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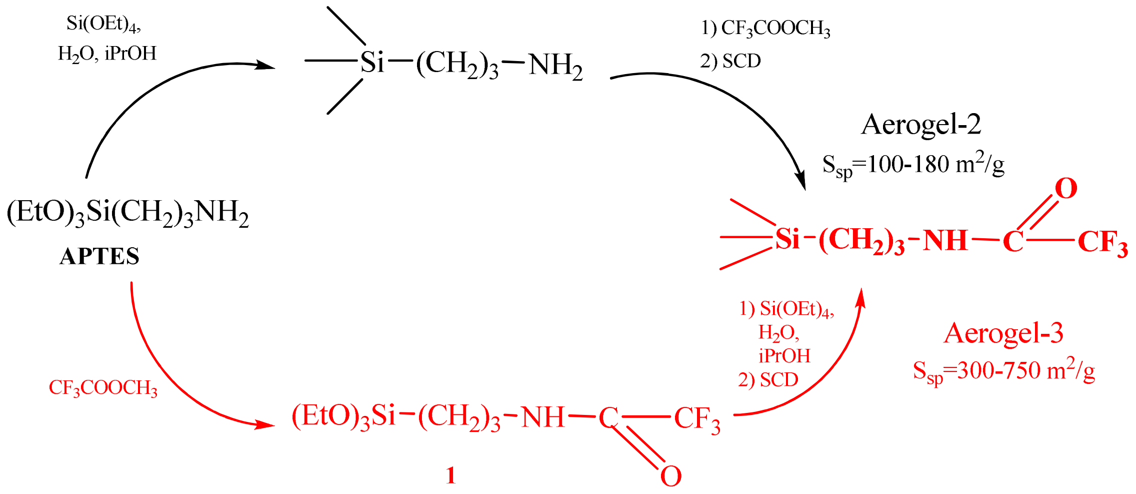
Si(OEt)4, H2O, iPrOH
Si–(CH2)3–NH2
1) CF3COOCH3
2) SCD
(EtO)3Si(CH2)3NH2
APTES
Aerogel-2
Ssp=100-180 m2/g
Si–(CH2)3–NH–C(=O)–CF3
1) Si(OEt)4, H2O, iPrOH
2) SCD
Aerogel-3
Ssp=300-750 m2/g
CF3COOCH3
(EtO)3Si–(CH2)3–NH–C(=O)–CF3
1

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ARTICLE TYPE

Functionalization of aerogels by the use of pre-constructed monomers: a case of trifluoroacetylated (3-aminopropyl) triethoxysilane

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A novel strategy of aerogels' functionalization, based on the preliminary modification of monomers before gelation, is proposed. The strategy is illustrated by the synthesis of trifluoroacetylated (3-aminopropyl) triethoxysilane (APTES)-based aerogels. An aerogel sample prepared by cogelation of APTES with tetraethoxysilane (TEOS), followed by trifluoroacetylation of free aminogroups, had a BET-surface area of 100-180 m^2/g, while the samples prepared by cogelation of a preliminary trifluoroacetylated monomer with TEOS had a 2-5 times larger specific surface area. Trifluoroacetylated aerogels' properties showed strong dependence on the supercritical drying media.

1. Introduction

Aerogels (AGs) are unique mesoporous materials possessing ultra-low density, high porosity and a high specific surface area. AGs are widely used as very effective thermal and acoustical insulators,[1] sorbents,[2-5] catalyst supports,[6] optical materials,[1,7] etc. The preparation of aerogels is a multistage process, typically involving gel synthesis by a sol-gel technique, aging and washing with a desired solvent, followed by supercritical drying (SCD). Alcohols and carbon dioxide (CO_2) are the most conventional types of SCD fluids for aerogels preparation,[8] while other solvents can also be used.[9,10]

