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Porous membranes for the preparation of magnetic nanostructures

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Abstract

This paper is a short review on the use of microporous membranes as templates for the preparation of nanomaterials using different synthetic approaches. Magnetic nanowires and multilayers have been synthesized by electrochemical deposition techniques. Hereby, we also report preliminary results to show the advantage of the chemical route as an alternative to template other nanostructures as for instance Co nanotubes.

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1. Introduction

Nowadays one of the most exciting areas in Materials Science is the study of nanomaterials due to their potential applications in fields as diverse as optics, electronics, catalysis, magnetism, electrochemistry, information processing and storage, etc. Preparation of inorganic, organic or organic–inorganic hybrid materials in the nanometer scale can be achieved either by physical or chemical methods and in many cases it requires the use of solids presenting voids or cavities in which the material can be synthesized [1]. Among the different preparation procedures, one of the most widespread is the *template method*, based on the use of the organized porosity of certain microporous membranes. C.R. Martin's group [2a–c] was pioneer in the use of this methodology and nowadays other teams are using it to prepare nanoparticles, nanotubes, nanofibrils and nanowires of different materials such as polymers, metal oxides, metals, etc.

Magnetic materials and other related structures have also been prepared at the nanoscale level using lithographic methods and template membranes [3]. Filling of pores of anodized Al with magnetic materials was firstly reported in 1975 [4] although the advantage of polymeric track-etch membranes for the preparation of arrays of magnetic nanowires was not reported till the 1990s [5]. Afterwards, the groups of Piraux [6] and Ansermet [7], and more recently others [8,9a,b,10a,b], have used track-etch and anodized Al_2O_3 membranes to prepare arrays of nanowires or multilayers of magnetic metals (Fe, Ni, Co…).

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This paper is organized starting with an introduction about membranes and methodologies to template nanomaterials including magnetic nanowires, then preliminary results are introduced on the use of the chemical route as an alternative approach to grow magnetic nanomaterials in membranes and finally some conclusions and prospects are included.

2. Membranes as templates of nanomaterials

Porous membranes are generally employed in filtration technologies for the separation of different species (polymers, colloids, molecules, salts, etc.), depending on their pore radii that may vary from μm to nm. Although they exhibit in general heterogeneous porosity, a few of them can be prepared with well-defined shape pores of a narrow distribution of diameters. Among these it is worth mentioning track-etch membranes and anodized Al_2O_3 membranes. Polycarbonate (PC) track-etch membranes (commercially available from Nucleopore, Poretics, Millipore) show cylindrical pores (Fig. 1a), mainly perpendicular to the membrane sheet although they could be tilted up to 34° (<5° in "home-made" membranes). Track-etch mica membranes present higher chemical and thermal stability with diamond-like cross-section pores (Fig. 1b). Anodic Al_2O_3 membranes are prepared by electrochemical oxidation of Al producing pores of asymmetric structure (Fig. 1c and d). Whatman (Anodisc) and Merck (Anotec) commercially sell anodic Al_2O_3 membranes but they are restricted to a very limited range of pore diameters. Consequently, many researchers prepare their own templates. Recently, the preparation of polycrystalline and monocrystalline pore arrays with large interpore distance in anodic Al_2O_3 has been reported [11]. Nanochannel glass templates (Corning) and porous silicon are two other types of porous membranes also used as templates for the synthesis of nanomaterials.

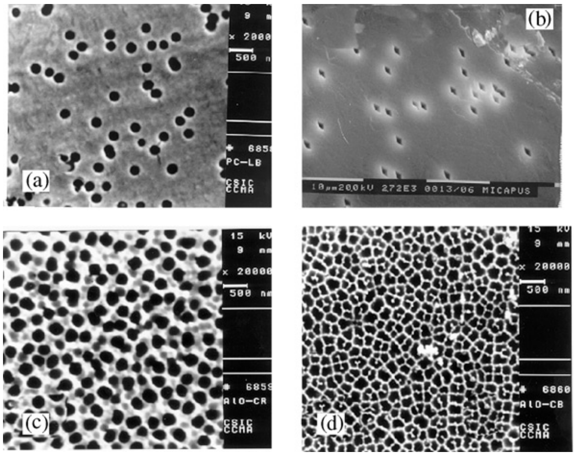

Fig. 1. SEM images of track-etch polycarbonate (a) and mica (b) membranes and both surfaces (c) and (d) of an anodized Al_2O_3 membrane.

