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ARTICLE

Electrochemical Method of Preparing Metallic, Polymeric and Organic-Inorganic Hybrid Nanowires inside Porous Anodic Alumina Templates

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Abstract: The fabrication of free standing silver, polypyrrole (PPy) and hybrid PPy–Ag nanowire arrays was reported. Silver, PPy and PPy–Ag nanowires were produced by electrochemical deposition/polymerization of metal/polymer in anodic aluminum oxide (AAO) templates. The home–made AAO templates were fabricated by two–step anodization of aluminum performed in oxalic acid, sulfuric acid and phosphoric acid at the anodizing potentials of 25 V, 45 V and 195 V, respectively. Silver nanowires with a diameter of ~40, 80 and 300 nm were synthesized by DC electrode position from a commercially available plating bath. PPy nanowires, ~80 nm in diameter, were synthesized by electropolymerization of a monomer in a solution containing pyrrole (Py) and $NaClO_4$ by applying a constant potential. The hybrid PPy–Ag nanowires, ~80 nm in diameter, were synthesized by a simple simultaneous cathodic electropolymerization of pyrrole and metal deposition in a solution containing HNO_3, $NaNO_3$, pyrrole (Py) and $AgNO_3$ by applying a constant potential. After the electrochemical deposition, free standing Ag, PPy and PPy–Ag nanowire arrays were obtained by a subsequent chemical etching of the AAO template in an aqueous NaOH solution. The morphology and structural characterization of fabricated nanowires were performed by FE–SEM and EDAX analyses.

Keywords: AAO templates; Electrodeposition; Electropolymerization; Nanowires.

Introduction

From a material viewpoint, the advancement of science and technology provides the smaller and smaller dimensions with higher precision and enhanced performance. The widespread interest in nanostructured materials is observed mainly due to the fact that their properties, such as: optical, electrical and mechanical, are usually different from those of the bulk materials. Different methodologies for conventional and unconventional fabrication of nanomaterials, such as photolithography, imprinting, molding and methods based on self–organization, have been developed in the past [1]. For nanotechnological applications of materials, a high order of obtained nanostructures and reproducibility of fabrication method are very important. It is not insignificant that the method of fabricating nanomaterials should be of low cost, and easily performed. Most of the methods listed above, are expensive and time–consuming and thus, difficult for adaptation in the industry [2].

Different methods have been used for preparing 1D nanomaterials [2]. Among these

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methods, a template–based synthesis is one of the most simple and low–cost fabricating ways. This method of fabrication of metallic or polymer nanotubes, nanowires and nanofibers is very promising. The template–assisted method, using porous AAO membranes, allows to control precisely the morphology and dimensions of nanowires.

Porous anodic aluminum oxide (AAO) can be fabricated electrochemically through anodic oxidation of aluminum [3]. AAO membranes have a wide range of applications in both the macro– and nano–world. For example, AAO in the macro–world, can be used as a protective and decorative cover, and in the nano–word in molecular filtration, template synthesis, catalysis, sensing, electronics, photonics, energy storage and drug delivery [4]. However, the most important application of AAO, from the perspective of nanotechnology, is its utilization as a matrix to produce a number of nanomaterials: metal nanostructures (nanodots, nanowires, nanorods and nanotubes), oxide nanostructures (nanodots, nanotubes and nanowires), semiconductor nanostructures (nanodots, nanowires and nanopores), polymer nanostructures (organic and inorganic nanowires and nanotubes) [2]. AAO formed by self–organized anodization of aluminum in acidic electrolytes consists of regularly arranged hexagonal cells with nanopores at their centers (Figure 1) [2]. Depending on the used electrolyte and anodizing conditions, this simple electrochemical process results in nanoporous structures with a pore diameter ranging from about 10 to over 300 nm and the interpore distance ranging from about 35 to 500 nm.

In this study, porous anodic alumina membranes with different pore diameters and interpore distances were fabricated by self–organized process occurring during the anodization of aluminum in sulfuric, oxalic and phosphoric acids.

