Correction

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ABSTRACT

No Abstract.

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ERRATUM


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Since this article was published it has been brought to the authors’ attention that a relevant reference was unintentionally omitted. The article, published by Kumara et al. in the Journal of Nanoscience and Nanotechnology (2007, 7, 2260), reported the use of the FliTrix system to form silica bionanotubes. We believe that this article should have been cited, although it did not report the formation of nanoholes or the production of variable morphologies of silica nanotubes, and our work used a different peptide display system. Kumara et al. have also used the FliTrix system to assemble nanoparticles (Chem. Mater. 2007, 19, 2056; J. Phys. Chem. C, 2007, 111, 5276).

We would also like to amend the author list as follows:

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Genetically Modifiable Flagella as Templates for Silica Fibers: From Hybrid Nanotubes to 1D Periodic Nanohole Arrays**

By Fuke Wang, Dong Li, and Chuanbin Mao*

Bacterial flagellum is a protein nanotube that is helically self-assembled from thousands of a protein subunit called flagellin. The solvent-exposed domain of each flagellin on the flagella is genetically modifiable, in that a foreign peptide can be genetically inserted into this domain, leading to the high-density display of this foreign peptide on the surface of flagella. In this work, wild-type and genetically engineered flagella (inner diameter of ~2 nm and outer diameter of ~14 nm) detached from the surface of Salmonella bacterial cells are used as templates to site-specifically form silica sheaths on the flagellar surface, resulting in the formation of double-layered silica/flagella nanotubes. The flagella templates inside the silica/flagella nanotubes can be removed to obtain silica nanotubes by calcining the nanotubes at high temperature (550 °C). Further calcination of the silica nanotubes at a higher temperature (800 °C) leads to the formation of a periodic nanohole array along the silica fibers with a center-to-center nanohole spacing of ~79 nm. It is demonstrated that the double-layered silica-flagella nanotubes can be used for selective CdTe quantum dot uptake into the inner channels or selective Au nanoparticle coating on the outer wall of the nanotubes due to the different chemistry between inner flagellum core (protein) and outer silica wall of the nanotubes. It is also found that flagella displaying different peptides result in different morphologies of the silica nanotubes. This work suggests that the monodisperse diameter and genetically tunable surface chemistry of the flagella can be exploited for the fabrication of silica nanotubes with uniform diameter and controllable morphologies as well as silica nanofibers decorated with periodic nanohole arrays.

1. Introduction

Nanotubes combine the interesting characteristics of both hollow and one-dimensional nanostructures. Among the nanotubes made of different materials such as metal, silica, and semiconductor, silica nanotubes are especially useful in nanobiotechnology applications due to their intrinsic biocompatibility and simple chemical modification.[1–4] Compared with silica nanoparticles (NPs), silica nanotubes have inner and outer surfaces that can be independently modified with functional groups,[5] leading to the development of multifunctionalized nanotubes for potential applications in drug and gene delivery, single molecular detection, single-molecule sensing, and bioseparation.[6–11] To date, two main templating methods have been used to fabricate silica nanotubes. C. R. Martin first reported the preparation of silica nanotubes by using anodic aluminum oxide (AAO) membranes as templates,[12] and since then, porous materials have been extensively employed as templates to grow silica nanotubes within the pores.[12–14] Recently, silica deposition on the outer surface of templates has been employed in silica nanotube fabrication, as pore size and architecture can be tuned by modification of the templates used. Both hard templates such as gold or silver nanorods[15,16] and silicon nanowires[17] and soft templates such as biological substrates,[18] peptides,[19,20] organogelators,[21,22] surfactants,[23,24] and lipids[25–27] have been applied. By tuning the concentration of the tetraethoxysilane (TEOS) in solution and the reaction time, the thickness of the silica shell could also be controlled in both methods. However, it is still a great challenge to fabricate silica nanotubes with monodisperse pore sizes and precisely controlled diameters in the whole batch. Here we solve this problem by using a genetically modifiable protein nanotube called bacterial flagellum as a template because of its uniform diameter and genetically controlled reproducibility (Scheme 1).