The surface composition of aerogels depends on the conditions of SCD treatment. For instance, the surface of aerogels dried in alcohols is covered by corresponding alkyl groups.[8] CO_2-dried aerogels are hydrophilic, as their surface bear highly polar OH-groups. We have recently shown that SCD drying in hexafluoroisopropanol gives an opportunity to obtain aerogels bearing fluoroalkyl groups on the surface.[10]

High hydrophobicity is of critical importance for aerogels, as poor humidity resistance is considered to be one of the major drawbacks preventing their practical use. Usually, hydrophobic aerogels are prepared by trimethylsilylation of surface M-OH groups of SiO_2 and Al_2O_3 based aerogels,[11,12] or by using methyltrialkoxysilanes $CH_3Si(OR)_3$ as gel-forming precursors.[13-15] Polyorganofluorination is another direct way to increase the materials' hydrophobicity. We could find only a few papers concerning the preparation of fluorinated aerogels. In all the cases, polyfluoroalkylsilanes were used as surface modifiers[16] or as co-precursors for AGs' preparation.[3,17,18] The resulting aerogels demonstrated high hydrophobicity and could remove non-polar organics (e.g. oil spills) from water. However, the high cost of starting materials limits the use of thus obtained materials.

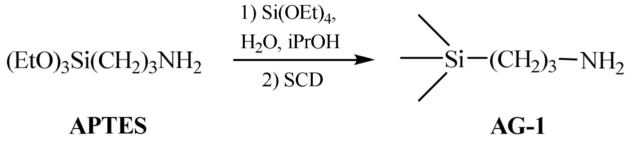
A number of methods for making non-aerogel type SiO_2-based materials hydrophobic via fluorination are known.[19-23] They are commonly based on commercial (3-aminopropyl) trialkoxysilanes ($NH_2(CH_2)_3Si(OR)_3$, R=Me, Et) treatment by polyfluorocompounds, mainly polyfluorocarbonic esters and polyfluorosilanes. Upon hydrolysis, superhydrophobic materials were obtained but no aerogels of this type were reported.

The present work is focused on the elaboration of novel types of fluorinated aerogels, namely those ones bearing a stable trifluoroacetylamide bond, on the basis of (3-aminopropyl) triethoxysilane (APTES). APTES-based aerogels have been recently described in a number of works.[24-31] The presence of reactive amino-groups can be used for further modification of aerogels properties: for instance, the cross-linking of the aerogels network by isocyanates,[24] epoxides[25-27] and styrene[28] increased the strength, hydrophobicity and flexibility of these materials. The fluorinated derivatives of APTES aerogels have not been studied yet. The preparation of such derivatives is of undoubted interest, since the presence of trifluoromethyl groups could increase the hydrophobicity of aerogel materials in an easy and affordable way.

To prepare trifluoroacetylated aerogels, we have used two protocols, namely the preparation of aerogels bearing aminogroups, with their subsequent acetylation, or the synthesis of trifluoroacetylated monomers and their subsequent gelation and SCD. The latter route is the first example of our new strategy of preparation of functionalized aerogels by using pre-constructed monomers. Several solvents were used for SCD of aerogels to determine the influence of SCD media on the chemical composition and texture properties of the fluoroamide aerogels.

2. Results and discussion

Silica-based aerogels modified by 20% mol of APTES were prepared by a two-step co-gelation procedure[27] (Scheme 1).



Scheme 1

SCD of wet gels in different solvents (Table 1) results in the formation of white opaque fragile monoliths. They sink and crack immediately when placed into water.

The specific surface area of thus prepared aerogels (**AG-1** series) only slightly depends on the solvent used for SCD (Table 1).

