Bottom-up nanofabrication using self-organized porous templates

A. Apolinário*, P. Quitério*, C.T. Sousa, M. P. Proença, J. Azevedo, M. Susano, S. Moraes, P. Lopes, J. Ventura and J.P. Araújo
IFIMUP-IN, Departamento de Física e Astronomia, Faculdade de Ciências, Universidade do Porto, 4169-007 Porto, Portugal
* These authors have contributed equally.
E-mail: jearaujo@fc.up.pt

Abstract. The great advances in nanoscience and nanotechnology in the last decade have led to the development of new platforms where all physical properties such as size, porosity, geometry and surface can be controlled at the nanoscale. Self-organized nanostructuring using template synthesis is a very promising and rapidly expanding field for the preparation of many different ordered structures ranging from the micrometer to the nanometer size. Porous aluminium, titanium, iron or hafnium oxide templates demonstrated real potential as well-controlled self-organized nanostructured materials for various applications. They are also an elegant tool to fabricate two- or three-dimensional arrays of periodic nanostructures. This work presents detailed methods to implement and fabricate nanoporous templates by anodic oxidation of Al and Ti metal substrates (that can be further used for Fe or Hf anodization). The characterization of nanowires grown in the pores of the synthesized Al₂O₃ and TiO₂ templates is also discussed.

1. Introduction
Precise control of the physical and chemical properties of materials at the nanometer scale is a central issue of current nanotechnology research. For practical nanoscience and nanotechnology applications, nanostructures with one, two, or three-dimensional architectures must be synthesized with controlled shape and size. In fact, since a broad range of material’s properties depend critically on the chemical composition, size, shape and regularity at the sub-nanometer scale, it is of increasing importance to develop structurally and dimensionally well-defined nanomaterials [1-4].

Basically, there are two nanofabrication approaches to create materials with the desired structural, mechanical, optical, magnetic and/or electronic properties: the top-down and the bottom-up. In the former one, large structures are machined in an attempt to build practical devices at the nanoscale [1]. Such nanostructures are produced from a bulk material or a continuous sheet-film with subsequent milling or lithography of the desired pattern [5-7]. Recent advances in various lithographic techniques, such as X-ray, ion-beam or electron-beam [1, 8,9], have provided access to the sub-100 nm size scale. However, these techniques have a crucial disadvantage: they are expensive, requiring state-of-the-art facilities and time consuming processes for the production of nanostructures on large scales.

On the other hand, the bottom-up approach starts with individual sub-nm or nm-sized building units such as atoms, molecules, polymers and colloids and assembles them, in a controlled way, creating the desired nanostructured materials. In the last two decades, a wide variety of techniques have been developed to control the size, shape, and crystalline structure of nanoparticles, including co-
precipitation in solution [10], chemical vapour deposition [11], sol-gel process [12] and electrochemical deposition [13]. The chemical reactions involved in these growth techniques can be performed in confined nanoreactors, where the nucleation and growth processes occur inside small spaces, such as micelles [14] or porous templates [15], increasing the nanoparticles homogeneity and organization. The bottom-up growth process from small molecules to big particles involves several steps. All processes start with the nucleation stage, which takes place in a very short period of time. Nuclei activation can be achieved after supersaturation of the reagents or with temperature or external electric field application. Subsequent growth needs to be diffusion-controlled, which is achieved with the efficient domain of all experimental parameters. These techniques often result in nanomaterials with a broad size distribution and limited control of the nanoparticles shape. Nevertheless, the exhaustive research in this field showed that nanomaterials obtained using the bottom-up approach have promising applications in a diversified set of fields as a result of their ability to form organized one-, two- and three-dimensional periodic nanostructures.

Among the various methods used for the fabrication of nanostructures using a bottom-up approach, template assisted fabrication is a practical physical-chemical method and a reliable alternative to top-down techniques [16-18]. In this methodology, a membrane with micro or nanometer pores acts as template for subsequent material deposition, adopting its shape. Several natural and synthetic materials with pores or voids in the micro- or nanoscale have been used as templates, from which Al₂O₃ and TiO₂ templates are excellent examples [19, 20].

