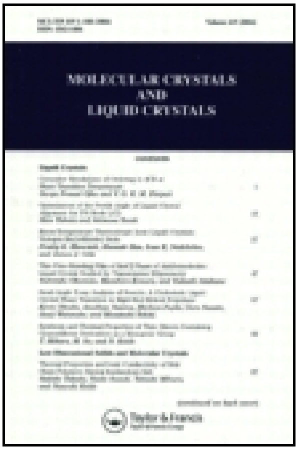

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# Preparation, Characterisation and Modification of Ammonium Tartrate Templated Organosilicate Nanotubes

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# Preparation, Characterisation and Modification of Ammonium Tartrate Templated Organosilicate Nanotubes

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*Silica nanotubes have been prepared by room temperature sol-gel chemistry, using crystalline ammonium tartrate as the tube-forming template. In this study, hybrid organosilicates have been prepared by incorporating methyltriethoxysilane (MTES), polydimethylsiloxane (PDMS) and 3-aminopropyl triethoxysilane (APTES) precursors during sol formation. The synthetic conditions have been systematically studied and a range of hybrid organosilicate tubes prepared. The physical characteristics of the materials were examined by scanning electron microscopy (SEM) and the aging of the tubes due to slow post-gelation condensation reactions was investigated. The morphology of the nanotubes changes when organosiloxanes are incorporated as precursors. Two methods of labeling the nanotubes, fluorescein labeled tubes and rhodamine B-dextran encapsulated in silica nanotubes, were demonstrated. The adsorption of enzyme proteins on nanotube walls is readily observed by SEM.*

**Keywords:** ammonium tartrate; hybrid organosilicates; scanning electron microscopy; silica nanotubes; sol-gel chemistry

## INTRODUCTION

Tubular nanostructure materials with a unique properties have attracted considerable attention because of their potential applications in catalysis, sensors and advanced storage materials [1–3]. Most inorganic hollow tubes such as carbon, boron nitride and silica have been synthesized under high temperature reaction conditions [4–6].

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Recently, single nanotubes have been prepared at room temperature by using the sol-gel template-directed approach. In this approach, a crystalline template acts as a directing agent, around which inorganic precursors are generated in situ and shaped into a nanostructure with its morphology complementary to that of the template [7]. The templates transcription into inorganic materials generally occurs by means of electrostatic or hydrogen bonding interaction between the template and the inorganic precursors and the surface of the template contains moieties that can catalyze the formation of the inorganic materials [8]. So far, silica nanotubes have been synthesized by utilizing some organic templates such as surfactants [9], organogelators [10] and some hydroxycarboxylic acids including DL-tartaric acid [11,12], oxalic acid [12] and citric acid [13,14]. Organically functionalized hybrid silica tubes, with the exception of C18-TMS tubes [8], however, have not yet been reported.

Organically modified silicates have recently received a great deal of interest as they enable either the surface or bulk to be modified with functional groups such as alkyl, phenyl, vinyl, cyano, thiol and others. These materials can be prepared by post-grafting of a preformed silica or by co-condensation of tetraalkoxysilanes and organotrialkoxysilanes [15]. The properties of these hybrid organic–inorganic silicates are versatile in their composition and processing as well as in their optical and mechanical properties [16]. This paper reports the preparation and properties of hybrid organic–inorganic silica nanotubes prepared by controlled hydrolysis of tetraethyl orthosilicate and organosiloxanes in the presence of ammonium DL-tartrate crystals as the structural directing agents and its use for the incorporation of proteins.

## EXPERIMENTAL

The silica nanotubes were prepared using the procedure of Nakamura and Matsui [11] with some modifications. In general, 0.73 g of silica precursor (tetraethyl orthosilicate, TEOS:organosiloxanes, 1:0.02) was dissolved in 5 mL of absolute ethanol containing 0.02 g of DL-tartaric acid and 0.06 g of water. The solution was permitted to stand for 30 minutes and finally 2 mL of 28% $NH_3$ solution was added. An opal white suspension formed after 1 h which was recovered by filtration, washed with water and dried in vacuum oven. Fluorescein labeled tubes were prepared by reaction of preformed tubes containing 2 mol% aminopropyl groups with fluorescein isothiocyanate solution, with the weight ratio of 1:0.1. Rhodamine B-dextran labeled tubes were prepared by dissolving 0.08 mL of rhodamine B-dextran

(MW 10,000) 0.1 mg/mL into the 0.73 g of TEOS with the same procedure as described above.

