

A STUDY OF THE SYNTHESIS OF HYBRID ORGANOSILICATE NANOTUBES

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ABSTRACT

Hybrid organosilicate nanotubes have been prepared by sol-gel chemistry, using crystalline ammonium tartrate as the tube-forming template. The nanotubes were prepared by controlled hydrolysis and co-condensation of tetraethyl orthosilicate (TEOS) and methyltriethoxysilane (MTES) at room temperature. The synthetic conditions have been systematically studied. The physical characteristics of the materials were examined by scanning electron microscopy (SEM) and the aging times of the tubes due to slow post-gelation condensation reactions was investigated. The morphology and microstructure of the nanotubes are greatly influenced by the synthetic conditions.

Keywords: organosilicate, nanotube, ammonium tartrate crystals.

INTRODUCTION

The synthesis of tubular silica nanostructure materials have attracted considerable attention because of their potential applications in catalysis, sensors and advanced storage materials [1-5].

Unlike the well-known carbon nanotubes [6,7], which are usually synthesized by a high temperature method, most silica nanotubes have been prepared at room temperature by sol-gel processing in the presence of a template. The kinds of templates that have been used so far include porous or fibrous materials such as carbon nanotubes [8,9], nanoporous membranes [10] and organic molecules [11-18]. Porous and fibrous materials are used in direct template method to act as a guides to the formation of nanotubes, while the organic molecules are used to bring about self-assembly between inorganic precursors and organic templates. The organic molecules that have been used so far are surfactants [19], organogelators [20] and some hydroxycarboxylic acids including DL-tartaric acid [16,17, 21], oxalic acid [21] and citric acid [17,18].

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 [22]. In comparison with the growing research on silica nanotubes, with the exception of C18-TMS tubes [23], relatively little

work on organically functionalized hybrid silica tubes has been reported until recently despite their versatility in composition and processing as well as good optical and mechanical properties. This paper reports the synthesis 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. A detailed evaluation of the synthetic parameters that play an important role in determining the microstructure of the nanotube formed was also reported.

EXPERIMENTAL SECTION

The silica nanotubes were prepared using the procedure of Nakamura and Matsui [16] 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% NH₃ solution was added. An opal white suspension formed after 1 h which was recovered by filtration, washed with water and dried in vacuum oven.

The effect of synthesis conditions on the microstructure and morphology of hybrid silica (MTES/TEOS) nanotubes was studied at various concentrations of template, ratios of water to precursor, concentrations of NH₃ and time before addition of NH₃. The dependence of the nanotube morphology on the concentration of templates was

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conducted at room temperature with the concentration of d,l-tartaric acid in the range 0–10 mol%. The effect of water to precursor ratio (in the range of 0.5-3) on the morphology of hybrid silica nanotubes was studied at a fixed concentration of d,l-tartaric acid (4 mol%). The reaction time before NH_3 addition was varied at room temperature with the concentration of template at 4 mol% and the ratio of water to precursor 1:1 with the time varied from 20–240 minutes. The effect of concentration of ammonia on the morphology of the tubes was examined with a range of 0-29% at the concentration of template was 4 mol%, water to precursor ratio of 1 and delay time before addition of the NH_3 was 30 minutes.

The electron micrographs were collected using a Hitachi S-900 Field Emission Scanning Electron Microscope. Samples were coated with a chromium coating using an EMITECH K575X High Resolution Sputter Coater. The accelerating voltage was 2 kV for the 10000 to 50000 times magnification. A Dynamic Stigmator Monitor (DSM) was used to correct the astigmatism. All of the photographs were taken using rolls of black and white film which took 10 exposures, 60 mm x 80 mm per roll of Agfa APX 100 film.

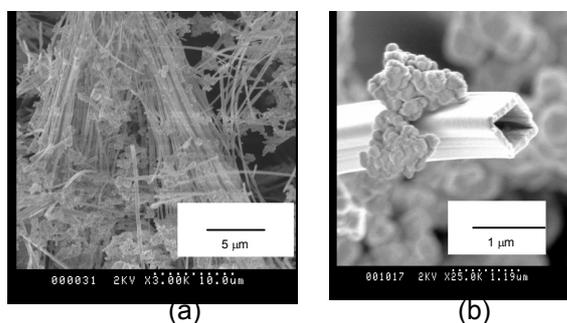


Figure 1 Electron micrographs of silica nanotubes. (a) low magnification, (b) high magnification

