Tunable synthesis of copper nanotubes

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Abstract. Simple method of tunable synthesis of copper nanotubes based on template synthesis was developed. A comprehensive study of the structural, morphological and electrical characteristics of the obtained nanostructures was carried out. Characterization of structural features was made by methods of scanning electron microscopy, energy dispersive spectroscopy and X-ray diffractometry analysis. Evaluation of wall thickness is made by methods of gas permeability. Electrical conductivity of nanotubes was define in the study of their current-voltage characteristics. The possibility to control of copper nanotubes physical properties by variation of the deposition parameters was shown.

1. Introduction
Over the past few years, much effort was directed to the synthesis of metallic micro- and nanostructures. Special attention is paid to copper nanostructures due to the low price, easy synthesis and high performance. Nowadays, a large number of techniques described in [1-5] allow to synthesize Cu nanocrystals with different morphologies (cubes [6], nanorods [7], nanodiscs [8], nanowires [9], and etc.). However, due to the specific structure and unique properties, more attractive for the practical application is hollow nanostructures. Due to a low density and large surface area, hollow nanostructures are very promising for use as elements of nanoelectronic devices, catalysts, targeted drug carriers, biomedical agents and chemical reactors [10-16]. The main problem to prepare Cu hollow micro- and nanostructures is the lack of a reliable method for their synthesis with the given parameters, all the above determine the relevance of the current search for an appropriate approach. To solve this problem, we propose method of template synthesis of copper nanotubes with the predetermined parameters, also a comprehensive characterization of morphological and electrical properties were carried out.

2. Experimental
Track-etched membranes based on poly(ethylene terephthalate) (PET) were used as templates with a thickness of 12 microns nominal pore diameter of 380 nm and a density of $4 \times 10^7$ cm$^{-2}$. Deposition of Cu was carried out by electrochemical method in potentiostatic mode with a potential difference $U$ in
the range of 1.0 to 1.5 and steps of 0.25 V. Control of the deposition was carried out by chronoamperometry using a multimeter Agilent 34410A.

Characterization of structural features was carried out by scanning electron microscopy (SEM, Hitachi TM3030), energy dispersive analysis (EDA, Bruker XFlash MIN SVE) and X-ray diffraction (XRD, D8 ADVANCE) using Cu Kα-irradiation. Determination of internal diameters of Cu nanotubes (NTs) was carried out by manometric method by determination of gas permeability (Sartocheck® 3 Plus 16290). Evaluation of electrical conductivity of nanotubes was carried out in the study of their current-voltage characteristics using a current source HP 66312A and amperemeter 34401A Agilent.

3. Results and Discussion

For the electrochemical pore filling of metal, the surface of PET templates was covered by gold layer with thickness of 10 nm using magnetron sputtering in vacuum deposition, this gold layer served as the working electrode (cathode) during deposition. The selected thickness of the deposited metal provides a partial penetration of Au on the pore walls, allowing formation of nucleation center of Cu on the cathode and initiating growth of the NTs. Electrolyte for the synthesis of NTs was: CuSO$_4$·5H$_2$O (238g/l), H$_2$SO$_4$ (21g/l). The deposition time $t$ was determined based on chronoamperograms. It corresponded to complete filling of the pores and was $t=120$ s for $U=1.0$ V, $100$ s for $1.25$ V and $30$ s for $1.5$ V. It is obvious, that we can tune the length of NTs by changing of deposition time. SEM pictures of the prepared nanostructures after chemical dissolution of the polymer matrix are presented in figure 1.

![Figure 1. SEM microphotographs of Cu nanotubes.](image)

SEM studies show that Cu nanostructures have a hollow NTs shape with a length corresponding to the original template thickness of PET ($11.8 \pm 0.2$ mm) and an outer diameter $D$ corresponding to the pore diameter of PET – $380\pm20$ nm. Taking into account the lack of resolution of SEM, definition of inner diameters $d$ of nanostructures in the pores of PET templates was carried out by manometric method using gas permeability at pressures in the range of 0.008 to 0.020 MPa at a pitch of 0.004 MPa. The inner diameter of synthesized nanotubes were calculated according to the equation [17]:

$$d^3 = \frac{Q \cdot 6l}{\sqrt[3]{2\pi R \cdot T \cdot M \cdot \Delta p \cdot n}},$$

where, $Q$ – gas flow rate, $l$ – thickness of the film, $\Delta p$ – applied pressure, $R$ – gas constant, $M$ – the molar mass of air, $n$ – pore density, $T$ – temperature. Obtained results are presented in figure 2.

