

Membrane Techniques for the Preparation of Nanomaterials: Nanotubes, Nanowires and Nanoparticles – A Review

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ABSTRACT

The large interest in nanostructures results from their numerous potential applications in various areas such as biomedical sciences, composite materials, electronic, optic, magnetism, energy storage, and electrochemistry. The present review deals with the preparation of nanomaterials including nanotubes, nanowires and nanoparticles on the basis of two processes using membranes as shaping tools: the membrane template method and the membrane contactor. This report is focused on a description of the type of membranes and of the synthesis techniques which are used to produce a large variety of nanomaterials in terms of morphology and chemical composition. In the membrane template method, a nanoporous membrane with oriented nanochannels is used as mould (hard template) and filled with the desired material or precursors. Subsequently, the membrane is removed to generate a panel of desired nanostructures (nanotubes or nanowires) with a size-replication effect. The spatial distribution of the ensuing nanoobjects is governed by the pore distribution in the starting membrane. In the second process, the membrane contactor, a first solution flows tangentially to the membrane surface and then mixes/reacts with a second solution coming from the membrane pores. Using this technique, polymeric nanoparticles, solid lipid nanoparticles, and nanocrystals have been prepared. Selected examples will be presented.

Keywords: 1D nanostructures, carbon nanotubes, inorganic nanotubes, membrane contactor, membrane template, nanocapsules

Abbreviations: AAM, anodic alumina membranes; CVD, chemical vapour deposition; MWCO, molecular weight cut-off; NC, nano capsule; NP, nanoparticle; PDCs, polymer-derived ceramics; SLN, solid lipid nanoparticles; SPG, Shirasu porous glass; UF, ultra filtration

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INTRODUCTION

Since the discovery of the carbon nanotubes in 1991 by Ii-

jima (Iijima 1991), interest in one-dimensional (1D) nanomaterials has grown remarkably, and an impressive number of research articles has been published on nanotubes as well

as nanowires of various chemical composition (Rao and Govindaraj 2005). A wide range of interesting physical properties have been reported for these nano-objects. Compared with bulk materials, low-dimensional nanoscale materials, with their large surface areas and possible quantum confinement effects, exhibit distinct mechanic, optic, electronic, chemical and thermal properties. For instance, cyclic voltammetric detection limits for electroactive species at an array of cylindrical gold nanoelectrodes (10 nm in diameter) could be three orders of magnitude lower than those observed at a conventional disk microelectrode made of gold (Menon and Martin 1995). Valuable properties derived there from have been envisaged in various domains ranging from automotive, aerospace, electronics to biomedical sciences. In electronics, smaller dimensions have historically allowed the production of denser, faster circuits, and the ability to produce nanostructures may lead to new types of devices to be operated on quantum mechanical principles. Other examples may include, for instance, ultrasmall chemical and mechanical sensors that are based on nanoelectrodes and nanoelectromechanical systems, solar cell and field emitter systems, and nanostructures for implants (Asuri *et al.* 2006; Cheng *et al.* 2007; Liu and Webster 2007; Saif and Abdel-Mottaleb 2007; Vamvakaki and Chaniotakis 2007). For a more fundamental view, these 1D nanostructures also display fundamental interests in the field of mesoscopic physics.

Several strategies have been developed for the synthesis of 1D-nanomaterials, based on both chemical and physical approaches including: i) use of the intrinsically anisotropic crystallographic structure of a solid to accomplish 1D growth; ii) introduction of a liquid-solid interface to reduce the symmetry of a seed; iii) use of various templates with 1D morphologies to direct the formation of 1D nanostructures; iv) use of supersaturation control to modify the growth habit of a seed; v) use of appropriate capping reagent(s) to kinetically control the growth rates of various facets of a seed; vi) self-assembly of 0D nanostructures; and vii) size reduction of 1D microstructures (i.e. Xia *et al.* 2003; Foyet *et al.* 2007; Langer and Golczak 2007; Zhao *et al.* 2007). Because many of these methods were not demonstrated until recently, most of their characteristics (such as reproducibility, product uniformity and purity, potential for scaling up, cost effectiveness, and in some cases, mechanism) are not well known (Xia *et al.* 2003). Among these strategies, the template-directed synthesis represents a straightforward route to 1D nanostructure. In this approach, the template serves as a scaffold within a different material is generated *in situ* and shaped into a nanostructure with its morphology complementary to that of the template (i.e. Martin 1996; Hulteen and Martin 1997; Huckzo 2000; Schmid 2002). A wealth of templates have been successfully demonstrated by various research groups, including step edges present on the surfaces of a solid substrate, channels within a membrane material, biological macromolecules such as DNA strains or rod-shaped viruses, and existing nanostructures synthesized using other approaches (Xia *et al.* 2003).

From a biomedical point of view, nanoparticles (nanospheres and nanocapsules) can be seen as colloidal delivery systems, which show great potential as a mean of efficiently delivering a drug to its site of action, thereby minimizing any unwanted toxic effects. Nanoparticles range in

size from about 10 to 1000 nm (Douglas *et al.* 1987; Kreuter *et al.* 1994; Basak *et al.* 2007; Mykhaylyk *et al.* 2007). Nanospheres have a matrix type structure with drugs adsorbed at their surface, entrapped in the particle or dissolved in it (Fessi *et al.* 1989). Nanocapsules have a polymeric shell and an inner liquid core, the drugs being dissolved in the inner core, or adsorbed at their surface (Allémann *et al.* 1993). Nanoparticles have been investigated for the entrapment of a wide variety of drugs, for applications ranging from ophthalmic delivery to carriers in chemotherapy (Allémann *et al.* 1993). Several methods for the preparation of nanoparticles are available, involving either a dispersion of preformed polymers or a polymerization of dispersed monomers (Fessi *et al.* 1989). Despite the numerous methods available to produce nanoparticles on a small scale, there are still problems in the establishment of large-scale production methods. This is considered to be one of the reasons preventing the successful introduction of nanoparticles to the clinic and the pharmaceutical market (Mehnert and Mäder 2001).