Raman spectra were recorded using a Renishaw 2000 Raman Microscope equipped with an $Ar^+$ ion laser. SEM micrographs were performed using a Hitachi S900 field emission SEM.

## RESULT AND DISCUSSION

The SEM pictures of hybrid silica tubes, shown in Figure 1, reveal numbers of open ended hollow rectangular tubes along with aggregated silica spheres. The diameter of the tubes varied from 300–960 nm with length from 10–100 µm and wall thickness around 50–120 nm. These dimensions are consistent with those reported previously [11].

Silica materials prepared in the absence of template gave only aggregated silica particles several microns in size, indicating the particular effect of tartaric acid template in formation of the tube. This observation is confirmed by the formation of needle-like crystals of ammonium tartrate for samples prepared in the absence of silicate precursor. It has been considered that the incipient crystallization of ammonium tartrate filaments is responsible for patterning the tubular structure through specific interactions involving inorganic deposition on the external surface of the organic crystal filaments [12].

Synthetic conditions are known to influence the morphology of the silica tubes. It was demonstrated in this work that the amount of tartaric acid introduced into the reaction mixture affects the diameter of the hybrid silica tubes. When the tartaric acid content is increased, the ammonium tartrate filaments formed become larger and the silica then deposits on the surface of the larger filaments leading to larger diameters upon removal of the template. The tube diameter increased from 460 to 980 nm on increasing the tartaric acid to silicate precursor ratio from 2 to 10%. As reported for the silica nanotubes [12], the dimensions of the hybrid silica tubes is also influenced by the water to precursor ratio and the time of hydrolysis. Low levels of water to silica precursor ratio favors crystal growth producing hybrid silica tubes with decreased tube diameter and high aspect ratio. The condensation process also affects the particular morphology of the tubes. A slight decrease in wall thickness was observed during aging at room temperature for several weeks. The wall thickness tended to decrease on increasing aging time due to slow post-gelation condensation reactions. Since the silica tubes will be used for the incorporation of biomolecules, in the present work we prefer to avoid high temperature processing.

Silica nanotubes were modified by co-condensation of siloxane and organosiloxane precursors. The organic groups enable either surface

