



Scaling-up of mesoporous silica films via an eco-efficient UV processing method. Part 2: Photoinduced calcination



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ABSTRACT

We describe a fast photocalcination process to prepare highly ordered silica mesoporous films through the use of a low-pressure amalgam arc (λ : 185/254 nm). Because radiant power is 2–3 times higher than conventional low-pressure UV lamps, the elimination of the PEO-*b*-PPO-*b*-PEO copolymer template in the 2D hexagonal hybrid film has been completed within 50 min, without damage to the mesostructure. The degradation kinetics are impacted by film thickness and irradiance, but hardly copolymer concentration. Compared to thermocalcination, a narrower pore size distribution and lower energy consumption have been found. Photodegradation mostly originates from a photoablation mechanism induced by radiation at 185 nm, while oxidation due to photo-generated reactive oxygen species plays a minor role. Photocalcination has been combined with an initial photoinduced mesostructuration (detailed in Part 1: *Microporous Mesoporous Mater.*, 257 (2017) 42–50), resulting in an unprecedented “all UV” method to mesoporous silica films. The final process relies on dual wavelength photoactivation: UV_B to form the hybrid copolymer/silica network, a flash intermediate thermal consolidation, and UV_C to decompose the copolymer chains.

1. Introduction

In recent years, inorganic and hybrid ordered mesoporous materials have been the focus of extensive studies through their broad scope of applications [1–3]. Thanks to both mesopores and functionalized pore surface, mesoporous materials in the form of films have been applied in various fields, including catalysis, separation, electronic and optical devices [4]. To fully tap their potential of delivering valuable products in the near future, further efforts are nevertheless necessitated in terms of easing scalability, processability, handling and storage of sol-gel precursors [5]. In this respect, we have recently proposed an eco-efficient Light Induced Self-Assembly (LISA) pathway to mesostructured copolymer/silica films, proceeding in the order of minutes, and using photolabile sol-gel precursors formulation reacted in a compact UV irradiation chamber [6]. However, much of the interest of a surfactant-templated synthesis is to ultimately obtain a mesoporous network surrounded by a self-standing silica or organosilica framework [2]. To achieve this, a subsequent removal of the templating agent, as complete as possible, is necessary. High temperature calcination, also referred to as *thermocalcination*, is currently the most conventional method to get

rid of the templating agent [7]. It involves sample heating at sufficiently high temperature to decompose the organic template, typically in the 300–500 °C range, while preserving the integrity of the oxide network [8]. Although ubiquitous, this method may be regarded as energy-intensive and slow. Especially, if one considers that the cycle times last between 4 and 8 h, whereas the synthesis of the hybrid silica/surfactant sample by photopolymerization may be complete in the order of minutes. Depending on the oven type, the consumption can reach up to 1 kWh⁻¹. Alternatively, more energy-saving muffle furnaces can be employed, but they have a much higher cost. Additionally, heat is not a selective stimulus, making the preparation of mesoporous ordered organosilica challenging [9,10]. Therefore, in most applications where a hybrid mesostructure is needed, grafting of organic moieties is performed by post-functionalization of preformed mesoporous inorganic materials [2]. In the case of films, other issues include loss of mechanical integrity due to network distortions and residual constraints arising during calcination. Finally, high temperatures exclude the use of thermally-sensitive surfaces such as plastic substrates [11,12]. Solvent extraction is the second most widespread method for surfactant removal [13]; it relies on appropriate solvents in which the

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Table 1
Main studies on photocalcination for the preparation of mesoporous films.

References	[18]	[19]	[20]	[21]	[22]	[23]
Film thickness	100 nm	200 nm	~ 100 nm	n/a	7 μm	n/a
Templating agent	Brij 56	CTAB or CTAC	Brij 56	Brij type	P123	Brij 56
Irradiation source	185/254 nm. Low-pressure Hg arc	172 nm Xe ₂ * excimer lamp	185/254 nm. Low-pressure Hg arc	Low-pressure Hg arc	254–800 nm medium-pressure Hg arc	185/254 nm low-pressure Hg arc
Irradiance	n/a	10 mW cm ⁻²	n/a	n/a	400 mW cm ⁻²	n/a
Photocalcination duration	60 to 120 min	30 min (10 ⁵ Pa) 3 h (10 Pa)	90 min	45 min	190 min	180 min

surfactant is soluble or has good affinities [14,15]. However, this strategy involves a high amount of mostly organic solvent and can pollute the sample by swelling the silica network. Its efficiency is highly dependent on surfactant structure and may be hindered when the hydrophilic portion of the surfactant molecule is intimately embedded into the silica network [14]. Typically 10–80% of surfactant can be removed after 6–24 h [15].

To overcome these limitations, other methodologies have been introduced, among them, the oxidation of the surfactant template using ozone [16] or hydrogen peroxide [17]. Even more promising is *photocalcination* because of its potential to improve processing conditions and efficiency [18]. Introduced for the first time in 2000, surfactant template photocalcination relies either on low-pressure Hg arcs [18] or excimer lamps [19], both emitting in the UV_C range (100–280 nm). Limited radiation penetration of short-wavelengths has focused interest on thin films (thickness < 1 μm). Very few studies have been reported in the literature, which are detailed in Table 1. All of them are affected by slow decomposition rates in the order of hours, incomplete characterization of the photocalcined sample in particular as regards to specific surface area, and there is no systematic comparison with thermocalcination in terms of structure, but also energetic performances and environmental impact. In general, photochemical degradation was attributed to a *photochemical effect* [18,20] — electronic excitation resulting in direct chemical bond dissociation— and/or *photooxidation effect* [21–23] driven by photogenerated reactive oxygen species (ROS), such as ozone, through well-established photochemical reactions [24].

