Template-Free Synthesis of Chemically Asymmetric Silica Nanotubes for Selective Cargo Loading and Sustained Drug Release

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ABSTRACT: SiO$_2$ nanotubes (NTs), with uniform diameter (~25 nm) and tailored shell thickness (1–5 nm), and featuring chemically asymmetric surfaces (a silane-functionalized exterior surface and a negatively charged (~Si–O–) interior surface) are prepared by a facile, template-free approach. Owing to their chemically asymmetric properties, positively charged cargoes can be selectively loaded with high content into the SiO$_2$ NTs via electrostatic interaction. With the mediation of polyamidoamine dendrimer pre-assembled in the NTs, different noble metal nanoparticles can be selectively deposited inside the NTs with high density and uniform size. Owing to their high specific surface area and elongated pore structure with lengths up to several micrometers, the SiO$_2$ NTs exhibit a high loading capacity (80 wt.%) for positively charged therapeutic agents, which exhibit sustained cargo release properties on the order of several months if the NTs are assembled into a membrane structure.

INTRODUCTION

Nanoarchitected silica materials have received widespread interest in a range of applications (e.g., catalysis,‡,‡§ sensing,¶ drug delivery‡,‡§ and templating synthesis‡,‡§) owing to their unique morphologies, high surface areas, tunable pore structures, easily modifiable surface properties and high biocompatibility. The past two decades have witnessed the rapid development of silica materials with diverse architectures, ranging from ordered mesoporous frameworks,‡,‡§,‡,‡§,‡,‡§ nanorods,‡,‡§,‡ nanowires (NWs),‡,‡§ nanocages,‡,‡§ nanobottles‡,‡ to nanotubes (NTs).‡,‡§ NTs are of particular interest in nanoreactor and drug delivery applications owing to their elongated structures and multiple functionalities as a core material, which provide further opportunities to design nanoreactors with desirable geometric morphologies (e.g., assemblies of NT membranes) and unique reaction features,‡,‡§ as well as the ability to control the biodistribution and release profiles of therapeutic agents.‡,‡§ SiO$_2$ NTs are typically prepared using either a hard template (e.g., nickel-hydrazine nanorod,§ anodic aluminum oxide membrane‡,‡§,‡) or a soft template (e.g., threadlike block polymer micelles‡,‡§) as a porogen to generate the hollow channels. However, these preparation methods largely depend on the availability of suitable templates. Furthermore, multiple process steps and harsh conditions (e.g., aggressive chemical etching or calcination) are typically required to remove the templates from the products to generate the hollow channels.‡,‡§ These limitations largely affect the scale-up synthesis and often compromise the quality of the NTs produced. Therefore, developing a template-free technique that yields high quality SiO$_2$ NTs is of particular importance, both for technological applications and fundamental research.

Herein, we introduce a facile, template-free method to synthesize uniformly sized SiO$_2$ NTs via an emulsion linear-merging growth (ELMG) approach. To the best of our knowledge, this is the first report on the synthesis of SiO$_2$ NTs via a template-free approach. The postulated ELMG mechanism for the formation of the SiO$_2$ NTs is illustrated in Figure 1a. The synthesis involves three stages: i) formation of ultrathin, metastable water droplets; ii) collision and merging of the water droplets into linear chains; and iii) shell growth and development of the chains into hollow NTs. The SiO$_2$ NTs are highly transparent with uniform diameter (~25 nm), tailored surface properties, tunable shell thickness (1–5 nm) and high aspect ratio (~100). More importantly, the SiO$_2$ NTs possess chemically asymmetric surfaces (an organic silane-capped exterior surface and a negatively charged, –Si–O–-terminated interior surface), which allow the selective loading of positively charged cargoes in the hollow channels through electrostatic interaction.
RESULTS AND DISCUSSION

