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Preparation of self-supporting mesostructured silica thin film membranes as gateable interconnects for microfluidics

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ABSTRACT

A methodology for the preparation of self-standing 100–200 nm thick mesoporous silica membrane interconnects is reported. Interconnects may become an important component in future microfluidic device technology since it allows extension of microfluidic architectures into the third dimension. The silica film was mechanically supported by a perforated silicon nitride microsieve and covered a hexagonal array of 500 nm-sized holes. The potential applicability of these films as gateable interconnects for controlled dosing of ions was demonstrated. The permeability of ionic species can be controlled by the ionic strength.

1. Introduction

The development of thin semipermeable gates through which certain molecular or ionic species can be transferred at will from one compartment into the other may ultimately lead to new switchable interconnects for microfluidic device technology to carry out functions such as separation, detection or dosing. In recent years a substantial number of works appeared in which such interconnects were demonstrated [1–7]. Well-known examples are thin polycarbonate track etched (PCTE) membranes [8] and anodic aluminum oxide (AAO) membranes [9], which both have straight parallel pores of uniform diameter. Under conditions in which the diffuse double layer is thick enough to span the width of the pores or channels, the channel become selectively permeable to anions or cations only. The type of selectivity depends on the sign of the surface charge on the pore wall. The thickness of the double layer can be estimated from the Debye length

$$\kappa^{-1} = \sqrt{\frac{\varepsilon k_B T}{2e^2 I}}, \qquad (1)$$

with ε the permittivity of the solution, k_B the Boltzmann constant, T the temperature, and e the elementary electron charge [10]. The parameter I is the ionic strength, and is defined by

$$I = \frac{1}{2}\sum_j z_j^2 c_j \qquad (2)$$

where c_j and z_j are the concentration and ionic charge of species j in the solution, respectively. The concept was first introduced in 1995 in a study in which it was shown that the semipermeability of gold-coated PCTE membranes can be modulated from anion-selective to cation-selective [11]. The selectivity was set by the ionic strength of the solution, while the type of selectivity depends on the sign of the surface charge of the pores, and was controlled by the electrical potential of the gold layer relative to the solution in which it was placed. The driving force for ionic transport through the membrane was a concentration gradient. In later studies it was demonstrated how external electrodes placed on both sides of the interconnect can be employed to create a driving force for ion migration through the membrane [10].

An alternative class of materials to make semipermeable gates are mesoporous oxides, especially mesostructured mesoporous silica [12,13]. These materials have a less well-defined pore structure than PCTE and AAO, but they have very high porosities of typically 55% or more, which makes them very permeable, and a narrow pore size distribution between 2 and 10 nm, which renders them a high permselectivity. Moreover, since mesoporous oxides are made by sol–gel synthesis, their composition, pore structure and film thickness can be controlled and modified at will. Self-standing thin films of this material could find application as a

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semi-permeable membrane in sensors and microreactors. To provide the thin film with sufficient mechanical strength, it needs to be supported by a permeable support structure. In a previous study, we employed silicon nitride microsieves with hexagonally ordered perforations of 1.2 μm width as support for MCM-48 silica films [10,14]. These sieves have an extremely low resistance to fluid flow [15], because of the high density of perforations and thickness of only 1 μm. The MCM-48 layer was deposited by spin coating, yielding a silica film which covered the entire sieve, and with a final thickness that was similar to that of the microsieve.

The aim of the current study was to develop a methodology to deposit thin silica films on top of the perforated microsieves with 500 nm pores, without any penetration of silica into the perforations of the support. This should result in a substantial reduction of layer thickness. We employed a sacrificial layer approach to accomplish this [5,16]. Mesostructured silica was chosen as model material, but the same strategy should also be possible with other materials.

