Assembling Photoluminescent Silicon Nanocrystals into Periodic Mesoporous Organosilicas

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ABSTRACT: A contemporary question in the intensely active field of periodic mesoporous organosilicas (PMO) materials is how large a silsesquioxane precursor can be self-assembled under template direction into the pore walls of an ordered mesostructure. An answer to this question is beginning to emerge with the ability to synthesize dendrimer, buckyball, and polyhedral oligomeric silsesquioxane PMOs. In this paper, we further expand the library of large-scale silsesquioxane precursors by demonstrating that photoluminescent nanocrystalline silicon with the porous structure of the PMO. This integration of two functional components makes ncSi-PMO a promising multifunctional material for optoelectronic and biomedical applications.

INTRODUCTION

Since the first reports on the synthesis of periodically ordered mesoporous silica and aluminosilica through template-directed self-assembly,1−3 the concept of using a sacrificial template to direct the self-assembly has been extended to a rich compositional array of periodic mesoporous materials, which now includes metal oxides,4,5 metal chalcogenides,6,7 metal phosphates,8 metals and semimetals,9−14 carbon,15,16 and organosilicas.17−21 In most syntheses, an amphiphilic template drives the separation of mesodomains and organizes small molecular precursors into ordered mesostructures. The ability of an amphiphilic template to organize and the ability of a precursor to diffuse put a practical limit on the size of the precursor for a successful coassembly. It is expected that large precursors are more difficult to assemble than small precursors. However, polymers,22 dendrimers,23 polyhedral oligomeric silsesquioxane,24 C60 molecules,25 and nanoparticles26 have been incorporated into the mesoporous framework through template-directed self-assembly. Although they are mostly the results of pure scientific curiosity, these synthetic feats have further extended the horizons of mesoporous materials and inspired the design of properties and functions for applying these materials in such areas as sensors, catalysis,27 nanoelectronics,28−30 light harvesting,31 energy storage and conservation,32 water purification,33 drug delivery,34 and biomedical imaging.35

The use of mesostructured materials in optical applications promises versatile processing strategies for fibers, spheres, films, and lithographic patterns with designed mechanical stability, wettability, and high loading of photoactive species.36,37 Early reports on the incorporation of photoactive species placed dye species in the hydrophobic regions of the micelle templates.36,37 Recent efforts focusing on the synthesis of luminescent forms of periodic mesoporous organosilicas (PMO) have aimed at the inclusion of large conjugated structures in the pore walls31 in

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order to preserve the pore space for further materials designs, such as the loading of another photoactive species to enable light harvesting.38 The chromophores in these luminescent PMOs are conjugated π structures. Compared with these organic chromophores, photoluminescent inorganic nanocrystals have the advantage of high resistance against photobleaching and tunable size-dependent absorption and emission spectra.39 Nanocrystalline silicon (ncSi) is particularly attractive because of its expected biocompatibility, which makes it one of a growing class of “green” nanomaterials.40 The current methods of making photoluminescent ncSi-embedded mesoporous thin films and powders involve the growth of nc-Si in/on the pore walls by either chemical vapor deposition41 or metamorphic transformation of mesoporous hydridosilica (meso-HSO1.5) into mesoporous ncSi/SiO2, with the latter exhibiting stronger photoluminescence (PL).42 Incorporating ncSi into mesoporous materials may further hold promise in areas such as lighting, lasers, drug delivery, and bioimaging.

Here we report the synthesis of photoluminescent nanocrystalline silicon periodic mesoporous organosilica (ncSi-PMO) through template-directed self-assembly. The hydride-terminated surface of the ncSi was first capped with triethoxysilylethylene (TESE) oligomers through hydrosilylation (Figure 1). The oligo(TESE) layer makes the ncSi precursor soluble in ethanol (Figure 2a), and its ethoxysilane groups, after being hydrolyzed and polycondensed, provide bonding that stabilizes the porous gel network. The PL spectrum of the pure ncSi:(CH2CH2Si(OEt)3)H dissolved in ethanol (Figure 2b) displays a peak at 615 nm upon excitation at 330 nm.