The synthetic approaches used for the preparation of nanomaterials inside the pores of membranes are variable, due to the large variety of materials and leading purposes. Martin [2a–c] and more recently Hucko [12] have extensively reviewed the subject, and therefore we will just shortly refer to the most commonly employed methodologies. The strategy consists in finding out the right pathway leading to the wanted nanomaterial (nanorods, nanotubes, nanowires, nanocomposites, multilayers...) presented in a particular final form, i.e., as an ordered array with individual components more or less separated, single nanoparticles, etc. Strategies of synthesis must consider: (i) nature of precursors and affinity to interact with the pore wall (e.g., hydrophobic/hydrophilic character of solvents); (ii) characteristics of the deposition reaction (rate, sequence of steps, etc.) and (iii) chemical and thermal stability of the host membrane. The synthetic approaches can be summarized as follows:

- *Electrochemical deposition* is perhaps the most employed method and requires the coating of one face of the template with a metal film to act as cathode for electroplating. The volume of the pore is continuously filled from the pore bottom up allowing the control of the total length of wires or even the preparation of multilayers. A large variety of metal nanowires (Au, Ag, Ni, Co, Cu, etc.) have been prepared following this method although preparation of metal nanotubes requires previous modification, e.g., silanization of Al_2O_3 pore walls [2a–c]. Conducting polymers as polypyrrole (PPy), polyaniline (PANI), etc. have been electropolymerized using different templates resulting either nanofibers or nanotubes depending on factors like experimental conditions, polymer nature or template membrane [2a–c].

- *Chemical deposition* usually requires either a chemical reducing agent, to plate a metal from solution onto a surface, or a catalyst, which promotes the reaction of the reagents filling the pores. As the deposition starts at the pore wall, it is possible to obtain hollow tubes of selected inside diameter with length and outside diameter determined by the characteristics of the template membrane. Other methods to prepare metal arrays (e.g., Au) or more complicate structures as $LiMn_2O_4$ nanotubes have been reported [12]. In certain cases, it is also possible the incorporation of fluids or melts (In, Sn, Al, Se, Te, GaSb, Bi_2Te_3) by high-pressure injection [13].
- *Chemical polymerization* is accomplished by simply immersing the membrane into a solution containing the monomer and a polymerization reagent. The polymer growth starts on the pore walls allowing the preparation of either tubes or fibers. Conducting polymers as PPy, PANI, etc., showing enhanced conductivities have been prepared by this method. PPy nanotubes can be used for bioencapsulation of enzymes to prepare, for instance, biosensors of glucose [2a–c]. Insulating polymers as polyacrylonitrile can be grown into Al_2O_3 membranes and thermally transformed into carbon nanotubes and fibrils [2a–c]. Poly(methylmetacrylate) has been prepared inside the pores of Al_2O_3 membranes to produce a "negative" polymeric membrane by dissolution of the Al_2O_3 template. This "new template" can be then used for the synthesis of nanoporous structures of metals as Au or Pt [14].
- *Sol–gel deposition* is a relatively easy way to prepare metal oxides (TiO_2, ZnO, WO_3, V_2O_5, etc.) tubules and fibers [2a–c,12]. As the sol–gel method involves thermal treatments among other steps (hydrolysis of precursors, gel formation, etc.) only inorganic membranes such as Al_2O_3 templates can be used.
- Chemical vapor deposition (CVD) is a technique widely used for preparation of solid thin films, but barely applied to produce templated nanostructures because of its usually fast deposition rates. However, carbon nanotubes of variable wall thickness can be produced by CVD passing a gas (ethene or propene) through Al_2O_3 membranes placed inside a high-temperature furnace [15].

