ChemComm
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Synthesis of a mesoporous composite material prepared by the self-assembly of mineral liquid crystals

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Received (in Cambridge, UK) 21st June 2002, Accepted 18th July 2002
First published as an Advance Article on the web 30th July 2002

Here we describe the synthesis of a mesoporous composite material using the self-assembly of well defined tubular building blocks obtained from the exfoliation of $[Nb_6O_{17}^{4-}]_n$ sheets.

The synthesis of mesoporous materials has attracted increasing attention due to their use as catalysts, molecular sieves and hosts for inclusion of compounds. Since the characterization by Kresge *et al.* of ordered materials with nanometer-scale periodicities, synthesized from the self-organization of inorganic precursors and organic surfactants,[1] the use of organic liquid crystals has become a standard procedure to synthesize inorganic mesoporous materials. Concurrently, the research field on mineral liquid crystals has grown during the last few years.[2] The use of the properties of such mineral complex fluids, which can have conductimetric or magnetic properties, as templating agents[3] could also permit the synthesis of inorganic–inorganic structured composite materials. In this communication, we report a first attempt at preparing a new mesoporous composite material with large pores based on the direct assembly of hollow tubular inorganic building blocks characterized by large cavities. Our interest turned toward rigid tubular structures with an inner diameter larger than 100 Å because an organized assembly of such objects can directly lead to the synthesis of mesoporous materials (Fig. 1).

Recently, Mallouk *et al.* reported that the exfoliation of the acid-exchanged $K_4Nb_6O_{17}$ with tetra(n-butyl)ammonium hydroxide in water lead to the formation of stable colloidal suspensions of well defined tubular structure formed by scrolling of the niobium sheets.[4] These tubules are 0.1–1 μm in length and have outer diameters ranging from 15 to 30 nm. The wall thickness ranges from 2.4 to 6 nm with a *d*-spacing between the sheets of the wall of 1.05 nm. Moreover, they showed that these tubules are perfectly scrolled at pH = 7 and that, at higher pH, flow uncoils the structure. Lower pH induces a flocculation of the colloids. Physicochemical studies of these colloidal suspensions at higher concentrations are in progress in our laboratory in order to compare their behavior to clays and other mineral layered mesogenic systems.[5]

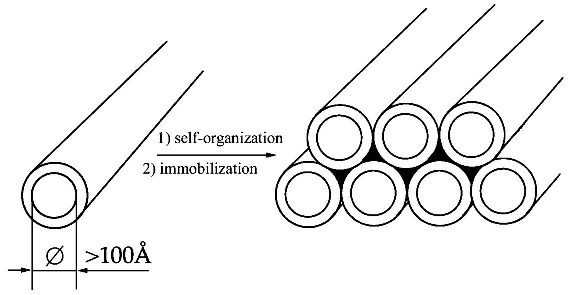

Fig. 1 Schematic representation of a novel route to the synthesis of mesoporous materials by self-assembling of tubular structures. The black zones between cylinders represent a glue, here an aluminosilicate.

The synthesis of our inorganic–inorganic composite material (CMI-1) was adapted from the procedure reported by Goltsov *et al.*,[6] using the tubules of $[Nb_6O_{17}^{4-}]_n$ instead of an organic surfactant. A suspension at 5.6% w/w $[Nb_6O_{17}^{4-}]_n$ tubules was prepared by exfoliation of the acid-exchanged $K_4Nb_6O_{17}$ (as described in ref. 4) with tetra(n-butyl)ammonium hydroxide in water at pH = 12. The pH was adjusted to 7 with 0.1 M HCl. Then, 49.2 mg of an aqueous solution of aluminium sulfate (Aldrich, $n\mathrm{Al_2O_3}$ = 0.14 mmol) was added to 0.5 g of a commercial aqueous solution of sodium silicate (Aldrich, $n(\mathrm{SiO_2})$ = 2.33 mmol, $n(\mathrm{Na_2O})$ = 0.72 mmol, $n(\mathrm{H_20})$ = 17.53 mmol). This mixture was then added, with stirring to 4.53 g of the aqueous colloidal suspension of tubules. The hydrothermal synthesis was performed at 423 K for 48 h in a 60 mL custom-made Teflon-lined stainless steel autoclave. After filtration, the homogenous white powder obtained was washed with distilled water and dried in the presence of P_2O_5.

