Three-Dimensional Niobium Nanopillar based Electrode for Energy Storage Devices

Nevin Taşaltın [1,2,3*], Elif Tüzün[4], Selcan Karakuş[4*]

[1]Maltepe University, Dept. of Electrical and Electronics Eng., Istanbul, Turkey.
[2]Maltepe University, Dept. of Basic Sciences, Istanbul, Turkey.
[3]Maltepe University, Dept. of Renewable Energy Tech. and Management, Istanbul, Turkey.
[4]Istanbul University-Cerrahpasa, Dept. of Chemistry, Istanbul, Turkey.

Abstract: In this study, aluminum (Al) film with high purity was coated on the Niobium (Nb) sheet by thermal evaporation under ultra-high vacuum. An Anodic Aluminum Oxide (AAO) nanotemplate was prepared on the Nb sheet. During AAO nanotemplate preparation, three-dimensional (3D) Nb nanopillars were grown on the Nb sheet. We performed a simple 3D Artificial Intelligence (AI) analysis of Nb nanopillars. According to the experimental results, the width of the prepared Nb nanopillars is in the range of 100–120 nm, and the length is approximately 150 nm. The Electron Diffraction Spectroscopy (EDS) results confirmed that the nanopillars are Nb. The prepared Nb nanopillars can be a potential candidate for energy storage applications.

Keywords: Energy storage; nanopillar; niobium; artificial intelligence.

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***Corresponding authors:** Nevin Taşaltın, Selcan Karakuş. **E-mails:** nevintasaltin@maltepe.edu.tr, selcan@iuc.edu.tr

INTRODUCTION

Current global economic conditions make it essential that energy resources should not be consumed excessively. Environmental pollution should be prevented for a moment (1–3). Renewable energy resources should be used more frequently in order to meet the increasing energy demand. Energy should be stored effectively and energy storage technologies should be developed rapidly (4–6). Therefore, it is extremely urgent to develop sustainable and efficient materials for energy storage devices, especially for supercapacitors and lithium-ion batteries (7–9). Among the materials used in energy devices, Niobium (Nb)-based materials (10–12) constantly maintain their attractiveness due to their unique crystal structures and high performance. A number of researchers have reported that the kinetics of anodic oxide film growth on the surface of Nb is commonly clarified with the high-field electrical conductivity measurements due to the hopping transmission between charged imperfections (13,14). This study set out with the aim of assessing the synthesis of the self-assembly Anodic Aluminum Oxide (AAO). In this study, high purity aluminum-Niobium (Al-Nb) was synthesized from the formation of barrier type Al_2O_3 layers on substrate metal using the controlled anodic oxidation method. It was experimentally observed that the metal film coating on the substrate metal during the controlled anodic oxidation process and the substrate metal was directed towards the finger-shaped alumina barrier layers due to the formation of Al_2O_3 layers (15,16). Nb nanostructures were prepared using the AAO nanotemplate (17–21). The current study found that the shape of the prepared Nb nanostructure depended on the anodizing conditions. In reviewing the literature, a few studies have been reported on the preparation of Al-Nb (22–24). Inspired by the previous studies, in this study, Nb nanopillars were prepared via anodic oxide growing kinetics on the surface of Nb and characterized.

EXPERIMENTAL

The Nb sheet (99.99%) was purchased from American Elements Company (USA). Hydrofluoric acid (HF) (38–40%), oxalic acid (98%), and phosphoric acid (85%) were purchased from Merck Company (Germany). Scanning Electron Microscopy (SEM) and Electron Diffraction Spectroscopy (EDS) results of samples were obtained using a Quanta 250 FEG SEM model.