2. Experimental

2.1. Silica sol synthesis

The synthesis of mesostructured silica thin films has been described elsewhere [17]. Aqueous nitric acid (0.05N) was dropped under vigorous stirring in a conical flask containing a solution of tetraethylorthosilicate (TEOS, ≥99% purity, Aldrich), in 1-propanol (analytical grade, Acros). After 5 min the templating agent cetyltrimethylammonium bromide (CTAB, ≥99% purity, Aldrich) was added. The molar ratio of the final mixture was TEOS:CTAB:1-propanol:H_2O:HNO_3 = 1:0.13:15:15.5:0.14. All reagents were mixed under nitrogen atmosphere in order to avoid hydrolysis of TEOS before the start of the reaction. The mixture was heated at boiling temperature for 2 h under reflux. Then it was allowed to cool down. The transparent sol was kept at 5 °C for a few days until it was used for thin film preparation. The film preparation procedure is described below.

2.2. Ion transport experiments

The experimental set-up for ion transport experiments consists of two halves of a U-shaped tube between which the interconnect is clamped. The interconnects were positioned in such a way that the oxide layer was in direct contact with the feed side of the interconnect. Aqueous electrolyte solutions (250 ml total volume) were added to the feed and receive side cells. Both cells were stirred vigorously. The pH was kept constant at 7.2 using Na_2HPO_4/NaH_2PO_4 buffer solutions.

A dc potential difference ΔV over the interconnect was set using a potentiostat and external Pt gauze electrodes separated by 20 mm. Here ΔV is defined as $\Delta V = V_{\mathrm{receive}} - V_{\mathrm{feed}}$, with V_{feed} and V_{receive} the electrode potentials at the feed and receive side, respectively. ΔV was kept between −2 and +2 V to prevent the electrolysis of water. The setup is described in more details in Ref. [10]. All experiments were performed at room temperature. Fluxes were calculated from concentration changes in the receive side cell with time, after reaching steady state conditions. The membranes were left in the receive side electrolyte solution for 12 h prior to the experiment to ensure full wetting of the oxide layer. Ion transport experiments were carried out with fluorescein (Fl^{2-}) as divalent anion (fluorescein disodium, Fluka), and methylviologen (MV^{2+}) as divalent cation (methyl viologen dichloride hydrate, 98%, Aldrich). These probes were added at the silica side of the membrane to a concentration of 0.77 mM. Analysis of MV^{2+} was carried out by UV spectroscopy (Agilent Technologies) at 257 nm.

3. Results and discussion

3.1. Preparation of self-supporting silica films on microsieves

The silicon nitride microsieves (Aquamarijn Micro Filtration B.V.) had a functional surface area of 3 mm × 3 mm and circular perforations of 500 nm diameter in hexagonal setting. A picture of a sieve is shown in Fig. 1. The process we developed for the formation and transfer of a silica film onto a perforated microsieve is shown schematically in Fig. 2. In the first step, the perforations of the sieve were filled to avoid penetration of the silica sol in the subsequent film deposition step. We infiltrated the perforations with a polymeric solution of appropriate viscosity. A solution containing 10 wt% polymethylmethacrylate (PMMA, M_w = 120 kg/mol) in acetyl acetone with a viscosity of 3.8×10^{-3} Pa s (3.8 cP) at 25 °C was found to be optimal. Solutions with a lower viscosity did not fill the pores properly, while more viscous solutions were comparatively thicker and harder to remove in later processing stages. Prior to infiltration, the microsieves were oxygen-plasma treated to remove residual organics. This improved the homogeneity of the PMMA film.