![Figure 1. Three dimensional (3D), two-dimensional (2D) and one-dimensional (1D) structures.](image)

Self-assembled templates, depending on their architecture, are typically classified taking into account the dimensionality of the resulting template structure: three-, two- and one-dimensional, as illustrated in Fig. 1. Three-dimensional templates include micelles, zeolites, glasses and block copolymers [17]. Two-dimensional templates are layered materials [21] being some minerals as the Langmuir-Blodgett films and ionic polymer multilayer, the most representative examples. One-dimensional templates are typically membranes with one-dimensional pores running through the sizeable thickness of the membrane. One of the most used one-dimensional template is the porous anodic oxide of metals like Al, Ti, Fe and Hf [15, 22-24]. When grown under appropriated conditions, cylindrical pores are formed perpendicularly to the surface of the membrane. The pores resulting from the electrochemical anodization of these metals present highly monodispersed pore diameters varying from 10 to 350 nm depending on the applied voltage. Obtainable pore density ranges from 10⁹ to 10¹² pores/cm² whereas porosity varies in the range of 3 - 70%. By carefully adjusting the anodization conditions, these templates can also present a highly ordered hexagonal array of pores.

Furthermore, it is possible to manipulate the templates as to grow different nanostructures inside their pores. Figure 2 illustrates some of the possible fabrication steps proposed for porous anodic alumina (PAA) templates, which can also be used for other metal oxides. Several post-treatments can be employed after PAA fabrication in order to change the pore dimensions and architecture, such as pore widening (with chemical etching), barrier layer removal, branched pores or dendrites formation (Fig. 2). Afterwards, several types of nanostructures, such as nanotubes, nanowires, dots and anti-dots,
can be grown inside (or at the surface) of PAA templates using for example electrodeposition, sol-gel or sputtering techniques, as also illustrated in Fig. 2. Such wide diversity of applications of the PAA membranes, as templates or replication masters, provides flexible and realistic opportunities to create well-defined nanostructured materials.

Figure 2. Processing steps in the PAA manipulation and fabrication of arrays composed of high aspect ratio nanoparticles.

2. Experimental

2.1 Anodization of Al and Ti

Both porous anodic alumina (PAA) and porous anodic titania (PAT) films were grown under regulated anodic bias using a Pt mesh as cathode. The anodization potentials ($V$), electrolyte concentration ($C$), anodization temperature ($T$), pore diameter ($D_p$), interpore distance ($D_{int}$), porosity ($P$) and anodization rates ($AR$) are displayed in Table 1.

| Electrolyte                  | $C$ (M) | $V$ (V) | $T$ ($°C$) | $D_p$ (nm) | $D_{int}$ (nm) | $P$ (%) | $AR$ ($\mu$m/h) |
|------------------------------|---------|---------|------------|------------|----------------|---------|-----------------|
| H$_2$SO$_4$ (aq)             | 0.3     | 25      | 2          | 20         | 65             | 10      | 2              |
| C$_2$O$_4$H$_2$ (aq)         | 0.3     | 40      | 4          | 35         | 105            | 10      | 2.5             |
| H$_3$PO$_4$ (aq)             | 0.1     | 195     | 1          | 200        | 500            | 9       | 2              |
| Ethyleneglycol +NH$_4$F (0.3 wt%) + H$_2$O (2 wt%) | 60 | 21 | 37 | 160 | 5 | 7.9 (3 hours) |
| Ethyleneglycol +NH$_4$F (0.3 wt%) + H$_2$O (2 wt%) | 60 | 21 | 38 | 160 | 5 | 4.1 (17 hours) |

A typical electrochemical cell used in the anodization process is depicted in Fig. 3. The anodization cell consists of a teflon container with a hole at the bottom, where the metal substrate is placed (working electrode), and a Pt mesh inserted on top of the teflon cell (counter electrode). The anodization was conducted under constant potential and the current monitored as a function of time using a digital source meter (Keithley 2400C) controlled by a home-developed LabVIEW program.
During the anodization, the temperature of the electrolyte solution was maintained constant using a copper cooling plate. The electrolyte was gently stirred at 200 rpm in the case of the PAA and 75 rpm for PAT.

