LITERATURE REVIEW

Silica

Silica is a polymer of silicic acid consisting of inter-linked SiO_4 unit in tetrahedral fashion with general formula SiO_2 (Fig 1). In nature it exists as sand, glass, quartz etc. Naturally occurring silica is crystalline where as synthetically obtained silica is amorphous in nature (Fig 2). The word "nano" means 10^{-9} so a nanometer is one billion of a meter. One definition of nanoscience is that it concerns itself with the study of objects which are anywhere from hundreds to ten nanometer in size. Nanosilicas can be in various forms such as silica nanoparticles, silica nanowires, silica nanorod and silica nanotube depending on the synthetic techniques.

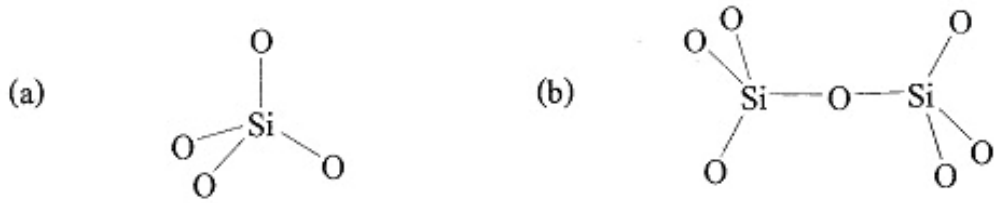

Figure 1 Structure of silica (a) A unit structure of silica containing SiO_4 unit in which one silicon is surrounded by four oxygen atoms in a tetrahedral geometry. (b) The expanded structure showing the coordination of oxygen atom between two silicon atoms.

Source: (Stebbins *et al.*, 1995)

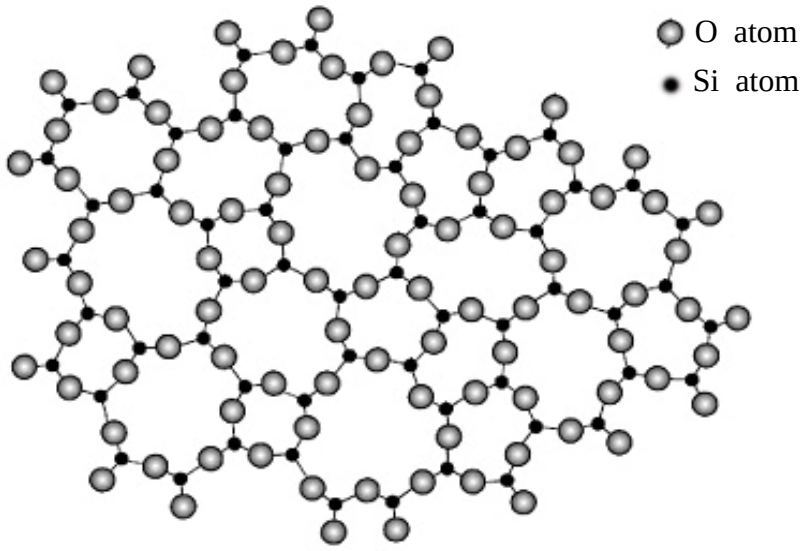

Figure 2 Structure of amorphous silica (SiO_2).
Source: (Stebbins *et al.*, 1995)

Silica used in chemical applications is synthesized by various techniques such as sol-gel method, precipitation and template method. Sol-gel is a useful self assembly process for nanomaterial formation. The sol-gel process is the most widely used and developed one among various synthetic powder precipitation methods. This process involves the evolution of networks through the formation of a colloid suspension (sol) and gelation of the sol to form a network in a continuous liquid phase (gel). The precursors for synthesizing these colloids normally consist of metal ions in the form of salts or metal organic compounds, for example metal alkoxides and alkoxysilanes. Additionally, a mutual solvent such as an alcohol is used because water and alkoxides are immiscible. In sol-gel formation, a solution of the appropriate precursors is formed first, followed by conversion into homogeneous oxide networks (gel) after hydrolysis, condensation and polymerization of monomers occur (Fig 3).

$$\text{Hydrolysis : } OH^- + ROSi(OR)_3 \xrightarrow{\text{base}} RO^- + HSi\text{-}O\text{-}Si(OR)_3$$

$$\text{Condensation : } 2HOSi(OR)_3 \longrightarrow (OR)_3\text{-}Si\text{-}O\text{-}Si\text{-}(OR)_3 + H_2O$$

