

Fabrication and Characterization of Metal and Metal Oxide Nanostructures Grown by Metal Displacement Deposition into Anodic Alumina Membranes

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Displacement deposition reactions were used to fabricate metal and metal oxide nanostructures inside the channels of alumina template. This type of template synthesis is based on the galvanic contact between a sputtered metal film, covering the bottom of the template, and a less noble metal, partially exposed to the solution. The deposition can be carried out at room temperature without using energy or specific equipments. Consequently, the present route for the preparation of nanostructures is cheap and simple, and it can also be applied to the synthesis of a wide range of different materials.

1. Introduction

Nanostructured materials are usually named those having at least one dimension of the order of nanometers. The nanoscale dimension induces properties different from those of bulk materials (Kelsall et al., 2005), and this makes use of such nanostructures highly attractive for several technological applications. Among nanostructured materials, one-dimensional ones, like nanowires (NWs) and nanotubes (NTs), are of particular interest. This kind of materials can be fabricated using different techniques. Among these, synthesis within nanoporous membranes is particularly simple and flexible (Martin, 1996). In fact, this technique allows producing one-dimensional nanostructures with different aspect ratios and different shapes (Inguanta et al., 2009a). In this context, anodic alumina membrane (AAM) is considered an almost ideal "template" for the synthesis of nanostructured materials, to be used in various applications such as optoelectronics, magnetic sensors and electronic circuits (Shingubara, 2003). In addition, the interest in anodic alumina membranes is also due to the simplicity of their fabrication process. In fact, they can be obtained by anodizing aluminum in appropriate acidic baths, and this leads to the formation of nanoporous honeycomb structures, whose morphological parameters (membrane thickness, pore diameter and density) can be easily controlled by adjusting the anodization parameters (anodization voltage and time, bath temperature and composition) (Inguanta et al., 2007a). For these reasons, a variety of nanostructures (metals, alloys, semiconductors, oxides and polymers) with different morphologies (tubules, fibers or wires, rods) have been fabricated using AAM as template. The most common techniques used for synthesis are the sol-gel process (Zhang et Chen, 2005), the microwave plasma chemical vapor deposition (Chen et al.,

2007), the electrodeposition and the electroless deposition (Inguanta et al., 2007a, 2007b, 2010). A drawback common to these techniques is that their implementation requires use of expensive reagents and equipment: as an example, electroplating needs an external power source. By contrast, electroless deposition does not require electrical energy, but it needs use of specific reagents that lead to deposition of metal nanostructures. Therefore, this process presents particular drawbacks: cost of reagents (chelating agent, bath stabilizers, buffers for pH control), long deposition times (steps for cleaning and activation of the substrate), control of the kinetic of reaction. Besides, in the case of deposition inside membrane pores, it is essential to avoid that reduction occurs in the bulk of the solution, which should lead to the formation of a thick deposit layer onto the external surface of the membrane, blocking pore mouth and thus preventing NWs formation. In addition, metal deposits obtained by electroless deposition display in many cases low purity, because they contain foreign species deriving from the deposition bath. In this work, we present the fabrication of nanostructures of metal (Inguanta et al., 2008, 2009b) and metal oxide, by a novel technique, based on the cementation reaction of metal ions in solution (Inguanta et al., 2007c) using a sacrificial anode as a reducing agent. The purpose of this study is to verify the potential of this technique for the fabrication of nanostructured materials with high purity, using alumina membrane templates and an appropriate precursor salt solution.

2. Experimental Details

The active metals used as sacrificial anode for the cementation process were aluminum (foil, thickness: 1.5 mm, purity: 99.99%) and zinc (foil, thickness: 2 mm, purity: 99.99%). These two metals were chosen because they have very low standard potential (-1.66 and -0.76 V/NHE, for aluminum and zinc respectively). Commercial anodic alumina membranes (Whatman, Anodisc 47) were used as template, having a mean pore diameter of about 210 nm, nominal thickness of 60 μm , porosity of about 28% and pore surface density of 10^{13} pores/ m^2 . The cementation solutions were prepared using deionised water and high purity chemical reagents. In table 1 the composition of cementation solutions used for the fabrication of metal and metal oxide nanostructures are reported. In order to investigate the kinetics of the metal deposition process, samples with different ratios of anodic to cathodic area were prepared. Moreover, cementations were performed for different immersion times. Chemical composition and morphology of nanostructures were investigated by SEM, EDS, XRD and RAMAN spectroscopy. These characterization methods are detailed elsewhere (Inguanta et al., 2007b, 2010).

