

## XPS CHARACTERIZATION OF NIOBIUM-OXIDE NANOCOLUMN ARRAYS VIA SELF-ORGANIZED ANODIZING IN SELENIC ACID

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### Abstract

As previously reported, arrays of Nb<sub>2</sub>O<sub>5</sub> nanocolumns on substrates may be synthesized by anodizing Al-on-Nb bilayers in oxalic, sulfuric, malonic, or phosphoric acids. Here, for the first time, we employed a new anodizing electrolyte - selenic acid (H<sub>2</sub>SeO<sub>4</sub>) due to a unique morphology of porous anodic alumina (PAA) formed in this electrolyte featuring extremely narrow pores and therefore, the minimal possible porosity (~3%) among the PAA films prepared in the usual solutions. Such a morphology may result in distinctive structural, physical, and chemical properties of the niobium-oxide nanoarrays complemented by the specific dielectric, optical, electro-optical, catalytic, and antibacterial properties in case the selenium species are incorporated into the column structure during the anodizing. The columns were prepared from the magnetron-sputtered Al/Nb bilayers by anodizing at 12 or 40 V, followed by re-anodizing to 80 or 120 V, respectively, and selective dissolution of the alumina overlayer. Detailed XPS characterization confirmed that selenium species is present in the column material. The fitting of the narrow-scan Se 3d spectra, complicated by overlapping with Nb 4s peaks, shows that selenium is incorporated in the form of selenate (SeO<sub>4</sub><sup>2-</sup>) and selenide (Se<sup>2-</sup>) anions, likely creating a core-shell structure. Quantitative analysis reveals that about 1.5-3.0% of O<sup>2-</sup> anions in the oxide structure are replaced by selenate or selenide anions. Further investigation is in progress to understand the formation-structure-morphology relationship and explore the functional properties of the arrays.

**Keywords:** Anodizing, porous anodic alumina, niobium pentoxide, selenium

### 1. INTRODUCTION

Nanostructuring is beneficial or crucial for many applications of metal oxides due to an increased surface-to-volume ratio and a shorter distance to the surface [1,2]. One-dimensional nanostructures (nanowires, nanorods, or nanocolumns), anchored to the substrate, can be synthesized in various ways, including sol-gel synthesis and other wet-chemical methods, physical and chemical vapor deposition, and electrodeposition [1,3]. An alternative approach, the so-called PAA-assisted anodizing [4], may be applied to a thin film of aluminum deposited on a layer of another valve metal (i.e. Nb, Ta, W, Ti, Hf, or Zr). Initially, the Al layer is converted into porous anodic alumina (PAA) by anodizing in an acidic electrolyte, immediately followed by self-organized growth of the underlying metal oxide locally into the barrier layer of the PAA film beneath the alumina pores. This results in the formation of short nanoprotusions of the underlying metal oxide, mixed to some extent with alumina. Further, re-anodizing to a higher voltage may be carried out to prolong the oxide protrusions within the alumina pores. In this way, metal-oxide nanocolumns, upright standing on a substrate, attaining the morphology of the initially formed PAA layer may be created.

Niobium pentoxide (Nb<sub>2</sub>O<sub>5</sub>) is a wide-bandgap *n*-type semiconductor [5]. It is a non-toxic metal oxide with excellent chemical stability and corrosion resistance [5], suitable for applications including photocatalysis, gas sensing, electrochemical energy storage, electrochromic devices, or photoanodes. The PAA-assisted

anodizing has been used to synthesize arrays of  $\text{Nb}_2\text{O}_5$  nanocolumns of various dimensions [4], with diameters ranging between 30 and 150 nm, depending on the electrochemical and electrical conditions applied during the Al anodizing. So far, various electrolytes have been tested, including oxalic, sulfuric, malonic, or phosphoric acids [4]. However, anodizing in *selenic acid* ( $\text{H}_2\text{SeO}_4$ ), which offers a unique morphology of PAA with extremely narrow pores and very low porosity of ~3% [6], may result in arrays of very thin  $\text{Nb}_2\text{O}_5$  nanocolumns possessing specific structural, physical, or chemical properties. In addition, if selenium species are incorporated into the column material, altering the dielectric, optical, catalytic, or antibacterial properties may be achieved.