In this study, Nb sheet was chemically cleaned by immersion washers in a 10 to 90% hydrofluoric acid (HF)/deionized water solution. After cleaning in HF/deionized water solution, the Al layer (thickness:700 nm) was evaporated on the Nb sheet under the ultra high vacuum ($1x10^{-7}$ Pa) medium and annealed at 200 ^{0}C for 15 min. The controlled anodic oxidation treatment of the solution with a 0.3 M oxalic acid solution at constant 40 V for 15 min; the sample was immersed in a phosphoric acid solution (3 wt. %) at 25 ^{0}C for 15 min. Then, the second anodic oxidation was performed under the same experimental conditions to obtain a novel AAO nanotemplate on Nb sheet. During the formation of the AAO nanotemplate, Nb nanopillars were grown on the surface of the Nb sheet. The AAO nanotemplate/Nb sample was vertically dipped in a 0.1 M NaOH solution for 10 min to dissolve the AAO nanotemplate, and then Nb nanopillars were obtained. The schematic illustration of the preparation of the Nb nanopillars is given in **Figure 1**. SEM and EDS measurements were carried out for the morphological and compositional analysis of Nb nanopillars.

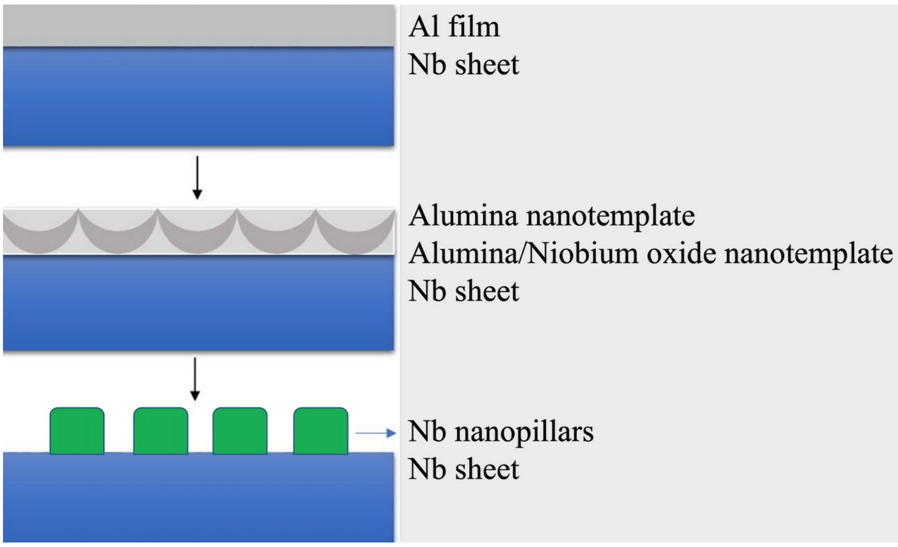

Figure 1: The schematic illustration of the preparation of the Nb nanopillars.

RESULTS AND DISCUSSION

The SEM image and EDS analysis of the obtained Nb nanopillars are shown in **Figure 2**. As clearly seen from the SEM image given in the inset of **Fig.2a-f**, the obtained Nb nanopillars are approximately 100 nm in diameter. Sometimes, material analysis techniques may not be sufficient for the analysis of materials, or the necessary infrastructure for the analysis is not available. In such cases, the Artificial Intelligence (AI) technique really comes to the rescue. It was not possible to determine the size of the Nb nanopillars prepared in this study by SEM analysis due to the infrastructure. Therefore, we performed a 3D AI analysis of Nb nanopillars. According to the experimental results, the width of the prepared Nb nanopillars is in the range of 100–120 nm, and the length is approximately 150 nm (**Fig. 2f**). The EDS spectrum confirmed that the nanopillars are Nb (**Fig. 2c**).

