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Organic low molecular weight aerogel formed in supercritical fluids

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Aerogels of 2,3-didecyloxyanthracene (DDOA) are prepared from supercritical fluids in two different ways. In the first, the gel is formed by mixing DDOA and ethanol, and dried by flushing with supercritical CO_2. This process produces a white, light and friable aerogel (density of 6×10^{-3} g cm^{-3}), constituted of fibers with diameters ranging from 100 to 200 nm. In the second, DDOA is solubilized in supercritical CO_2 to give a gel which is dried under the same experimental conditions. The resulting very low density aerogel (2×10^{-3} g cm^{-3}), has a specific surface equal to 10 m^2 g^{-1}, and constitutes a network of long fibers with diameters varying from 100 to 200 nm.

Introduction

Aerogels are of interest for various applications.[1,2] Thus Cherenkov detectors or micrometeorite receptors are based on silica aerogels and carbon aerogels are useful as insulators or electrodes in supercapacitors. These aerogels are formed following a chemical reaction process, the molecules being linked *via* chemical bonds (covalent, ionic, *etc.*).

Only a few non H-bonding small organic molecules are known to produce physical gels with organic solvents,[3] the gels constructed without any chemical reaction are stabilized through van der Waals force interactions. The 2,3-didecyloxyanthracene (DDOA, see Fig. 1) belongs to this series and, with it, organogels are formed with various solvents at very low concentration.[4] For example, 1 molecule of DDOA gelifies 40 000 molecules of methanol (MeOH) at 25 °C. These gels are made up of a 3D network of fibers with a section of 100 nm.[4] As only van der Waals interactions are required for the 3D network cohesion, the sol–gel transition is thermo-reversible.

However, a gel formed by DDOA and an organic solvent always provides upon drying a xerogel, where the fiber network collapses to a white and dense solid ($\rho = 1.1$ g cm^{-3}) (Fig. 2a), which does not retain the original tridimensional structure of the fibers within the gel. As supercritical fluids have been already used for inorganic[5–7] and organic[8,9] aerogel synthesis (for example, a monolithic aerogel is synthesized by sol–gel polymerization of alkoxysilanes[5]) in order to prevent this collapse and maintenance of the 3D network architecture, we discuss here the use of supercritical fluids as a drying solvent or as a processing medium.

In this paper, original aerogel materials built from a small organic molecule (DDOA) are presented and two methods for production of DDOA aerogels are described. The first method consists of the drying of a DDOA–EtOH gel with supercritical CO_2 (Fig. 2b), in the second, the fiber network formation occurs directly in the supercritical CO_2 medium as no organic solvent is required because CO_2 is gelified.

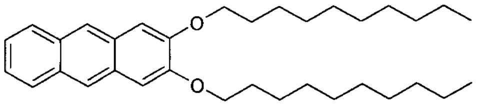

Fig. 1 2,3-Didecyloxyanthracene (DDOA).

Experimental

Materials

The experimental setup (Fig. 3) for the supercritical conditions (30 MPa and 200 °C) essentially consists of a high pressure pump (Thermoseparation - Model 39/2398), a heat exchanger which brings the fluid to the working temperature, and a steamjacket to heat the experimental cell. Temperature (Fe–constantan thermocouple) and pressure sensors control the working conditions. Three different cells are used for the experiments:

(1) A metallic 20 cm^3 vessel.
(2) A sapphire cell for the visual control of the gel drying.
(3) A UV-visible cell equipped with sapphire windows (1 cm optical path length).

The UV spectra are recorded with a Cary-1 (Varian) UV-Visible spectrometer equipped with optical fibers for connecting the spectrometer to the cell. This UV experimental setup was detailed previously.[10]

SEM images were generated with a JEOL 840A, samples were deposited on a conductive surface and covered with vaporized gold. Optical and fluorescent images were performed using a Nikon microscope.

