

Micro-emulsion synthesis of monodisperse surface stabilized silicon nanocrystals

Richard D. Tilley,^{*a} Jamie H. Warner,^a Kazushige Yamamoto,^b Isao Matsui^b and Hiroyuki Fujimori^c

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Silicon nanocrystals with a uniform size distribution were synthesized in inverse micelles using powerful hydride reducing agents. The silicon nanocrystals surfaces were then stabilized with 1-heptene to produce particles with strong blue photoluminescence.

Nanoscale materials have been shown to behave quite differently from their bulk counterparts due to the effect of quantum confinement imposed upon the charge carriers.¹ Bulk silicon has an indirect band gap, resulting in a low photoluminescence yield in the near IR.² The bulk excitonic radius for silicon is ~ 4 nm, thus the effects of quantum confinement should be observed for nanocrystals with radii smaller than 4 nm.³ An increase in the photoluminescence yield along with a shift towards the visible spectrum has been observed in nanocrystalline clusters of silicon.¹⁻⁵ These small nanocrystals have considerable potential for many optoelectronic applications and also in biological imaging.⁶⁻⁷

Recently silicon nanocrystals have been synthesized using a variety of techniques such as laser pyrolysis,⁸ aerosols,⁹ plasma deposition,¹⁰ electrochemical etching of silicon wafers¹¹ and colloids.²⁻⁴ Colloidal techniques for growing silicon nanocrystals hold the most promise as they allow with relative ease the manipulation of the surface chemistry.^{4,12} Modifying the surface chemistry through the attachment of molecular ligands to the surface of the silicon nanocrystals acts to stabilize, protect and determine their functionality and solubility.⁴

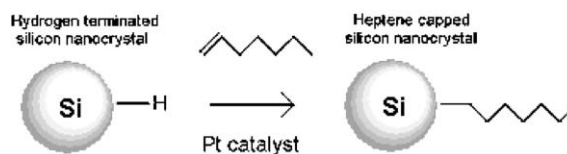
Currently, the most successful colloidal techniques for growing silicon nanocrystals depend on the solution reduction of silicon halides.^{3,12} For example, Kauzlarich and co-workers recently reported the room temperature solution synthesis of relatively monodisperse silicon nanocrystals (4.5 ± 1.1 nm) by reduction of silicon tetrachloride with sodium(naphthalide).⁴ The major drawback of colloidal techniques to synthesize silicon nanocrystals thus far has been the relatively large size distributions produced (~ 20 – 40%). The large range of size prevents a simple interpretation of the optical spectra and is undesirable for device applications.³

Here we report a method using powerful hydride reducing agents for the production of silicon nanocrystals in the strong confinement regime. The silicon nanocrystals formed have a far smaller mean size and at least a two-fold decrease in the size distribution and the FWHM of the photoluminescence as compared to previous studies.⁴ The narrow size distribution eliminates the need for any post synthesis treatment, such as

HPLC, that has been used previously to obtain narrow size distributions but at dramatically reduced silicon nanocrystal yields.³

Silicon nanocrystals are formed in inverse micelles by the solution reduction of silicon tetrachloride with strong hydride reducing agents at room temperature and pressure. The silicon nanocrystals are then capped with 1-heptene, purified and redispersed into hexane, according to Scheme 1.[†]

Fig. 1 shows the HRTEM image of a number of 1-heptene capped silicon nanocrystals on a holey carbon grid. The inset shows an enlarged image of a single silicon nanoparticle with clearly visible (0.22 nm) lattice fringes consistent with the (211) plane in diamond crystalline silicon. The grid was prepared by placing a single drop of the 1-heptene capped silicon nanocrystals suspended in hexane onto a grid and leaving to dry. The mean size and size distribution was determined by measuring 802 nanoparticles from different regions of the grid. The silicon nanocrystal mean size is 1.8 ± 0.2 nm (0.2 nm being the standard deviation), which is significantly better than previous reports.^{3,12} The standard deviation of nanoparticle sizes of 0.2 nm is equivalent to a single atomic spacing in silicon and highlights the highly monodisperse size distribution synthesized.



Scheme 1 Capping of silicon nanocrystals with 1-heptene.

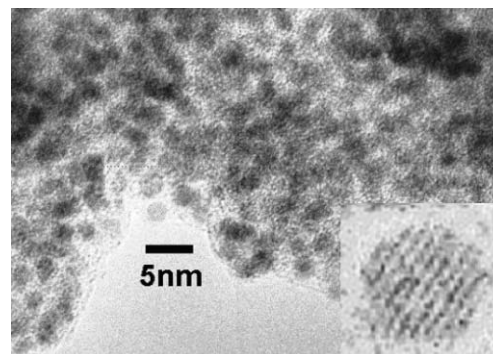


Fig. 1 HRTEM of 1-heptene capped silicon nanocrystals on a holey carbon grid. Bottom right inset shows lattice fringes in a single 1.8 nm silicon nanocrystal.

*Richard.tilley@vuw.ac.nz

A selected area electron diffraction pattern was obtained and was consistent with diamond cubic crystalline silicon. Energy dispersive X-ray spectroscopy also confirmed the presence of silicon.

The bonding of 1-heptene onto the surface of the silicon nanocrystals was confirmed by FTIR spectroscopy shown in Fig. 2. We observed peaks at 1463 cm^{-1} and 1288 cm^{-1} attributed to vibrational scissoring and symmetric bending of Si-CH₂. The peak at 1463 cm^{-1} is broadened by the inclusion of the C-CH₂ and C-CH₃ vibrational modes at 1455 cm^{-1} and 1488 cm^{-1} . Peaks at 2852 cm^{-1} , 2920 cm^{-1} and 2965 cm^{-1} are attributed to C-CH₃ symmetric, C-CH₂ asymmetric and C-CH₃ asymmetric vibrations, respectively, of the 1-heptene.¹³ The peaks between $1000\text{--}1100\text{ cm}^{-1}$ correspond to Si-OR stretching vibrations and the relatively low magnitude of these peaks indicate minimal oxidation of the silicon nanocrystals has occurred.

