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Hybrid Nanoparticles

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Molecularly Designed Nanoparticles by Dispersion of Self-Assembled Organosiloxane-Based Mesophases**

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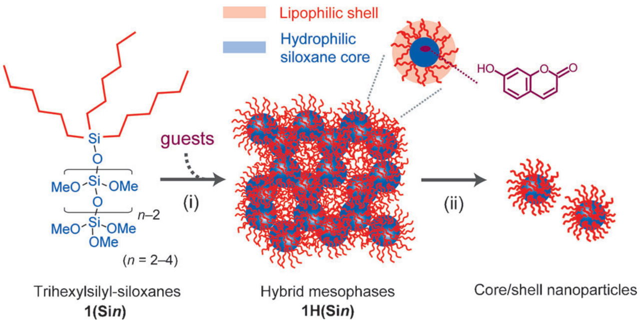
Abstract: *The design of siloxane-based nanoparticles is important for many applications. Here we show a novel approach to form core–shell silica nanoparticles of a few nanometers in size through the principle of "dispersion of ordered mesostructures into single nanocomponents". Self-assembled siloxane–organic hybrids derived from amphiphilic alkyl-oligosiloxanes were postsynthetically dispersed in organic solvent to yield uniform nanoparticles consisting of dense lipophilic shells and hydrophilic siloxane cores. In situ encapsulation of fluorescent dyes into the nanoparticles demonstrated their ability to function as nanocarriers.*

Functionalized nanoparticles have found many applications including in biomedicine,[1–5] optics,[6,7] electronics,[8,9] and catalysis.[10] As host or coating matrices, silica is widely utilized because of its transparency, biocompatibility, insulating property, and controllable porosity. Fine control of the particle sizes and surface properties while retaining a high dispersibility is crucial for various new applications. For example, the optimal nanoparticle size for drug delivery systems is limited to the range of 3–7 nm to avoid an inflammatory immune response.[5] Control of these factors is also crucial for the alignment and dispersion of the nanoparticles to provide unique functions for electronic and optical devices.[10] The methodology for the preparation of uniform and stable silica nanoparticles with tailored sizes and surface properties as well as with the ability to accommodate various guest species thus addresses an important need in these fields.

The self-assembly of amphiphilic organosilanes has attracted growing interest as a direct approach to silica–organic hybrid nanomaterials.[11–14] Micellar and vesicular particles have been prepared from lipids or block copolymers bearing $Si(OEt)_3$ groups;[13,14] however, difficulty remains in precisely controlling their dimensions, particularly in the 1–10 nm range. In this context, we focused on the formation of a periodic and extended reverse-type mesophase where siloxane spheres surrounded by an organic shell are arranged periodically to establish a straightforward dispersion process yielding uniform and discrete nanoparticles of a few nanometers in size.

Herein, we report a novel approach to form core–shell silica nanoparticles of a few nanometers in size through the principle of "dispersion of ordered mesostructures into single nanocomponents" (Scheme 1). Self-assembled siloxane–organic hybrids derived from amphiphilic trialkyl-substituted oligosiloxanes were postsynthetically dispersed in organic solvent to yield uniform nanoparticles consisting of dense lipophilic shells and hydrophilic siloxane cores. To explore their ability to function as nanocapsules, we demonstrate the in situ encapsulation of hydrophilic dyes into the nanoparticles. The synthetic development of such a molecularly designed nanoparticle is a promising step toward various advanced applications.



Scheme 1. Self-assembly/dispersion approach to organically modified silica nanoparticles: (i) an evaporation-induced self-assembly process involving hydrolysis and polycondensation of **1(S*in*)**; (ii) dispersion of a hybrid mesophase (**1H(S*in*)**) in a nonpolar solvent to form single nanoparticles. Hydrophilic guest species can be loaded into the nanoparticles during the self-assembly process.