In the present work, we have anodized and re-anodized the Al-on-Nb bilayers in selenic acid to synthesize arrays of Se-doped  $\text{Nb}_2\text{O}_5$  nanocolumns of various morphologies. The chemical composition of the films, focusing on the presence of selenium species, has been examined by X-ray photoelectron spectroscopy (XPS).

## 2. EXPERIMENTAL PART

### 2.1. Sample preparation

Thin Al-on-Nb bilayer film was used as a precursor for anodizing. It was prepared on oxidized Si wafers by magnetron sputtering of a 140-nm thick Nb layer followed by a 1- $\mu\text{m}$  thick Al layer from the Nb (99.95%) and Al (99.999%) targets, respectively. Pieces of 1 cm  $\times$  1 cm cut from the wafers were anodized and re-anodized in 1.5 M  $\text{H}_2\text{SeO}_4$  aqueous solution at room temperature. The anodizing was performed galvanostatically at 0.5 or 5  $\text{mA}\cdot\text{cm}^{-2}$ , followed by a short potentiostatic hold at 12 or 40 V, respectively, to anodize Nb through the barrier layer. For selected samples, potentiodynamic re-anodizing was carried out at 10  $\text{V}\cdot\text{s}^{-1}$  to 80 or 120 V, respectively, followed by a short voltage stabilizing period. To obtain PAA-free samples, the PAA overlayer was selectively dissolved away in  $\text{Cr}_2\text{O}_3/\text{H}_3\text{PO}_4$ -based etchant [7]. Field emission SEM was employed to examine the morphology of the films.

### 2.2. XPS characterization

XPS analysis was carried out for the PAA-free films on a Kratos Axis Ultra DLD spectrometer using a monochromatic Al  $K\alpha$  source. The X-ray emission power was 150 W with a 15 kV accelerating voltage focused to a spot of 300  $\mu\text{m}$   $\times$  700  $\mu\text{m}$ . The emitted electrons were detected at fixed pass energies of 160 eV for the survey spectra and 20 eV for the high-resolution spectra. The Kratos charge neutralizer system was used for all specimens.

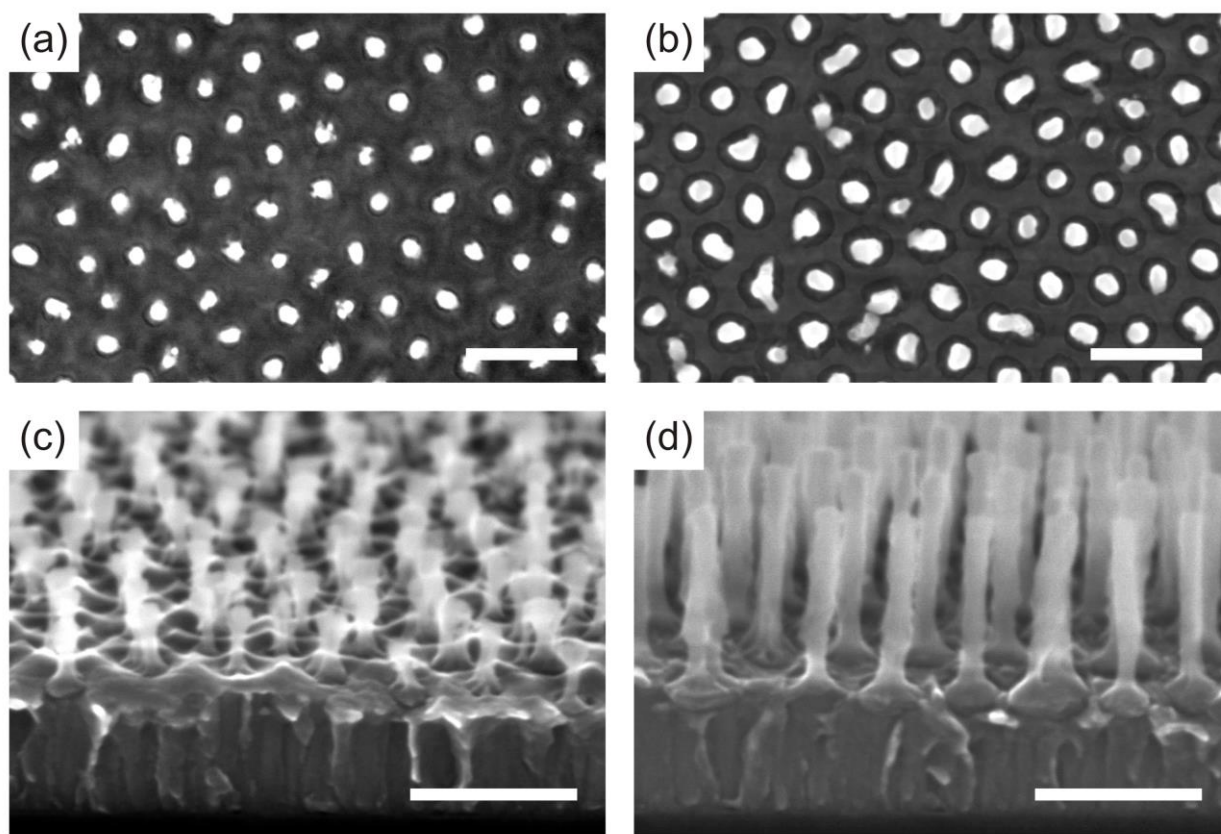
The spectra were analyzed using CasaXPS. GL(30) profiles were used for all components except the metallic core lines of Nb 3d, for which asymmetric profiles in the form of LA(1.2,5,12) were applied. A standard Shirley background was used in all fitted spectra. Spectra from all samples have been charge corrected to give the adventitious C 1s spectral component (C–C, C–H) binding energy of 284.8 eV. The deconvolution of C 1s spectra was performed as described in previous works [4].

