

Direct syntheses of functionalized mesostructured silica by using an inexpensive silica source†‡

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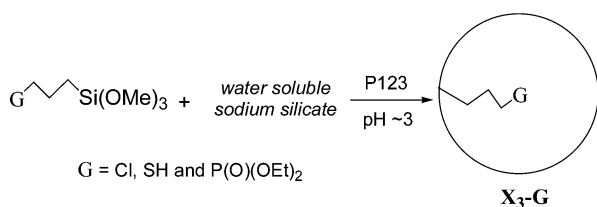
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The co-condensation of water soluble sodium silicate and different organotrialkoxysilanes in the presence of non-ionic triblock copolymers under acidic conditions provides a very convenient, general and economic one step synthesis methodology for the preparation of organically functionalised mesostructured silica.

In the last few years, considerable attention has been focused on the organic tailoring of the internal surface of mesoporous silica, due to applications of such materials in different fields as catalysis, sensing and adsorption. For that purpose, post synthesis grafting of a organotrialkoxysilane *via* SiOH groups of MCM-41 was very often used.^{1–4} More recently, direct synthesis involving co-condensation of tetraethylorthosilicate (TEOS) and organotrialkoxysilane in the presence of different templating surfactant has been shown to be a promising alternative to the grafting procedure mainly as this method allows the control of the organic groups loading as well as their regular distribution within the channel pores.^{5–10} The synthesis of mesoporous silica using sodium silicate as the silica source in place of tetraalkoxysilane and in the presence of different surfactants has been described in several reports.^{11–16} Such silica can be subsequently functionalised *via* grafting giving rise to functionalised materials of low cost. In contrast, to the best of our knowledge, there was no preparation of organically functionalised mesostructured silica by direct synthetic approach using an inexpensive silica source in place of tetraalkoxysilane. That renders this methodology commercialisable with difficulty at the moment. As both methods of functionalisation of the internal surface of mesoporous silica are not equivalent, both of them being interesting to some respect, it was of importance to show that functionalised mesostructured silica can be obtained by direct synthesis using also an inexpensive silica source.

Here we report the one-step synthesis of organically functionalised mesostructured silica in the presence of Pluronic P123 (EO₂₀PO₇₀EO₂₀) as structure directing agent under acidic conditions using the low cost soluble sodium silicate (Scheme 1) in place of tetraalkoxysilane.¹⁷ This new methodology is illustrated with three different organotrialkoxysilanes: 3-chloropropyltrimethoxysilane **1**, 3-mercaptopropyltrimethoxysilane **2** and 3-trimethoxysilylpropyl-diethylphosphonate **3**.



† Electronic supplementary information (ESI) available: ¹³C NMR for X₃-SH, ²⁹Si CP MAS NMR (solid state) spectrum of material X₃-SH and ³¹P HP DEC NMR (solid state) spectrum of material X₃-PO(OEt)₂. See <http://www.rsc.org/suppdata/cc/b3/b314415a/>

‡ Following the submission of our manuscript a paper reporting related results has been published by J. Shah, S. S. Kim, T. J. Pinnavaia, *Chem. Commun.*, 2004, 572 (see ref. 18)

In a first attempt, the basic sodium silicate solution was acidified at pH = 0.4 and added to the micellar solution of P123 at pH = 1.5 containing the organotrimethoxysilane. The solids obtained were named X for xerogel with in index the value of the pH of the sodium silicate solution followed by the organic function. Some physicochemical data of hybrid materials prepared from the organotrimethoxysilanes **1**, **2** and **3** under these experimental conditions are reported in Table 1.

The *S*_{BET} and pore volumes of the samples are relatively weak. Furthermore, the N₂ adsorption–desorption isotherms point to a solid predominantly mesoporous but with irregularities at the desorption in all cases. The N₂ adsorption–desorption isotherm for X_{0.4}-Cl is given as an example in Fig. 1a. We explained the irregularities in N₂ adsorption–desorption isotherms to a too fast condensation reaction. Therefore, in order to have a better control of the condensation rate of materials, the pH of the initial silicate solution was modified. Hybrid materials were prepared from silicate solutions of pH 1.5, 3 and 7. The results of this study revealed that when the pH of the silicate solution is 3, N₂ adsorption–desorption isotherms are typical for mesoporous materials with a rather narrow pore size distribution. That is illustrated in Fig. 1b.