This manuscript presents an updated review devoted to membrane techniques used for the preparation of nanomaterials (nanotubes, nanowires, and nanoparticles). Excellent reviews can be found on general aspects of 1D-dimensional nanostructures: general synthesis methods, characterization and applications (i.e. Xia *et al.* 2003; Rao *et al.* 2004; Rao and Govindaraj 2005). The template method, which is a very general approach, has been used to prepare nanotubes and nanowires of polymers, metals, semiconductors, carbons, ceramics and other materials (i.e. Martin 1996; Hulteen and Martin 1997; Huckzo 2000; Schmid 2002). The membrane template technique is shown in Fig. 1. Because the membranes contain cylindrical pores with a narrow size distribution in terms of diameter and length, monodispersed nanocylinders of the desired material, with carefully controlled dimensions, are obtained. These nanocylinders may be either hollow (nanotubes) or solid (nanowires). The second method uses a membrane contactor to prepare nanoparticles: a first phase is introduced through the membrane pores, while a second phase flows tangentially to the membrane surface (Sirkar *et al.* 1999; Drioli *et al.* 2003). The contact between the two phases allows nanoparticles to be formed. Polymeric nanoparticles (nanospheres and nanocapsules), solid lipid nanoparticles, and nanocrystals have been prepared in this way. The membrane contactor process is represented in Fig. 2.

TEMPLATE SYNTHESIS OF NANOMATERIALS

In the membrane-based template method, a membrane that contains a large number of straight cylindrical pores is used as mould (hard template). Nanochannels are filled with the desired material such as precursors, polymers, metals, semiconductors or carbon. Subsequently the membrane is removed to leave the desired nanotubes, nanorods and nanowires (e.g. Martin 1996; Hulteen and Martin 1997; Huckzo 2000; Schmid 2002) that replicate the size and the morphology of the template (Fig. 1). The dimensions and the morphology of the nanostructures are defined by the membrane support. Various chemical compositions can be targeted for the nanostructures ranging from carbon, metal and polymer to inorganic materials. Electrochemical and electroless depositions, chemical polymerization, sol-gel de-

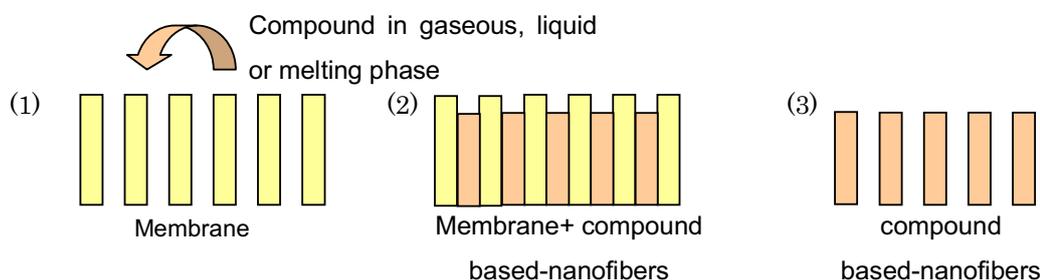


Fig. 1 Schematic principle of the membrane template method. The various steps are: (1) initial membrane, (2) material deposition i.e. by capillarity or under pressure, and final treatment (thermal and/or chemical), (3) membrane dissolution.

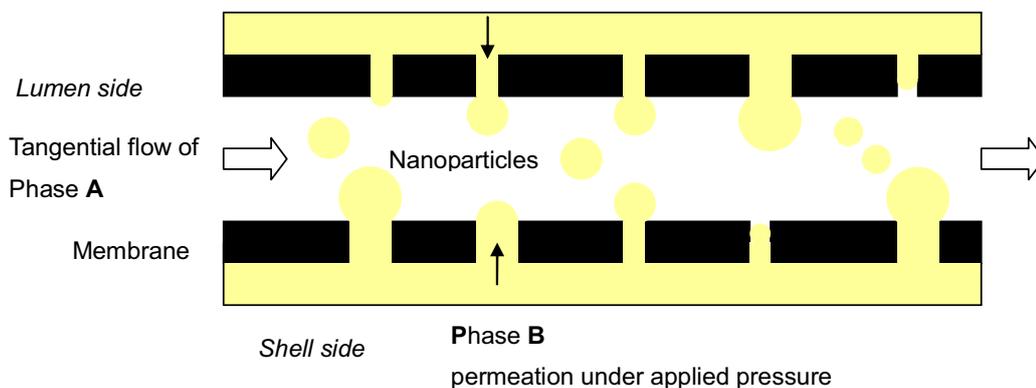


Fig. 2 Schematic principle of the membrane contactor process. Phase A is introduced through the membrane pores, while phase B flows tangentially to the membrane surface. Nanoparticles are formed either by reaction between the two phases, or by solidification of the droplets of A formed at the pore outlets.

position, chemical vapour deposition, and polymer-derived ceramics are major chemical strategies employed.

Membranes used as template supports

Most of the work in template synthesis has entailed the use of two types of nanoporous membranes: track-etch polymeric membranes and porous alumina membranes.

Track-etch membranes

A number of companies (e.g., Millipore, Nuclepore and Poretics) sell microporous and nanoporous polymeric filtration membranes that have been prepared by the track-etch method (Martin 1996). This method entails bombarding a non-porous sheet of the desired material with nuclear fission fragments to create damage tracks in the material, and then chemically etching these tracks into pores. The resulting membranes contain cylindrical pores of uniform diameter which are randomly distributed in the volume of the membrane (Fig. 3A). Membranes with a wide range of pore diameters (down to 10 nm) and pore densities approaching 10^9 pores/cm² are commercially available (Martin 1996). The most commonly used materials are polycarbonate or polyester. Other materials (for example mica) are amenable to the track-etch process (Huczko 2000).

Anodic Alumina Membranes (AAM)

Porous alumina membranes are electrochemically prepared from an aluminum sheet in an appropriate aqueous solution (Schmid 2002). The pore structure of a porous alumina membrane is a self-ordered hexagonal array of cells with cylindrical pores of almost uniform diameter and length, which can be controlled by changing the experimental conditions (Fig. 3B). Pore densities as high as 10^{11} pores/cm² can be achieved (Martin 1996). Such membranes are commercially available (e.g. Whatman[®]) in a limited number of pore diameters (20, 100, 200 nm). Membranes of this type have also been prepared at the lab scale with pore size as small as 5 nm (Martin 1996).

