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ORIGINAL PAPER

Ordered arrays of copper nanowires enveloped in polyaniline nanotubes

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Abstract Copper nanowires enveloped in polyaniline (PANI) nanotubes were obtained by 'second order' electrodeposition into the pores of anodic porous alumina. The templated synthesis of copper nanowires was performed by both potentiostatic and galvanostatic methods. The morphology of the polyaniline nanotubes, copper nanowires as well as the copper-filled polyaniline nanotubes was investigated by means of scanning electron microscopy. The copper nanowires were protected from corrosion and oxidation by the PANI nanotubes. Energy-dispersive X-ray spectroscopy was performed for the microanalysis of the copper deposition into the polyaniline nanotubes. Cyclic voltammetry was employed to assess the electrochemical properties of the obtained nanostructures as well as the influence of the copper nanowires synthesis method on the properties of filled polyaniline nanotubes.

Keywords Copper nanowires · Polyaniline (PANI) nanotubes · Potentiostatic and galvanostatic methods · Cyclic voltammetry · SEM · EDAX

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1 Introduction

Fabrication of high performance devices at small scale depends on building controlled nanostructures. Amongst the wide range of nanostructured materials, the nanotubes of conducting polymers and metallic nanowires received a high interest. The conducting polymers nanotubes represent an interesting material for electrochemical applications including microelectronics [1, 2] and biosensor construction [3] due to their good conductivity and increased surface area. The copper nanowires [4–8] attracted increased attention because of their potential application in several devices such as in wire-grid polarizers [9], electrostatically dissipative devices [10] and current collectors for Li-ion batteries [11]. Amongst the numerous kind of conducting polymers, polyaniline (PANI) has attracted the highest interest due to its wide range of conductivity from insulating to metallic regime, unique redox tunability, good environmental stability, low cost, ease of synthesis and promising applications in various fields, such as metallic corrosion protection [12, 13], electromagnetic interference shielding [14], electrostatic discharge [15], sensors [16] and actuators [17]. Templates with nanosized pores, such as an aluminium oxide substrate [18], a polycarbonate (PC) membrane [19] or a mica single crystal [20], were used to fabricate nanostructures arrays. The main advantage of a typical template synthesis relies on the simplicity to control the nanotube diameter.

With an alumina membrane as the hard-template, the copper nanowires enveloped in PANI nanotubes were prepared by a two-step process. The copper nanowires were protected from corrosion and oxidation by the PANI nanotubes, rendering the nanostructured composite promising material for some applications such as microelectronics.

2 Experimental

All chemicals of the highest quality commercially available: aniline (Aldrich, >99.5%), H_2SO_4 (Wako Chemicals), CuSO4, $(NH_4)_2SO_4$, HCl and KCl (Aldrich) were used as received.

Anodic aluminium oxide (AAO) membranes (Whatman) with the nominal pore size of 200 nm and thickness of 60 µm were used as the nanostructured template. The working electrode for the electrodepositions was achieved by depositing a 120-nm thick Au layer on the branched side of the template with a BOC Edwards magnetron sputter coater. The electrode (effective area 0.283 cm^2) was placed in such a way that the electrolyte could access the working electrode only through the pores of the membrane.

Electrochemical experiments were carried out with PC-controlled AMEL 5000 instrument, in a one-compartment three-electrode cell at room temperature, using a platinum net as a counter electrode and saturated calomel electrode (SCE) as a reference electrode. All potential are measured with respect to the SCE. Morphological characterization of samples was performed using a scanning electron microscope FEI Quanta 200 3D scanning electron microscope equipped with an X-ray energy-dispersive spectrometer.

Polyaniline nanotubes were obtained by potentiostatic method. The copper nanowires were deposited into the AAO membranes as well as into the PANI nanotubes by both potentiostatic and galvanostatic methods. After electrodeposition, the samples were rinsed with Milli-Q water. In order to observe the morphology of the nanostructures, the template was dissolved in 1 M NaOH for 15 min and then the samples were repeatedly rinsed with deionized water in order to remove residual NaOH, followed by drying at 100 °C for 30 min. The properties of the obtained nanostructures were assessed by cyclic voltammetry (CV) in a solution of 1 M HCl and 1 M KCl.

