

## Electrochemical method for rapid synthesis of Zinc Pentacyanonitrosylferrate Nanotubes

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### ABSTRACT

In this paper, a rapid and simple approach was developed for the preparation of zinc pentacyanonitrosylferrate nanotubes (ZnPCNF NTs) within the cylindrical pores of anodic aluminum oxide (AAO) template by electrochemical method. The AAO was fabricated in two steps anodizing from aluminum foil. The first anodization of aluminum foil was performed in 0.2 mol L<sup>-1</sup> H<sub>2</sub>C<sub>2</sub>O<sub>4</sub> followed by removal of the formed porous oxide film by a solution of 6 wt% of phosphoric acid. The second anodization step was then performed using the same conditions as the previous step. Scanning electron microscope (SEM) and X-ray diffraction (XRD) method were employed to characterize the resulting highly oriented uniform hollow tube array which its diameter was in the range of 25-75 nm depending on the applied voltage and the length of nanotubes was equal to the thickness of AAO which was about 2 μm. The growth properties of the ZnPCNF NTs array film can be achieved by controlling the structure of the template and applied potential across the cell.

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## 1. Introduction

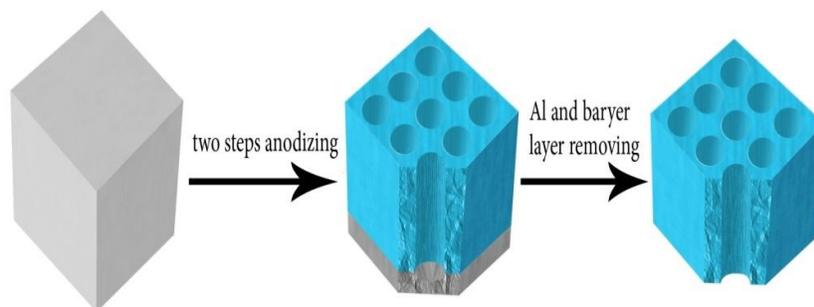
Since the first discovery of carbon<sup>1</sup> and WS<sub>2</sub> nanotubes<sup>2</sup> more attention has been given to the preparation, properties, and applications of inorganic nanotubes. Several strategies, such as sulfurization by heating, decomposition of precursor crystals, or solvothermal synthesis, have been employed for the synthesis of inorganic nanotubes<sup>3-9</sup>. Among those, template synthesis is one of the rationalized methods for the production of inorganic nanotubes<sup>10-14</sup>. The templates can be porous membranes of alumina or polycarbonate. The pores are used to deposit the relevant materials or precursors, after which the annealing and removal of the template takes place. A variety of membranes are now commercially available for various purposes<sup>15-16</sup>. Polymeric and inorganic membranes are most frequently used. Only the latter can be used under high temperature conditions.

Metal pentacyanonitrosylferrate (MPCNF) as an inorganic compound have been used in the form of a thin layer on electrodes; in these studies different transition metals such as: Cd<sup>17</sup>, Co<sup>18</sup>, Ni<sup>19</sup>,

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$\text{Pd}^{20}$  and  $\text{Zn}^{21}$  have been used. However, to the best of our knowledge, there is no report on preparation of ZnPCNF nanotubes. In this work, we report an approach for electrochemical synthesis of ZnPCNF nanotubes using deposition in AAO template. Fig. 1 outlines our fabrication strategy for the synthesis of AAO membrane using aluminum foil by two-step anodizing, where ZnPCNF was used as a model to demonstrate the approach, although other MPCNFs could also be used. The method is based on the use of AAO as a template for electrochemical synthesis of ZnPCNF. The SEM and XRD techniques were employed to characterize the resulting highly oriented uniform hollow tubes.

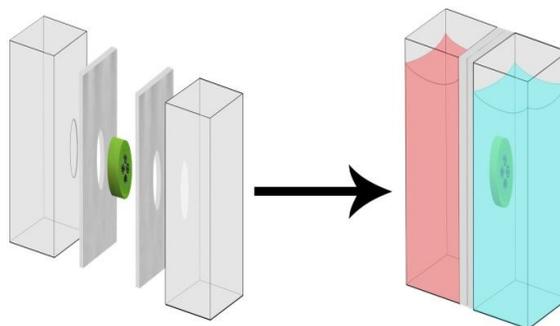


**Fig. 1.** The scheme of template synthesis of AAO membrane by aluminum foil using two-step anodizing. From left to right: Aluminum foil, two-step anodized aluminum and Al and barrier layer removing from the bottom of AAO membrane