$$\downarrow$$

$$(OR)_2OH\text{-}Si\text{-}O\text{-}Si(OR)_3 + HOR$$

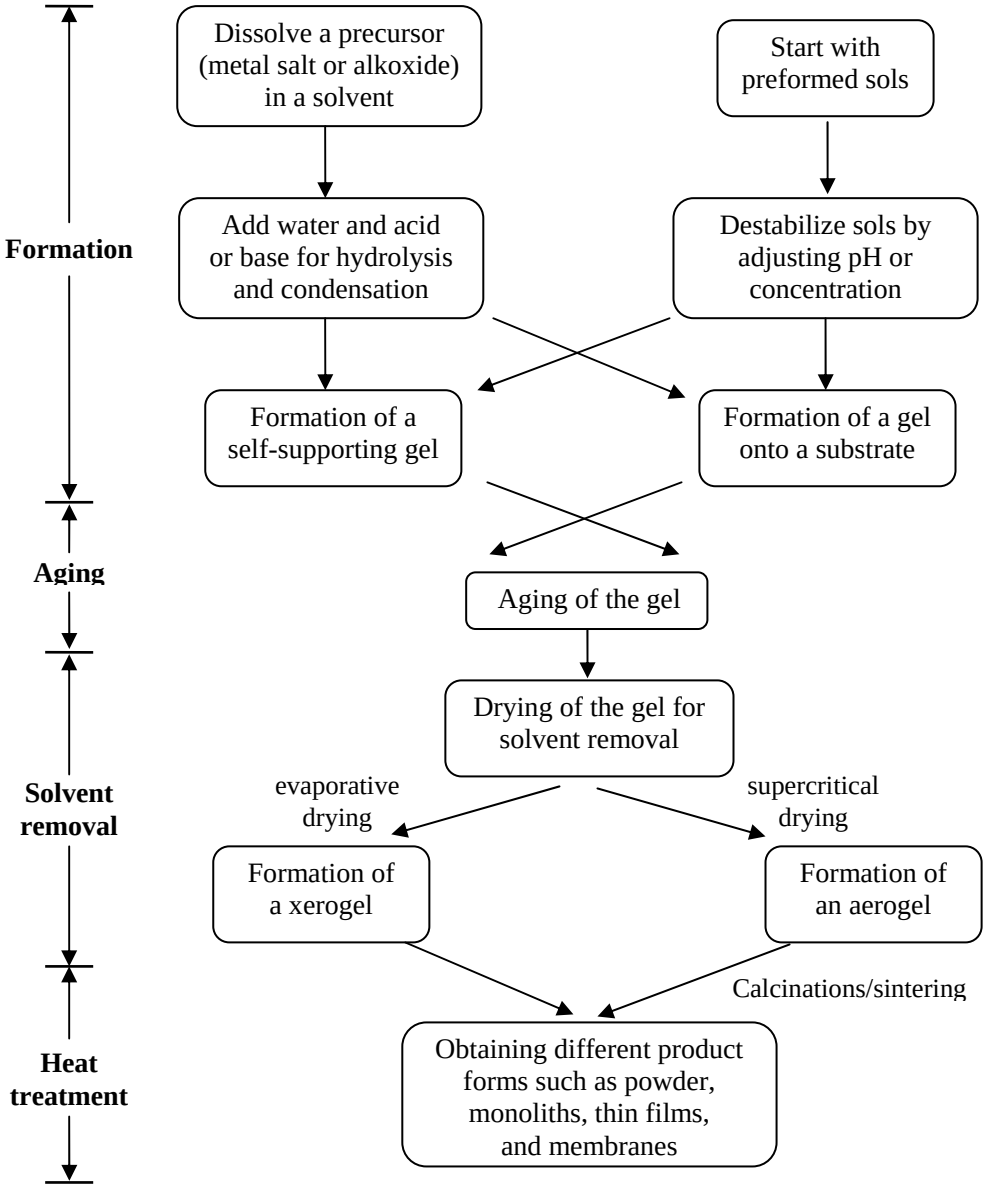

Figure 3 Schematic diagram showing the various steps of a sol-gel process.

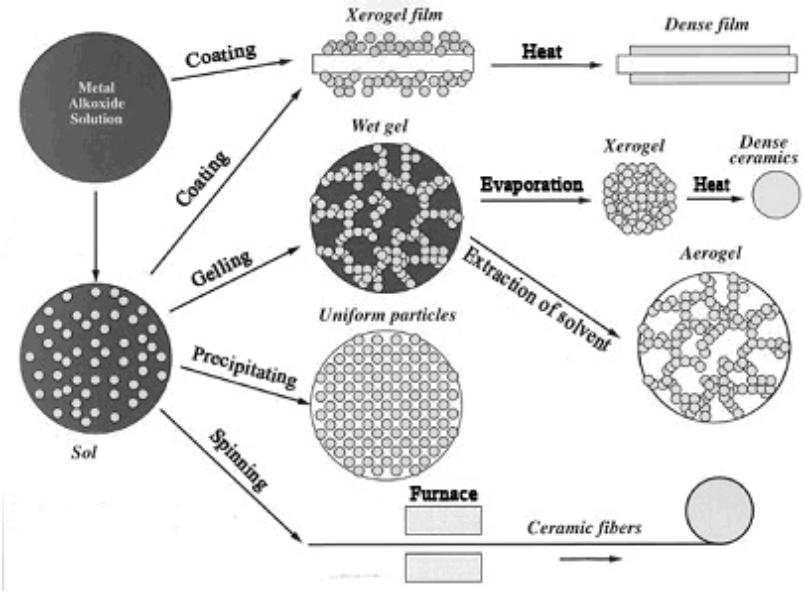

Figure 4 Summarizes sol-gel technologies and their products.
Source: (www.chemat.com)

