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Superhydrophobic silica aerogels by fluorination at the gel stage

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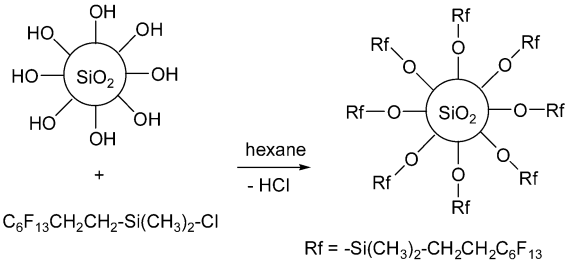
Superhydrophobic silica aerogels are obtained by surface modification of standard silica gels prepared by a two-step process with a heavily fluorinated silyl chloride followed by supercritical evacuation of the solvent.

The preparation and testing of highly hydrophobic materials is a topic of current interest because repellence of water or other liquids confers practical applications, such as self-cleaning, to the modified materials.[1] The wettability of a material depends on both the physical and chemical nature of the surface, *i.e.* surface roughness and the chemical functional groups of the surface. Large surface area materials (>200 m^2 g^{-1}) usually absorb important amounts of molecular gases, *i.e.* silica aerogels can contain up to 15 wt% of absorbed air and water vapour. In order to decrease the pores affinity to absorption and make aerogels less hydrophilic, a number of strategies have been used, such as avoiding the presence of terminal hydroxyl groups by co-gelling some silicon precursors containing at least one non-polar chemical group *i.e.*, CH_3–Si.[2]

Incorporation of fluorinated chains covalently bound onto the surface has been used for organic[3,4] or inorganic materials.[5] To the best of our knowledge only one report deals with fluorinated aerogels; Coronado and co-workers have described the co-polymerization of $(CH_3O)_4Si$ (TMOS) with a fluorinated trialkoxysilane in the preparation of an aerogel.[6]

With the aim of getting a high repellence to water, we have modified hydroxyl-rich silica aerogel pores by incorporating a fluorinated periphery. Our strategy differs from the one adopted by Coronado *et al.*[6] Thus, two-step acid–base catalyzed gels were obtained following a modification of the synthesis reported by Tillotson *et al.*[7] (see experimental†). Afterwards, the solvent was exchanged with hexane and the gels, suspended in hexane, were treated with 1*H*,1*H*,2*H*,2*H*-perfluorooctyldimethylchlorosilane (Scheme 1). Then, hexane was replaced again with ethanol. One portion of the gels obtained by this procedure was dried under ambient conditions to afford material XF (Table 1). The rest was dried with $scCO_2$ to afford material AF (Table 1).

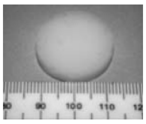
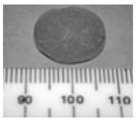
In order to test hydrophobicity we have added a drop of water on top of a sample of fluorinated aerogel AF (Fig. 1a). The contact angle has been estimated from the photograph as *ca.* 150° that is within the range found in hydrophobic or superhydrophobic materials.[4] Moreover, we have covered the surface of aerogel AF with carbon aerogel powder. The water droplet was moved across the dirty surface with the aid of a needle. This operation resulted in the cleaning of the surface (Fig. 1b).



Scheme 1 Modification of the silica surface.

We have made initial estimates of the amounts of vapour solvents absorbed by materials A and AF. The results of Fig. 2 have been obtained by exposing samples of aerogels A and AF to a saturated atmosphere of the indicated liquids in a closed system. Quick weighing was performed at the indicated times. Therefore, the obtained values have a high degree of uncertainty. However,

Table 1 Pertinent properties of the prepared materials

	Aerogel (A)	Fluorinated aerogel (AF)	Fluorinated xerogel (XF)
Density/g mL^{-1}	0.15	0.31	1.23
Surface area/m^2 g^{-1}	624	457	286
%F	Not determined	35–37	42–45
%C		18	23
%H		1.8	2.4
Photograph			

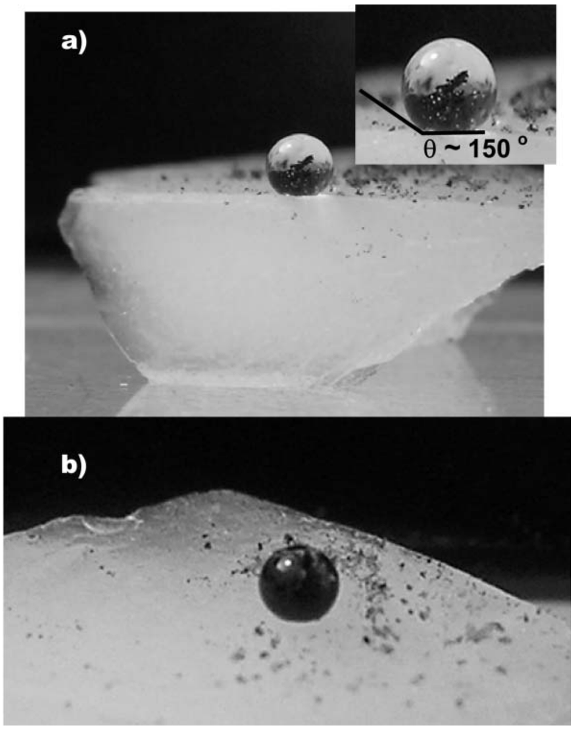


Fig. 1 a: Drop of water on top of material AF, inset shows a close-up. b: Carbon aerogel powder accumulated in the water droplet.