Other nanoporous membranes

A variety of other membrane templates have been used. Ionomer membranes have been used as templates for the preparation of various nanoparticles (Rollins *et al.* 2000). The ionomer membrane was obtained by wet casting from a solution of the sulfonimide ionomer in dimethylformide, followed by careful annealing at high temperature. Nafion ionomer membranes are provided by DuPont Co. Biomembranes have been used for template synthesis of nanomaterials, i.e., living bio-membrane bi-templates of the mung-bean sprout to prepare semiconductor lead selenide nanorods and nanotubes (Li *et al.* 2004), and lamellar DNA-cationic membrane complexes to form CdS nanorods (Liang *et al.* 2003). Mesoporous zeolite membranes have been

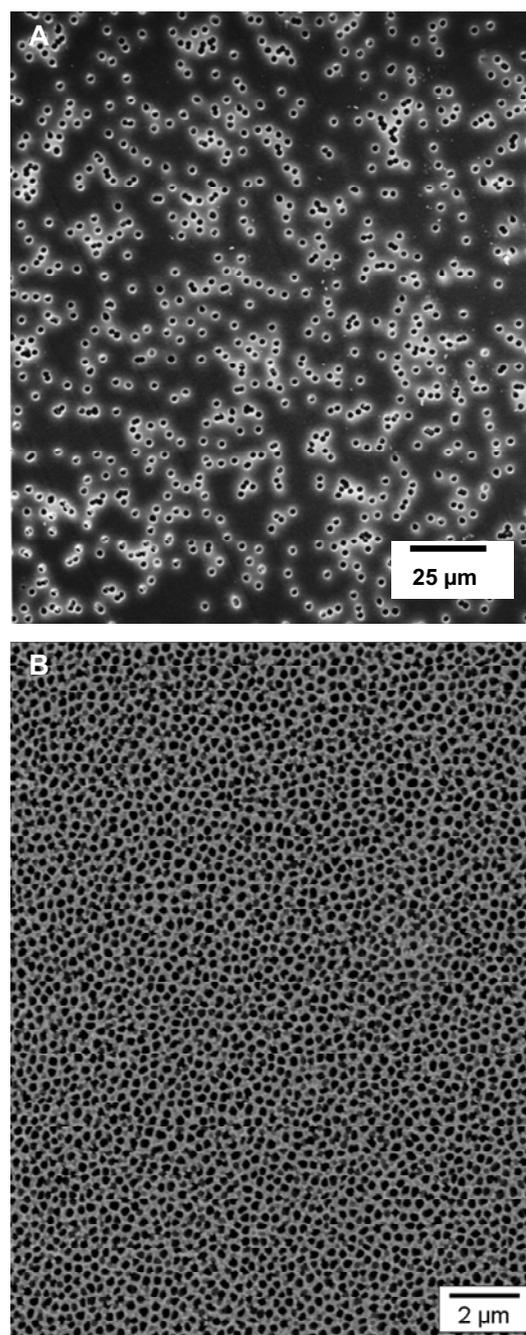


Fig. 3 Membranes used with the membrane template method. Two membranes are shown: (A) Isopore[®] track-etched polycarbonate membrane (Millipore) (Charcosset and Bernengo 2000) and (B) Anopore[®] alumina membrane (Whatman[®]). Reprinted from Charcosset C, Bernengo JC (2000) Comparison of microporous membrane morphologies using confocal scanning laser microscopy. *Journal of Membrane Science* 168, 53-62, ©2000, with kind permission from Elsevier.

Table 1 Examples of nanostructures prepared by the membrane template method. (d: nanostructure diameter, L: nanostructure length, d_p : diameter of the membrane pores)

