

A simple three step method for selective placement of organic groups in mesoporous silica thin films



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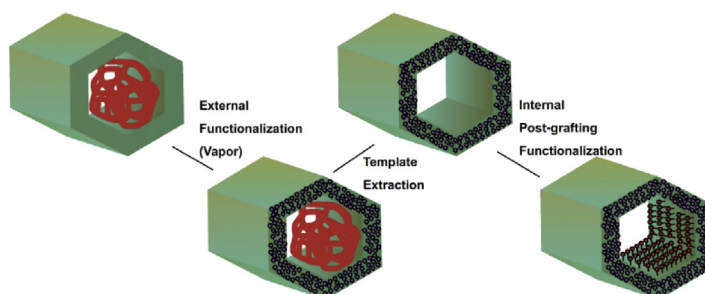
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HIGHLIGHTS

- Selective functionalization of mesoporous silica thin films was achieved using a three step method.
- A volatile silane group is anchored by evaporation on the outer film surface.
- A second silane is deposited in the inner surface of the pores by post-grafting.
- Contact angle, EDS and XPS measurements show different proportions of amino groups on both surfaces.
- This method can be extended to a combination of silane chlorides and alkoxides functional groups.

GRAPHICAL ABSTRACT



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ABSTRACT

Selective functionalization of mesoporous silica thin films was achieved using a three step method. The first step consists in an outer surface functionalization, followed by washing off the structuring agent (second step), leaving the inner surface of the pores free to be functionalized in the third step. This reproducible method permits to anchor a volatile silane group in the outer film surface, and a second type of silane group in the inner surface of the pores. As a concept test we modified the outer surface of a mesoporous silica film with trimethylsilane ($-\text{Si}-(\text{CH}_3)_3$) groups and the inner pore surface with propylamino ($-\text{Si}-(\text{CH}_2)_3-\text{NH}_2$) groups. The obtained silica films were characterized by Environmental Ellipsometric Porosimetry (EEP), EDS, XPS, contact angle and electron microscopy. The selectively functionalized silica (SF) shows an amount of surface amino functions 4.3 times lower than the one-step functionalized (OSF) silica samples. The method presented here can be extended to a combination of silane chlorides and alkoxides as functional groups, opening up a new route toward the synthesis of multifunctional mesoporous thin films with precisely localized organic functions.

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1. Introduction

Mesoporous hybrid thin films (MHTF) with high surface area, periodically organized porosity and versatile pore surface functionalization constitute a thriving field in current materials chemistry [1–3]. In the last years, significant advances have been reported in the reproducible MHTF production and properties control, which bring up potential advanced applications in energy, sensing, prosthetics and information technology, among others. In addition, MHTF can be easily integrated in electronic or micro/nanofluidic platforms [2–4]. The incorporation of active organic groups in nanosized materials is the basic principle of the rational design of “on-demand” hybrid assemblies for multiple applications [5,6]. The physically constrained environment plays a central role in determining the molecular organization and chemical reactivity, mainly due to interfacial interactions, symmetry breaking, and confinement-induced entropy losses [7,8].

Chemical strategies to preparing organo/inorganic nanostructured materials following the concepts of soft chemistry and assembled materials have been widely reported [9–11] and include the access of grafting reagents as organo-chloro or alkoxy-silanes to the internal Si–OH groups located in the pore surface of meso-ordered materials [12–14]. Liz-Marzán et al. had successfully carried out silane grafting in mesoporous particles using a solvent-free method at room temperature comprising the volatilization of (3-aminopropyl)-dimethyl-ethoxysilane (APDMES) with bubbling N₂ [15,16]. This route was preferred over solution-phase silanization, since it proved to have no effect on the adhesion of the silica particles, and improves the efficiency of silane grafting.

The processes that take place in the internal surface of a mesopore can be significantly different to the processes occurring in the external surface of the mesoporous material, which is in contact with the bulk solution. This is particularly important in the design of sophisticated nanosystems, for example gated nanoporous architectures, in which the outer groups control long-range interactions and wetting, while inner groups control molecular transport [17].