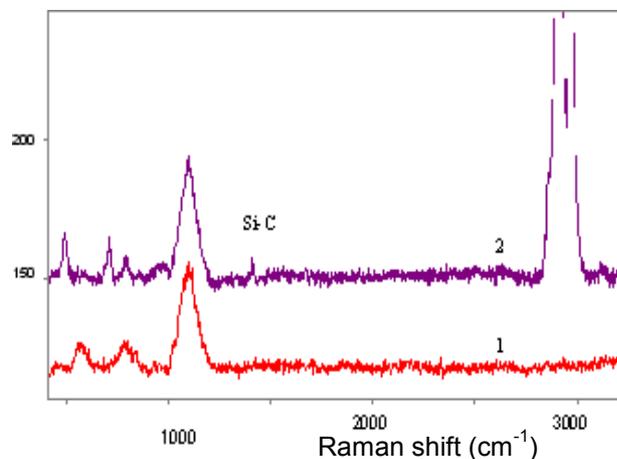


Figure 2 Raman spectra for TEOS nanotube (1) and TEOS/MTES nanotube (2)

Raman spectra were recorded using a Renishaw 2000 Raman Microscope equipped with an Ar^+ ion laser at 514 nm.

RESULTS AND DISCUSSION

The SEM images shown in Fig 1 gives an overview of the morphology of the synthesized product. A number of open ended hollow rectangular tubes were formed along with aggregated silica spheres. The diameter of the tubes varied from 300-900 nm with length from 10-100 μm and wall thickness around 50-120 nm. This indicates that the incipient crystallization of ammonium d,l-tartrate filaments is responsible for patterning the tubular structure. These dimensions are consistent with those reported previously for the silica nanotubes [16].

In order to verify that the methyl groups have been incorporated into the silica nanotubes, the product was characterized using Raman microscopy. Using this method, the laser can be focused on a single tube enabling the spectra of individual tubes to be obtained. The spectra in Fig 2 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 cm^{-1} and 1080 cm^{-1} , respectively. The presence of bands at 2964, 2924 and 2887 cm^{-1} are due to the asymmetric and symmetric C-H stretching of methyl. This result suggests that the hybrid organosilicate nanotubes have been formed.

Synthetic conditions are known to influence the morphology of the organosilicate tubes. It is demonstrated in this work that the amount of tartaric acid introduced into the reaction mixture affects the diameter of the organosilicate nanotubes. Table 1 shows effect of concentration of d,l-tartaric acid on the morphology of hybrid organosilicate tubes. As can be seen in Fig 3, when the tartaric acid content is increased, the ammonium d,l-tartrate filaments formed become larger and the silica then deposits

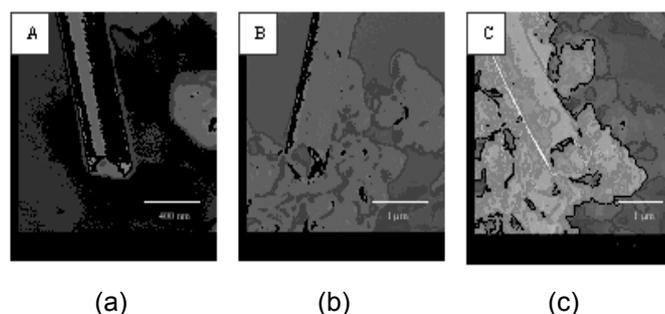


Figure 3 Effect of template concentration on the morphology of hybrid silica tubes. (a) 2 mol%, (b) 4 mol% and (c) 10 mol%.

Table 1 Effect of template concentration on the morphology of hybrid organosilicate nano-tubes

d,l-Tartaric acid (mol%)	Particle size (μm)
0	Spheres
2	Width: 0.19-0.34, length: 8.30-67.40, thickness: 0.05-0.09
4	Width: 0.30-0.63, length: 6.80-60.00, thickness: 0.07-0.12
8	Width: 0.50-0.80, length: 4.50-45.80, thickness: 0.10-0.11
10	Width: 0.50-0.89, length: 5.40-27.90, thickness: 0.09-0.10

on the surface of the larger filaments leading to larger diameters upon removal of the template. The tube diameter increased from 380 to 890 nm on increasing the tartaric acid to silicate precursor ratio from 2 to 10 mol%. As reported previously [21,24], the dimensions of the silica tubes are also influenced by the water to TEOS precursor ratio, the time of hydrolysis and the concentration of NH_3 .