PMMA was deposited by spin-coating 100 μl of polymer solution at 33.33 Hz (2000 rpm) for 120 s. After drying, the deposition step was repeated. The microsieve was then heated to 80 °C for 15 min to evaporate the solvent completely. In the next step, 50 μl of silica sol was spin-coated at 33.33 Hz (2000 rpm) for 60 s and dried overnight in a furnace at 50 °C to allow condensation of the sol. This increased the coherence of the silica film and avoided crack formation in the next step. This procedure yielded a 100–200 nm thick silica membrane, which is noticeably thinner than the width

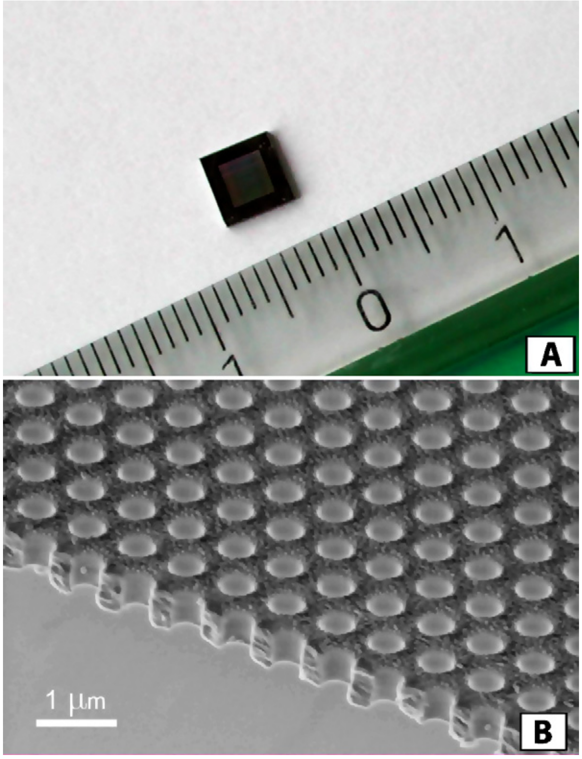

Fig. 1. Images of the microsieve. (A) Picture of the 5 mm × 5 mm microsieve. Patterned area is 3 mm × 3 mm. (B) SEM image of the perforated area of the microsieve. The perforations have a diameter of 500 nm.

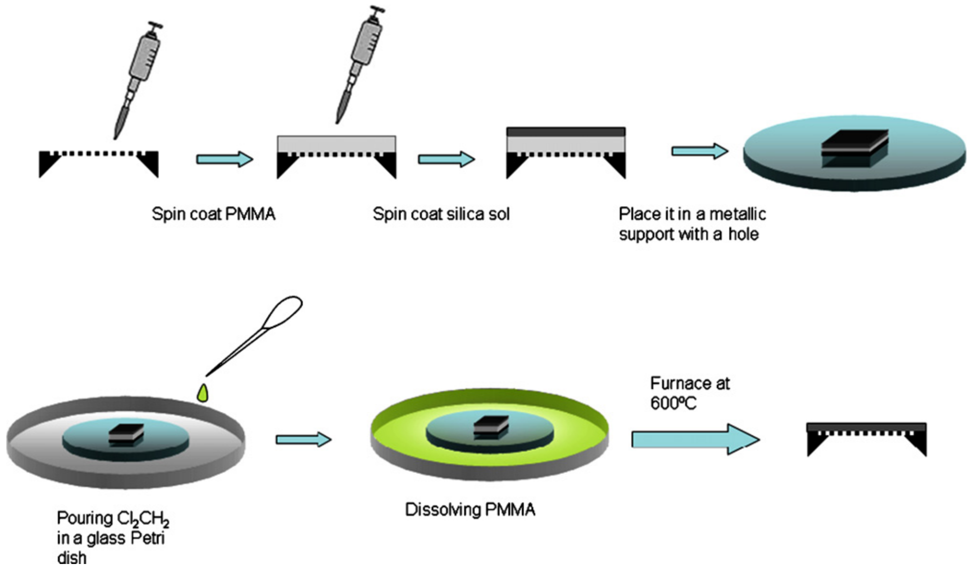

Fig. 2. Scheme showing the developed procedure used to deposit self-standing silica membranes on highly permeable porous microsieves.

