Hollow nanoparticle nanotubes with a nanoscale brick wall structure of clay mineral platelets

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Long hollow inorganic nanoparticle nanotubes have been synthesized by templating of block copolymer electrospun fibers with clay mineral platelets followed by interlinking of the platelets using condensation reactions.

Construction of well-defined inorganic nano- and mesoscale structures using organic templates has aroused considerable recent interest.[1–3] As a simple basic geometry, hollow inorganic nanotubes are typically constructed based on vapor phase techniques or sol–gel chemistry and they could find many applications (*e.g.* fluid transportation, sensors or nanoscale structural parts).[4–8] Encouraged by specific biological inorganic hierarchical structures,[9] inorganic nanoparticles could be considered for the tube walls. Nanoparticle nanotubes (NPNTs) made from presynthesized nanoparticles could become an important class of nanomaterials as they combine the peculiar properties of nanoparticles with the hollow one-dimensional structures of nanotubes.[10,11] The use of presynthesized nanoparticles as precursor for NPNTs could have significant advantages over conventional nanotubes, made from vapor phase techniques or sol–gel chemistry, because the synthesis methods for inorganic nanoparticles are quite well-developed and allow the fine-tuning of various characteristics including particle size, shape and optical, electrical and magnetic properties.[12,13] The construction of inorganic NPNTs from presynthesized nanoparticles is rarely demonstrated, however, probably due to a lack of methods to interlink the discrete nanoparticles in the tube wall, which is an essential requirement for mechanical tube stability. To the best of our knowledge, the only reported long NPNTs from presynthesized nanoparticles have been prepared by the metal nanoparticle adsorption on the pore walls of amino-modified alumina membranes, their coalescence, and by the dissolution of the membrane.[10,11] The interlinking of the nanoparticles occurred through room temperature coalescence, a process restricted to metal nanoparticles. The challenge is to form NPNTs from other types of nanoparticles, which is non-trivial as it requires mechanisms to interlink the nanoparticles. Clay mineral platelets, for example, have been interlinked using condensation reactions to prepare hollow spheres in which the walls are sufficiently strong to prevent collapse.[14] On the other hand, construction of long, self-supporting, one-dimensional cavities would, in addition, require stability against tube breakage. Therefore, it is not evident that condensation reactions can also be applied for the synthesis of NPNTs.

In this work, we demonstrate a novel and facile method for the synthesis of long, self-supporting, and thin-walled hollow nanotubes using clay mineral nanoscale platelets as building blocks. This way we combine two concepts in a novel manner. First we demonstrate that electrospun block copolymer nanofibers can be coated with a thin layer of clay minerals. Secondly, we demonstrate that condensation reactions are applicable for the synthesis of NPNTs. Furthermore, non-spherical particles with a high aspect ratio, such as nanoscale clay mineral platelets, have an additional advantage of a large overlap between neighbouring particles allowing multiple mutual bonds and leading to strong but thin tube walls. In this way a "brick wall" inorganic structure is demonstrated for tube walls, like a "nanoscale masonry".

The procedure for construction of long tubes from clay mineral building blocks is as follows (Fig. 1). First electrospun fibers were prepared from a solution of poly(4-vinyl-*N*-methylpyridinium iodide-*block*-methyl methacrylate) (P4VPQ-*b*-PMMA) diblock copolymer (M_n (P4VPQ) = 37600 g mol^{-1}, M_n (PMMA) = 167000 g mol^{-1} and M_w/M_n = 1.28, Polymer Source, Inc.) in *N*,*N*-dimethyl formamide according to a procedure described in literature.[15] These fibers were coated with a thin layer of clay mineral platelets by placing them for 30 s in an aqueous dispersion of 0.05 wt% Laponite RD clay minerals (Rockwood Additives Ltd, UK) which are ~1 nm thick disks with a mean diameter of 17–24 nm.[16] The fibers were thoroughly washed with water to remove excess clay minerals. Consequently the clay particles on the polymer fiber surface are covalently linked using tetraethyl orthosilicate (TEOS, Fluka) in a 50/50 water–ethanol mixture at pH 2. Finally the polymer template is removed by heating for 5 h

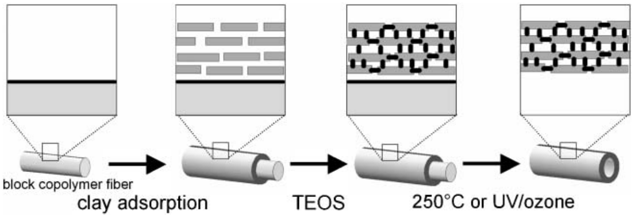

Fig. 1 A route for the synthesis of hollow nanotubes with clay mineral brick walls. First electrospun block copolymer fibers are coated with clay mineral platelets by a cation exchange mechanism. Consequently the clay platelets are covalently interlinked using TEOS, forming a brick wall structure in which clay minerals are the nanoscale "bricks" and Si–O bonds between the clay platelets are "the cement". Finally the polymer template is removed by heat or UV/ozone treatment.