Table 1: Cementation solutions

Deposit	Solution
Cu	$\text{CuSO}_4 + \text{H}_3\text{BO}_3$
Pd	$\text{Pd}(\text{NH}_3)_4(\text{NO}_3)_2 + \text{H}_3\text{BO}_3$
$\text{Mn}(\text{OH})_x/\text{MnO}_x$	$\text{Mn}(\text{NO}_3)_3$ (Mn = Co, Ni, Pb, Zn)
$\text{Ln}(\text{OH})_3/\text{Ln}_x\text{O}_y$	$\text{Ln}(\text{NO}_3)_3$ (Ln = La, Ce, Sm, Er)

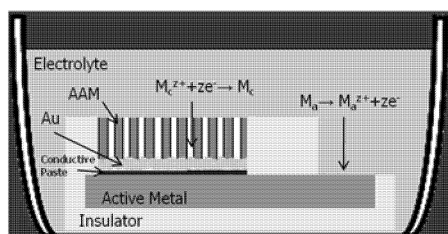


Figure 1: Schematic representation of the galvanic cell appropriately designed for the fabrication of nanostructured materials inside the channels of an alumina template.

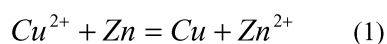
3. Results and Discussion

The galvanic deposition process allows obtain high-purity nanostructures in a rapid and inexpensive way. The procedure is based on a galvanic deposition reaction (cementation), which produces the desired nanostructures inside the pores of the AAM template. In particular, one membrane external surface is covered with gold and coupled electrically to a less noble metal (M_a).

After immersion of the bimetallic couple into an electrolytic solution, containing metal ions to be deposited (M_c), a micro-battery is formed, where gold acts as cathode and the less noble metal as anode. In this last area the anodic reaction (less noble metal dissolution) occurs, while on the cathode surface the cathodic reactions (ions reduction and eventual concurrent reactions, like hydrogen evolution) happen. A scheme of the cell is shown in Figure 1. One advantage of this configuration is the possibility to vary the ratio between anode and cathode surface to control the current ratio. The peculiarity of this method is that the electromotive force for the deposition process must not be supplied from an external source. Besides, we will show that this method is very flexible because can be used for both deposition of metal and metal oxide nanostructures with different shapes (NWs and NTs).

3.1 Cementation of metal nanostructures

In the case of metal cementation, the metal M_a is oxidized and passes into the solution providing electrons for the reaction of M_c deposition (reduction), as shown in Figure 1. The overall reaction for the deposition of copper NWs by displacement of Zn is:



After one week of cementation, this reaction leads to a complete pore filling and to the growth of an external metal layer of about 100 μm .

In all deposition conditions, morphology of Cu NWs was similar the FEG-SEM image of Fig. 2(a): NWs are straight with a cylindrical shape; their uniform diameter (about 210 nm) is almost equal to the size of the AAM channels. The template dissolution does not alter the alignment between NWs, which are firmly hammered in the thin gold layer. The presence of some broken NWs is due to sample preparation before FEG-SEM analysis. Since the Cu deposition occurred in all pores, NWs surface density was equal to pore population of the AAM, i.e. of the order of 10^{13} wires m^{-2} .