of the perforations of the sieve. In the next step, the PMMA phase was removed by dissolving it in dichloromethane (Merck) [18]. To this end, the microsieve was placed on a metallic film with a small hole which was located below the sieve. The hole provided entrance for the solvent to dissolve PMMA from the bottom up, and avoided unnecessary direct contact and possible flooding of the silica layer by the solvent. The main PMMA layer was dissolved during 20 min at 40 °C. Residual traces of PMMA were eliminated from the microsieve in the following steps. The membrane was finally annealed in air at 600 °C for 2 h (heating and cooling rates 0.5 °C/min). The resulting interconnect is shown in Fig. 3. The darker stripes in the middle of the sieve depicted in Fig. 3A indicate regions with 500 nm perforations, while the areas surrounding are dense and impermeable and act as mechanical support. The cross sections shown in Fig. 3B and C were made by breaking a sieve.

3.2. *Structural characterization of mesostructured silica film*

Fig. 4 shows the XRD spectrum of the silica film after deposition and heat treatment. A broad peak is visible at 2θ 2–3°. This peak indicates the presence of long-range order in the material in the form of an ordered mesopore architecture [19]. The nitrogen sorption isotherm of powdered silica material is shown in Fig. 5. From the analysis, a BET area of 1380 m^2/g, a total porosity of 61%, and a pore diameter (BET average) of ∼1.8 nm were calculated.

3.3. *Ion transport experiments*

We applied the thin film as an electrophoretic gate to demonstrate its potential applicability in microfluidic device technology. Doubly charged methyl viologen ions (MV^{2+}) were transported through the membrane with a concentration gradient and/or an electrical field as driving forces. The influence of electrical field and ionic strength on methyl viologen transport rate was investigated, as shown in Fig. 6.

At low ionic strength, i.e., $I = 0.045$ M, where $\kappa^{-1} = 2.0$ nm, the diffusional (Fick) flux of doubly charged methyl viologen ions was 17 $\mu mol\ m^{-2}\ s^{-1}$. No additional electric field was present. The flux increased by a factor of 4 when an additional potential difference of −2 V was applied over the interconnect. Upon reversing the field by setting ΔV at +2 V, the flux decreased to a value of only 2 $\mu mol\ m^{-2}\ s^{-1}$. This clearly indicates that transport of MV^{2+} through the interconnect can be modulated by application of an external field. The response of the flux on ΔV suggests that the dominant modes of ion transport are Fick diffusion and ion migration [10].

The value of κ^{-1} exceeded the radius of the pore $r_p \sim 1$ nm in these experiments, so the transport of methyl viologen occurred under conditions of double layer overlap. Since the isoelectric point of silica is about 2–3 and the experiments were carried out at pH 7.2, the surface of silica was negatively charged. The diffuse double layer inside the pores should therefore be positively charged, i.e., it should consist mainly of cations such as sodium and methyl viologen. The local concentration c_j^p inside a pore is related to the concentration in the surrounding bulk c_j^b and local electrical potential V (relative to that of the bulk) at a location inside the pore according to [20]

$$c_j^p = c_j^b \exp\left(-\frac{z_j eV}{k_B T}\right). \qquad (3)$$

Since silica is negatively charged ($V < 0$), the concentration of anions ($z_j < 0$) in the double layer is depleted. This was indeed confirmed by the observation that no measurable rate of transport of (negatively charged) fluorescein occurred under similar conditions as described above. Consequently, the membrane exhibits a much higher permeability for cations than for anions.

