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## Size Controlled Synthesis of Silicon Nanocrystals within Inverse Micelles

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### ABSTRACT

Alkyl-terminated Si nanocrystals (NCs) are synthesized at room temperature by hydride reduction of  $\text{SiCl}_4$  within inverse micelles. Highly monodisperse Si NCs (2 – 6 nm) are produced by variation of the cationic quaternary ammonium salts used to form the inverse micelles. Transmission electron microscopy imaging confirms the NCs are highly crystalline, while FTIR spectra confirm that the NCs are passivated by covalent attachment of alkanes, with minimal surface oxidation. The photoluminescence intensity of the Si NCs exhibits an inverse relationship with the mean NC diameter, with a quantum yield of 12 % recorded for 2 nm NCs.

### INTRODUCTION

Research interest in the preparation of oxide-free Si NCs has been steadily increasing, because the momentum requirements due to the indirect band gap structure of bulk Si are relaxed in the 1–5 nm size range as a result of quantum confinement effects.[1-2] This allows for their excellent photophysical properties, such as size-tunable and narrow luminescence and high quantum yields, to be combined with the richness of silicon surface chemistry. A large variety of both physical and chemical methods have been reported for the preparation of Si NCs, including physical and chemical vapor deposition, thermal annealing, laser induced-heating of gaseous precursors, electrochemical etching of crystalline silicon wafers, thermal decomposition of silane precursors and the reduction of silicon halides by various reducing agents.[3-8] The preparation of Si NCs within inverse micelles was first reported by Wilcoxon *et al.*, which resulted in 2 – 10 nm Si NCs with hydrogenated surfaces.[9] This method was later refined using a Pt-catalyzed hydrosilylation process to chemically passivate the nanocrystal surface and allows addition of various functionalities.[10-12] More recently, alkyl trichlorosilanes have been utilized as both reductant and ligand, resulting in formation of both alkyl- and alkene-functionalized Si NCs.[13-14] However, despite the number of reports describing the preparation of high quality Si NCs, no studies have been carried out on the effect of the surfactant in determining the size and shape of the resultant Si NCs. Here we report a simple method for the synthesis of Si NCs within inverse micelles having well defined core diameters ranging from 2 to 6 nm. Through controlling the size of the nanocrystals, their resulting photophysical properties can be tuned.

