

Short communication

Mesostructured fluorocarbon–silica hybrid materials with a low dielectric constant

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Received 15 September 2006; received in revised form 6 November 2006; accepted 7 November 2006

Available online 15 November 2006

Abstract

The properties of a fluorocarbon–silica hybrid prepared by sol–gel hydrolytic polycondensation using a non-ionic fluorocarbon surfactant as a structure-directing agent are studied by small angle X-ray scattering, scanning electron microscopy, ²⁹Si MAS-NMR, thermogravimetric analysis and dielectric relaxation. The obtained hybrid material consists mainly of micron-sized spherical particles with an internal two-dimensional hexagonal (*p6mm*) nanostructure. The material is thermally stable (with a high proportion of fully cross-linked silica) and shows a very low dielectric constant (about 2.15), which can be interesting from the point of view of applications.

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Keywords: Fluorocarbon surfactant; Mesostructured silica; Small angle X-ray scattering; Thermogravimetric analysis; Dielectric behavior

1. Introduction

The functionalization of silica with fluorocarbon chains is interesting for applications such as protective coatings [1] and low dielectric constant materials for semiconductors [2]. Although ultra-low dielectric constants (values lower than 2) have been reported for high-porosity silica aerogels or xerogels [3,4], the weak structural stability of these materials is unsuitable for the actual manufacturing processes. In this case, hybrid materials could be an interesting alternative because the component with low dielectric constant is an organic compound instead of air, and therefore an improvement in mechanical properties could be expected. Recently, it has been shown that fluorinated surfactants can act as structure-directing agents in the formation of mesostructured inorganic materials by cooperative self-assembly [5–7]. Most reports on this subject have been focused on the characterization of mesoporous materials after surfactant removal, and comparatively little has been published on the properties and possible applications of inorganic–organic hybrids containing embedded surfactant molecules.

In this context, we present here a brief report on a hybrid fluorocarbon–silica material prepared by sol–gel hydrolytic polycondensation of an alkoxysilane in the presence of a non-ionic fluorinated surfactant, which acts as a structure-directing agent. To our knowledge, this is the first report on the dielectric behavior of these kind of materials.

2. Experimental

2.1. Materials

Tetraethyl orthosilicate (TEOS), 99.999%, was supplied by Aldrich. A fluorinated surfactant, with the general structure $\text{CF}_3(\text{CF}_2)_7\text{SO}_2-[\text{CH}_3(\text{CH}_2)_2\text{N}-(\text{C}_2\text{H}_4\text{O})_{10}\text{H}]$, designated commercially as EF122B, was kindly provided by Mitsubishi Materials (Japan). Milli-Q purified water was used in all the experiments.

2.2. Synthesis of mesoporous silica

The hybrid fluorocarbon–silica material was obtained by a procedure based on the well-known precipitation method [6]. The synthesis was carried out by adding TEOS to an aqueous

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solution containing surfactant and hydrochloric acid. The mass ratios were surfactant/HCl(aq.) 5 M/TEOS = 5/90/5. The samples were kept at 60 °C for 24 h, stirred by magnetic agitation. Afterwards, they were aged at 80 °C, without agitation, for 24 h to increase silica cross-linking. Finally, the precipitate was dried for 24 h at 60 °C. Pure silica was prepared following the same procedure but without adding surfactant.

2.3. Characterization

Small angle X-ray scattering (SAXS) measurements were performed in a Nanoviewer Instrument, from Rigaku Corporation (Japan), equipped with point collimation and a CCD Camera as detector, operated with a 40 kV and 20 mA power beam. The samples were placed in a sample holder 1 mm thick and sealed by Mylar film. Bragg spacings were calculated by $d = \lambda/2 \sin(\theta)$ where λ is the radiation wavelength (0.159 nm) and θ is the scattering angle.

^{29}Si MAS-NMR spectra of powdered samples were recorded at the magic angle in an Inova 750 spectrometer. The spinning frequency was 7 kHz. Time intervals of 5 s between successive accumulations were selected for the Si nuclei and 1600 accumulations were recorded. Tetramethylsilane was used as internal reference.

Scanning electron microscopy (SEM) images were taken using a LEO-435VP instrument operating at a maximum voltage of 30 kV.

Thermogravimetric analysis (TGA) (Perkin-Elmer TGA 7) was conducted in air at a heating rate of 5 °C/min to monitor the calcination process of composites.