The chemical structure of ncSi:(CH2CH2Si(OEt)3)H was analyzed by FT-IR spectroscopy, UV−vis spectroscopy, liquid-phase NMR spectroscopy, and gel-permeation chromatography (GPC) (Figure 3). The IR spectrum of ncSi:(CH2CH2Si(OEt)3)H (Figure 3a) shows characteristic C−H vibrations at around 2900 and 1390 cm−1, Si−O−C vibrations at around 1100 cm−1, very weak Si−H vibrations at around 2100 cm−1, and, as anticipated, little evidence for C=C vibrations at 1600–1700 cm−1, suggesting almost complete reaction of the surface hydride groups on the ncSi and of the monomeric TESE. The UV−vis absorption spectrum of pure ncSi:(CH2CH2Si(OEt)3)H (Figure 3b) has a broad absorption in the 200–500 nm region, predominantly originating from the ncSi core. The 1H NMR spectrum in CDCl3 (Figure 3c) shows resonances due to the ethoxy groups at 3.79 and 1.20 ppm and resonances due to the oligomer backbone at 0.56 and 1.48 ppm, the latter overlapping with a broad resonance attributed to water (1.59 ppm). The samples contained less than 2% unreacted TESE, as calculated by integrating the vinyl...
protons (5.6−5.9 ppm). The spectrum appears virtually identical to that of pure oligo(TESE). The additional peak in the high-molecular-weight region (log \( M_w \) ≈ 4.5) in the chromatogram of ncSi:(CH\(_2\)CH\(_2\)Si(OEt)\(_3\))\(_n\)H (Figure 3d), in comparison with that of pure oligo(TESE), indicates successful grafting of the oligomer onto the surface of ncSi.

The precursor ncSi:(CH\(_2\)CH\(_2\)Si(OEt)\(_3\))\(_n\)H was further analyzed using high-resolution transmission electron microscopy (HRTEM) and energy-filtered TEM (EFTEM).\(^{44}\) EFTEM collects only electrons that have lost a specific amount of energy as a result of the electron−specimen interaction and is advantageous over the other techniques for characterization of Si nanoclusters and nanoparticles.\(^{45}\) It generates a chemical map of the species of interest with a very high spatial resolution.\(^{46,47}\) The plasmon loss of ncSi is centered at ∼17 eV and that of silicon dioxide at ∼24 eV. This difference allows us clearly to distinguish silicon from silicon dioxide. The plasmon map at 17 eV (Figure 4a) proves the existence of silicon nanoparticles in the precursor. For comparison, the bright-field TEM image (Figure 4a inset) shows a uniform gray background without any appreciable intensity contrast. Other representative nanoparticles showing crystal lattice fringes indicate the ncSi to be ∼2 nm in width and ∼5 nm in length. However, we emphasize here that the sizes of the nanocrystals prepared by high-temperature treatment of hydridosilicate glass are polydispersed. Our recent study of monodisperse silicon nanocrystals prepared using the same method and separated using density gradient ultracentrifugation suggests a lack of crystallinity for nanoparticles smaller than 2.5 nm.\(^{48}\) A comparison of the HF etching time used in our previous report (∼1.5 h) and the time used here (∼2.5 h) suggests that there is an appreciable number of silicon nanoparticles having sizes below 2.5 nm.

The precursor ncSi:(CH\(_2\)CH\(_2\)Si(OEt)\(_3\))\(_n\)H was then coassembled with TEOS using P123 as the template to form ncSi-PMO (Figure 5). The assembly of pure ncSi:(CH\(_2\)CH\(_2\)Si-(OEt)\(_3\))\(_n\)H with TEOS also gave a mesostructured film, but as expected, it collapsed upon template removal (Figure S1 in the Supporting Information). To minimize any oxidation of
ncSi, mild thermal treatments at 85 °C under vacuum or under a reductive H2/Ar atmosphere were used to increase the degree of polycondensation in the framework before the template removal. The PL of ncSi was preserved throughout the synthesis and surfactant removal processes. The ncSi-PMO showed visible PL under 400 nm light excitation, with a broad emission peak at 605 nm (Figure 6).