Two synthetic strategies were further used to prepare **AG-2** and **AG-3** fluorinated aerogels (Scheme 2):

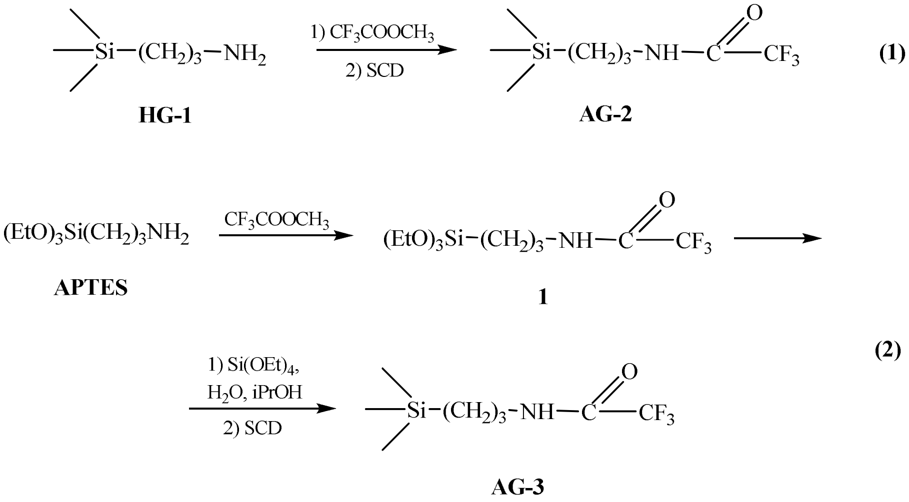
1. Acylation of **AG-1** by methyltrifluoroacetate (**AG-2**) (Scheme 2, Equation 1);
2. Preliminary acylation of APTES, followed by gelation and SCD (**AG-3**) (Scheme 2, Equation 2).

The **AG-2** sample was supercritically dried in isopropanol only; samples belonging to the **AG-3** series were dried in different solvents (Table 1).

Table 1 Texture properties of aerogels

Sample	APTES:TEOS mol	Specific surface area (m^2/g) SCD solvent							bulk density (g/cm^3)
		MeOH	i-PrOH	HFIP	TFE	CO_2	Et_2O	MTBE	
AG-1	1:4	120±15	100±10	110±10	140±15	135±15	140±15	180±20	0.15*
AG-2	1:4	-	130±15	-	-	-	-	-	-
AG-3	1:4	280±30	500±60	640±80	590±70	750±90	320±40	375±40	~0.5*

* for isopropanol dried samples



Scheme 2

According to low temperature nitrogen adsorption data, **AG-1** and **AG-3** aerogels prepared by supercritical drying in isopropanol have specific surface areas of 100 and 500 $m^2 \cdot g^{-1}$ respectively. Adsorption–desorption isotherms presented in Figure 1 show that absolute adsorption values for the **AG-1** sample are significantly lower than for the corresponding **AG-3** sample. The adsorption-desorption isotherm for the **AG-1** sample is close to Type II, with the H3 type hysteresis loop corresponding to slit-like mesopores. The adsorption–desorption isotherm for the **AG-3** sample is of Type IV, with a pronounced hysteresis loop close to the H2 type, indicating a presence of ink-bottle mesopores.

