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SYNTHESIS AND CHARACTERISATION OF TiO_2 NANOTUBES WITH EC-AFM

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The formation process of auto-organised titanium oxide nanotube structures is presented using the electrochemical atomic force microscopy (EC-AFM). The images recorded in real time during the formation process of the auto-organised titanium oxide structures in two electrolytes, one inorganic and one hybrid organic-inorganic highlighted differences in the formation of nanotubes and lead to the deduction mechanisms occurring at the liquid-electrode interface.

Keywords: Auto-organized TiO_2, nanotubes, EC-AFM, growth mechanism.

1. Introduction

TiO_2 is one of the most studied compounds in materials science in the last years. Owing to some outstanding properties it is used for instance in photo-catalysis [1; 2], dye-sensitized solar cells [3; 4], and biomedical devices [5; 6; 7]. In 1999, first reports showed the feasibility to grow highly ordered arrays of TiO_2 nanotubes by a simple but optimized electrochemical anodizing of a titanium metal sheet [8; 9]. This finding stimulated intense research activities that focused on growth, modification, properties, and applications of these auto-organized nanostructures [10; 11; 12].

Synthesis of TiO_2 nanostructure involves different methods, anodic oxidation being a convenient electrochemical method, which can be easily used to grow various oxide layers on titanium surface by using appropriate anodizing conditions.

The presence of fluorides in the electrolyte strongly affects the anodizing process, as fluorides form water soluble $[TiF_6]^{2-}$ species [13; 14]. On one hand, Ti^{4+} ions are ejected at the oxide–electrolyte interface after migration through the oxide film; and on the other hand new TiO_2 is formed on the surface by chemical attack.

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In this study, we used two aqueous electrolytes (inorganic and organic) to demonstrate that the nature of the electrolyte affects the migration of fluoride ions on the surface of the electrode and thus, the resulting structures are different.

2. Experimental

Liquid mode AFM is a technique used mainly in biological and electrochemical experiments. The cantilever and the sample are completely submerged in liquid and images can be recorded without the removal of the solution. This technique has the advantage of removing any contact with the atmosphere, thus reducing to a minimum sample-air interactions and contaminations.

A custom-made electrochemical cell was designed and used with the A.P.E. Research A100- SGS EC-AFM. The three electrode system was made of a Titanium working electrode, a Ag/AgCl reference electrode and a Platinum counter electrode.

The working electrode was previously polished with SiC paper of granularity up to 4000 until a mirror surface was achieved and then cleaned with ethanol and deionized water before each experiment.

The electrochemical cell and Liquid mode AFM permitted real time and in-situ analysis. Synthesis of Titanium Oxide nanotubes was realized using two types of aqueous electrolytes: a mixture of fluoride salts for an inorganic solution $(NH_4)_2SO_4$ +NH_4F 0.5 wt% (electrolyte 1) and a hybrid inorganic organic components as glycerol + 4% H_2O + NH_4F 0.36 wt% (electrolyte 2).

A MATRIX MPS-7163 single channel adjustable DC power supply electrochemical source was used to input 20V for 1 h.

AFM data were processed using Gwyddion, a modular program for SPM data visualization and analysis.

Scanning Electron Microscopy (SEM) – FEI/Phillips XL30 ESEM was also used for surface characterization.

3. Results and discussion

Fig. 1 presents the chronoamperograms for titanium oxide nanotubes formation in both electrolyte 1 and electrolyte 2 solutions:

The chronoamperograms evolution shows that the formation of nonotubes can be divided into three stages:

- First stage: the formation of a titanium oxide layer on the surface, which lowers the current in the circuit.

- In the second stage the partial dissolution of titanium dioxide begins and random pores appear on the surface, reducing the thickness of the oxide layer and increasing the active surface of the electrode.

- In the last stage, as pores develop in optimum conditions, self-organized nanotubes form on the surface.

