

## Time-resolved SAXS studies of periodic mesoporous organosilicas in anodic alumina membranes

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### ABSTRACT

A method for producing oriented periodic mesoporous organosilica filaments within the confined channels of anodic alumina membranes is presented. Deposition of the mesoporous filaments were performed under a variety of conditions, which favoured the evaporation induced self-assembly of the mesoporous material. The experimental conditions examined included different drying rates, over a range of humidity values, and sol compositions, e.g. varying the amount of the organosilica component. The deposition process was followed *in situ* by time resolved small angle X-ray scattering which was essential for evaluating the formation mechanism of the mesophase structures. Through careful control of the deposition environment, the structure and orientation of the mesoporous filaments could readily be varied.

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### 1. Introduction

Periodic mesoporous organosilicas (PMOs) are an attractive class of ordered mesoporous materials consisting of hybrid structural units, i.e.  $-[_{1.5}\text{OSi}-\text{R}-\text{SiO}_{1.5}]_n-$  (where R is a bridged group, such as  $-\text{CH}_2\text{CH}_2-$ ,  $-\text{CH}=\text{CH}-$ , or phenyl) where the inorganic and organic moieties in the structure are covalently linked to each other [1–5]. PMO materials offer novel porous structures with different chemical characteristics to the traditional inorganic-based mesoporous materials. These materials combine the rigidity of the silica framework with the added functionality of the organic counterpart. The organo-silica functionality is generated during the initial synthesis of the material by hydrolysis of an appropriate organo-silica precursor which results in the formation of a material with a repeating organic bridging unit [6]. PMOs have found use in a wide range of applications including catalysis [5], chromatography [7] and as high  $k$  dielectrics [8] as reviewed by Wight and Davis [9] and Hoffmann et al. [10]. Thin films of PMO materials have also been prepared by the deposition of suitable gels onto substrates, for example Wu et al. [11] have reported the production of PMO thin films on silicon substrates. The formation of mesopor-

ous materials within the confined architecture of a structured template, for example anodic alumina membranes (AAMs) [12,13] provides a unique opportunity to spatially align the mesopores in a particular orientation due to the directional alignment of the pores within the template. Similar mesoporous silica filaments were reported by Huo et al. in 1997 [14]. Two common mesoporous structures have been identified within the confines of AAMs: (i) circular hexagonal – where the mesopores wind around the main axis of the AAM channels and (ii) columnar hexagonal – where the mesopores run parallel to the main axis of the AAM channels. Recently another confined mesoporous structure has been postulated, i.e. a lamellar structure which is composed of concentric silica sheets [12]. In terms of applications, mesoporous silica filaments in AAMs have been used as templates for the synthesis of carbon filaments [15] and in the controlled delivery of drugs [16,17].

The analysis of PMO filaments confined within the porous structure of AAMs has also been studied in the past, most recently using small angle X-ray scattering (SAXS) and transmission electron microscopy (TEM) by Keilbach et al. [18]. Electrophoretic deposition of PMO materials within AAM channels was investigated by Hill et al. [19] and depositions using a PMO gel with two different structural directing agents was reported by Lee et al. [20]. Ku et al. [21] and Lai et al. [22] both reported the deposition of various mesoporous materials within the channels of AAMs and the growth of nanowires within the pores of mesoporous silica

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confined within the channels of AAMs was reported by Petkov et al. [23]. Marlow et al. also studied circular mesoporous silica filaments synthesised in the absence of AAMs using SAXS [24].

In this paper we report the synthesis of PMOs, through a sol–gel process, within the pores of AAMs. The effects of the deposition conditions, e.g. reduced humidity as well as the organic–inorganic ratio, on the resultant porous structure were investigated to enable a detailed understanding of the dynamics of the disorder-to-order transitions in these systems and to subsequently control the orientation of the mesostructured phases.

## 2. Experimental

P123 was supplied by BASF. Tetraethyl orthosilicate (TEOS), 2-bis-(triethoxysilyl) ethane (BTESE) were supplied by Sigma–Aldrich. All chemicals were used as received. Ethylene-bridged PMO materials within the AAMs were prepared from a sol–gel method similar to that reported previously by Platschek et al. [25]. In a typical synthesis 2.08 g w/w of silica (TEOS) and organo-silica (BTESE) precursors, 3 ml of 0.2 M aq HCl, 1.8 ml of H<sub>2</sub>O and 5 ml of ethanol were mixed at 60 °C for 1 h. To this solution, 15 ml of a 5 wt% P123 in ethanol was then added and left to stir at room temperature for 1 h, after which the gel was filtered. The gel was then dropped onto a Whatman AAM, with 100 nm pores, until the membrane was completely covered and left to dry under vacuum or in a controlled humidity atmosphere. Dry AAM–PMO composites were calcined at 450 °C in air to lift off any excess film material from the surfaces of the membrane. It should also be noted that the calcination step also reduces the size of the PMO filament within the AAM pores and adhesion between the PMO filament and the AAM wall is lost. The SAXS experiments were first conducted *ex situ* on already structured (dry) membranes followed by *in situ* time resolved experiments on some selected samples. This however resulted in a mesoporous film deposited on top of the membrane which interfered with, but did not obstruct, the analysis of the mesoporous filaments within the AAM channels. This surface film is unavoidable when conducting *in situ* measurements, where otherwise it would be removed via calcination or polishing.