3 Results and discussion

Successful electropolymerization of polyaniline nanotubes was previously studied [21] by CV, potentiostatic and galvanostatic methods. It was observed that the diffusion rate of monomers to the electrode is increased at higher H_2SO_4 concentration leading to a higher oxidation current maximum. Polyaniline nanotubes were deposited potentiostatically into the pores of AAO membranes from a solution of 0.1 M monomer and 1 M H_2SO_4. The concentration of H_2SO_4 was chosen at this value in order to allow a faster diffusion rate of the monomer to the electrode. The electropolymerization was performed at a constant potential of 900 mV for 20 min.

Figure 1a shows the morphology of the PANI nanotubes. It can be observed from Fig. 1a that PANI has a significantly high filling ratio in the AAO template, which indicates the homogeneous polymerization of PANI in the pores of the template. The estimated diameter of the PANI nanotubes was around 250 nm, which is consistent with the pore size of the AAO template. The length of the PANI nanotubes assessed from scanning electron microscopy (SEM) studies was 7 µm for 20 min of deposition.

The behaviour of the PANI nanotubes within the AAO template was studied by CV in a solution of 1 M HCl and 1 M KCl at a scan rate of 10 mV s^{-1}. Cyclic voltammetry is widely used for the characterization of electrochemical properties of the conducting polymers. The advantage of CV originates from its ability to provide considerable information on the thermodynamics of redox process and the kinetics of heterogeneous electron-transfer reactions, as well as on coupled chemical reactions. In particular, it offers a rapid way for locating the redox potentials of the electroactive species, and a convenient method to observe the effect of media on the redox process.

Figure 2 presents the cyclic voltammograms at different cycles of PANI nanotubes without removal of the AAO template. There can be observed an anodic peak at 0.16 V and a cathodic peak at 0.01 V corresponding to the first redox couple of conventional PANI [22]. Upon cycling, the shapes of the cyclic voltammograms are very similar.

Further, the PANI nanotubes were used as template for the electrodeposition of the copper nanowires. For comparison, the copper nanowires were also deposited into the pores of AAO template under constant potential of −0.3 V. The value of the deposition potential was chosen considering the concurrent cathodic reaction of H_2 evolution ($E_{eq} = -0.47$ V at pH 3), in order to realize copper electrodeposition in the absence of hydrogen evolution. The electrolytic bath contained 150 g L^{-1} CuSO4 + 25 g L^{-1} H_2SO_4 + 5 g L^{-1} $(NH_4)_2SO_4$. The morphology of the obtained free-standing copper nanowires after removal of the template can be observed in Fig. 1b. It shows that electrochemical process is effective in the deposition of copper nanowires uniformly over the exposed area.

The electrochemical behaviour of the copper nanowires in 1 M HCl + 1 M KCl was studied as well, by means of CV as it can be seen in Fig. 3. A redox couple was observed, the anodic peak at −0.065 V and the corresponding cathodic one at −0.29 V. Upon cycling, the anodic peak shifts to slightly more negative values and the anodic current is slightly decreased. The cathodic current increases with continuous cycling.

Further, the copper nanowires were electrodeposited into the PANI nanotubes by the ‘second order template’ method. The PANI nanotubes were electropolimerized

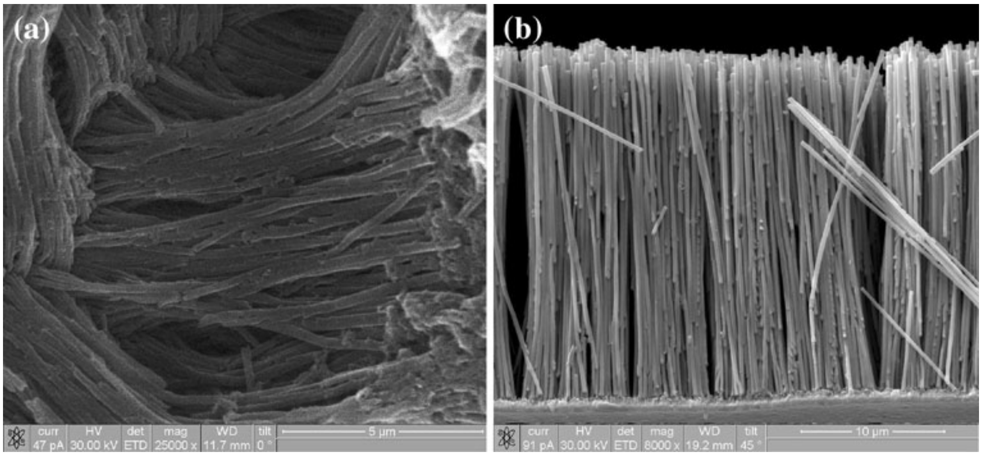

Fig. 1 SEM images of template-electrodeposited **a** PANI nanotubes and **b** copper nanowires