Stöber et al. (1968) reported the reproducible production of uniform spherical silica particles with diameters in the range of 0.05-2 μm. The spherical silica particles were made by hydrolyzing tetraethylorthosilicate (TEOS) in a mixture of ammonia, water, and ethanol. Porous spherical silica particles were formed by the hydrolysis of TEOS in acetonitrile solution with organic carboxylic acids (Nakamura and Matsui, 1995b). Millimeter-sized mesoporous silica spheres were prepared directly from the reaction of tetraethoxysilane with tartaric acid in cyclohexanol by the sol-gel process (Izutsu *et al*., 1997). The hallow tubes and spiral fibers of amorphous silica were synthesized under high temperature conditions.

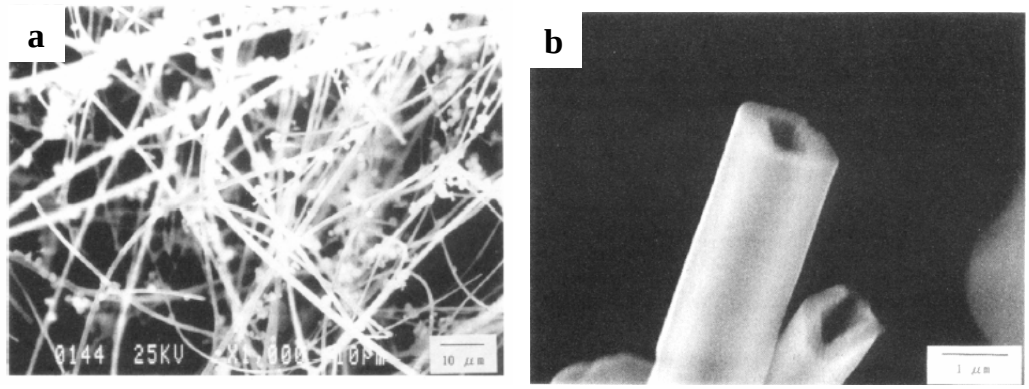

Figure 5 Electron microscopic view of silica nanotubes. (a) SEM image of silica nanotubes (1000 X). (b) SEM image of silica hallow tubes. Source: (Nakamura *et al*., 1995a)

Silica nanotubes synthesized by sol-gel method at room temperature were reported (Nakamura and Matsui, 1995a and 1995b). These amorphous tubes were synthesized by hydrolyzing tetraethylorthosilicate (TEOS) in a mixture of ethanol, ammonia, water and organic acid (tartaric or citric acid). When tartaric acid was used, the reaction products were hallow tubes which contained small spherical particles and aggregates (Fig 5). The cross section of the tubes showed square shapes with an outer diameter of 0.8 – 1.0 μm and were 200 – 300 μm in length. The diameter of the tubes decreased with low reaction temperature. The efficiency of the reaction depended on the presence of certain isomer. Only the racemic isomer of tartaric acid and mixture of L- and D-isomer of tartaric acid were effective in the reaction. The yield was very sensitive to the purity of the tartaric acid. In the case of citric acid, a worm-type silica hallow tube were produced, mostly with one end closed. Occasionally tubes both ends closed were observed. The cross section of the tubes was circular and inner shapes were square. The tubes were porous with an outer diameter of 0.6 – 1.2 μm and a length of 8 – 12 μm. The specific surface area was 250 – 350 m^2/g and the yield was almost 100%. It was found that the

morphologies of silica nanotubes were sensitive to the synthetic condition (Wang *et al*., 2001). Rapid addition of ammonia and citric acid under static conditions gave only uniform micrometer sized bone-like rods with well-defined morphologies and under stirring condition gave only nanoparticles. The slow addition of ammonia and citric acid under stirring was effective for the formation of single nanotubes. Under stirring condition, numbers of long single nanotubes together with some nanoparticles coexisted in the material. The outer diameter of nanotubes varied from 50 – 500 nm with the majority around 100 – 150 nm. The length of tubes ranged from hundreds of nanometer up to tens of micrometers. Therefore the synthetic conditions also influence the particular morphologies of material (Fig 6).

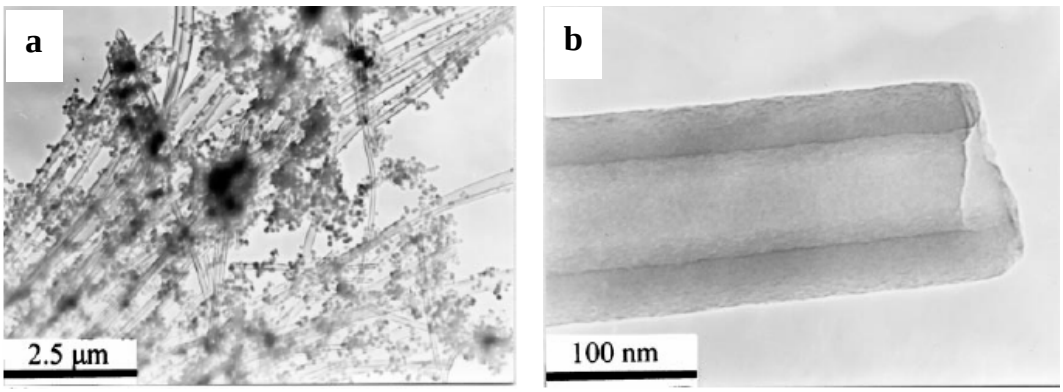

Figure 6 TEM images of single silica nanotubes. (a) Low-magnification and (b) high-magnification