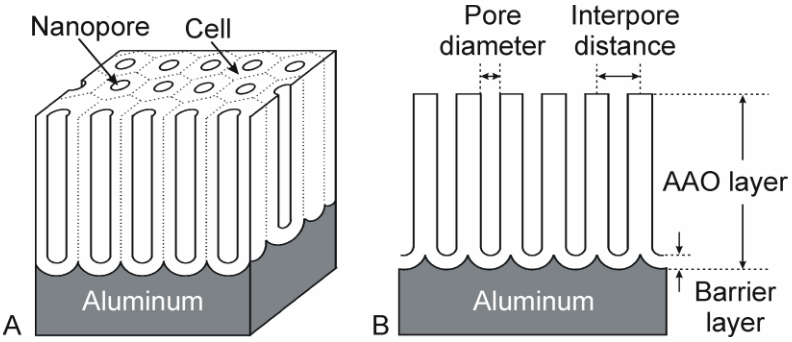

FIG. 1: Idealized structure of anodic porous alumina (A) and cross-sectional view of the anodized layer (B) [2].

It is noteworthy that nanofibers and nanowires have shown higher conductivity and strength over conventional bulk forms. As one of the most promising 1D nanomaterials, silver and polypyrrole nanowires have exhibited many interesting properties that can be exploited in various fields of science and engineering.

Silver nanoparticles are of special interest, because they are potential electrocatalysts for fuel cells [3] and reduction of organic halides [4, 5]. They also can be used in surface plasmon resonance (SPR) [6, 7] and surface–enhanced Raman scattering (SERS) [8, 9], as well as in chemical and biological sensing [10]. Conducting polymers, such as PPy, combining the advantages of organic polymers and the electronic properties of semiconductors, are attractive materials for use in data storage and photovoltaic cells. They also can be used as electrochromic devices, chemical sensors and biosensors, logic or switching elements and supercapacitors [11]. PPy nanostructures could also be utilized as a matrix for the formation of metal–polymer hybrid electrodes [12, 13 and 14], metal oxide–polymer composite nanowires [15, 16] and for embedding or dispersing of metal particles with electrocatalytic properties [17, 18 and 19].

Methodology

In general, the electropolymerization of a monomer and electrode position of metal have been performed at nanochannels of lab–made AAO templates with an average pore diameter of about 40, 80 or 300 nm. The AAO templates were prepared by two–step anodizing as described previously [2], in operating conditions collected in Table 1. Due to a relationship between the pore diameter of AAO and the type of electrolyte used for anodization [2], three types of templates with different pore diameters were fabricated in sulfuric acid (0.3 M), oxalic acid (0.3 M) and phosphoric acid (2 wt.% in CH_3OH water system 1:4 vol.) solutions at different anodic voltages. A high purity (99.999%) aluminum foil was used as a starting material. After degreasing in ethanol and electropolishing in a mixture of perchloric acid (60 wt.%) and ethanol (1:4 vol.), performed at the constant current density of $0.5\ A\cdot cm^{-2}$ for 1 min at 10 °C, aluminum sheet (25 × 5 × 0.5 mm) was first anodized at a constant voltage. Then, the formed AAO was removed by a wet chemical etching in a mixture of phosphoric acid (6 wt.%) and chromic acid (1.5 wt.%) at 45 °C for about 12 h. After that, the samples were anodized again at the same conditions as during the first anodization. After anodization, the remaining aluminum substrate was chemically removed by immersion in a saturated $HgCl_2$ solution. Subsequently, alumina barrier layer at the pore bottoms was removed in a 5% H_3PO_4 solution at 45 °C. In order to fabricate Ag, PPy and PPy–Ag nanowires, a thin Au conducting layer was sputtered at the bottom side of through–hole AAO membranes.

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

Electrolyte	Anodizing voltage [V]	Temperature [^oC]	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	40	~60	~40
0.3 M $H_2C_2O_4$	45	25	1/4	80	~108	~36
2 % H_3PO_4 in CH_3OH – water system (1:4 vol.)	195	0	8/30	~300	~390	~50

Silver nanowires with different diameters (40, 80 and 300 nm) have been successfully fabricated into the anodic alumina oxide (AAO) membranes by a direct–current electro deposition from a commercially available plating solution with a metal content of $28.7\ g/dm^3$. Polymer nanowires with a diameter of 80 nm have been synthesized by electropolymerization of a monomer in a solution containing 0.1 M $NaClO_4$ and 0.05 M pyrrole by applying a constant potential of 1.5 V vs. the saturated calomel electrode (SCE). The hybrid PPy–Ag nanowires were synthesized by a simple simultaneous cathodic electropolymerization of pyrrole and metal deposition in a solution containing 0.4 M HNO_3, 0.5 M $NaNO_3$, 0.2 M pyrrole (Py) and 0.1 M $AgNO_3$ by applying a constant potential of –0.625 V vs. the saturated calomel electrode (SCE). With prolonged electrodeposition time, the AAO template changed the color from gold to brown.