Bacterial flagellum is a naturally occurring protein nanotube that can be detached from bacterial cells. It has an outer diameter of 12–25 nm and an inner diameter of ~2 nm.[28] It is helically assembled from more than 20000 copies of identical protein subunits called flagellin, with 11 subunits per turn.[28,29] During the biosynthesis of flagella, the flagellin is expressed inside the bacterial cells, transported across the cell membrane,
and then assembled on the cell surface, leading to the formation of highly ordered protein nanotubes (i.e., flagella) attached to the bacterial surface, which enable bacterial cells to swim. The flagellar filaments can be detached from the bacterial cell surface by a simple vortexing process, allowing us to obtain purified flagella for materials synthesis. The solvent-exposed domains (D2 and D3) of the flagellin subunits are genetically variable, making it possible to site-specifically insert a foreign peptide into these domains. Flagella detached from the same host are biologically assembled nanotubes with uniform diameter (diameter of the flagella used in the present work is 14 nm as measured from electron microscopy). Therefore, all the obtained silica nanotubes prepared by using flagella as templates are expected to have uniform and precise pore sizes. Also, since flagella are naturally occurring hollow nanotubes, the resulting hybrid materials are expected to be double-layered nanotubes. That is, the inner organic protein nanotube will be coated with a sheath of silica as shown in Scheme 1. The hybrid inorganic/organic nanotubes may offer a unique opportunity for studying drug and gene delivery and building bio-devices, stemming from the independent functions of the two layers (i.e., silica and protein).

In addition, relatively few studies have been conducted on the control of the spacing of nanoholes or NPs along the fibers due to the technical difficulties inherent to the process.\cite{30,31} Such control could lead to their potential applications in photonic crystals and optical switching.\cite{31,32} In the present study, we report novel pearl-necklace-like silica nanotubes prepared by using bacterial flagella as templates, which are further converted into a 1D periodic alignment of nanoholes simply by calcinations at higher temperature (Scheme 1). This 1D nanohole array is promising for applications in optical and photonic sensing.\cite{38}

2. Results and Discussion

Wild type flagella were prepared by vortexing flagellated Salmonella cells.\cite{39} To control the resulting silica morphologies and gain a better understanding of the silica growth mechanism, flagella were genetically engineered with peptides of different surface-charge properties and functional groups inserted into the solvent-exposed domain of each flagellin. One type of genetically engineered flagella (termed Fla-KKCC) surface-displayed a peptide with a sequence -Lys-Lys-Lys-Lys-Lys-Lys-Lys-Lys-Lys-Lys-Cys-Cys-Cys-Cys-Cys-Cys-, which has two domains (positively charged due to the Lys and thiol-rich due to Cys). Another type of engineered flagella (termed Fla-OCN) surface-displayed a peptide with a sequence -Asp-Pro-Glu-Pro-Arg-Arg-Val-Cys-Val-Leu-Asp-Pro-Asp-Cys-Asp-Glu-, which has negatively charged residues (Asp and Glu) and strong nucleophilic residues (Arg and Cys). Oligonucleotides that encoded the peptide sequences were genetically inserted into the flagellin gene, leading to the expression of the foreign peptides in the solution-exposed domains of the flagellins. The engineered flagellins are assembled to form engineered flagella on the bacterial cell surface that present foreign peptides on the side wall. The engineered flagella were detached from the bacterial cell surfaces, stained with uranyl acetate (1%), and then characterized by transmission electron microscopy (TEM). As shown in Figure 1, both wild type and engineered flagella show the characteristic nanofibrous morphology, with a uniform diameter of 14 ± 0.5 nm.

Hybrid silica/flagella nanotubes were fabricated by addition of aminopropyltriethoxysilane (APTES) and TEOS in turn to the aqueous solution of flagella. White precipitates generally appeared in about 15 min and the products were purified by several cycles of centrifugation and washing. Figure 2a shows the typical scanning electron microscopy (SEM) images of silica-flagella hybrid nanotubes produced by using wild-type flagella as templates. Novel pearl-necklace-like fibrous structures (~170 nm wide and a few micrometers long) were observed. The pearl-necklace-like structures indicate that the silica nucleation does not occur simultaneously all over the flagellar filaments but probably begins on some specific points along flagella, and grows in a spherical manner until adjacent spheres meet and fuse together. We believe that the flagella-directing silica growth might follow the “surface mechanism”
silica prepared by using flagella solution and thus the templated silica fibers. On the contrary, domains on the flagella straightens the flagella templates in Consequently, the charge repulsion between neighboring increases the density of the positive charges on the surface.