Dielectric properties of the prepared materials at room temperature were determined by means of the parallel-plate capacitor method. The capacitance (C) and loss factor (D) were measured with a commercial Agilent 16451B test fixture coupled to an Agilent 4284A LCR-meter, in a frequency range of 10^4 to 10^6 Hz. Prior to the measurement, the powder sample was compacted into circular pellets (typically 10 mm in diameter and 1 mm thick), applying a uniaxial pressure of 6 t/cm². The samples were dried at 60 °C before performing all the measurements. The dielectric constant was calculated from the following expression:

$$\epsilon'_r = \frac{h}{A} \frac{C}{\epsilon_0}$$

where h is the thickness of the pellet (measured with a digital caliper), A the contact area between the sample and the electrode, ϵ_0 the permittivity of the free space (8.85×10^{-12} F/m) and C is the capacitance obtained at each frequency.

3. Results and discussion

The X-ray diffraction spectrum of the fluorocarbon–silica hybrid material is shown in Fig. 1. Three reflections were obtained indicating the existence of a supramolecular structure. The positions of peak maxima correspond to d spacings with approximate ratios $d_1 : d_2 : d_3 = 1 : \sqrt{3} : 2$, which can be assigned to a two-dimensional hexagonal ($p6mm$) struc-

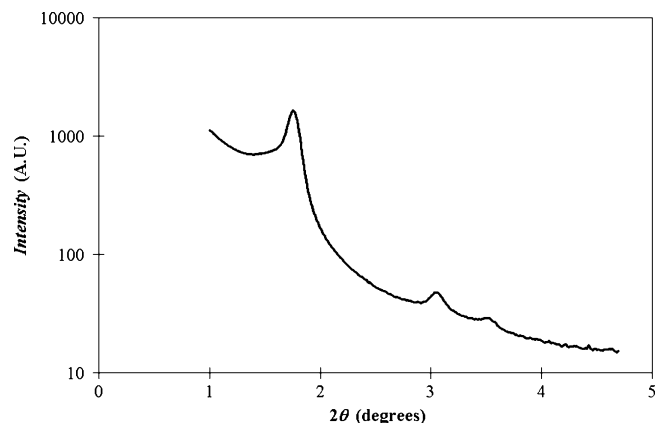


Fig. 1. SAXS pattern of fluorocarbon–silica hybrid material.

ture, similar to that of mesoporous materials prepared using the same surfactant [6,7]. According to such a structure, the hybrid material would be made (at nanoscale) of aligned fluorinated cylinders embedded in a silica matrix. The distance between the centers of the cylinders in the hexagonal array, given by $2d_1/\sqrt{3}$, is 6.7 nm.

According to the SEM image of Fig. 2, the hybrid material mainly consists (at micron scale) of spherical particles, although some short rods are also present. The spherical particle shape suggests that the surfactant–silica mixture has sufficient time and driving force to reorganize at the interface and to minimize the surface area of contact between the particle and the surrounding fluid [8]. It is apparent that in the present case there is no direct relationship between the structure at nano- and micro-scales, as in other mesostructured siliceous materials [5].

The ^{29}Si C-MAS spectrum of the hybrid material is presented in Fig. 3. Two peaks corresponding to full cross-linked Q₄ Si(OSi)₄ tetrahedra (−110 ppm) and to Q₃, HOSi(OSi)₃, sites (−98 ppm) are found [9]. From the Q₄/Q₃ ratio, it is estimated that about 70% of the silica is fully cross-linked.

As can be seen Fig. 4, TGA results indicate that there are two thermal decomposition events, one starting at around 100 °C

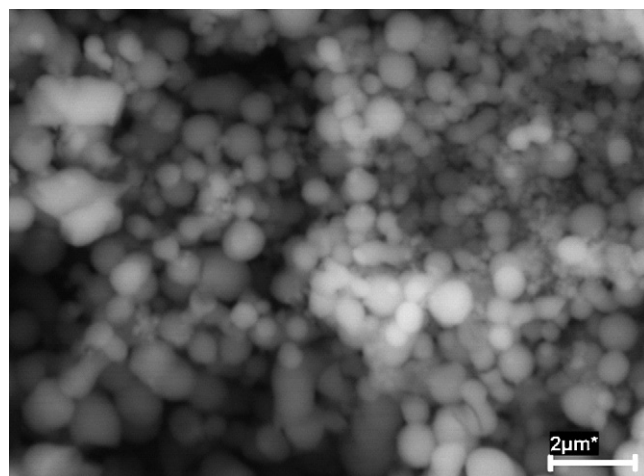


Fig. 2. SEM image of the fluorocarbon–silica hybrid material.