We report herein a new photocalcination process intended to provide many improvements compared to the current short-wavelength systems described in the literature [20]. Our method uses for the first time, a low-pressure Hg amalgam arc, emitting two lines at 185 and 254 nm, which represents an inexpensive and readily available commercial radiation source. As a special feature, it provides a radiant power 2–3 times higher than conventional low-pressure Hg arcs. This lamp is already in use for air purification [25], surface desinfection [26], as well as water purification [27]. Our original photocalcination process is characterized by the possibility to treat micrometer thick films ($\geq 1 \mu\text{m}$) and its rapidity (30 min in the best conditions). Another advantage is the possibility to treat large surface areas ($\geq 100 \text{ cm}^2$) because this lamp is available in various lengths and shapes, opening avenues for upscaling. Another indirect advantage is to be able to obtain at least grams of mesoporous materials, enabling analyses that have never been performed in the past with photocalcined samples, such as the determination of specific surface areas by N₂ adsorption/desorption isotherms and silica network's degrees of condensation by ²⁹Si Solid-State NMR spectroscopy. These characterizations are very important to shed light onto the photoinduced degradation process, which has remained so far elusive in the literature. Last but not least, adding this photocalcination to the initial photoinduced mesostructuring process (see Ref. [6] for details) leads, for the first time, to an “all UV method” to mesoporous thin films. Clearly, the challenge is to achieve a complete surfactant removal from a mesostructured copolymer/silica film in the shortest possible time, without affecting the mesophase's integrity.

Our complete irradiation process relies on dual wavelength photoactivation: UV_B (280–320 nm) to form the hybrid mesostructured network, then UV_C (165/254 nm) to decompose the structuring agent with a flash intermediate thermal consolidation (150 °C), which has proven to be essential to preserve the mesostructure. Our starting material is a 4 μm -thick photolent liquid film composed of alkoxy silane precursor (poly (dimethoxysiloxane), PDMOS) and 45 wt% of a Pluronic triblock copolymer (P123) acting as templating agent. In the best possible conditions, only 70 min were necessary to achieve a 2D hexagonal mesoporous silica film with this 3-step method. Several parameters, such as film thickness, irradiance, copolymer content have been investigated to determine the best conditions for surfactant elimination and mesostructure preservation. Investigation of the impact of radiation wavelength (λ : 185/254 nm) and atmosphere composition on degradation kinetics shed light into a photocalcination mechanism proceeding mainly through photoablation.

2. Materials and methods

2.1. Materials

Mesoporous silica films were synthesized on polished silicon wafers (Siltronix) or 10 × 10 cm glass substrate (Brot). Photoacid generator diphenyliodonium hexafluorophosphate ($\Phi_2\text{I}^+\text{PF}_6^-$) and surfactant Pluronic 123 (P123) were provided by Sigma Aldrich. Poly (dimethoxysiloxane) (PDMOS) is an oligomeric methoxy precursor provided by ABCR with a proportion of Q₀/Q₁/Q₂/Q₃ species: 4.5/26.5/48.5/20.5% as determined by ²⁹Si liquid-state NMR spectroscopy.

2.2. Preparation of mesoporous silica films through a coupled photoinduced mesostructuring and calcination process

A homogeneous and photolent solution containing PDMOS (1 g), P123 (0.45 g, otherwise mentioned in the text), $\Phi_2\text{I}^+\text{PF}_6^-$ (60 mg) and acetone (1 g) was prepared. After deposition on a glass or silicon wafer using a 4 μm bare coater, the films were placed into an environmental chamber (Memmert HCP 108 hygrometric chamber) where temperature (T) and relative humidity (RH) were set to T = 30 °C and RH = 60%. Film irradiation inside the chamber was performed for 30 min through two fluorescent UV bulbs UV 6 (UV236 system, Waldmann, 280–380 nm, electrical power: 36 W) ensuring a homogeneous irradiance of 3 mW cm⁻² at film surface. After irradiation, the resultant P123/silica film was dry and optically transparent. Samples were then treated thermally during 8 min at 150 °C in a Memmert UM400 oven (1.4 kW). Thermocalcination was performed with a Nabertherm Controller P330 (1.2 kW), by heating the samples during 4 h at 300 °C after a 1 °C min⁻¹ ramp. Alternatively, photocalcination was carried out at ambient conditions under air during periods spanning from 60 min to 180 min. As shown in Fig. S1 of the data in brief article, the setup was composed of two indium-mercury amalgam low-pressure arcs (NIQ 60/35XL, Heraeus Noble light, electrical power: 85 W) fixed on a reflective metal panel, and exhibiting two irradiation lines at 185 and 254 nm. Replacement of the synthetic quartz (Suprasil[®]) envelope by a conventional quartz enabled to have a single

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