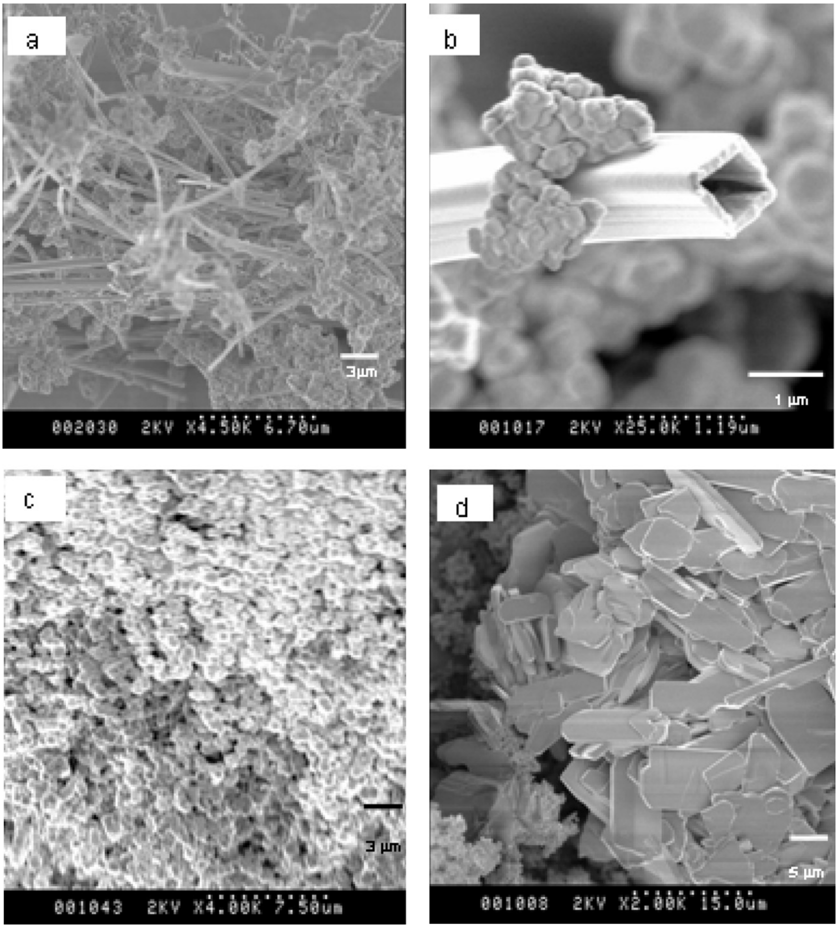

**FIGURE 1** SEM images of MTES containing silica nanotubes at low magnification (a), high magnification (b), silica materials formed without template (c) and ammonium tartrate crystals (d).

or bulk modification of the nanotubes to be carried out. SEM images of the modified nanotubes shown in Figure 2 indicate that incorporation of organic groups changes the morphology of the nanotubes. Addition of up to 2 mol% of either methyltriethoxysilane (MTES), polydimethylsiloxane (PDMS, MW 300) or 3-aminopropyl triethoxysilane (APTES) leads to narrower tube dimensions, presumably due to a decrease in the crosslinking density of the inorganic network. Different mechanisms and transition states cause the organically substituted compounds to react slower in base-catalyzed systems. When

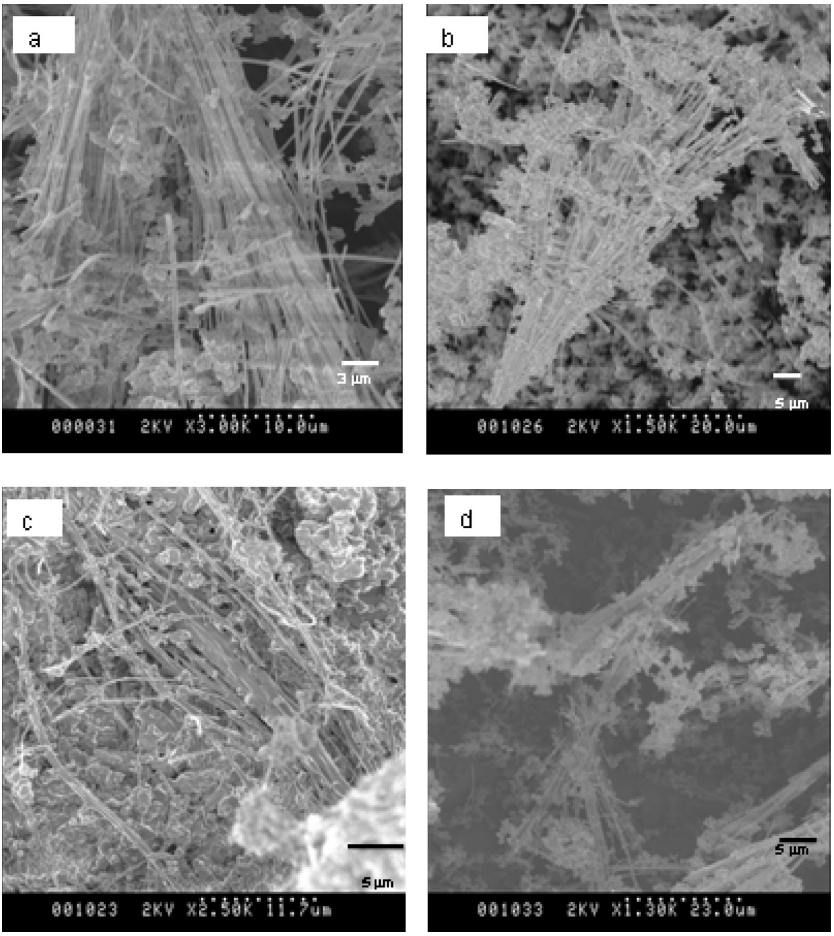

**FIGURE 2** SEM images of silica nanotubes prepared by using different precursors. TEOS (a), TEOS/MTES (b), TEOS/PDMS (c) and TEOS/APTES (d).

the tetraethyl orthosilicate and alkyl triethoxysilane mixture is reacted under basic condition, the inorganic network is predominantly formed from TEOS because it reacts faster. The alkyl triethoxysilane units then condense onto the network [17].