| Product type | Membrane material | Technique | Reference |
|--|--|--|--|
| Co nanotubes and nanowires d=220 nm, L=25 μ m | Modified alumina (Whatman) d_p =100 nm | Electrodeposition | Bao <i>et al.</i> 2004 |
| Au nanotubes d=200 nm, L=2 μ m | Alumina (Anotech Ltd.) d_p =200 nm | Electrochemical deposition | Brumlik and Martin 1991 |
| Au, Ag, Au/Ag nanotubes d=200-400 nm, L=3 μ m | Alumina (Anopore) Track-etch (Nuclepore) d_p =200-400 nm | Electrodeposition; chemical deposition | Brumlik <i>et al.</i> 1994 |
| Polypyrrole, poly(3-methylthiophene) nanowires d_p =1 μ m | Track-etch (Nuclepore) | Chemical synthesis | Cai and Martin 1989 |
| CdS nanowires L=60 μ m | Alumina d_p =100 nm | Sol-gel synthesis | Cao <i>et al.</i> 2001 |
| C nanotubes and nanowires d=75-100 nm | Alumina (Whatman) d_p =200 nm | Chemical vapour deposition of carbon | Che <i>et al.</i> 1998a, 1998b |
| Fluorescent silica nanotubes d=200 nm, L=2 μ m | Alumina (Whatman) d_p =200 nm | Sol-gel synthesis | Chen <i>et al.</i> 2005b |
| α -Fe ₂ O ₃ nanotubes d=200 nm, L=60 μ m | Alumina (Whatman) d_p =200 nm | Thermal decomposition of a precursor within the pores | Chen <i>et al.</i> 2005a |
| SiC nanotubes and bamboo-like structures d=200-300 nm, L=60 μ m | Alumina, d_p =250 nm | CVD or liquid precursor infiltration followed by pyrolysis | Cheng <i>et al.</i> 2005 |
| Au nanotubes d=60-150 nm | Polycarbonate track-etched (Nuclepore) d_p =30-400 nm | Electroless deposition of metal within the pores | Curulli <i>et al.</i> 2005 |
| Polypyrrole nanotubes d=100-250 nm L=3-10 μ m | Polycarbonate d_p =50-200 nm | Chemical synthesis by oxidative polymerization of the pyrrole monomer within the pores | de Vito and Martin 1998 |
| C nanotubes d=200 nm, L=60 μ m | Alumina, d_p =200 nm | Chemical synthesis by via polymerization of acrylonitrile within the pores followed by heat treatment | Hulteen <i>et al.</i> 1997 |
| C nanotube d=30-230 nm L=60-75 μ m | Alumina (Whatman) d_p =230 nm | Pyrolytic carbon deposition on the pore wall by exposition to propylene at 800°C | Kyotami <i>et al.</i> 1996 |
| CeO ₂ nanowires | Alumina prepared by the authors, d_p =60 nm | Migration of Ce ³⁺ and C ₂ O ₄ ²⁻ ions by diffusion conversely | La <i>et al.</i> 2004 |
| TiO ₂ , V ₂ O ₅ , MnO ₂ , Co ₃ O ₄ , ZnO, SiO ₂ nanotubes, nanowires d=200 nm, L=50 μ m | Alumina (Whatman) d_p =200 nm Alumina prepared by the authors, d_p =10 nm | Sol-gel synthesis | Lakshmi <i>et al.</i> 1997 |
| TiO ₂ nanotubes | Alumina (Whatman) d_p =20-200 nm | Sol-gel synthesis | Lee <i>et al.</i> 2004 |
| PbSe nanotubes, | Living bio-membrane bi-templates of the mungbeam sprout | Chemical deposition | Li <i>et al.</i> 2004 |
| CdS nanostructures | DNA-cationic membrane complexes | Chemical synthesis | Liang <i>et al.</i> 2003 |
| Au, Au-poly(pyrrole), Poly(pyrrole) d=50 nm, L=500 nm | Polycarbonate (Poretics) d_p =30 nm | Electrodeposition | Marinakos <i>et al.</i> 1998 |
| C nanotubes L=50 μ m | Alumina (Anopore) d_p =260 nm | Chemical synthesis via the polymerization of acrylonitrile within the pores, followed by heat treatment | Parthasarathy <i>et al.</i> 1995 |
| B ₄ C nanotubes, nanowires d=250 nm, L=45-50 μ m | Alumina d_p =250 nm | Molecular and polymeric precursors to B ₄ C within the pores followed by heat treatment | Pender <i>et al.</i> 2003; Sneddon <i>et al.</i> 2005 |
| CdS, PbS nanoparticles d=4-7 μ m | Perfluorinated ionomer (Nafion, DuPont Co.) and made by the authors | Chemical synthesis | Rollins <i>et al.</i> 2000 |
| Poly[M(Schiff)] (M=Ni, Pd; Schiff=tetradentate Schiff bases) nanowires d=20-200 nm | Alumina (Anopore) d_p =20, 40, 100, 200 nm | Electrochemical deposition | Tchepournaya <i>et al.</i> 2003 |
| Co, Fe nanotubes, nanowires d=30 nm, L=6 μ m | Track-etch polycarbonate (Poretics) d_p =30 nm | Electrochemical synthesis | Tourillon <i>et al.</i> 2000 |
| Polypyrrole (PPy/CNT)/ carbon nanotubes, composite nanowires d=200 nm, L=10 μ m | Alumina (Anodisc, Whatman) d_p =200 nm | Electrochemical synthesis, by plating PPy into the pores in presence of carboxylated CNT dopants | Wang <i>et al.</i> 2005 |
| Polyaniline nanofibers | Mesoporous aluminosilicate MCM-41 d_p =3 nm | Adsorption of aniline vapor into the pores | Wu and Bein 1994 |

used for the template synthesis of nanomaterials: polyaniline nanowires have been prepared in the 3-nanometer-wide hexagonal channel system of the aluminosilicate MCM-41 (Wu and Bein 1994).

Template synthesis techniques

In principle, nearly any solid material can be synthesized within nanoporous membrane template since a convenient synthesis strategy is developed. We can distinguish six main strategies to carry out template synthesis of 1D nanostructures (**Table 1**).

Electrodeposition

Electrodeposition of a material within the membrane pores is preceded by coating one face of the membrane with a metal film and using this metal film as a cathode for electroplating (Huckzo 2000). The volume of the pore is continuously filled up beginning from the pore bottom. Thus, the length of the nanostructures can be controlled by varying the amount of material deposited. Both metal and conductive polymer nanotubes and nanowires have been synthesized using this method (i.e. Brumlik and Martin 1991; Brumlik *et al.* 1994; Tchepournaya *et al.* 2003; Wang *et al.* 2005).

Electroless deposition

Metal nanotubes have been prepared by electroless deposition involving a chemical agent to plate a material from the surrounding phase onto a template surface (i.e. Brumlik *et al.* 1994; Curulli *et al.* 2005). This method differs from the previous one, since the surface that must be coated does not need to be electrochemically conductive. The material deposition in the pores starts from the pore walls. Two types of 1D nanostructure are provided. After short decomposition times, nanotubes are obtained within each pore, whereas long deposition times result in solid nanowires. Electroless deposition yields structures that run the complete thickness of the template membrane, unlike the electrochemical deposition method where the length of metal nanowires can be controlled at will (Huczko 2000).

Chemical polymerization

Different conductive polymers can be template-synthesized by the polymerization of the corresponding monomer to yield tubular nanostructures (i.e. Wu and Bein 1994; de Vito and Martin 1998; Marinakos *et al.* 1998). The process can be accomplished by simply immersing the membrane into a solution containing the desired monomer and a polymerization reagent. The polymer preferentially nucleates and grows on the pore walls, resulting in nanotubes at short deposition times and nanofibers at long times. For polymeric precursors (e.g. polyacrylonitrile, PAN), the nanostructures can be further thermally processed to create carbon nanotubes and nanofibers (Hulteen *et al.* 1997).

Sol-gel deposition

Sol-gel synthesis within the pores of a membrane template involves preparation of a solution of a precursor molecule to obtain first a suspension of colloid particles (the sol) and then a gel composed of aggregated sol particles. The gel is then thermally treated to yield the desired nanostructures within the membrane pores (Hulteen and Martin 1997). The process can be conducted to synthesize for example semiconductor nanotubes and nanowires (i.e. Lakshmi *et al.* 1997; Cao *et al.* 2001).