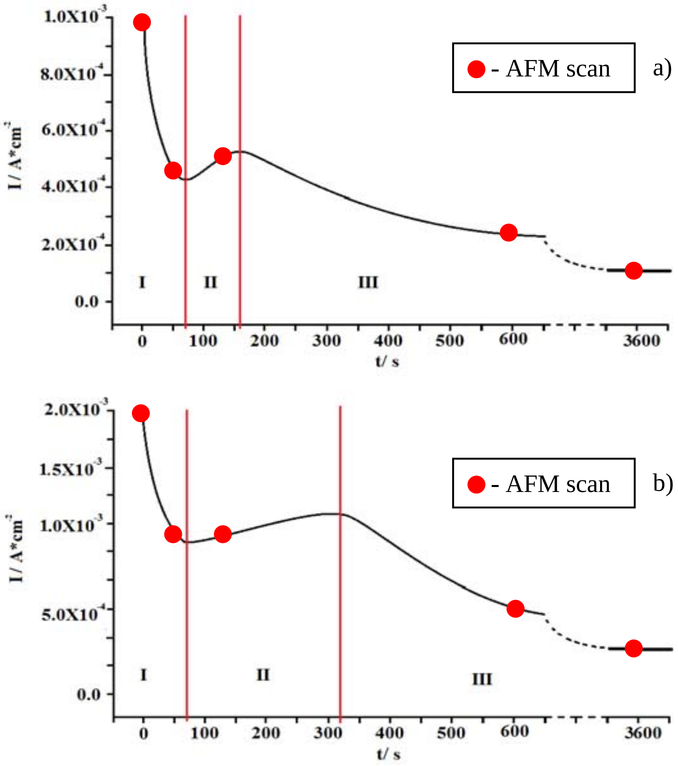


Fig. 1. Chronoamperograms for Titanium oxide nanotubes formation in electrolyte1 (a) and electrolyte2 (b).

3.1. AFM imaging

AFM images were taken during the process at key time intervals to observe in detail the process described above for both electrolytes at 0s, 60s, 120s, 600s and 3600s.

The initial image shows the surface of pure titanium after immersion and before voltage application. Note the presence of natural oxide structures already present on both of the surfaces (Fig.2).

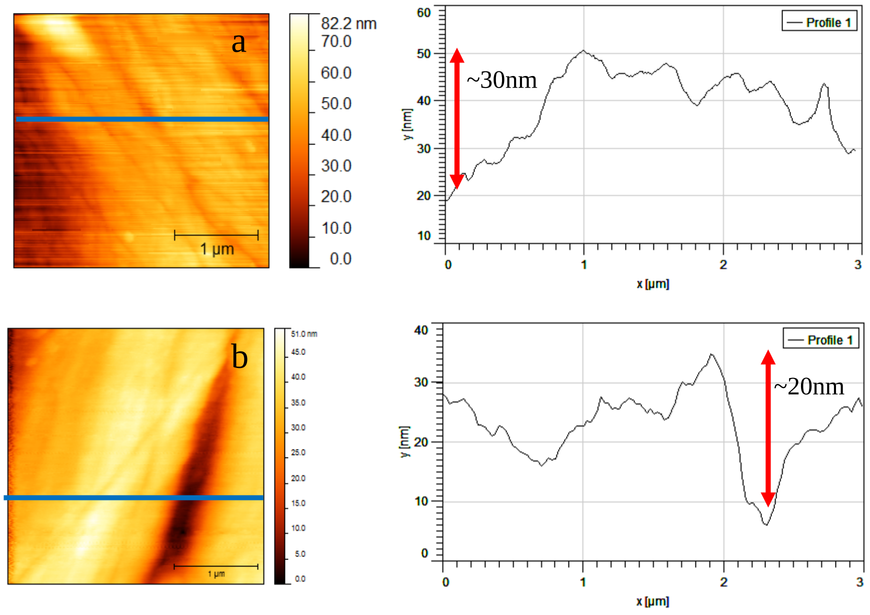


Fig. 2. AFM scans (T=0s) and linear profiles of Titanium in electrolyte1(a) and electrolyte2(b)

In the first stage, after 60 seconds of applying the voltage, there is a full coverage of the surface with a layer of titanium oxide. The topographic images confirm the appearance of granular structures with size of about 100-200 nm, which form a compact and uniform layer (Fig.3). In this stage, the current density decreases for both samples at about 45 % from initial value due to compact oxide layer formation.

After two minutes, at the final second stage of the sample anodized in electrolyte 1, scans were again performed. The linear profile shows the start of the pores formation, pores which will become centres of the nanotubes formation. The resulted nanopores have a diameter of about 100 nm (Fig.4) and are more visible for the sample anodised in electrolyte 1.