2,3-Didecyloxyanthracene has been synthesized, as previously described.[2] CO_2 (critical temperature and pressure

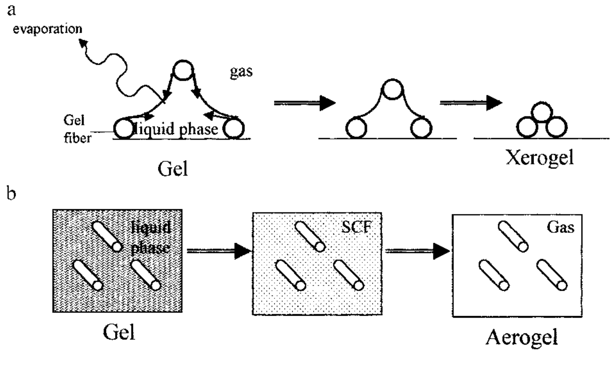

Fig. 2 (a) Schematic representation of the collapse of a network of fibers during the drying of a gel by the usual way; (b) Schematic representation of the drying of a gel using a supercritical route.

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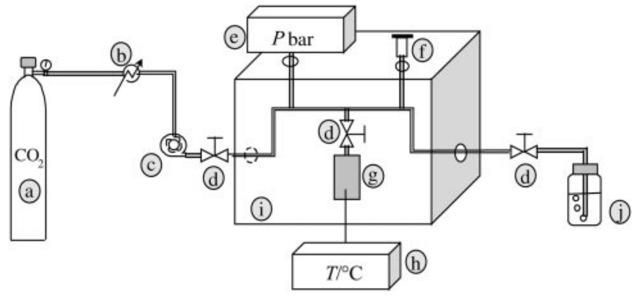

Fig. 3 Experimental apparatus: a CO_2 bottle; b heat exchanger; c high pressure pump; d valve; e pressure sensor; f pressure security; g experimental cell; h temperature sensor; i steam-room; j gas reception.

equal to 31 °C and 7.38 MPa, respectively) was provided by Air Liquide.

Experimental procedures

Liquid gel drying. The DDOA xerogels are obtained by drying a small sample of gel (DDOA–EtOH) under reduced pressure on a conductive surface. The resulting xerogel was treated in the usual way with gold vapor for SEM measurements.

Supercritical gel drying. The drying of ethanol gels by supercritical CO_2 was performed using the following procedure: a sample of gel (4 ml, [DDOA] = 1.2 mol l^{-1}) is introduced to the sapphire cell. At this DDOA concentration the gel is stable up to 62 °C. The pressure and the temperature are taken up to 10 MPa and 47 °C, respectively. These conditions are kept constant for 12 hours. Then a CO_2 flow is applied through the gel during 1 hour to replace ethanol by CO_2. At the end of the procedure, the pressure is first released to atmospheric and then the temperature is decreased to 20 °C. The resulting aerogel, delicately extracted out of the cell, is a light, white and friable solid.

Gel formation in supercritical medium. The formation of DDOA aerogel in supercritical CO_2 requires both higher pressure and temperature than for the drying process in order to obtain the solvation properties of CO_2. A small quantity of DDOA (20 mg) is introduced in a 20 cm^3 steel vessel with a Teflon liner. A summary of the experimental thermodynamic path is depicted in Fig. 4. The system is first heated up to 80 °C (point 1 to point 2) and, after temperature stabilization, the pressure and temperature are increased to 25 MPa and 90 °C, respectively (point 2 to point 3). At this temperature, DDOA is liquid (melting point 87 °C). After keeping these conditions for 1 hour, the system is cooled down to 40 °C (point 3 to point 4) and slowly depressurized to ambient conditions (0.1 MPa and 20 °C) (point 4 to point 1). One must be careful not to cross the liquid–vapor CO_2 curve. At the end of the procedure, a white, light and fragile solid, is obtained. DDOA solubility measurements were performed at 90 °C. The same thermodynamic pathway, as previously described, is followed but pressure at point 3 (Fig. 4) varies from 17 to 30 MPa.

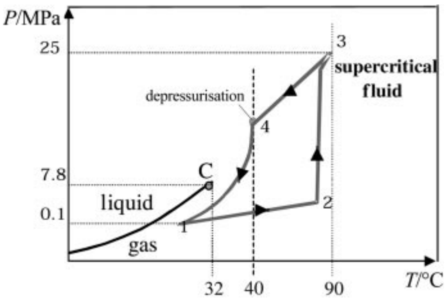

Fig. 4 Thermodynamic path used for DDOA aerogel synthesis using supercritical CO_2 as solvent.