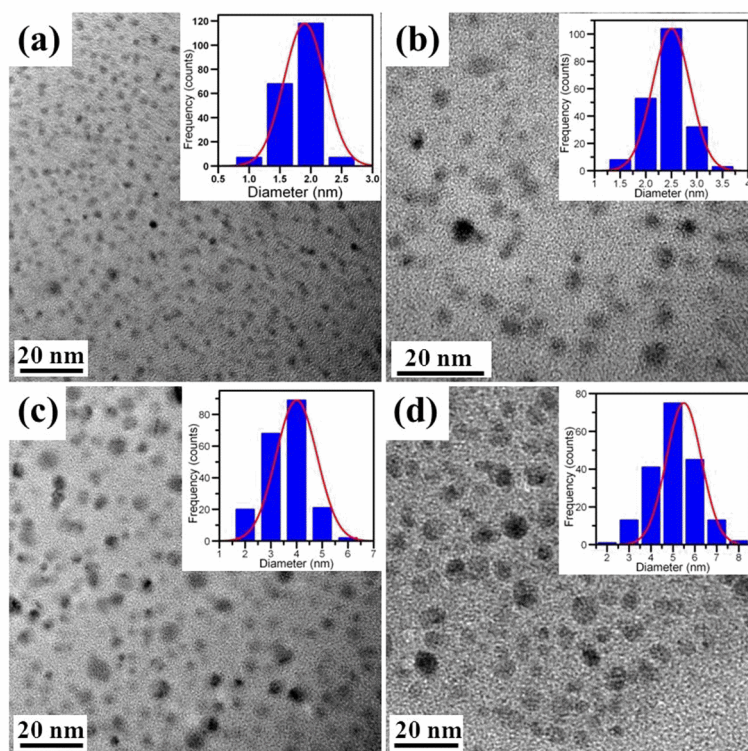
### EXPERIMENT

The synthesis of the Si NCs was adapted from previously reported methods and carried out in an inert atmosphere glove-box.[10] In a typical preparation, 2.74 mmol of the surfactant was dissolved in 100 mL anhydrous toluene. 0.1 mL (0.87 mmol)  $\text{SiCl}_4$  was then added to the solution and left to stir for 30 min. Si NCs were formed by the dropwise addition of 6 mL of 1 M lithium aluminum hydride in THF over a period of 2 min. The solution was then left to react for 2.5 h. The excess reducing agent was then quenched with the addition of 60 mL anhydrous methanol. The NCs were subsequently-passivated by modifying the silicon-hydrogen bonds at

the surface *via* the addition of 200  $\mu\text{L}$  of a 0.1 M  $\text{H}_2\text{PtCl}_6$  in isopropyl alcohol as a catalyst, followed by 6 mL of 1-heptene. After stirring for 2.5 h, the Si NCs were removed from the glove box and the organic solvent removed by rotary evaporation. The resulting dry powder was then redispersed in 20 mL hexane and sonicated for 30 min. The solution was then filtered twice, washed 4 times with 100 mL of *n*-methyl formamide and once with distilled water. Alkyl-terminated Si NCs remain in the hexane phase. The Si NCs were further purified by column, chromatography, using Sephadex gel LH-20 as the stationary phase and eluted with THF. UV-Vis absorption spectra were recorded using a Shimadzu UV PC-2401 spectrophotometer with a 60 mm integrating sphere (ISR-240A, Shimadzu). Photoluminescence (PL) spectra of the Si NCs were recorded using a Perkin Elmer LS 50 luminescence spectrophotometer; quantum yields (QY) were measured using the comparative method.[15] FT-IR spectra were recorded on a Bio Rad Excalibur FTS 3000 spectrometer. Transmission electron microscopy (TEM) images and energy dispersive x-ray spectra (EDX) were acquired on JEOL 2100 electron microscope equipped with an Oxford INCA x-sight detection spectrometer. NC size analysis was carried out using the Particle Size Analyzer macro for ImageJ (r12, <http://code.google.com/p/psa-macro/>).

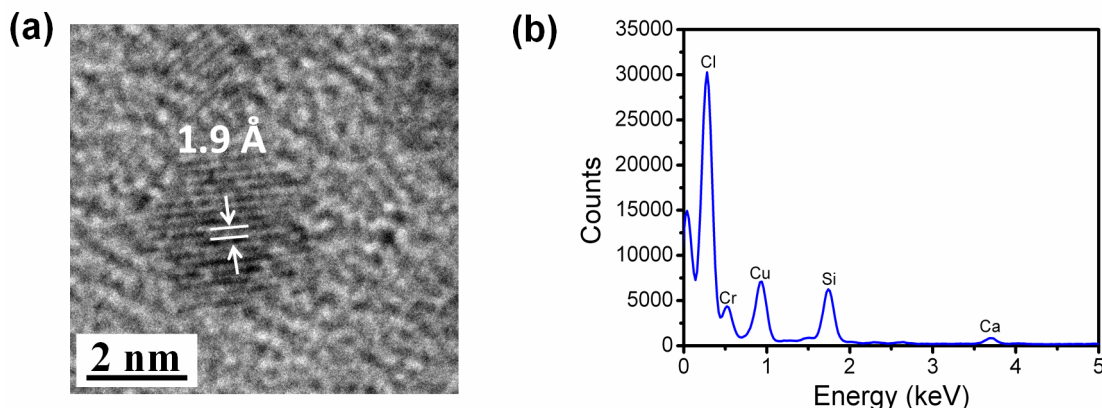
## DISCUSSION

TEM images of Si NCs prepared in the presence of tetraoctyl ammonium bromide (TOAB), tetrabutyl ammonium bromide (TBAB), dodecyltrimethyl ammonium bromide (DTAB) and tetradodecyl ammonium bromide (TDAB) are shown in Figure 1. Si NCs prepared with TOAB as the surfactant template are highly size and shape monodisperse, see Figure 1(a). A histogram of NC diameters, determined by analysis of *ca.* 200 NCs located at random