The formation mechanism of the SiO₂ NTs. A feature of the ELMG approach for silica NTs synthesis is that it affords the formation of ultrafine, metastable water nanodroplets (~10–20 nm) that merge into linear chains to reduce the surface energy. The metastable water nanodroplets were prepared through modification of the recently reported water/1-pentanol emulsion system, which has been used for anisotropic growth of high-aspect ratio silica particles from single water droplets with a size of ~100 nm. To obtain the metastable water nanodroplets, distinct changes from the previous formulation were made that include: (i) no addition of polyvinylpyrrolidone as a stabilizer and (ii) the use of ethanol (EtOH) as cosolvent to produce ultrafine water nanodroplets (~10–20 nm). Owing to the ultrafine size, the emulsified nanodroplets have a high interfacial tension and are thermodynamically metastable. The subsequently added (3-chloropropyl)trimethoxysilane (CPTMS) molecules hydrolyze upon contact with the water droplets under basic conditions. After hydrolysis, CPTMS forms amphiphilic CICH₂–(CH₂)₂–Si(–O–)₃ species, which play a surfactant-like role at the water droplet interface in stabilizing the droplets through insertion of the hydrophobic tail into the 1-pentanol phase while the polar head (–Si–O–) faces the water droplets.

The collision of two droplets with soft, amphiphilic CICH₂–(CH₂)₂–Si(–O–)₃ arranged at the droplet surface leads to the merging of the droplets into a dumbbell-like shape (Figure 1a). A worm-shaped chain is subsequently obtained with continuous collision and merging of the droplets in a linear direction. Meanwhile, hydrolysis of the added tetraethyl orthosilicate (TEOS), after migrating into the water droplets, and condensation with the hydrolyzed CPTMS at the interface occur to stabilize the shell. Continuous deposition of the hydrolyzed TEOS on the shell from the inner-side of the water droplets extrude the water and produce an elongated nanochannel in center of the chains.

The proposed ELMG mechanism for the NT synthesis is supported by monitoring the shape of the intermediate products through scanning electron microscopy (SEM) (Figure 1b–e). Worm-shaped particles formed within a time as short as 5 min after addition of TEOS and CPTMS to the nanoemulsion (Figure 1b). Wire structures with grainy, rough surfaces were obtained within 15 min (Figure 1c, d). As the reaction proceeded to 30 min, wires with smooth surfaces were obtained (Figure 1e). These results suggest that the growth of the SiO₂ NTs is rapid, which was also confirmed by the dynamic light scattering (DLS) experiments, wherein changes in the particle size as a function of reaction time were monitored (Figure S1).

The shell thickness of the NTs was determined from transmission electron microscopy (TEM) images. The NTs had an ultrathin shell (~1 nm) after a growth time of 30 min, and showed a partly collapsed, belt-like shape after air-drying (Figure 2a, S2a). The shell thickness increased to ~2 nm after 1 h of growth (Figure 2b, S2b). Prolonged growth (3 h) led to free-standing NTs with a distinct hollow structure (Figure 2c, d, S2c). The measured outer diameter, inner diameter and shell thickness of the NTs obtained after a growth time of 3 h were ~25, ~15 and ~5 nm, respectively (Figure 2c, d, S2c). SEM images revealed the size homogeneity of the NTs with length up to several micrometers (Figure 2e, f). Capping of the NTs with a layer of 3-chloropropyl groups was confirmed by the elemental mapping profiles shown in Figure 2g–j. Nitrogen sorption analysis revealed that the SiO₂ NTs displayed type IV sorption isotherms, with a hysteresis loop within the relative pressure range of 0.50–0.90 (Figure 2k), indicating the presence of abundant mesopores in the NTs. The NTs had a high surface area of 618 m²·g⁻¹ (Brunauer–Emmett–Teller method) and pore volume of 1.17 cm³·g⁻¹. The pore size distribution curve was centered at ~12 nm (Figure 2l), coinciding with the inner tube...
diameter of ~15 nm measured from TEM analysis.