In the case of mesoporous films with highly uniform and open pore systems, a precise separation between both types of functions (e. g. hydrophobic/ion complexing, hydrophilic/hydrophobic, bioactive/drug release) is required for advanced applications in fields such as micro- and nanofluidics, separation membranes, biopore mimetic systems, controlled cell adhesion or drug delivery membranes. Mesoporous thin films present typical thicknesses in the order of 100 nm, hence diffusion is a fast process [3]. To date, very few simple and reproducible techniques have been reported that enable the separate selective grafting of two different functions on the external film and the inner pore surface [18–21]. A careful control of the reactivity must be achieved in the case of films, because if the surface function penetrates along the mesopores, the precision in the function distribution can be lost, or even pore clogging can occur. Thus, promoting a fast anchoring of a first function in the presence of the template in the first step seems to be essential. Alternatively, one can resort to multi-step processes relying on the control of wetting and capillary effects of solvents with different polarity that block the pores as a kind of “nano stoppers” [22,23].

Ruiz-Hitzky and De Juan were the first to present a route to produce mesoporous particulated silica with a selective functionalization of the internal and external surfaces of the material. In this method, the selective intra (aryl)- or extra (alkyl)- pore functionalization was carried out [18].

Control of transport and reactivity of functional groups has been used to selectively place organic functions along the mesoporous

channels. Lim and Stein showed that post-grafting leads to a gradient in function incorporation, which was enriched at the pore outlets [19]. Brühwiler et al. developed techniques to follow in-situ the functionalization [24], and established the kinetics. Shephard et al. [25] developed a method to passivate the external surface of MCM-41 with small amounts of diphenyldichlorosilane. Subsequent grafting of APTMS would then lead to an exclusive amino-functionalization of the pore surface. The position of the surface-grafted amino groups was determined by high resolution TEM and following adsorption of a ruthenium cluster compound. Bein and coworkers [20,21] have developed a selective functionalization procedure with a sequential co-condensation approach via functionalized oligosilicates. Using this strategy, they achieve an outer and inner surfaces functionalization in mesoporous silica particles with spatial control of organic groups without significantly decreasing the pore accessibility. These strategies are well suited for mesoporous particles, in which the particle size, geometry and tortuosity of the pores result in relatively long diffusion times that would allow its use in, for instance, the design of drug delivery systems [26]. However, it must be recalled that incorporation of organic functions by co-condensation methods often leads to the burying of such functional groups within the mesopores walls, precluding their full exposure to the pore interior or the external surface [19,36].

As far as we know, the usual methods presented in literature adapted for powders have limitations when applied to supported thin films. Repeated exposure to high temperatures and solution media containing functional molecules such as silanes can lead to pore clogging or partial silica dissolution [18]. These effects might represent a minor loss in a powdered material, but can seriously degrade the performance of a thin coating, which presents very low masses (in the order of magnitude of mg cm⁻²) [27–30].

In this work we propose a soft alternative method that enables the rapid and selective functionalization of mesoporous silica thin films from controlled vapor deposition of alkoxydes. This method does not affect the stability of the material, and leaves the pore surface intact. In addition, this simple three-step method does not require high working temperatures nor aggressive media, allowing the functionalization with a wide variety of volatile silanes. The first step of the method consists in the functionalization of the outer surface of a mesoporous silica thin film in which the pore template has not been removed. The second step consists in washing off the template, thus leaving the inner surface of the pores free to be functionalized in a third step, with a silane different to the one used in the first step. Targeted groups for the selective functionalization were trimethylchlorosilane (TMCS), and (3-Aminopropyl)triethoxysilane (APTES). These silanes were chosen as model groups since they have large physical-chemical differences as a result of the different functional groups. These chemical differences allow to probe the location of the groups in the porous matrix by techniques such as EDS and XPS, and additionally confer to the surfaces measurable properties such as different degrees of hydrophobicity/hydrophilicity. In addition, they present marked reactivity differences, in order to optimize their positioning. The synthesized materials were characterized using superficial and bulk analysis techniques in order to evaluate the chemical functions present on the film surface, and the interior of the mesopores. The possibility of separately functionalizing the inner and outer surfaces of these materials has important consequences in relevant issues regarding mesoporous coatings, such as adhesion control, microfluidics, selective sensing, catalysis and drug delivery systems.

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