

Tunable One-Dimensional Helical Nanostructures: From Supramolecular Self-Assemblies to Silica Nanomaterials

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Herein, one-dimensional double helix is fabricated via supramolecular self-assembly of a sugar-based amphiphile, which can be utilized as soft template to synthesize silica double helices and nanotubes through sol–gel reaction of tetraethyl orthosilicate (TEOS). The self-assembled double helix can be rationally transformed into nonhelical fibers with the aid of conventional ionic surfactants. It is suggested that the introduction of ionic surfactant will impart electrostatic repulsion inside double helix and shape double helices into nanofibers. Interestingly the nonhelical fibers coassembled by C₄AG and cationic surfactants have been proven to direct the preparation of single-stranded helical SiO₂ through sol–gel polycondensation. This is the first time that both double and single-stranded silica helix have been created in one system.

Introduction

Nature has the unique power to create sophisticated architectures, spanning from organisms to inorganic species and from nanoscale to macroscopic scale. The exquisite examples of well-defined structures in nature involve DNA double helix, twisted β -sheet, bones, teeth, and diatoms shells. Attracted by nature's works, chemists have endeavored in mimicking natural synthetic process and creating novel architectures of similar functionality and complexity. Among these studies, helix is a central structural motif because of its significance in biological process and biological evolution, as well as its versatile applications in material science, asymmetric synthesis, sensing, and chiral devices.^{1–6} Therefore, the study of building helical architectures has drawn intense interest.

During past few years, considerable attention has been focused on the design of supramolecular self-assembled helix based on noncovalent interactions (e.g., hydrophobic effect, hydrogen bond, van der Waals force, and

coordination effect).^{7–15} The building blocks for supramolecular helix include polypeptides,^{16,17} OPes,^{18,19} OPVs,²⁰ model bile,^{21,22} synthetic polymers,^{23,24} sugarlipids,^{25–29} hexabenzocoronene amphiphiles,^{30,31} and

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lipids.^{32,33} One of the appealing advantages of self-assembled helical structures is their high tunability and controllability with respect to size, shape and chirality in response to environmental conditions.

In contrast, the creation of inorganic helical materials seems to be more difficult although they are appealing subjects during past decade.^{34–41} Recently soft template method has emerged as one of effective strategies to transcribe chiral supramolecular self-assembles into diverse helical nanomaterials including single-strand helical nanotubes, double helical nanotubes, helical bundles, and inner helical structure.^{42–52} Different from other preparative methods, soft template strategy possess its own advantages such as simple procedures (especially one-pot synthesis), variability of the template sources, and easy removal of the templates by washing at low temperature. The pioneering work has been conducted by Hanabusa and Shinkai, who reported a novel creation method of helically structured silica by sol–gel reaction in chiral diaminocyclohexane-based organogel systems. In their work, both right- and left-handed helical silica and transition-metal oxide structures can be created by transcription of

right- and left-handed structures in the organogel fibers.^{53–55} Shimizu and co-workers has transcribed self-assembled double helix in sugar-based gelator into a novel double-helical silica nanotubes.⁵⁶ Recently Stupp has synthesized single and double nanohelices of cadmium sulfide (CdS) utilizing supramolecular templates.^{57,58}

Despite the studies dedicating to helical nanomaterials, the transcription of organic helical aggregates into inorganic helix with tunable shape, size, porosity, and helicity remains a research interest to chemists. In this paper, we have demonstrated a rational design of artificial nanohelices, both in organic and inorganic materials. Double-stranded helical fibers are fabricated via supramolecular self-assembly of a synthetic sugar-lipid C₄AG,⁵⁹ which can serve as soft template to create silica double-stranded nanohelices and nanotubes. By introducing interchain repulsion through chemical approach, organic double-stranded nanohelices can transform into nonhelical nanofibers, which are further utilized to direct the synthesis of silica single-stranded nanohelices.

Experimental Section

Materials. The surfactants dodecyltrimethyl ammonium bromide (C₁₂TAB), tetradecyltrimethyl ammonium bromide (C₁₄TAB), cetyltrimethyl ammonium bromide (C₁₆TAB), cetylpyridinium bromide (C₁₆PyB), and sodium dodecylsulfate (SDS) are bought from Acros Organics Co. and used as received. Octadecyltrimethyl ammonium bromide (C₁₈TAB) and cetyltriethyl ammonium bromide (C₁₆TEAB) are prepared by the reaction of bromoalkane and corresponding trialkylamine. Cetyltrimethylimidazolium bromide (C₁₆MinB) is synthesized from methylimidazolium and bromohexadecane. The amphiphiles C₄AG is synthesized according to our previous paper.⁵⁹

Preparation of Self-Assembled Nanostructures. (1) To prepare self-assembled double helix, C₄AG solid is added into pure water, sealed and heated to 70–80 °C until the solid is totally soluble in water. Then the solution is cooled at room temperature and a viscous solution is formed. (2) To obtain the nanofiber solution, C₄AG solid is added into pure water and heated to become a clear homogeneous solution at 70–80 °C. Later, a desired amount of surfactant stock solution (ca. 100 mM) is added into C₄AG solution and the sample is slowly cooled to room temperature.