The results showed that calculating pore diameter of PET template is $380\pm5$ nm that is corresponding to the data obtained from SEM pictures. Analysis of the data obtained for Cu NTs at different $U$ showed an interesting relationships: increasing the deposition potential from 1 V to 1.5 V led to increasing of inner diameter of NTs from 170 and 200 nm that corresponds to a reduction of the wall thickness from 100 nm to 85 nm.
Determination of elemental composition by EDA showed that all the samples are contained 100% copper without any impurities. Analysis of the crystal structure of Cu NTs was carried out by XRD. Figure 3 shows obtained radiographs.

According to the analysis of XRD, all samples of Cu NTs have the FCC structure with a cell parameter $a$ differ from the standard (3.6130 Å). The peak with the angular position of $2\theta=20–33^\circ$ belongs to PET template [18]. Table 1 shows the lattice parameters and the average size of crystallites calculated by Scherrer equation [19].

**Table 1. Parameters of Cu NTs obtained at different deposition potentials.**

| $U$, V | $a$, Å         | The average size of crystallites, nm |
|--------|----------------|-------------------------------------|
| 1.0    | 3.6124±0.0009  | 32.23                               |
| 1.25   | 3.6132±0.0009  | 28.82                               |
| 1.5    | 3.6135±0.0007  | 43.85                               |

Orientation of polycrystalline nanotubes was investigated by calculation of texture coefficient $TC(hkl)$, which was calculated using Harris equation [20]:

**Figure 2.** Pore diameter of PET template and the inner diameters of Cu NTs at various applied pressure using manometric method of gas permeability determination.

**Figure 3.** XRD spectra of Cu NTs in PET template at different deposition potentials.
where $I(hkl)$ – experimentally obtained relative intensity, $I_0(hkl)$ – the standard relative intensity according to the database JCPDS, $n$ – number of planes. The results are presented in table 2.

### Table 2. Data on the texture coefficients.

| $2\theta$ $^\circ$ | (hkl) | $U=1.0$ V | $U=1.25$ V | $U=1.5$ V |
|-------------------|-------|-----------|-----------|-----------|
| 43.39             | (111) | 1,584974  | 1,775872  | 1,780566  |
| 50.53             | (200) | 0,826349  | 1,030679  | 1,121368  |
| 74.18             | (220) | 1,145673  | 0,825306  | 0,902701  |
| 90.00             | (311) | 0,687315  | 0,661072  | 0,848477  |
| 95.20             | (222) | 0,755689  | 0,707071  | 0,897925  |
| 116.99            | (400) | -         | -         | 0,448962  |

The values of texture coefficients larger than one indicate a preferred orientation along the array of nanotubes in the planes, that indicate increasing the number of grains along the plane. The values of about 1 indicates that this structure has a polycrystalline nature with a preferred direction [111]. The increasing of the deposition potential leads to increasing of texture coefficients values for the plane [111] within 10%.

To determine the influence of the synthesis conditions on the electrical properties, conductivity $\sigma$ of Cu NTs array in PET template were studied. The electrical conductivity was calculated by the formula:

$$\sigma = \frac{dl}{dU} \frac{l}{A},$$

(4)

where $l$ – length of nanotube, $A$ – conducting surface area, $dl/dU$ – tangent of the angle depending $I$–$U$. Graph of dependence $\sigma$ from deposition potential is shown in figure 4.

![Figure 4. Dependence of Cu NTs conductivity on deposition potential.](image)

As seen from the presented dependence, increasing deposition potential on the 0.25 V leads to increasing conductivity of Cu NTs of about 2%. The results are in good agreement with the data of XRD analysis: with increasing of the deposition potential, crystallite size of copper is increased, of
which the NTs contains, that is accompanied by decreasing in the scattering of conduction electrons on these boundaries.

4. Conclusions
Using PET track-etched membranes with thickness of 12 µm as template, polycrystalline copper nanotubes were synthesized by electrochemical method with outer diameter of 380 nm and wall thickness in the range from 85 to 100 nm. A comprehensive study of the structural, morphological and electrical characteristics was carried out, the ability to control parameters of Cu NTs such as length and thickness of the wall by variation of deposition time and potential. It was found that the change in the potential of electrochemical deposition leads not only to decreasing the wall thickness of Cu NTs, but also to increasing the size of copper crystallite.

Changes in the degree of crystallinity is accompanied by decreasing in conduction electron scattering at the grain boundaries, that causes increasing conductivity of NTs. Relative availability and reliability of the proposed method, along with the ability to control physical properties of the nanostructures defines the prospects for their further application as catalysts or components for modern electrical circuits, including on flexible substrates.

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