This observation is consistent with recorded chronoamperograms which show that point three is at the end of the stage two for sample anodized in electrolyte 1, where the pores are already formed on the surface and contrary at the start of stage two for the sample anodized in electrolyte 2, where the pores are during formation.

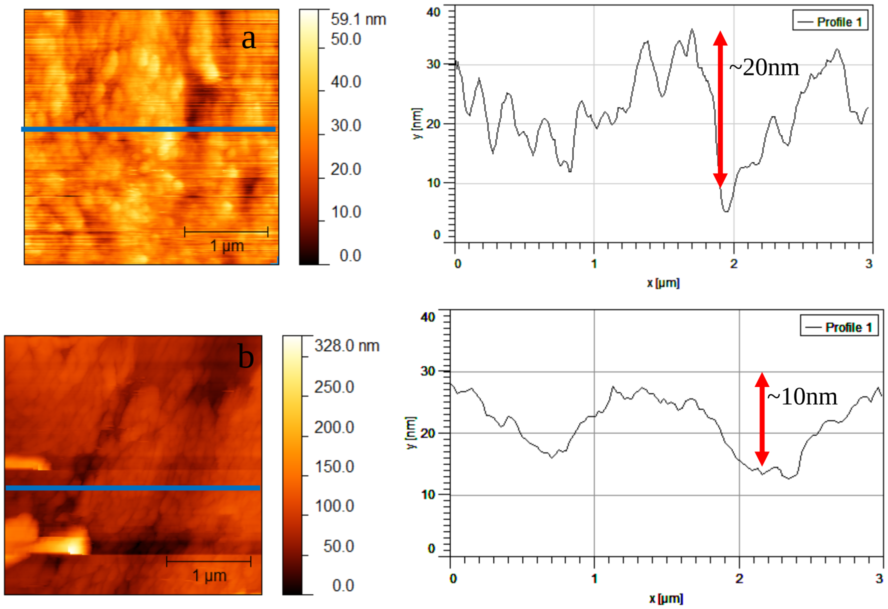
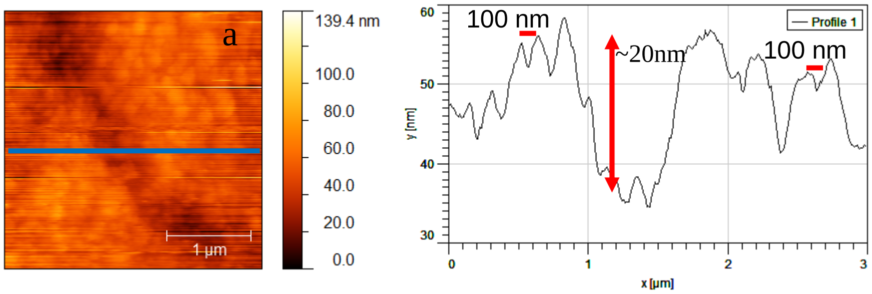


Fig. 3. AFM scans (T=60) and linear profiles of Titanium in electrolyte1(a) and electrolyte2(b)

The third stage, corresponding to the actual increase of nanotubes, the images were taken at 600 and 3600 seconds. At 10 minutes after voltage application, topographical images show a further increase of the titanium oxide layer on the surface. The cantilever could not directly capture the formation of nanotubes, because of their very small size. However, linear profile indicates further growth of nanotubes in the cavities of about 50nm surrounded by small peaks. A big difference was observed for the sample anodized in electrolyte 2, in which the Titanium oxide formed very fast in this stage, filling the top of the nanotubes (Fig.5).



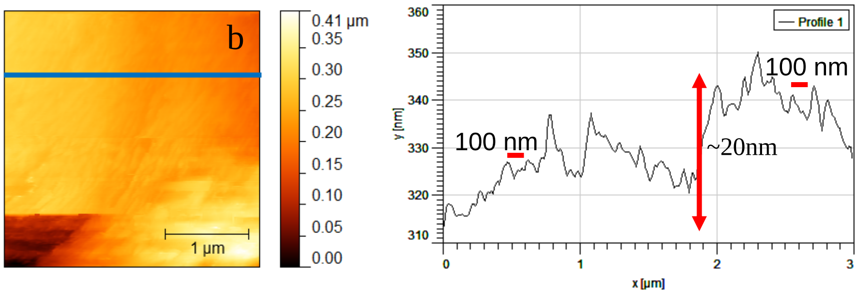


Fig. 4. AFM scans (T=120) and linear profiles of Titanium in electrolyte1(a) and electrolyte2(b)