Preparation of Silica Nanomaterials. Typically, to prepare double helical SiO₂, 50 μL of ammonia (2 wt %) solution is added into 3 mL C₄AG solution in test tubes. The sample is vortex mixed to ensure complete mixing. After that, 30 μL TEOS is fed into the amphiphilic solution under magnetic stirring. Then the mixed solution is incubated under static conditions in thermostat container. If not specific mentioned, the TEOS hydrolysis reaction is performed at 25 °C for 48 h. Subsequently, the as-formed silica gel is washed with ethanol for three times, collected after centrifugation, and further applied to TEM and SEM observations. For nitrogen adsorption and desorption experiments, the SiO₂ products are dried at 70 °C and moved to a furnace to be calcined. The annealing procedure is performed at a heating rate of 5 °C/min and kept at 550 °C for

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2 h to remove surfactants and organic residua. After cooling naturally to room temperature, a large quantity of white powder is obtained as source material.

The single-stranded helical SiO₂ is prepared in C₄AG/cationic surfactant mixtures. The molar ratio of C₄AG, surfactants, TEOS, and ammonia is C₄AG/C₁₂TAB/TEOS/NH₃ (1:1.2:9:0.8); C₄AG/C₁₄TAB/TEOS/NH₃ (1:0.8:9:0.8); C₄AG/C₁₆TAB/TEOS/NH₃ (1:0.4:9:0.8); C₄AG/C₁₈TAB/TEOS/NH₃ (1:0.2:9:0.8); C₄AG/C₁₆PyB/TEOS/NH₃ (1:0.4:9:0.8); C₄AG/C₁₆TEAB/TEOS/NH₃ (1:0.4:9:0.8); C₄AG/C₁₆MinB/TEOS/NH₃ (1:0.4:9:0.8). The pH value of C₄AG/surfactant/NH₃ solution is controlled at pH = 9.29.

Cryo-TEM. A small drop of sample is placed on a 400 mesh copper grid, and a thin film is produced by blotting off the redundant liquid with filter paper. This thin film is then quickly dipped into liquid ethane, which is cooled by liquid nitrogen. Observation of the cryo-sample is carried out at -183 °C.

Negative-Staining TEM. TEM micrographs are obtained with a JEM-100CXII transmission electron microscope (working voltage of 80–100 kV) by the negative-staining method with uranyl acetate solution (1%) as staining reagent.

Circular Dichroism (CD). CD spectra are recorded using a JASCO J-810 spectrometer. The path length of the quartz cell is 0.1 mm. The experiment is conducted at room temperature and each measurement is repeated for three times.

Field Emission-Scanning Electron Microscopy (FE-SEM). Silica materials in ethanol are dropped on silicon plate and air-dried before applied to SEM observation (SEM, Hitachi S4800).

Nitrogen Adsorption and Desorption. Nitrogen adsorption and desorption isotherms are measured using a Micromeritics ASAP 2010 system at -196 °C. The samples are degassed at 350 °C overnight under vacuum (10⁻⁵ Torr) before measurement. The specific surface area is obtained by Brunauer–Emmett–Teller (BET) method.

Results and Discussion

Transcription from C₄AG Double Helix into Chiral SiO₂ Nanomaterial. According to our previous work,⁵⁹ the novel sugar-lipid C₄AG is synthesized which can self-assemble into well-defined double helix in aqueous solution through multiple noncovalent interactions (Figure 1). As shown in TEM images, the supramolecular self-assembled double helices in C₄AG solution are exclusively left-handed, with the pitch of approximately 25 nm, the diameter of 14–16 nm and the extended length of several micrometers. It is expected that they can be further exploited as soft template to design chiral inorganic nanomaterials because these double helices are highly stable and can be facily prepared

Herein, the sol–gel polycondensation of TEOS is conducted in C₄AG solution to prepare helical SiO₂, in which ammonia solution serves as a catalyst. It is important that C₄AG double helix can maintain their morphology with the addition of ammonia solution (Figure S1). Following the procedure in Experimental Section, double-stranded helical silica can be replicated from C₄AG double helix with different C₄AG/TEOS/NH₃ molar ratios (Figure 2). These nanohelices are exclusively left-handed with the pitch of 25 nm, in agreement with that of organic template. Besides, the duplex width of silica materials is approximately