**Figure 1.** TEM images of the Si NCs synthesized in the presence of the following surfactants: a) TOAB, b) TBAB, c) DTAB, and d) TDAB. Insets: Size histograms of the mean NC diameters with curves fit to the data using a Gaussian model.

locations on the TEM grid, is shown inset in Figure 1(a). Fitting the histogram to a Gaussian model gave a mean diameter of  $1.9 \pm 0.3$  nm, in good agreement with previous results.[10,16] The standard deviation closely matches the Si (111) interplanar spacing, emphasizing the size monodispersity nature of the NCs. Si NCs synthesized with TBAB and DTAB resulted larger NCs, with mean diameters of  $2.6 \pm 0.3$  nm and  $4.0 \pm 0.9$  nm respectively, see Figures 1(b) and 1(c). The largest NCs ( $5.8 \pm 1.8$  nm) were obtained when TDAB was employed as the surfactant, though a large increase in size and shape polydispersity is observed.

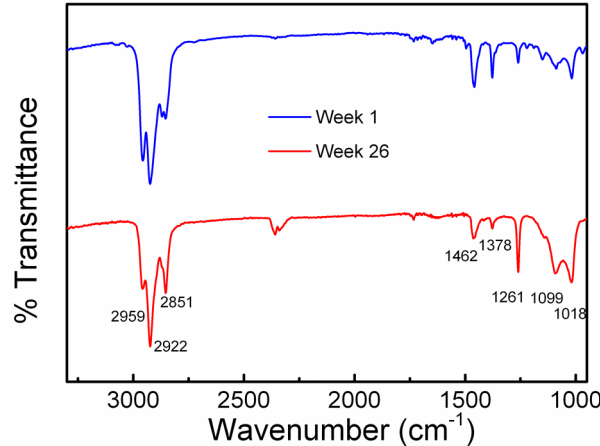


**Figure 2.** (a) HR-TEM image and (b) EDX profile of Si NCs synthesized with DTAB as the surfactant.

High-resolution TEM (HR-TEM) imaging was used to confirm the crystallinity and establish the crystal phase of the as-synthesized NCs; see Figure 2(a). HR-TEM images of Si NCs showed that the Si NCs formed a single contiguous crystalline phase, without the presence of packing defects. The lattice fringes shown inset in Figure 2 (a) correspond to a  $d$  spacing of 1.9 Å, matching the (220) spacing reported for the silicon unit cell. Figure 2(b) shows the energy dispersive X-ray (EDX) spectrum, where the Si peak corresponding to the presence of the NCs is evident. Other elemental peaks assigned to the presence Cl and Ca are probably due to solvent artifacts, while C and Cu peaks are due to the carbon-coated copper grid. No peaks for Br or Pt were observed, indicating that the surfactant and catalyst were removed during purification.