Chemical Vapour Deposition (CVD)

Chemical vapour deposition has been extensively applied in the commercial production of solid thin films (Huczko 2000). The technique entails surface solidification of desired reactants resulting from their gas-phase chemical transformations. The method has successfully been developed for the template synthesis of carbon nanotubes (i.e. Che *et al.* 1998a, 1998b). The starting reactants, i.e. ethylene and pyrene, acetylene, tripropylamine, methane, propylene, or 2-amino-4,6-dichloro-s-triazine, were thermally activated and decomposed to solid carbon within porous templates while traversing the length of the pore. Thermal decomposition of the gas occurred throughout the pores, resulting in the deposition of carbon films along the length of the pore walls and formation of carbon nanotubes within the pores.

Polymer-Derived Ceramics (PDCs)

This chemical approach can be seen in a first view as the analogue of the sol-gel process for the fabrication of non-oxide ceramics (Cornu *et al.* 2005). In the PDCs route, a polymeric or molecular precursor is first synthesized, then formed into the desired shape and subsequently decomposed into the final solid-state material with retention of this shape. This chemical route has been shown to be a promising method for producing many 1D non-oxide nanostructures in a wide range of processed forms and sizes (Pender *et al.* 2003). A liquid, soluble or meltable preceramic polymer prepared from a molecular precursor is

deposited on the surface of membrane until saturation of the template and formation of a thin film covering it. The polymer-membrane composite is then pyrolyzed at high temperature to yield the desired ceramic nanomaterial within the nanochannels. Nanotubes and nanowires can be prepared according to this strategy.

Compositions and morphologies of the template-synthesized nanomaterials

Various 1D nanomaterials have been prepared using the membrane template method, including semiconductor, metal, polymeric, carbon and ceramics.

Semi-conductor nanostructures

Much attention has been paid to the preparation of oxide nanowires for their interesting optical and electrical properties. For example TiO₂ nanostructures are known for their catalytic properties and are used as electrodes for solar cells (Lee *et al.* 2004). The concepts of sol-gel synthesis and membrane template have been used to prepare nanostructures of semiconductors materials (Huczko 2000). For example, TiO₂ nanotubes and nanowires of the anatase phase have been synthesized (Lakshmi *et al.* 1997; Lee *et al.* 2004). The high surface area offered by these TiO₂ nanostructures has been used for photodecomposition of salicylic acid in sunlight (Lakshmi *et al.* 1997). Other oxide semiconductor nanostructures such as MnO₂, Co₃O₄, ZnO, WO₃, and SiO₂ (i.e. Lakshmi *et al.* 1997; La *et al.* 2004), chalcogenide semiconductors such as CdS, CdSe, ZnS (i.e. Cao *et al.* 2001), and other nanostructures such as α -Fe₂O₃ nanotubes have been prepared (Chen *et al.* 2005a).

Metal nanotubes

Metal nanotubes are of interest because they can have good electrical conductivity and low electron work functions. Vacuum deposition with an electroplating method was used to prepare Au and Ag nanotubes in the pores of track-etch membrane with 400 nm pore diameter (Brumlik *et al.* 1994). Co and Fe nanotubes 6 μ m long were fabricated in the pores of track-etched polycarbonate membrane by using pulse voltage during electrodeposition (Tourillon *et al.* 2000). Another interesting strategy to fabricate metal nanotubes is the pore-wall modification method, which was first developed by Martin and coworkers (Brumlik and Martin 1991). Au nanotubes as long as 6 μ m with a 1 nm inside diameter were synthesized by using (2-cyanoethyl)triethoxysilane as a pore-wall modifying agent of the alumina membrane. Shape-controllable cobalt nanostructures in alumina membrane using methyl- γ -diethylenetriaminopropyl-dimethoxysilane as pore-wall modifying agent by electrodeposition were also obtained (Bao *et al.* 2004).

Polymeric nanostructures

Conducting polymer nanotubes have been attracting considerable attention because of their potential applications as nanosized transistors, displays, sensors and molecular wires. They were prepared using membrane template and electrochemical or oxide polymerization, i.e., polyaniline nanowires (Wu and Bein 1994), polypyrrole nanotubes (de Vito and Martin 1998; Marinakos *et al.* 1998), and redox polymers poly[M(Schiff)] (M=Ni, Pd; Schiff=tetradentate Schiff bases) nanowires (Tchepournaya *et al.* 2003). By controlling the polymerization time, conductive polymer nanotubes with thin or thick walls were obtained. For polypyrrole, the nanotubes ultimately formed solid nanowires. In contrast, the polyaniline nanotubes never closed up, even at long polymerization times (Martin 1996). Using the same technique, one-dimensional Au-polypyrrole nanoparticles arrays were obtained (Marinakos *et al.* 1998).

Carbon nanotubes

Carbon nanostructures are of tremendous interest, from both a fundamental and an applied perspective. Applications investigated include use for storage of hydrogen and other gases, as a catalyst support and as a tip for scanning probe microscopy. Templating methods have been successfully applied to produce ensembles of aligned and mono-dispersed nanotubes of graphitic carbon. CVD technique was applied and hydrocarbons were pyrolyzed in alumina templates yielding graphitic carbon nanofiber and nanotube ensembles (with diameters as small as 20 nm and lengths around 50 μm) (Parthasarathy *et al.* 1995; Kyotani *et al.* 1996; Che *et al.* 1998a, 1998b). Carbon nanotubes have also been prepared via the polymerization of acrylonitrile within the pores of aluminium oxide membranes followed by a series of heat treating conditions converting the polymer structure into carbon nanostructures (Hulteen *et al.* 1997). Carbon nanotube/polymer composites have been explored for possible improvement in the electrical and mechanical properties of polymer, i.e. polypyrrole/carbon nanotube composite nanowires were prepared by electrochemical polymerization, involving plating of polypyrrole into the pores of an alumina membrane in the presence of carboxylated carbon nanotubes (Wang *et al.* 2005).

Ceramic nanostructures

Boron carbide B_4C is a highly refractory material that is of great interest for both its structural and electronic properties (Pender *et al.* 2003). Some selected properties are its high-temperature stability, high hardness, and high-temperature thermoelectric properties. Boron carbide nanostructured materials have been prepared with single-source boron carbide precursors in conjunction with a membrane templating method (Pender *et al.* 2003; Sneddon *et al.* 2005). Other ceramic nanostructures, like silicon carbides SiC nanostructures, were obtained with carbosilane and polycarbosilane precursors by using a membrane templating method (Cheng *et al.* 2005).