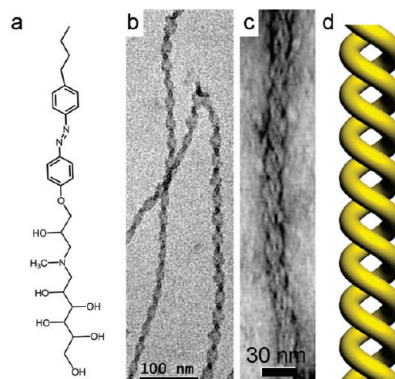


Figure 1. (a) Molecular structure of C₄AG amphiphile; (b) cryo-TEM image of double helix in C₄AG solution; (c) TEM image of double helix stained with uranyl acetate; (d) Representative scheme of left-handed double helix. The concentration of C₄AG is 5 mM. (*T* = 25 °C).

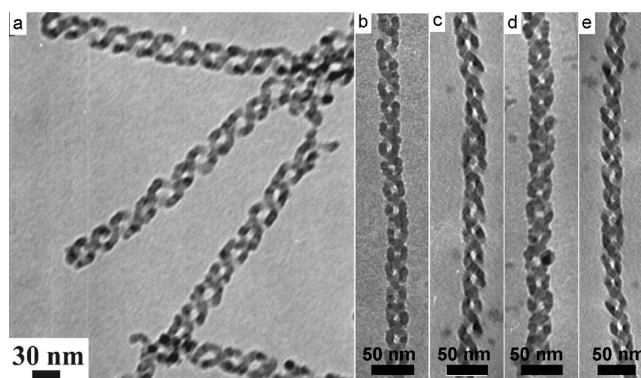


Figure 2. As-prepared double helical SiO₂ templated from C₄AG solution with different molar ratios: (a, b) C₄AG/TEOS/NH₃ (1:9:4, pH = 10.52); (c) C₄AG/TEOS/NH₃ (1:9:5, pH = 10.60); (d) C₄AG/TEOS/NH₃ (1:9:6, pH = 10.64); (e) C₄AG/TEOS/NH₃ (1:9:7, pH = 10.66). The concentration of C₄AG solution is fixed at 5 mM. (*T* = 25 °C).

30 nm which is slightly larger than organic helix. It is therefore believed that as-prepared silica nanomaterials are good replicas from C₄AG double helix. EDS (energy dispersive X-ray spectroscopy) result demonstrates the composition of Si and O element (Figure 3a). N₂ adsorption–desorption isotherms shows the BET surface area of around 367 m²/g (Figure 3b).

It has been realized that the transcription of soft templates into silica materials should satisfy two requirements:⁵⁶ (1) The self-assembled morphology of organic molecules should be stably maintained during the sol–gel reaction. As shown in Figure S1, the addition of ammonia did not interfere the self-assembly behavior of C₄AG and double helix can still exist. (2) The presence of strong intermolecular interactions (such as electrostatic forces or efficient hydrogen bond) is required in order to adsorb “anionic” inorganic precursor moieties onto the organic molecular assemblies. As proposed in our previous results,⁵⁹ self-assembled C₄AG double helix is fabricated with the sugar moiety exposed on the surface; in other words, the surface of helical fibers has a large amount of hydroxyl groups. During the sol–gel process, silica precursors of anionic oligomeric siloxanes are adsorbed onto the self-assembled helix through hydrogen bond between