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This concept has been realized by the design of linear and alkoxylated oligosiloxane precursors, in which three alkyl chains are attached to the terminal Si atom (**1(Si*n*)** in Scheme 1). The larger volume of the hydrophobic trialkylsilyl group relative to the linear oligosiloxane chain should favor the formation of reverse micelles and their assemblies. The self-assembly and siloxane network formation are induced by the evaporation of solvent from the solution containing the hydrolyzed precursor, which allows the synthesis of monodisperse silica nanoparticles stabilized against irreversible aggregation by the organic outer shell. This strategy is fundamentally different from the conventional approaches that use reverse micelles or block copolymer assemblies as templates for the confined growth of inorganic nanoparticles.[15,16]

The precursors **1(Si*n*)** were synthesized by the reaction of trihexyl(hydroxy)silane with alkoxylated oligosiloxanes (see the Supporting Information for details) and were hydrolyzed in tetrahydrofuran (THF) under acidic conditions. After complete hydrolysis of the constituent Si–OMe groups, the solutions were cast onto a glass substrate to evaporate the volatile components so that self-assembly of the hydrolyzed molecules and the concomitant polysiloxane formation could proceed. The resulting film was solid, but exhibited some plasticity. The resulting hybrid material **1H(Si4)** from the **1(Si4)** precursor was characterized in detail by electron microscopy, X-ray diffraction (XRD), and solid-state NMR spectroscopy.

The scanning electron microscopy (SEM) imaging of the surface of the cast film revealed hexagonally arranged spherical particles with a uniform diameter of ca. 3.3 nm (Figure 1 a). The particle size roughly corresponds to twice the extended molecular length of **1(Si4)** (ca. 1.7 nm). This film exhibits an XRD peak corresponding to a *d* spacing of 2.7 nm (Figure 1 b). Assuming that this peak is assigned to the (111) plane of a face-centered cubic structure, the calculated particle size (3.3 nm) is in good agreement with that determined by SEM. The solid-state ^{29}Si magic-angle spinning (MAS) NMR spectrum of **1H(Si4)** shows the Q^3 and Q^4 signals along with the M^1 and Q^2 signals (Q^m: $Si(OSi)_m(OH)_{4-m}$, M^1: $C_3Si(OSi)$; Figure 1 c), confirming the formation of crosslinked siloxane networks with a certain degree of uncondensed silanols. The presence of the alkyl chains as well as the elimination of alkoxy groups were confirmed by ^{13}C cross-polarization magic-angle spinning (CP-MAS) NMR spectroscopy (see the Supporting Information, Figure S1).

The hybrid material **1H(Si4)** was readily dispersed in hexane to give a colloidal solution. When the clear solution is allowed to dry, island-shaped aggregates (Figure 2 a) and discrete nanoparticles (Figure 2 b) are clearly observed by SEM and the relative proportion of these two forms depends on the dilution ratio. The discrete particles are also observed by transmission electron microscopy (TEM) (inset of Figure 2 b). The affinity of these nanoparticles to the nonpolar solvent strongly suggests that they have a reverse micellar structure with the alkyl chains facing outward and the hydrophilic silanol groups inward. Furthermore, these nanoparticles can be re-assembled into various macroscopic morphologies, such as spherical particles (ca. 200 nm in diameter) through the addition of ethanol to the hexane solution (Figure S2), and as thin films by coating the hexane solution onto substrates (data not shown). These secondary structures can again be re-dispersed in hexane. The ability of these nanoparticles to undergo reversible assembly/dispersion illustrates their chemical stability.