To obtain free–standing silver and polypyrrole nanowire arrays, the AAO templates were dissolved by chemical etching in a 1 M NaOH solution. The structural characterization and morphology of silver and polypyrrole nanowires were performed by FE–SEM and EDAX analyses.

Results and discussion

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 conditions, especially chosen electrolyte, anodizing voltage and duration of the process. A self-organized process of aluminum anodization is usually performed in sulfuric, oxalic or phosphoric acid solutions. Figure 2 shows FE–SEM micrographs of AAO templates synthesized in different electrolytes with different pore diameter and interpore distance. Self-organized anodizing of aluminum in acidic electrolytes can result in an almost perfectly ordered nanopore array. The regular nanohole arrangement can be obtained only in the narrow range of anodizing potentials and this potential window varies between 15 and 25 V for sulfuric acid, 30 and 80 V for oxalic acid and 100 and 200 for phosphoric acid, respectively. The structural features of prepared AAO templates are collected in Table 1.

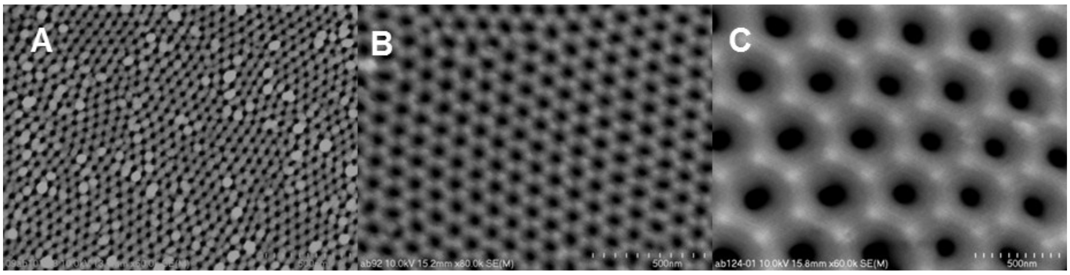

FIG. 2: FE-SEM images of porous alumina templates obtained by anodization of aluminum in sulfuric acid at 25 V (A), oxalic acid at 45 V (B) and phosphoric acid at 195 V (C).