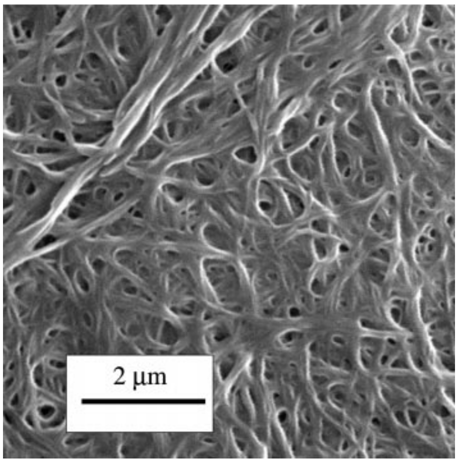

Fig. 5 SEM image of the xerogel of DDOA (gel DDOA–EtOH desolvated under low pressure).

Results and discussion

Liquid gel drying

The drying process with evaporation of a classical solvent leads to a xerogel where all the fibers collapsed into a white and dense solid, the 3D network is destroyed and fibers cannot be extracted from this material. This is showed by the SEM picture (Fig. 5). The characteristics of the resulting solid are due to interfacial forces that emerge during the drying process. A thin film of DDOA appears on the surface of the fibers, it might originate from a post precipitate of DDOA solubilized into supercritical CO_2 in the drying process.

Supercritical gel drying

A microscopic image showing the 3D texture of the fiber network is given in Fig. 6 for material obtained from the supercritical drying conditions. The fibers have a regular and cylindrical shape with diameters ranging from 100 to 200 nm. It indicates that this drying method is probably not so drastic as the classical drying process. Moreover, the DDOA aerogel exhibits a density of 6×10^{-3} g cm^{-3} and a specific surface of 10 m^2 g^{-1}. This surface is estimated from the hypothesis of compacted fibers using a solid density of 1.1 g cm^{-3}. However,

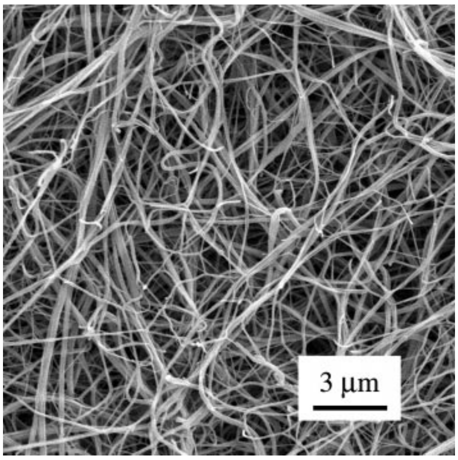

Fig. 6 SEM picture of the DDOA aerogel (gel DDOA–EtOH desolvated under supercritical CO_2 and formed in supercritical CO_2).

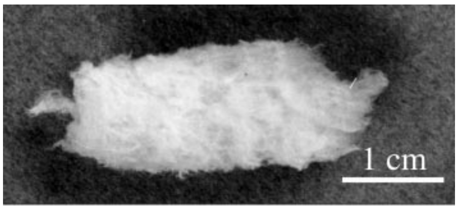

Fig. 7 View of a DDOA aerogel distaff.

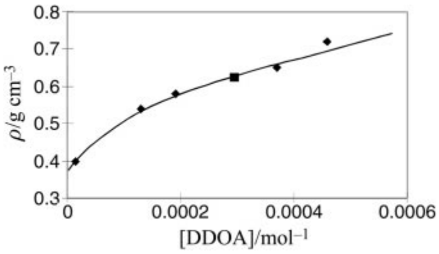

Fig. 8 Solubility of DDOA in supercritical CO_2 *versus* the fluid density at 90 °C.

treatment of the gel is time and CO_2 consuming since the ethanol has to be removed by CO_2 extraction.