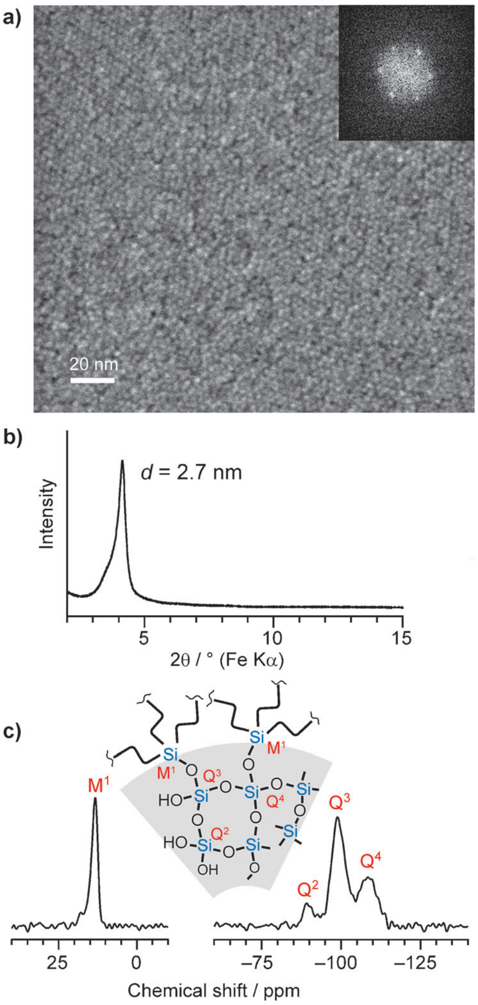

Figure 1. a) Typical SEM micrograph and its Fourier transform image of the hybrid mesostructure **1H(Si4)**. The sample was imaged without prior deposition of a conductive metal top-coat. b) XRD pattern and c) solid-state ^{29}Si MAS NMR spectrum of **1H(Si4)**.

Thus, core–shell hybrid nanoparticles as small as 3.3 nm in diameter have been obtained. The maximum thickness of the organic shell is ca. 0.7 nm when the C6 chains are in an extended state, and the diameter of the siloxane core is then calculated to be ca. 1.9 nm. A recent report on the templated synthesis of silica nanospheres in metal complex capsules confirmed that a nanosphere of 2.9 nm in diameter is composed of roughly 170 SiO_2 units.[17] Considering that our nanoparticles have a similar degree of condensation (i.e. Q^3 unit is predominant), as confirmed by ^{29}Si MAS NMR spectroscopy, the number of SiO_2 units in our case is estimated to be 48. Therefore, each nanoparticle of **1H(Si4)** is presumed to be composed of at least 12 molecules of **1(Si4)**.

Our previous studies have shown that the structural periodicity of the alkylsiloxane mesophase is dependent on

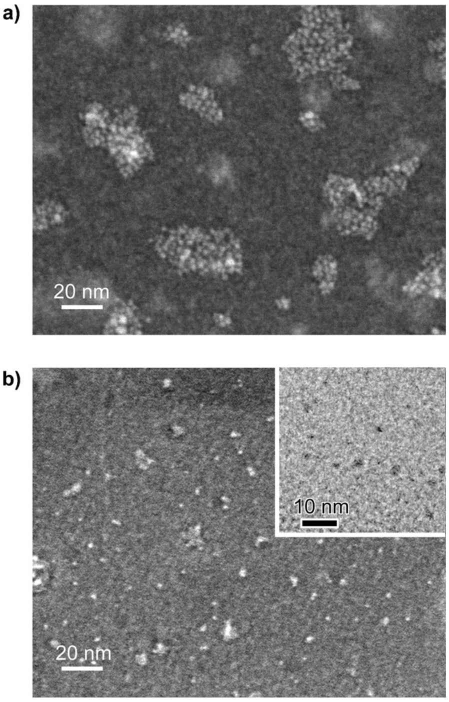

Figure 2. Direct observation of the nanoparticles deposited from a hexane solution. SEM images of a) island-shaped aggregates and b) discrete nanoparticles. The samples were prepared by applying drops of the solutions on copper TEM grids followed by drying in air. The inset of (b) shows the TEM image of the discrete nanoparticles.

the alkyl chain length of the precursors.[11] In the present case, precise size control of the nanoparticles can be achieved by varying the length of the oligosiloxane chains in the presence of trihexyl groups. Homologous precursors with a disiloxane unit, **1(Si2)**, as well as a linear trisiloxane unit, **1(Si3)**, form mesophases with smaller d spacings (Figure S3), which indicates a decrease of the resultant particle size. These mesophases were fully dispersible in hexane. Notably, **1H-(Si2)** was a viscous liquid mainly consisting of the trimer of hydrolyzed **1(Si2)** having a cyclic trisiloxane core, as confirmed by liquid-state ^{29}Si NMR spectroscopy and matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF-MS, Figure S4). The smaller number of crosslinkable units available with this disiloxane precursor should result in a decreased number of the molecular components in a particle. Hence, the direct observation of individual nanoparticles has not been achieved mainly because of their extremely small numbers of SiO_2 units.