## 2. Results and Discussion

### 2.1. Electrochemical synthesis of ZnPCNF nanotubes

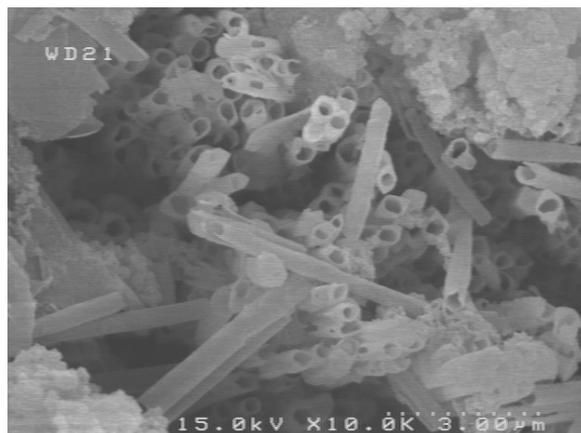
As mentioned above, AAO membrane was synthesized by anodizing aluminum foil in two steps. After the removal of aluminum metal from the bottom of the membrane, the hole opening of the oxide barrier film on the bottom side was performed using phosphoric acid. The prepared AAO membranes were used as templates for electrochemical synthesis of ZnPCNF nanotubes. The AAO membrane was clamped between two spectroscopic cells with holes in one side (Fig. 2). According to the experimental data increasing the voltage, caused acceleration of tube fabrication but in high voltages, the holes in nanotube become smaller compared to lower voltages. Ions in one half cell could be diffused to the other cell; when voltage was applied the electromigration of ions could occurs much faster than the diffusion rate. Diffusion and electromigration of ions in opposite directions caused the ions to meet each other through the nanochannels of AAO membrane and a reaction zone was generated, consequently the ZnPCNF nanoparticles were deposited on the inner walls of the AAO membrane.



**Fig. 2.** Schematic diagram for synthesis of ZnPCNF by electrochemical method. Two half cells with membrane before and after clamping and solutions in cells.

## 2.2. Structural characterization of ZnPCNF nanotubes

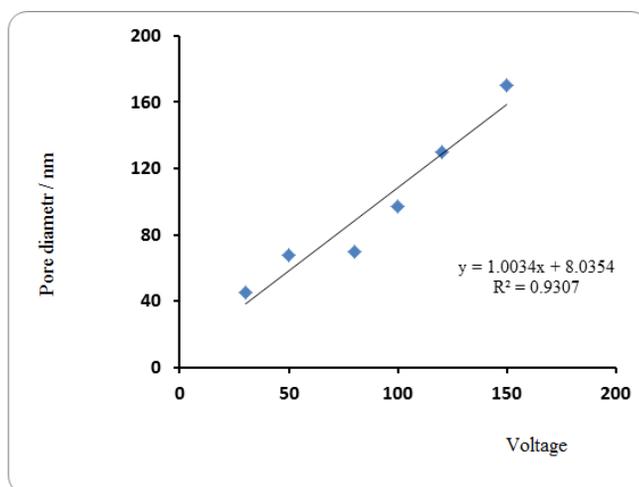
The ZnPCNF nanotubes were obtained after dissolving AAO template in  $H_3PO_4$ . Then, the raw products were centrifuged and rinsed several times with distilled water. The obtained nanotubes were studied by SEM. Figure 3 shows typical ZnPCNF nanotubes. As can be seen in Figure 3, the nanotubes have lengths of up to a few micrometers and diameters of a few hundred nanometers. The diameters of nanotubes and their lengths depend on the template morphology. The outer diameter of nanotubes depends on the AAO template hole diameters, one can obtain the AAO films with average pore diameter of 100 nm (up to 200-300 nm after further pore widening process).



**Fig. 3.** SEM images of ZnPCNF nanotubes prepared by the electrochemical approach. Applied potential was 50 V for 30 min. Far view of nanotubes after chemically dissolving AAO template

## 2.3. The effect of voltage on AAO pore diameters

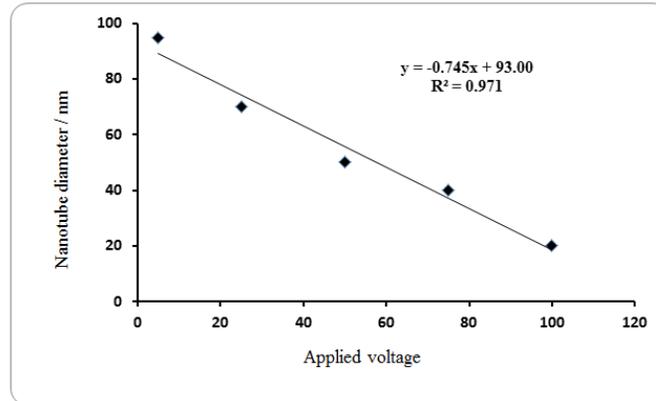
The study of the anodizing potential effect on the pore diameter in AAO was performed for cell potentials from 30 to 160 V. The pore diameter in porous alumina formed by the anodization in oxalic acid was increased linearly by increasing the potential, which was applied to the cell. Experimental data of the pore diameter obtained in this study are shown in Fig. 4. The rate of  $Al_2O_3$  etching is closely related to a composition of solution, temperature, time of anodising and hydrodynamics conditions. In each step, one can do widening of holes using electrolytes such as phosphoric acid solution.



