

Synthesis and Characterization of Silica Nanotube by Glycyldodecylamide as a Template

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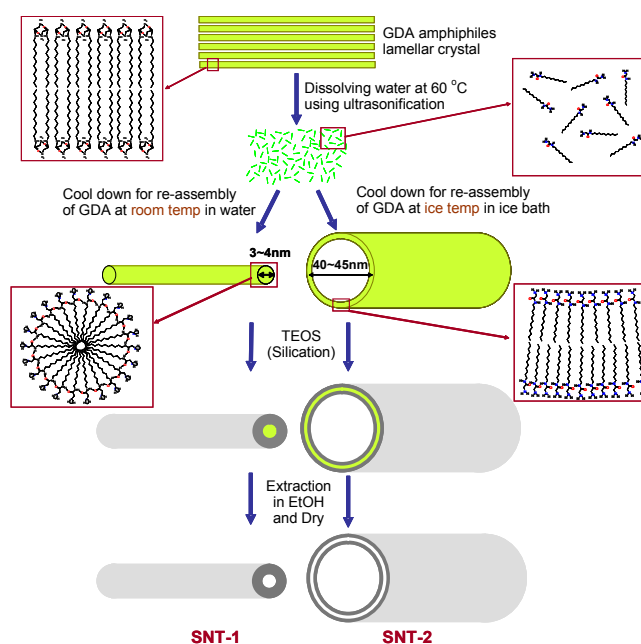
Many efforts have been devoted to synthesize various kind of inorganic nanotubes¹ due to their numerous significant applications.²⁻⁴ Among them hollow silica nanotubes (SNTs) have drawn considerable interest because of their advantages such as biocompatibility, controllable size, and accessible for the modification of surfaces⁵⁻⁷ increasing its utility in areas of nanofluidic, drug delivery, adsorption, catalysis, hydrogen storage, and bioseparation.⁸⁻¹¹

Several methods have been developed for synthesizing hollow silica nanotube. However, normal synthetic methods of silica nanotube are mainly through the sol-gel transcription process using various kinds of templates. These methods relied on severe conditions such as extreme pH, difficult template preparation and high pressure. For synthesizing silica nanotube, an organic templates including biomolecules and lipids which leads to gelation through the self-assembly of amphiphiles is required.¹²⁻¹⁹ Nowadays, research has increasingly focused on finding new templates for producing well-defined structures in terms of pore diameters, wall thickness, and aspect ratios *etc.* But several difficulties lie on the high orderness and creation of well-defined morphology.

One of attractive method for synthesizing silica nanotube is *via* neutral templating route²⁰⁻²⁴ due to formation of mesoporous structures with neutral amine and neutral silica precursors.²¹ Moreover this method is simple, based on ambient conditions facilitate easy recovery of the surfactant, yielding a thick silica wall and hydrothermally stable materials. This finding inspired us to develop a new glycyldodecylamide (GDA) surfactant as template for synthesis of silica nanotube.

The aim of our study was to undertake bio-silication through assembly in an aqueous solution using glycyldodecylamide surfactant. Two types of silica nanostructure (SNT-1 and SNT-2) were synthesized with narrow (3 - 4 nm) and wide (45 nm) diameters, respectively by temperature dependent self assembly (Scheme 1). The silica nanotubes were synthesized by the hydrolysis of TEOS as a silica source after dissolving the surfactant in a water/ethanol (10: 1) solution.²¹

The XRD pattern of SNT-1 showed the broad band at the small-angle scattering regime ($2\theta < 2^\circ$), which could indexed as a lattice constant, $a = 4.1$ nm (Figure S1 red line). The self-assembled GDA gel in a dry form also shows the periodical diffraction peaks, indicating its assembled structure as a lamellar organization (Figure S1 black line). The d-spacing of the aggregates were approximately 4.1, 2.06, 1.38, 1.05 nm and corresponded to the twice of the extended molecular length of GDA



Scheme 1. Schematic representation of tubular nanostructure by self assembled GDA amphiphilic templating process (left: SNT-1, right SNT-2)

(2.05 nm, by the Chemdraw 3D molecular modeling) that is quite similar to the length of two molecules of GDA surfactant.²⁵ These results indicated that a gelation material maintained a bilayered structure with a 4.1 nm of bimolecular sheet which was corresponded to the (100) plane (Figure S1A). The SEM image strongly supported the lamellar structure, which could be explained due to the hydrogen bonded bilayered assembly of GDA dimeric amphiphile (Figure 1A). The measured diameter of 48 nm of GDA gel in D₂O solution at 4 °C from SANS (Small Angle Neutron Scattering) was corresponded to the 45 nm of diameter of SNT-2 (Figure S1B).