Thus, in a typical experiment (Scheme 1), 2.0 g of EO₂₀-PO₇₀EO₂₀ were dissolved in an aqueous solution (70 mL of H₂O)

Table 1 Physicochemical data for materials prepared from a silicate solution at pH = 0.4

Sample	<i>S</i> _{BET} /m ² g ⁻¹	<i>D</i> <i>p</i> ^a /Å	<i>V</i> <i>p</i> /cm ³ g ⁻¹
X _{0.4} -Cl	129 ± 5	45 and 35	0.13
X _{0.4} -SH	293 ± 8	46 and 36	0.35
X _{0.4} -PO(OEt) ₂	271 ± 8	61 and 35	0.38

^a Calculated from the desorption branch using the BJH method.

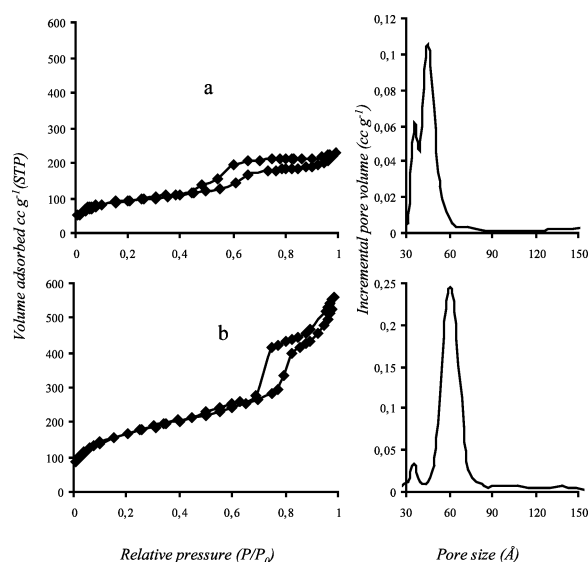


Fig. 1 Nitrogen adsorption–desorption isotherms and pore size distribution plots of X_{0.4}-Cl (a) and X₃-Cl (b).

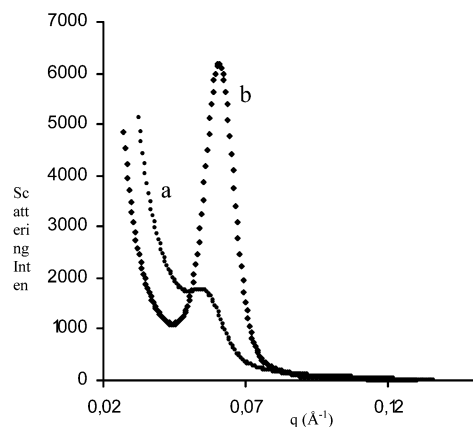
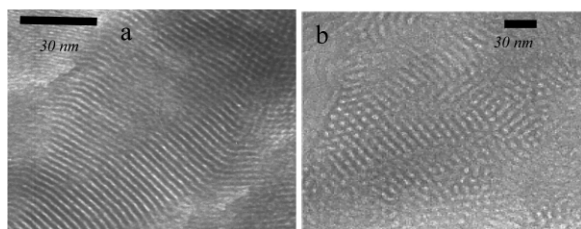
Table 2 Physicochemical data for materials prepared from a silicate solution at pH = 3

Sample	Organic content ^{a/} mmol g ⁻¹	Si/ Σ molar ratio	$S_{\text{BET}}/\text{m}^2 \text{g}^{-1}$	$Dp^e/\text{\AA}$	$Vp/\text{cm}^3\text{g}^{-1}$	$d_{100}/\text{\AA}$	Wall thickness/ \AA ^f
X ₃ -Cl	1.24 (1.49)	9.7 ^b (10)	590 ± 20	60	0.75	120	78.5
X ₃ -SH	1.28 (1.49)	9.3 ^c (10)	410 ± 12	60	0.61	106	62.4
X ₃ -P(O)(OEt) ₂	1.00 (1.29)	11 ^d (10)	517 ± 12	71	0.87	119	66.4