Advantages and limits of the membrane template synthesis

Each method of 1D nanostructures synthesis has its specific merits and inevitable weakness. The template-directed synthesis is generally accepted to provide a simple, high throughput, and cost-effective procedure that allows the complex topology of a template to be duplicated in single step. The major advantage is that both the dimensions and compositions of nanowires and nanotubes can be easily controlled by varying experimental conditions. The main limits of the template-directed synthesis are the following. Removal of the template through a post-synthesis process may cause damage to the nanowire and nanotube products. In addition, most nanowires synthesized using template directed methods are polycrystalline in structure, an unwanted feature that may limit their use in device fabrication and fundamental studies (Xia *et al.* 2003). Moreover, the use of a template limits the quantity of structures that can be produced in each run of synthesis. Therefore the yield and the efficiency of the membrane template-directed synthesis may be not sufficient for industrial standards. To solve this major limitation, research studies will have to focus on the scaling-up ability of the technique, i.e. by using superposed membranes of higher thickness, and on its automatization.

MEMBRANE CONTACTORS FOR NANOMATERIALS

Membrane contactors represent an emerging technology in which the membrane is used as a tool for inter-phase mass transfer operations. These membrane systems provide a high interfacial area between two phases to achieve high overall rates of mass transfer (Sirkar *et al.* 1999; Drioli *et al.* 2003). Liquid-gas membrane contactors have attracted considerable attention recently, for simultaneous extraction and injection of gases in natural water production, and membrane distillation for desalination and wastewater treatment (Drioli *et al.* 2003). Liquid-liquid phase membrane contactors are reported for the preparation of nanoprecipitates (Jia and Liu 2002; Jia *et al.* 2003; Chen *et al.* 2004), polyaluminium chloride nanoparticles (Fei *et al.* 2003; Jia *et al.* 2004a),

Table 2 Examples of nanostructures prepared using the membrane contactor process. (d: nanostructure diameter, d_p : diameter of the membrane pores, J: flux through the membrane pores, NC: nanocapsules, NP: nanoparticles, MWCO: molecular weight cut-off)

| Product type | Membrane material | Technique | Reference |
|---|---|---|--|
| Polycaprolactone (PCL) NP d=280-320 nm | Ceramic (Kerasep, Rhodia Orelis, France) $d_p=0.1\mu\text{m}$ | Shell: acetone/PCL lumen: water/Tween 20 | Charcosset and Fessi 2005a |
| PCL/vitamin E NC d=250 nm | MWCO= 1 and 150 kDa | Same with vitamin E in the shell | |
| Hexyl laurate/sebacoyl chloride NC d=250-350 nm | | Shell:acetone/span 80/hexyl laurate/sebacoyl chloride lumen: water/Tween 20 J=0.1-1.5 $\text{m}^3/\text{h.m}^2$ | |
| PCL/indomethacin NC, d=250 nm | Ceramic (Kerasep, Rhodia Orelis, France) MWCO= 150 kDa | Shell: acetone/PCL/ indomethacin/Mygliol lumen: water/Tween 20 J=0.5 $\text{m}^3/\text{h.m}^2$ | Charcosset and Fessi 2005b |
| Solid lipid NP (SLN) Gelucire 44/14 vitamin E d=70-200 nm | Ceramic (Kerasep, Rhodia Orelis, France) $d_p=0.1, 0.2, 0.45\mu\text{m}$ | Shell: Gelucire 44/14 lumen: water/Tween 20 J=0.1-0.4 $\text{m}^3/\text{h.m}^2$ | Charcosset <i>et al.</i> 2005c; El-Harati <i>et al.</i> 2006 |
| BaSO ₄ NP d=10-200 nm | Stainless steel (Central Iron and Steel Institute, Chine) $d_p=0.2, 0.9\mu\text{m}$ | Shell: BaCl ₂ lumen: Na ₂ SO ₄ | Chen <i>et al.</i> 2004 |
| BaSO ₄ NP d=70 nm | Hollow fiber UF polysulfone/polyether- sulfone MWCO= 3, 10, 30 kDa (Zhongke Membrane, China) | Shell: Na ₂ SO ₄ lumen: BaCl ₂ J=0.2-50 10^3 ml/min.cm ² | Jia and Liu 2002; Jia <i>et al.</i> 2002 |
| CaCO ₃ NP d=60 nm | Hollow fiber UF polysulfone/polyether- sulfone MWCO= 1, 10, 30 kDa | Shell: Na ₂ CO ₃ lumen: CaCl ₂ | Jia <i>et al.</i> 2003 |
| PAC (polyaluminium chloride) NP d=50 nm | Hollow fiber UF polysulfone MWCO= 10, 30 kDa | Shell: NaOH lumen: AlCl ₃ J=0.1-3 10^3 ml/min.cm ² | Jia <i>et al.</i> 2004a |
| Perylene NP d=55-300 nm | Hollow fiber UF polysulfone (Amicon) MWCO= 3 kDa | Shell: ethanol/perylene lumen: water J=1.5-50 10^3 ml/min.cm ² | Jia <i>et al.</i> 2004b |
| PCL/spironolactone NC, d=250 nm | Ceramic (Kerasep, Rhodia Orelis, France) $d_p=0.1\mu\text{m}$ | Shell: acetone/PCL/ spironolactone/ Labrafac hydro lumen: water/Tween 20 | Limayem Blouza <i>et al.</i> 2006 |
| SiO ₂ NP d=70 nm | Alumina made by the authors | Frontal mode Preparation of an emulsion Shell: Na ₂ SiO ₃ Lumen: hexane/cyclohexane Added to (NH ₄) ₂ CO ₃ solution | Yanagishita <i>et al.</i> 2004 |

perylene nanoparticles (Jia *et al.* 2004b), polymeric nanoparticles (Charcosset and Fessi 2005a), and solid lipid nanoparticles (Charcosset *et al.* 2005) (Table 2).