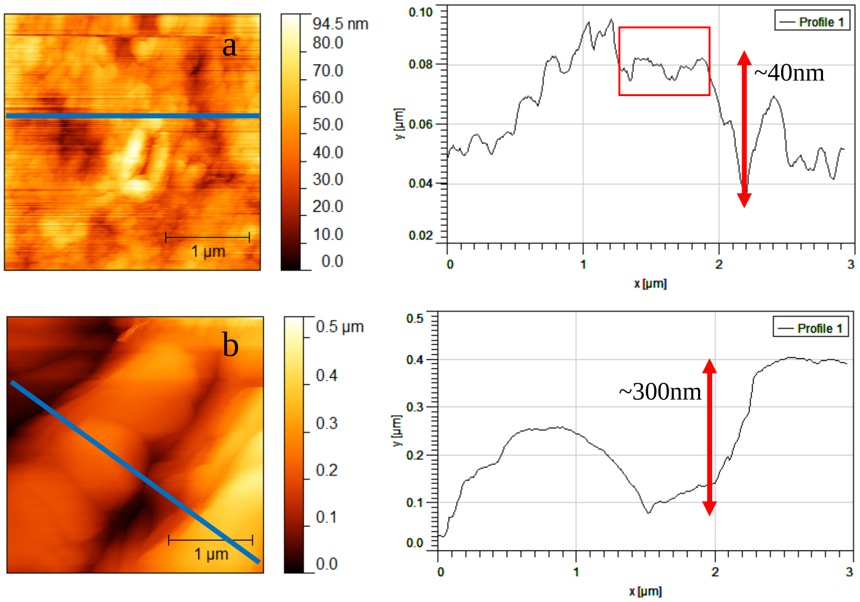


Fig. 5. AFM scans (T=600) and linear profiles of Titanium in electrolyte1(a) and electrolyte2(b)

The last image was taken at the end of the experiment, after one hour of applying voltage. The topographic image shows a uniform surface on the electrode. Extracted linear profile shows the formation of oxide layer and its partial dissolution. Again, small peaks appear indicating the presence of nanotubes on the surface. As expected, in the case of the organic electrolyte, the growth of the oxide layer continued, until it became uniform on the surface.

After topographic analysis, statistical data and electrochemical measurements, the mechanisms of formation of self-organized structures of titanium oxide could be proposed for the sample anodize in both electrolytes. (Fig.6)

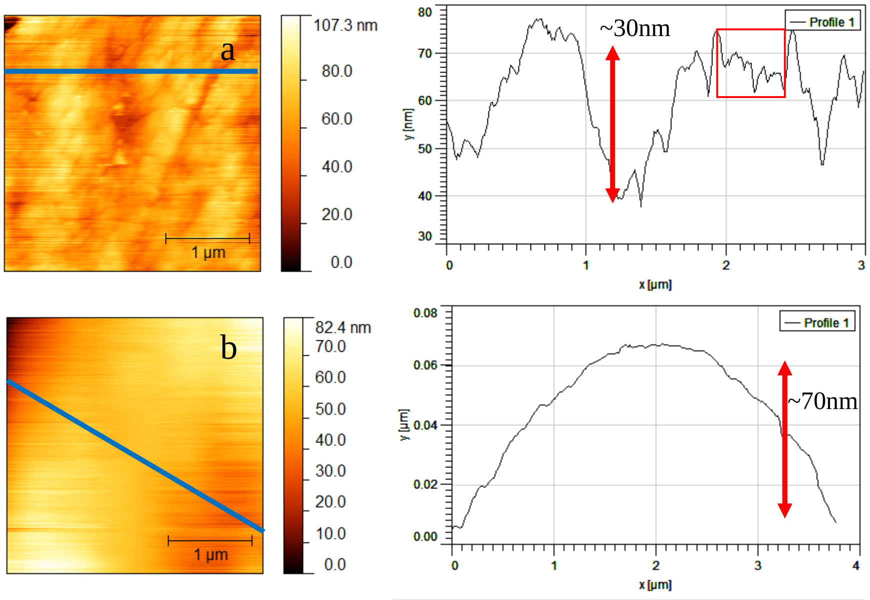


Fig. 6. AFM scans (T=3600) and linear profiles of Titanium in electrolyte1(a) and electrolyte2(b)

The first stage is identical for both electrolytes and contains only the formation of a natural layer of titanium oxide on the surface of both samples.