Source: (Wang *et al*., 2001)

Mokoena and coworker (Mokoena *et al*., 2003) performed a systematic study of the use of DL-tartaric acid in the syntheses of silica materials by sol-gel method. The parameter studied were (1) reaction temperature, (2) concentration of NH_4OH solution, (3) reaction time (aging), (4) stirring and (5) solvent. Among the synthesis conditions investigated it was found that temperature, stirring and reaction time played the largest effect on the

morphology. These factors had a direct bearing on template formation. The formation of the tubes was more enhanced at lower temperatures than elevated ones. It was due to the fact that at the lower temperature molecules diffused more slowly and thus had enough time to self-assembly. TEM and SEM images showed that the yield and microstructure of the silica was influenced by the synthetic conditions (Fig 7)

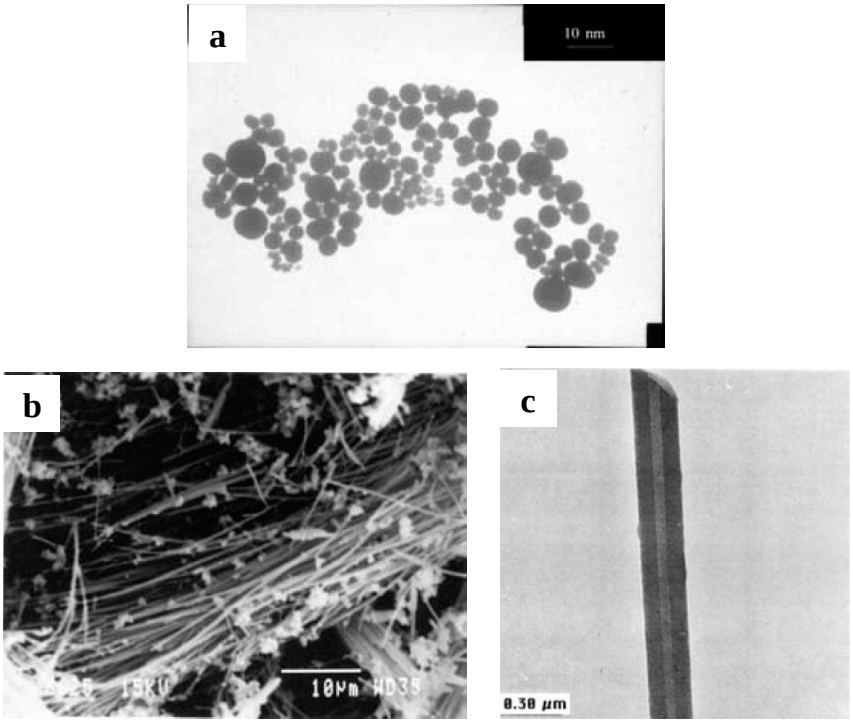

Figure 7 Electron microscopic view of silica products (a) TEM image of spherical silica particles obtained at 75°C (b) SEM image of silica tube formed at 0°C (c) TEM image of hollow silica tube obtained at 0°C

Source: (Mokoena *et al.*, 2003)

Silica nanotubes were synthesized from kaolin clay using surfactant, sulfuric acid and hydrothermal treatments (Dong *et al.*, 2003). White powder of silica nanotubes obtained was amorphous silica. The well-defined structure of

silica nanotubes was clearly seen in TEM image (Fig 8) which showed irregular rod-shaped hallow tubes. High resolution TEM images showed tubular structures with open ends, inner diameter of about 50 nm, outer diameter of 80 nm and an average length of less than 1 μm.

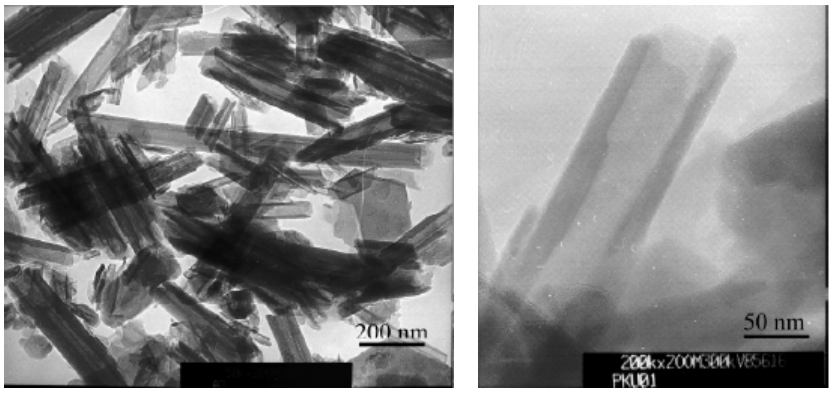

Figure 8 TEM image of the final silica nanotubes synthesized from kaolin clay.