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as proposed by van Bommel and Shinkai. That is, the addition of APTES to the flagella solution leads to the absorption of APTES on the surface of flagella, through hydrogen bonding or electrostatic interaction between the amino group of APTES and surface protein of flagella. The close contact of APTES with the surface protein enhances the hydrolysis of APTES to form silicic acid, which functions as nuclei for subsequent silica growth. Polycondensation of TEOS will proceed on the surface of these nuclei, ultimately resulting in the formation of silica fibers. The formation of pearl-necklace-like silica fibers may be ascribed to the helical arrangement of the protein subunits (i.e., flagellins) along the length of the flagella. APTES will be absorbed on the helically assembled flagellins, resulting in the formation of silica nuclei wrapping the flagellum. Subsequently, silica particles grow on these nuclei until neighboring silica particles meet.

To have a better understanding of the silica growth mechanism and the control of morphologies of resulting silica, engineered flagella \((\text{Fla-KKCC} \text{ and } \text{Fla-OCN})\) were used as templates to fabricate silica fibers. Under the same conditions as those of wild type flagella, both engineered flagella gave pearl-necklace-like silica fibers due to the intrinsic helical arrangement of flagellins in flagella. However, SEM images of silica fibers (Fig. 2) templated with wild type or engineered flagella showed obvious morphological difference. For examples, silica fibers templated by wild type flagella are cyclic (Fig. 2a) while those templated by engineered flagella \(\text{Fla-KKCC} \) are more straight (Fig. 2b). We ascribed the cyclic silica fibers to the naturally coiled shapes of the wild-type flagella in solution. On the surface of engineered flagella \(\text{Fla-KKCC} \), insertion of 10 cationic Lys residues into each flagellin greatly increases the density of the positive charges on the surface. Consequently, the charge repulsion between neighboring domains on the flagella straightens the flagella templates in solution and thus the templated silica fibers. On the contrary, silica prepared by using flagella \(\text{Fla-OCN} \) as templates showed tadpole structures, which was attributed to the high density of negative charge and the strong nucleophilic residues in the foreign peptides inserted into the flagellins. Within the peptide sequence displayed on the surface of flagella \(\text{Fla-OCN} \), 8 negatively charged acidic amino acids (4 Asp and 4 Glu) enhance the absorption of APTES to the flagellar surface and the strong nucleophilic residues (2 Arg and 2 Cys) catalyze the hydrolysis of APTES to form nuclei with positive amino groups on their surface (see Scheme S1 of the Supporting Information). The electrostatic interaction between the positively charged nuclei and the negatively charged flagella \(\text{Fla-OCN} \) results in coiling of flagella around the already formed nuclei (see Scheme S2 of the Supporting Information), which leads to the formation of extremely large silica spheres at one end of the fiber (Fig. 2c). These results suggest that the morphologies of the silica fibers can be facilely tuned by genetic engineering of flagellar surface.

Silica-flagella hybrid nanotube structures were recognized by TEM. As shown in Figure 3a and b, uniform pore size of 14 ± 0.5 nm was observed in all the resulting silica nanotubes. The pore size is in agreement with the diameters of flagella (Fig. 1), indicating the successful mineralization on the flagella templates which results in the formation of silica nanotubes. In each individual silica nanotube, the inner surface is very smooth, and the inner diameter (14 ± 0.5 nm) is uniform along the whole silica nanotube, which is ideally suited for nanofluidic studies and single biomolecule sensing. Uniform pore sizes also indicate that our silica growth method can faithfully transcribe the sizes and morphologies of templates, giving rise to silica nanotubes with uniform pore sizes due to the intrinsic monodispersity of the flagella templates.