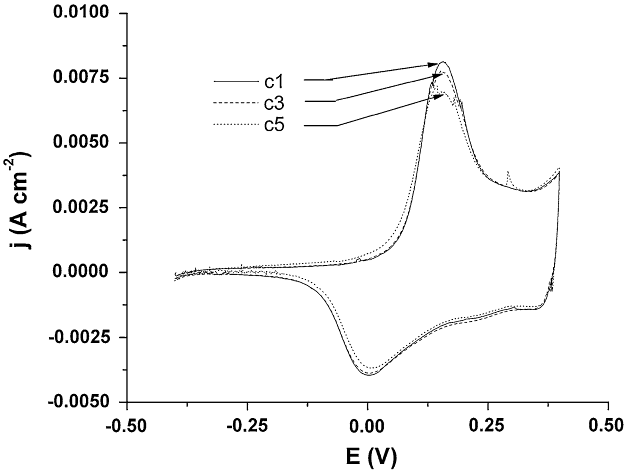

Fig. 2 Cyclic voltammograms of PANI nanotubes with AAO template at a scan rate of 10 mV s^{-1}

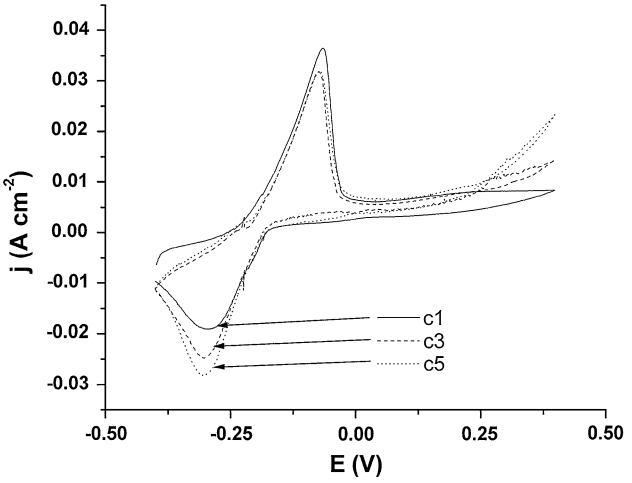

Fig. 3 Cyclic voltammograms of Cu nanowires with AAO template at a scan rate of 10 mV s^{-1}

potentiostatically, and the Cu nanowires were grown into them both potentiostatically at −0.3 V and galvanostatically at −10 mA cm^{-2}. The effect of the deposition method on the electrochemical properties of the Cu nanowires enveloped in PANI nanotubes was assessed by CV. Figure 4 shows the morphology of the PANI encapsulated Cu nanowires deposited by both methods.

To assess the deposition of the copper nanowires into the polyaniline nanotubes, energy-dispersive X-ray spectroscopy (EDAX) microanalysis was performed for the polyaniline nanotubes obtained by potentiostatic deposition, before the copper deposition and after it, as it is shown in Fig. 5. The template was partially removed, and the samples were Au sputtered before the EDAX analysis. As it can be seen in Fig. 5, the obtainment of the polyaniline is clear by the content in the correspondent elements. After the copper deposition, it is observed that the samples contain Cu, fact which confirms the deposition of the copper nanowires into the polyaniline nanotubes.

The electrochemical behaviour of the enveloped copper nanowires deposited potentiostatically, for a period of time corresponding to a theoretical height of 7 μm, was studied in 1 M HCl + 1 M KCl by CV at a scan rate of 10 mV s^{-1} and it is presented in Fig. 6. Two oxidation peaks can be observed on the anodic curve, the first one (A1) at −0.06 V which corresponds to copper and the second one (A2) at 0.18 V corresponding to PANI. The cathodic curve exhibits two reduction peaks: the first one (C1) at 0.1 V corresponding to PANI and the second one (C2) at −0.02 V corresponding to copper. Upon cycling, the current A1 slightly decreases, as well as the current A2. The decrease of the current is clearly evident in the case of the cathodic currents C1 and C2. The cathodic peak C2 corresponding to the growth of copper nanowires into PANI nanotubes was shifted to more positive values in comparison with the non-enveloped copper nanowires.