Source: (Dong *et al.*, 2003)

Silica fiber-composite were obtained by using long chain carboxylic acid as template (Sudheendra and Raju, 1999). Experiments with different long chain carboxylic acid (octanoic, decanoic and lauric acids) were carried out. The SEM images showed the beautiful fiber structure, with diameter of 50 – 100 nm range. Heating the carboxylic acid silica fiber-composite in air at 400 °C for 2 hours removed the carboxylic acid and made the long fiber-like structure collapsed. The presence of the acid was found to be necessary for the formation of the fibrous structure.

Nanosized $CaCO_3$ particles with cubic and needle-like morphologies were employed as novel inorganic structure directing template to produce the hallow particles instead of the normally used organic templates (Chen *et al.*,

2004). The sodium silicate ($Na_2SiO_4.9H_2O$) was used as silica source. The hydrolysis and condensation of sodium silicate occurred, then silica was deposited over the surface of aggregate $CaCO_3$ cores to from core-shell structures. The spherical hallow silica particles with a diameter of 10 – 100 nm and wall thickness of approximately 10 nm (Fig 9) were obtained after calcining and dissolving $CaCO_3$ in diluted HCl solution. There were three IR characteristic peaks at 1081.15, 798.51 and 456.65 cm^{-1} belonging to three fundamental vibration bands for the silica structure (Bell *et al*., 1970, Sen and Thrope, 1977 and Gallener, 1979). The BET specific surface area of the hallow silica sphere was found to be as high as 725.2 m^2/g.

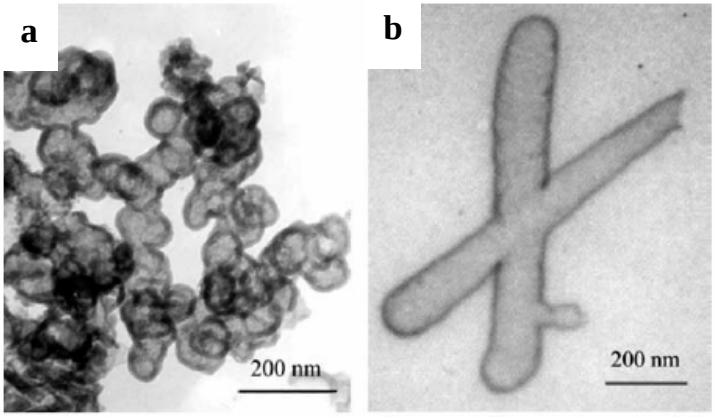

Figure 9 TEM images of hollow silica particles: (a) spherical particles using cubic $CaCO_3$ template; (b) tubular particles using needle-like $CaCO_3$ template.

Source: (Chen *et al.*, 2004)

The nanotubes, bamboo-like nanofibers and nanowires with uniform diameter of ~30 nm were synthesized using an ordered nanochannel of anodic alumina as templates (Zhang *et al*., 1999). Different morphology of the silicon oxide nanostructures was determined by the aging time and temperature of sol. A large number of nanotubes with uniform diameter of 30 – 50 nm was also

synthesized (Zhang *et al*., 2002). The photoluminescence (PL) spectra had maxima at 2.55 and 2.33 eV for the as-grown and annealed nanotube flakes. The strong emission might be due to the Si-OH complex located on both the inner and outer surfaces of the nanotubes.

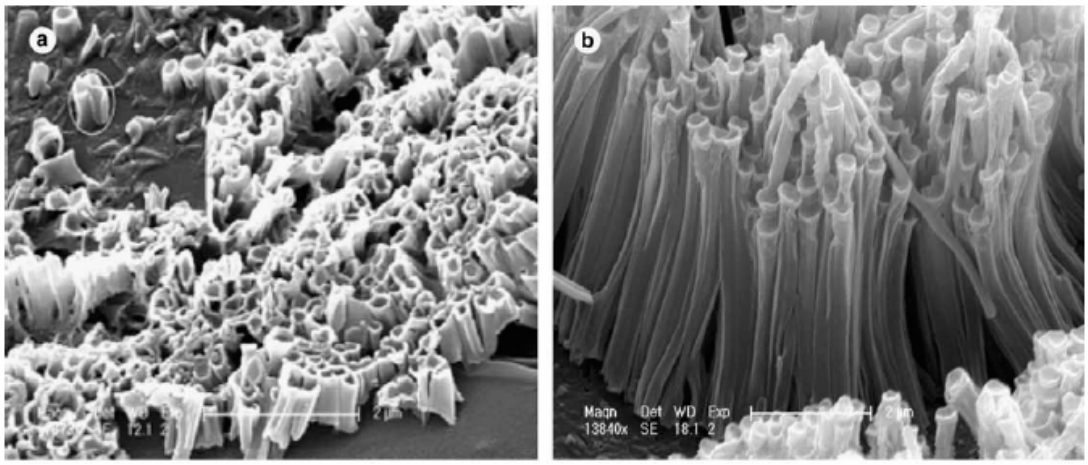

Figure 10 FE-SEM images of the silica nanotubes have been annealed at 100 ^{o}C for (a) 2h, and (b) 5 h after calcination and complete removal of the alumina template.