## 3. RESULTS AND DISCUSSION

### 3.1. Film morphology

The PAA-assisted anodizing of Nb bilayers in selenic acid at 12 and 40 V was expected to result in arrays of  $\text{Nb}_2\text{O}_5$  nanocolumns of two dissimilar diameters. **Figure 1a** and **c** shows the top-view and cross-fractional SEM images of the PAA-free 40V columns. Protrusions of presumably  $\text{Nb}_2\text{O}_5$  are observed, about 70 nm long and 20 nm in diameter. They are anchored to the Nb metal below through oxide bases and are separated from each other by the remainings of Al and possibly Nb metals. Increasing the voltage during the re-anodizing to

120 V results in the lengthening and widening of the protrusions to 260 and 30 nm, respectively (**Figures 1b,d**). The nanocolumns are still connected to metal oxide bases below them and are separated by the residues of the metals, evidently of a smaller amount than in the case of the anodized 40V sample. The nanocolumns obtained by anodizing at 12 V followed by re-anodizing to 80 V (i.e., 12+80V columns, SEM images not shown) are thinner and shorter than the 40+120V columns, as expected, having a diameter of 12 nm and a length of 120 nm. However, they are not separated by metal residues. They are standing on a continuous layer of metal oxide residing between the columns and the unoxidized Nb on the substrate. In the following, we will focus on the wider, 40V and 40+120V nanocolumns.

