

## Silica Gel Nanotubes Obtained by the Sol–Gel Method

Hidenori Nakamura and Yasushi Matsui\*

Central Research Laboratory, Showa Denko K.K.  
1-1, Ohnodai 1-chome, Midori-ku Chiba 267, Japan

Received November 30, 1994

The inorganic hollow tubes known to date are composed of carbon,<sup>1–6</sup> boron nitride,<sup>7–9</sup> and silica.<sup>10,11</sup> The carbon tubes have been known for several years and are usually prepared by the catalytic decomposition of organic vapors such as acetylene or benzene at high temperatures. Ferromagnetic metals such as Fe, Co, and Ni are commonly used as catalysts. Recently, needle-like carbon tubes (carbon nanotubes) were produced using an arc-discharge evaporation method similar to that used for fullerene synthesis,<sup>5</sup> and amorphous boron nitride tubes were obtained from the reaction between cesium and *B,B,B*-trichloroborazine ( $B_3Cl_3N_3H_3$ ) under vacuum at 1100 °C.<sup>7</sup>

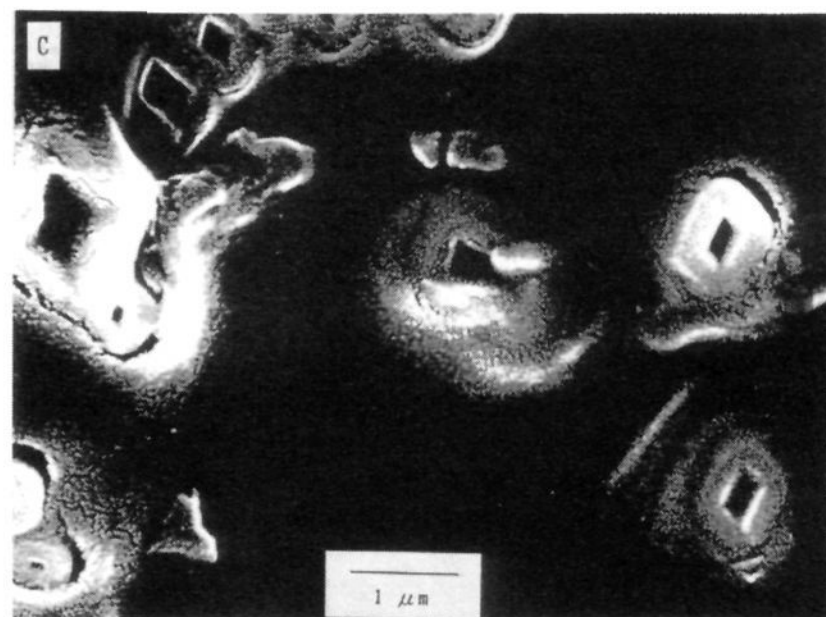
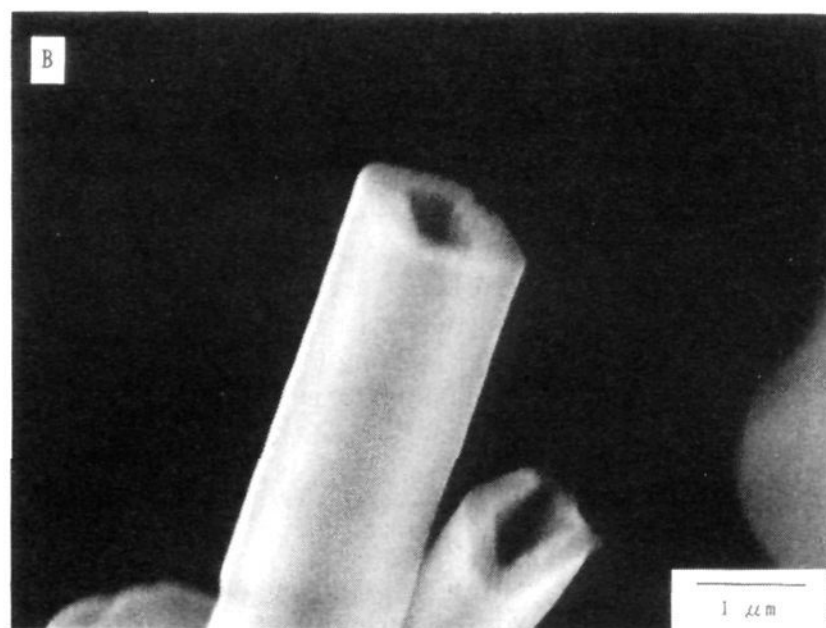
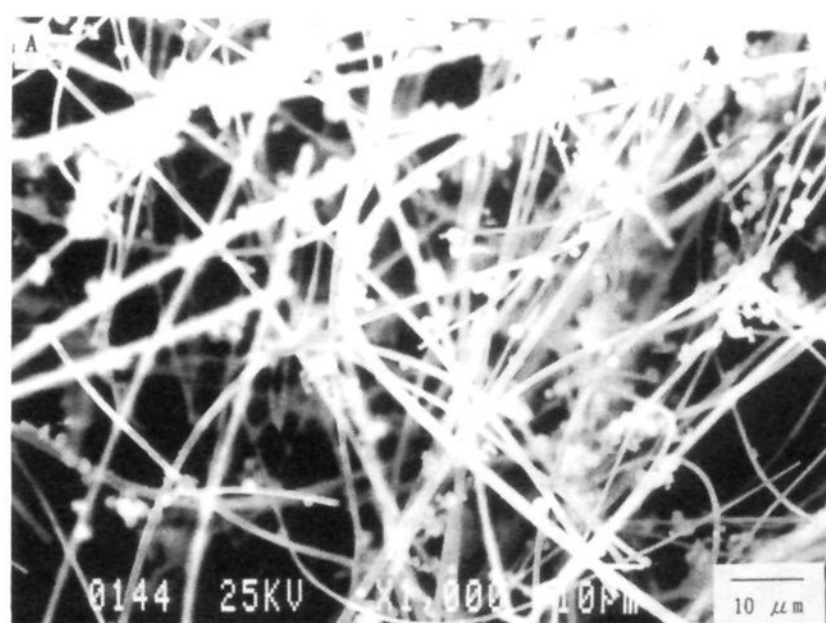
Nemetschek and Hofmann investigated the SiO disproportionation reaction<sup>10</sup> and the reaction of silica and silicon metal in high vacuum at 1200 °C.<sup>11</sup> In their investigation, they found that these reactions generated hollow tubes and spiral fibers of amorphous silica.