Source: (Zhu *et al*., 2005)

Zhu successfully developed a simple and effective method for preparing mesostructured silica nanotubes by using porous alumina membrane as a template (Zhu *et al*., 2005). Annealing time had an influence on the formation and growth of the nanotubes. The nanotubes were perpendicular to the substrate and the formed mesopore channels arranged over the whole nanotube sheath were parallel to each other (Fig 10). The nanotubes prepared could remain their sizes confined within the pores of alumina membranes and still attached to their growth substrate after the template has been removed.

A novel double-helical structure of the silica nanotube was produced using a binary sugar-based gel system as template (Jung *et al.*, 2002). The binary template consisted of a sugar-based gelator *p*- dodecanoyl-aminophenyl-*β*-D-glycopyranoside acting as an amphiphilic gelator and p-aminophenyl glucopyranoside whose amine moiety functioning as a binding site for hydrolyzed tetraethoxysilane (TEOS) (Fig 11). This adduct induced the formation of helical superstructure as a result of strong rigid and chiral packing of the sugar moieties through intermolecular hydrogen bonding interaction (Fig 12). The helicity of silica was transcribed from that of the template. Jung also used dimeric azobenzene appended cholesterol organogel (Fig 13a), which has two cholesterol skelatons as a chiral aggregate-forming site and two amino groups as an acidic proton or cationic binding site as a template. Sol-gel polymerization of TEOS was carried out to transcribe the superstructure formed in the organogel into the silica structure. The silica nanotube showed the fibrous structure with about 30 nm outer diameters and a few micrometers length (Fig 13b). The results obtained indicated that such organogel was successfully transcribed into the silica nanotube by the intermolecular hydrogen-bonding interaction between the amino group of the gelator and anionic silica particles (Jung *et al.*, 2003). The creation of the helical structure of the silica from the organogel was schematic presented in Fig 14. Luminescent silica nanotubes loaded with coumarion laser dye, 1, and with anthracene laser dye, 2, were prepared by sol-gel cocondensation of functional dyes and TEOS in a cholesterol-based organogel system (Han *et al*, 2005). The cholesterol-based organogel acted as a template to produce the tubular structure of the silica nanotubes (1 and 2) (Fig 15). There was a great difference in the PL spectrum of silica nanotubes loaded with functional dyes between ethanol and the solid state. In the former, a strong green light emission was achieved in dye 1,while a strong bluish green light emission was in dye 2; whereas in the

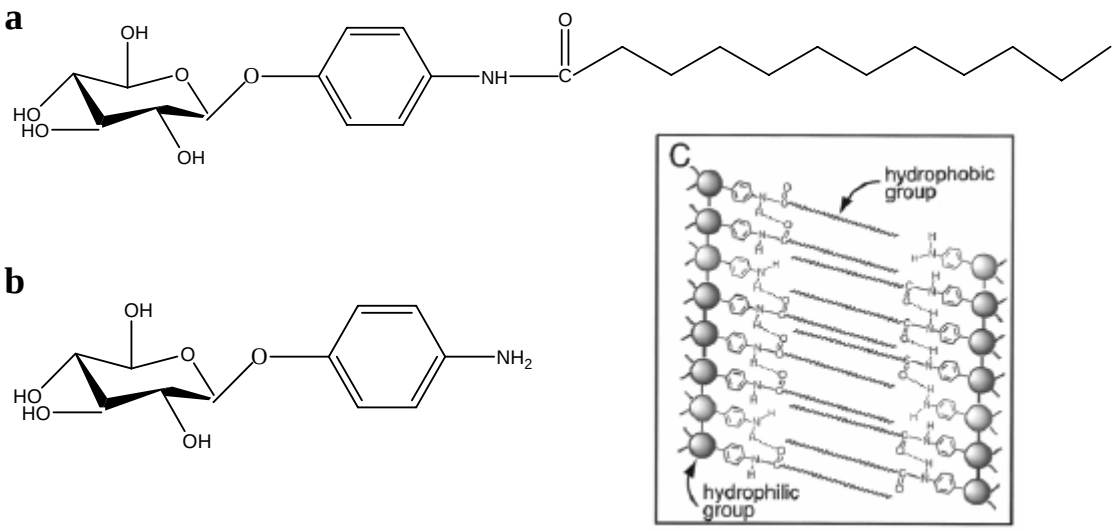

Figure 11 Structure of molecule for self-assembly process (a) structure of *p*-dodecanoyl aminophenyl-β-D-glucopyranoside (b) structure of *p*-aminophenyl glucopyranoside and (c) a possible self-assembling model in the bilayered chiral fiber from the mixed gel of a and b.

