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Solution reduction synthesis of surface stabilized silicon nanoparticles

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This paper describes the preparation of air and moisture stable octanol derivatized crystalline silicon nanoparticles by room temperature sodium naphthalenide reduction of silicon halides.

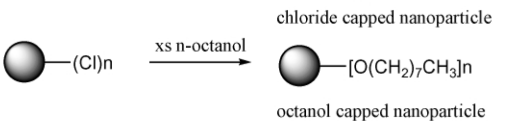
Nanoscale materials have recently received a great deal of attention, due in part to the fundamental differences in properties between nanoscale and bulk material. Elemental silicon, being the cornerstone of the computer revolution, is of enormous technological importance. Nanoparticles of silicon have displayed particle size dependent optical and electronic properties[1,2] as well as a lowering of melting temperature with decrease in size.[3] Such properties are thought to have important applications in the development of optoelectronic devices and as solubilized crystalline silicon.

Silicon nanoparticles can be made by a range of different methods including the gas and solution phase decomposition of silanes,[4–7] the electrochemical etching of silicon wafers,[8] the reaction of Zintl salts with silicon halides,[9–13] as well as the solution reduction of silicon halides by sodium,[14] lithium naphthalenide,[15] hydride reagents[16,17] or the reduction of $Si(OEt)_4$ with sodium.[18] While solution reductions have given rise to crystalline nanoparticles[16,17,19] it has been suggested that both the high temperatures and pressures of bomb reactions[7,14] or ultrasonication[18] are required to obtain crystalline silicon. Recently we reported the room temperature and pressure solution reduction synthesis of crystalline silicon tetrahedra in the 40–80 nm size range.[19] While these particles are too large to exhibit the desired size dependent properties, the fact that these particles were crystalline piqued our interest in solution reduction as a means of generating crystalline silicon nanoparticles.

Previous routes to silicon nanoparticles in this group have relied on the metathesis reaction of $SiCl_4$ with metal silicides. The yields were generally low, the reaction is difficult to scale up and the heterogeneous nature of the reaction mixture leads to little potential for control over the size, as the initiation of the reaction and thus nucleation occurs over an extended time. We report here a reaction of the inexpensive and readily available silicon tetrachloride with sodium naphthalide in 1,2-dimethoxyethane to give a halide capped silicon nanoparticle that can then be terminated with n-octanol, according to Scheme 1.†

The nanoparticles are obtained as a waxy orange hexane soluble solid. Solution ^1H NMR is consistent with the presence of octanoxide groups on the surface of the nanoparticles. This is supported by the IR spectrum, in which bands corresponding to alkyl C–H stretching at ~3000 cm^{-1} and Si–OR stretching at ~1080 cm^{-1} can be observed.

Fig. 1 shows the HRTEM image of a number of the octanoxide capped silicon nanoparticles on a holey carbon grid. The grid was prepared by suspending the nanoparticles in hexane, sonicating and then dipping the grid into the solution. The nanoparticles show some faceting. The size distribution was determined by measuring 718 nanoparticles from different regions of the grid. A histogram of the particle sizes is given in Fig. 2. The mean diameter is 5.2 ± 1.9 nm (1.9 nm being one standard deviation). Such a distribution compares favourably with those obtained through the use of inverse micelles.[16,17] The sample exhibits photoluminescence in the 410–430 nm range with an excitation at 320 nm. The range of sizes present and the non-linear size dependence of the phonon interaction required for silicon photoluminescence prevents a simple interpretation



Scheme 1 Reduction with sodium naphthalide followed by termination.

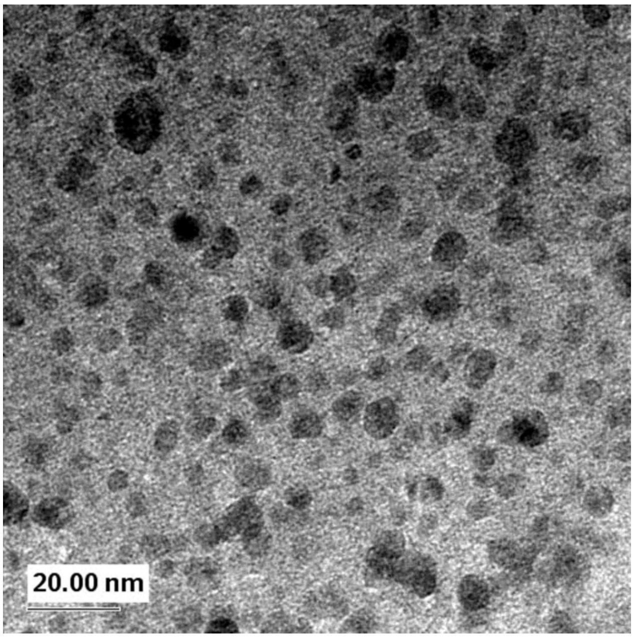


Fig. 1 HRTEM of n-octanol capped silicon nanoparticles on a holey carbon grid (Phillips CM200 operating at 200 keV). Darker circular regions are silicon nanoparticles.