We note that the use of EtOH as a cosolvent is important in the NT synthesis. Without the addition of EtOH, spherical silica particles with a diameter of ~100 nm were obtained (Figure S3a, b), likely due to the relatively large water droplets formed in the absence of EtOH. When a small amount of EtOH (EtOH/1-pentanol, 1:10 v/v) was added to the emulsion system, both SiO$_2$ NTs and a few spherical particles (~50 nm) formed in solution (Figure S3c, d). Further increases in the EtOH/1-pentanol ratio over 3:10 resulted in the formation of homogeneous SiO$_2$ NTs, with the outer diameter of the NTs decreasing from 20 to 15 nm as the EtOH/1-pentanol ratio increased from 3:10 to 1:2 (Figure S3e–h). These results suggest that EtOH plays a key role as cosolvent in controlling the emulsion droplet size—the presence of EtOH in the water phase would suppress interfacial instabilities, ultimately resulting in the formation of ultrafine water nanodroplets in 1-pentanol.

The amount of CPTMS used in the synthesis was also studied. When the CPTMS/TEOS volume ratio was less than 1:20, a mixture of NTs and spherical particles were obtained (Figure S4a–d), likely because the CPTMS amount was insufficient to stabilize the nanoemulsion. When the CPTMS/TEOS ratio increased to 1:10, homogeneous NTs were obtained (Figure S4e, f). A further increase in the CPTMS/TEOS ratio to 1:5 resulted in numerous nanoparticles being deposited on the NT surface (Figure S4g, h).

Optical transparency of the SiO$_2$ NTs. Owing to the ultrathin shell (<5 nm), suspensions of the SiO$_2$ NTs were almost optically transparent in water. The suspension of SiO$_2$ NTs with a silica concentration of 2.0 mg·mL$^{-1}$ had a transmittance of ~84 % (at 550 nm), which is almost 10 times higher than that of a suspension of SiO$_2$ NWs with a diameter of ~80 nm (Figure 3a). The flexible and high aspect ratio features of the SiO$_2$ NTs make the assembly of the NTs into a monolithic NT membrane (NTM) through vacuum filtration of the NT suspension possible. The assembled NTM with a thickness of around 200 μm (Figure 3e) was highly transparent (Figure 3b–d). As observed from Figure 3f, the SiO$_2$ NTs were intertwined into a three-dimensional network and the structure of the NTs was well preserved within the NTM network.

Capping of the SiO$_2$ NTs with other organic groups. Of particular significance is that the ELMG strategy is applicable to the preparation of SiO$_2$ NTs capped with a variety of organic groups through substituting the CPTMS with another silane group (i.e., phenyltrimethoxysilane, trimethoxysilylpropanethiol, allyltrimethoxysilane) (Figure 4a–f). The phenyl-capped SiO$_2$ NTs can be verified by the FTIR characterization. The silica NTs capped with phenyl groups has skeleton vibrates (C-C) at 1431 cm$^{-1}$, and bending vibration of C-H at 698 cm$^{-1}$ and 740 cm$^{-1}$ (Figures S5). UV–
vis spectra of 3-carboxy-4-nitrophenyl disulfide (DTNB) solution with the addition of thiol-capped silica NTs has a strong absorption at 412 nm,

Figure 3. (a) Transmittance spectra of suspensions of SiO$_2$ NTs and SiO$_2$ NWs at different silica concentrations. Optical images of a SiO$_2$ NT membrane (NTM) and a SiO$_2$ NW membrane (NWM) on tweezers (b, c), respectively, and on color-printed paper (d) (NTM is circled on the color-printed paper). Top-view (e) and cross-sectional (f) SEM image of the SiO$_2$ NTM.

indicating that sulfhydryl groups are successful capped on the silica NTs (Figures S6). The amount of capped sulfhydryl silane is calculated to be 10.2 wt.% based on the weight of silica NTs. When a silane group with a longer hydrophobic chain (e.g., trimethoxy-7-octenyl-silane) was used, particles with a variety of shapes were obtained (Figure S7a, b).

