

# A general one-pot process leading to highly functionalised ordered mesoporous silica films

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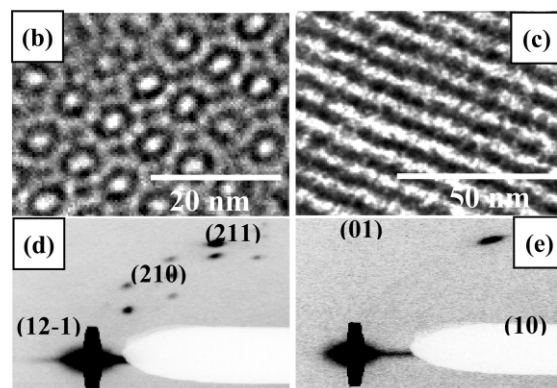
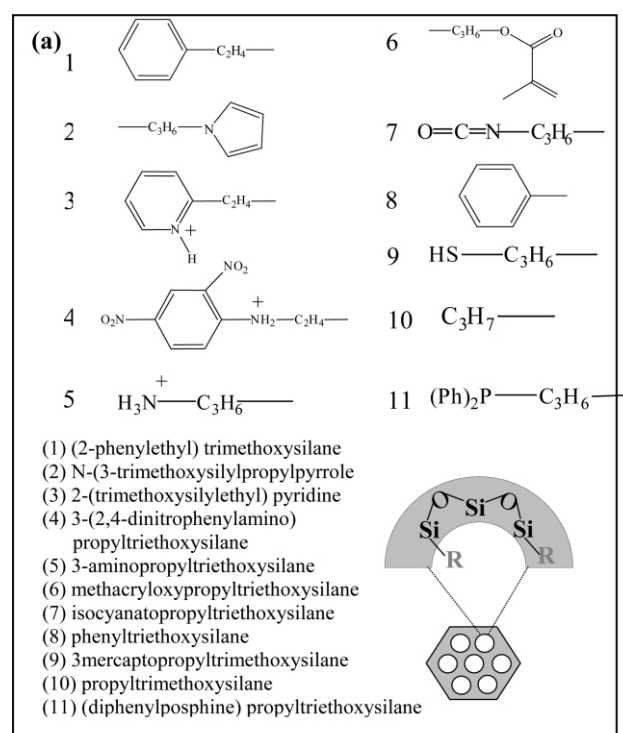
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Various organic moieties are homogeneously introduced in high quantities into mesostructured porous silica films through a general co-condensation process, which influences the self-assembly mechanism, depending on the physico-chemical properties of each function.

Functionalised mesoporous silica materials are highly interesting because they combine a high surface area and a narrow pore size distribution with the additional properties of organic functions. This expands the range of potential applications<sup>1</sup> in separation, catalysis, sensing, *etc.* Such materials can be prepared either by post-grafting or, alternatively, by one-pot co-condensation of organotrialkoxysilane and tetraalkoxysilane. The advantage of the post grafting route is the thermal stabilisation of the silica network before grafting, which is not possible through the co-condensation path. However, the one-pot synthesis is, to date, the only way to homogeneously disperse the organic functions within the matrix. Most of these hybrid mesoporous materials obtained by one-pot synthesis are precipitate powders.<sup>2</sup> With regard to films, one-pot preparation of functionalised thin layers requires the Evaporation-Induced-Self-Assembly (EISA) process,<sup>3</sup> which offers the advantage of an accurate control of the stoichiometry. Indeed, the initial solution's chemical composition in non-volatile compounds is retained after evaporation, fixing the  $R-Si/Si_{total} = r$  ratio in the mesoporous film. Brinker's group<sup>4</sup> used this one-pot method to prepare ordered aminopropyl functionalised silica thin films as pH sensors. However, the effect of the organic function on the self-assembly has not been discussed.