Source: (Jung *et al*., 2002)

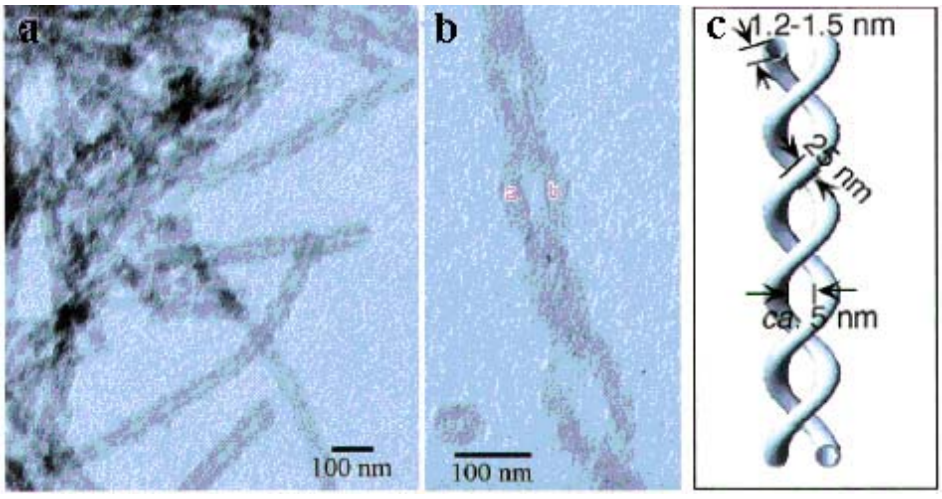

Figure 12 TEM images of the double-helical silica nanotube after calcinations (a and b), and (c) schematic representation of the double-helical structure of the silica nanotubes.

Source: (Jung *et al*., 2002)

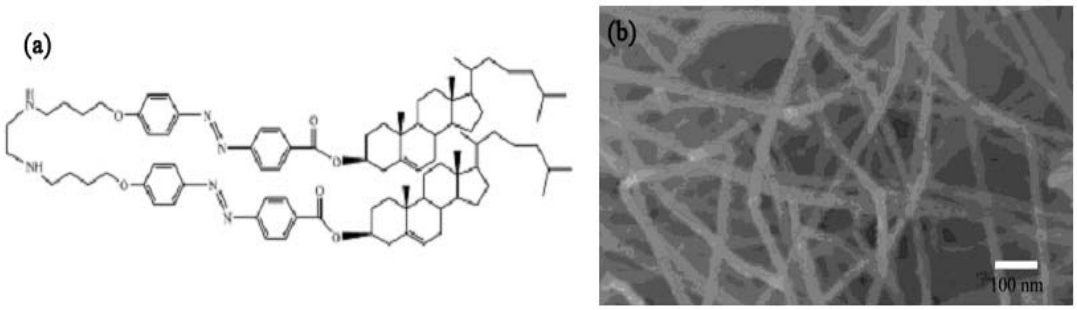

Figure 13 The structure of product appended cholesterol (a) The structure of dimeric azobenzene and (b) SEM picture of the silica nanotube obtained from 1-octanol gel 1 after calcinations.

Source: (Jung *et al*., 2003)

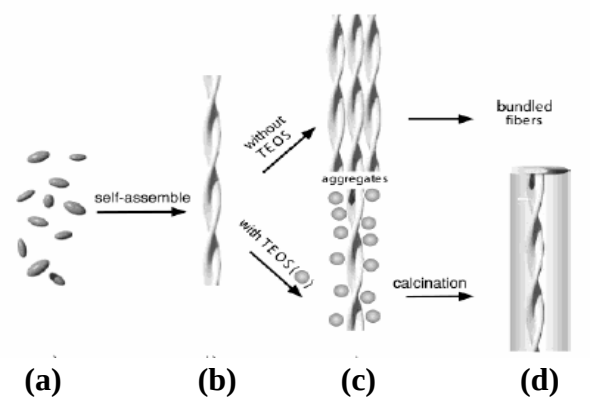

Figure 14 Schematic representation for the creation of the helical structure of the silica from the organogel state **1.** (a) gelator, (b) incipient organogel fiber, (c) silica adsorption (lower) and aggregation of organogel fiber (upper), and (d) the inner helical structure of the silica formed after calcination.

Source: (Jung *et al*., 2003)

latter, strong blue light emissions of dye 1 and dye 2 were observed at 482 and 483 nm, respectively.