Ordered mesopores were revealed using small-angle X-ray diffraction (XRD) patterns and high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM). The small-angle XRD patterns showed increased signal-to-noise ratios and decreased peak widths after template removal (Figure 7a,b), indicating that the porous structure was preserved upon template removal in the ncSi-PMO films. The d spacings decreased slightly, from 87.4 to 77.4 Å in the spin-coated film and from 76.1 to 66.9 Å in the drop-cast films. The HAADF-STEM images of ncSi-PMO directly confirmed the ordered mesoporous structure (Figure 7c,d). The ordering is anisotropic, with a larger lattice spacing along the direction parallel to the interfaces than along the direction perpendicular to the interfaces. The quasi-2D hexagonal symmetry (compressed in the direction perpendicular to the substrate) is evident in layers close to the substrate–film and film–air interfaces. The repeat distances obtained from the corresponding fast Fourier transform (FFT) are ~6 nm in the direction parallel to the interfaces and 5–5.5 nm in the direction perpendicular to the interfaces. The images display wormlike disorder mesoporous structures between the ordered regions originating from substrate and air interfaces, with average lattice parameters of ~10 nm parallel to the substrate and ~5.8 nm perpendicular to it. The difference in the d spacings calculated from the small-angle XRD patterns (measured in the Bragg–Brentano geometry, corresponding to the out-of-plane direction) and from the top spot of the FFT of electron microscopy image (also corresponding to the out-of-plane direction) can be attributed to a different degree of anisotropy caused by the additional thermal treatment used to increase the degree of polycondensation in preparing the sample for STEM imaging. Furthermore, a slight reduction of the lattice spacings during focused ion beam (FIB) preparation cannot be excluded, but the mesoporous structure was quite stable with respect to the electron beam during TEM and STEM imaging.

Information on the porosity of ncSi-PMO was obtained from nitrogen sorption measurements on powders produced by scratching drop-cast films off their substrates (Figure 8a,b) as well as from ellipsometric porosimetry (EP) measurements on spin-coated films (Figure 8c,d). The nitrogen sorption measurements showed type IV isotherm, with a Brunauer–Emmett–Teller (BET) surface area of 256 m2/g, a total pore volume of 0.35 cm3/g, and a pore size of ~5.8 nm [as estimated from thickness profile in Figure 8d]. This Young’s modulus value is much lower than those of PMOs made from smaller molecules, and the difference can be attributed to the low degree of polycondensation as well as the flexibility of the bridging Si–CH2CH2−Si groups in the matrix.

The relative amount of ncSi in ncSi-PMO was analyzed by solid-state NMR spectroscopy (SSNMR) (Figure 8). Because of the small amount of ncSi incorporation, together with the long relaxation time of Si atoms in ncSi, a quantitative method for determining the relative amount of ncSi, such as Bloch decay acquisition accompanied by high-power proton decoupling (HPDEC) SSNMR, was unsuitable for the ncSi-PMO films (Figure S2 in the Supporting Information). Thus, we used cross-polarized magic-angle-spinning (CP MAS) SSNMR with conditions optimized for Si atoms with no close protons (a direct comparison of the two methods on an ncSi silica composite before HF etching is given in Figure S3 in the Supporting Information). The samples before and after surfactant removal both showed a small but distinguishable signal from the ncSi at around ~79.2 ppm (Figure 9a,b). As a control sample, we also measured the spectrum of an ncSi:(CH2CH2Si(OEt)3)3:H gel that was hydrolyzed and polycondensed under the same acidic conditions without P123 and TEOS. This spectrum (Figure 9c) showed only peaks due to T and ncSi sites, indicating no cleavage of C–Si bonds. Semiquantitative analysis showed that 2–3% of the silicon atoms in the ncSi-PMO films are ncSi and that 50–55% of the silicon atoms are at the T sites, with the remaining 42–48% of the silicon atoms at the Q sites (Table 1). These values are consistent with the initial ncSi:(CH2CH2Si(OEt)3)3:H and TEOS precursor composition of the films, which provides the ncSi, T, and Q sites, respectively. The oligomeric carbon chains provide additional structural connectivity that increases the loading amount of Si T sites beyond the usual 25% limit.21

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The Raman spectra provided the most direct evidence for the presence of ncSi in ncSi-PMO. Figure 10 compares the spectrum of the initial ncSi−silica composite before HF etching (the step in which ncSi first appears) and the spectrum of the ncSi-PMO end product. Both spectra show the transverse optical (TO) mode at \( \sim 500 \text{ cm}^{-1} \), indicating that ncSi is preserved throughout the entire synthesis.\(^{52,53} \) The red shift from the typical crystalline Si TO mode observed at \( 520 \text{ cm}^{-1} \) is due to the phonon confinement effect in the ncSi.\(^{53} \) The broadening in the full width at half-maximum is attributed to surface modification by HF etching and TESE capping. For interested readers, we provide additional UV−vis spectra of ncSi-PMO in Figures S4 and S5 in the Supporting Information.

