



# Arrays of rhodium nanowires based on anodic alumina: Preparation and electrocatalytic activity for nitrate reduction



Alexey P. Leontiev<sup>a</sup>, Oleg A. Brylev<sup>a,b</sup>, Kirill S. Napolskii<sup>a,b,\*</sup>

<sup>a</sup> Department of Materials Science, M.V. Lomonosov Moscow State University, 119991 Moscow, Russia

<sup>b</sup> Department of Chemistry, M.V. Lomonosov Moscow State University, 119991 Moscow, Russia

## ARTICLE INFO

### Article history:

Received 27 September 2014

Received in revised form 10 December 2014

Accepted 11 December 2014

Available online 15 December 2014

### Keywords:

rhodium  
anodic aluminium oxide  
nanowires  
electrodeposition  
nitrate reduction

## ABSTRACT

Rhodium nanowires with an average diameter of 55 nm and a length of 1.5–11  $\mu\text{m}$  have been prepared by electrodeposition in the pores of anodic aluminium oxide (AAO) membranes which were fabricated by two-step anodization technique. Rh/AAO nanocomposites have been investigated by the combination of instrumental and electrochemical methods. The electrochemical surface area of Rh nanowires is about one order of magnitude higher than the geometrical one that is beneficial for catalytic applications. The efficiency of both isolated Rh nanowires and Rh/AAO nanocomposites towards nitrate electrochemical reduction in acidic medium has been demonstrated. The preliminary annealing of AAO templates allows us to obtain nanocomposites that are suitable for long-term catalytic applications in aggressive medium.

© 2014 Elsevier Ltd. All rights reserved.

## 1. Introduction

Elevated nitrate concentrations in drinking water sources or food products present a potential threat to people's health. While nitrate is considered to be relatively nontoxic to adults, it could be harmful to infants causing a "blue baby syndrome" [1]. For the nitrate removal, different treatment processes including ion exchange, biological denitrification, chemical denitrification, reverse osmosis, electrodialysis, and catalytic denitrification have been developed [2]. However, these techniques exhibit considerable drawbacks, and the electrocatalytic conversion of nitrate ions proved to be a more efficient and environmentally friendly method. Rhodium is the most active catalyst among platinum group metals for this application [3] and it can be used in a wide pH range [4].

Many attempts were reported to improve the efficiency of Rh catalysts for the electrochemical nitrate reduction by changing metal morphology. Various rhodium structures such as spherical particles [5], nanotubes [6], cubes, horned particles and nanodendrites [7] were synthesized and tested as catalysts. But recently, the arrays of vertically aligned metal nanowires have attracted a great attention of researchers due to their promising geometry, allowing a high electrocatalytic activity to be achieved. In particular, the arrays of Pt nanowires have been successfully

utilized in industrial process of methanol electrooxidation which is crucial for fuel cells [8].

In order to prepare the arrays of metal nanowires, the template synthesis is often applied. For this purpose, the most popular templates are track-etched membranes [9,10] and porous anodic aluminum oxide (AAO) films [11–13]. Both types of templates possess uniform cylindrical channels which are aligned perpendicularly to the film surface. For the formation of AAO matrices, the two-step anodization technique is widely used. It allows a uniform pore structure with hexagonal arrangement of cylindrical channels to be produced [14–16]. The structural parameters of AAO matrix such as pore diameter and interpore distance can be easily changed by varying an electrolyte composition, voltage and duration of the anodization. Moreover, AAO provides a mechanical stability for the nanowires. If necessary, AAO can be readily removed by chemical dissolution [17].

Concerning Rh nanowires, there are only few works devoted to their preparation [18–20]. In [18] the authors describe the atomic structure of Rh nanowires (an average diameter of 40 nm, a length of 3–5  $\mu\text{m}$ ) which have been fabricated by electrodeposition in the pores of track-etched polycarbonate membranes. Individual Rh nanowires obtained from commercial Rh plating solution in commercial AAO membranes with disordered porous structure have been used as cantilevered resonators [19]. In both cases, the properties of individual nanowires were tested, but no data on the electrochemical response of Rh nanowire arrays have been reported.