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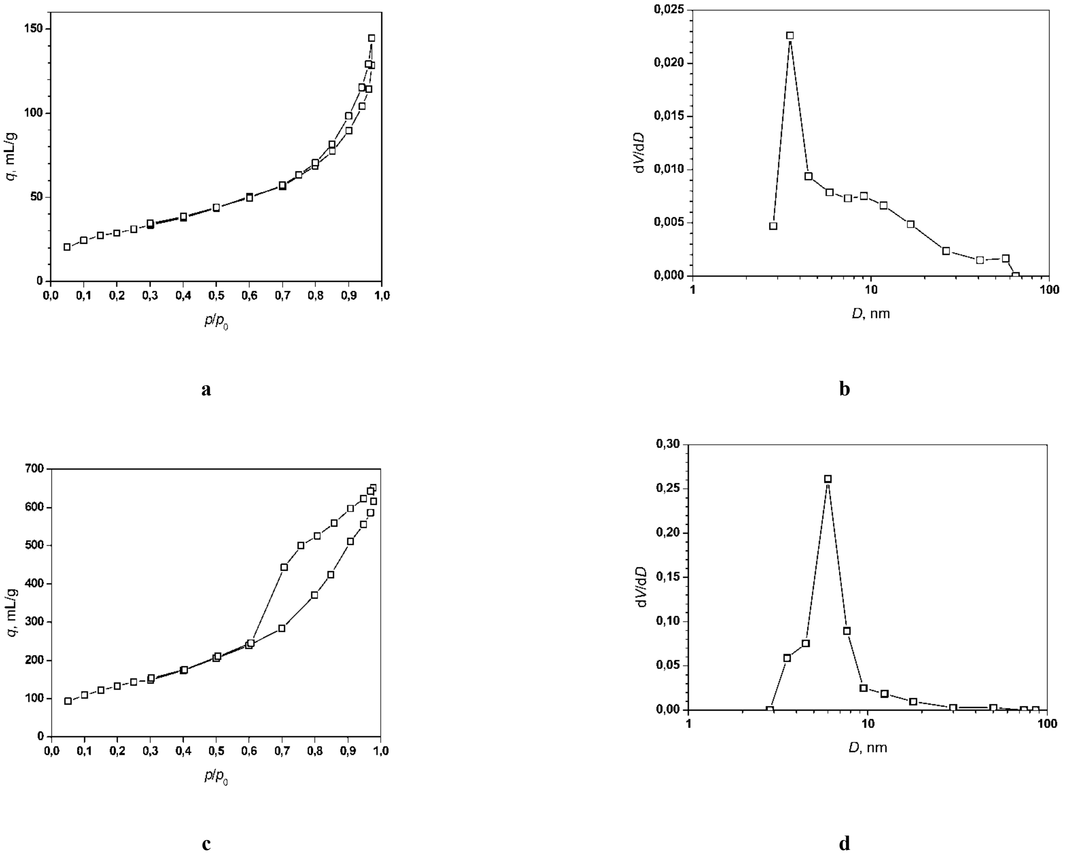


a

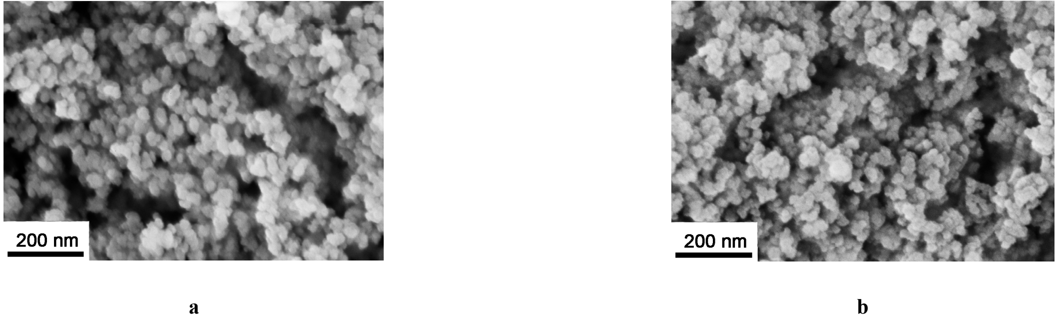
b

c

d

Fig. 1 Adsorption–desorption isotherms and pore size distributions for **AG-1** (**a**, **b**) and **AG-3** (**c**, **d**) aerogels prepared by supercritical drying in isopropanol.

High resolution SEM images of **AG-3** samples are shown in Figure 2 (c,d). The particle size of CO_2-dried aerogel (~10 nm) is considerably smaller than the particle size of isopropanol-dried one (~15-20 nm), being in good agreement with nitrogen adsorption data (higher specific surface area corresponds to smaller particle size). The interparticle pores size is close to the particles size in both cases. SEM data for **AG-1** samples dried in various solvents (Figure 2 a,b) are also in a good coincidence with BET surface area measurements. The particle size in the latter samples is much greater than in **AG-3** aerogels.