^a Calculated from elemental analysis. ^b $\Sigma = \text{Cl}$. ^c $\Sigma = \text{S}$. ^d $\Sigma = \text{P}$. ^e Calculated from the desorption branch using the BJH method. ^f Calculated by $a_o - \text{pore size}$ ($a_o = 2d_{100}/3^{(1/2)}$). In parentheses, theoretical values.

of pH 1.5 adjusted by addition of 1 mL of H₂SO₄ 2 M. 0.89 g (4.48 mmol) of the organotrimethoxysilane **1** was put into this solution. A solution containing 9.0 g (40.35 mmol) of a basic sodium silicate solution (27% SiO₂, 14 % NaOH, Aldrich) acidified at pH = 3 by adding 50.6 mL of distilled water and 1.60 mL of concentrated H₂SO₄ was quickly prepared and immediately added under stirring to the previous mixture. A white precipitate was observed immediately and the suspension was then heated under reflux and stirring for 3 days. The resulting solid was filtered off and washed 3 times with ethanol (3 × 20 mL) then the surfactant was removed by Soxhlet extraction with ethanol (500 mL) heated under reflux for 36 h. The solid was again washed three times with ethanol (3 × 20 mL), acetone and ether before drying under 0.1 mm Hg at 120 °C for 12 h affording 2.83 g of a white solid (95% yield). The physicochemical data for the three materials are reported in Table 2. The composition of the final materials was inferred from the results of elemental analyses of Si, Cl, S, or P depending on the organic groups. They were found to be close to those for the original mixtures. The specific surfaces and pore volumes of materials obtained at pH = 3 are notably larger than those of the corresponding materials prepared with an initial silicate solution of pH = 0.4.

Small-angle X-ray scattering patterns of different samples exhibit an intense diffraction peak corresponding to d_{100} spacing. Fig. 2 shows how critical for the structure is the initial pH of the silicate solution. A TEM image of the material X₃-SH and X₃-P(O)(OEt)₂ (Fig. 3) provides evidence for a 2D hexagonal structure.

**Fig. 2** SAXS diffraction patterns of X-SH at pH 0.4 (a) and pH 3 (b).**Fig. 3** TEM image of X₃-SH (a) and X₃-P(O)(OEt)₂ (b) after surfactant extraction.

It is worth noting that starting from a silicate solution of pH = 7 slowed down the condensation rate but did not give rise to a mesostructured materials probably because the pH of the solution was not acidic enough to achieve a good structuration.

Solid-state ¹³C MAS-NMR spectra[†] of materials display distinctly the three signals assigned to the propyl group (11.5, 16.6, 27.6 ppm). ²⁹Si CP MAS NMR spectra[†] of materials indicate a high degree of condensation for the organic precursor (T³ resonance is the major one) as well as a high degree of condensation of the silica (with a major Q³ and Q⁴ resonances). The ³¹P HP DEC NMR spectra[†] of material X₃-P(O)(OEt)₂ display only one signal at 33.5 ppm assigned to the phosphonate group.

In conclusion, we have shown that it is possible to obtain by direct synthesis ordered mesoporous silica functionalised with various organic groups using sodium silicate in place of TEOS and amphiphilic block copolymers as the structure-directing agents. The role of the pH of the initial silicate solution was proved to be crucial. The materials were obtained under moderated acidic conditions, pH = 3 being the value giving N₂ adsorption-desorption isotherms typical for mesoporous materials with narrow pores sizes distribution. Up to now, functionalised ordered mesoporous silica could be obtained with a low cost production only by post-synthetic grafting of a organotrialkoxysilane on ordered mesoporous silica prepared from sodium silicate. Therefore, this new synthetic method corresponds to a real advance in materials science as the direct synthetic approach allows the control of the organic loading and a regular distribution of organic groups within the channel pores.

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