

## Supplementary Information

### Synthesis of Silicon Nanocrystal by Magnesium Directed Reduction of the Silica Nanoparticle Formed in Micro-Emulsion of Reverse Micelle

Thu-Huong Le and Hyun-Dam Jeong\*

Department of Chemistry, Chonnam National University, Gwangju 500-757, Korea. \*E-mail: hdjeong@chonnam.ac.kr  
Received April 18, 2014, Accepted August 19, 2014

#### Experimental

**Synthesis of Silica Nanoparticle (SiO<sub>2</sub> NPs).** The size-controlled SiO<sub>2</sub> NPs were synthesized from tetraethylorthosilicate (TEOS) molecules by a micro-emulsion method using reverse micelles, as shown in Scheme 1. Brij® L4 surfactant (12 g, 0.033 mol) was mixed with cyclohexane (200 mL) and 1-hexanol (3.2 mL) by sonication for 30 min until the mixture changed to a clear solution. Distilled water was then added, and the reaction mixture was sonicated for 10 min. When the water was added, a white solid was generated in the reaction mixture, which was completely re-dissolved by sonication. TEOS (5 mL, 0.022 mol) was then added with stirring, and the reaction mixture was further stirred for 30 min at room temperature. For the hydrolysis and condensation of TEOS, NH<sub>4</sub>OH (1 mL) was slowly added while stirring the reaction mixture, which was then stirred for an additional 12 h at room temperature. After the reaction had been completed, the reverse micro-emulsion was de-stabilized by adding acetone (20 mL), followed by centrifugation at 12,000 rpm for 5 min. The synthesized SiO<sub>2</sub> NPs were washed with ethyl alcohol (1 mL for each wash) 3–10 times. To investigate how the concentration of water affects the size of SiO<sub>2</sub> NPs in our synthetic procedure, these reactions were carried out with two different volumes of distilled water (1 mL and 4 mL), without changing the other conditions (supplementary material) The two samples of Si NCs obtained were labeled Si-1 and Si-2 for the addition of 1 or 4 mL of water, respectively.

**Synthesis of Silicon Nanocrystal (Si NCs).** In Scheme 1, SiO<sub>2</sub> NPs (0.60 g, 0.01 mol w.r.t Si content) and magnesium powder (0.5 g, 0.22 mol) were mixed and ground together manually to give a grayish brown-colored powder, then heated at 670 °C for 15 hours under an argon atmosphere in a quartz tube furnace. The resulting dark brown-colored powder product was treated with hydrochloric acid (20 mL) for 12 hours to remove magnesium oxide (MgO). A brown precipitate was obtained by vacuum filtration. The solid was washed with distilled water until the washings resulted in a neutral pH (*ca.* 7). The precipitate was then washed with ethanol (20 mL) and acetone (3 × 20 mL), and air dried to yield oxide coated Si NCs. Finally, the Si NCs were obtained as a brown powder.

**Synthesis of Octadecyl Terminated Silicon Nanocrystal (ODE-Si NCs).** The hydride-terminated Si NCs (H-Si NCs) were synthesized only from sample Si-2 (0.2 g) through an etching reaction using 1:1:1 mixture of hydrofluoric acid, ethanol and distilled water for 2 hours. After completing the etching process, H-Si NCs were isolated by extraction with 20 mL of anhydrous toluene. The H-Si NCs were collected from the solvent by centrifugation at 10000 rpm for 4 min. After centrifugation, the solution was discarded, and the brown precipitate was rinsed twice with ethanol and once with toluene before dispersion in 1-octadecene. The H-Si NCs solution was capped with octadecyl-terminated Si NCs (ODE-Si NCs) by thermal hydrosilylation at 190 °C. The reaction mixture was degassed by three cycles of evacuation and purging with argon to eliminate water, and stirring for 10 hours. After the functionalization, the reaction mixture was filtrated to yield a clear, bright yellow liquid. Next, all solvents was removed at 40 °C under reduced pressure using a rotary evaporator. To remove free capping molecules, the product was washed three times by precipitation with acetone as an antisolvent, and dispersed in toluene. The final product was obtained as a yellow resin after evaporation of the toluene solvent.