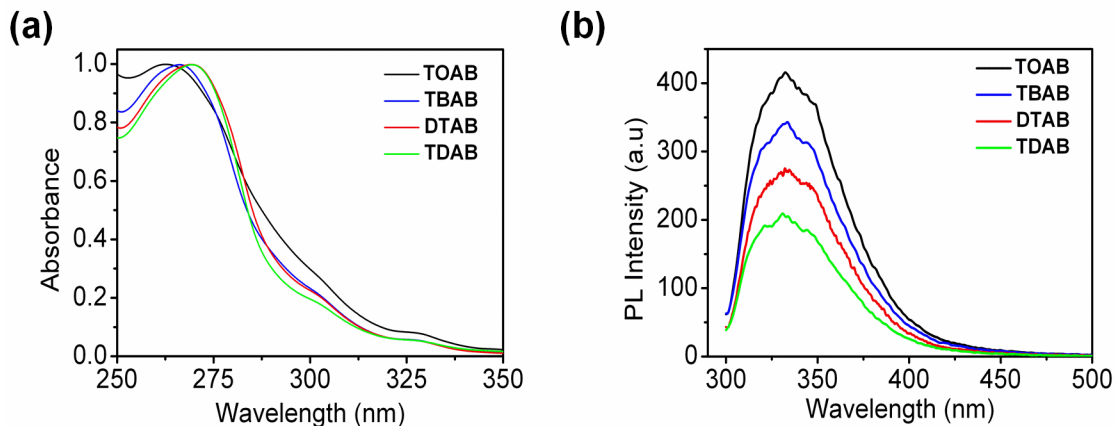
The surface chemistry of the Si NCs was characterized by FTIR spectroscopy; see Figure 3 for typical spectra recorded 1 week (blue line) and 26 weeks (red line) after storage under ambient atmospheric and lighting conditions. Both spectra show C-H stretching signals due to the presence of the alkyl ligands at the nanocrystal surface, with symmetric CH<sub>2</sub>, asymmetric CH<sub>2</sub>, and the asymmetric C-CH<sub>3</sub> stretching vibrations at 2851, 2922, and 2959 cm<sup>-1</sup>, respectively. The peak at 1378 cm<sup>-1</sup> is assigned to the C-CH<sub>3</sub> symmetrical bending mode, while the peaks at 1261 and 1462 cm<sup>-1</sup> are attributed to the symmetric bending and scissoring vibration of the Si-C bond, respectively. The absence of the CH=CH<sub>2</sub> peaks at 3080 and 1640 cm<sup>-1</sup>, combined with the formation of the Si-C bond at 1460 cm<sup>-1</sup>, confirms covalent attachment of the alkyl groups to the NC surface.[3,10,16] Two additional peaks at 1099 and 1018 cm<sup>-1</sup>, attributed Si-OR stretching vibrations, are clearly seen in the spectrum recorded after 26 weeks, indicating oxidation of the nanocrystal surface.[10,16] The low intensity of these peaks recorded after 1 week indicates that only minimal oxidation of the silicon core has taken place, indicating that the surface of as-synthesized Si NCs have well passivated.

Figure 4(a) shows the UV-Vis absorption spectra of dilute dispersions of Si NCs in hexane. The spectrum of the smallest nanocrystals (1.9 nm), showed a broad absorption band



**Figure 3.** FT-IR spectra of alkyl-terminated Si NCs recorded 1 week (blue line) and 26 weeks (red line) after storage under ambient conditions.

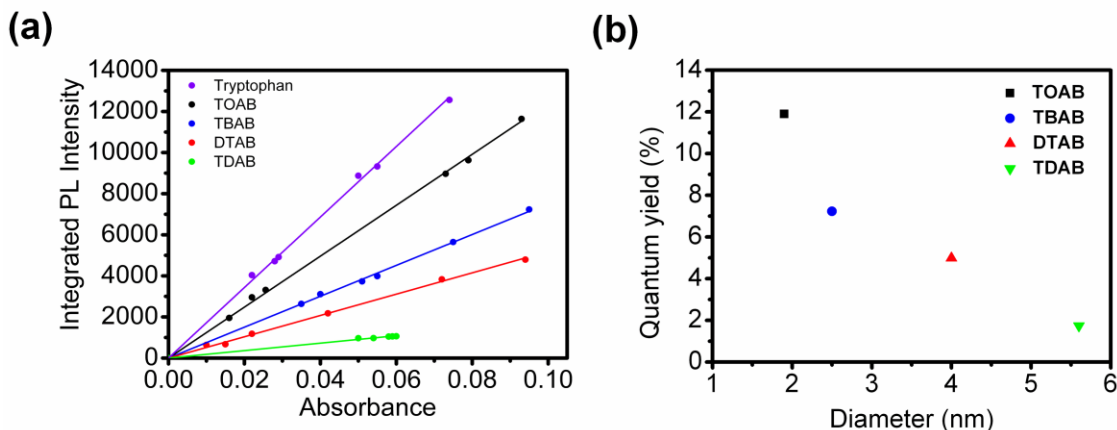
centered at *ca.* 260 nm with an onset of absorbance located at 350 nm, considerably blue shifted from that of bulk silicon. Previous reports for similarly sized alkyl-terminated Si NCs, which have assigned this feature to the direct  $\Gamma$ - $\Gamma$  band gap transition.[9,17] Increasing the mean NC diameter to *ca.* 2.6 nm resulted in a distinct red-shift in the wavelength position of the absorption band to 267 nm. Further red shifts in the absorption spectrum were observed for increasing nanocrystal sizes, with the largest size nanocrystals (5.8 nm) showing a strong peak centered at 272 nm, corresponding to a 12 nm shift compared to the smallest (1.9 nm) nanocrystals.