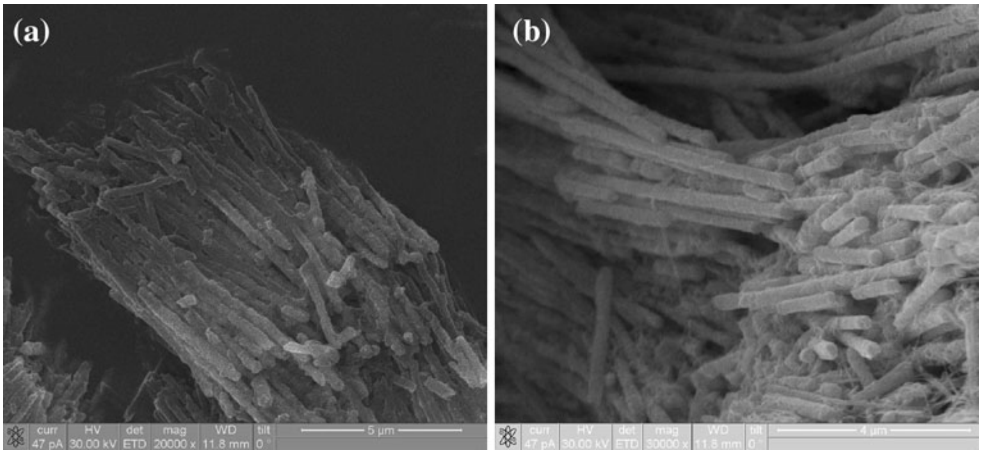

Fig. 4 SEM images of the Cu nanowires into the PANI nanotubes grown **a** potentiostatically and **b** galvanostatically

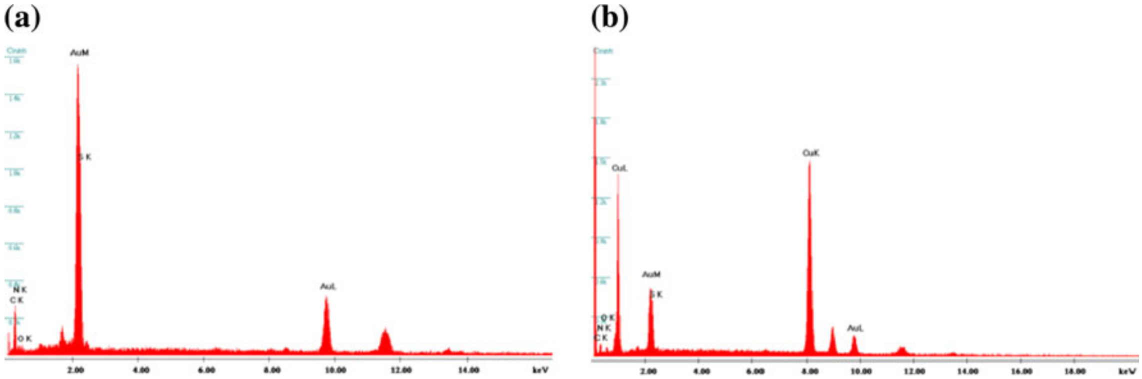

Fig. 5 EDAX microanalyses of the polyaniline nanotubes **a** before and **b** after the copper nanowires deposition

One possible explanation for the shift can be given by the properties of the metal/polymer interface and the growth of the copper nanowires at smaller current.