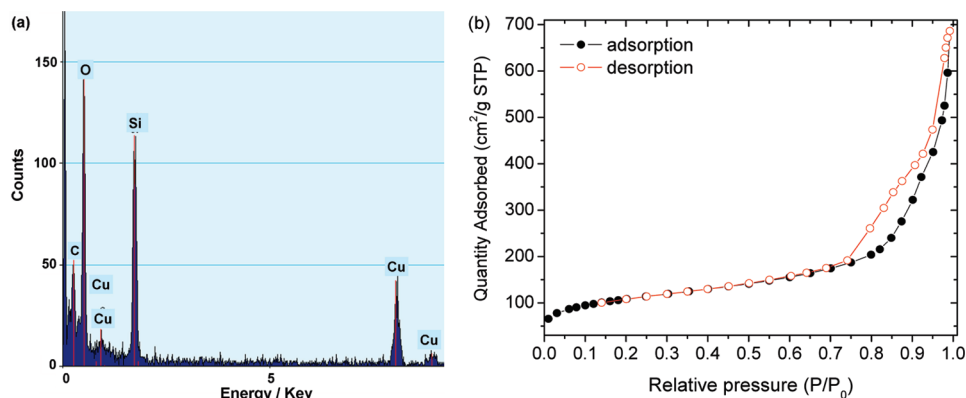
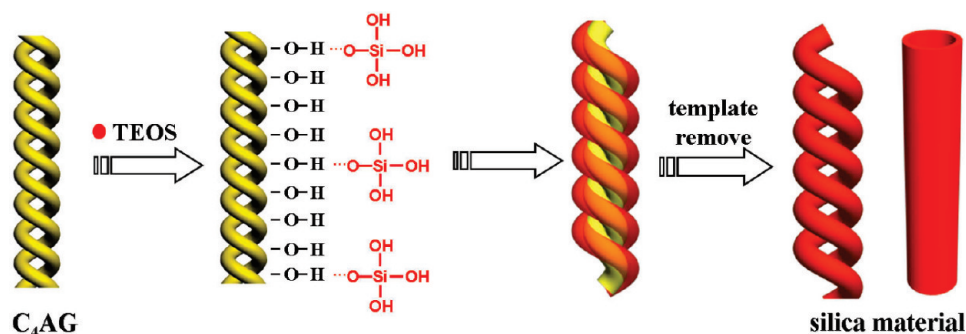


Figure 3. (a) EDS result of the as-prepared double helical silica; (b) N₂ adsorption–desorption isotherms of calcined silica double helix. The silica nanomaterials are obtained from the system of C₄AG/TEOS/NH₃ with the molar ratio of 1:9:4. The concentration of C₄AG solution is fixed at 5 mM.

Scheme 1. Possible Scheme of Sol–Gel Reaction into Double Helical SiO₂ Nanomaterials



Si–OH and sugar hydroxyl (Scheme 1).⁶⁰ Consequently the morphology of C₄AG double helix can be transcribed to SiO₂ nanomaterials. Enlarge TEM images are taken during the sol–gel reaction to display the adsorption of silica on the helical fibers (Figure S2).

Transcription of the organic templates is carried out under different conditions to assess the role of each parameter on the morphology of replicated objects. Specifically, the ammonia concentration and transcription temperature is varied. First, the concentration of catalyst ammonia seems to be an essential factor that influences TEOS polycondensation. When the ammonia concentration is lowered, silica nanotubes rather than double helices can be obtained (Figure 4). The nanotubes diameter is approximately 30 nm and the inner diameter is 15–20 nm. As indicated by arrows, the hollow nanotubes can exhibit obvious chiral character (Figure 4c). N₂ adsorption–desorption isotherms gives the BET surface areas of 423, 438, and 464 m²/g for the calcined silica nanotubes prepared from C₄AG/TEOS/NH₃ system with the molar ratio of 1:9:0.2, 1:9:0.4, and 1:9:0.8 (Figure S3). The important role of ammonia on the formation of silica nanotubes and helix may be rationalized as below. At higher alkali condition, siloxanes particles become negatively charged and the electrostatic repulsion between siloxanes particles is relatively strong. As a result, the siloxane particles cannot pack closely on the fiber surface. Only a small amount of siloxane particles will adsorb

on C₄AG double helix through hydrogen bond which results into double helical SiO₂ (Figure 2). At lower alkali condition, the electrostatic repulsion between siloxanes particles is relatively low. Thus, large amounts of siloxane particles will adsorb on C₄AG double helix and continuous Si–O–Si network covering organic helices are favored. Consequently, SiO₂ nanotubes can be obtained (Figure 4). Second, the sol–gel reaction temperature is found to affect the diameter of SiO₂ nanotubes. When the polycondensation temperature is raised from 25 to 40 °C, the nanotubes diameter increases from 30 to 50 nm and the nanotube wall becomes thicker (Figure S4). This is because the sol–gel reaction is promoted at higher temperature and more silica can be deposited on the surface of soft template.

Surfactant-Induced C₄AG Double Helix to Nonhelical Fiber Transition. It is supposed that the mesoscopic chirality of self-assembled double helical fibers in C₄AG solution arises from the intrinsic helicity of sugar groups and the double strands are held together by the interchained affinity of hydrogen bond.⁵⁹ Therefore, when interchained repulsion is introduced, it is reasonable that double-stranded helix can be destroyed. To test our hypothesis, conventional cationic surfactant cetyltrimethyl ammonium bromide (C₁₆TAB) is introduced into the C₄AG solution. Cryo-TEM is performed to reveal the self-assembled structures in solution without artifacts. It is interesting to find that double helix in 5 mM C₄AG solution (see Figure 1) transforms into nonhelical fibers in the solution of C₄AG/C₁₆TAB (5 mM/2 mM) (Figure 5a).