After 60 seconds, there is a full coverage of the surface with a compact oxide layer with granule size ranging between 100-200 nm for electrolyte1 and between 100-400 nm for electrolyte2.

At 120 seconds - second stage - the precursors of nanotubes start to form, the two processes begin to differ from one another, by the fact that dissolution occurs slower in electrolyte2, and less fluoride ions penetrate the surface because of the lower diffusion rate.

The third phase is very different between the two electrolytes: oxide formation and dissolution have almost the same rate in electrolyte1 after 600 seconds, fact which leads to the formation of nanotubes without oxide layer on top. In electrolyte2, because the dissolution rate is lower than the oxide formation rate, nanotubes are covered by the newly formed oxide layers. At 3600 seconds, the process continues for both electrolytes directions as observed. With electrolyte1 relatively oxide-free structures have been obtained, opposite with electrolyte2, which lead to a completely titanium oxide covered surface.

The calculated values for roughness in the two environments have led to very different values, but the evolution is similar in the two cases.

At the end of Stage I (T=60s), there is a decrease in roughness values as a result of the Titanium electrode being covered with oxide from 10.38 nm to 7.24 nm (electrolyte1) and from 77.58 nm to 23.0 nm (electrolyte2).

During the second stage, the roughness values have an increasing trend due to the partial dissolution of the surface oxide, but they do not reach the initial values.

In the third stage (T>600s) the evolution of roughness values have different trends for both electrolytes due to the different ratios of oxide forming and disolving.

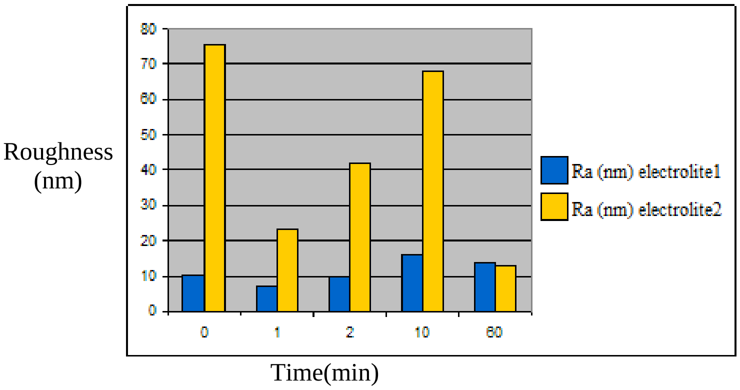


Fig.7. Roughness values (nm)/time (min) for Titanium electrode for the two electrolytes

The AFM provided insights during the process, and it was observed that the forming of nanotubes was affected by the nature of the electrolyte which could facilitate or hinder the migration of fluoride ions on the surface of the electrode.

Although the nanotube growth is not so well highlighted in the AFM images topography, the formation mechanism is still fairly well outlined in the linear profile of the surface.

However, for better investigation of the TiO_2 nanotube surface morphology the SEM analysis was performed for the two electrodes used in the above tests.

SEM analysis shows the presence of self organised tubular structures on both electrode surfaces (fig.8). As it was evident by the AFM analysis, the nanotubes formed in the aqueous electrolyte are not covered by a compact oxide layer. In contrast, the anodising performed in hybrid electrolyte led to the formation of the TiO_2 nanotube covered with a shielding layer.