Varying the chemical composition of the outer organic layer plays a key role in tuning the surface and therefore the nanoparticles' properties with regard to interparticle interactions, solubility, and functionality.[19,20] As an example, we performed the reaction of the precursor bearing C=C bonds at the terminus of the hexyl groups forming a periodic structure that exhibits an XRD peak at $d = 2.3$ nm (Figure S5). The slightly shorter periodicity compared to that of **1H(Si4)** aggregates may be attributed to the different packing due to the presence of C=C bonds. The C=C bonds should allow further reactions, such as hydrosilylation, coupling reactions, and radical polymerizations. For biomedical applications, grafting of hydrophilic PEG chains to the terminal C=C bonds is of great significance. Our direct-assembly method thus provides a versatile route for the production of organically modified nanoparticles. This is superior to the conventional method based on the postsynthetic modification of bare silica nanoparticles,[18,19] which is often complicated by self-condensation of the silylating agents and/or irreversible aggregation of the nanoparticles during modification.

To demonstrate the ability of our silica nanoparticles to serve as nanocapsules, we investigated the encapsulation of a hydrophilic fluorescent dye, 7-hydroxycoumarin, into the siloxane core by dissolving the dye in the solution of hydrolyzed **1(Si4)** prior to evaporation-induced self-assembly. The obtained particles can be dispersed in hexane, and the resulting clear solution exhibits absorption at $\lambda_{max} = 327$ nm (Figure 3), suggesting that the dyes are incorporated in the nanoparticles. The fluorescent peak at 390 nm suggests that the incorporated dye molecules are not aggregated and in their neutral state,[20] implying that the dyes are fixed to the siloxane core through a weak hydrophilic interaction and/or hydrogen bonding. This represents a new method to "dissolve" hydrophilic dyes in nonpolar solvents and such an encapsulation of dyes in silica matrices is expected to enhance their stability against degradation.[21] Similar results were observed for different types of hydrophilic dyes (Figure S7), confirming that this encapsulation capability is of general versatility.

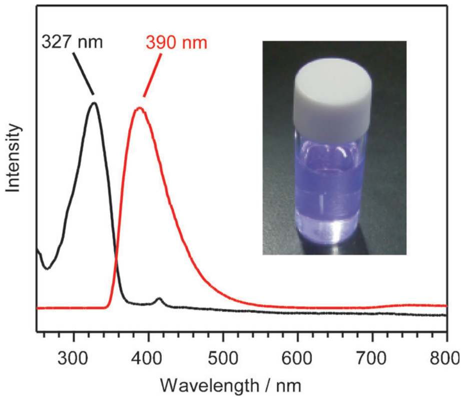

Figure 3. UV/Vis spectrum (black line) and fluorescence spectrum (red line, excitation wavelength: 327 nm) of the hexane dispersion of 7-hydroxycoumarin-containing **1H(Si4)**. The inset shows the photograph of the dispersion under UV irradiation (365 nm).

In conclusion, we have developed a novel route to organically modified silica nanoparticles with diameters of a few nanometers from well-defined single-molecule precursors. The small silica core is covered with a dense layer of alkyl chains, which allows for the dispersion of the bulk mesophase into its individual nanoparticle building blocks without the occurrence of irreversible nanoparticle aggregation. Furthermore, we succeeded in encapsulating a fluorescent dye into the siloxane cores. This study paves the way to new possibilities for designing functionalized hybrid nanoparticles through the targeted tailoring of the chemical and physical properties of the core and shell components.