Gel formation in supercritical medium

DDOA aerogel formation is performed using supercritical CO_2 as solvent in order to obtain final material without any other solvents. The aerogels formed look like cotton material (Fig. 7) with a density of 2×10^{-3} g cm^{-3}. The DDOA solubility in supercritical CO_2, at 90 °C and variable pressures, is measured using DDOA UV absorption properties ($\varepsilon = 5400$ L mol^{-1} cm at $\lambda = 367$ nm). Solubility values are reported *versus* CO_2 density (Fig. 8). The experimental data are fitted by a logarithmic function as observed classically for the solubility in supercritical solvents. For a CO_2 density of 0.72 g cm^{-3}, the solubility is found equal to 0.47 mmol L^{-1} which corresponds to the maximal concentration detection allowed by our experimental setup.

UV measurements are also useful for determining the sol–gel transition temperature of the DDOA–CO_2 mixture. DDOA electronic transitions show a bathochromic effect when the gel formation occurs. As in liquid solvents, this property is used to define the fiber growing in the supercritical fluid. Fig. 9 shows UV spectra at different temperatures. A weak light diffusion occurs at 83 °C certainly due to a deposition of DDOA on the surface of the cell. Between 83 °C and 75 °C, diffusion strongly increases due to growing of fibers of DDOA and an electronic transition appears at 387 nm which is characteristic of the DDOA solid phase. For saturated concentrations of the gelling agent, the temperature corresponding to fiber growing (between 83 °C and 75 °C) remains constant when the CO_2 density varies. This temperature is 10 degrees lower than the DDOA melting point (87 °C). This behaviour is also observed for gels prepared *via* the liquid process.

DDOA fibers are observed both by optical and SEM analysis. The optical analysis shows long fibers with 1 µm diameter. SME detail of one long fiber evidences the presence of smaller fibers with 100 to 200 nm diameters as reported in Fig. 6. These fibers present a regular cylindrical shape over a relatively large distance.

Various tridimensional flasks can be filled with the DDOA aerogel but due to the mechanical fragility of the material it is necessary to introduce directly the UV cells of 3 cm^3 volume inside the vessel.

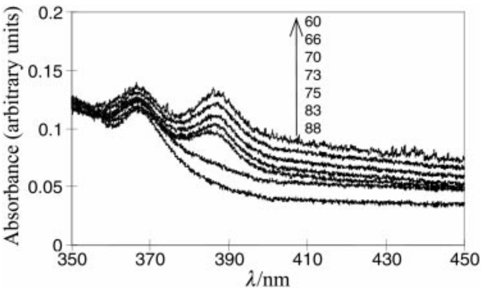

Fig. 9 UV spectral changes of the system DDOA–CO_2 *versus* temperature ([DDOA] = 2.2×10^{-5} M; $\rho CO_2 = 0.4$ g cm^{-3}).

Since DDOA is fluorescent, the fibers in the aerogel can be observed with a microscope at 350 nm excitation light. The fibers display fluorescence and each fiber end is strongly emitting. This suggests that DDOA fibers act as wave guide material. Different applications of these systems can be investigated for example the utilization of fibers as nano-fluorescent detectors.

Conclusion

In conclusion, we have shown that it is possible to obtain DDOA aerogels using two different processes: 1) drying liquid gels with supercritical CO_2; 2) forming the aerogel *in situ* using supercritical CO_2 as solvent. To our knowledge, it is the first time that this type of gel was obtained from small non H-bonding organic molecules and a supercritical process. The characteristics of the aerogels, *i.e.*, low density (2 to 6×10^{-3} g of DDOA cm^{-3}), presence of a network of fibers with diameters ranging from 100 to 200 nm, relatively high specific surface (10 m^2 g^{-1}), allow us to envisage different applications. These materials are soluble in organic solvents and could be used as particle collectors, the particles can be easily separated after solubilisation of the aerogel. The fluorescent capacities of anthracenic groups give interesting properties for the fibers to capture and spread light, which could be used in photo-detectors. Moreover, this highly dispersed material has an important surface, which could be covered with a metal or other compounds and give interesting material catalysis.

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