SiO$_2$ NTs for selective cargo loading. The hollow architecture along with the asymmetric surface properties make the SiO$_2$ NTs interesting candidates for selective cargo loading. As a proof-of-principle study, the loading of the NTs with dendritic polyamidoamine (PAMAM) was studied because of the well-defined molecular structure and abundant chemical

Figure 4. SEM images of the products obtained after replacing the siloxanes (CPTMS) with different silanes: (a,b) phenyltrimethoxysilane; (c,d) trimethoxysilylpropanethiol; (e,f) allyltrimethoxysilane. The reaction time was 1 h and all other synthesis conditions were the same as described in the 3-chloropropyl groups-capped silica NTs preparation.

groups of this dendrimer for subsequent material functionalization.$^{41,44}$

As illustrated in Figure 5a, amine-terminated PAMAM (denoted as PAMAM-NH$_2$) dendrimers impregnate the NTs through electrostatic interaction with the negatively charged (−Si−O−) interior surface of the NTs. PAMAM-NH$_2$ (3.0 G, 3256 Da, 2.9 nm) could be loaded in the NTs at a loading as high as 63.6 wt.%), as determined by thermogravimetric analysis (Figure S8). Given the excellent metal ion complexing ability, the loaded PAMAM-NH$_2$ dendrimers were then used as a matrix to enrich the interior of the NTs with noble metal ions from the outer solution for in situ reduction of noble metal nanoparticles (NPs) inside the NTs. This “ship-in-a-bottle” strategy for noble metal NP deposition afforded a high loading density of Au NPs with uniform size in the NTs. TEM (Figure 5b, S10a) and elemental mapping (Figure 5c−f) images revealed that the Au NPs (dark dots in Figure 5b, S10a) generated inside the NTs were uniform in size (~2.5 nm) and evenly distributed inside the NTs. The Au content was 22.4 wt.%, as determined by inductively coupled plasma atomic absorption spectroscopy (ICP-AAS). In contrast, when the NTs were not pre-loaded with PAMAM-NH$_2$, the formation of Au NPs in the NTs did not occur to an appreciable extent (Figure 5g), thus highlighting the importance of PAMAM-NH$_2$ pre-loading in enriching Au(III) ions in the NT. Notably, using the same procedure, Au NPs were generated on both the external and internal surfaces of the NTs provided the capped 3-chloropropyl groups were removed (via calcination) (Figure 5h). Furthermore, this indicates the importance of the asymmetric surface properties of the SiO$_2$ NTs in achieving selective loading of the NTs. SiO$_2$ NTs loaded with different noble metals (Pd, Pt) were also prepared, demonstrating the generality of the present approach (Figure S9). TEM images revealed that the Pd NPs and Pt NPs deposited inside the NTs had uniform diameters of about 2 and 1 nm, respectively (Figure S10b, c). The measured contents of Pd and Pt loaded in the NTs were 37.8 and 19.4 wt.%, respectively, as determined by ICP-AAS.

The catalytic activity of the Au NP-loaded NTs was evaluated through the hydrogenation of 4-nitrophenol (4-NP). The reaction was monitored by measuring decreases in the absorbance at 400 nm using UV−vis spectroscopy (Figure 5i). As deduced from Figure 5j, the reaction could be considered a pseudo-first-order reaction with an apparent rate constant ($k_{app}$) of 0.33 min$^{-1}$ and a calculated turnover frequency of 2328 h$^{-1}$. These results indicate that the Au NPs (of which the formation was directed by pre-loading the NTs with PAMAM-NH$_2$ inside the NTs were catalytically active and accessible to the reaction molecules in the bulk solution.

SiO$_2$ NTs for therapeutic agents loading and sustained release. The performance of the chemically asymmetric SiO$_2$ NTs as nanocarriers for therapeutic agents loading was assessed; positively charged doxorubicin (DOX) and lysozyme were examined. DOX is a widely used, small molecule anticancer drug, while lysozyme is often used as a model protein to simulate the in vitro release profile of expensive brain-derived neurotrophic factor (BDNF) owing to the similar physical properties (molecular weight, isoelectronic point) that lysozyme and BDNF share.$^{45}$ Dendritic mesoporous silica nanoparticles (DMSNs),$^{45}$ with similar pore size (~13 nm) and
pore volume (1.36 cm$^3$ g$^{-1}$) to those of the present SiO$_2$ NTs, are used as a control for comparison studies of loading and release performance. Comparison of the performance of DMSNs and the SiO$_2$ NTs revealed that the latter achieved a high DOX loading of 81.3 wt.%, which was more than twice that (36.8 wt.%) achieved in the DMSNs. Similarly, lysozyme loading in the SiO$_2$ NTs (67.6 wt.%) was significantly higher than that obtained for DMSNs (24.1 wt.%). These results suggest that electrostatic attraction could be used to efficiently load the SiO$_2$ NTs with a high content of positively charged therapeutics. The high loading capacity of the SiO$_2$ NTs is attributed to the elongated pore structure that suppresses cargo leakage during the washing step, which is undertaken after loading to remove any loosely adsorbed drug molecules on the particle surface.

