



Scaling-up of mesoporous silica films via an eco-efficient UV processing method. Part 1: Photoinduced mesostructuration

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ABSTRACT

Designing sustainable and industrially viable processing methods to synthesize ordered mesoporous films is a necessary condition to tap their full potential of applications. In order to respond to this challenge, well-established photoacid-catalyzed sol-gel photopolymerization has been harnessed to prepare large (>100 cm²) and micrometer-thick porous silica films possessing a 2D hexagonal mesostructure. Our UV irradiation system consists of two inexpensive and low radiant power fluorescent UV tubes (3 mW cm⁻², 280–380 nm) enclosed in a hygrometric chamber. Precise conditions to promote copolymer/silica hybrid film mesostructuration have been determined as regards relative humidity, film thickness and templating agent concentration. The mesostructured films have been analyzed using an extensive range of techniques including electron microscopy, grazing-incidence small-angle X-ray scattering (GISAXS), and N₂ sorption measurements, and solid-state NMR spectroscopy. Mesoporous silica films with a specific surface area up to 314 m² g⁻¹ have been achieved with a very low level of microporosity. Coupling of X-ray diffraction (XRD) and FTIR spectroscopy has enabled to shed light into the photoinduced self-assembly mechanism.

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1. Introduction

25 years of intense and massive research in ordered mesoporous materials have led to two major outcomes [1,2]. Firstly, a thorough understanding of the self-assembly mechanism has been achieved, leading to robust processing methods to control *chemical composition* (silica, oxide, hybrid ...), *texture* (pore organization, specific surface area ...) and *morphology* (film, monolith, fiber, powder ...). Secondly, their potential for delivering innovative and useful applications in extremely varied fields has been established [3–7]. Today, we are at the eve of a gradual integration of these mesoporous materials into marketable products. However, their development at very large scale will only be possible in the future if emerging methods readily transferable from the laboratory to the industry are introduced [8,9]. Although mesoporous materials are backed up with soft-chemistry sol-gel routes [10], scalability but

also eco-design are currently two issues that have not been sufficiently raised or discussed so far. This is mainly attributed to complex experimental conditions and the high cost products involved in the synthesis [11].

The preparation of mesostructured silica or organosilica materials in the form of film is particularly representative, since it involves many constraints: multiple steps including heating for silica network stiffening and template removal, high concentration of solvents whose recovery has been rarely addressed, limited film thickness up to a few hundred nanometers only, and mostly high cost and fossil-based alkoxy silane reactants [12,13]. Up to now, the most complicated step is certainly to master film deposition due to a short pot-life formulation, and the need to control both the external environmental conditions — temperature, relative humidity (RH) — as well as the deposition parameters. Nonetheless, obtaining mesoporous materials with a net-shaped film morphology is highly desired for many advanced functional applications, including sensors, supercapacitors, or photonic devices [14]. Today, a scalable, efficient, energy-saving and environmentally benign process to mesoporous silica films has yet to be developed.

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In the search for environmental improvements in the processing method that could also yield parallel economic benefits, we present an eco-efficient UV process to design large surface area of micrometer-thick ordered silica mesoporous films. The concept of thin-layer radiation curing has been extensively investigated, but essentially for the preparation of organic polymer films intended for use as industrial coatings, inks and adhesives [15]. Harnessing radiation energy to synthesize inorganically cross-linked silica or metal oxide films needs to be further developed because it may provide similar technical advantages: fast production rates, low or no volatile organic compounds (VOC) formulation, and ambient temperature reaction. In 2012, UV radiation was proved to drive the synthesis of disordered silica network mesostructures [16]. More recently, ordering was even achieved upon optimizing irradiation conditions [17]. Other recent studies showed the interest of photoinduced inorganic polymerization for the synthesis of silica particles [18,19], membranes [20], hybrid films [21,22], and dental materials [23]. In this report, we have taken a further step forward and designed an energy-saving, scalable, and fully-photoinduced process where UV radiation has two consecutive roles: i. the formation of silica/surfactant mesostructured film and, ii. the selective and fast photodegradation of the copolymer templating agent. For the sake of clarity, each UV process — induced by two different wavelength ranges — is dealt in a separate study. This study entitled *Part 1 Photoinduced Mesostructuring* focuses on the first UV_B-driven (280–320 nm) condensation of methoxysilane oligomer precursors to form ordered copolymer/silica hybrid films. In this report, mesoporous silica films have, therefore, been produced by thermal calcination. A separate forthcoming study *Part 2: Photoinduced Calcination* will describe the second stage based on UV_C-driven (160–280 nm) calcination to synthesize the final mesoporous silica film.