A large number of nanocomposites as metal multilayers, concentric-tubular nanostructures, etc. [2a–c,3,12,16] can be synthesized by combining properly the anterior strategies enlarging in this way the scope of applications of nanomaterials.

Anodized Al_2O_3 was the first porous structure used to grow magnetic nanostructures [4] although the limitations to reach complete filling of the pores determined the use of nanoporous Al_2O_3 sheets detached from the electrode, i.e., membranes. In this way, Al_2O_3, track-etch PC and mica membranes, and nanochannel glass templates have been employed to prepare a large variety of magnetic nanostructures as arrays of nanowires and multilayers [3–8,9a,b,10a,b,17,18]. PC track-etch membranes is the template most extensively employed, as they are easy to handle and exhibit relatively low porosity limiting magnetic interaction among individual wires, but defects (di-, tri-pores, surface roughness, tilting of pores…) could cause detriment in the searched properties. Mica track-etch membranes [9a,b] are fragile and show pores, i.e., nanowires, with a curious shape but its higher thermal stability allows the study of magnetic properties with temperature and nanowires modified by previous thermal treatments. Al_2O_3 membranes are also thermally stable and show better parallel alignment of perpendicular pores but their higher porosity and smaller interpore distance could introduce magnetic interaction among the nanowires. The general procedure to produce arrays of nanowires (Co, Ni, Fe, CoNi, NiFe…) is electrochemical deposition, which also allows production of multilayers (Co/Cu, Ni/Cu, etc.) [6,7,17]. Magnetic nanowires (Ni, Fe) have also been encapsulated on hollow nanotubes of conducting polymers (PPy, PANI) chemically prepared on PC or Al_2O_3 membranes [19a,b]. Structures such as carbon nanotubes [20], biomolecular entities [21] or mesoporous silica [22] have also been used to grow magnetic metal nanowires and nanotubes. These last approaches could be of interest as they introduce methods of synthesis that might be alternatives to electrodeposition for growing other type of nanostructres than nanowires.

3. Chemical preparation of Co nanostructures

As we have reported elsewhere [10a,b] electrochemical synthesis allows the preparation of Co nanowires (Fig. 2a) whose crystalline structure, cubic or hexagonal, depends on the nature of the membrane support, Al_2O_3 or PC templates, respectively. Despite these differences both types of arrays show similarities in the magnetic behavior. The easy direction is along the wire axis due to the strong shape anisotropy. The coercivity is minimum in such direction as a consequence of the dipolar interaction among the wires increasing for arrays templated on PC membranes because their interpore distance is greater (porosity: 25% for PC and 80% for Al_2O_3) [10a,b].

In a new approach we have used the chemical route to template Co nanostructures in Al_2O_3 (Anodisc™) and track-etch PC (Nucleopore™) membranes. As it is well known, certain organometallic complexes and coordination compounds are used to generate metal particles for catalytic purposes [23]. We have selected the $Co_2(CO)_8$ as precursor. This compound is very sensitive to moisture and thermally decomposes to Co ($<90^\circ C$) in an inert atmosphere [24]. Incorporation of the precursor inside the pores of the membrane is achieved by two procedures, working always in a dry box ($<0.2\,ppm$ H_2O, Ar atmosphere). The membranes are previously treated under dynamic vacuum for 24 h to remove adsorbed water. In the first procedure a membrane (e.g., Al_2O_3 200 nm pore diameter) is immersed ≈ 5 min in 10 ml of 5×10^{-2} M $Co_2(CO)_8$/n-hexane