Using Raman microscopy, the laser can be focused on a single tube enabling the spectra of individual tubes to be obtained. The spectra in Figure 3 show that the Si$-$C containing precursors are incorporated into the tubes. The silanol and silicon oxide bands in the surface layers of the silica are observed at 976 $\text{cm}^{-1}$ and 1080 $\text{cm}^{-1}$, respectively. The

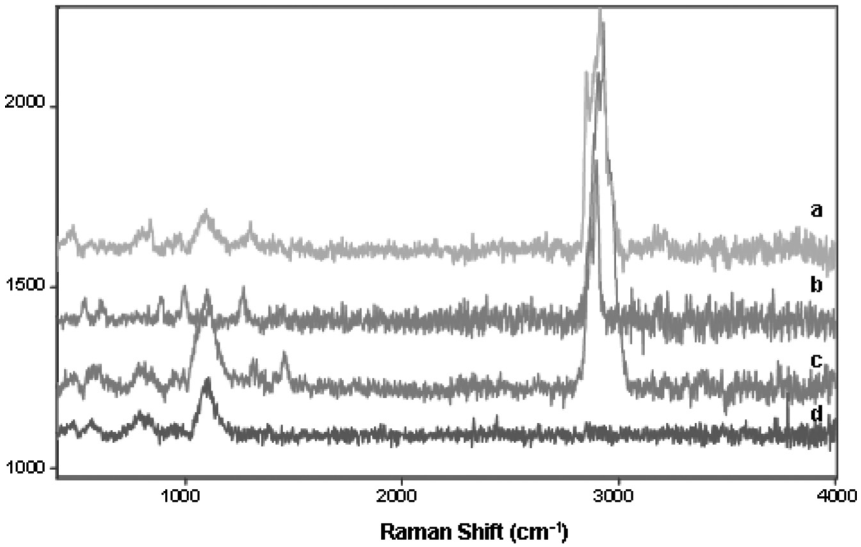

**FIGURE 3** Raman spectra for TEOS/MTES tube (a), TEOS/PDMS tube (b), TEOS/APTES tube (c) and TEOS tube (d).

presence of bands at 2964, 2924 and 2887 cm$^{-1}$ are due to the asymmetric and symmetric C–H stretching of methyl and terminal propyl groups.

Modification of these nanotubes with fluorescent markers was then investigated. Two methods of labeling silica nanotubes, fluorescein labeled tubes and rhodamine B-dextran doped silica tubes, were demonstrated. The fluorescein labeled silica tubes, where the fluorescein is covalently attached to the tubes, was obtained from the reaction of pre-formed tubes containing 2 mol% of aminopropyl groups with fluorescein isothiocyanate.

Rhodamine B-dextran encapsulated in silica tubes are achieved by dissolving the rhodamine B labeled dextran molecules in the precursor solution. During the hydrolysis and polycondensation reactions, the dextran molecules are encapsulated in the silica matrix. The dextran molecular weight (10,000 Da) is high enough that it does not wash out from the gels during template removal.

The Raman microscope was also used to obtain fluorescence spectra of individual tubes. The spectra confirmed that the fluorescein isothiocyanate and rhodamine B emissions are observed at 528 nm and 590 nm, respectively.

Bovine serum albumin, BSA, was added to the suspension of the silica nanotubes. The SEM picture (Fig. 4) shows that the BSA is

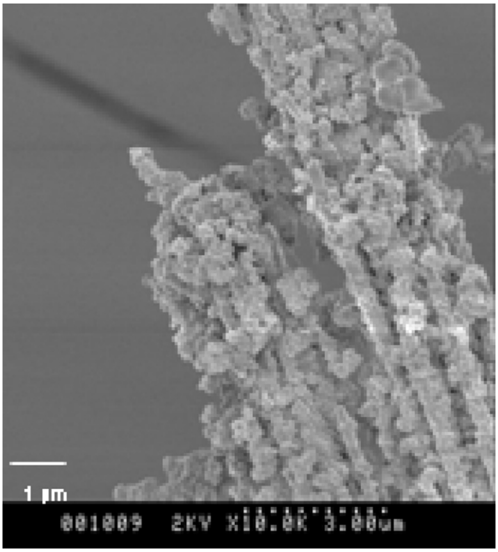

**FIGURE 4** SEM image of bovine serum albumin adsorbed on TEOS tubes.

adsorbed on the silica tube walls. Further work to confirm whether BSA can be incorporated into the tubes rather than simply adsorbing on the surface is under investigation.