Furthermore, it is desirable to be able to tune the properties of these nanotubes by accurately controlling their pore...
We have successfully demonstrated the growth of silica nanotubes with precise pore sizes by using 14-nm-diameter flagella as templates. Thus, it should not be difficult to prepare silica nanotubes with different pore sizes by using different types of flagella as templates, since nature has provided various types of flagella with monodisperse diameters, ranging from tens nanometers to micrometers (see Table S1 of the Supporting Information). Here we show a different strategy to tune the pore sizes of silica nanotubes by using the assembly of engineered flagella. As shown in Figure 3, silica nanotubes prepared by using engineered flagella Fla-KKCC without dithiothreitol (DTT) protection displayed different pore sizes with diameters that are several times that of single flagellum (14 nm) (Fig. 3c). The larger pore sizes were attributed to the formation of flagellar bundle through the formation of disulfide bonding between neighboring Cys-presenting flagella in the absence of DTT.[43] As illustrated in the Supporting Information (Scheme S3), the formation of disulfide bond between cysteine residues on neighboring flagella drives the self-assembly of flagella that is mediated by the dissolved oxygen in the reaction media.[44] The assembly of flagella in the silica nanotubes was also confirmed by the cross-sectional TEM images (Fig. 3c, inset), which show that two or more flagella were assembled to direct the silica nanotube formation. It is noteworthy that silica nanotubes templated by flagella Fla-KKCC in the presence of DTT protection show that nearly all silica nanotubes were templated with single flagellum (Fig. 3a and b).

Interestingly, we have found that some of the silica nanotubes are interconnected with each other, forming branched silica nanotube structures. Also, it was found that larger silica spheres were formed at these intersection points (Fig. 2d and 3d). As we have described above, the silica growth follows the “surface mechanism.” That is, APTES was first absorbed on the surface of flagella and then hydrolyzed to form nuclei, followed by subsequent TEOS polymerization on these nuclei. Therefore, one can imagine that more nuclei will be formed at the intersection points of two or more flagella, and thus faster growth of silica at these points than other sites is expected. These branched silica nanotubes can constitute valuable candidates for nanofluidic and nanoelectronic 2D networks.

In addition, the as-prepared hybrid silica/flagella nanotubes are in fact multi-functional nanotubes, with inner protein nanotubes and outer silica nanotube sheath. Such double-layered nanotubes with distinct functional inner (protein) and outer (silica) surfaces will impart different functions to the nanotubes, such as drug loading, biocompatibility and biorecognition. As a proof of concept, we have developed the following procedures to take advantage of the different functionalities of the inner and outer walls of these nanotubes. First, 1.4-nm cadmium telluride (CdTe) quantum dots (QDs) coated with cysteine,[45] were incubated with the as-prepared silica/flagella nanotubes in a phosphate buffer solution (PBS) (pH = 7.4) for 12 h. After that, the nanotubes were separated out by repeated centrifugation and washing. Selective uptake of QDs into the inner channel of the as-prepared nanotubes was observed, probably because the surface of the cysteine-coated QDs behaves like a protein and preferentially interacts with the protein outlining the inner channel of flagella. As shown in TEM images (Fig. 4a), the uptake and aggregation of CdTe QDs occurred mainly in the channels of the silica nanotubes, resulting in the formation of CdTe nanowires in the protein channel. The uptake of QDs was also confirmed by the energy dispersive X-ray (EDX) analysis of samples, which shows elemental composition of Si, O, Cd, and Te (Fig. 4b). Furthermore, no uptake of cysteine-coated QDs was found
after the silica/flagella nanotubes were calcined at 550 °C to remove all the organic composition (see Fig. S1 of the Supporting Information), indicating the selective uptake of QDs by the channels of the flagella inside the nanotubes through the interaction between protein subunits of flagella and the cysteine-coated QDs.

Also, as the inner channel of the silica nanotubes was occupied by flagella, it was easy to selectively modify the silica nanotube outer surface with functional materials such as NPs. To demonstrate this concept, the hybrid silica/flagella nanotubes were dispersed in ethanol with 1 mg mL⁻¹ of APTES for 12 h to functionalize the silica-nanotube surfaces with amino groups. The surface-modified silica nanotubes were purified and then added to a solution of 13-nm gold NPs. The wine-red gold NP solution changed to purple immediately when the surface-modified silica nanotubes were added, suggesting that aggregation of gold NPs occurred. TEM images of the resulting silica nanotubes show the aggregation of gold NPs exclusively on the surface of silica nanotubes (Fig. 4c).