We report a general route for the direct synthesis of functionalised CTAB-templated silica thin films, using eleven organotrialkoxysilanes (see Fig. 1(a)), differing by their physico-chemical properties (*e.g.* hydrophobic, acid/base, aromatic, polymerisable). We show that highly ordered 2D-hexagonal and cubic structures can be obtained and are strongly dependent on the amount of the organosilane and the nature of R. Initial solutions were prepared by adapting the synthetic protocol used for pure silica systems.<sup>5,6</sup> Cetyltrimethylammonium bromide (CTAB), ethanol, water, and HCl are mixed in a first solution to which the prehydrolysed solution of TEOS and then the organotrialkoxysilane are added. Final molar ratios are  $1 - x\text{TEOS} : x\text{RSi}(\text{OR}')_3 : 22\text{EtOH} : 0.15\text{HCl} : 5\text{H}_2\text{O} : 0.18\text{CTAB}$  with  $x = 0-0.15$ . When the organosilane carries a basic function (**3**, **4** and **5**), this latter must be protonated (*via* addition of HCl) before its incorporation in order to prevent gelation. Solutions are aged in sealed vessels for three days previous to dip-coating on silicon wafers at the withdrawal rate of  $2.5\text{ mm s}^{-1}$  and in controlled relative humidity (RH). It has been reported that RH was a crucial parameter for the mesostructure during evaporation.<sup>6</sup> Here, RH was maintained at 40% during the first 60 s of evaporation and was then raised to 70%, which corresponds to the best mesoorganisation for pure CTAB/silica films.<sup>6</sup> In order to allow accessibility to the functions, films were then heated at  $130\text{ }^\circ\text{C}$  for 48 h in air followed by CTAB extraction by ethanol leaching. For the ammonium compounds **3**, **4** and **5**, their deprotonation generates a reactive amino function and is achieved through an  $\text{NH}_3$  post-treatment. Film structures were deduced from 2D-SAXS patterns obtained at the SAXS beamline of the ELETTRA synchrotron.<sup>5</sup>

Structures were confirmed by TEM and the incorporation of the organic compound was assessed by FTIR and UV-vis spectroscopies. Fig. 1 (b–e) shows that highly ordered 2D-hexagonal and (or) 3D cubic mesoporous structures can be formed by co-condensation of various types of alkoxy silane depending on  $r$  value. These are listed in Table 1 with the corresponding compositions. These results reveal that all functionalised films are highly organised,



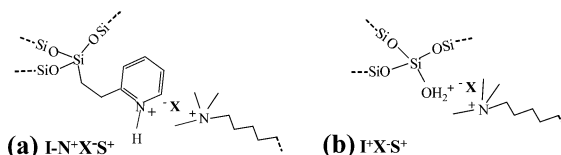
**Fig. 1** (a) Lists of organic functions covalently bonded to the  $\text{Si}(\text{OR})_3$  coupling agent that are used during the one-pot film formation. (b) and (c): TEM pictures of a  $Pm3n$  structure in the [210] axis view plane, and a  $P6m$  structure in the [10] axis view plane respectively; and their corresponding 2D-SAXS patterns, (d) and (e). The  $Pm3n$  film is functionalised with **8**, while the  $P6m$  film is functionalised by **3**.

even with loadings as high as 36% weight (see  $w$  in Table 1). It is important to stress that when  $r$  reaches 0.15, 1 molecule of organic function (R) is coexisting with 1.2 molecules of surfactant (CTAB).

Considering that the pure CTAB system leads to a cubic structure, three main tendencies can be proposed depending on the organic group. For most functions, the 2D hexagonal mesophase is observed whatever the value of  $r$ . For others, such as **2** and **8**, they behave like the pure silica system promoting a  $Pm3n$  mesophase whatever the value of  $r$ . The last behaviour concerns the phenylethane function. In this particular case, the mesostructure depends on the value of  $r$ . Indeed, a  $Pm3n$  mesophase is obtained for  $r < 0.02$  whereas a  $P6m$  structure is promoted above 0.02. These different results could be related to the nature of the organic functions. Indeed,  $Pm3n$  mesostructured films are only obtained when the organosilane carries an aromatic function (*i.e.* with phenyl (**8**) and/or pyrrol (**2**) groups). However this aromatic criterion cannot fully explain the promotion of the cubic mesostructure, since other aromatic functions that promote the 2D hexagonal structure have been incorporated (*i.e.* pyridinium (**3**) and phenyl- $C_2H_4$  (**1**) groups). Consequently the role of the organic function during the self-assembly is complex, mainly because we do not yet know accurately its localisation with respect to the micelle/silica interface. Indeed, according to its physicochemical properties, the function may interact more or less strongly with the silica wall, with the surfactant head group, and with its hydrocarbon tail, affecting or not the curvature of the interface. Few works deal with the localisation of the organic group inside mesostructured materials.<sup>7,8,9</sup> It has been shown that the phenyl function develops direct interactions with surfactant-head groups,<sup>8</sup> the organic functionality acting like a sort of co-surfactant. These interactions increase the area of the surfactant's head group promoting higher curvature of the  $Pm3n$  structure. The opposite effect on the curvature would be obtained by increasing the volume of the hydrophobic micelle core (swelling effect). However, in our system, the effect of each function given in Table 1 seems to be more subtle and cannot be explained in these two extreme schemes only.