Experimental Section

Synthesis of **1(Si4)**: All reactions were performed under nitrogen atmosphere using standard Schlenk techniques. The alkoxytrisiloxane was synthesized by adding H_2O (17.5 mL) and 6 N HCl (12.5 mL) to a mixture of tetramethoxysilane (TMOS, 500 g) and tetrahydrofuran (THF, 300 mL), followed by heating at reflux for 3 h. After removal of the solvent in vacuo, octamethoxytrisiloxane [$(CH_3O)_3SiOSi(OCH_3)_2OSi(OCH_3)_3$] was isolated by vacuum distillation. Partial replacement of −OMe groups with −Cl was then performed by stirring a mixture of octamethoxytrisiloxane (25 g), tetrachlorosilane ($SiCl_4$; 1.3 mL), and $AlCl_3$ (0.32 g) at RT for 1 day. Removal of $AlCl_3$ followed by vacuum distillation gave a mixture of $(CH_3O)_3SiOSi(OCH_3)_2OSi(OCH_3)_3$ and $(CH_3O)_2ClSiOSi(OCH_3)_2OSi(OCH_3)_3$ (approximate molar ratio of 1:1, as shown in Figure S8). Trihexylsilanol was synthesized by stirring a mixture of trihexylsilane (5.0 g), THF (60 mL), H_2O (2.0 mL), and Pearlman's catalyst (22 mg) for 30 min in an ice bath. The resulting solution was filtered to remove the catalyst and the solvent was evaporated. The resulting solid (trihexylsilanol) was dissolved in hexane (50 mL) and added to a stirred mixture of alkoxytrisiloxane (20 g), pyridine (5.2 mL), and THF (100 mL), and the mixture was stirred at RT. To eliminate the residual −Cl groups, methanol (1.3 mL) was added to the mixture. After removal of pyridine hydrochloride by filtration, the residue was distilled under vacuum to yield **1(Si4)** as a clear, colorless liquid (8.5 g). Spectroscopic data for **1(Si4)**: ^{1}H NMR (500 MHz, [D$_8$]THF): $\delta = 0.61$–0.64 (m, 2H), 0.88–0.89 (t, 3H; CH_3), 1.31–1.39 (m, 8H), 3.51–3.55 ppm (s, 21H; OCH_3); ^{13}C NMR (125.7 MHz,$^{[D8]}$THF): $\delta =$ 14.42, 15.88, 23.42, 23.73, 32.43, 34.18, 50.96, 51.08, 51.10 ppm; ^{29}Si NMR (99.3 MHz, [D$_8$]THF): $\delta = -93.97$ (Q^2), −92.76 (Q^2), −86.17 (Q^1), 10.21 ppm (M^1); MS (MALDI-TOF): $[M+K^+] = 672$, $[M+Na^+] = 656$.

Synthesis of **1(Si2)** and **1(Si3)**: Compounds **1(Si2)** and **1(Si3)** were synthesized by the reaction of trihexylsilanol with monochlorinated alkoxysilane and alkoxydisiloxane, respectively. The silylating agent used for the synthesis of **1(Si2)** was the mixture of $SiCl(OCH_3)_3$ (> 60%) and $Si(OCH_3)_4$ obtained by adding methanol dropwise to $SiCl_4$ in a N_2 flow. The silylating agent for **1(Si3)** was the siloxane dimer with a Si−Cl group.[12] Other procedures were the same as those for the synthesis of **1(Si4)**. Spectroscopic data for **1(Si2)**: ^{1}H NMR (500 MHz, [D$_8$]THF): $\delta = 0.60$–0.63 (m, 2H), 0.88–0.90 (t, 3H; CH_3), 1.30–1.39 (m, 8H), 3.48 ppm (s, 9H; OCH_3); ^{13}C NMR (125.7 MHz, [D$_8$]THF): $\delta = 14.40$, 15.90, 23.36, 23.70, 32.39, 34.10, 50.95 ppm; ^{29}Si NMR (99.3 MHz,$^{[D8]}$THF): $\delta = -84.84$ (Q^1), 9.93 ppm (M^1). Spectroscopic data for **1(Si3)**: ^{1}H NMR (500 MHz, [D$_8$]THF): $\delta = 0.61$ (m, 2H), 0.89 (t, 3H; CH_3), 1.30 (m, 8H), 3.48–3.52 ppm (s, 15H; OCH_3); ^{13}C NMR (125.7 MHz, [D$_8$]THF): $\delta = 14.35$, 15.83, 23.25, 23.58, 32.29, 34.01, 50.82, 51.85, 50.94 ppm; ^{29}Si NMR (99.3 MHz, [D$_8$]THF): $\delta = -92.58$ (Q^2), −86.15 (Q^1), 10.14 ppm (M^1); MS (MALDI-TOF): $[M+K^+] = 566$, $[M+Na^+] = 550$.