Calcinations of the obtained silica nanotubes at different temperatures (550–1 000 °C) were carried out in air in a tube furnace. Fourier transform infrared (FT-IR) spectra (data not shown) of the resulting silica showed that the organic material was completely removed from the silica nanotubes when the calcination temperature went above 550 °C. The silica fibers obtained above this temperature were pure inorganic silica. TEM images of the calcined silica nanotubes at 550 °C showed that there was no obvious shrinkage as observed in most silica materials produced by the sol–gel technique. In fact, no obvious shrinkage was observed even when the calcination temperature was increased to 700 °C, indicating the high thermal stability of the resulting silica nanotubes.

Collapse of the silica occurred when the calcination temperature was above 750 °C. In the range of 750–850 °C, the resulting silica fibers displayed 1D periodic array of nanoholes along the fibers (Fig. 5a). The average center-to-center spacing between the nanoholes was 79.1 nm and the deviation is illustrated in Figure 5a (inset). The diameter of the nanoholes, calculated by measuring 270 nanoholes, was 32 ± 5 nm when the silica was calcined at 750 °C for 4 h. No obvious size change of the nanoholes was observed within the calcination temperature range from 750 to 850 °C. We believe that the formation of the 1D periodic nanohole arrays was due to the special pearl-necklace-like silica structure (see Scheme S4 of the Supporting Information). Upon calcinations at a temperature higher than 800 °C, the silica begins to collapse first at the intersecting points of two adjacent silica nanospheres, forming segregated cavities in the silica fibers. Further calcination led to the reconstruction of the silica network at calcination temperature and formation of the 1D periodic nanohole array. To have a better understanding of the formation of the nanoholes from the silica nanotubes, silica nanotubes calcined at 800 °C for 1 h were quenched to room temperature quickly (10 °C min⁻¹). TEM images (Fig. 5b) of the resulting samples showed various stages of the process of nanohole formation: the already-formed nanoholes, the segregated tubular structures, and the less-affected silica nanotubes. It is important to note that the formation of the 1D periodic nanohole array along the silica fibers is reproducible and can be achieved simply by keeping the calcination temperature in the range of 750–850 °C. To the best of our knowledge, this is the first example of a 1D periodic nanohole array along a silica fiber, prepared by using a facile and reproducible method. One may also consider growing metal NPs in each nanohole by using a repeated templating method, which could fabricate functional optical devices such as photonic crystals and plasmonic waveguides.

When the calcination temperature was higher than 900 °C, the nanoholes began to disappear, leading to the formation of solid silica fibers. A typical TEM image of the solid silica fibers after calcination at 950 °C in air for 4 h is displayed in Figure 5c, showing the fusion of silica into a solid fiber. Increase of calcination temperature seems to induce a corresponding reconstruction of the silica net structures. Selective area electron diffraction (SAED) patterns of the silica calcined at 550 °C show that the formed silica is amorphous. On increasing the calcination temperature to 800 °C, the SAED pattern (Fig. 5b, inset) suggests that the sample is amorphous. Crystalline silica was obtained when the calcination temperature was higher than 950 °C, as revealed by the electron diffraction pattern (Fig. 5c, inset).
3. Conclusions

In summary, hybrid silica/flagella nanotubes with uniform and precise pore sizes have been prepared by flagella-directed silica growth in aqueous media. Pore sizes and morphologies of the resulting silica nanotubes can be tuned by using flagella genetically engineered with different surface charge density and functional groups. Since flagella are naturally occurring nanotubes, the as-prepared hybrid silica/flagella nanotubes show distinct inner and outer functionalities. Selective uptake of QDs with a protein-like surface to the inner channels and selective modification of silica nanotube outer wall with gold NPs were successfully demonstrated in the present work. Furthermore, we also provide a facile and reproducible way to prepare periodic 1D arrays of nanoholes along silica nanofibers by calcination of the silica nanotubes, which may find potential applications in the fabrication of photonic crystals and plasmonic waveguides.