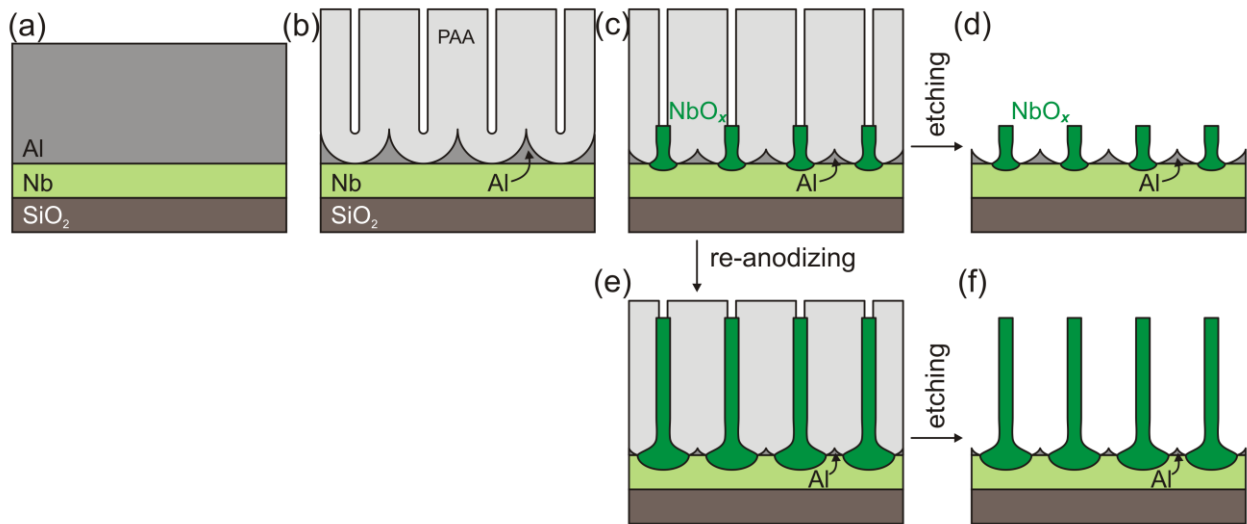


**Figure 1** (a,b) Top-view and (c,d) cross-sectional SEM images of the PAA-free (a,c) 40V (anodized) and (b,d) 40+120V (re-anodized) nanocolumns. The scale bar is 200 nm.

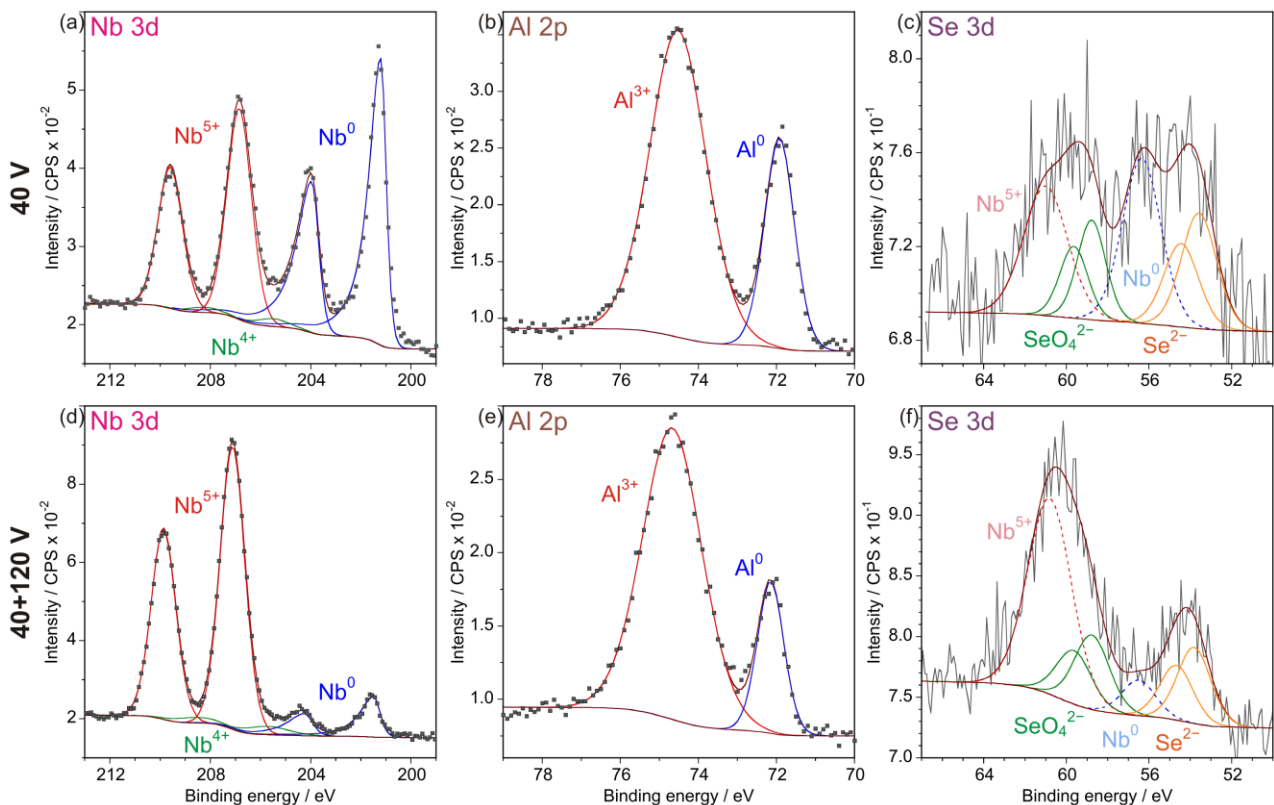
Based on the SEM observation, schematic images of the formation of the 40V and 40+120V films were developed (**Figure 2**). Major features of the  $\text{Nb}_2\text{O}_5$  nanocolumns formed in this way in the selenic acid are their smaller diameter (compared with that of the columns formed at similar electrical conditions in oxalic acid [4]) and their separation from each other by the residual Al and Nb metals. These characteristics may influence the possible utilization of the nanocolumn arrays, in addition to the expected presence of selenium species in the columns, as investigated by XPS.