Energy dispersive X-ray analysis (EDX) experiments performed on an EDAX-equipped JEOL JSM-5800LV scanning electron microscope give the following elemental composition at various points: 1 K : 8 Na : 8 Nb : 3 Al : 24 Si : 79 O. The Si/Al ratio of 8 corresponds well with the initial ratio in the synthesis. It also confirms the incorporation of niobium in the material (Si/Nb = 3). The deduced formulation for CMI-1 is $(\mathrm{Cation})_6^{+}\,[(\mathrm{Al_2O_3})(\mathrm{SiO_2})\mathrm{O_3}]^{6-}$. The charge balance indicates a deficit in alkali cations which is likely to be compensated by tetra(n-butyl)ammonium cations and protons that are initially present in the solution.

TEM experiments were performed on a HITACHI H9000-NAR operated at 300 keV by depositing a 5 μL drop of a suspension of the composite material in ethanol onto a perforated carbon-film covered grid. Fig. 2a shows the border of a grain of aluminosilicate. Qualitative EDX experiments performed during TEM experiments confirmed the presence Si, Al, K, Na and Nb. At high magnification one can observe striations that are coming from an organized set of tubes (Fig. 2b). The tubes have an outer diameter of 25.5(3.0) nm and an inner diameter of 15.5(3.0) nm. High resolution images of the walls of these tubes show that they are formed by the scrolling of sheets with a *d*-spacing between each roll of 1.0(0.2) nm. All these dimensions are in good agreement with those determined by Mallouk *et al.* These TEM results show that the tubules of $[Nb_6O_{17}^{4-}]_n$ do not uncoil during the synthesis and that they are well inserted in the aluminosilicate composite. It appears from Fig. 2 that the tubes self-organize by orientating their main axis in the same direction. This organization seems to extend into the bulk of the material. This nematic-like frozen organization was confirmed from other images obtained at various points of the sample (see Graphical abstract). It can be easily explained because such a nematic structure is to be expected in the case of concentrated suspensions of high aspect ratio colloids. Indeed, as described by the Onsager model[7] and DLVO theory[8] in the case of a colloidal suspension of charged cylinders, above a critical concentration, the tubes reduce their physical interactions by spontaneously aligning their main axis in the same