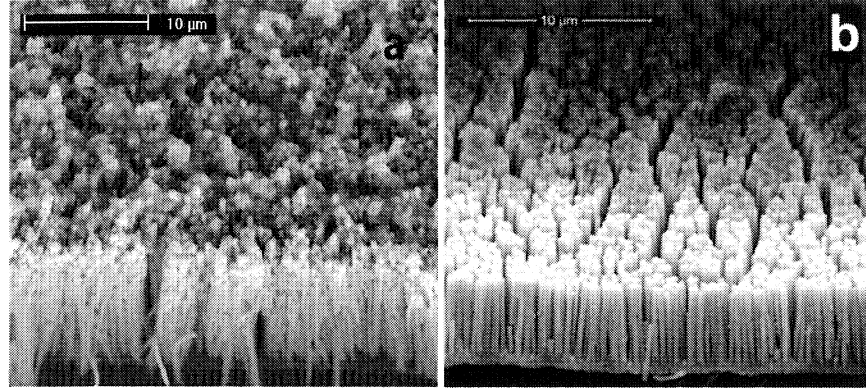
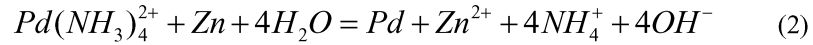


Figure 2: SEM images, taken after dissolution of the AAM template, (a) of copper nanowires obtained by displacement deposition reaction and (b) of palladium nanowires obtained by displacement deposition reaction

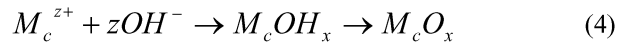
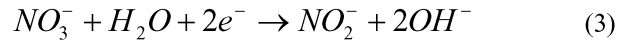
EDS spectra showed that NWs consist of pure copper metal. This finding was confirmed by X-ray diffractograms revealing a polycrystalline structure of the deposited metal. Identification of peaks, which are relative to the cubic structure of copper, was performed by comparison with the ICDD data-base (card n. 4–836). Similar results were obtained in the case of fabrication of palladium NWs by displacement of Zn. In this case the overall reaction is:



Also in this case, NWs consist of pure and polycrystalline (ICDD card n. 46–1043) palladium metal. Figure 2(b) shows an array of Pd NWs obtained by this way: NWs are straight with a cylindrical shape. The diameter is uniform and almost equal to the size of the AAM channels and the contour is very smooth. NWs length varied with the cementation time from about 1.5 μm to 9 μm.

3.2 Cementation of metal oxide/hydroxide nanostructures

More recently, we have extended successfully the displacement deposition technique to the fabrication of large arrays of self-standing oxide nanostructures. To obtain a metal oxide/hydroxide by galvanic deposition, the metal salt contained in the electrolytic bath plays a key role. In fact, when a metal nitrate solution was used, reduction of the NO_3^- anion is able to guide the deposition reaction towards formation of oxide phases instead of metal ones. In particular, precipitation of oxide/hydroxide happens when the standard potential for NO_3^- reduction is higher than that of the corresponding metal phase. The reactions running at cathode surface are:



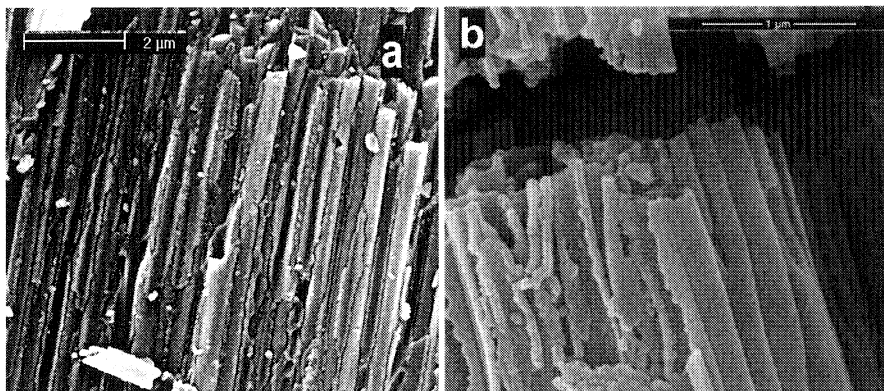


Figure 3: (a) SEM image $\text{ZnO}/\text{Zn}(\text{OH})_2$ nanowires inside the channels of AAM template obtained by displacement deposition; (b) SEM image, taken after dissolution of the AAM template, of $\text{CeO}_2/\text{Ce}(\text{OH})_3$ nanotubes obtained by displacement deposition.