Fig. 3 presents the photoluminescence spectrum from the monodisperse colloidal suspension of silicon nanocrystals capped with 1-heptene, shown in Fig. 1.

The photoluminescence spectrum was obtained using an excitation at 290 nm. The emission has a peak at 335 nm (3.7 eV) and a FWHM of 47 nm (0.5 eV). The narrow FWHM of the photoluminescence confirms the monodisperse nature of the silicon nanocrystals. The photoluminescence is attributed to be direct e-h recombination in the silicon nanocrystals across the $\Gamma\text{--}\Gamma$ direct gap, similar to the observations of Wilcoxon *et al.*³ The position of the photoluminescence peak at 335 nm is in

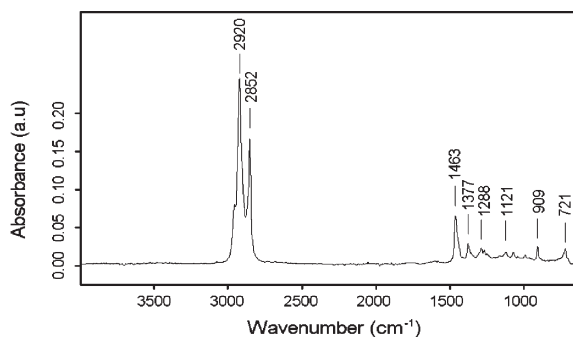


Fig. 2 FTIR spectrum of 1-heptene capped silicon nanocrystals.

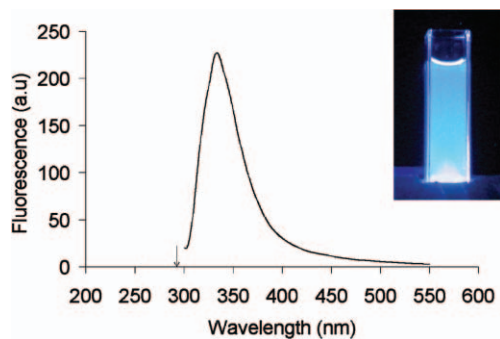


Fig. 3 290 nm photoluminescence spectrum of 1-heptene capped silicon nanocrystals. Arrow indicates the wavelength of excitation used for the photoluminescence spectrum. Top right inset shows a fluorescence image of a cuvette of silicon nanocrystals when excited with a UV lamp.

good agreement with previous reports of silicon nanocrystals of similar size. The shift in the photoluminescence from 1.1 eV in bulk silicon to 3.7 eV in these small silicon nanocrystals is direct evidence of the presence of quantum confinement in these structures.³

The absence of photoluminescence from defect or trap state recombination, which typically occurs near 600 nm, supports the notion that the observed photoluminescence presented in Fig. 3 is due to direct e-h recombination in the silicon nanocrystals.³ Colloidal suspensions of the 1-heptene silicon nanocrystals were stable and photoluminescent for at least 6 months in air, showing their resistance to photo-oxidization.

In conclusion, we have successfully synthesised monodisperse 1.8 nm colloidal silicon nanocrystals capped with 1-heptene with strong photoluminescence in the visible regime. The ability to synthesise photoluminescent monodisperse silicon nanocrystals in the strong confinement regime should enrich the applicability of these nanocrystals in future opto-electronic devices.

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Richard D. Tilley,^{*a} Jamie H. Warner,^a Kazushige Yamamoto,^b Isao Matsui^b and Hiroyuki Fujimori^c

^aSchool of Chemical and Physical Sciences, MacDiarmid Institute of Advanced Materials and Nanotechnology, Victoria University of Wellington, P.O. Box 600, Wellington, New Zealand.

E-mail: Richard.tilley@vuw.ac.nz; Fax: + 64 4 463 5237; Tel: + 64 4 463 5016

^bToshiba Corporate Research and Development Center, 1, Komukai Toshiba-Cho, Saiwai Ku, Kawasaki, Japan

^cResearch & Development Center, Toshiba Ceramics Co. Ltd., 30, Soya, Hadano, Kanagawa prefecture 257-8566, Japan

Notes and references

† Experimental: In a nitrogen filled dry-box, 92 μL of SiCl_4 was added to 1.5 g of tetraoctylammonium bromide (TOAB) in 100 mL of anhydrous toluene and stirred for 1 h. 2 ml of 1 M lithium aluminium hydride in THF was added dropwise over a period of 2 min. The solution was then left to react for 3 h. The excess reducing agent was then quenched with 20 mL of methanol, upon which the solution became transparent. At this stage of the reaction the silicon nanocrystals are terminated by hydrogen and encapsulated in a TOAB micelle. 100 μL of a 0.1 M platinum catalyst (chloroplatinic acid hexahydrate) was then added dropwise to the solution followed by 2 mL of 1-heptene. The solution was then left to stir for 3 h. All solvents were then removed from the solution by rotary evaporation. The resulting dry powder was then redispersed in 20 mL of hexane and sonicated for 20 min. The hexane solution was subsequently purified by first filtering and then washing with 100 mL of *n*-methyl formamide and finally with distilled water.¹⁴ Pure silicon nanocrystals capped with 1-heptene remain in the hexane phase. The final product typically yielded 20 mL of 1 μM solution of 1-heptene capped silicon nanocrystals.

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