In the present paper, we report the preparation of Rh nanowires by templated electrodeposition into AAO matrices with ordered

\* Corresponding author. Tel.: +7 495 9395248; fax: +7 495 9390998.  
E-mail address: [knapolsky@gmail.com](mailto:knapolsky@gmail.com) (K.S. Napolskii).

porous structure. A special attention has been paid to the structural characterization of nanowires and the determination of influence of structural features (e.g. aspect ratio, specific surface area and roughness) on the electrocatalytic activity for the reduction of nitrate ions. The length of Rh nanowires was varied in a wide range by adjusting the electric charge spent for metal electrodeposition. To the best of our knowledge, this is the first demonstration of the preparation of ordered arrays of Rh nanowires and their systematic study by electrochemical methods. A comparative analysis of the catalytic activity of Rh/AAO composites towards nitrate reduction has been performed.

## 2. Experimental part

### 2.1. Sample preparation

The arrays of rhodium nanowires were fabricated by potentiostatic electrodeposition using porous anodic alumina films as templates.

The two-step anodization technique was applied for the preparation of AAO membranes [14]. Firstly, high purity aluminum foil (99.999 %, Goodfellow, 0.5 mm thick) was electrochemically polished in a solution containing 880 ml/l  $\text{H}_3\text{PO}_4$  (IREA 2000, 85%) and 185 g/l  $\text{CrO}_3$  (Vekton, 99.7%) at 80 °C in an impulse mode. 40 impulses for 3 s were imposed at a current density of  $0.4 \text{ A cm}^{-2}$  with a voltage limit of 20 V. Subsequently, the anodization was realized in a two-electrode cell in 0.3 M  $\text{H}_2\text{C}_2\text{O}_4$  (Aldrich, 98%) at a constant voltage of 40 V using Pt wire as a counter electrode. The electrolyte was continuously stirred and its temperature was maintained in the range of 0–5 °C during anodization. After the first anodization for 48 h, alumina films were selectively etched away in a solution containing 35 ml/l  $\text{H}_3\text{PO}_4$  and 20 g/l  $\text{CrO}_3$  at 70 °C. The second anodization was carried out under the same

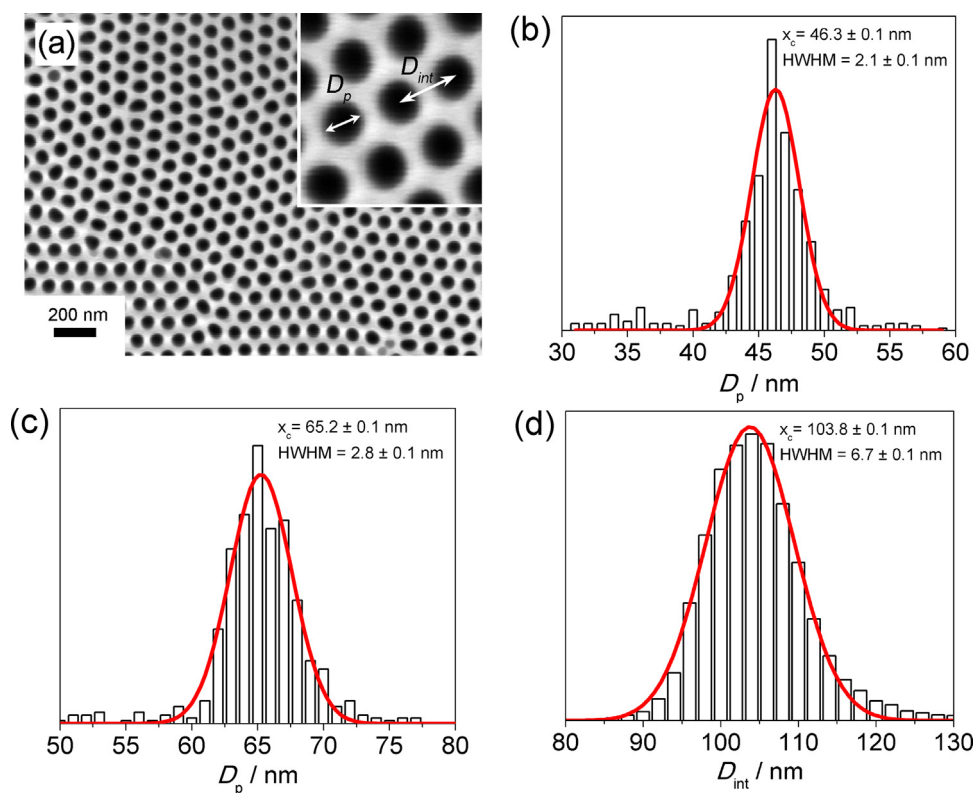
conditions. The anodization duration was varied from 12 to 24 h to prepare the templates with different thicknesses. An oxide film was separated from aluminum substrate by selective dissolution of Al in 10 vol.% solution of  $\text{Br}_2$  in methanol (99.6%). Subsequently, the pore bottoms were opened by chemical etching in a 3.6 vol. % aqueous  $\text{H}_3\text{PO}_4$  solution at 60 °C for 5 min.