The formation of hybrid silica tubes is sensitive to the amount of water present in the system during the reaction. Low levels of water to silica precursor ratio favors crystal growth along the needle axis by blocking sites on the side faces, which in turn produces hybrid organosilicate nanotubes with reduced channel size and longer tube dimension [21]. The tubes formed only when the ratio of water to MTES/TEOS is ≤ 1.5 . More water content gave only small amounts of tubes and more spherical silica particles were formed. Table 2 gives the effect of water concentration on the morphology of silica tubes.

The formation of the silica tubes was reported to depend on the extent of silica condensation present at the onset of ammonium d,l-tartrate

Table 3 Effect of delay time before the addition of ammonia on the morphology of hybrid organosilicate nanotubes

Time (min)	Particle size (μm)
0	spheres
20	Width: 0.16-0.40, length: 11.56-35.75, thickness: 0.04-0.08
30	Width: 0.29-0.80, length: 36.30-128.60, thickness: 0.04-0.09
45	Width: 0.30-0.87, length: 30.20-135.10, thickness: 0.05-0.10
60	Width: 0.40-1.00, length: 21.90-142.00, thickness: 0.06-0.11
120	Width: 0.32-0.98, length: 25.80-128.30, thickness: 0.05-0.08
300	spheres

Table 2 Effect of water to precursor ratio on the morphology of hybrid organosilicate nanotubes

Water to MTES/TEOS ratio	Particle size (μm)
0.50	Width: 0.19-1.47, length: 14.20-118.05, thickness: 0.05-0.49
0.75	Width: 0.20-0.82, length: 6.50-86.00, thickness: 0.04-0.45
1.00	Width: 0.38-1.15, length: 15.00-105.17, thickness: 0.15-0.39
1.50	Width: 0.28-0.83, length: 6.00-18.09, thickness: 0.10-0.19
3.00	spherical

crystal growth [21] which occurred immediately on addition of ammonia. Table 3 depicts the effect of time prior to the addition of ammonia on the formation of hybrid organosilicate nanotubes. The Figure shows that more tubes are formed, with the lengths between 37 and 129 μm , when the time is 30 minutes. There was no tube formed when the NH_3 was added immediately after the addition of precursor, probably due to the absence of condensed silicate during crystallization of the ammonium d,l-tartrate which subsequently coalesced into polycrystalline aggregates [21]. Only a few tubes were obtained at delay times of 20 minutes. Increasing delay time results in decreasing numbers of tubes formed and increasing tube length and width. It appears that increasing the delay time means that the inorganic precursor oligomers can more efficiently self-assemble around the template leading to longer and thicker tubes. The results are consistent with a recent study by Mokoena et al. [24], who found that the yield of tubes decreases from 85% to 10% as the delay time increases from 0.25 hours to 6 hours.

The concentration of ammonia is another important factor affecting the formation of organosilicate nanotubes. Table 4 indicates that the yield and tube lengths increase with concentration of ammonia. In the absence of NH_3 and in the presence of low concentrations of NH_3 only

Table 4 Effect of the concentration of NH_3 on the morphology of hybrid organosilicate nanotubes

$[\text{NH}_3]$ (%)	Particle size (μm)
0	spheres
7.5	spheres
14.5	Width: 0.27-0.65, length: 5.50-40.10, thickness: 0.06-0.08
20	Width: 0.17-0.78, length: 17.00-60.00, thickness: 0.04-0.10
29	Width: 0.15-0.87, length: 28.00-132.50, thickness: 0.02-0.12

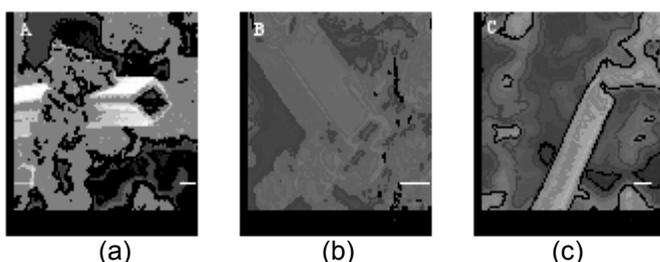


Figure 4 Effect of aging on the morphology of silica tubes. (a) 1 week, (b) 8 weeks, and (c) 12 weeks. Bar: 300 nm

spherical particles were obtained while long tubes were produced when higher concentrations of NH_3 were used. These observations confirm that ammonia plays an important role in the formation of silica tubes not only as the initiator of ammonium d,l-tartrate crystallization which is responsible for the templated growth of individual filaments, but also as the catalyst for the condensation of the silica sol [21].