**CONCLUSION**

In summary, we have successfully incorporated photoluminescent ncSi into periodic mesoporous organosilica through a creative design of the precursor with an oligomeric capping
ligand, ncSi,(CH₂CH₂Si(OEt)₃)ₓH, and careful tuning of its template-directed self-assembly conditions. Comprehensive structural and property characterizations indicate that ncSi-PMO gainfully combines the optical properties of ncSi and the porous structure of PMO. This integration of purposeful components makes ncSi-PMO a promising multifunctional material for optoelectronic and biomedical applications.

### EXPERIMENTAL SECTION

#### Reagents and Materials.
Trichlorosilane (HSiCl₃, 99%), TEOS [Si(OC₂H₅)₄, ≥ 99%], and TESE [C₂H₃Si(OC₂H₅)₃, 99%] were purchased from Sigma-Aldrich and used as received. Pluronic P123 surfactant (P123 triblock copolymer) was purchased from BASF Corporation. Decane (C₁₀H₂₂), hydrochloric acid (HCl, 36−38%), and hydrofluoric acid (HF, 48%) were obtained from Caledon Laboratories Ltd.

#### Characterization.
UV−vis absorption spectra were obtained using either a Cary 100 BIO, PerkinElmer Lambda 900, or Beijing Puxi TU-1810 UV−vis spectrophotometer. PL spectra of surface-functionalized ncSi were obtained on a Varian Cary fluorospectrophotometer.

Small-angle X-ray scattering (SAXS) patterns were collected on a Nanostar SAXS diffractometer equipped with a high-power point-focus Cu Kα source and low-intensity-background substrates. Small-angle XRD patterns of thin-film samples were acquired on a Siemens D5000 diffractometer using Cu Kα radiation (λ = 1.5418 Å).

SEM images were obtained on Hitachi S5200 microscope operated at 30 kV. TEM images were obtained on an image-corrected FEI Titan 80−300 microscope operated at 300 kV and equipped with a Gatan Tridiem energy filter providing an information limit of 0.08 nm in TEM mode. HAADF-STEM operation was performed with a nominal probe size of 0.19 nm. TEM sample preparation of the ncSi:(CH₂CH₂Si(OEt)₃)ₓH precursor gel was done by diluting the material in ethanol and dispersing it on a carbon-coated Au grid (Quantifoil). Cross-section TEM samples of the mesoporous ncSi-PMO were prepared by in situ lift-out in an FEI Strata 400S DualBeam FIB instrument using 30 kV Ga ions for rough cutting and 5 kV Ga ions for fine polishing.

Nitrogen sorption data were collected on a Quantachrome Autosorb-1C instrument. Samples were degassed at 100 °C overnight under vacuum before measurements. Raman spectra were collected on LabRam 300 spectrometer equipped with a confocal microscope (100 μm slit width and 300 μm pinhole), a 532 nm diode laser source, an electronically cooled CCD camera, and a 1200 groove/mm monochromator. Calibration was done using a crystalline silicon wafer.

### Table 1. Integrated Intensities from CP MAS SSNMR Experiments Corrected for Differences in T₁ρ and T₂Si−H (mol %)

<table>
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<th>signal intensity (mol %)</th>
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<th>−56 to −58 ppm</th>
<th>−64 to −66.5 ppm</th>
<th>−77 to −79 ppm</th>
<th>−91 to −92 ppm</th>
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Figure 8. Porosity information obtained from nitrogen sorption EP measurements: (a) nitrogen sorption isotherm and (b) the corresponding BJH pore size distribution; (c) EP isotherm and (d) the corresponding thickness profile.

Figure 9. ²⁹Si CP MAS SSNMR spectra (spinning speed of 5000 Hz and relaxation delay of 3 s) of (a) ncSi-PMO before template removal, (b) ncSi-PMO after template removal, and (c) a gel of hydrolyzed and polycondensed ncSi:(CH₂CH₂Si(OEt)₃)ₓH synthesized under the same conditions as ncSi-PMO but without P123 and TEOS. The signal positions highlighted in red correspond to signals originating from the ncSi core.