The template-free growth of isolated ultralong and straight amorphous silica nanotubes in bulk quantity with a part of the tubes filled with indium sulfide nanorods was reported (Liang *et al*., 2004) (Fig 16). Transmission electron microscopy, scanning electron microscopy and X-ray diffraction analysis demonstrated, (1) the formation of hollow cylindrical amorphous silica tube with length up to hundreds of micrometers and outer diameters range of 70 to 300 nm, (2) silica tubes encapsulating indium sulfide nanorods with a cubic structure and (3) S-filled silica tubes with high sensitivity to a focused electron beam. A modified vapor-liquid-solid (VLS) process was proposed for the formation of amorphous silica nanotubes under the coexistence of low melting point indium (In) and sulfur (S). Indium sulfide nanorods were passively formed from capillary-induced filling. A similar process might be used to synthesize other sulfide nanorod filled silica nanotubes or other nanotubes.

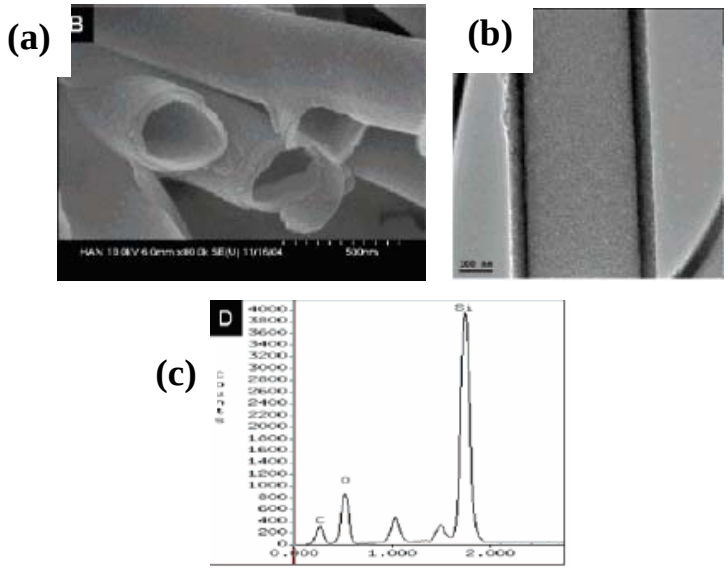

Figure 15 Image of silica tubes from cocondensation method. (a) FE-SEM image. (b)FE-TEM image and (c) EDX spectrum of dye 1 prepared in 1-butanol.

Source: (Han *et al*, 2005)

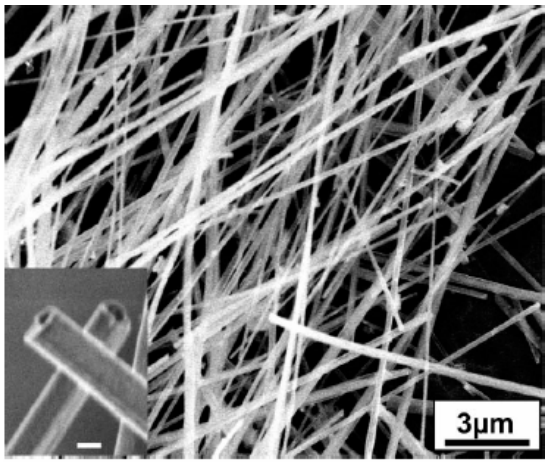

Figure 16 FE-SEM images illustrating the whisker-like morphology of the synthesized product. And small picture is a high-magnification image of the ends of two single hollow whiskers with a scale bar of 100 nm.

Source: (Liang *et al*., 2004)

Nanosilica was prepared by precipitation method and was characterized by various analytical tools (Jal *et al*., 2004). From transmission electron micrograph the silica particles were found to have almost spherical shape with a dimension of ~50 nm (Fig 17). The surface area was found to be 560 m^2g^{-1} and density 2.2 gcm^{-3}. From thermogravimetric analysis the total silanol density in the silica was found to be 7.68 nm^{-2}. A two tier hydration model was proposed from the results of thermogravimetric analysis. The number of reactive silanols that formed hydrogen bond with water molecules is found to be 2.48. The infrared spectral data supported the presence of the hydrogen bonded silanol group and the siloxane groups in silica.

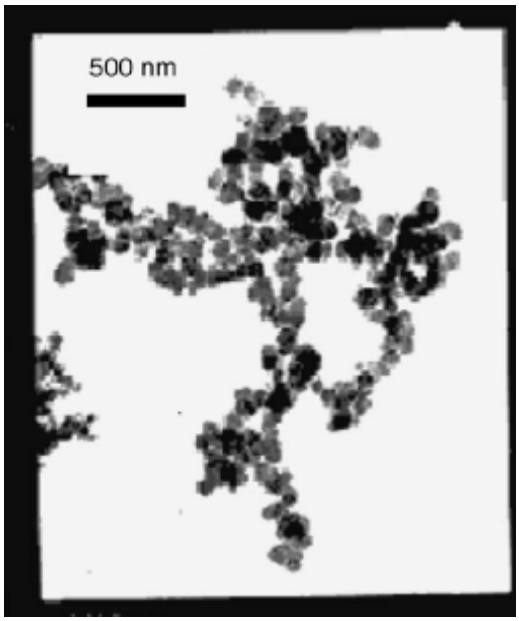

Figure 17 TEM images of nasnosilica particles ; 50,000X

Source: (Jal *et al*., 2004)