Our study begins with a description of the new UV radiation system to produce silica/surfactant ordered films. The added values compared to a conventional set-up based on evaporation-induced self-assembly (EISA) methodology have been emphasized. Secondly, the photogenerated sol-gel films prepared with a triblock copolymer based on poly(ethylene oxide) (PEO) and poly(propylene oxide) (PPO) ((EO)₁₉-(PO)₆₉-(EO)₁₉) have been thoroughly characterized using a range of techniques: transmission electron microscopy, X-ray diffraction (XRD), grazing-incidence small-angle X-ray scattering (GISAXS), N₂ adsorption and ²⁹Si and ¹H solid-state NMR. The influence of copolymer concentration, relative humidity (RH) and film thickness have been examined in a view of optimizing the process. To understand the light controlled self-assembly mechanism, XRD and FTIR have been conducted in parallel to show the interplay between the progress of the sol-gel process and the onset/evolution of the mesophases.

2. Materials and methods

2.1. Materials

Pluronic 123 (P123), an amphiphilic triblock copolymer based on PEO and PPO ((PEO)₁₉-(PPO)₆₉-(PEO)₁₉) and diphenyliodonium hexafluorophosphate ($\Phi_2\text{I}^+ \text{PF}_6^-$), a photoacid generator, were purchased from Sigma Aldrich. Poly(dimethoxysiloxane) (PDMOS) is an oligomeric methoxy precursor provided by ABCR (Fig. 1 depicts a simplified structure, and Figure S1 in supplementary material provides the ²⁹Si liquid state NMR spectrum). Polished silicon wafers from Siltronix and 10 × 10 cm glass substrate from Brot were previously washed with acetone and used as substrates.

2.2. UV processing method to mesoporous silica films

The starting formulation is prepared by mixing PDMOS, P123, $\Phi_2\text{I}^+ \text{PF}_6^-$ and acetone with a 1/x/0.06/1 wt ratio ($0.1 < x < 1$). The resulting homogenous and stable solution is either deposited on silicon wafer with a spin coater (15 s at 1000 rpm then 30 s at 10000 rpm) or onto a 10 × 10 cm glass substrate using a 6 μm bar coater, leading to ~ 3.6 μm films (see characterization section for details on film thickness measurement). The formulated system is photolabile when stored in a vial at ambient temperature, and insensitive to visible light. Irradiation was performed inside a Memmert HCP 108 hygrometric chamber, with a careful monitoring of temperature and RH: 30 °C and 60% in standard conditions, respectively. Even when the samples were stored in the environmental chamber, no sign of early hydrolysis was observed within 1 h in absence of UV radiation. Irradiation was provided by a compact system UV 236 (dimensions: 470 × 280 × 100 mm) placed inside the chamber. This radiation system was purchased from Waldmann SA, and includes two fluorescent tubes (UV6, 36 W, Philips). These lamps cover a broadband spectrum, spanning from 280 to 380 nm (see full spectrum in Figure S2), with a total irradiance of approximately 3 mW cm⁻² at a distance of 6 cm from the lamp. After 30 min exposure, transparent and solid hybrid films were obtained. Calcination of the surfactant was then performed under air at 250 °C for 4 h with a preliminary 2 h step at 100 °C (heating rate of 1 °C min⁻¹).

2.3. Characterization

Film thickness was measured by an optical profilometer (Altisurf 500). Two different X-ray diffraction (XRD) experiments were performed. The acquisition of simple θ -2 θ diffractograms was performed with a X'Pert Pro (PANalytical) diffractometer using Cu K α radiation ($\lambda = 0.15418$ nm; $0.5^\circ < 2\theta < 10^\circ$; $0.017^\circ \text{ s}^{-1}$). However, the information provided with this technique is restricted to scattering vectors perpendicular to the substrate. As result, 2D-GISAXS patterns were used additionally when it was necessary to remove ambiguities in the interpretation of the formed mesostructures. 2D-GISAXS analysis was performed on a homemade SAXS apparatus mounted on a rotating anode generator (Cu K α radiation, 40 kV, 20 mA, small focus). The alignment of the sample was performed with position-sensitive detector so as to visualize the location of the reflected beam. The sample was oscillated by ca. 1° in grazing incidence during acquisition; diffraction patterns were recorded on photostimulable imaging plates. XRD and GISAXS patterns were directly taken on the sample deposited on silicon wafer or glass substrate. Transmission FTIR spectra were obtained directly on films deposited on silicon wafer using an IR Equinox with a resolution of 4 cm⁻¹ and 32 spectra accumulation. All spectra were baseline corrected and integrated under OPUS 7.0 software. For measuring XRD patterns and IR spectra at different irradiation times (see section 3.3), similar and minimum time intervals were taken between the sample removal from the UV chamber and its analysis: 5 min (FTIR) and 10 min (XRD). Such conditions are meant to limit the effect of dark post-reactions (hydrolysis and condensation). Morphology of the as-synthesized and calcined products was observed by transmission electron microscope TEM (JEOL JEM-ARM200F). N₂ adsorption and desorption isotherms were performed on a Tristar 3000 (Micrometrics). Calcined samples were degassed under vacuum at 150 °C during 12 h. Surface area was determined by BET method, average pore diameter and distribution were evaluated from desorption branch by BJH method. ²⁹Si MAS NMR spectra of hybrid materials were recorded on a Bruker AVANCE II 300WB spectrometer ($B_0 = 7.1$ T)

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