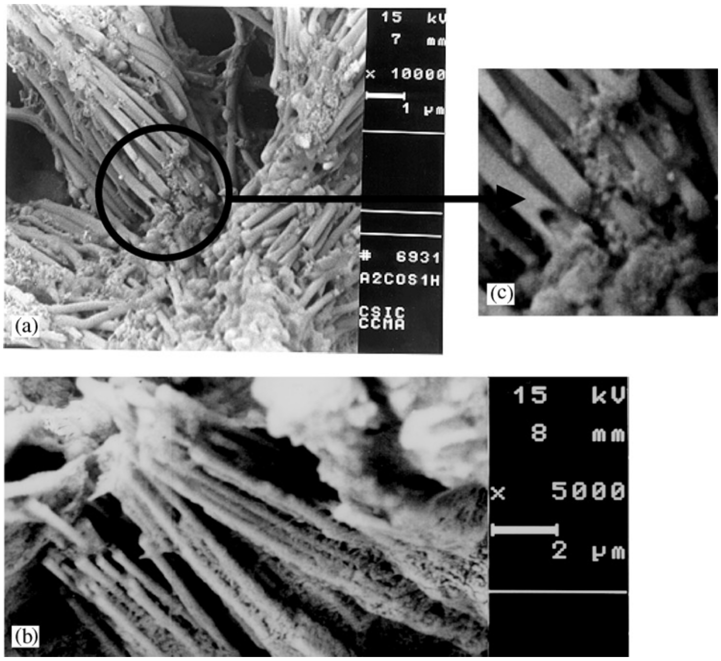

Fig. 2. SEM images of Co nanostructures templated in Al_2O_3 membranes by chemical (a) and electrochemical methods (b), detail of a hollow nanocylinder (c).

solution and then dried at room temperature. The process is repeated several times, typically 5, to increase the loading of the pores. The second procedure profits from the relatively high vapor pressure of the carbonyl complex to pass it through the pores using the experimental setup shown in Fig. 3. In both the cases the precursor is deposited inside the pores and the membrane turns brown-black. Once the membrane had the precursor incorporated, the system was alternatively left to evolve several days at room temperature or heated at 90°C to produce the formation of Co particles. The SEM study coupled with EDX microanalysis indicates the presence of Co inside the pores of the membrane. From the FTIR and DRX data we deduce that the amount of adsorbed compound must be very small, since we could not detect the precursor, metallic Co or cobalt oxide. After dissolution of the membrane the formation of Co hollow cylinders could be observed (Fig. 2a and c), in contrast to the nanowires resulting from electrochemical deposition (Fig. 2b). Magnetism of the arrays of Co nanotubes prepared by the two procedures, measured by means of VSM using a LDJ magnetometer, is undetectable. It could be that the strong interaction of Co particles with the Al_2O_3 substrate induces oxidation of the metal but the same behavior is showed by arrays prepared using PC membranes. Probably the method induces formation of very small particles of metal that oxidize when exposed to air during the magnetic measurements. Besides, we believe that the small amount of deposited Co might also be a reason of this lack of magnetic properties. The method of synthesis, including the use of other precursors in order to prepare nanocomposite structures, are currently being optimized.

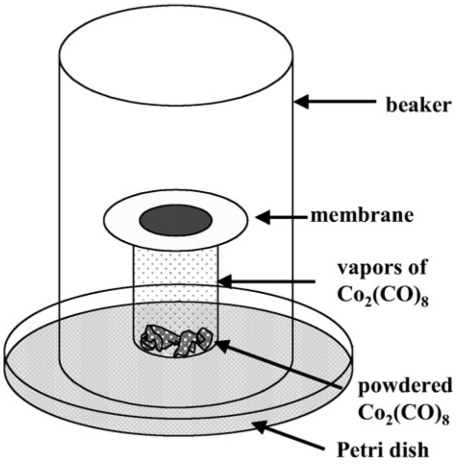

Fig. 3. Experimental setup for chemical growth of Co nanotubes inside microporous membranes.

4. Conclusions and perspectives

The versatility of the membrane template method allows the exploration of new routes to prepare new magnetic systems. In this way, we have showed that the chemical route is an alternative to electrochemical deposition to obtain Co nanotubes instead of nanowires. This new approach opens a way to the preparation of composite structures, as for instance ferromagnetic/non-magnetic nanotubes, with potential novel properties, although there are still experimental difficulties to obtain nanostructures with reproducible magnetic behavior.

Acknowledgements

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