#### Results and Discussion

The surface chemistry of H-Si NCs was confirmed based on FT-IR spectroscopy. Figure S1 (supplementary information) shows the presence of a Si-H stretching vibration mode of the H-Si NCs sample at 2122.8 cm<sup>-1</sup>. The peak at 2917.1 cm<sup>-1</sup> was attributed to the C<sup>sp3</sup>-H stretching vibration of the toluene solvent used in the extraction process of the H-Si NCs. The Si-O stretching vibration in the range of 1100 to 1000 cm<sup>-1</sup> was also observed in the spectrum, which was due to the brief air exposure of the sample during preparation for FT-IR measurement. As shown in the FT-IR spectrum of the ODE-Si NCs (Figure S1 in supplementary information), asymmetric stretching, symmetric stretching, and bending the C-H in the octadecyl group were obtained at 2917.1 cm<sup>-1</sup>, 2847.7 cm<sup>-1</sup>, and 1372.0 cm<sup>-1</sup>, respectively.<sup>1</sup> We observed a peak at 1466.5 cm<sup>-1</sup>, which is attributed to the symmetric bending vibration of an Si-C bond, confirming the formation of the Si-C covalent bond between the Si

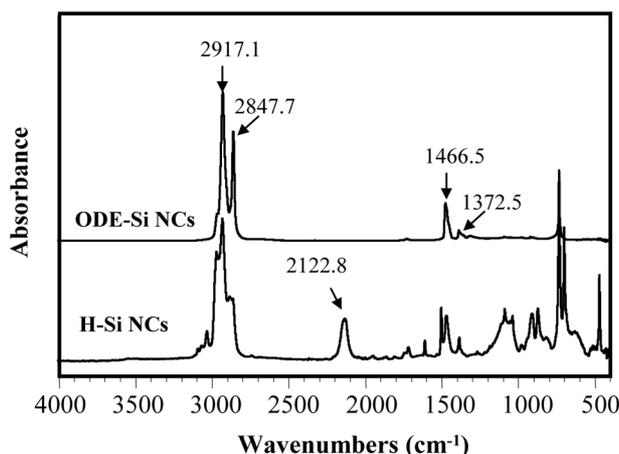


Figure S1. FT-IR spectra of ODE-Si NCs and H-Si NCs.

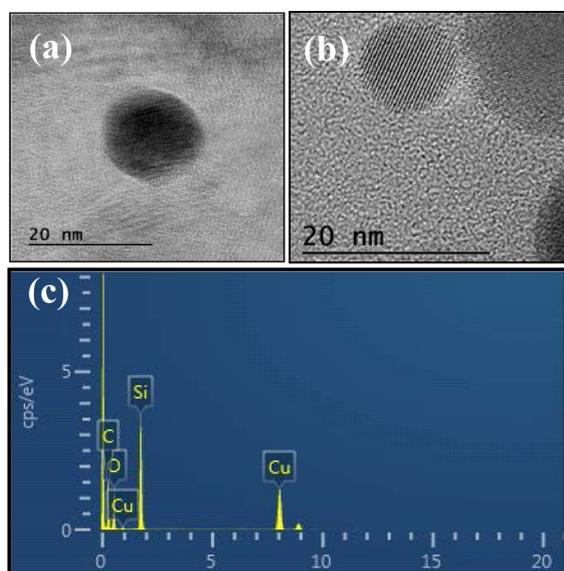


Figure S2. (a) Transmission electron microscopy (TEM) image of Si NPs (Si-1). (b) Transmission electron microscopy (TEM) image of Si NPs (Si-2). (c) Energy dispersive X-Ray (EDX) spectra of the Si NCs.

NCs and octadecyl group.<sup>1</sup> The absence of a peak due to an Si-O bond in the range of 1000-1100  $\text{cm}^{-1}$  indicated no oxygen involved on the surface of the Si NCs.