The in vitro release profiles of the loaded drugs were investigated by incubating the DOX- and lysozyme-loaded carriers in phosphate-buffered saline (PBS, pH 7.4) at 37 °C. The amount of DOX and fluorescein isothiocyanate isomer I (FITC)-labeled lysozyme released from the NTs was monitored by fluorescence spectroscopy. The driving force for the release is a concentration gradient of the drug between the nanocarriers and the surrounding PBS medium. DOX and lysozyme release from the DMSNs was rapid, with $>$80% of the loaded cargoes released within 24 h (Figure 6). This result was attributed to the radial pore structure of DMSNs, which affords a relatively short diffusion path ($<$100 nm) for the loaded cargoes to diffuse out of the particles. In contrast, cargoes loaded in the SiO$_2$ NTs showed sustained release profiles, with $\sim$80% of the cargoes released within 2 weeks. The sustained release was attributed mainly to the elongated nanochannel (up to several micrometers) with a narrow diameter ($\sim$15 nm), which could suppress diffusion of the cargoes out of the NTs.

Notably, the release period can be further prolonged through assembling the cargo-loaded SiO$_2$ NTs into a monolithic NTM (diameter: 5.0 mm, thickness: 200 μm). Both DOX and lysozyme release from the NTM were considerably prolonged and showed a near-zero order release profile. Cumulative release amounts of $\sim$40% for DOX and $\sim$30% for lysozyme was achieved within a period of 3 months (Figure 6, insets), suggesting the synergistic role of pore structure and geometric size on influencing the release profiles of the SiO$_2$ NTs. These results suggest that the SiO$_2$ NTs and NTM are promising candidates for local drug delivery applications, particularly in implants with highly loaded drugs for achieving a very sustained drug release pro-
CONCLUSION

In conclusion, optically transparent silica NTs with uniform diameter and asymmetrically tunable surface properties were synthesized in the absence of a sacrificial template. Ethanol and CPTMS played key roles in controlling the size and maintaining the metastable state of the water nanodroplets, and subsequently the diameter of the NTs generated. Owing to the asymmetric surface properties of the SiO \(_2\) NTs, guest molecules were selectively loaded in the NTs via electrostatic interaction. Using the pre-infiltrated PAMAM-NH\(_2\) dendrimer as a matrix, various noble metal nanoparticles were selectively deposited inside the NTs with high density and uniform size. Benefitting from their high specific surface area, large pore volume, and elongated pore structure in the micrometer-scale, SiO \(_2\) NTs displayed a high loading capacity for positively charged therapeutic agents and achieved sustained release profiles. The sustained release period could be tuned to last for several months provided the NTs are assembled into a membrane structure. Further studies on the SiO \(_2\) NTs for loading various substances and thus generating multifunctional NTs and NTM for nanocatalysis, sensing and biomedical applications are underway.

EXPERIMENTAL SECTION

Chemicals. Tetraethyl orthosilicate (TEOS), 1-pentanol, gold(III) chloride trihydrate, fluorescein isothiocyanate isomer I (FITC), (3-chloropropyl)trimethoxysilane (CPTMS), allyltrimethoxysilane and trimethoxy-7-octenyl-silane were purchased from Sigma-Aldrich. Ethanol (EtOH, 99.7%), ammonia (25 wt.% solution), sodium borohydride (96%), and ethylenediaminetetraacetic acid disodium (EDTA-2Na) were obtained from Sinopharm (China). Doxorubicin hydrochloride (DOX), p-nitrophenol (4-NP), trimethoxysilane and chloroplatinic acid hexahydrate were purchased from Aladdin (Shanghai, China). Polyamidoamine (PAMAM, 2.0 G) with ethylenediamine as core and amine groups as terminal (denoted as PAMAM-NH\(_2\), 2 wt.% in ethanol) was obtained from Dendritech Inc. (USA). Lysozyme from hen egg white was purchased from Fluka.