a

b

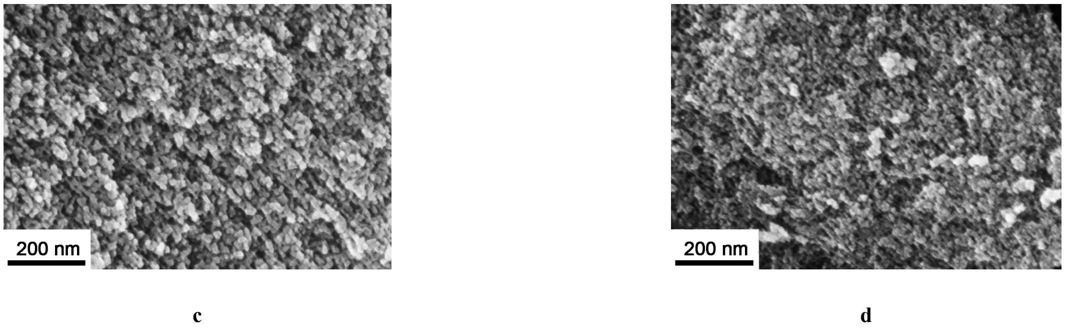
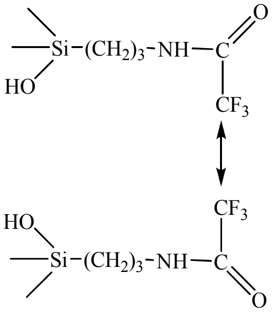


Fig. 2 SEM images of **AG-1** aerogels dried in isopropanol (**a**) and MTBE (**b**), and **AG-3** aerogels dried in isopropanol (**c**) and CO_2 (**d**)

Upon SCD the matrix of aerogels becomes rigid enough. This can be illustrated by comparison of the texture properties of **AG-1** and **AG-2** aerogels dried in isopropanol (Table 1). One can see that acetylation of the pre-formed **AG-1** aerogel doesn't result in any notable change of its surface area. In contrast, the specific surface area of **AG-3** samples prepared from the preliminary acetylated precursor **1** is 2-5 times higher, thus indicating formation of a new matrix. This phenomenon can be explained by a strong repulsion of surface CF_3-groups, preventing the thickening of the aerogels' walls (Scheme 3):



Scheme 3

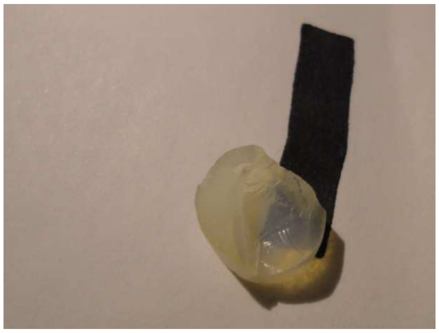
We can conclude that the preparation of fluorinated aerogels of the same chemical composition but having a different matrix is possible simply by changing the synthetic procedure.

It is worth noting that the specific surface area of **AG-3** amide-modified aerogels dried in alcohols - hexafluoroisopropanol. trifluoroethanol and isopropanol is considerably higher compared to the samples dried in methyl tert-butyl and diethyl ethers. We have recently shown that a solvent used for SCD indeed affects aerogels' texture characteristics, including specific surface area and porosity.[9,10] The mechanism of such an influence is not clear yet, while the data presented here confirm this phenomenon. We suppose that some kind of aerogel structure rearrangement could occur during SCD of wet gels (*i.e.* dissolution – precipitation in supercritical fluid), causing the change in the aerogels' properties. We can also state that this influence is not universal, since the change of SCD fluid does not affect the **AG-1** properties.

AG-3 aerogels are much more transparent compared to opaque **AG-1** samples (Figure 3). The optical transmittance of 4 mm thick isopropanol-dried **AG-3** sample was 65% at 600 nm. There are only a few data on hydrophobic aerogels transmittance, silylated silica aerogels being the most transparent (up to 90-94% at 550-700 nm, thickness not defined)[11,32].