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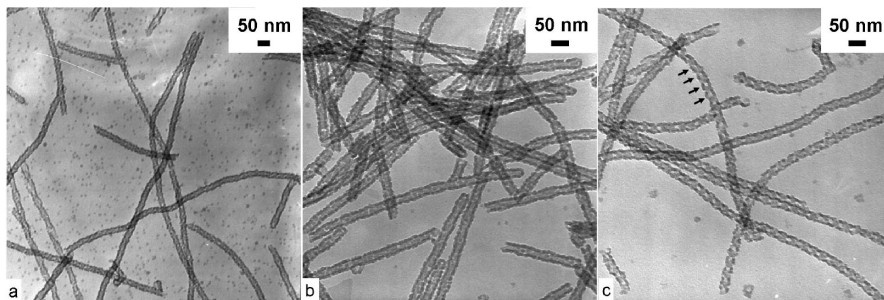


Figure 4. As-prepared silica nanotubes through sol-gel process with $C_4AG/TEOS/NH_3$ molar ratio of: (a) 1:9:0.2, pH = 9.29; (b) 1:9:0.4, pH = 10.52; (c) 1:9:0.8, pH = 10.60. The concentration of C_4AG solution is fixed at 5 mM. ($T = 25\text{ }^\circ\text{C}$).

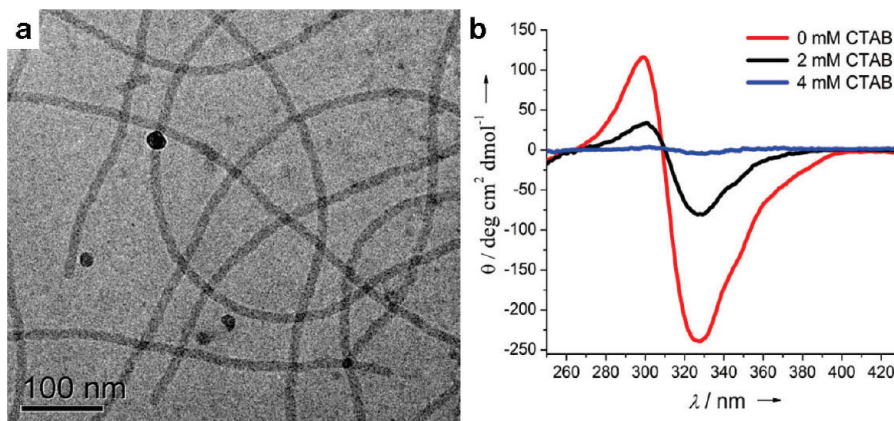


Figure 5. (a) Cryo-TEM images of $C_4AG/C_{16}TAB$ solution (5 mM/2 mM); (b) Circular dichroism of C_4AG solution (5 mM) with the addition of cationic surfactant $C_{16}TAB$. ($T = 25\text{ }^\circ\text{C}$).

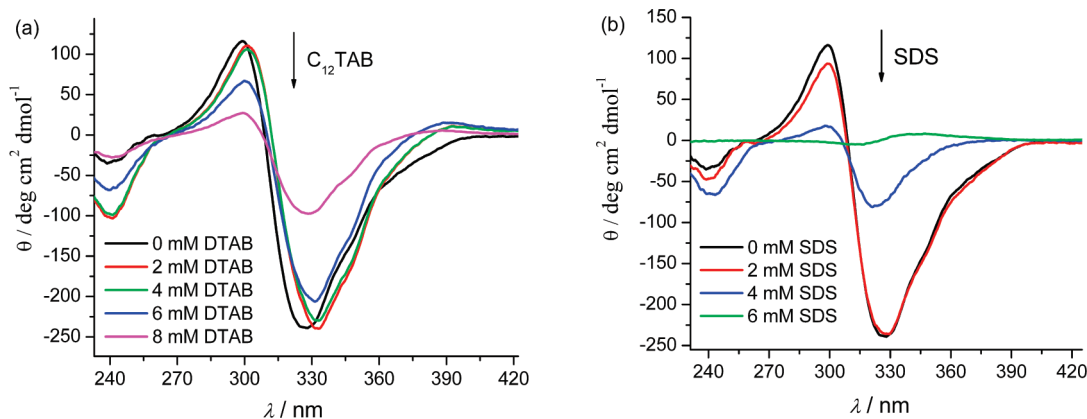


Figure 6. Circular dichroism of C_4AG solution (5 mM) with the addition of ionic surfactants: (a) $C_{12}TAB$; (b) SDS.