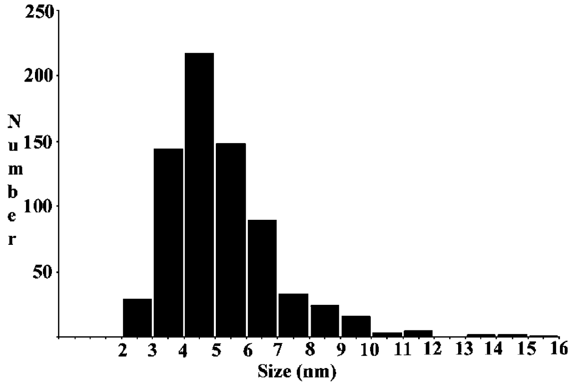


Fig. 2 Histogram of particle sizes from a survey of 718 particles from different regions of the grid.

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of the data.[2] Further size control is necessary to probe the optical properties and relate band edge to photoluminescence.

Fig. 3 gives a HRTEM image of a single large nanoparticle (~10 nm). The diagonal striations on the particle are lattice fringes. The lattice fringe spacing (0.314 nm) is consistent with the <111> plane of diamond crystalline silicon. Several smaller nanoparticles, more consistent with the overall size distribution (~3.5 nm) can also be seen in the image.

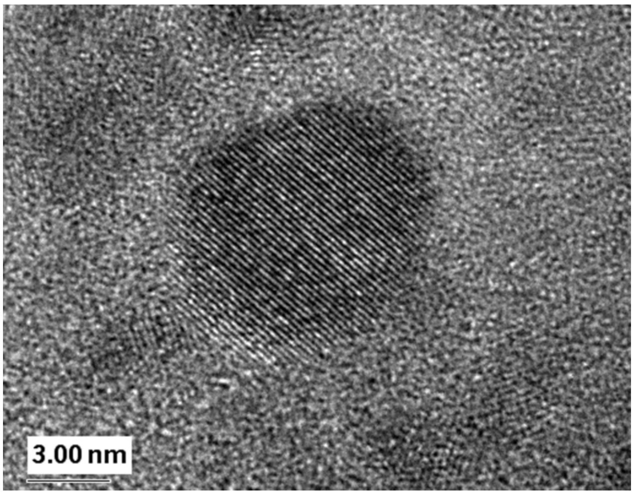

Fig. 3 HRTEM image of a n-octanol capped silicon nanoparticles on a holey carbon grid (Phillips CM200 operating at 200 keV). Dark striated region is a 10 nm silicon nanoparticle with lattice fringes clearly visible.

The selected area electron diffraction pattern is consistent with diamond cubic crystalline silicon. This is further confirmed by energy dispersive spectroscopy (EDS), in which silicon was seen to be present, as well as some residual chlorine. EDS did not show the presence of sodium. It is possible that some chlorine is bonded to the silicon surface and the termination is incomplete. More aggressive reaction conditions for the termination, or the use of an alkali metal alkoxide may achieve more complete termination.

The solid state ^{29}Si{^{1}H} CP MAS NMR of the octanoxide terminated Si nanoparticles displays three broad peaks, centered at δ values of −7, −60 and −90 ppm with respect to TMS (Fig. 4). The two narrow resonances at δ values of −95 and −102 ppm are consistent with Si–O bonding on the surface of the nanoparticles. Due to the very long longitudinal relaxation times of the ^{29}Si nucleus (bulk crystalline silicon exhibits a T_1 relaxation time of 1000 s) and the enhancment of proton coupled surface Si with a CP pulse sequence, the core atoms in the nanoparticles are presumably not contributing to the NMR spectrum. The ^{29}Si MAS spectrum shows three broad peaks similar to those observed in the ^{29}Si{^{1}H} CP MAS NMR spectrum. Previous ^{29}Si NMR studies on oxidized silicon nanoparticles have shown peaks at around 100 ppm for oxide associated surface silicons.[10]

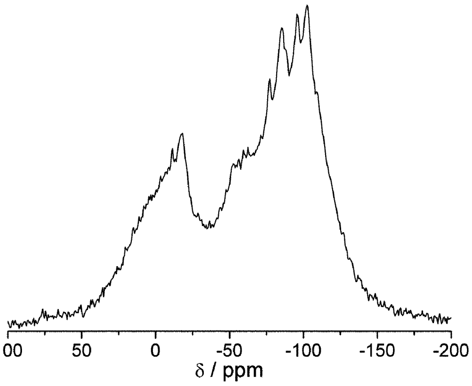

Fig. 4 ^{29}Si CP MAS NMR of octanol capped nanoparticles. (The ^{29}Si CP MAS NMR was recorded with a Chemagnetics CMX-400 spectrometer using a standard Chemagnetics cross polarization MAS probe assembly configured for rotors having an outer diameter of 7.5 mm. The spectra were measured at a Larmor frequency of 79.49 MHz and spinning speeds of 5 kHz. Spectrum pulse lengths of 8 μs were used at a 31 kHz B_1 field for both ^{29}Si and ^{1}H, the recycle delay was 5 s. The chemical shift was externally referenced to tetramethylsilane.)