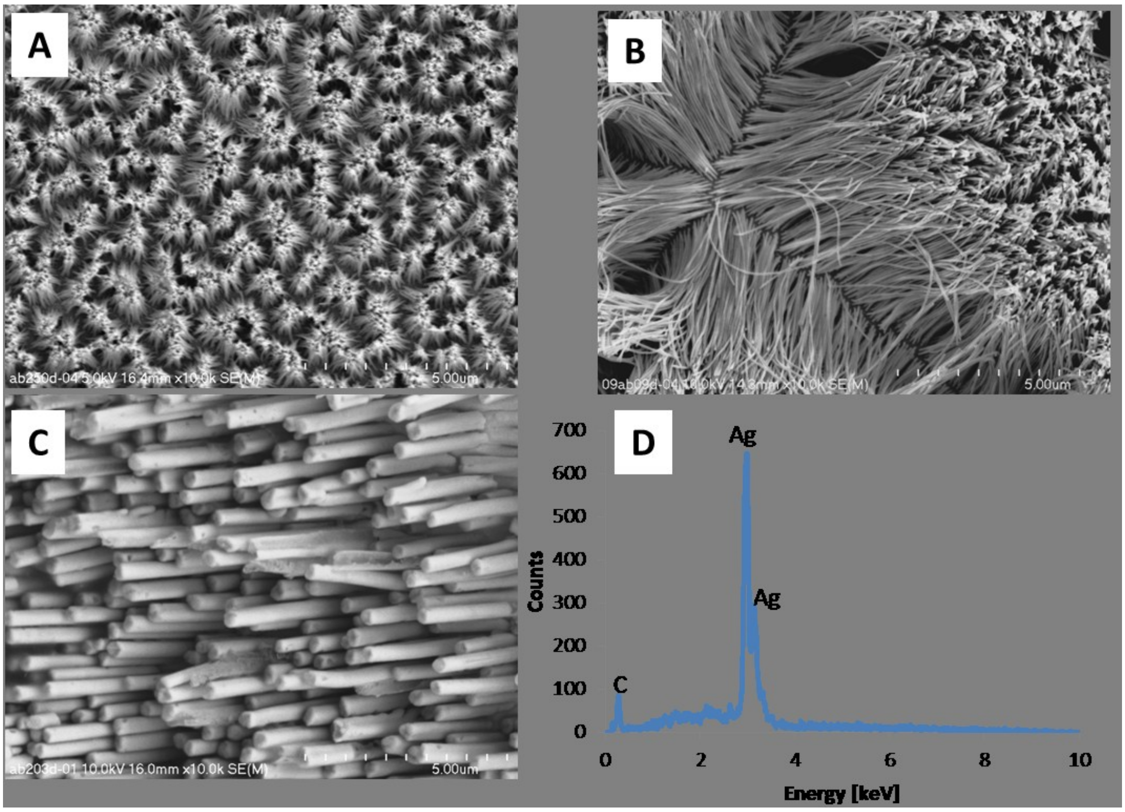

FIG. 3: FE–SEM images of free–standing silver nanowires obtained by DC electrode position inside AAO templates with diameters of about: 40 (A), 80 (B) and 300 nm (C) together with EDAX analysis (D).

FE–SEM images (Figure 3) of the free–standing silver nanowires liberated from the AAO templates show an uninterrupted silver nanowire structure up to approximately 1.0 µm (Figure 3A), 2.8 µm (Figure 3B) and 2.2 µm (Figure 3C) length. The average diameter of nanowires is approximately: 40, 80 and 300 nm for sulfuric, oxalic and phosphoric acid templates, respectively. Consequently, Ag nanowires have an aspect ratio of about 25, 35 and 7, respectively. To confirm the chemical composition of obtained Ag nanowires, the EDAX analysis was performed (Figure 3D). As can be expected, the spectrum showed that Ag nanowires are composed of silver. The spectrum display also carbon peaks as a result of the presence of the thin, conducting C layer attached to the bottom of the sample in order to improve its mechanical stability and electrical conductivity during SEM analysis. The PPy nanowires after dissolution of the AAO template in a NaOH solution are shown in Figure 4(A-C).

The fabricated PPy nanowires have a uniform diameter of about 80 – 85 nm and the length of 17.6 µm that gives an aspect ratio of about 207. In order to confirm the composition of PPy nanowires, IR analysis was performed in the range of 450 – 4000 cm^{-1} (Figure 4C). For the PPy nanowire spectrum, the bands at 2917 cm^{-1} are related to the carbonyl group C=O stretching. The broad band at 3420 cm^{-1} is attributed to the N-H stretching in pyrrole. The presence of the absorption band at 1620 cm^{-1} in the PPy spectrum is assigned to the axial deformation of C = C bond.