The self-assembled nanofibers have uniform diameter of ~ 10 nm and micrometer scale length. It is worthwhile that single-stranded nanofibers are the exclusive aggregates in $C_4AG/C_{16}TAB$ (5 mM/2 mM) mixture as revealed by cryo-TEM. There are no other structures, such as double helix or vesicle under TEM scope. When the concentration of surfactant $C_{16}TAB$ is further increased to 4 mM, self-assembled nanofibers are broken down. Circle dichromom spectrum is applied to illustrate chiral molecular packing inside self-assembled nanostructures (Figure 5b). In the absence of $C_{16}TAB$, the CD spectrum of C_4AG solution (5 mM) exhibits negative Cotton effect, which is

in agreement with left-handed double helix. With addition of 2 mM $C_{16}TAB$, the Cotton signal can be still detected while the intensity is decreased. When the concentration of $C_{16}TAB$ is increased to 4 mM, the Cotton effect in CD spectrum is unobservable.

In further experiments, the transition from double helix to nonhelical fibers can be triggered by other ionic surfactants. As Figure 6a shows, the CD signal of C_4AG solution (5 mM) exhibits gradual decrease with the addition of dodecyltrimethyl ammonium bromide ($C_{12}TAB$). TEM image demonstrates the formation of nonhelical nanofibers in $C_4AG/C_{12}TAB$ (5 mM/6 mM)

mixture (Figure S5). Similar results can be observed in C_4AG/SDS system (Figure 6b). The effect of ionic surfactants can be rationalized as below. Ionic surfactants such as $C_{16}TAB$ can coassemble with C_4AG amphiphile in solution, mainly driven by hydrophobic effect. This imparts electrostatic repulsion to double helix, which is unfavorable for close chiral packing of amphiphiles. As a result, double helix will be destroyed and transforms into nonhelical fibers, accompanied by the decrease of CD signal in $C_4AG/C_{16}TAB$ solution. When ionic surfactant concentration was increased to a threshold value (such as 4 mM $C_{16}TAB$), the nonhelical nanofibers can be further broken down because of the solubilization effect of surfactants, accompanied by the disappearance of CD signal.

Transcription from Self-Assembled Nonhelical Fiber to Helical SiO_2 . Furthermore, the self-assembled nonhelical fibers in $C_4AG/C_{16}TAB$ system (5 mM/2 mM) can be utilized as a soft template to synthesize single-stranded silica nanohelix with high yields (Figure 7). The width of resulting silica helix is about 40–50 nm and the pitch of 30 nm. EDS data shows these single nanohelices are composed by Si and O with roughly 1:2 Si/O ratio (Figure 8a). The BET surface area calculated from N_2 adsorption–desorption isotherms is around 671 m^2/g (Figure 8b). Similar to the situation of the $C_4AG/C_{16}TAB$ system, silica nanohelix can be prepared in C_4AG solution with a series of cationic

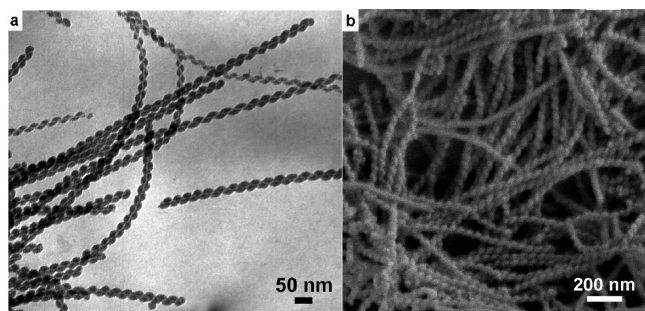


Figure 7. As-prepared single-stranded silica helix prepared from $C_4AG/C_{16}TAB$ (5 mM/2 mM) solution by sol–gel transcription: (a) TEM and (b) SEM image. The $C_4AG/C_{16}TAB/TEOS/NH_3$ molar ratio is 1:0.4:9:0.8, pH = 9.29.

