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# Synthesis of copper nanocone array electrodes and its electrocatalytic properties toward hydrogen peroxide reduction



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## ABSTRACT

The copper nanocone (Cu-NC) array electrodes were successfully synthesized by metal sputtering on Al<sub>2</sub>O<sub>3</sub>/Al substrate with conical nanopores followed by electrodeposition of Cu. To fabricate the conical pores on aluminum substrate, repeated and alternating anodizations and pore widening treatments were performed. Each anodization step was conducted at 45 V in a 0.3 M oxalic acid solution at 9 °C. After that, the holes were widened by immersion in a 5 vol% phosphoric acid solution at 30 °C. The effect of different number of alternating anodization-etching cycles on the shape, diameter and height of pores in anodic aluminum oxide (AAO) template was studied. After the electrochemical deposition of Cu, free standing Cu-NC arrays were obtained by chemical etching of Al<sub>2</sub>O<sub>3</sub> templates in dilute phosphoric acid. The dimensions of copper nanocones correspond closely with used Al<sub>2</sub>O<sub>3</sub> templates. The morphology and structural characterization of fabricated Al<sub>2</sub>O<sub>3</sub> templates and Cu-NC arrays were performed. The electrocatalytic activity of the Cu-NC array electrodes toward hydrogen peroxide reduction was investigated.

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## 1. Introduction

Due to their special properties and small dimensions, nanostructured materials are of interest of the world's scientists. Materials in the nanoscale are increasingly used in many areas of science and everyday life. Recently, one dimensional metallic nanostructures (e.g.: nanowires, nanotubes, nanocones, and nanorods) have been studied as potential electrocatalytic materials [1,2]. These nanostructured materials can offer great opportunities to improve catalytic performance due to a small geometrical size and large active surface area. As electrode materials, metallic (e.g., Ag, Au, Pt, Cu, Pd), composite (e.g., Cu-Pt, Pt-Pd, Au-Pt, Pt-Ni, Pt-Ag, Au-Pd), and alloyed (e.g., PtCu, AuCu, PtPd, PtRu, PtCo, NiCu, PdAu, PtPd, PdAg, PtAg) nanostructures were used in electrocatalysis [2].

Porous anodic aluminum oxide (AAO) is the most versatile template for synthesis of ordered arrays of nanowires [3–6], nanotubes [6], nanodots [6], nanopillars [6], nanopores [6], nanocones [7–12], etc. The internal pore structure of nanoporous AAO can be engineered by controlling anodization conditions or by applying an appropriate post-anodization treatment. For instance, by control of the applied anodizing potential it is possible to obtain Y-branched pore structures [13], modulated pore diameter

[4,14,15], and periodically branched nanopores [16]. Another approach to alter the internal pore structure of AAO is based on alternating repetition of the anodization and pore widening process. This method can result in step-shaped pores (conical nanopores) [17–20].

Porous anodic alumina with conical nanopores can be used for synthesis of metallic nanocone arrays [9–12]. The fabrication of the metallic nanocone arrays based on anodic alumina templates with conical nanopores can be realized by electroless deposition of metals [9–11] or by sputtered deposition of metals on the top side of the AAO template followed by electrochemical deposition [12].

In this work we describe the synthesis of well-ordered copper nanostructures and their electrocatalytic properties towards hydrogen peroxide detection. Copper nanostructures belong to the group of the most important metallic nanomaterials, and they are characterized by the large working surface area that exhibits good electrocatalytic properties [21–23].

## 2. Experimental

### 2.1. Fabrication of the Al<sub>2</sub>O<sub>3</sub>/Al template with conical nanopores

A general synthesis procedure of the Al<sub>2</sub>O<sub>3</sub>/Al substrate with conical nanopores and copper conical array electrode is shown in Fig. 1. It consists of repeated steps of alternating anodization and pore widening processes. Briefly, a high purity (99.999%,

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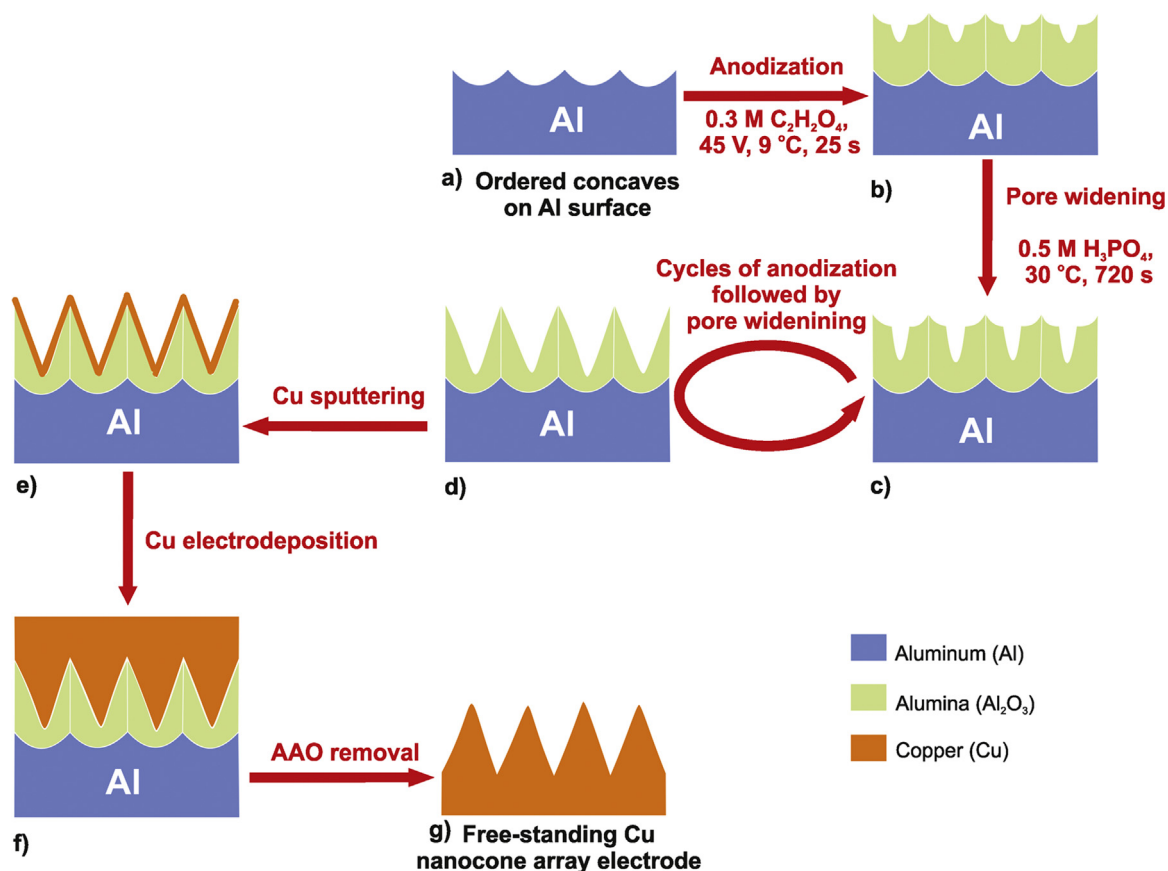