Figure S2(a), (b), and (c) show the transmission scanning electron microscopy (TEM) image and energy dispersive X-Ray (EDX) spectra of the Si NCs sample. The average sizes of the Si NPs are  $20 \pm 2.09$  nm for sample Si-1 (Figure S2a and Figure S3a), and  $10.66 \pm 1.66$  nm for sample Si-2 (Figure S2b and Figure S3b). The TEM image clearly shows that highly spherical Si NPs are formed, and their size distribution is narrow. The composition of these nanocrystals is also analyzed by energy dispersive X-ray spectroscopy (EDX). Figure S2(c) shows that these nanocrystals are composed of C element (27% from the remaining solvent and carbon film on the TEM copper grid), Cu element (27% from the copper TEM grid), O element (16% from  $\text{SiO}_2$  on surface Si NCs) and Si element (31% from Si NCs).

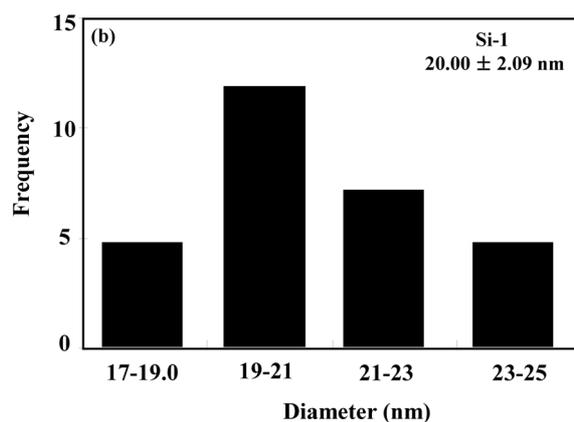


Figure S3. (a) Size distribution of Si-1 sample. (b) Size distribution of Si-2 sample.

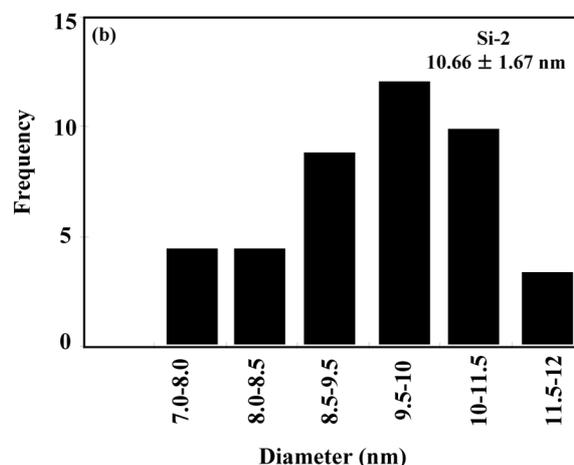


Figure S4. (a) TEM image for ODE-Si NC of 5.2 nm, exhibiting 680 nm emission band in the PL spectrum, (b) TEM image of ODE-Si NC of 3.2 nm, exhibiting 470 nm emission band in the PL spectrum, (c) bimodal size distribution indicating mixing of different sized ODE-Si NCs, where the right part corresponds to the TEM images for about 5.2 nm while the left one for about 3.2 nm, (d) contrast histogram of TEM image for the 3.2 nm ODE-Si NC, confirming the lattice spacing of 2.2 Å due to (211) lattice plane of diamond crystal structure.

Furthermore, no magnesium is detected in the EDX result, showing that unreacted Mg metal is removed completely after treatment with hydrochloric acid (HCl).

In Figure S4(c), we can see fairly wide size distribution, indicating mixing of different sized ODE-Si NCs. In the bimodal size distribution in Figure S4(c), the right part corresponds to the TEM images for about 5.2 nm (Figure S4(a)) of lattice spacing of 2.7 Å, while the left one for about 3.2 nm (Figure S4(b)) of lattice spacing of 2.2 Å. The two lattice spacings are originated from (200) and (211) lattice planes in diamond crystal structure, respectively. In addition, the lattice spacing of 2.2 Å due to (211) lattice plane of diamond crystal structure was confirmed from contrast histogram of TEM image for the 3.2 nm ODE-Si NC, as shown in Figure S4(d).

**References**

1. Yang, C. S.; Bley, R. A.; Kauzlarich, S. M.; Lee, H. W. H.; Delgado, G. R. *J. Am. Chem. Soc.* **1999**, *121*, 5191-5195.