AG-3 aerogels appear to be hydrophobic: CO_2- and MTBE-dried **AG-3** samples floated on water surface for at least several weeks. According to water drop contact angle (θ) measurements, the θ values for CO_2- and HFIP-dried **AG-3** aerogels are 99° and 139° respectively (see Figure S1). It should be noted that the variation of the contact angle with the change of the supercritical drying media has never been reported before. A detained study of this phenomenon will be published elsewhere.

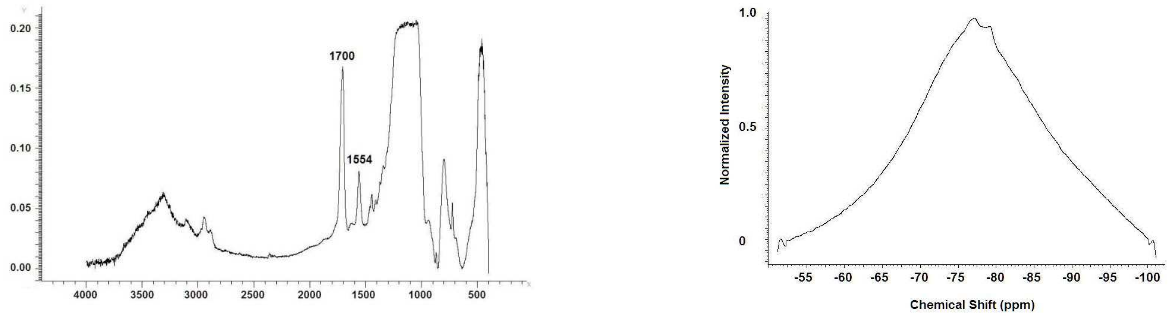
Our data indicate that introduction of only 20% mol. of CF_3-groups allows overcoming a very high hydrophilicity of the silica matrix and to produce hydrophobic aerogels. The most hydrophobic aerogels reported to date in the literature are made from methyltrialkoxysilans $CH_3Si(OR)_3$ (θ = 150-172°).[2,13,15,33] The contact angle values for polyfluoroalkyl-modified aerogels vary from 128 to 150°.[3,4,16,17] For APTES-based hydrophobic aerogels, the contact angle reported are 150° (perfluorophenyl-substituted aerogel,[28] and 91° (isocyanate-modified aerogel containing the $(CH_2)_3$-NH-C(O)-moiety.[30]



a b

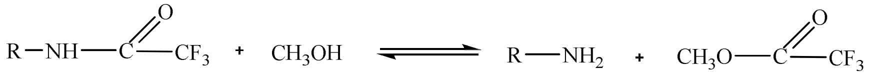
Fig. 3 Pictures of **AG-1** (**a**) and **AG-3** (**b**) aerogels supercritically dried in isopropanol.

IR spectra of amide-modified **AG-2** and **AG-3** aerogels dried in ethers, CO_2, trifluoroethanol, hexafluoroisopropanol and isopropanol, contain the signals of amide groups (1700 and 1554 cm^{-1}, Figure 4a), and ^{19}F NMR spectra contain a broad signal of the CF_3-group (Figure 4b), evidencing the presence of CF_3CONH-moiety. The EDX spectra of **AG-3** samples dried in isopropanol and methyl tert-butyl ether reveal the ratio F:Si = 0.52 and 0.77, respectively, which is reasonably close to the theoretical value of 0.6 for trifluoroacetylated aerogels containing 20% mol of APTES. Only traces of trifluoroacetylamide fragments could be found in methanol-dried **AG-3** aerogels, so we can conclude that SCD of **AG-3** in methanol leads to a nearly complete removal of trifluoroacetamide groups from aerogels. Evidently, alcoholysis by the most nucleophilic methanol is the main reason for the amide groups' disappearance (Scheme 4).



a b

Fig. 4 Typical IR (**a**) and ^{19}F NMR spectra (**b**) of **AG-3** aerogel (sample supercritically dried in methyl tert-butyl ether).



$$R{-}NH{-}C(=O){-}CF_3 + CH_3OH \rightleftharpoons R{-}NH_2 + CH_3O{-}C(=O){-}CF_3$$