Moreover, it was confirmed that GDA surfactant could be easily extracted by simple extraction with hot ethanol. After extraction of the GDA surfactant the obtained SNT-1 was investigated with FE-SEM and FE-TEM (Figure 1B, 1C). This mesoporous silica displays a wormhole structure with an inner diameters *ca.* around 3 nm. This result was similarly to the typical HMS typed mesoporous silica from long chain alkylamine surfactant.²¹ However, SNT-2 that had an around 45 nm of inner porosity and 85 nm of outer diameter was prepared after gelation (Figure 1E, 1F). Also SNT-2 had pretty long ranged straight-channeled structure having a high aspect ratio with one dimen-

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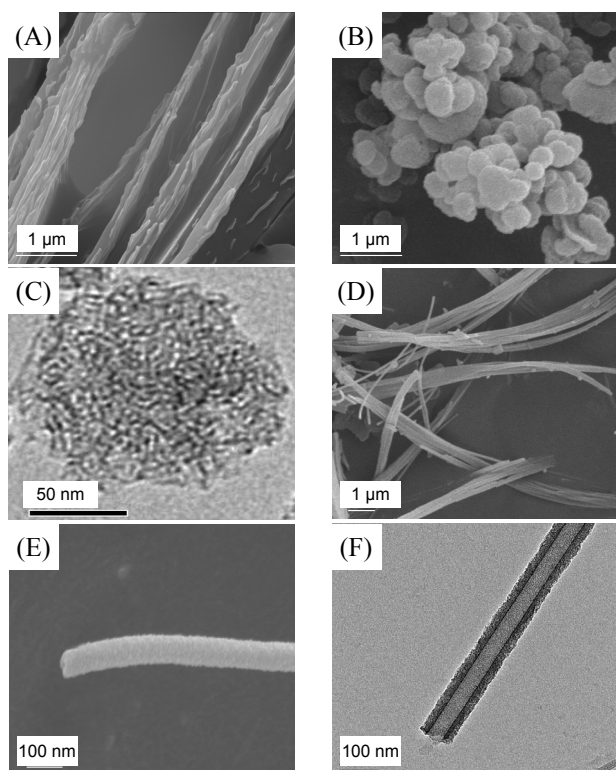


Figure 1. (A) SEM image of GDA gelator (B) SEM image of SNT-1 (C) High resolution transmission electron micrograph (FE-TEM, JEOL, JEM 2100F) of SNT-1 (D) SEM image of SNT-2 bundles (E) Enlarger SEM image of SNT-2 (F) TEM image of SNT-2.

sionality (Figure 1D). The preformed GDA structures in aqueous solution into the rigid and large-sized nanotubes were accurately transcribed into the relatively large pore silica nanotube.

The mesoporosity of the samples were analyzed by using nitrogen sorption study. The SNT-1 showed type IV isotherm with narrow mesopore distributions at 2.8 nm. However, this pore size of SNT-1 did not match with the linear length of GDA molecule. We assumed that the GDA micelles were densely packed in the aqueous solution cause by hydrophobic interaction of long tails of amphiphiles. Whereas in the case of SNT-2 showed the presence of big sized mesopore tubes. The ethanol extracted SNT-1 and SNT-2 materials had a BET (Brunauer-Emmett-Teller) surface area of 685 m²/g and 395 m²/g and pore volumes of 0.85 cm³/g and 1.12 cm³/g, respectively. The pore size distribution clearly confirmed that the pore volume corresponding to the 2.8 nm pore diameter decreased with increasing pore volume around 45 nm (Figure S2).

The FT-IR shows the stretching modes of the GDA amphiphile at 1638 and 1674 cm⁻¹ assigned to hydrogen bonded amide stretch and amide stretch induced by non-hydrogen bond, respectively²⁶ inferring β -sheet like character. In the as-synthesized SNT-1 material, the hydrogen bonding peak (named as Amide Band I) was strongly observed at 1655 cm⁻¹ indicate that the peptide region also adopts significant α -helix or random coil hydrogen bonding conformations. However, the as-synthesized SNT-2 material shows similar peaks as those of amide peaks of GDA. So, it revealed that the bilayered structured GDA amphiphiles easily converted to GDA dimer structure under drying condition (Figure S3).

In summary, controlled diameters and morphology of the mesoporous silica nanotubes were formed at neutral conditions by temperature dependent self-assembly of GDA amphiphile and moreover surfactant recyclability. The hydrogen bonded self-assembly of the GDA crystal in a polar solvent gave a well-ordered GDA lamellar structure. This seemed to be due to the primary amine group in GDA, which gave stronger hydrogen bonded moiety with oxygen from the carbonyl group than with amide proton during the drying process. In an aqueous solution the micelle of GDA amphiphile formed at before gelation, showed 3 - 4 nm diameter wormhole like structure (SNT-1). In contrast, at 0 °C GDA formed was bilayered large tubular structure after gelation having around 45 nm (SNT-2).²⁷ These findings might open a great opportunity for appropriate use of such materials for molecules storage and as nanoreactor.

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