Figure 10. Raman spectra of (a) ncSi−silica composite before HF etching and (b) ncSi-PMO.
EP measurements were performed using a Sopra GESSE instrument. Liquid-phase NMR spectroscopy was performed on a 400 MHz Varian Mercury NMR spectrometer at 25 °C. Samples were prepared by diluting Si nanocrystals in CDCl₃, and the spectra were referenced to tetramethylsilane (TMS) (0 ppm).

²⁹Si NMR measurements were carried out on a Bruker Avance 200 NMR spectrometer with a magnetic field of 4.7 T and a ²⁹Si Larmor frequency of 39.75 MHz using a BL7 double-resonance MAS probe and 7 mm ZrO₂ spinners. All of the NMR measurements were performed at room temperature at a spinning speed of 5000 Hz. Signal of liquid TMS was used as an external reference (0 ppm). The spectra were acquired both in Bloch decay mode and using CP to protons. The Bloch decay spectra were acquired using a short ²⁹Si pulse of 1 μs (τ/10) and high-power composite pulse proton decoupling. The delay between the scans was set at 100 s, which should be sufficient for complete relaxation of all of the signals and quantitative measurements, and 2000–3000 scans were commonly acquired. Fitting and deconvolution/integration of the spectra were performed using the DMFit simulation program. In quantitative measurements, the absolute intensities of the spectra were normalized to the total number of scans acquired. Since the Bloch decay spectra could not provide a sufficiently high signal-to-noise ratio, quantitative measurements were performed using the data from the CP experiments. The CP spectra were acquired on the same MAS probe using a ¹H RF field of 62.5 kHz and a relaxation delay of 3 s. To quantify the CP spectra, the variations in the signal intensity I with the CP contact time τ (0.1–50 ms) were obtained for all of the samples. The experimental dependencies were fit simultaneously using the equation

\[
I(\tau) = \frac{I_0}{1 - \frac{\tau}{\tau_C}} \left[ \exp -\frac{\tau}{\tau_C} - \exp -\frac{\tau}{T_{1CH}} \right]
\]

and the signal intensities at thermal equilibrium, I₀, together with relaxation constants T₁ Hir and T₁CH were obtained.

**Synthetic Procedures.** Synthesis of H(SiO₁.₅)ₙ Sol−Gel Glass. In a typical synthesis, 10 mL of HSiCl₄ was added to a round-bottom flask equipped with a magnetic stirrer bar and cooled in an acetone/dry ice bath (−78 °C). An excess amount of deionized water was rapidly injected into the cooled HSiCl₄ with vigorous stirring, and a white precipitate immediately formed. Hydrolysis of the precursor was confirmed by verifying the pH of the reaction mixture (pH <=1). After the reaction, the precipitate was separated by vacuum filtration, washed with distilled water, and dried under vacuum at 85 °C overnight. The resulting white solid (H(SiO₁.₅)ₙ), sol−gel polymer (yield >95%) was kept under vacuum.

Synthesis of Bulk ncSi/SiO₂. Silicon nanocrystals were prepared by thermally induced disproportionation reactions. The white solid (H(SiO₁.₅)ₙ) was placed in a quartz glass reaction boat and transferred to a high-temperature tube furnace with minimum air exposure. Samples were heated for 1 h at 1100 °C under a flowing 5% H₂/95% Ar atmosphere. After it was cooled to room temperature, the brown ncSi/SiO₂ composite was mechanically ground in an agate mortar and pestle to obtain a fine powder.

Synthesis of Hydro-terminnted Freestanding ncSi. A representative etching procedure involved transferring ncSi/SiO₂ composite (0.6 g) to a Teflon beaker containing a mixture of 9 mL of deionized water, 18 mL of ethanol, and 30 mL of 48% aqueous HF. The mixture was stirred for 2.5 h to etch the SiO₂ matrix and gradually decrease the size of the ncSi. Hydrophobic, hydro-terminated freestanding silicon nanocrystals were isolated by extraction from the aqueous solution into 30 mL of decane.

**REFERENCES**