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at 250 °C in air or by treatment in a UV/ozone reactor (BioForce Nanosciences, USA).

A dual functionality is required for the polymer of the electrospun fibers in the present case: (1) the fibers must have an affinity to adsorb clay minerals and (2) the fibers must not dissolve in the aqueous clay mineral dispersion. These properties are present in poly(4-vinyl-*N*-methylpyridinium iodide-*block*-methyl methacrylate) (P4VPQ-*b*-PMMA) diblock copolymer. Whereas the P4VPQ homopolymer is water soluble, the block copolymer is not and the P4VPQ-*b*-PMMA fibers remain stable in water. The ability of P4VPQ-*b*-PMMA to adsorb clay is separately demonstrated using thin films by quartz crystal microbalance (Q-Sense E4, AT-cut 5 MHz quartz crystals, Sweden). Thin films of PMMA do not adsorb clay minerals (Fig. 2). By contrast, in the case of thin films of P4VPQ-*b*-PMMA in water, the frequency shifts up linearly probably due to hydration effects. Changing water to an aqueous clay mineral dispersion results in a decrease of the resonance frequency indicating adsorption of clay minerals to the polymer surface. Most likely the adsorption mechanism is cation exchange in which the Na^+ cations originally present at the clay mineral surface are replaced by the cationic methylpyridinium units of the block copolymer. Adsorption of clay minerals reaches saturation in a few minutes, until the exposed cationic polymer chains become occupied by clay minerals.

Adsorption of clay platelets on the fibers is also evident from transmission electron microscopy (TEM) (Fig. 3). Bright-field TEM was performed using a FEI Tecnai 12 transmission electron microscope operating at an accelerating voltage of 120 kV. The P4VPQ-*b*-PMMA block copolymer fibers have diameters of a few hundreds of nm and the surfaces are smooth (Fig. 3a). The fibers that were immersed in a Laponite RD clay mineral aqueous dispersion have more rough surfaces due to adsorbed clay platelets (Fig. 3b). TEM images of fiber cross-sections show that the coating has a layered structure (Fig. 3c + d). The coating was typically between three and six clay mineral lamellae thick, although locally also some thicker clay coating could be observed.

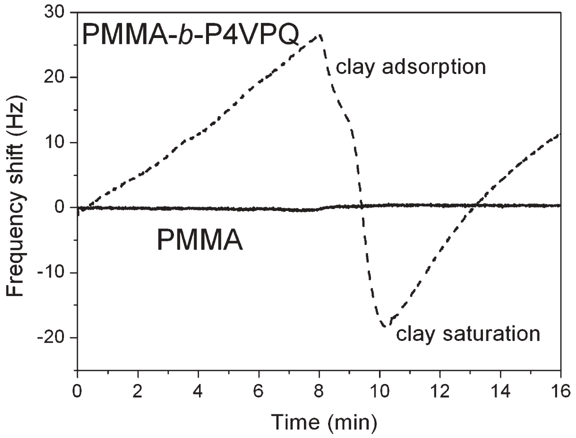

Fig. 2 Quartz crystal microbalance sensogram of laponite clay mineral adsorption on thin films of PMMA homopolymer (solid line) and PMMA-*b*-P4VPQ block copolymer (dashed line). First water was used and replaced by an aqueous Laponite clay mineral dispersion after 6 min. No clay adsorption takes place on PMMA. Clay adsorption occurs rapidly on PMMA-*b*-P4VPQ and leads to saturation.