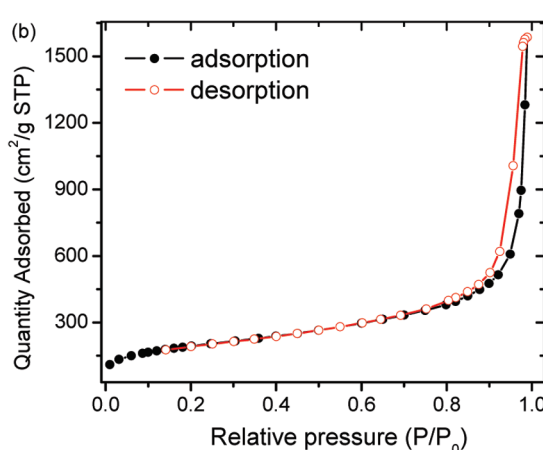
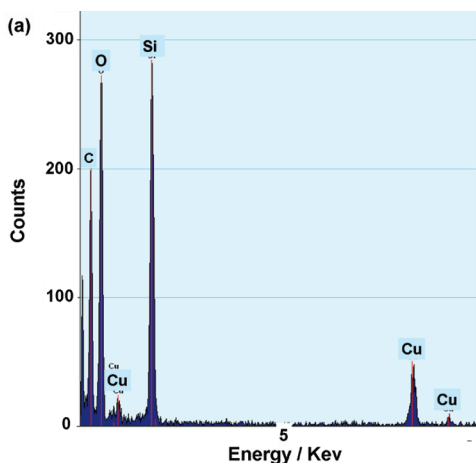


Figure 8. (a) EDS and (b) N_2 adsorption–desorption isotherms of calcined single helical silica prepared from $C_4AG/C_{16}TAB$ (5 mM/2 mM) solution by sol–gel polycondensation.

surfactants with different hydrocarbon chain lengths and hydrophilic headgroups, that is, $C_{12}TAB$, $C_{14}TAB$, $C_{16}TAB$, $C_{18}TAB$, $C_{16}EAB$, $C_{16}PyB$, and $C_{16}MinB$ (Figure 9). SEM images are also provided to confirm the formation of well-defined SiO_2 helix (Figure 10). A small amount of silica nanotubes can be also obtained in these systems (see Figure 10).

It is surprising that helical SiO_2 is prepared in the nonhelical C_4AG /surfactant fibers. Herein, the possible mechanism of helical SiO_2 formation is discussed (Scheme 2). As illustrated above, the addition of ionic surfactants imparts cationic charges to self-assembled C_4AG double helix which is unfavorable for double helix formation and gives rise to nonhelical nanofibers. Because of the introduction of cationic charge, the affinity of silica precursor to nanofiber surface can be facilitated through electrostatic attraction between cationic surfactant and anionic silica precursor, resulting in a higher yield of silica nanomaterials. On the other hand, the nonhelical nanofibers self-assembled by $C_4AG/C_{16}TAB$ (5 mM/2 mM) exhibit notable Cotton effect in CD spectrum. It is therefore supposed that cationic surfactants arrange a chiral packing inside $C_4AG/C_{16}TAB$ nanofibers (Scheme 2). As a consequence, anionic silica precursor can deposit on

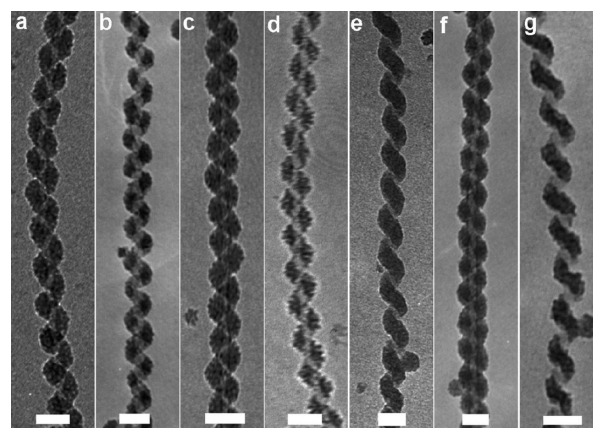


Figure 9. TEM images of as-prepared single-stranded helical SiO_2 prepared from 5 mM C_4AG solution with the addition of cationic surfactant. The C_4AG /surfactant/ $TEOS/NH_3$ molar ratio is listed in Experimental Section. (The scale bar is 50 nm).