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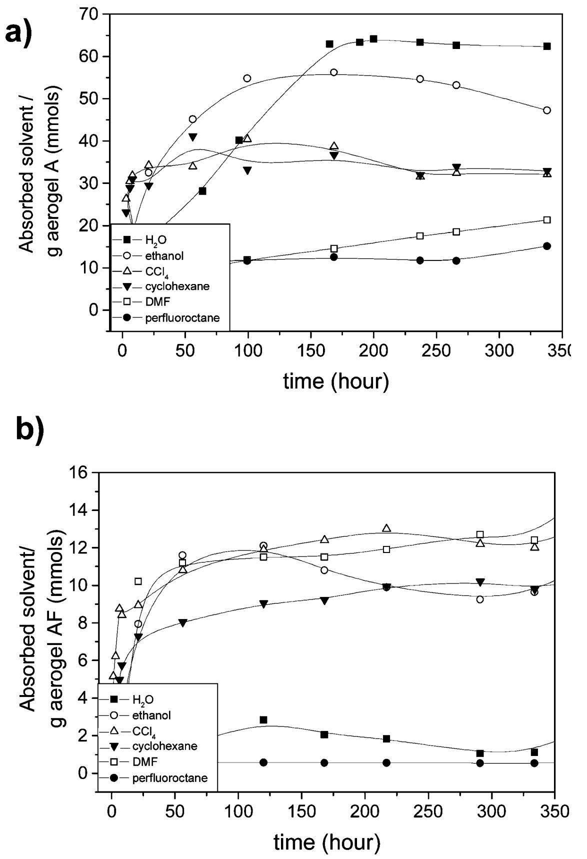

Fig. 2 a: mmols of solvents absorbed per gram of material A; b: mmols of solvents absorbed per gram of material AF.

some conclusions could be drawn when comparing values of solvent absorbed at saturation time, such as, non-fluorinated aerogel A absorbs water with preference to other solvents due to the high hydrophilic character of its surface. Ethanol is second among the series tested. Polarity and ability to participate in hydrogen bonds determines the amount of solvent absorbed (Fig. 2a). On the contrary, fluorinated aerogel AF shows a decreased ability to absorb solvents. In particular, it is reluctant to absorb water whereas non-polar carbon tetrachloride is the solvent more absorbed, albeit in much lower quantities than the non-fluorinated material (Fig. 2b).

Capillary stress is a key point in destroying the gel structure during conventional non-supercritical drying. Thanks to supercritical conditions (no difference between liquid and gaseous phase) an aerogel maintains the wet gel structure. However, for practical reasons alternatives to supercritical drying are sought. Fluorination at the porous surface can avoid shrinkage. In this respect, it is noteworthy to consider the properties of material XF dried at ambient conditions. Although XF was considered in Table 1 as a xerogel, because it was ambiently dried, its properties reveal that it is a highly porous material and it preserves the monolithicity. Therefore, our procedure resembles that of Smith *et al.* who have silylated aerogels surfaces with trimethylchlorosilane to obtain materials that under conventional drying did not experience much-reduced shrinkage.[8]

In summary, we have prepared superhydrophobic highly porous silica aerogels by fluorinating the terminal hydroxyl functions. The aerogels were obtained either by conventional ambient conditions drying (XF) or by supercritical drying (AF). Hydrophobicity test revealed that these materials are very efficient in rejecting water and surface self-cleaning. They are potentially useful and further research is in progress.

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Notes and references

† Typical experimental procedure: a solution of 14 mL of ethanol (Carlo Erba 99,8 v/v), 14 mL of water and a drop of conc. ammonia (Merck 32%) was added dropwise to a stirred mixture of 14 mL (5 mmol of Si) of commercial prepolymerised tetraethoxysilane (TEOS) (H5 from Silbond Corp., 98+) and 10 mL of ethanol. The sol was gellified in cylindrical plastic moulds (*ca.* 2.5 cm diameter) for 15 min. Gels were aged for 5 days while covered with ethanol. The solvent was changed once per day over two days with pure ethanol to eliminate residual water. One sample was not further manipulated for comparison purposes (A, $scCO_2$ drying, *vide infra*) and all the rest were successively treated with ethanol–hexane mixtures with increasing hexane content until complete replacement of the ethanol. Finally, 10 mL (33.15 mmol) of 1*H*,1*H*,2*H*,2*H*-perfluorooctyldimethylchlorosilane were added to a bath containing seven gels immersed in 92 mL of hexane. An immediate reaction took place with liberation of HCl. Initially the gels floated to submerge again at the end. The gel pieces lost transparency during the process. Solvent exchange to ethanol was performed as above with mixtures of solvents with increasing amounts of ethanol. One sample was dried at ambient conditions (XF). The remaining samples (A and AF) were dried with $scCO_2$ under these conditions: autoclave pressure 100 bar at room temperature, exchange of ethanol by liquid CO_2 over 5 h at 4 kg h^{-1}, raising the temperature to 50 °C to reach supercritical conditions, and finally slowly depressurizing to afford samples labelled as AF. Table 1 gathers some physico-chemical properties of the obtained materials.

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