The intermediate halide capped silicon nanoparticle will allow for a large range of surface functionality, a distinct advantage over other methodologies. It may also be possible to obtain further control over the size of the nanoparticles through the use of micelle techniques.

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Notes and references

† Experimental: sodium naphthalide in 1,2-dimethoxyethane (prepared from 0.69 g of sodium and 2.93 g of naphthalene stirred in 70 cm^3 of 1,2-dimethoxyethane overnight) was added rapidly *via* cannula to a stirred solution of 1.04 g of $SiCl_4$ in 250 cm^3 of 1,2-dimethoxyethane. The dark brown suspension obtained was stirred for 30 minutes then 5 cm^3 of 1-octanol was added. A yellow solution with a white precipitate was obtained immediately. The solvent and naphthalene were removed under reduced pressure with heating in a water bath, the naphthalene being collected on a liquid nitrogen cooled probe. The resulting orange solid was extracted with hexane and washed three times with slightly acidic distilled water. The hexane layer was collected and pumped down to give a waxy orange hexane soluble solid.

1 L. Tsybeskov, *MRS Bull.*, 1998, **23**, 33.
2 H. W. H. Lee, P. A. Thielen, G. R. Delgado, S. M. Kauzlarich, C. S. Yang and B. R. Taylor, *Crit. Rev. Opt. Sci. Technol.*, 2000, CR77 (Novel Materials and Crystal Growth Techniques for Nonlinear Optical Devices) 147.
3 A. N. Goldstein, *Appl. Phys. A*, 1996, **62**, 33–37.
4 D. Zhang, R. M. Kolbas, P. Mehta, A. K. Singh, D. J. Lichtenwalner, K. Y. Hsieh and A. I. Kingon, *Mater. Res. Soc. Symp. Proc.*, 1992, 35–40.
5 K. A. Littau, P. J. Szajowski, A. J. Muller, A. R. Kortan and L. E. Brus, *J. Phys. Chem.*, 1993, **97**, 1224.
6 A. Fojtik and A. Henglein, *Chem. Phys. Lett.*, 1994, **221**, 363–7.
7 J. D. Holmes, K. J. Ziegler, R. C. Doty, L. E. Pell, K. P. Johnston and B. A. Korgel, *J. Am. Chem. Soc.*, 2001, **123**, 3742–3748.
8 For example G. Belomoin, J. Therrien, A. Smith, S. Rao, R. Twesten, S. Chaieb, M. H. Nayfeh, L. Wagner and L. Mitas, *Appl. Phys. Lett.*, 2002, **80**, 841–843 and references contained therein.
9 R. A. Bley and S. M. Kauzlarich, *J. Am. Chem. Soc.*, 1996, **118**, 12461–12462.
10 D. Mayeri, B. L. Phillips, M. P. Augustine and S. M. Kauzlarich, *Chem. Mater.*, 2001, **13**, 765.
11 C.-S. Yang, R. A. Bley, S. M. Kauzlarich, H. W. H. Lee and G. R. Delgado, *J. Am. Chem. Soc.*, 1999, **121**, 5191.
12 C.-S. Yang, Q. Liu, S. M. Kauzlarich and B. Phillips, *Chem. Mater.*, 2000, **12**, 983.
13 R. A. Bley and S. M. Kauzlarich, *Nanopart. Nanostruct. Film*, ed. J. H. FendlerWiley-VCH, Weinheim, Germany, 1998, pp. 101–118.
14 J. R. Heath, *Science*, 1992, **258**, 1131–1133.
15 A. Kornowski, M. Giersig, R. Vogel, A. Chemseddine and H. Weller, *Adv. Mater.*, 1993, **5**, 634.
16 J. P. Wilcoxon and G. A. Samara, *Appl. Phys. Lett.*, 1999, **74**, 3164.
17 J. P. Wilcoxon, G. A. Samara and P. N. Provencio, *Phys. Rev. B*, 1999, **60**, 2074.
18 N. A. Dhas, C. P. Raj and A. Gedanken, *Chem. Mater.*, 1988, **10**, 3278.
19 R. K. Baldwin, K. A. Pettigrew, J. C. Garno, P. P. Power, G.-Y. Liu and S. M. Kauzlarich, *J. Am. Chem. Soc.*, 2002, **124**, 1150–1151.