A simple sol–gel route for the preparation of silica–surfactant mesostructured materials

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Hexagonal silica–surfactant nanocomposite films are successfully prepared by a novel sol–gel process in which alkyltrimethylammonium salts are directly dissolved into pre-hydrolysed tetramethoxysilane.

Self-organization of molecules into highly ordered architectures has attracted a wide range of scientific and practical interests.[1–3] The preparation of mesostructured materials from a cooperative organization of inorganic species and surfactants[4–7] is a current topic mainly because of the possible use of the mesoporous materials derived from the mesostructured composites in molecular sieves, catalysis, and host–guest chemistry.[8–10] The preparation of porous films[11–13] is another key technology for constructing novel advanced materials with specific functions based on their unique microstructures. If the periodic silica–surfactant nanocomposites can be obtained as films, the composite films might be applied to sensors, optical and electronic materials, *etc.* to which powder samples are not accessible.[14] Here I report a novel and simple synthetic route to transparent films of the hexagonal phase of periodic silica–surfactant nanocomposites.

A sol–gel process[15] was employed for the sample preparation. Tetramethoxysilane (TMOS) was partially hydrolysed by a substoichiometric amount of water (molar ratio TMOS : H_2O = 1 : 2) under acidic conditions. Then a given alkyltrimethylammonium salt [$C_nH_{2n+1}N(Me)_3{}^+X^-$ C_nTAC (X = Cl) (n is the number of C atoms in the alkyl chain)] was dissolved directly into the solution, and the mixture vigorously stirred. The solution was spin-coated on a glass substrate and dried; in this manner, transparent films were obtained.

The X-ray diffraction pattern [Fig. 1(*a*)] of the film prepared using C_{16}TAC (molar ratio TMOS : C_{16}TAC in the starting solution = 4 : 1) showed a very sharp diffraction peak at d = 3.7 nm and weaker reflections in the range $4.0 < 2\theta < 7.0°$. (The thickness of the film was determined with a surface profilometer to be *ca.* 2 μm.) These peaks can be indexed on a hexagonal phase, where peaks with d values of 3.7, 2.2, 1.9, 1.4 and 1.3 nm were attributed to (100), (110), (200), (210) and (300) reflections, respectively. This XRD pattern indicates that a hexagonal silica–surfactant nanocomposite can be formed on the substrate as a transparent film by a simple method. The preparation of the inorganic–surfactant composite films has been reported previously for constructing molecularly ordered architectures.[16] The present silica–surfactant composite films can be regarded as a new class of materials owing to their unique structures, transparency, *etc.*

Gel- or glass-like samples were obtained by casting the precursor solution, prepared by the same procedure as above, on a substrate. The XRD pattern [Fig. 1(*b*)] can also be indexed to a hexagonal phase. The powdered samples were used for the following characterization, and conversion to porous materials.

The composition of the product is C, 38.0; N, 2.3; Cl, 5.9%; ash, 41.0%. The Si : C_{16}TAC ratio (4.1 : 1.0) is consistent with the ratio in the starting mixture (4.0 : 1.0). The IR spectrum of the silica–C_{16}TAC nanocomposite showed absorption bands characteristic of C_{16}TAC and silica [*e.g.* ν_{sym} (Si–O–Si) at *ca.* 1230 and 1080 cm^{-1}]. Thermogravimetric analysis of the composites showed a mass loss corresponding to that expected for C_{16}TAC starting from 200 °C and the DTA curve showed an exothermic peak around 300 °C due to oxidative decomposition of C_{16}TAC. These observations indicate that most of the TMOS was converted to silica and quantitatively complexed with C_{16}TAC to form the hexagonal mesostructure. It should be noted here that an advantage of the present reaction is that all the starting components are converted to the product.

The silica–C_{12}TAC and silica–C_{14}TAC nanocomposites also showed X-ray reflections attributable to hexagonal phases. The d_{100} values (3.2 and 3.6 nm for C_{12}TAC and C_{14}TAC composites, respectively) were chain-length dependent, indicating that the surfactant aggregates played an important role in the formation of mesostructures, as reported for other periodic silica–surfactant composite systems.

When the starting solution containing TMOS and surfactant was allowed to react in a closed vessel until gelation, the product was amorphous. Therefore, the periodic structure obtained in the present study is thought to form during the evaporation of volatile components (methanol from TMOS and water), although the state of surfactant in the starting solution is not clear at present.

The hexagonal silica–C_{16}TAC composite was heated in air at 873 K for 1 h, in order to remove surfactant from the composite. No special precautions were required before thermal treatment. The X-ray diffraction pattern of the calcined product is shown