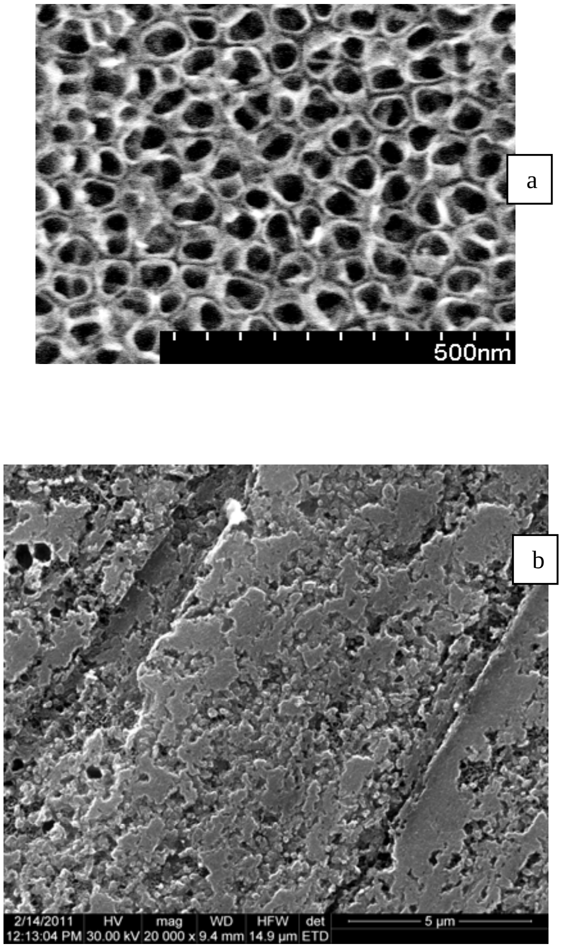
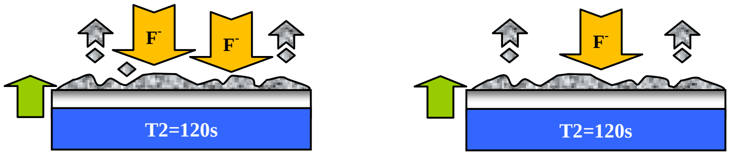


Fig 8. SEM images for titanium oxide structures formed in electrolite1(left) and in electrolite2 (right)

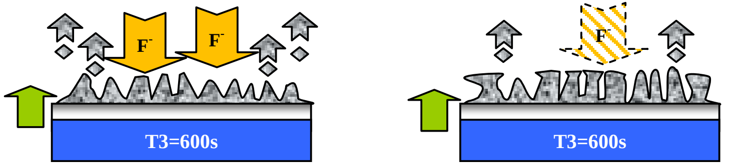
From the topographical analysis, statistical data and electrochemical measurements, a forming mechanism of self-organized titanium oxide structures could be sketched for the two electrolytes (Fig. 9). For the inorganic electrolyte, Titanium oxide formation speed is approximately equal to the dissolution speed induced by F^- ions, thus resulting a well-organized Titanium nanotube array. In the hybrid electrolyte however, the dissolution speed is much lower than in the previous case, leading thus to the formation of covered nanotubes.

Polished surface: only traces of TiO_2 are present

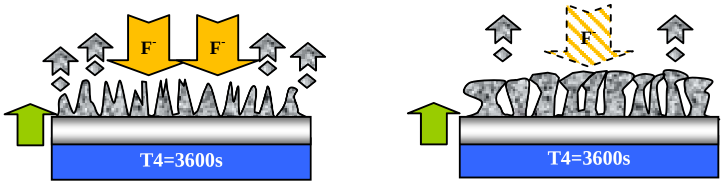
First stage: a compact TiO_2 layer covers the surface



Second stage: TiO_2 continues to form on the surface; TiO_2 nanotube precursors appear; TiO_2 dissolution speeds are different for the two electrolytes



Third stage: TiO_2 nanotubes start to form; the TiO_2 dissolution speed is close to the TiO_2 forming speed in electrolyte1 and much slower in electrolyte2



The processes continue leading to the formation of mostly uncovered nanotubes in electrolyte1 and covered nanotubes in electrolyte2

Fig. 9. Mechanisms for TiO_2 structure formation in electrolyte1 (left) and electrolyte2 (right)

4. Conclusions

Titanium oxide nanotubes have been successfully growth and analyzed with the EC-AFM.

The TiO_2 nanotube synthesis is very different between the two electrolytes, the anodization in electrolyte 1 leads to the formation of nanotubes without oxide layer on top and anodization in electrolyte 2 leads to the formation of nanotubes which are covered by the new formed oxide layers.

The AFM provided further insights during the process, and it was observed that the formation of nanotubes was affected by the nature of the solution, which could facilitate or hinder the migration of fluoride ions on the surface of the electrode. A growth mechanism of self-organized titanium oxide structures for the two different electrolytes was proposed.

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