The double layer overlap was removed by increasing the ionic strength to a value of $I = 1.2$ M, which corresponds to $\kappa^{-1} = 0.4$ nm. No field was applied and the MV^{2+} concentration gradient remained the same. Nevertheless, the MV^{2+} flux without external bias increased by a factor of 8.5, to a value of 146 $\mu mol\ m^{-2}\ s^{-1}$. Apparently, the permeability of MV^{2+} is much lower under conditions of double layer overlap. The permeability P_j of a species is proportional to mobility and concentration:

$$P_j \propto b_j c_j \qquad (4)$$

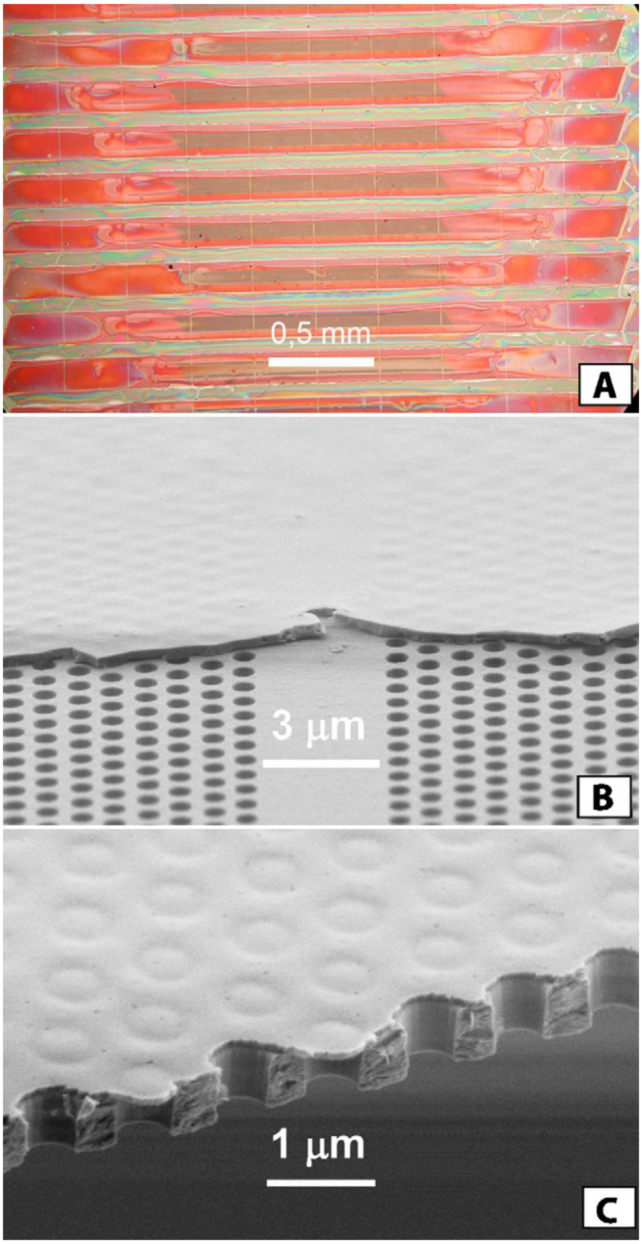

Fig. 3. Images of the silica coated microsieve. (A) Optical microscope image of the microsieve with the silica membrane after heat treatment. (B) SEM image of the microsieve with a self-standing silica membrane after heat treatment. (C) SEM image of the self-standing silica membrane at high magnification.

where b_j is the mobility of a species. The physical conditions at high ionic strength are such that the local negative potential V at any location inside the pore is smaller (in absolute terms), so that the relative accumulation of cations is less [21]. Since $P_{MV^{2+}}$ is smaller under conditions of double layer overlap and $c_{MV^{2+}}$ is higher, the mobility $b_{MV^{2+}}$ of methyl viologen under conditions of double layer overlap must be much smaller than at high ionic strength. Probably methyl viologen is retarded in its mobility due to attractive Columbic interactions with the negatively charged pore wall, and/or to repulsive interactions with similarly charged species elsewhere in the double layer. In more concentrated systems with a higher ionic strength, such interactions are more effectively screened.