Scheme 4

3. Materials and methods

3.1. Materials

Methyl trifluoroacetate (MTFA, Acros, 99%), tetraethylorthosilicate (TEOS, Acros, 98%), (3-aminopropyl) triethoxysilane (APTES, Acros, 99%), isopropanol (Acros, 99.5+%), methanol (MeOH, Acros, 99.9%), hexafluoroisopropyl alcohol (HFIP, Aldrich 99%), trifluoroethanol (TFE, Acros, 99.8%), methyl tert-butyl ether (MTBE, Acros 99%), diethyl ether (Et_2O, Acros 99+%), HF (Acros, 40% aqueous solution) were used without further purification.

3.2. Synthesis of (3-trifluoroacetylaminopropyl) triethoxysilane (1)

3.27 g (0.0255 mol) of MTFA and 4.71 g (0.0213 mol) of APTES (the molar ratio MTFA:APTES=1.2:1) were separately cooled in an ice-water bath, placed into a stainless steel autoclave and heated at 110° C for 2 hours. The product obtained was evacuated (25° C, 0.0067 MPa) to remove all volatile products.

The ^1H NMR spectrum ($CDCl_3$), δ_H (ppm): 0.63 t (2H, $^3J_{HH}$ 7.83 Hz CH_2-Si), 1.19 t (8.2H, $^3J_{HH}$ 6.85 Hz CH_3-CH_2-O), 1.69 qui (2H, $^3J_{HH}$ 7.34 Hz CH_2-CH_2-CH_2), 3.32 qua (2H, $^3J_{HH}$ 6.36 Hz CH_2-NH), 3.52 s (0.8H CH_3-O), 3.79 qua (5.4H, $^3J_{HH}$ 7.34 Hz CH_2-CH_2-O), 7.34 broad s (1H CH_2-NH). ^{19}F NMR: -77.7 s.

3.3. Preparation of aerogels

3.3.1 Amine-modified silica hydrogel (HG-1) and aerogel (AG-1)

2.78 g (0.0134 mol) of TEOS and 0.74 g (0.0033 mol) of APTES (the molar ratio TEOS:APTES=4:1) were dissolved in 3.0 g (0.05 mol) of isopropanol, followed by the addition of 1.2 g (0.067 mol) of deionized water. The solution obtained was stirred for 2-3 minutes and then poured into cylindrical polypropylene containers, sealed and allowed to gelate and age for 24 h. The resulting hydrogel (**HG-1**) was soaked in isopropanol, methanol, 2,2,2-trifluoroethanol, hexafluoroisopropyl alcohol, diethyl ether, or methyl tert-butyl ether for 24 h to exchange the mother liquor for the solvent chosen. This procedure was repeated five times. The gels formed were then placed into an autoclave or supercritical CO_2 extraction chamber for supercritical drying.

3.3.2 Amide-modified silica hydrogel (HG-2) and aerogel (AG-2)

Hydrogel (**HG-1**) obtained as described above, and a solution of 0.508 g (0.004 mol) MTFA in isopropanol (6 ml) (the molar ratio MTFA:APTES=1.2:1), were placed into a stainless steel autoclave and heated at 125° C for 2 h. The hydrogel obtained (**HG-2**) was soaked in isopropanol for 24 h to remove unreacted products. This procedure was repeated five times. Then the gel formed was placed into an autoclave for supercritical drying.

3.3.3 Amide-modified silica hydrogel (HG-3) and aerogel (AG-3)

6.96 g (0.0334 mol) of TEOS and 2.67 g (0.0084 mol) of (**1**) were mixed with 7.54 g (0.1254 mol) of isopropanol in a plastic beaker. 3 g (0.167 mol) of deionized water and 0.2 g of 40% HF solution were mixed in another plastic beaker. The second solution was added to the first solution in one portion, stirred for 2-3 minutes and then poured into cylindrical polypropylene containers, sealed and allowed to gelate and age for 24 h. The resulting hydrogels (**HG-3**) were soaked in isopropanol, methanol, 2,2,2-trifluoroethanol, hexafluoroisopropyl alcohol, diethyl ether, or methyl tert-butyl ether for 24 h to exchange the pore liquid for the solvent chosen. This procedure was repeated five times. The gels formed were placed into an autoclave or supercritical CO_2 extraction chamber for supercritical drying.