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DOI: 10.1039/b205947a

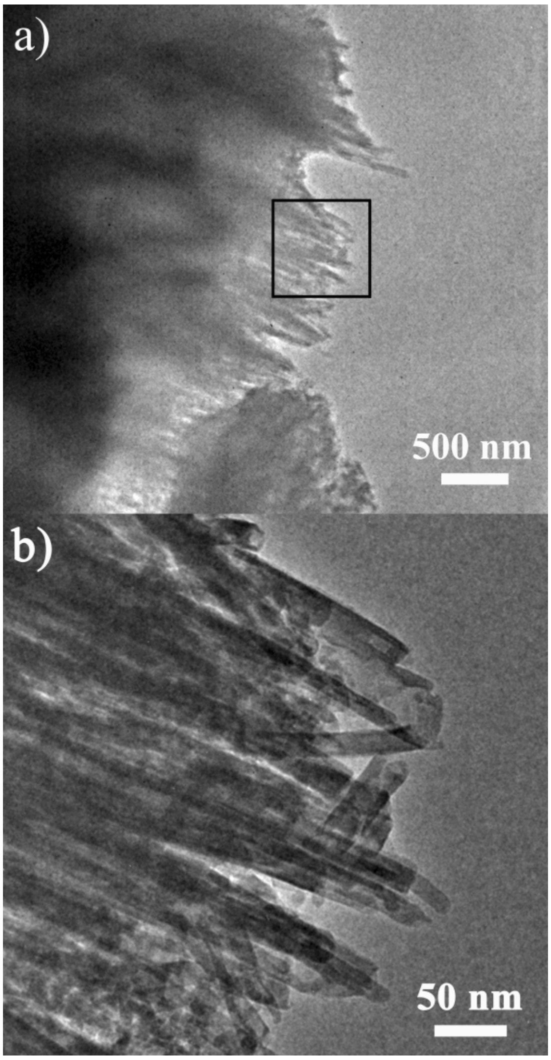

Fig. 2 (a) TEM image of the composite material aluminosilicate–niobium oxide tubules. (b) Zoom of the border of a grain showing the frozen nematic-like organization of tubules along the edge of this composite material.

direction (excluded volume effect). The anisotropic signal obtained by small angle X-ray scattering (LURE, Orsay) confirms the presence of large objects oriented parallel in this material. No correlation peak has been detected, probably due to the polydispersity in diameter of the tubules, which precludes the occurrence of long range positional ordering (in the plane perpendicular to the long axis of the rolls).

To verify the presence of non-filled tubules and accessible space, nitrogen physisorption experiments (determined at 77 K by means of a micromeritics ASAP 2010 porosimeter) were performed. This composite exhibited type IV behaviour (hysteresis), typical of materials with large pores with restricted openings (ink bottle) (Fig. 3). This material has a N_2 Brunauer–Emmett–Teller (BET) surface area of 102 $m^2\ g^{-1}$, a mean pore size of 14.6 nm and a single point ($p/p_0 = 0.965$) pore volume of 0.32 $cm^3\ g^{-1}$. This mean pore size (insert Fig. 3) is in agreement with the mean inner diameter determined by TEM (15.5(3.0) Å). The total surface area of this material is larger than the BET surface area measured on dried precipitated tubular colloids (37 $m^2\ g^{-1}$).[4] The determined mean pore size and the observed hysteresis show that all the tubules are not filled with aluminosilicate and characterizes this composite as mesoporous. We are currently working on ways to open the pores further.

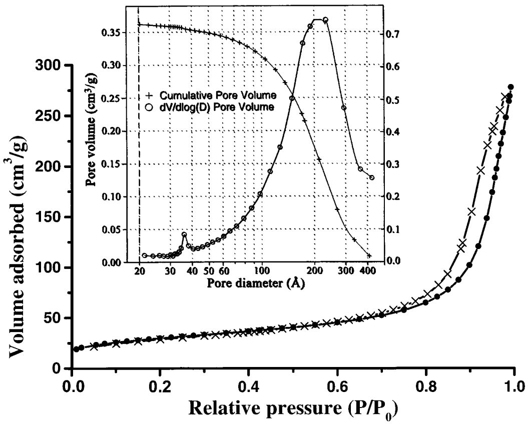

Fig. 3 Nitrogen adsorption and desorption isotherms for this mesoporous composite material synthesized by direct assembling of well defined tubular building blocks. (Insert) The pore size distribution of the mesoporous composite aluminosilicate–niobium oxide tubules using the Barrett–Joyner–Halenda (BJH) model from the desorption branch of the isotherm. (The peak centred at 37 Å is an artifact).

The presence of the tubules in the material is further confirmed by the observation of a thin X-ray diffraction peak at 11.1 Å, which corresponds to the *d*-spacing between layers in the scrolled sheets making the walls. Other diffraction lines are also observed that arise from the long-range two-dimensional atomic positional order within the niobium oxide layers.

We have shown that it is possible to synthesize a mesoporous composite material by direct assembly of anisotropic hollow objects. This use of mineral liquid crystals represents a new approach for the synthesis of composite porous materials and thus diversifies the types of objects that can be assembled in this way, offering the possibility of synthesizing new materials with a variety of properties. Self-assembly of these charged inorganic tubules is currently explored *via* the ionic self-assembly route.[9]

We would like to thank Dr P. Davidson and Dr C. Bourgaux for helpful discussions and their help in performing the SAXS experiment while at LURE; S. Grolleau for TGA and adsorption–desorption measurements; the LURE for the award of beamtime and the Ministère de l'Education Nationale for financial support.

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