Synthesis of hybrid material **1H(Si*n*)**: Hydrolysis and polycondensation of **1(Si*n*)** were performed in a mixture with the molar ratio of **1(Si*n*)**/THF/H_2O/HCl = 1:30:$(2n-1) \times 2$:0.01. The mixture was stirred at room temperature until complete hydrolysis was confirmed by liquid-state ^{13}C NMR spectroscopy. In the cases of $n = 2$ and 4, hydrolyzed solutions were diluted with H_2O to the final molar compositions of **1(Si2)**/THF/H_2O/HCl = 1:30:12:0.01 and **1(Si4)**/THF/H_2O/HCl = 1:30:29:0.01, respectively. These solutions were cast on glass substrates and air-dried at RT for 1 day. In the case of **1H(Si2)**, the film was aged for 1.5 h at 80 °C to form the structure with a better arrangement.

Synthesis of dye-containing hybrid materials: 7-Hydroxycoumarin was added to the hydrolyzed solution of **1H(Si4)** with the molar ratio of **1(Si4)**/THF/H_2O/HCl/dye = 1:30:15:0.002:0.2. The mixture was stirred for 30 min to completely dissolve the dye, and then cast on glass substrates and air-dried.

Dispersion of hybrid materials (**1H(Si4)**) into nanoparticles: The hybrid materials derived from **1(Si4)** can be well dispersed in hexane (regardless of whether they contain dyes). A tiny amount of undispersed polymeric species was removed by filtration to give clear and colorless solutions.

Characterization: Liquid-state ^{29}Si, ^{13}C, and ^{1}H NMR spectra were recorded on a JEOL Lambda-500 spectrometer at resonance frequencies of 99.3, 125.7, and 500 MHz, respectively. The solution was put in a 5 mm glass tube, where a small amount of [D$_8$]THF was added for obtaining lock signals, and a small amount of chromium(III) acetylacetonate was added for the relaxation of ^{29}Si nuclei. Solid-state ^{29}Si MAS NMR and ^{13}C CP/MAS NMR spectra were recorded on a JEOL JNM-CMX-400 spectrometer at resonance frequencies of 79.42 and 100.5 MHz with recycle delays of 100 s and 12 s, respectively. The θ–2θ XRD patterns of the mesostructured hybrid materials were recorded on a Mac Science M03XHF22 diffractometer with Mn-filtered Fe Kα radiation or on a Rigaku RINT 2000 diffractometer with Ni-filtered Cu Kα radiation. TEM studies were carried out on a JEOL JEM-2010 electron microscope operated at 200 kV. SEM observation was carried out on a HITACHI S-5500 microscope operated at 30 kV. For TEM and SEM observation, mesostructures were directly formed by applying drops of the hydrolyzed solution on a carbon-supported grid. In the case of the particle observation, the hexane solutions of particles were applied dropwise onto the same grid and air-dried. UV/Vis absorption spectra were obtained with a Shimadzu UV-3100PC instrument. Fluorescence spectra were recorded on a Hitachi F-4500 spectrofluorophotometer at the excitation wavelength of 327 nm. For spectroscopic data, transparent hexane solutions were measured, after filtration of the solution with a 0.2 μm filter. MALDI-TOF mass analysis was carried out with a Shimadzu AXIMACFR instrument. The matrix of 1,8,9-anthracenetriol and the sample in hexane were spotted on the MALDI-TOF MS source target and allowed to dry in air prior to analysis.

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