In order to enhance the template chemical stability, AAO films were annealed in air in a muffle furnace [21,22]. They were placed between two corundum plates and then gradually heated from room temperature to 800 °C at a rate of  $1^\circ\text{C min}^{-1}$ . The samples were annealed at the target temperature for 6 h and then slowly cooled down to the room temperature.

To provide an electric contact a layer of Au (150 nm thick) was deposited onto one side of AAO membrane by magnetron sputtering (Q150T ES, Quorum Technologies). The Rh electrodeposition was carried out in a three-electrode cell from the solution containing 0.01 M  $\text{Na}_3\text{RhCl}_6$  (Alfa Aesar, Rh 17.27%) + 0.5 M NaCl (Reachem, 99.9%) at  $E_d = -0.3 \text{ V}$  versus saturated (KCl) Ag/AgCl reference electrode using Autolab PGSTAT302 N potentiostat. Before each electrodeposition, the initial potential of  $-0.8 \text{ V}$  vs. Ag/AgCl was maintained during 0.1 s. The working electrode area was restricted by a viton o-ring with an internal diameter of 6 mm. Hereinafter, this area ( $0.28 \text{ cm}^2$ ) is designated as an apparent electrode area ( $A_a$ ).

The reference electrode was connected with the cell via Luggin capillary. All the potential values hereinafter are referred to the saturated (KCl) Ag/AgCl electrode. A Pt wire ring was used as a counter electrode located in parallel to the surface of the working electrode to provide a homogeneous current distribution.

In this work, all the solutions were prepared using deionized water ( $18.2 \text{ M}\Omega \text{ cm}$ ) obtained by water purification system WaterPro PS (Labconco). The experiments were performed at room temperature (20–25 °C).



**Fig. 1.** Morphology of porous anodic alumina templates. (a) SEM image of the top surface of as-prepared AAO film obtained by two-step anodization in 0.3 M  $\text{H}_2\text{C}_2\text{O}_4$  at 40 V. Geometrical parameters of AAO structure are depicted on inset in panel (a).  $D_{\text{int}}$  is an interpore distance,  $D_p$  is a pore diameter. The results of numerical treatment of SEM micrographs: pore size distribution at bottom (b) and top (c) parts of AAO porous film, interpore distance distribution (d).

Download English Version:

<https://daneshyari.com/en/article/184599>

Download Persian Version:

<https://daneshyari.com/article/184599>

[Daneshyari.com](https://daneshyari.com)