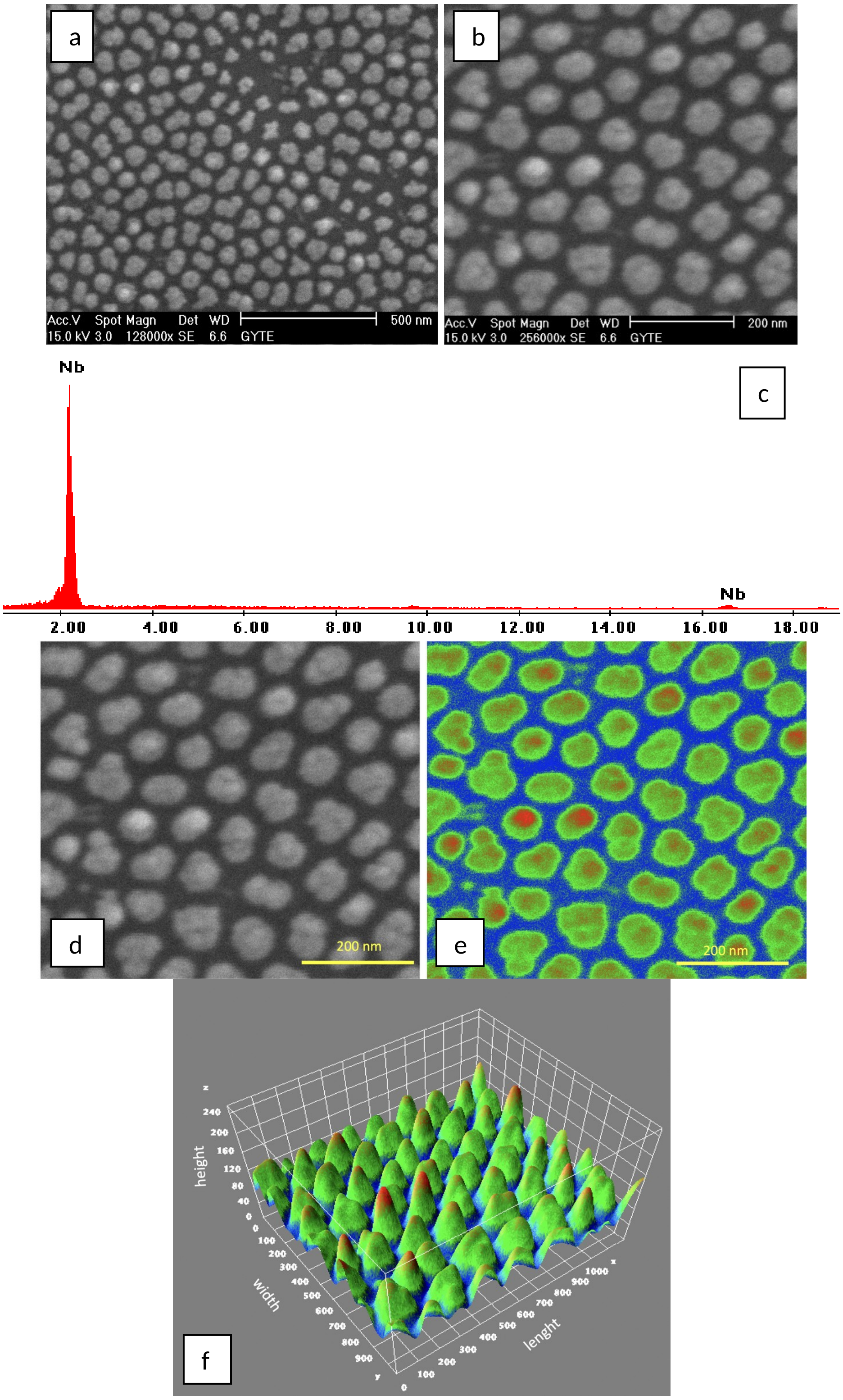

Figure 2. (a-b) SEM images and **(c)** EDS analysis of the prepared Nb nanopillars, **(d)** Artificial Intelligence (AI)-powered SEM image (8-bit) **(e)** SEM image (8-bit/rainbow RGB), and **(f)** 3D surface plot of Nb nanopillars.