Preparation of Chemically Asymmetric SiO \(_2\) NTs. In a typical synthesis, 3.0 mL EtOH and 0.42 mL ammonia aqueous solution were added to 10 mL 1-pentanol. The ammonia aqueous solution contained 13 M ammonia and 17 mM EDTA-2Na for catalyzing the hydrolysis and gelation of the silane. After 5 min of vigorous shaking the above solution, 0.1 mL TEOS and 0.01 mL CPTMS were added. The mixture was shaken vigorously for 2 min and then rotated (60 rpm) at room temperature for 3 h. The obtained SiO \(_2\) NTs were centrifuged and washed three times with a water/EtOH mixture (50%/50% v/v).

Preparation of Phenyl-, Thiol-, Allyl-, Octenyl-Capped Silica NTs. In a typical synthesis, 3.0 mL EtOH and 0.42 mL ammonia aqueous solution (containing 17 mM EDTA-2Na) were added to 10 mL 1-pentanol, and the mixture was vigorously shaken for 5 min. Then, 0.1 mL TEOS and 0.01 mL phenyltrimethoxysilane, trimethoxysilylpropanethiol, allyltrimethoxysilane or trimethoxy-7-octenyl-silane were added to the above solution and shaken vigorously for 2 min. The mixture was rotated (60 rpm) at room temperature 3 h. The obtained SiO \(_2\) NTs were centrifuged (8000 g, 10 min) and washed three times with a water/EtOH mixture (50%/50% v/v).

Preparation of SiO \(_2\) NT and SiO \(_2\) NW Membrane. SiO \(_2\) NWs were synthesized according to our previously reported method.\(^{25}\) The vacuum filtration method was used to prepare the free-standing SiO \(_2\) NT and SiO \(_2\) NW membranes. An appropriate amount of diluted NT or NW suspension was vacuum-filtered through a cellulose acetate filter paper (pore size 0.45 µm) to form free-standing SiO \(_2\) NT and SiO \(_2\) NW membranes, respectively.

Characterization. The formation of the SiO \(_2\) NTs was monitored by TEM on an H-600 transmission electron microscope (Hitachi, Japan) and SEM on an Ultra 55 field-emission microscope (Zeiss, Germany). Energy-dispersive X-ray spectroscopy elemental mapping was performed on a Tecnai G2 F20 S-Twin STEM instrument (FEI, USA). Particle size of SiO \(_2\) NTs was measured by dynamic light scattering (Zetasizer Nano-ZS (Malvern)). Thermogravimetric analysis of SiO \(_2\) NTs and PAMAM-NH\(_2\)-loaded SiO \(_2\) NTs was performed on an SDT Q600-SDT simultaneous thermal analyzer (USA). The organic groups capped on the silica NTs were determined by FT-IR spectroscopy using a Spectrum Two FT-IR spectrometer (PerkinElmer, USA). Nitrogen sorption isotherms were measured on a Micromeritics Tristar 3000 analyzer. The amount of the noble metal (i.e., gold, palladium and platinum) NPs loaded in the SiO \(_2\) NTs was determined by inductively coupled plasma atomic adsorption spectrophotometry on an iCAP 7400 spectrophotometer. The amount of DOX or FITC-lysozyme loaded was monitored by a fluorescence spectroscopy (Shimadzu RF-5301).

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website.

Experiment detail of synthesis of noble metal NP-loaded SiO \(_2\) NTs, catalytic hydrogenation of 4-nitrophenol by Au NP-loaded SiO \(_2\) NTs, drug loading and in vitro release, SEM images, HRTEM images of SiO \(_2\) NTs and noble metal NP-loaded SiO \(_2\) NTs (PDF)

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Notes

The authors declare no competing financial interest.

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