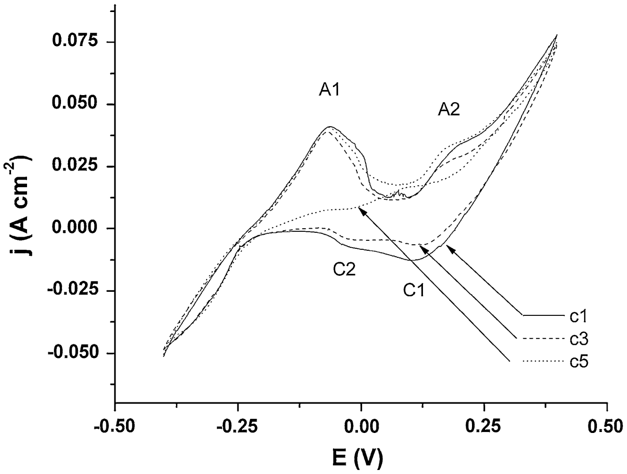

Fig. 6 Cyclic voltammograms of Cu nanowires grown potentiostatically into the PANI nanotubes, at a scan rate of 10 mV s^{-1} at different scan cycles

Next, the CV at a scan rate of 10 mV s^{-1} was performed for the enveloped copper nanowires deposited galvanostatically at a constant current density of -10 mA cm^{-2}. The corresponding voltammograms are presented in Fig. 7. Two redox couples were observed again: A1 at -0.09 V and A2 at 0.13 V and C1 at -0.03 V and C2 at -0.34 V. The peaks A1 and C2 correspond to the copper nanowires, and the couple A2 with C1 corresponds to the PANI nanotubes.

As it can be seen, by comparing the cyclic voltammograms in Figs. 2, 3 and 7, the peak couples are positioned almost at the same potential values. The cyclic voltammogram corresponding to the enveloped copper nanowires can be considered as a sum of the cyclic voltammograms of the PANI and Cu studied separately.

Nevertheless, the current corresponding to the anodic peak of the PANI-enveloped copper nanowires is decreased in the case of galvanostatic deposition of the copper with respect to the bare copper nanowires, fact that suggests the nanowires grown by this method are protected by the PANI envelope.

Nevertheless, the current corresponding to the anodic peak of the copper nanowires grown galvanostatically into

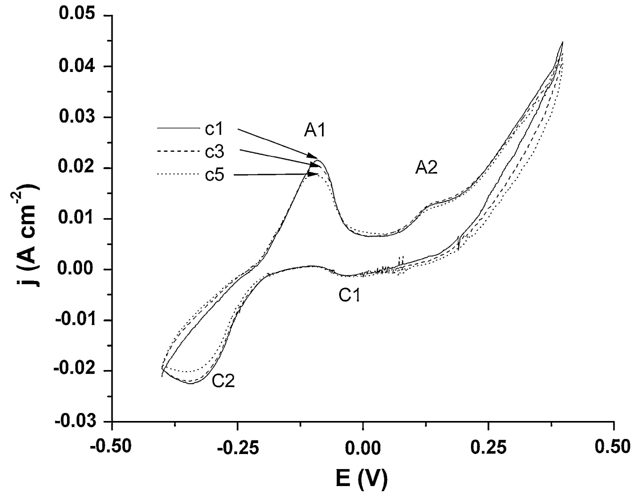

Fig. 7 Cyclic voltammograms of Cu nanowires grown galvanostatically into the PANI nanotubes, at a scan rate of 10 mV s^{-1} at different scan cycles

the PANI nanotubes was lower in comparison to the peak current of the non-enveloped copper nanowires, fact that suggests the copper nanowires grown by this method are protected by the PANI envelope.

4 Conclusions

One-dimensional nanostructured PANI is one class of the most promising candidates for development of nanosized electronic devices, energy storage or sensor technologies.

Arrays of polyaniline-encapsulated copper nanowires were successfully electrodeposited by ‘second order template’ method into the pores of anodic porous alumina. The templated synthesis of copper nanowires was performed by potentiostatic and galvanostatic methods. The SEM images and EDAX microanalysis confirmed the growth of copper nanowires into the polyaniline nanotubes. The electrochemical properties of the obtained nanostructures were assessed by CV. The peaks observed in the cyclovoltammograms of the copper-filled polyaniline nanotubes are positioned almost at the same potential values as those of the compound nanostructures studied separately. The CV studies also revealed that the copper nanowires synthesized at constant current density into the polyaniline nanotubes are protected against corrosion by PANI in the solution of 1 M HCl and 1 M KCl.

The nanostructured material obtained in this study represents a promising one for some applications such as microelectronics and sensors. Further research to optimize the fabrication of these nanostructures is undergoing.

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