**Table 1** Synthesis conditions ( $r = R-Si/Si_{total}$ ), final mesophases (P = H ( $P6m$ ), or P=C ( $Pm3n$ )), and corresponding  $d$ -spacing ( $\text{\AA}$ ) at maximal  $r$ , ( $d(01)$  for the  $P6m$ , and  $d(211)$  for the  $Pm3n$ ). The weight ratio  $w = 100 \times r \times M_R / (r \times M_R + M_{SiO_2})$  is also given for each incorporated function.

	R-Si(OEt) <sub>3</sub>	$r$	P	$w(\%)$	$d/\text{\AA}$
Hydrophobic	None	0	C	0	35
	(1)Phenyl- $C_2H_4$	0–0.02	C	3	31
	(1)Phenyl- $C_2H_4$	0.02–0.15	H	3–20	31
	(8)Phenyl	0–0.15	C	16	32
	(11)(phenyl) <sub>2</sub> P- $C_3H_6$	0.15	H	36	33
	(10) $C_3H_7$	0.15	H	9	32
	(2)Pyrrol- $C_3H_6$	0–0.15	C	21	35
	(9)HS- $C_3H_6$	0.15	H	15	34
	(6)Metacrylate	0.15	H	24	31
	(7)OCN- $C_3H_6$	0.15	H	17	34
	(4)NPATES	0.15	H	35	38
	(5) + $NH_3-C_3H_6$	0.15	H	13	40
	Hydrophilic	(3)Pyridinium- $C_2H_4$	0.01	H	2
(3)Pyridinium- $C_2H_4$		0.08	H	12	41
(3)Pyridinium- $C_2H_4$		0.15	H	21	45



**Fig. 2** Representation of coulombic interactions that occur in acidic medium (a) (I-N<sup>+</sup>X<sup>-</sup>S<sup>+</sup>), (b) (I<sup>+</sup>X<sup>-</sup>S<sup>+</sup>).

Moreover, we observed an interesting effect concerning the interplanar distances with protonated ammonium organic functions in Table 1. Most of the interplanar distances  $d(01)$  are around 34  $\text{\AA}$  which is close to that of the 2D hexagonal mesophase obtained for pure silica system and for RH = 40%. There is an exception for the three systems that carry an ammonium group (*i.e.*, **3**, **4** and **5**) for which the  $d$ -spacings are higher. With the 2-(trimethoxysilyl)ethyl pyridinium (**3**) function,  $d$  increases from 34  $\text{\AA}$  to 45  $\text{\AA}$  when  $r$  varies between 0 and 0.15. These results are mainly attributed to the cationic character of the incorporated functions. Usually, in acidic conditions, the bromide is intercalated between the ammonium head group and the silica wall through electrostatic interactions (I<sup>+</sup>X<sup>-</sup>S<sup>+</sup>)<sup>10</sup> (see Fig. 2(b)). Here we suggest a (I-N<sup>+</sup>X<sup>-</sup>S<sup>+</sup>) mechanism where the pyridinium is located between the bromide and the silica wall (I-N<sup>+</sup> embodies the ammonium function carried by the organosilane), (see Fig. 2(a)). More investigations are under way to understand these behaviours.

In conclusion, we have prepared highly organised functionalised thin films by dip-coating where the organic moiety is covalently bonded to the silica network. Various organic compounds differing by their hydrophilicity are used: cationic species, aromatic or hydrophobic systems. Their introduction lead to highly organised mesostructure films presenting a  $P6m$  or a  $Pm3n$  ordered mesophase even at high organosilane/silica ratio. We have stressed that the organosilane moiety influences the final mesostructure through additional coulombic interactions between the organic and the surfactant head group.

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