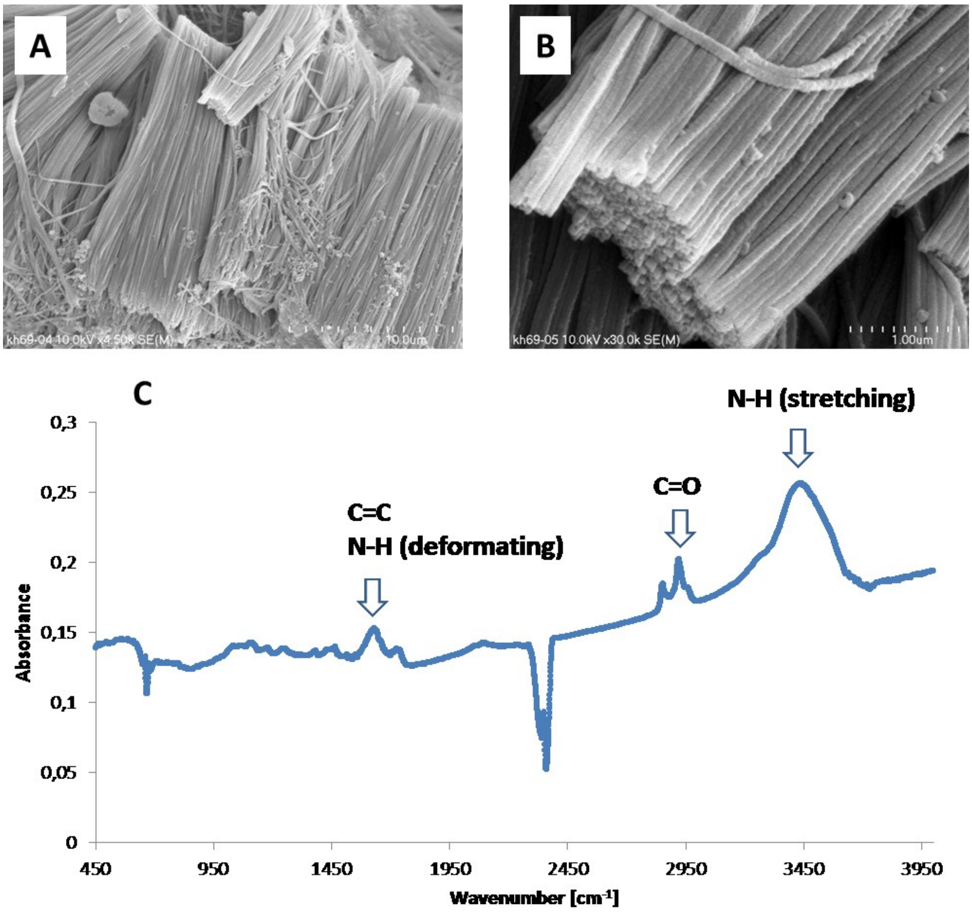

FIG. 4: FE-SEM images of the PPy nanowires after dissolution of the AAO template at different magnifications: 4500 (A) and 30000 (B) and its IR analysis.

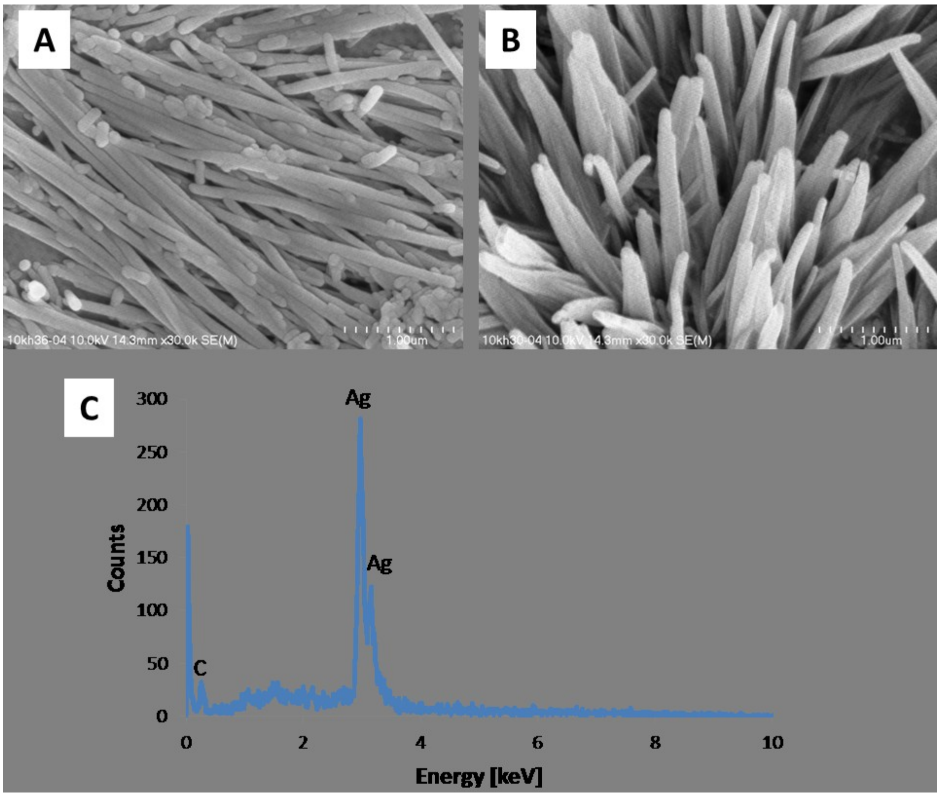

FIG. 5: FE–SEM micrographs of hybrid Ag (A) and PPy–Ag nanowires (B) with EDAX analysis of hybrid nanowires (C).