3.4 Supercritical drying

Supercritical drying was performed as follows: A gel sample in a glass tube containing ~ 14-16 mL of an appropriate solvent was placed into a stainless steel autoclave (V ~ 40 mL). The autoclave was sealed and heated to a temperature exceeding the critical temperature of the solvent. The heating rate was approximately 100 °C/h. For isopropanol, methanol, diethyl ether, hexafluoroisopropyl alcohol, methyl tert-butyl ether and 2,2,2-trifluoroethanol, the drying temperatures were 250–260 °C (the measured pressure in the autoclave at the beginning of the drying procedure reached 6.0–7.0 MPa), 255–265 °C (9.0–10.0 MPa), 210–220 °C (5.0–6.0 MPa), 240–250 °C (4.5–5.5 MPa) and 240–250 °C (6.0–7.0 MPa), respectively. After reaching the desired temperature, the valve was opened; the pressure was evenly decreased to the atmospheric pressure over 2 hours. The hot autoclave was then evacuated for 30 min, cooled to room temperature and opened.

SCD in CO_2 was performed at 50º C and 15 MPa.

3.5 Characterization of aerogels

The specific surface area of aerogels was determined by low-temperature nitrogen adsorption measurements with an ATX-06 analyzer, by an 8-point BET method. Experimental values were plotted against P/Po according to the BET equation; the correlation coefficient, r, of the linear regression was not less than 0.9975.

High resolution ^1H and ^{19}F NMR spectra were obtained in $CDCl_3$ on a Bruker DPX-200 spectrometer at the Larmor precession frequencies of 200 and 188 MHz, respectively, relative to TMS and $CFCl_3$.

Solid state ^{19}F NMR experiments were performed on a Bruker Avance III 400 spectrometer, with $CFCl_3$ as the external reference. Larmor precession frequency was 376.5 MHz. ^{19}F NMR spectra were recorded using 9 μs pulse length, accumulating 64 repetitions for each spectrum.

Infrared Fourier spectroscopy (IR) was performed on a Bruker IFS-113V spectrometer in a 4000–350 cm^{-1} region (KBr pellets, 0.25-0.5 % mass sample content).

Microstructure of the samples was studied using Carl Zeiss NVision 40 scanning electron microscope (SEM) at 7 kV acceleration voltage. Before measurements samples were coated with Au/Pd conductive layer. Energy dispersive X-ray analysis (EDX) was performed using an Oxford Instruments X-MAX analyzer operating at 20 kV accelerating voltage.

Transmittance spectra of specially fabricated isopropanol dried **AG-3** sample having plane parallel surfaces (4 mm thick) were obtained using Ocean Optics USB 4000 UV-vis spectrometer equipped with DH 2000 halogen-deuterium light source.

Sessile water drop (~3 μL) contact angles were measured on a FTÅ200 (First Ten Angstroms, Inc., USA) instrument. Images obtained were analyzed using standard FTÅ200 software.

Conclusions

We have demonstrated that the surface modification of silica-based aerogels can be easily achieved by the formation of stable amide bonds. This strategy was illustrated by two different approaches, leading to the formation of fluorinated aerogels, e.g. acylation of APTES aerogels or preliminary preparation of acylated APTES, followed by gelation and supercritical drying in alcohols, ethers or CO_2. Aerogels prepared by different techniques possess notably different characteristics – the specific surface area of samples made from a pre-constructed acetylated precursor is 2-5 times larger than that of post-acetylated aerogels. Trifluoroacetylated APTES aerogels are much more transparent, hydrophobic and stable in water compared to non-fluorinated ones.

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Notes and references

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