### 3.2. Film composition

Examination of the chemical composition and bonding states in the surface layer of the PAA-free 40V and 40+120V films was performed by XPS. The presence of C, Nb, O, Al, Se, P, and Cr was identified in the survey spectra of the samples; the last two elements were present due to the PAA dissolution in the  $\text{Cr}_2\text{O}_3/\text{H}_3\text{PO}_4$ -based etchant. Narrow-scan C 1s, Nb 3d, O 1s, Al 2p, and Se 3d spectra were collected to analyze the bonding states. The experimental and fitted Nb 3d, Al 2p, and Se 3d spectra are shown in **Figure 3**.



**Figure 2** Schematic images of the processes for forming the 40V and 40+120V nanocolumn arrays: (a) the sputter-deposition of an Al/Nb bilayer onto an oxidized Si wafer, (b) the anodizing of the Al layer to form a PAA film, (c) the anodizing of the Nb underlayer into the barrier layer (the anodized, 40V film), (d) possible etching of the PAA overlayer to obtain the PAA-free 40V film, (e) the re-anodizing of Nb layer to 120 V (the re-anodized, 40+120V film), (f) possible etching of the PAA overlayer to obtain the PAA-free 40+120V sample



**Figure 3** Experimental and fitted XPS spectra of the surface of the PAA-free (a-c) 40V and (d-f) 40+120V anodic films. (a,d) Nb 3d, (b,e) Al 2p, and (c,f) Se 3d high-resolution spectra are shown.

The *Nb 3d spectra* of the two samples (**Figures 3a,d**) are both fitted with three doublets of appropriately constrained peaks ( $\text{Nb } 3d_{5/2}$  and  $3d_{3/2}$  with fixed peak separation energy of 2.75 eV and with fixed intensity ratio of 3:2 [4]). The highest binding energy (BE) doublet is due to the presence of  $\text{Nb}^{5+}$  cations, whereas the lowest BE doublet is associated with metallic  $\text{Nb}^0$  [4], separating the column bases. The relative amount of the metallic  $\text{Nb}^0$  is much smaller in the 40+120V anodic film than in the 40V sample (12% vs. 53% of all Nb species), which is in agreement with the SEM observations (**Figure 1**). The third, lowest-intensity doublet, shifted to  $-1.35$  eV from the  $\text{Nb}^{5+}$  component, is attributed to the presence of  $\text{Nb}^{4+}$  cations in the film [4]. The ratio of  $\text{Nb}^{5+}:\text{Nb}^{4+}$  cations is 97:3 and 95:5 for the 40V and 40+120V films, respectively, indicating the presence of a substoichiometric  $\text{Nb}_2\text{O}_5$  in the columns. The presence of  $\text{Nb}^{4+}$  cations (and lower-oxidation-state metal cations in general) at the surface of re-anodized PAA-assisted films seems to be a common feature [4,7].

The *Al 2p spectra* (**Figures 3b,e**) are fitted with two single peaks: a high-intensity peak associated with  $\text{Al}_2\text{O}_3$  and a low-intensity peak associated with metallic Al. The metallic Al and a portion of the alumina seen in the spectra are attributed to Al metal residues (covered with native oxide) situated around the columns and over the metallic Nb residues. These metallic contributions can be subtracted from both the Nb 3d and Al 2p spectra to obtain an approximate amount of Nb and Al present only on the column surface. For Al, also the corresponding native oxide was taken into account and subtracted [8]. The result is 65 and 61 at.% of Al for the 40V and 40+120V films, respectively (providing at.%(Al+Nb) = 100%). Similarly larger amounts of Al in the outer layer of PAA-assisted oxide columns of about 75 at.% have been reported for N-doped  $\text{TiO}_2$  surfaces [7]. These results mean that the outmost column material is composed of mixed alumina-niobia, whereas the column interior is alumina-free  $\text{Nb}_2\text{O}_5$  [4].