Membranes used for membrane contactors

Polymeric hollow fibers devices and tubular inorganic membranes have been used to prepare nanoparticles using a membrane contactor technique. For example, mixed polysulfone and polyethersulfone hollow fibers ultrafiltration membranes (1 000, 3 000, 10 000, and 30 000 daltons cutoff) have been used to prepare BaSO₄ nanoparticles (Jia and Liu 2002). Kerasep ceramic membranes (1 000 and 150 000 daltons cutoff, 0.1 µm mean pore size) with an active ZrO₂ layer on an Al₂O₃-TiO₂ support (Rhodia Orelis, France) have been used to prepare polymeric and solid lipid nanoparticles (Charcosset and Fessi 2005a; Charcosset *et al.* 2005). A very large range of membrane materials and membrane devices may be tested for membrane contactor applications. In particular, membranes with narrow pore size distributions could be used for these applications, such as the Shirasu porous glass (SPG) membrane (Ise Chemical Co., Japan) (Vladisavljević and Williams 2004). The SPG membrane is synthesized from CaO-Al₂O₃-B₂O₃-SiO₂ type glass which is made from “Shirasu”, a Japanese volcanic ash. The SPG membrane is characterized by uniform cylindrical interconnected micropores, a wide spectrum of available pore sizes (0.05-30 µm), and a high porosity (50-60%).

Membrane contactors techniques

The membrane contactor allows one phase to be introduced through the membrane pores into another phase which flows tangentially to the membrane surface. The technique may rely on the formation of small droplets at the pore outlets. The droplets formed are then solidified in the second phase flowing tangentially to the membrane surface. The process is similar to the “membrane emulsification” technique for which water in oil, oil in water and multiphases emulsions have been prepared (Vladisavljević and Williams 2004). The membrane contactor method may also rely on mixing and reaction between the two phases inside the membrane device, with reactions such as polymerization and precipitation. The membrane contactor is used in a tangential configuration (one phase circulates tangentially to the membrane surface), although a frontal configuration may be chosen for membrane emulsification to prepare emulsions (Vladisavljević and Williams 2004).

Nanoparticles prepared using membrane contactors

Polymeric nanoparticles

Nanoparticles (nanospheres and nanocapsules) range in size from about 10 to 1000 nm (Douglas *et al.* 1987; Kreuter *et al.* 1994). Several methods for the preparation of polymeric nanoparticles are available, involving either a dispersion of preformed polymers or a polymerization of dispersed monomers (Allémann *et al.* 1993). The nanoprecipitation method developed by Fessi (Fessi *et al.* 1989) is based on the interfacial deposition of a polymer following displacement of a semi-polar solvent miscible with water from a lipophilic solution. The interfacial polymerization is a technique in which two monomers, one oil-soluble and the other water-soluble, are employed and a polymer is formed on the droplet surface (Hincal and Kas 2000).

Various polymeric nanoparticles were prepared using a membrane contactor technique. Nanoparticles were obtained using a nanoprecipitation reaction (Charcosset and Fessi 2005a, 2005b). The organic phase contained a solvent, a polymer, eventually an oil, and a drug and the aqueous phase a surfactant. With this technique, polyacrylonitrile nanospheres, nanocapsules, and vitamin E-loaded nanocap-

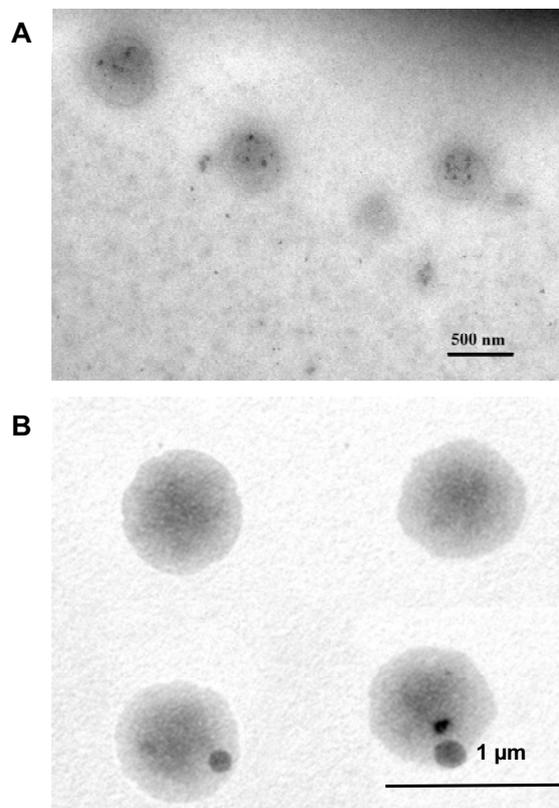


Fig. 4 Examples of nanoparticles prepared using a membrane contactor. Two types of nanoparticles are observed by TEM: (A) vitamin E-loaded nanocapsules prepared with a Kerasep® 150,000 Da membrane (Orelis, France) (Reprinted from Charcosset C, Fessi H (2005a) Preparation of nanoparticles with a membrane contactor. *Journal of Membrane Science* 266, 115-120, ©2005, with kind permission from Elsevier); (B) spironolactone-loaded nanocapsules prepared with a Kerasep® 0.1 µm membranes (Reprinted from Limayem I *et al.* (2006) Preparation and characterization of spironolactone-loaded nanocapsules for paediatric use. *International Journal of Pharmaceutics* 325, 124-131, ©2006, with kind permission from Elsevier).

sules were prepared (Fig. 4A). Nanoparticles were also obtained using interfacial polymerization (Charcosset and Fessi 2005a). The organic phase contained a solvent, a monomer, eventually an oil, and a drug and the aqueous phase a co-monomer and a surfactant. Nanocapsule-loaded spironolactone (a diuretic for children) has been also prepared (Fig. 4B) (Limayem *et al.* 2006).

The obtained fluxes through the membrane were high (between 0.1 and 1.6 m³/h.m²) (Charcosset and Fessi 2005a, 2005b; Limayem *et al.* 2006). The higher dispersed phase flux, 1.6 m³/h.m², was obtained with the 0.1 µm pore size membrane. This high flux leads to the preparation of 1.8 10⁻³ m³ of nanoparticles in 4 min, which confirms the potentiality of this process for industrial applications. An extrapolation to membranes with larger surface area (i.e. Kerasep membrane module with a membrane area of 0.34 m²) would lead to the preparation of 0.082 m³ of nanoparticles in the same time. This high flux was explained by the organic phase formulation for which the main component was the solvent, which lead to a low viscosity and to favourable interfacial tensions in membrane pores (Charcosset and Fessi 2005a).