**Figure 4.** (a) Normalized UV-Vis absorption spectra of dilute dispersions of the Si NCs in hexane. (b) PL spectra of the Si NCs recorded on samples with the same optical densities.

Figure 4(a) shows the PL spectra (280 nm excitation) of Si NC dispersions prepared with the same optical densities for comparison. Luminescence from the Si NC dispersions is observed over a narrow spectral range between 300 – 420 nm, with a wavelength maximum at *ca.* 330 nm, similar to other reports.[10,18] The full width at half maximum (FWHM) was found to be *ca.* 60 nm, emphasizing the monodispersity of the nanocrystals.[10] While the luminescence intensity decreases monotonically with increasing nanocrystal diameter, there is no change in the PL spectra of the Si NCs over the size range reported here. The origin of PL from nanocrystalline silicon remains controversial, complicated by presence of both direct and indirect band gap transitions.[12,19] The underlying mechanism is usually described in terms of quantum

confinement within the nanocrystal core, or surface phenomena at the interface between the crystalline core and the host matrix. While size dependency observed in the UV-Vis spectra (Figure 4(a)) agrees with the quantum confinement model, the PL spectra shown in Figure 4(a) exhibit a blue emission that is independent of nanocrystal size, implying that the nanocrystal surface must be involved in the emission process. This interpretation is in agreement with recent reports by Yang et al., who concluded that excitons are first formed within Si NCs by direct transitions at  $\Gamma$  or X point, which transfer to and recombine at states close to the surface.[20]



**Figure 5.** (a) Integrated PL intensity versus absorbance for various dilute dispersions of Si NCs in hexane and aqueous solutions of tryptophan (pH 7.0) recorded under identical excitation conditions. (b) Quantum yields of the Si NCs versus average core diameter.

Figure 5(a) shows the integrated PL intensity (280 nm excitation) of dilute dispersions of Si NCs in hexane compared with an aqueous solution (pH 7.0) of the reference emitter tryptophan recorded under identical excitation conditions. Linear regression analysis was employed to determine the relative PL intensities of the sample and reference solutions over the range shown. Figure 5(b) shows the calculated quantum yields of the Si NCs plotted against average core diameter. The quantum yield of the 1.9 nm Si NCs was found to be 12 % at the optimal excitation wavelength of 280 nm, comparable with values reported for Si NCs of similar sizes reported in the literature.[16,21-22] The quantum yields of the Si NCs exhibit an inverse relationship with the mean NC diameter, decreasing to *ca.* 7% for 2.5 nm nanocrystals, with a minimum of less than 2% recorded for 5.8 nm NCs. The observed trend in the quantum yields of the Si NCs may be accounted for by a combination of less efficient generation of excitons and the presence of greater number of non-radiative traps and recombination pathways with increasing size.

## CONCLUSIONS

Alkyl-terminated Si NCs have been synthesized using a room temperature microemulsion synthesis method, with core diameters controlled between 2 to 6 nm. TEM imaging confirmed that the NCs are highly crystalline and size monodisperse, while FTIR confirmed that Si NCs were chemically passivated, with little surface oxidation. UV-Vis and PL spectroscopy showed significant quantum confinement effects, with moderate absorption in the UV spectral range, and a strong blue emission. The Si NC QY showed an inverse relationship with the NC core diameter, with a maximum of 12 % measured for 2 nm NCs.

## ACKNOWLEDGMENTS

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