When using the cell of Figure 1, these reactions lead to precipitation of oxide/hydroxide inside the channels of the alumina template. We have investigated the cementation process in nitrate solutions of Co, Ni, Zn, Pb and Ln (Ln= La, Ce, Sm, Er). Very short deposition times were necessary to grow large and ordered array of oxide nanostructures.

In these cases, XRD and Raman analyses showed that displacement reactions led to the growth of NTs and NWs of either amorphous or nanocrystalline oxides of different metals. In particular, oxides/hydroxides of Pb and Zn were obtained in form of NWs with the morphology shown in Figure 3(a), that is relative to $\text{ZnO}/\text{Zn}(\text{OH})_2$. The oxides/hydroxides of La and Sm presented a mixed morphology, consisting in both NWs and NTs, with predominance of NTs in the case of La. In the case of Co, Ni, Ce and Er, cementation reactions led to the formation of oxides/hydroxides with tubular shape (NTs), as shown in Figure 3(b), where a SEM image of $\text{CeO}_2/\text{Ce}(\text{OH})_3$ is reported. The formation of aligned NTs, having mean external diameter of 210 nm and a wall thickness equal to 70 nm, can be observed. Both the external diameter and the wall thickness were quite uniform along NTs length.

4. Conclusions

We have used displacement deposition reactions to fabricate metal and metal oxide nanostructures. The key advantage of this approach is to obtain nanostructured materials without using an external power source. It is sufficient to select a template and to build a bi-metallic contact to be immersed in an electrolytic solution containing the desired metal ions. It has been demonstrated that employing this technique it is possible to synthesize nanostructures with different shapes (nanowires and/or nanotubes) and aspect ratios (length/width).

5. References

- Chen M., Pan M., Hung I., Wu C. and Chen F., 2007, Amorphous carbon coated silicon nanotips fabricated by microwave plasma chemical vapor deposition using anodic aluminum oxide as the template, *J Electrochem. Soc.*, 154; D215-D219
- Inguanta R., Butera M., Sunseri C. and Piazza S., 2007a, Fabrication of metal nanostructures using anodic alumina membranes grown in phosphoric acid solution: Tailoring template morphology, *Appl. Surf. Sci.* 253, 5447-5456
- Inguanta R., Piazza S. and Sunseri C., 2007b, Template electrosynthesis of CeO₂ nanotubes, *Nanotechnology*, 18, 561-566.
- Inguanta R., Piazza S. and Sunseri C., 2007c, Metodo e apparato per la fabbricazione di nanowires metallici, Patent, I.P. VI2007A000275.
- Inguanta R., Piazza S. and Sunseri C., 2008, Novel procedure for the template synthesis of metal nanostructures, *Electrochem. Comm.*, 10, 506-509.
- Inguanta R., Ferrara G., Piazza S. and Sunseri C., 2009a, Nanostructures fabrication by template deposition into anodic alumina membranes, *Chem. Eng. Trans.* 17, 957-962.
- Inguanta R., Piazza S., and Sunseri C., 2009b, Synthesis of self-standing Pd nanowires via galvanic displacement deposition, *Electrochem. Comm.*, 11, 1385-1388.
- Inguanta R., Livreri P., Piazza S. and Sunseri C., 2010, Fabrication and photoelectrochemical behavior of ordered CIGS nanowire arrays for application in solar cells, *Electrochem. Solid State Lett.*, 13, K22-K25.
- Kelsall R. and Hamley I., 2005, *Nanoscale Science & Technology*. Wiley, Chichester.
- Martin C. R., 1996, Membrane-Based Synthesis of Nanomaterials, *Chem. Mater.*, 8, 1739-1746.
- Pauvonic M. and Schlesinger M., 2000, *Modern Electroplating*, Wiley, New York.
- Shingubara S., 2003, Fabrication of nanomaterials using porous alumina template, *J. Nanopart. Res.* 5, 17-30
- Zhang G. and Chen J., 2005, Synthesis and Application of La_{0.59}Ca_{0.41}CoO₃ Nanotubes, *J Electrochem. Soc.* 152, A2069-A2073