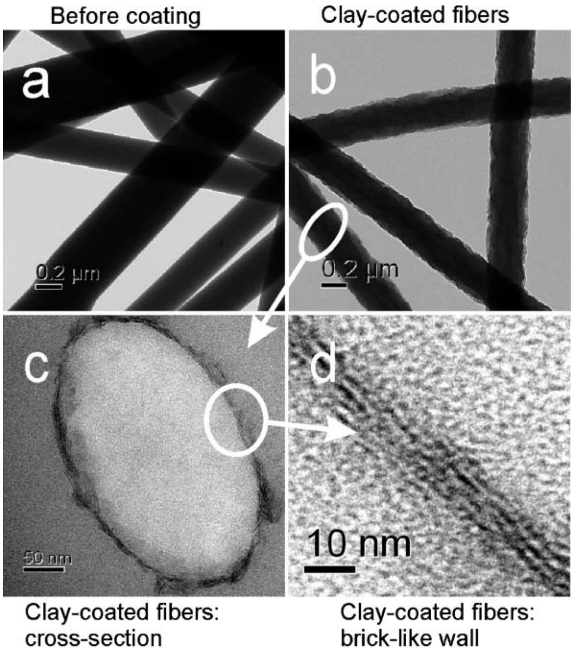

Fig. 3 Transmission electron micrographs of (a) uncoated electrospun P4VPQ-*b*-PMMA fibers and (b–d) clay-coated electrospun fibers before removing the P4VPQ-*b*-PMMA-template. Cross-sectional TEM images of the wall of a clay-coated electrospun fiber showing the individual clay mineral lamellae (c + d).

Next, the fibers are treated with TEOS to glue the clay platelets together. A related procedure was described for the synthesis of armored latex spheres.[14] TEOS most likely binds at the OH groups located at the edges of the clay platelets. Subsequent heating or UV/ozone treatment results in removal of the polymer template. TEM images (Fig. 4) show fibers that are transparent to electrons, indicating the polymer is removed and hollow purely inorganic tubes are obtained. Although the clay mineral building blocks have nanometer dimensions, the tubes are sufficiently strong not to

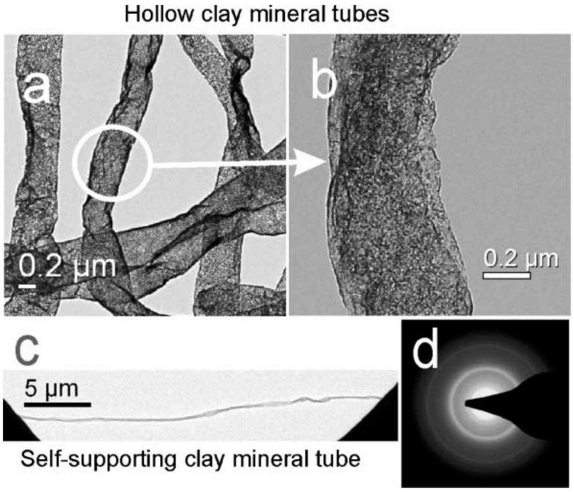

Fig. 4 (a–c) Transmission electron micrographs of the hollow clay mineral tubes formed by removal of the electrospun P4VPQ-*b*-PMMA fiber upon heating at 250 °C. (c) The clay mineral tubes have sufficient strength to be self-supporting over lengths of more than 25 µm. (d) Electron diffraction of the tubes is due to the crystallinity of the clay mineral building blocks.

break while unsupported over distances of tens of micrometer in an oyster-type of TEM grid (Fig. 4c). The aspect ratio of the tube in Fig. 4c exceeds 100. Importantly, removal of the polymer template from clay-coated fibers did not lead to stable tubes without the TEOS treatment. The condensation reactions using TEOS are thus essential to bind the clay platelets together and to preserve the structure given upon emptying. The anisotropic, layered structure of clay minerals is beneficial because multiple bonds can be formed between overlapping clay platelets. The tubes are typically open and in some cases collapsed, although all the tubes are sufficiently strong not to break. Still the open tubes demonstrate that NPNTs can be made from clay mineral platelets. The tubes exhibit electron diffraction from the crystallinity of the clay mineral building blocks (Fig. 4d).

In summary, we demonstrated a novel procedure for the synthesis of long inorganic nanotubes using clay mineral nanoplatelets as building blocks. Electrospun fibers of a cationic block copolymer were coated with a thin layer of clay minerals and importantly the clay platelets were subsequently interlinked using condensation reactions. Hollow tubes were obtained by removal of the polymer template. The wall structure can be considered as nanoscale masonry with clay mineral nanobricks. We foresee the importance of condensation reactions for the future synthesis of NPNTs from nanoplatelets with various electrical, optical or magnetic properties.

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