Fig. 1. Schematic representation of synthesis of the non-enzymatic free-standing Cu nanocone array electrode for  $\text{H}_2\text{O}_2$  detection.

Goodfellow) aluminum foil was electropolished in an unstirred mixture of perchloric acid and ethanol (v/v 1:4) at 0 °C. The electropolishing was performed in a two electrode system with Al working electrode and Pt counter electrode at a constant voltage of 20 V for 1 min. After electropolishing, the anodization was conducted in a 0.3 M oxalic acid solution under vigorous magnetic stirring. The first step of anodization was done for 1 h at 45 V and 9 °C. The formed oxide layer was removed by dipping of the  $\text{Al}_2\text{O}_3/\text{Al}$  substrate into a mixed solution of 6 wt%  $\text{H}_3\text{PO}_4$  and 1.8 wt%  $\text{H}_2\text{CrO}_4$  at 60 °C for 1 h (Fig. 1a).

The second step of anodization consisted of multistep alternating anodization (Fig. 1b) and chemical etching (Fig. 1c) in oxalic acid and phosphoric acid, respectively. Each anodization step of second anodization was conducted at 45 V in a 0.3 M oxalic acid solution at 9 °C. The duration of anodization in the first and next anodizing-etching cycles was 25 s and 20 s, respectively. The pores were widened by immersion in a 5 vol% phosphoric acid solution at 30 °C for 720 s. To control the aspect ratio of conical nanopores a number of alternating anodization and etching cycles was changed (Fig. 1d).

## 2.2. Fabrication of Cu-NC array electrodes

The copper nanocone (Cu-NC) array electrodes were successfully synthesized by metal sputtering on the  $\text{Al}_2\text{O}_3/\text{Al}$  substrate with conical nanopores followed by electrodeposition of Cu. When the anodization process was completed, a thin conductive Cu layer was sputter deposited (Fig. 1e) on the samples using a vacuum Sputter Coater (Emitech K575X). Then, the DC electrodeposition of copper was performed (Fig. 1f) in a three-electrode cell with a Pt wire and plate as a pseudo-reference and counter electrodes, respectively. The DC electrochemical deposition of copper into the

$\text{Cu}/\text{Al}_2\text{O}_3/\text{Al}$  template was performed at room temperature in an aqueous solution containing 0.5 M  $\text{CuSO}_4 + 0.5$  M  $\text{H}_2\text{SO}_4$  at  $5 \text{ mA cm}^{-2}$  for 60 min. The applied electrodeposition conditions provide a sufficiently thick Cu layer which allows to freely handle the electrode. After the electrochemical deposition, a free standing Cu nanocone array was obtained by chemical etching of the  $\text{Al}_2\text{O}_3$  template in a dilute phosphoric acid solution. The morphology and structural characterizations of fabricated  $\text{Al}_2\text{O}_3/\text{Al}$  templates and Cu nanocones were performed by SEM and EDX analyses.

## 2.3. Study of the electrochemical properties of Cu-NC electrodes

The electrocatalytic activity of the copper nanocone array electrodes for hydrogen peroxide reduction was investigated using cyclic voltammetry (CV) and chronoamperometry (CA). The electrochemical measurements were performed with a Reference 3000 potentiostat (Gamry Instruments) in a conventional three-electrode double-walled glassy cell with the Cu nanocone array as a working electrode, Pt grid and saturated calomel electrode (SCE) as counter and reference electrodes, respectively. All electrochemical measurement were carried out at 25 °C in a 0.1 M phosphate buffer solution (PBS, pH=7.4). Cyclic voltammograms were obtained in the potential range from  $-0.2$  to  $-1.0$  V vs. SCE with a scan rate of  $20 \text{ mV s}^{-1}$ . Amperometric experiments were carried out in a stirred system by applying a constant potential step to the working electrode. Typically, current-time curves were recorded after successive additions of 3.26 mM  $\text{H}_2\text{O}_2$ .

## 3. Results and discussion

### 3.1. Characterization of the $\text{Al}_2\text{O}_3/\text{Al}$ template with conical

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