In order to fabricate PAA templates with ordered nanopore arrays, in which the holes are straight and regularly arranged throughout the oxide film, a two-step anodization process, similar to that reported by Masuda et al., was employed [15]. During the first anodization process, the hexagonally ordered pores were formed only at the bottom layer by a self-organization process. Subsequently, a chemical dissolution of the resulting PAA was achieved by submerging the sample in an aqueous solution of H$_3$PO$_4$ (0.4 M) and H$_2$Cr$_2$O$_7$ (0.2 M) at 70 ºC for about 12 hours. The resulting periodic concave patterns on the Al substrate act as pore nucleation centers for the second anodization process. An ordered nanopore array is then obtained after anodizing for the second time under the same parameters as in the first step. In the case of the PAT, a two-step anodization process can also be employed to improve the structural order of the pore arrays [25, 26]. However, we developed a simple and efficient method to induce a high degree of organization in PATs using an electropolishing pretreatment of the Ti foil [26]. Before starting the anodization, the Ti foils were electropolished in a H$_2$SO$_4$/HF (8:3) solution, with an applied potential of 10 V between the Ti foil and an inert Pt mesh (distance 2.5 cm) for 4 min; the solution was mechanically stirred (300 rpm) and kept at room temperature.

![Figure 3. Home-made anodization cell.](image)

2.2 Electrodeposition in PAA and PAT pores

To electrodeposit inside PAA templates, the alumina barrier-layer present at the bottom of each nanopore (intrinsic to the anodization process; Fig. 2) needs to be removed or reduced [27]. To perform DC potentiostatic electrodeposition, the barrier-layer is totally removed in a chemical bath of 0.5 M H$_3$PO$_4$ at 21 ºC for 2 h (after chemically etching the Al substrate in an aqueous solution of 0.2 M CuCl$_2$ and 4.1 M HCl at room temperature). Finally, a layer of 100 nm of Au was sputtered on the bottom side of the open through porous membrane to serve as the working electrode (WE).

In order to use a pulsed electrodeposition method (PED) in PAA, the alumina barrier layer was thinned down to enable electrodeposition using the Al substrate as the cathode. To this end, the voltage was exponentially decreased from the second anodization potential until a final anodization potential corresponding to the desired thickness of the barrier layer is reached. In this method the applied potential was stepwise reduced to avoid discrete constant voltage drops, according to:

$$V_f = V_{anod} e^{-\eta}$$

where $\eta$ was phenomenologically determined and depends on the acid solutions used [28]. The pulses of $V_{anod}$ last only for a pre-defined amount of time, also depending on the used acid. This restrain prevents the anodization current density [$j(t)$] to reach 90% of the corresponding stable value, where $V_{anod}$ is again reduced and a new non-steady-state anodization step occurs.
In this work, Ni nanowires (NWs) were deposited in PAA and PAT pores using two different electrodeposition techniques: potentiostatic DC and pulsed electrodeposition. In both cases the depositions were performed in the so-called Watts bath [29], consisting of a mixture of 1.14 M NiSO$_4$·6H$_2$O, 0.19 M NiCl$_2$·6H$_2$O and 0.73 M H$_3$BO$_3$. During the electrodeposition, the solution was magnetically stirred at 250 rpm and kept at a constant temperature of 35 ºC with a pH ranging between 4 and 5.

**Potentiostatic DC electrodeposition:** A three-electrode cell was used, where the porous membranes serve as the WE, a Pt mesh was used as counter electrode (CE) and Ag/AgCl (in 4 M KCl) as reference electrode (0.197 V vs. standard hydrogen electrode – SHE). To deposit Ni nanowires, the electrodeposition potential of -1.5 V vs Ag/AgCl was optimized in a previous work [30].

**Pulsed electrodeposition:** To electrodeposit, a two-electrode cell was used. In this case the Al substrate acts as cathode and a Pt mesh as counter electrode. The PED was carried out by applying a modulated signal constituted by three consecutive pulses in the millisecond range supplied by a Source Metter Keithley 2400[27]. First, a pulse of 70 mA cm$^{-2}$ is applied during 8 ms to deposit the material, followed by a second one with opposite polarity to discharge the insulator barrier layer capacitance in 1 ms at 8 V (corresponding to the final applied potential in the dendrite formation process[31]), and finally a delay time of 0.7 s.

3. Results and discussion

3.1 **Influence of the electrochemical conditions on PAA and PAT formation**

The most important parameters that affect the anodic oxidation of Al and the oxide film properties are the applied voltage or current, pH, type/concentration of the electrolyte and temperature. Both types of Al oxide, barrier-type and porous-type, can be obtained at constant potential or current[32]. The shapes of the current and potential-time transient curves are well established and can give insightsof the growth process and its kinetics [32]. The thickness of the barrier-type alumina is mainly determined by the applied voltage, although there is a small dependence on the electrolyte and temperature [33]. The anodizing ratio, which is defined as oxide thickness formed per volt, demonstrates that the barrier-type films are also strongly influenced by the type of metal which is anodized. The maximum attainable thickness of the barrier-type alumina was reported to be less than 1µm, corresponding to voltages lower than 500 V, since above this value the breakdown of the barrier was observed [32].