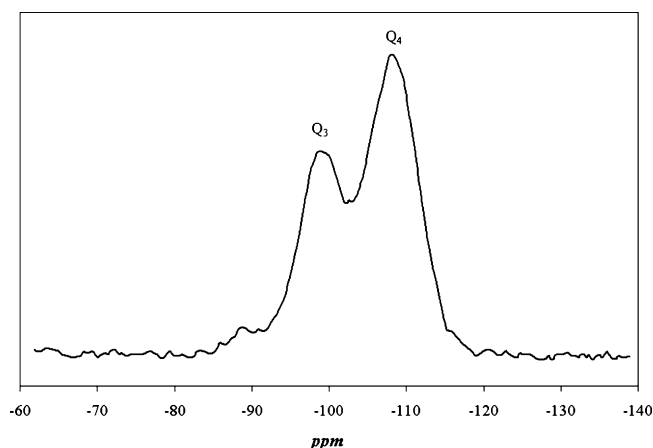


Fig. 3. ^{29}Si C-MAS spectra of the fluorocarbon-silica hybrid material.

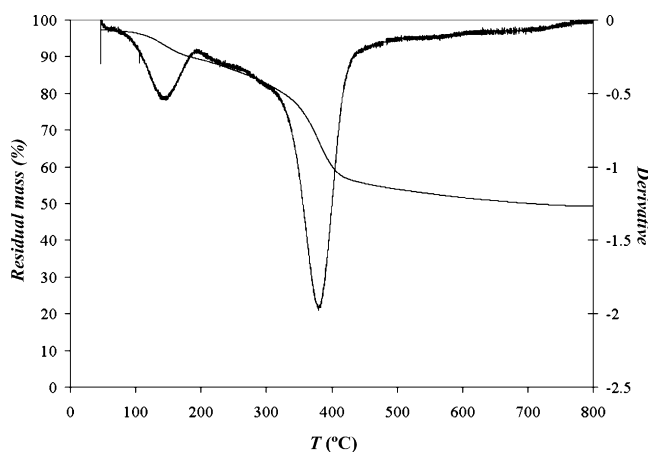


Fig. 4. TGA curve for the fluorocarbon-silica hybrid material.

and finishing at around 200 °C, and the other starting at around 300 °C and finishing at around 450 °C. The first event can be assigned to the release of water formed from the condensation of silanols in the silica framework [10], while the second is

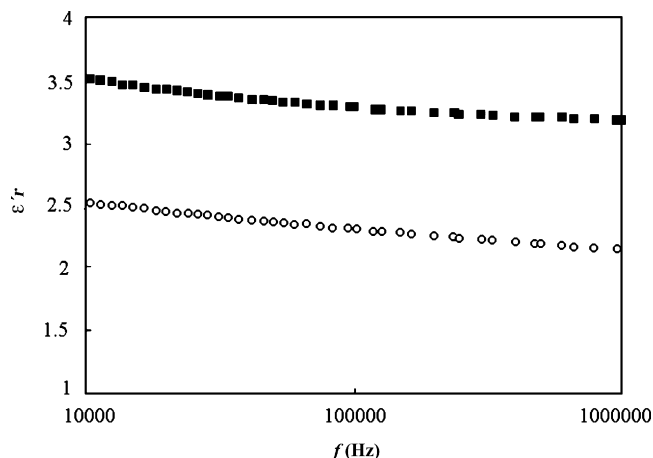


Fig. 5. Dielectric constant as a function of frequency for pure silica (squares), and fluorocarbon-silica hybrid material (circles).

attributed to the thermal decomposition of the embedded surfactant, which occurs at 380 °C according to derivative data. About 50 wt.% of the original mass still remains at 800 °C, indicating a relatively high thermal stability.

Fig. 5 shows the real part of the relative dielectric permittivity, the dielectric constant ϵ'_r , as a function of frequency for the hybrid material and pure silica (prepared as described in Section 2). An almost flat response can be observed, indicating the absence of any relevant dielectric relaxation in the experimental frequency range [11]. The dielectric constant for the hybrid material is significantly lower than that of pure silica, and near the value for polytetrafluoroethylene ($\epsilon'_r = 2$), which is attractive for possible applications such as protective coatings and semiconductors.

4. Conclusions

Hybrid fluorocarbon-silica materials consisting of micron-sized spherical particles with hexagonal nanostructure were synthesized by using a non-ionic fluorinated surfactant as a structure-directing agent. The prepared material is thermally stable and, more interestingly, has a very low dielectric constant (2.15), which is almost independent on frequency.

Acknowledgment

CR and PMB gratefully acknowledge the Ministry of Science and Education of Spain for financial support (J. de la Cierva Program).

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