## CONCLUSION

A range of new hybrid nanotubes have been prepared through the hydrolysis and condensation of tetraethyl orthosilicate and organosiloxanes in the presence of ammonium tartrate crystals. The dimensions of the tubes can be controlled by varying the synthetic conditions. Two methods of labelling the nanotubes, fluorescein labeled tubes and rhodamine B-dextran encapsulation were demonstrated. Preliminary experiments on the interaction of proteins with the silica nanotubes have been carried out.

## REFERENCES

[1] Hernadi, K., Thiên-Nga, L., Ljubović, E., & Forró, L. (2003). SWNTs as catalyst and/or support in the catalytic decomposition of hydrocarbons. *Chem. Phys. Letters*, *367*, 475–481.

[2] Delvaux, M. & Demoustier-Champagne, S. (2003). Immobilisation of glucose oxidase within metallic nanotubes arrays for application to enzyme biosensors. *Biosensor and Bioelectronics*, *18*, 943–951.

[3] Chen, J., Li, S. L., & Tau, Z. L. (2003). Novel hydrogen storage properties of $MoS_2$ nanotubes. *J. of Alloys and Compounds*, *356–357*, 413–417.

[4] Ebbesen, T. W. & Ajayan, P. M. (1992). Large-scale synthesis of carbon nanotubes. *Nature*, *358*, 220–222.

[5] Bae, S. Y., Seo, H. W., Park, J., Choi, Y. S., Park, J. C., & Lee, S. Y. (2003). Boron nitride nanotubes synthesized in the temperature range 1000–1200°C. *Chem. Phys. Letters*, *374*, 534–541.

[6] Wang, Z. L., Gao, R. P., Gole, J. L., & Stout, J. D. (2003). Silica nanotubes and nanofiber arrays. *Adv. Mater.*, *12*, 1938–1940.

[7] Xia, Y., Yang, P., Sun, Y., Wu, Y., Mayers, B., Gates, B., Yin, Y., Kim, F., & Yan, H. (2003). One-dimensional nanostructures: Synthesis, characterization, and applications. *Adv. Mater.*, *15*, 353–389.

[8] Kim, M., Sohn, K., Kim, J., & Hyeon, T. (2003). Synthesis of carbon tubes with mesoporous wall structure using designed silica tubes as templates. *Chem. Commun.*, 652–653.

[9] Adachi, M. (2003). Formation processes of silica nanotubes and integrated ordered microstructures. *Colloid Polym. Sci.*, *281*, 370–385.

[10] Jung, J. H., Shinkai, S., & Shimizu, T. (2003). Nanometer-level sol-gel transcription of cholesterol assemblies into monodisperse Inner helical hollows of the silica. *Chem. Mater.*, *15*, 2141–2145.

[11] Nakamura, H. & Matsui, Y. (1995). Silica gel nanotubes obtained by the sol-gel method. *J. Am. Chem. Soc.*, *117*, 2651–2652.

[12] Miyaji, F., Davis, S. A., Charmant, J. P. H., & Mann, S. (1999). Organic crystal templating of hollow silica fibers. *Chem. Mater.*, *11*, 3021–3024.

[13] Nakamura, H. & Matsui, Y. (1995). The preparation of novel silica gel hollow tubes. *Adv. Mater.*, *7*, 871–872.

[14] Wang, L., Tomura, S., Ohashi, F., Maeda, M., Suzuki, M., & Inukai, K. (2001). Synthesis of single nanotubes in the presence of citric acid. *J. Mater. Chem.*, *11*, 1465–1468.

[15] Noble, K., Seddon, A. B., Turner, M. L., Chevalier, P., & Ou, D. L. (2003). Porous siloxane-silica hybrid materials by sol-gel processing. *J. of Sol-Gel Sci. Tech.*, *26*, 419–423.

[16] Seçkin, T., Gültek, A., & Kartaca, S. (2003). The grafting of rhodamine B onto sol-gel derived mesoporous silicas. *Dyes and Pigments*, *56*, 51–57.

[17] Schubert, U. & Hüsing, N. (2000). *Synthesis of Inorganic Materials*, *Sol-Gel Processes*, Weinheim: Wiley-VCH, 222–227.