All inorganic hollow tubes previously mentioned were synthesized under high temperature reaction conditions.

Here, we report the preparation of a new type of silica-gel nanotube by a sol–gel method at room temperature. These tubes were synthesized by hydrolyzing tetraethyl orthosilicate (TEOS) in a mixture of ethanol, ammonia, water, and tartaric acid. The reaction was carried out as follows: 7.3 g (0.035 mol) of TEOS was dissolved in 50 mL of absolute ethanol containing 0.2 g (0.00133 mol) of DL-tartaric acid and 0.6 g of water. The solution was permitted to stand for 30 min to form SiO<sub>2</sub> sol, and finally 20 mL of ammonium hydroxide solution (28% NH<sub>3</sub> solution) was added. After 15–20 min, the reaction was observed to be completed.

The reaction products were hollow tubes that contained small spherical particles and aggregates (Figure 1A). These were washed on a 300 mesh net with a large amount of water, and the hollow tubes were collected on the net (Figure 1B). The cross section of the tubes showed interesting results (Figure 1C). They had square shapes with an outer diameter of 0.8–1.0 μm and were 200–300 μm in length. The products also contained small amounts of cylindrical tubes, with circular inner shapes. The diameter of the tubes decreased with low reaction temperatures, and the finest tube was 0.05–0.1 μm in diameter. The inner diameter of the tubes was 0.02–0.8 μm, and the shells were 0.015–0.3 μm thick.