Fig. 5 shows Ag (A) and hybrid PPy–Ag (B) nanowires synthesized by a simple simultaneous cathodic electropolymerization of pyrrole and metal deposition inside the pores of AAO membrane after dissolution of the AAO template. It is easily to notice that silver nanowires have smoother surface than hybrid PPy–Ag. In the composite material, aggregation of nanowires is stronger and nanowires have more rough side–surfaces as shown in Figure 5B.

After dissolution of metallic part of hybrid PPy–Ag nanowires, performed in HNO_3 at 0 ^{o}C for 1 h, the obtained PPy nanowires have a diameter of about 65 nm (Fig. 6).

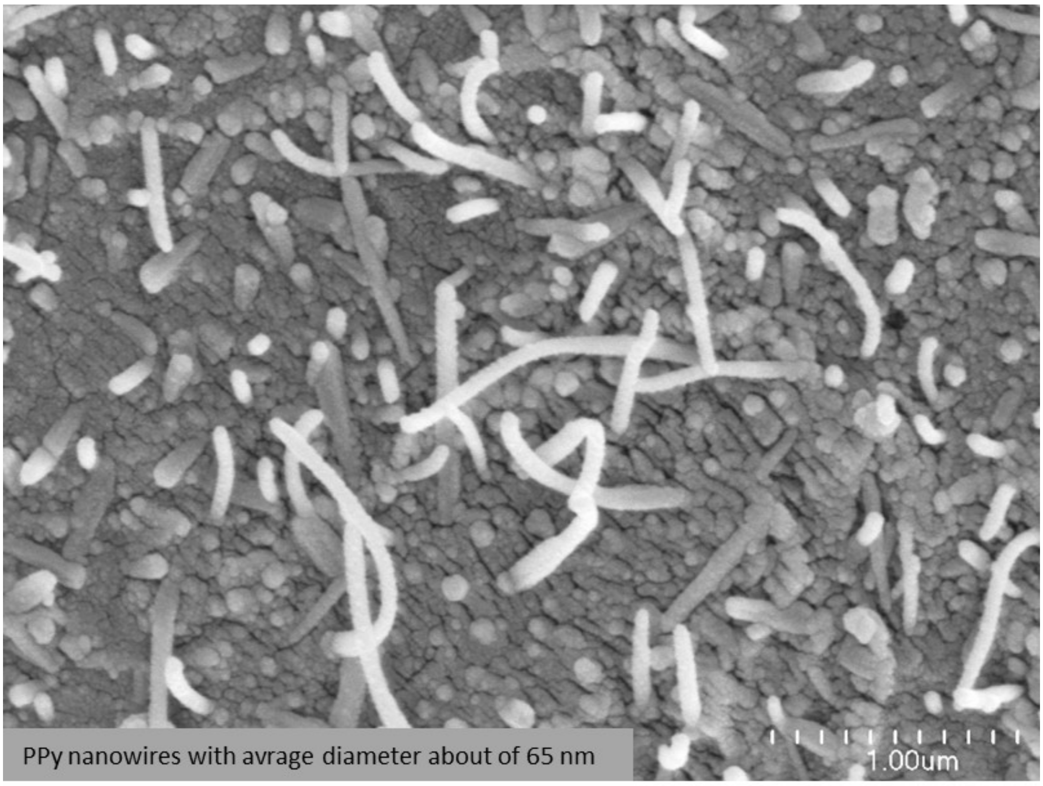

Fig. 6: PPy nanowires obtained after dissolution of silver part of hybrid PPy–Ag nanowires.

Conclusions

The following conclusions can be drawn:

- 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.
- Using DC electrode position, anodic electropolymerization and cathodic polymerization accompanied by electrochemical deposition of metals, silver, polypyrrole (PPy) and polypyrrole–silver (PPy–Ag) nanowires were successfully prepared. The diameter of synthesized nanowires corresponds with the diameter of the used AAO templates.

Acknowledgments

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