## 3. Characterisation

*In situ* SAXS experiments at grazing incidence angles of 1–2° were carried out at the Austrian SAXS beamline of the ELETTRA Synchrotron facility, Trieste, Italy using an image intensified 2D-CCD-camera (CV12, Photonic Science Ltd., Millham, UK) and 8 keV X-ray energy. The sample to detector distance was set to 1.478 m. Briefly, the AAMs were loaded with the PMO gel in a sealed chamber in which the humidity was controlled. In some cases the evaporation rate was accelerated by evacuating the chamber to a reduced pressure of approximately 1 mbar. *d*-Spacings were calculated using a standard (silver behenate) of known *d*-spacing.

TEM images were collected on a JEOL 2000FX transmission electron microscope operating at a voltage of 200 kV. The membranes were prepared for plan-view TEM imaging by dimple grinding, followed by Ar-ion polishing. The dimple grinding was accomplished using a Gatan model 656 dimple grinder using 5 μm diamond paste. Further Precision Ion Polishing (PIPS) reduces the thickness of the AAM for TEM analysis which was done at grazing angles of 6° with a 5 kV acceleration voltage on a Gatan, Precision ion polish system model 691.

## 4. Results and discussion

SAXS measurements of AAMs loaded with a mesoporous material will result in different diffraction patterns due to the orientation of the mesostructure within the AAM channels, see Fig. 1. These diffraction patterns are much like those reported for normal mesoporous thin films, as reported by Grosso et al. [26,27]. However due to the confinement effects of the AAM channels different scattering patterns are observed. A very good overview of such X-ray reflections and the responsible structures, in direct space and reciprocal space, are given by Platschek et al. [12] and briefly repeated here for completeness.

Fig. 1a shows the columnar hexagonal mesoporous structure and the scattering pattern which results from the high rotational symmetry of the columnar structure around the axis of the AAM channels. Fig. 1b illustrates the circular hexagonal mesoporous structure consisting of concentric circles of hexagonally arranged pores wound around the AAM channels and an example of the resulting scattering pattern from the circular hexagonal pores. The additional scattering spots are hidden from view due to the beam stop. Additionally, a lamellar mesophase (concentric lamellar sheets wound around the axis of the AAM channels) has also been reported [12,25], however such a structure was not observed in this work. SAXS data was not the only technique used to identify the mesoporous structures present in the AAM channels as SAXS data may lead to misleading conclusions. Therefore complementary TEM data was used to confirm the mesoporous structures within the AAM channels.

The evaporation induced self assembly (EISA) mechanism that determines the final structure of a PMO materials can be influenced by many factors [26], none more important than the chemical composition of the deposited gel [28]. Humidity plays a significant role during the condensation of a silica precursor during the deposition of any mesoporous material. Water is vital to both the condensation of the silica precursor and the formation of stable micelles of the structure directing agent (in this case P123). The effect of humidity on the final mesoporous structure within the AAM channels from a sol composed of 50% w/w organo-silica precursor and 50% w/w silica precursor measured *ex situ* is shown in Fig. 2.

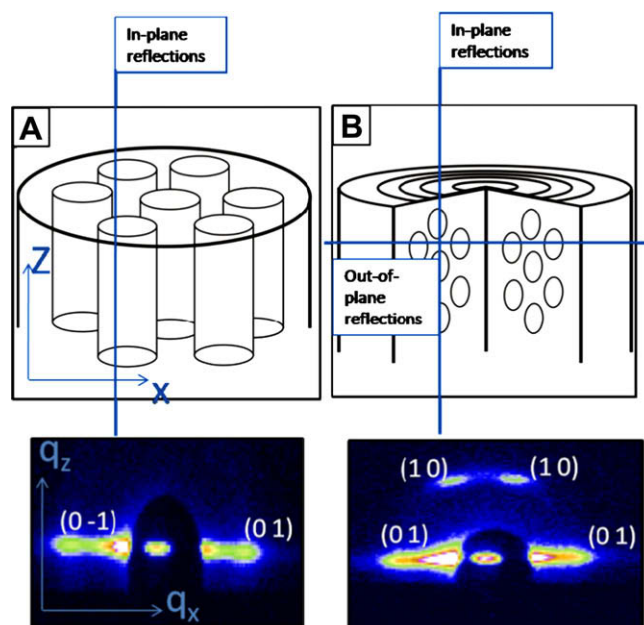


Fig. 1. Schematics of the mesoporous structures within the channels of AAMs with the corresponding SAXS patterns: (a) columnar hexagonal and (b) circular hexagonal orientated mesoporous structure.

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