The efficiency of the reaction depends on the presence of certain isomers. Our observation indicated that only the racemic isomer of tartaric acid and the mixture of L- and D-isomers of

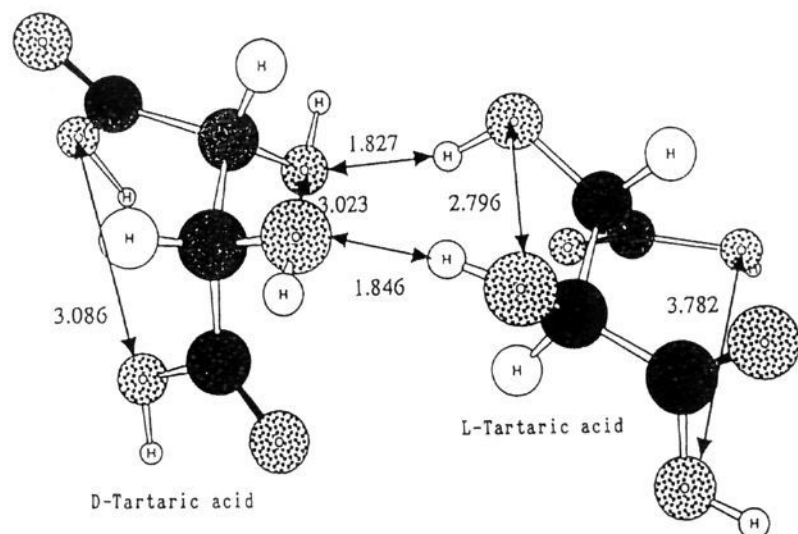


**Figure 1.** (A) Electron microscopic view (1000×) of the products of the reaction of TEOS dissolved in absolute ethanol containing DL-tartaric acid with ammonium hydroxide solution. (B) Close-up of the hollow tubes collected upon washing the reaction products. (C) Cross section of the tubes, showing the square inner shape and the outer diameter of 0.8–1.0 μm.

tartaric acid were effective in this reaction. The L-isomer, D-isomer, and *meso*-isomer of tartaric acid were not effective. The yield was very sensitive to the purity of the tartaric acid.

When freshly distilled TEOS dissolved in absolute ethanol containing DL-tartaric acid was added immediately to ammonium hydroxide solution, hollow tubes did not form. The products were instead spherical particles and aggregates. The fact that DL-tartaric acid is the only isomer showing this effect may be linked to the unique nature of the H-bonding in this case, and this is thought to play an important role in the reaction mechanism.

- (1) Bacon, R. *J. Appl. Phys.* **1960**, *31*, 283.
- (2) Baker, R. T. K.; Barber, M. A.; Harris, P. S.; Feates, F. S.; Waite, R. *J. J. Catal.* **1972**, *26*, 51.
- (3) Baker, R. T. K. *Carbon* **1989**, *27*, 315.
- (4) Motojima, S.; Kawaguchi, M.; Nozaki, K.; Iwanaga, H. *Carbon* **1991**, *29*, 379.
- (5) Iijima, S. *Nature* **1991**, *354*, 56.
- (6) Amelinckx, S.; Zhang, X. B.; Beraerts, D.; Zhang, X. F.; Ivanov, V.; Nagy, J. B. *Science* **1994**, *265*, 635.
- (7) Hamilton, E. J. M.; Dolan, S. E.; Mann, C. M.; Colijn, H. O.; McDonald, C. A.; Shore, S. G. *Science* **1993**, *260*, 659.
- (8) Gleize, P.; Herreyre, S.; Gadelle, P.; Caillet, M. *J. Mater. Sci.* **1994**, *29*, 1571.
- (9) Gleize, P.; Herreyre, S.; Gadelle, P.; Mermoux, M.; Cheynet, M. C.; Abello, L. *J. Mater. Sci. Lett.* **1994**, *13*, 1413.
- (10) Nemetschek, Th.; Hofmann, U. *Z. Naturforsch.* **1954**, *9b*, 166.
- (11) Nemetschek, Th.; Hofmann, U. *Z. Naturforsch.* **1953**, *8b*, 410.