The condensation process also affects the particular morphology of the tubes. Fig 4 illustrates the effect of aging on the morphology of silica tubes. A slight decrease in wall thickness from 119 nm to 80 nm was observed during aging at room temperature for several weeks. The wall thickness tended to decrease with increasing aging time due to slow post-gelation condensation reactions. Since the silica nanotubes will be used for the incorporation of biomolecules, in the present work it is preferred to avoid high temperature processing.

CONCLUSION

New hybrid organosilicate nanotubes have been prepared through the hydrolysis and co-condensation of tetraethyl orthosilicate and organosiloxanes in the presence of ammonium d,l-tartrate crystals. The template together with the synthetic conditions influences the formation of the particular morphologies. The dimensions of the tubes can be controlled by varying the synthetic conditions. This hybrid organosilicate nanotube is expected to have a wide range of applications, including catalysts, sensors, adsorbents and advanced storage materials. The presence of macro-cavity in the hybrid organosilica tubes facilitates the bidirectional diffusion of reactants to both interior and exterior surfaces of the tubes.

REFERENCES

- Mitcell, D.T., Lee, S.B., Trofin, L., Li, N., Nevanen, T.K., Soderlund, H. and Martin, C.R., 2002, *J. Am. Chem. Soc.*, 124, 11864-11868
- Hu, J.Q., Meng, X.M., Jiang, Y., Lee, C.S. and Lee, L.T., 2003, *Adv. Mater.*, 15, 70-76
- Martin, C.R., 1996, *Chem. Mater.*, 8, 1739-1746
- Obare, S.O., Jana, N.R. and Murphy, C.J., 2001, *J. Nano Lett.*, 1, 601-603
- Fan, R., Wu, Y., Li, D., Yue, M., Majumdar, A. and Yang, P., 2003, *J. Am. Chem. Soc.*, 125, 5254-5255
- Iijima, S., 1991, *Nature*, 354, 56-58
- Iijima, S. and Ichihashi, T., 1993, *Nature*, 363, 603-605
- Satishkumar, B.C., Govindaraj, A., Vogl, E.M., Basumallick, L. and Rao, C.N.R., 1997, *J. Mater. Res.*, 12, 604-606
- Ajayan, P.M., Stephan, O., Redlich, P. and Collex, C., 1995, *Nature*, 375, 564-565
- Lakshmi, B.B., Patrissi, C.J. and Martin, C.R., 1997, *Chem. Mater.*, 9, 2544-2550
- Adachi, M., Harada, T. and Harada, M., 1999, *Langmuir*, 15, 7097-7100
- Muhr, H.-J., Krumeich, F., Schonholzer, U.P., Bieri, F., Niederberger, M., Gauckler, L.J. and Nesper, R., 2000, *Adv. Mater.*, 12, 231-234
- Ono, Y., Nakashima, K., Sano, M., Kanekiyo, Y., Inoue, K., Shinkai, S. and Hojo, J., 1998, *Chem. Commun.*, 1477-1478
- Kobayashi, S., Hanabusa, K., Hamasaki, N., Kimura, M., Shirai, H. and Shinkai, S., 2000, *Chem. Mater.*, 12, 1523-1525
- Clavier, G.M., Pozzo, J.L., Bouas-Laurent, H., Liere, C., Roux, C. and Sanchez, C., 2000, *J. Mater. Chem.*, 10, 1725-1730
- Nakamura, H. and Matsui, Y., 1995, *J. Am. Chem. Soc.*, 117, 2651-2652
- Nakamura, H. and Matsui, Y., 1995, *Adv. Mater.*, 7, 871-872
- Wang, L., Tomura, S., Ohashi, F., Maeda, M., Suzuki, M. and Inukai, K., 2001, *J. Mater. Chem.*, 11, 1465-1468
- Adachi, M., 2003, *Colloid Polym. Sci.*, 281, 370-385
- Jung, J.H., Ono, Y. and Shinkai, S., 2000, *Langmuir*, 16, 1643-1649
- Miyaji, F., Davis, S.A., Charmant, J.P.H. and Mann, S., 1999, *Chem. Mater.*, 11, 3021-3024
- Noble, K., Seddon, A.B., Turner, M.L., Chevalier, P. and Ou, D.L., 2003, *J. Sol-Gel Sci. Technol.*, 26, 419-423
- Kim, M., Sohn, K., Kim, J. and Hyeon, T., 2003, *Chem. Commun.*, 652-653
- Mokoena, E.M., Datye, A.K. and Coville, N.J., 2003, *J. Sol-Gel Sci. Technol.*, 28, 307-317