For the PAT formation, also several anodization parameters, such as electrolyte type and concentration, pH, temperature and applied potential, influence the template structure and geometry: interpore distance, diameter, wall thickness, length, quality and organization [34-36]. In the case of PAT templates, the thickness of the oxide barrier layer, diameter and interpore distance depends linearly on the applied voltage [25, 26]. But differently from the Al case, the anodizing ratio is not constant, being strongly influenced by additional chemical dissolution processes during the anodization, resulting in a limitedPAT thickness[35, 37]. Thus, the maximum attainable PAT thickness was reported to be hundreds of microns (220 µm in 17h), obtained in fluoride and ethylene glycol-based electrolyte that has, for that reason, become the main choice for the growth of long and ordered arrays of PAT with TiO$_2$ nanotubes (NTs) [34, 35].

The porous-type oxide growth can be divided in several stages (Fig. 4) that are easily identified by monitoring the current transients during the anodization process (for anodizations at constant potential) [32] or that can be directly observed by high-resolution electron microscopy [38].

For both PAA and PAT cases, immediately after switching-on the anodic potential a barrier oxide layer starts to grow (stage 1). Relatively fine-featured pathways are then revealed in the outer regions of the barrier oxide prior to any true pore formation (stage 2). Further anodizing results in the propagation of individual paths through the barrier oxide with their heads becoming enlarged (stage 3). Finally, a steady-state pore structure is formed by cylindrical cells, each containing a pore at the center and separated from the valve metal by a layer of scalloped hemispherical barrier oxide (stage 4).
Figure 4. Current density vs time behavior during PAA and PAT formation and schematic diagram of porous structure growth.

The PAT growth mechanisms, evaluated from the current density transient curves, present the typical behaviour when compared to the PAA formation. However, at stage 4, the oxidation/dissolution processes are not quite in equilibrium, where the oxidation is seen to be stronger than the dissolution, leading to a slow decay of $j(t)$ during the Ti anodization (differently from the constant $j(t)$ for the PAA case). This is due to the progressively failure of $\text{F}^-$ ions from the electrolyte, at the NT bottoms, which are difficult to replace by new ones giving the high viscosity of the electrolyte and increasing length of the pores (diffusion limited process). Consequently, the oxidation process is faster than the dissolution ($j$ slowly decrease with time), leading to an increase of the oxide barrier layer thickness $\delta_b$ at the NTs’ bottom. This significantly extends the ionic diffusion paths along the oxide barrier[39], thus inhibiting the transport of $\text{F}^-$, $\text{Ti}^{4+}$ and $\text{O}_2^-$ ions across $\delta_b$ which subsequently limits the PAT growth. The result is a typical PAT non-steady-state anodization equilibrium between oxide formation and dissolution rate and a deceleration of the template growth [40, 41].

3.2 Nanoporous structures of PAA and PAT
Regarding the PAA structure, based on the SEM analysis, a direct dependence is observed between the applied voltage and the pore diameter ($D_p$), interpore distance ($D_{int}$) and barrier layer thickness ($\delta_b$), with a relationship of 0.85 nm/V, 1.29 nm/V and 2.77 nm/V, respectively[42], although these values depend on the pH, temperature and electrolyte used. Recently it was showed that the porosity also depends on the applied potential. Careful measurements and simulations showed a decrease in porosity with voltage, which implies a weaker dependence of the pore diameter on the applied voltage[25, 43]. Only at high voltages and in a self-ordered regime, was the porosity found independent of the applied voltage[25, 44]. The content of incorporated anionic impurities also increases with increasing voltage, as the driving force for anion adsorption and transport in the oxide increases[38].
Concerning the PAT pore morphology, one also observes the linear dependence between potential and $D_p$, $D_{int}$ and $\delta_b$, with respective proportionality constants of 0.50 nm/V, 2.41 nm/V and 1.21 nm/V. Our $D_p(V)$ and $D_{int}(V)$ values are similar to those reported in the literature\[41\]. However, the constant for the barrier layer differs from the one reported (2.2 nm/V)\[45\], since we used a different organic electrolyte composition, which confirms the dependence of these values on electrolyte composition. Similarly to the PAA templates, the porosity of PAT was also found to decrease with the applied voltage\[41, 46\].