**Figures 3c,f** shows the measured and fitted *Se 3d spectra* for the two anodic films. The spectra are noisy due to the low content of Se, which, in addition to overlapping with Nb 4s peaks, complicates the deconvolution of the Se 3d spectra. When comparing the spectra of the various samples (including the 12V and 12+80V films, not shown), fitting them, and verifying the peak positions with the literature [9,10], multiple components were well assigned: Nb 4s peak of  $\text{Nb}^{5+}$  cations ( $\sim 60.9$  eV), Nb 4s peak of  $\text{Nb}^0$  atoms ( $\sim 56.4$  eV), Se 3d peaks of selenate anions ( $\text{SeO}_4^{2-}$ , Se  $3d_{5/2}$  at  $\sim 58.8$  eV), and Se 3d peaks of selenide anions ( $\text{Se}^{2-}$ , Se  $3d_{5/2}$  at  $\sim 54.0$  eV). For fitting the Nb 4s peaks, the area below the peaks was considered proportional to the area of the corresponding Nb 3d peaks and the area of the  $\text{Nb}^0$  peak was constrained as a multiple of the  $\text{Nb}^{5+}$  peak to agree with the corresponding Nb 3d spectrum. The Se 3d peaks were fitted as doublets with a constrained spin-orbit splitting of 0.86 eV [10] and the ratio of the Se  $3d_{3/2}$  and  $3d_{5/2}$  components was fixed at 0.72 [10].

The ratio of selenate:selenide is found 39:61 and 51:49 for the 40V and 40+120V films, respectively. The amount of Se at the column surface was calculated using the area of the Se 3d components and after subtracting the metallic contributions from the Al 2p and Nb 3d spectra. 5.3 and 3.2 at.% of Se were obtained for the 40V and 40+120V samples, respectively (provided at.%(Al+Nb+Se) = 100%).

The chemical composition of the surface layer of the columns in the 40V and 40+120V anodic films can thus be expressed as a mixture of  $\text{Al}_2\text{O}_3$  and substoichiometric  $\text{Nb}_2\text{O}_5$ , with some percentage of the  $\text{O}^{2-}$  anions in both oxides replaced by  $\text{SeO}_4^{2-}$  and  $\text{Se}^{2-}$  anions. There are about 65 at.% of  $\text{Al}_2\text{O}_3$  and 3.0 and 1.8% of  $\text{O}^{2-}$  anions replaced by selenium species in the 40V and 40+120V samples, respectively.

Selenate anions in the columns originate from the anodizing electrolyte. They move within the growing oxide under the high electric field, with a slower velocity than the  $\text{O}^{2-}$  anions, and are incorporated into the oxide structure, similarly to other electrolyte anions during the PAA-assisted anodizing [11]. The presence of selenide anions is less obvious and may be explained by the reduction of  $\text{SeO}_4^{2-}$  anions at the cathode, their further diffusion inside the electrolyte, and incorporation into the growing anodic oxide in a similar way as in the case of the selenate anions. Most probably, the anions move more easily within the surface layer of the columns (which is mixed with alumina [4]). Therefore they form a kind of core-shell structure. The shell contains the Se species and alumina, while the core is free from them.



#### 4. CONCLUSIONS

The Al-on-Nb bilayers were anodized via the PAA-assisted anodizing in selenic-acid electrolyte for the first time. Varying the electrical conditions during the oxide growth resulted in the arrays of thinner and wider nanocolumns of niobium oxide, with diameters of 12 and 30 nm, respectively. XPS analysis of the wider columns revealed that their surface layer consists of substantial amounts of alumina (about 65 at.%) and substoichiometric Nb<sub>2</sub>O<sub>5</sub>. In both oxides, ~2.5% of O<sup>2-</sup> anions are replaced by selenate and selenide anions. Probably, the columns grow as a core-shell structure with the shell being alumina- and Se-species-rich and the core being free of them.

The presence of selenate and selenide anions in the column material may impact their functional properties, such as optical, catalytic, and antibacterial. Moreover, the self-formed heterojunctions may lead to even more advantages. Such promising properties of the anodic films prepared here may be investigated in future works.

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