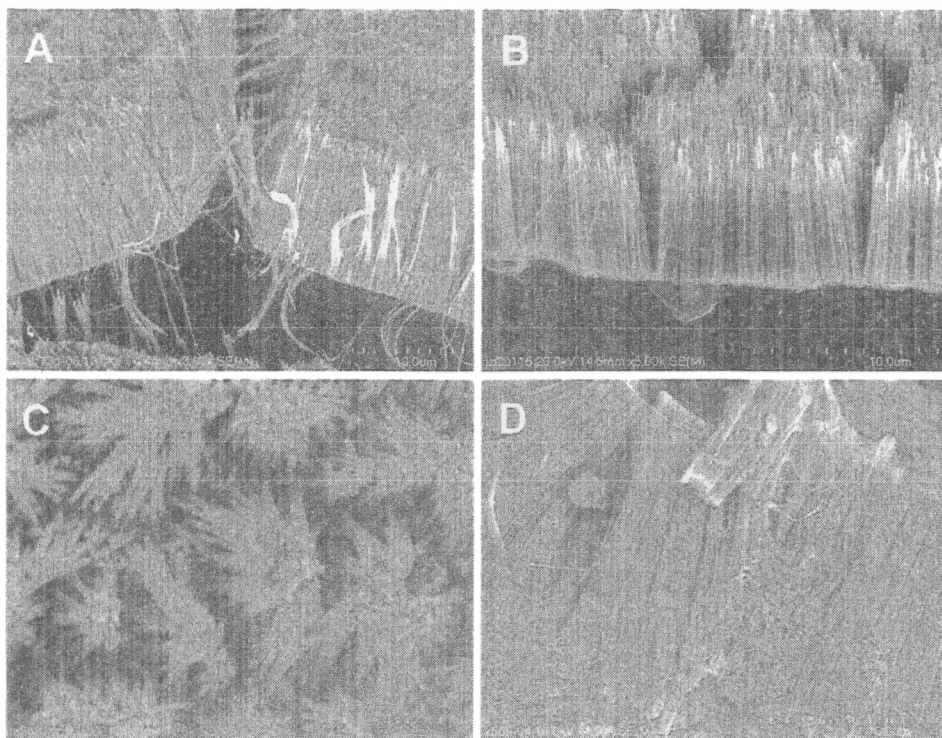

Figure 5. **Silver (A), copper (B), tin (C) and polypyrrole (D) nanowire arrays obtained by DC electrodeposition and electropolymerization inside porous AAO templates**

All nanowires have a nearly uniform diameter of about 80 nm independently on the type of electrodeposited metal and the value is consistent with the average pore diameter of AAO templates. The length of nanowires can be controlled in a range from several nanometers to a few tens of micrometers by varying the deposition time. However, despite a constant geometric surface area of all samples, the real current density for each individual samples can be different due to the presence of some pores blocked by air bubbles and impurities trapped inside the pores. Under the chosen electrodeposition conditions, the average length of Ag, Cu and Sn

nanowires was estimated at about 10.9, 6.8 and 1.1 μm, respectively. Consequently, Ag, Cu and Sn nanowires have a aspect ratio of about 136, 85 and 14, respectively. Vertical metallic nanowires have a strong tendency to aggregate into bundles after a complete dissolution of the alumina template due to existence of capillary forces between nanowires. Currently, we are working on using metallic nanowire arrays in electrocatalysis (Ag), and lithium ion batteries as current collectors (Cu) and active material (Sn).

Figure 5D shows polypyrrole (PPy) nanowires synthesized by simple electropolymerization of pyrrole inside the pores of AAO membrane after dissolution of the template. PPy nanowires have uniform diameters of about 80 – 85 nm and length of 17.6 μm that gives an aspect ratio of about 207. Recently, some investigations on employing functionalized PPy nanowire arrays as pH sensor have been performed in our group.

4. Conclusions

The following conclusions can be drawn:

1. Through–hole AAO membranes with pore diameters from tens to few hundreds of nanometers can be easily fabricated by a simple two- step anodization of aluminum and subsequent pore-opening procedure.

2. Nanoporous titania layers with well–arranged honeycomb structures can be synthesized via the three – step anodizing of titanium in an ethylene glycol solution containing NH_4F (0.38 wt%) and H_2O (1.79 wt%)

3. The structural features of AAO and ATO layers such as: pore diameter, interpore distance, "barrier layer" thickness, thickness of the oxide layer as well as pore arrangement depends on anodizing condition, especially on applied voltage, electrolyte composition and duration of the process.

4. AAO membranes can be successfully employed for fabrication of metallic or polymeric nanowire arrays. The diameters of nanowires are determined by diameters of pores of alumina templates.

Acknowledgments

5. References

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