When the two-step anodization technique (25) applied to Al film on Nb sheet, the anodic metal oxide was developed on the Nb_2O_5 layer by simultaneous growth at the Nb_2O_5 /Al_2O_3 interface by the migration of oxygen ions into the AAO layer (26). With the effect of anodization conditions, negative oxygen ions moved through the oxide layers in the direction of the Nb_2O_5 layers and the released Al^{+3} ions were expelled towards the electrolyte by passing through the barrier oxide layers. During the anodization of the metal substrate, some of Al^{+3} anions reacted with the O^{-2} ions at the interface of the AAO barrier layer/electrolyte and it was related to the formation of Al_2O_3 at the interface of metal oxide/electrolyte in the pores of AAO. Migrated electrolyte O^{-2} ions in the Nb_2O_5 layers were penetrated and oxidized the layer due to the formation of Nb_2O_5/Al_2O_3 using an electrochemical migration approach. At the same time, Nb^{+5} ions were directed outward to obtain new oxide layers at the interface of Nb_2O_5/Al_2O_3 by the electric field. Additionally, the thickness of the AAO barrier layer could be increased under the constant anodization voltage during the anodization due to the formation of the new oxide at the Nb_2O_5/Al_2O_3 and interfaces of Al_2O_3/electrolyte, and it was compensated by the ionic interface resistance of the interface of Al-Nb. It was also revealed that Nb_2O_5 were formed without direct contact between Nb metal and electrolyte due to the migration of O^{-2} ions and exition on the AAO barrier layer to Nb metal using a highly controlled process. At the beginning of the anodization process, the decrease in current was related to the O^{-2} ions on the Nb_2O_5 layer at the interface of Nb_2O_5/Al_2O_3 and the AAO layer on Al. Nb nanopillars with controlled morphologies could be easily achieved from AAO with the different electric field distribution. Finally, it was successfully presented the fabrication of a new the self-assembly AAO nanotemplate using a dilute NaOH solution, which yield the formation of Nb nanopillars with small nanopores.

CONCLUSIONS

The AAO nanotemplate was prepared on the Nb sheet. During AAO nanotemplate preparation, Nb nanopillars were grown on the Nb sheet. The proposed Nb nanopillars is a advanced energy storage material with superior advantages such as high surface area and electroactive regions. The diameter of Nb nanopillars is approximately 100–120 nm, and the length is approximately 150 nm. Nb-based materials are promising electrode materials for use in supercapacitors and batteries. The Nb nanopillar-based electrodes prepared in this study can overcome the following problems. Nb nanopillars can shorten the diffusion distance between ions, provide a fast transfer path for ions, increase the contact surface between electrolyte and electrode, and expand the specific surface area, which improves the efficiency of the active material. In this way, volume expansion can be experienced. The large lattice parameter in Nb nanopillars can show a high Li^+ diffusion coefficient in Li-ion batteries, providing low electrode polarization and charge transfer resistance. Modification of Nb nanopillars with metal nanoparticles can achieve a more satisfactory crystal structure that increases the unit cell volume and lattice parameters. Thus, it can result in superior lithium diffusion kinetics in the Li-ion battery. Therefore, improved conductivity and increased Li^+ ion diffusion coefficients can be achieved, resulting in improved electrochemical performance. Modifying Nb nanopillars with carbon-based nanomaterials can greatly improve conductivity and contribute to enough active sites and efficient conductive contacts during the electrochemical reaction process. In summary, it is predicted that Nb-based materials will have a wider application area in supercapacitors and batteries in the future.

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DECLARATION OF COMPETING INTEREST

The authors declare that they have no conflict of interest.

AUTHOR CONTRİBUTİONS

Nevin Taşaltın: Conceptualization, Methodology, Writing- Reviewing and Editing. Elif Tüzün: Methodology, Selcan Karakuş: Conceptualization, Methodology, Writing- Original draft preparation, Software.

CONFLICTS OF INTEREST

None.

DATA AVAILABILITY

The authors confirm that the data supporting the findings of this study are available within the article. Raw data that support the findings of this study are available from the corresponding author, upon reasonable request.

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