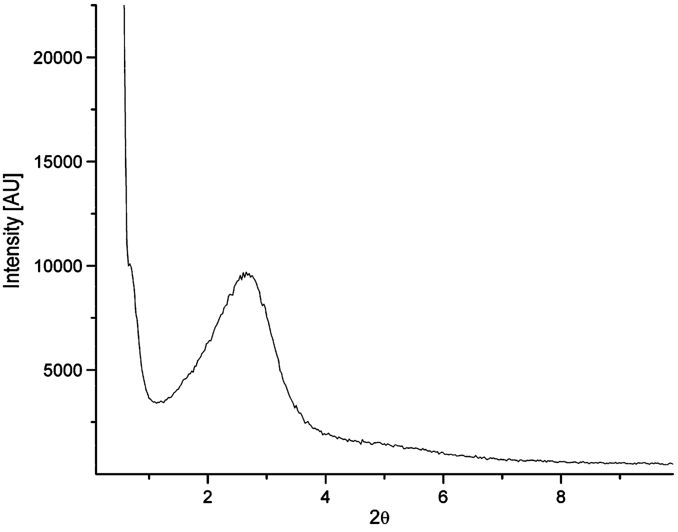

Fig. 4. XRD pattern (Cu Kα radiation) of mesostructured silica film after calcination at 500 °C.

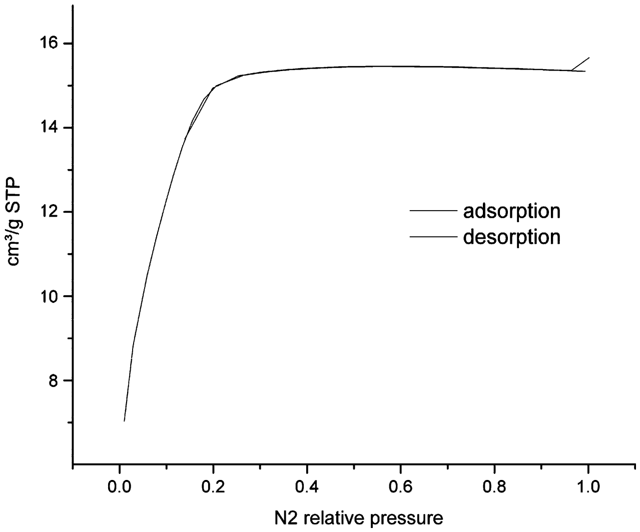

Fig. 5. Nitrogen sorption isotherm of mesostructured silica powder at 77 K.

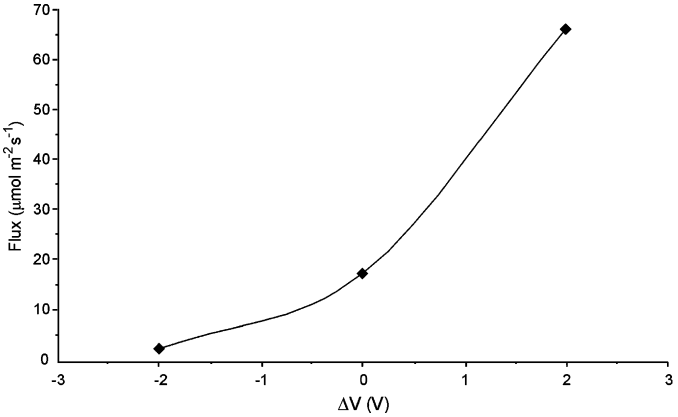

Fig. 6. Effect of variation of potential difference ΔV on flux of MV^{2+} ions through the membrane. $[MV^{2+}] = 0.77$ mM. Ionic strength was 45 mM.

4. Conclusions

We developed a methodology to deposit free standing sol–gel thin films of 100–200 nm thickness on silicon nitride microsieves, and demonstrated their potential applicability as a semipermeable functional component in microfluidic devices. The concentration and mobility of ionic species could be controlled by the ionic strength. Integration into smaller devices is a potential approach to establish communication between two microfluidic channels and may be an important component in future microfluidic devices since it allows extension of microfluidic architectures into the third dimension [22].

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