Figure 5. Surface SEM images of PAA grown at 40 V (left), at 195 V (middle) and cross section view of the PAA template grown at 195 V (right).

Figure 6. SEM images of PAT: top-view, grown at 50 V (left, top); bottom-view, grown at 60 V (right, top); cross section view of NTs template, grown at 60 V (left, bottom); and STEM image of a single nanotube, grown at 60 V (right, bottom).
3.3 Template-assisted growth of Nanowires using PAA

The growth of nickel nanowires inside the PAA pores was performed using DC potentiostatic electrodeposition (Fig. 7; left) and PED (Fig. 7; right). The PAA oxide barrier layer reduction or removal and the electrodeposition processes were described in detailed in section 2.2. Cross-section SEM micrographs show a uniform deposition with an apparent almost complete filling of the pores independently of the electrodeposition method used. However, top-view images revealed that many pores were not completely filled. To overcome such non-total filling of the template, the top surface can be consecutively physically etched by ion milling.

The nanowires grown by the DC method present 50 nm in diameter which corresponds to the PAA pore diameter (Fig 6; left). To use the DC method one requires thick templates (>20 μm) that allow easy handling and are able to endure the exothermic Al removal and barrier layer removal processes. By optimizing the DC electrodeposition potential, nanowires with length larger than 100 μm can be grown in PAA templates [30].

On the other hand, nanowires grown by PED showed a dendritic structure at the bottom (Fig 6; right) due to the tree-like nanopores created during the non-steady-state anodization method used to reduce the bottom of the barrier layer[47]. The PED nanowires also show the original diameter of the PAA pores of 35 nm. In this case one can usually only grow nanowires with lengths up to 20 μm due to the high potentials used which leads to hydrogen evolution. Nevertheless, careful tuning of the PED parameters can lead to high pore filling percentages in thicker templates [20].

![Figure 6. Cross-section SEM images of nickel nanowires grown by DC mode (left) and PED methods (right).](image)

3.4 Template-assisted growth of Nanowires using PAT

For the deposition of materials inside PAT templates, we used the DC electrodeposition technique. Nanotubes bottoms were previously opened, using the step increase potential. Previously to the anodization, we performed a chemical etching pre-treatment on the Ti foil in aqueous solution of HF (4%) during 15 minutes. A TiO₂ NTs free standing membrane was produced by anodizing at 60 V for 17 hours, immediately followed by prolongation of the anodization at 150 V for 5 minutes to open the NTs bottoms[48]. The use of a large increase of the applied potential at the end of the anodization process, drastically and suddenly increases the NTs diameter at the bottom, resulting in a weaker point for breaking and separate the NTs from the Ti foil. This results in free standing NT membranes with open bottoms [48].

The free-standing membrane with open bottoms was sputtered with gold (to act as an electrical contact for the metal electrodeposition). Finally, Ni was electrodeposited inside TiO₂ NTs, using the potentiostatic mode under a potential of -1.5 V vs Ag/AgCl. Figure 7 shows the 10 μm long Ni NWs electrodeposited inside TiO₂ NTs (formed mainly in the middle length region of the NTs). This unusual and non-uniform Ni deposition along the NTs might be related with the semiconducting properties of TiO₂ and with the fragile nature of the NTs membranes. Additionally, the presence of a double-layer between NTs makes them easily separable from each other[25], which may influence the
efficiency of the metal deposition. Compared with PAA, the process of PAT electrodeposition showed lower efficiency, indicating that it requires further optimization.

![Figure 7. SEM images of PAT with open bottoms (left), cross section view of template after electrodeposition (middle) and electrodeposited nickel inside nanotubes (right).](image)

4. Conclusions
This work was devoted to the detailed description of the design and implementation of a home-made anodization and electrodeposition set-up to fabricate nanoporous oxide templates and ordered arrays of nanowires. Porous anodic templates of aluminium and titanium were synthetized and morphologically characterized. We have also compared the results obtained for nanowires grown in PAA by DC potentiostatic electrodeposition and PED, which present similar morphological properties. The electrodeposition in the PAT nanotubes was also demonstrated using the DC electrodeposition in free-standing PAT membranes with open bottoms. All the fabricated nanostructures have potential applications in a large range of fields from solar cells to biotechnological applications.

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