4. Experimental

Engineering, Purification and Amplification of Salmonella Flagella: Two pairs of primers (forward and reverse) encoding the following two different peptides were designed and synthesized: 1) Flu-KKCC: -Lys-Lys-Lys-Lys-Lys-Lys-Lys-Lys-Lys-Lys-Cys-Cys-Cys-Cys-Cys-Cys-Cys-Cys-Cys-Cys-Cys-Cys; 2) Fla-OCN: -Asp-Pro-Glu-Pro-Arg-Arg-Glu-Val-Cys-Leu-Asp-Pro-Asp-Pro-Glu. The forward and reverse primers were annealed into a double-stranded DNA. At the same time, two restriction enzyme sites of XhoI and BglII were inserted into PCR amplified products. The resulting oligonucleotides with two sticky ends were inserted into the linearized plasmid PLS411 by XhoI and BglII Enzymes. Then the plasmids were transformed into flagellin deficient salmonella (strain SL5928). Individual colonies were picked on RMG-Amp (0.1%) plates and structures of the recombined plasmid with Flu-KKCC or Flu-OCN were confirmed by DNA sequencing. In order to increase the motility and length of engineered flagella, salmonella bacteria (SL5928) with Flu-KKCC or Flu-OCN were inoculated into LB-Amp (0.1%) media and grown at 37°C for 10 min. The cloudy cultures were then transferred to 1 L of LB-Amp (0.1%) media at 37°C. Finally, from the advancing edge of the growth on the semisolid media and grown at 37°C with shaking (250rpm) until the OD reached about 0.5. The culture was centrifuged at 7000g for 15 min at 4°C. The cell pellets were resuspended into 50 mL of PBS buffer (pH = 7.4) and centrifuged again at 7000g for 15 min at 4°C. This step was repeated twice to remove the impurity. Finally, the cell pellet was resuspended in deionized water and vortexed on a vortex mixer for 3 min. Due to the vortexing, the flagella were detached from the cells and suspended in the solution. The flagella were collected by centrifugation at 10000g for 15 min. The supernatant containing flagella was frozen at −20°C for further usage. It should be noted that for Fla-KKCC, reducing agent such as dithiothreitol was used to prevent flagella from cross-coupling due to the presence of thiol groups.

Silica Growth on Flagella Templates: In a typical synthesis of hybrid silica/flagella nanotubes, APTES (2 × 10⁻⁵ mmol) was added to flagella solution (500 µL). The solution was gently mixed on a vortex mixer. Then, it was put into an ice-water bath for ∼3–5 min. To this solution, TEOS (2.5 × 10⁻⁵ mmol) was added under stirring for still at 3 min. The mixed solution in a reaction tube was left in an ice-water bath for 3 min. The reaction tube was then left at room temperature for about 8 h. The obtained silica tubes were purified by centrifugation at 4500g for 10 min and washed with ethanol and water for several times.

Calcinations of Silica Nanotube and the Synthesis of 1D Nanohole Arrays: Calcinations of the silica nanotubes were carried out at different temperatures in air. In each calcination experiment, the air-dried silica nanotubes were transferred to a steel boat, heated at 120°C in a tube furnace for 12 h. Then, the temperature was increased (2°C min⁻¹) up to the desired point and maintained for 4 h. Finally, the samples were cooled down to room temperature with 5°C min⁻¹. The 1D nanohole arrays along silica fibers were prepared by calcining the silica nanotubes at 800°C for 4 h in air. Calcination was carried out in a Lindberg tube furnace (TF55030A).

Selective Uptake of CdTe QDs in the Inner Channels of Silica/Flagella Hybrid Nanotubes: Cysteine-coated CdTe quantum dots were prepared according to the reference with minor modification.[46] Silica/flagella nanotubes (10 mg) were added to as-prepared aqueous solution (2 mL) of CdTe QDs and incubated at room temperature for 12 h. The resulting silica nanotubes were purified by several rounds of centrifugation and washing, and then characterized by TEM.

Selective Absorption of Gold Nanoparticles (NPs) on the Outer Walls of Silica/Flagella Hybrid Nanotubes: The surface of silica/flagella nanotubes was first modified with APTES to form a layer of amino groups. Gold NPs were prepared by reduction of HAuCl₄ with sodium citrate.[46] The as-prepared gold NPs solution was mixed with the APTES-modified silica nanotubes and incubated at room temperature for 2 h. The resulting silica nanotubes were purified by several rounds of centrifugation and washing, and then characterized by TEM.

Materials Characterization: The morphologies of the as-prepared silica/flagella nanotubes were examined by using TEM JEOL 2000-FX and SEM JEOL JSM-850, both using LaB₆ source.

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