**Fig. 4.** The effect of applied potential on pore diameter of AAO membrane

#### 2.4. The effect of voltage on inner hole diameter of nanotubes

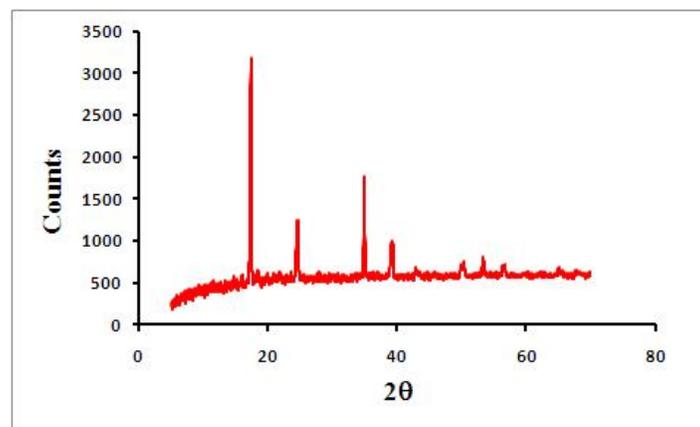
The effect of voltage on morphology of the prepared ZnPCNF nanotubes was studied. For this purpose the voltage between 5- 100 V was applied. Experimental data showed that by increasing voltage the inner hole diameter of nanotubes became smaller compared to the lower voltages. The reduction of inner diameter of ZnPCNF was due to fast transition of ions among AAO holes and accordingly their fast deposition inside the AAO holes. Figure 5 show the effect of applied potential on pore diameter of ZnPCNF nanotubes in constant time. As can be seen by increasing applied potential across the cells the nanotubes pore diameters decreased.



**Fig. 5.** The effect of potential on pore diameter of ZnPCNF nanotubes in constant time (10 minute potential applied)

#### 2.5. The morphology study using XRD

The phase and crystallographic structure of the ZnPCNF nanotube were determined by X-ray powder diffraction (XRD) technique using a D8 Discover by Bruker AXS with Cu K radiation ( $\lambda = 1.54178 \text{ \AA}$ ). The samples were mounted on an alumina sample holder. The X-ray diffraction pattern of ZnPCNF nanotubes were taken to examine the crystal structure of the nanotubes. The XRD pattern of ZnPCNF nanowires is shown in Fig. 6. As can be seen in Figure 6, the spectrum consists of a set of peaks. According to the standard JCPDS cards, this set corresponds to the hexagonal structure with a nominal composition of ZnPCNF.



**Fig. 6.** The XRD spectrum for the ZnPCNF nanotubes

### 3. Conclusions

In summary, we have developed a facile, low-cost electrochemical method for production of ZnPCNF nanotubes. In this research the AAO membrane was used as a template with desired channel diameter. The inner diameter of ZnPCNF nanotubes decreased with increasing applied voltage across the cell. The morphology of the nanotubes was studied using SEM, and the crystalline structures of ZnPCNF nanotubes was studied using XRD. According to the experimental results nanotubes of most transition metal salts with nitroprusside can be fabricated using this method.

### 4. Experimental

#### 4.1. Materials and Methods

All chemicals were of analytical grade from Merck. The oxalate buffer solution was made from oxalic acid and pH was adjusted by NaOH. The electrochemical experiments were carried out using a  $\mu$ -AUTOLAB potentiostat/galvanostat model TXPE III coupled with a personal computer. For anodizing a DC Power supply Agilent technologies model N5752A was used. For anodizing, two platinum sheets were used in each cell as anode and cathode electrode.

#### 4.2. Fabrication of AAO template

An Al sheet (20 mm  $\times$  20 mm  $\times$  0.15 mm) with the purity of 99.999% was ultrasonically degreased in acetone for 10 min, etched in 1.0 mol L<sup>-1</sup> NaOH at room temperature for 1 min to remove the native oxide, then washed thoroughly with distilled water. Afterward, the Al foil was anodized at 15-45 V in 0.2 mol L<sup>-1</sup> H<sub>2</sub>C<sub>2</sub>O<sub>4</sub> aqueous solutions at room temperature, using another two Al sheets in purity of 99.8% as the counter electrode.

After removal of AAO layer produced from the first anodizing step, a second anodization step was performed on these samples using the same conditions as the previous step. The remaining aluminum on the formed AAO layer was removed by a CuCl<sub>2</sub>/HCl solution. Finally, the oxide barrier film on the bottom was removed using 6 wt% solution phosphoric acid (0.5 h) to make self-standing membranes with through-hole morphology. Finally the porous alumina membrane was rinsed thoroughly with distilled water and dried.

#### 4.3. Fabrication of ZnPCNF nanotubes

The AAO membrane was clamped between two plastic spectroscopic cells with a hole in their sides. The ZnCl<sub>2</sub> solution was first added to the anodic half cell and sodium pentacyanonitrosylferrate with the same concentration (0.1 M) was added to the cathodic half -cell. Two platinum-sheet electrodes were used in each half cell, and potential was applied across the membrane. In order to obtain the pure ZnPCNF product, the AAO template was dissolved in 6 wt% H<sub>3</sub>PO<sub>4</sub> solution. Then, the raw products were centrifuged and rinsed several times with distilled water (Fig. 2). Morphology of nanotubes were analyzed by SEM microscopy (Philips ESEM, mod. XL30).

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