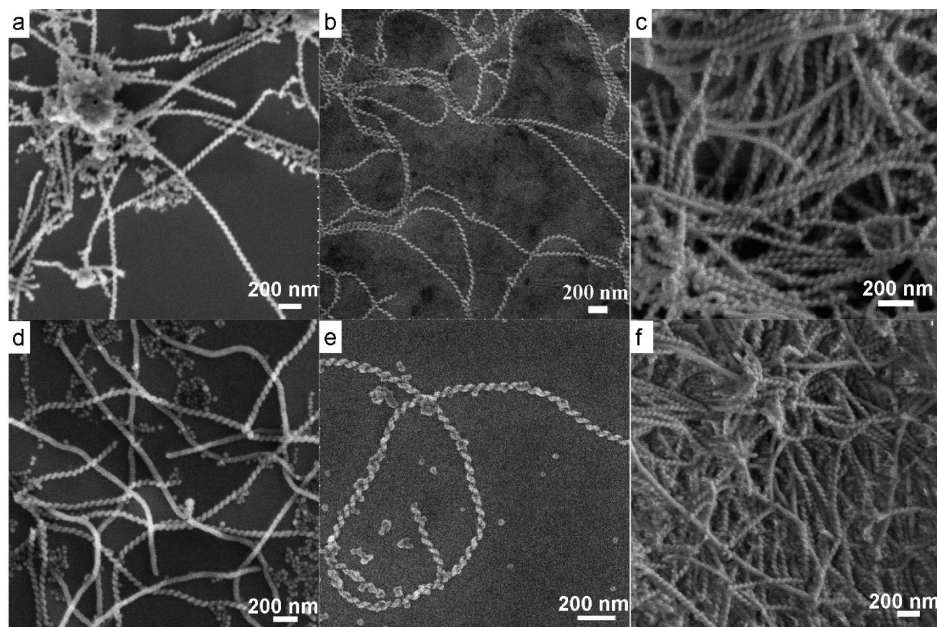
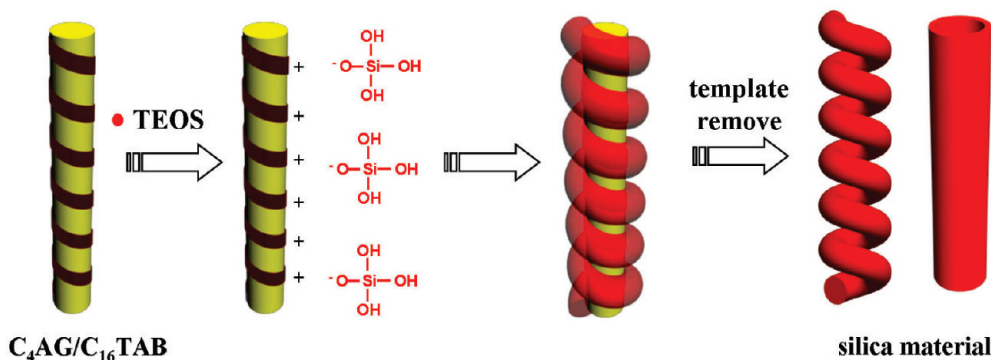


Figure 10. SEM pictures of as-prepared silica single helix prepared from 5 mM C_4AG solution with the addition of cationic surfactant: (a) $C_{12}TAB$; (b) $C_{14}TAB$; (c) $C_{16}TAB$; (d) $C_{16}MinB$; (e) $C_{16}PyB$; (f) $C_{16}TEAB$. The C_4AG /surfactant/TEOS/ NH_3 molar ratio is listed in Experimental Section.

Scheme 2. Possible Scheme of Helical SiO_2 Nanomaterials in the System of $C_4AG/C_{16}TAB^a$



^aThe brown ribbon on the $C_4AG/C_{16}TAB$ fiber gives a proposed location of $C_{16}TAB$, which can not be observed under TEM.

nanofiber surface in chiral patterns driven by electrostatic attraction between silica precursor and $C_{16}TAB$. In this way, single-stranded helical SiO_2 is prepared using nonhelical fibers as a soft template.

During the sol-gel process, two factors are significantly important: cationic charge and its chiral packing inside nanofibers. In control experiment, when cationic surfactant is replaced by anionic surfactants such as sodium dodecyl sulfate or sodium dodecyl sulfonate, the yield of silica is extremely low and irregular silica materials is produced. On the other hand, we have conducted sol-gel polycondensation of TEOS in $C_{16}TAB/NH_3/H_2O$ under similar conditions. The $C_{16}TAB$ concentration is fixed at 2 mM while the ammonia concentration ranges from 2 mM to 100 mM. However, no helical SiO_2 can be attained. So it is believed that the nonhelical nanofiber coassembled by $C_4AG/C_{16}TAB$ is indispensable for the creation of helical SiO_2 .

Conclusion

In conclusion, well-defined double helix is fabricated through supramolecular self-assembly of a synthetic

sugar-lipid, which can be transformed into nonhelical fibers by incorporation of ionic surfactants. The unwinding of double helix into single-stranded fiber can be viewed as a good example of building tunable hierarchical architectures via chemical self-assembly. The self-assembled double helix and nonhelical fibers are further exploited as soft templates to design SiO_2 double helices, single helices as well as nanotubes. This manifests the possibility of utilizing soft self-assemblies to synthesize inorganic nanomaterials in a controllable fashion. We hope this work can open a new opportunity toward self-assembled artificial nanostructures and template-directed synthesis of complex inorganic species.

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Supporting Information Available: N_2 adsorption-desorption isotherms, TEM, and SEM images. This material is available free of charge via the Internet at <http://pubs.acs.org>.