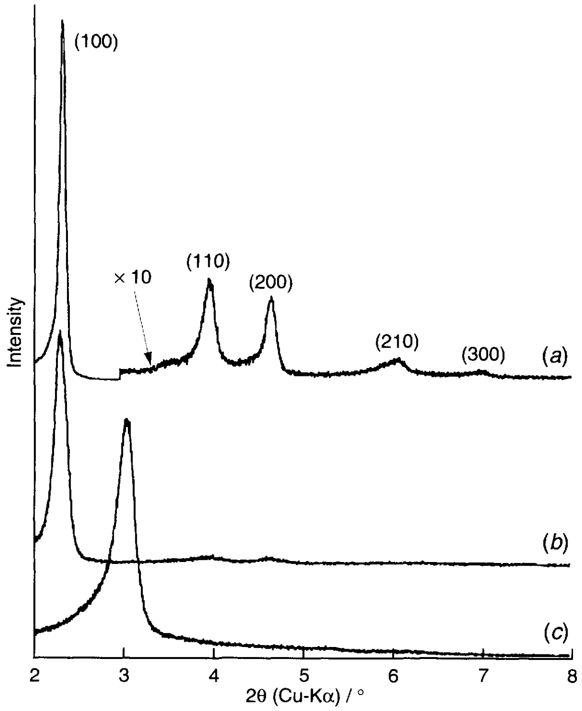

Fig. 1 X-Ray diffraction patterns of (*a*) the silica–C_{16}TAC composite film (TMOS : C_{16}TAC molar ratio = 4 : 1), (*b*) the silica–C_{16}TAC composite and (*c*) calcined (*b*)

in Fig. 1(*c*). The diffraction intensity does not change upon calcination, showing that the ordered structure is maintained even after the removal of the surfactant. The d_{100} value of the calcined product (2.9 nm) was smaller than that of as-synthesized product by *ca.* 0.8 nm. Although similar d_{100} spacings have been observed for a series of MCM-41 materials,[7,17] the origin of the shrinkage is not clear at present.

The nitrogen adsorption–desorption isotherms at 77 K of the calcined sample are shown in Fig. 2. The Brunauer–Emmett–Teller (BET) surface area was >1000 m^2 g^{-1}. From the Horváth–Kawazoe pore-size distribution curve[18] for the calcined product, the average pore diameter was determined to be *ca.* 1.8 nm. These observations indicate that the periodic silica–surfactant nanocomposites synthesized in the present study was successfully converted to porous solids. By subtracting the Horváth–Kawazoe pore size from the repeat distance (*a*) between pore centre (3.3 nm, calculated from XRD data by the relation $a = 2d_{100}/\sqrt{3}$), the framework wall thickness was estimated to be *ca.* 1.5 nm.

Transmission electron microscopy (Fig. 3) of the calcined sample confirmed the porous structure of the silica–C_{16}TAC nanocomposite.

In a further experiment, the precursor solution was cast on a Petri dish and dried slowly, so that a transparent self-standing film was obtained. The X-ray diffraction pattern of the film shows only a broad diffraction peak with $d \approx 4.0$ nm. The broad diffraction of the sample suggests that the composite is composed of an irregular array of cylindrical micelles of C_{16}TAC surrounded by silica. It should be noted that the morphology and the transparency of the film were preserved upon calcination at 873 K in air. The X-ray diffraction pattern of the calcined sample also showed a broad diffraction peak with $d = 3.0$ nm. The BET surface area of the heat-treated film is 1100 m^2 g^{-1}. Thus, a transparent porous self-standing film was obtained.

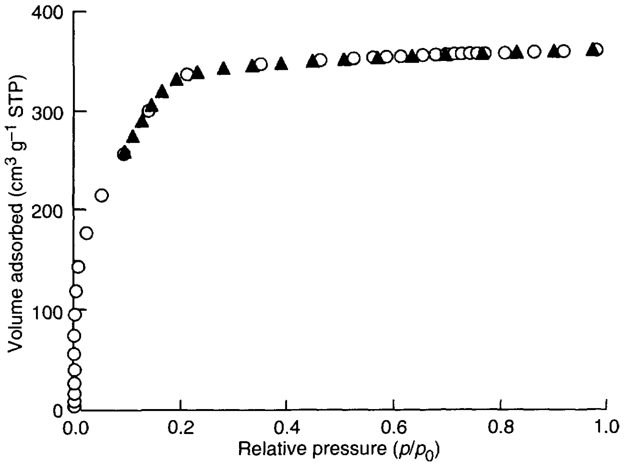

Fig. 2 Nitrogen adsorption–desorption isotherms for the calcined silica–C_{16}TAC composite. Before the measurement the sample was heated for 3 h at 393 K. The isotherms were measured at 77 K.

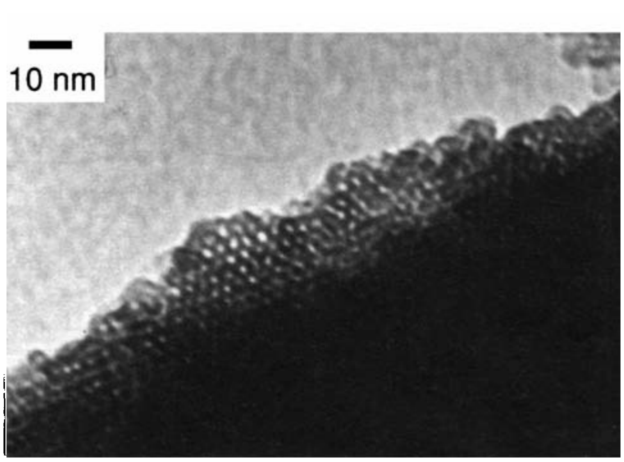

Fig. 3 Transmission electron micrograph of the calcined silica–C_{16}TAC composite

The present paper shows a new and simple way for the preparation of silica–surfactant mesostructures and their conversion to porous materials. Efforts are being made to control the pore size and the wall thickness of the porous materials as well as the morphology of the films, and results will be reported subsequently.

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