Solid lipid nanoparticles

As an alternative to polymeric nanoparticles, solid lipid nanoparticles (SLN) are realised by exchanging the liquid lipid (oil) of the emulsions by a solid lipid, which means lipids are solid at room temperature but also at body temperature (Müller *et al.* 2000a; Mehnert and Mäder 2001; Müller *et al.* 2002). The use of solid lipids instead of liquid

oils is a very attractive idea to achieve controlled drug release, because drug mobility in a solid is considerably lower compared with liquid oil. Solid lipid nanoparticles are prepared using high pressure homogenization techniques (Müller *et al.* 1995, 2000a). Two general approaches, the hot and the cold homogenization techniques, can be used.

Solid lipid nanoparticles were prepared using a membrane contactor (Charcosset *et al.* 2005c; El-Harati *et al.* 2006). The lipid phase was pressed, at a temperature above the melting point of the lipid, through the membrane pores allowing the formation of small droplets. The aqueous phase circulated inside the membrane module, and swept away the droplets forming at the pore outlets. SLN were formed by the following cooling of the preparation to room temperature. The influence of process parameters (aqueous phase and lipid phase temperatures, aqueous phase cross-flow velocity and lipid phase pressure, membrane pore size) on both the SLN size and the lipid phase flux were investigated. Vitamin E-loaded SLN were prepared, and their stability was demonstrated. The advantages of this new process were shown to be its facility of use, the control of the SLN size by an appropriate choice of process parameters, and its scaling-up abilities. Again, the obtained fluxes were high (between 0.1 and 0.4 m³/h.m²), making possible industrial applications.

Other nanoparticles

Barium sulphate BaSO₄ and calcium carbonate CaCO₃ nanoparticles have been successfully obtained using a membrane contactor (Jia and Liu 2002; Jia *et al.* 2003; Chen *et al.* 2004). Nanosized BaSO₄ particles, about 15 nm in size, were synthesized by a membrane contactor, in which NaSO₄ solutions were added into BaCl₂ solutions gradually through the pores of ultrafiltration membranes to control the saturation ratio, subsequently the nucleation and growth rates (Jia *et al.* 2003). The addition of additives such as methyl alcohol and ethanol favoured the synthesis of nanoparticles with small size. Polyaluminium chloride nanoparticles, which is an important flocculent in potable water and wastewater treatment, have been synthesized by a membrane contactor in which NaOH solution permeated through the pores of an ultrafiltration membrane into AlCl₃ solution gradually to reduce the NaOH droplet size to nanoscale (Jia *et al.* 2003; Jia *et al.* 2004). Also, the preparation of monodisperse SiO₂ nanoparticles with a mean size of 70 nm by membrane emulsification has been reported (Yanagishita *et al.* 2004). Using an anodic alumina membrane, a NaSiO₃ solution was pushed into a mixture of hexane and cyclohexane containing a surfactant in order to prepare monodisperse emulsions droplets. The resultant water-in-oil emulsion was added to a (NH₄)₂CO₃ solution and the mixture was agitated at 40°C for 8 h to solidify the sodium silicate droplets by interfacial polymerization of silicic acids.

Advantages and limits of membrane contactors

With the membrane contactor, the obtained fluxes are high, making possible scaling-up for industrial applications. The available membrane area may be easily increased by using several devices in parallel. High quantity of structures are produced in each run of synthesis, therefore the efficiency of the process may be very high. Other advantages of the membrane contactor are its versatility for the preparation of various types of nanoparticles (nanocapsules, nanospheres, and nanocrystals) by methods involving a polymerization or a precipitation. The average nanoparticles size can also be modified by an appropriate choice of the process parameters (membrane pore size, cross-flow velocity, pressure, formulations...). The drawbacks of the membrane contactor are related to those of classical membrane techniques, as ultrafiltration and microfiltration. After each run of synthesis the experimental set-up must be cleaned, especially the membrane has to recover its initial permeability before the next run. The cleaning is often time consuming. Moreover,

fouling of the membrane may occur during a run of synthesis (i.e. organic or inorganic molecules may deposit on the membrane surface and in the membrane pores). These mechanisms lead to decrease the flux versus time, and therefore decrease the yield and the efficiency of the process. A proper choice of the process parameters (i.e. concentrations not too high, high pressure and high cross-flow velocity) can limit the fouling mechanisms.

CONCLUSION

The membrane template method was introduced in the 1980s as a very simple and efficient technique for the synthesis of nanomaterials. A large range of chemical approaches are available for the template synthesis of a wide variety of nanomaterials including metals, polymers, carbon, and ceramics. The latter display a large range of physical and chemical properties. Applications range from gas sensor and lithium-ion battery applications with α -Fe₂O₃ nanotubes (Chen *et al.* 2005a) to gene delivery using fluorescent silica nanotubes (Chen *et al.* 2005b) and electrochemical sensors and biosensors gold nanotubes (Curulli *et al.* 2005). An important feature of the template synthesis method is the ability to control the dimensions of the nanotubes (or nanowires) obtained. The outside diameter of the nanotubes is determined by the diameter of the pores in the template, and the length of the nanotubes by the thickness of the template. The actual limitation of the membrane template method is the low amount of nanostructures prepared. Methods for mass producing template-synthesized nanostructures would be required for industrial applications.

Membrane reactors have increased in interest in recent years and are reported to have different functions, as separation of products from reaction mixtures and immobilization of catalysts (Sirkar *et al.* 1999; Drioli *et al.* 2003). The membrane reactor (contactor) controls the addition of one reactant into another reactant. The membrane contactor has been used to prepare a wide variety of nanoparticles including polymeric nanoparticles, solid lipid nanoparticles and nanocrystals. In the membrane contactor, the flux may be very high, making possible scaling-up for industrial applications. Other advantages of the membrane contactor are its versatility for the preparation of polymeric or lipid nanoparticles (nanocapsules or nanospheres), and the control of the average nanoparticle size by an appropriate choice of the process parameters.

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