**Figure 2.** Diagram of the D-L two-hydrogen-bonding tartaric acid complex, showing selected distances between the atoms, as discussed in the text.

In analyzing the reaction mechanism, we calculated the stability of hydrogen-bonding complex of two molecules of tartaric acid using MOPAC v. 6 (PM3). D-L, L-L, *meso-meso*, and L-*meso* complexes formed stable "two-hydrogen-bonding complexes"; however, D-D and D-*meso* complexes were not able to form "two-hydrogen-bonding complexes". In the D-L complex, the distances of the two oxygen atoms of the outer free hydroxy groups were 3.086 (D-side) and 3.782 Å (L-side), respectively (Figure 2). Therefore, D- and L-tartaric acid were able to form the ladder-type two-hydrogen-bonding complex, such as a D-L-D-L- complex. According to the calculation, the D-L-D-L complex was also stable. On the other hand, L-L, *meso-meso*, and L-*meso* complexes were not able to form the ladder-type two-hydrogen-bonding complex, because the distances of the two oxygen atoms of the outer free hydroxy groups were very long.<sup>12</sup>

The reaction mechanism of formation of the tubes is still unknown. In the usual hydrolysis reaction of TEOS using  $\text{NH}_3$

as catalyst, the products are nonporous spherical silica particles of uniform size.<sup>13</sup> We also observed that porous spherical silica particles were formed by the hydrolysis reaction of TEOS in acetonitrile solution with organic carboxylic acid.<sup>14</sup>

In this reaction, it is considered that  $\text{SiO}_2$  sol particles were the starting point for the formation of tubes, and the tubes are formed in the DL-tartaric acid matrixes. The essential conditions for the formation of tubes, therefore, are the presence of  $\text{SiO}_2$  sol and DL-tartaric acid, and the diameter of the tubes depends on the size of  $\text{SiO}_2$  sol particles.

These tubes could be converted to  $\text{SiO}_2$  glass tubes by heating them to 800 °C and 1000 °C in air. IR spectra of  $\text{SiO}_2$  gels have a 946  $\text{cm}^{-1}$  signal assigned to the Si-OH vibration and a 1102  $\text{cm}^{-1}$  signal assigned to the Si-O stretching vibration. The absorption peak of 946  $\text{cm}^{-1}$  diminishes, and the absorption peak of 1102  $\text{cm}^{-1}$  shifts to 1116  $\text{cm}^{-1}$  and becomes similar in shape and position to that found in conventional silica glass as the heating temperature increases to 800 °C and 1000 °C. This results are the same as those reported by Sakka.<sup>15</sup>

According to X-ray diffraction, silica gel tubes and silica glass tubes are amorphous silica.

**Acknowledgment.** We sincerely thank Y. Shibusa and M. Mori of the Production Technology Department of SDK for calculating tartaric acid complexes and colleagues K. Takahashi and Y. Miyasaka for performing electron microscopy.

JA943879P

(12) The distances of the two oxygen atoms for L-L were 3.934 and 5.377 Å, *meso-meso* were 4.134 and 4.167 Å, L-*meso* were 4.045 (L-side) and 4.185 Å (*meso*-side).

(13) Stöber, W.; Fink, A.; Bohn, E. *J. Colloid Interface Sci.* **1968**, *26*, 62.

(14) Nakamura, H.; Matsui, Y. Unpublished results.

(15) Sakka, S.; Kamiya, K. *Proc. Int. Symp. Factors Densif. Sinter. Oxide Non-oxide Ceramics, Jpn.* **1978**, 101.