

Low-Temperature Solution Route to Macroscopic Amounts of Hydrogen Terminated Silicon Nanoparticles

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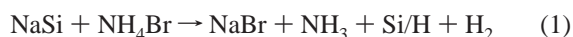
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The production of hydrogen terminated silicon (Si) nanoparticles is currently an area of intense research. The primary methods of producing large amounts of hydrogen terminated Si is either from the mechanical fracturing of porous Si¹ or the gas-phase decomposition of silane or organosilane gas.^{2–4} In both cases, further etching is necessary using nitric and hydrofluoric acid to produce a stable, well-passivated hydrogen surface.⁵ Once the surface is hydrogen passivated, further functionalization via hydrosilation is possible.⁵ This chemistry has been well-developed in the case of porous Si and opens the door for biological and technological applications, such as for quantum dot probes, optical and electronic applications, hydrogen storage, and solar energy.

Reports of ambient solution reduction have invigorated research to improve colloidal synthesis of Si nanoparticles.^{6–9} These reported syntheses provide new solution routes to free-standing Si nanoparticles that can be further functionalized. In addition, further doping and shape control of Si has been documented.^{9,10} However, the yields of nanoparticles from these methods are still very low, and physical methods, such as mechanical fracturing of porous Si and gas-phase decomposition of silanes, still provide significantly larger amounts of nanoparticles for further applications. A simple chemical synthesis of hydrogen-capped Si nanoparticles would provide a major advance in the application of functionalized silicon nanoparticles.

Metal silicides have been useful starting materials for the production of silicon nanoparticles. Si nanoparticles have been prepared by a metathesis route in solution using SiCl₄,^{11,12} by oxidation in solution using bromine,¹³ and by sonication.¹⁴ Metal silicides can produce amorphous Si with embedded nanocrystallites of Si by the solid-state reaction of metal silicides with metal and ammonium halides.¹⁵ However, size and shape control, along with further functionalization, is not possible via a solid-state reaction. Herein, we report a new solution route to the production of macroscopic amounts of either amorphous or crystalline hydrogen terminated silicon nanoparticles. This method provides a simple route that can be further optimized to control size and possibly shape and allows for additional surface functionalization with organic moieties.

All manipulations for the synthesis of Si nanoparticles were performed in a N₂-filled glovebox or Ar inert atmosphere Schlenk line. The silicon nanoparticles were prepared by a solution reaction using sodium silicide (0.5 g) and ammonium bromide (0.55 g) in dimethoxyethane (DME, 80 °C) and dioctyl ether (DOE, 260 °C) using standard Schlenk techniques. Sodium silicide was prepared by direct reaction of stoichiometric amounts of the elements in sealed niobium tubes, sealed under vacuum in fused silica tubes, at 650 °C for 3 days.¹⁶ The chemical reaction is provided in (1), where Si/H is used to indicate hydrogen terminated silicon nanoparticles.



There are two possible driving forces for this reaction to occur at

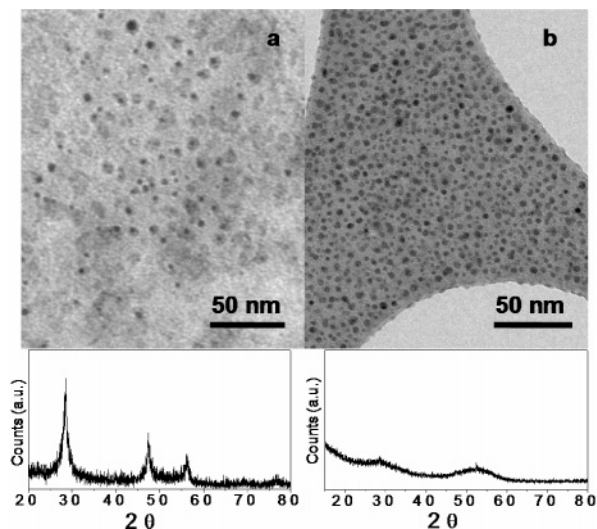


Figure 1. TEM and X-ray powder patterns for the powders obtained from the reactions in (a) DME and (b) DOE. The powder diffraction of (a) can be fully indexed as diamond-structured silicon.

temperatures less than 300 °C: the production of sodium bromide as a reaction byproduct and the generation of ammonia and hydrogen gases. The solvent provides a medium that allows for better mixing of the reagents and prevents the particles from agglomerating. In addition, the solvent allows for continuous access to the surface of NaSi, thus facilitating the reaction. In both of the investigated solvents, for a 1:1 molar ratio, the reaction product is a mixture of Si nanoparticles with Na₈Si₄₆ clathrate phase.¹⁵ The final product consists of a dry black hydrophobic powder (0.2 g) and a yellow solution (DME) or a brown-orange solution (DOE). The solutions can be dried into powders (0.016 g) and dispersed in chloroform for further characterization.

The X-ray powder patterns along with the TEM images for the solid product obtained from DME and DOE are presented in Figure 1. The TEM images show well-dispersed nanoparticles. The size distribution for the nanoparticles obtained in DME is 4.91 ± 1.23 nm and for the DOE is 3.85 ± 1.03 nm (based on 1000 nanoparticles). The TEM images for the solution products in DME and DOE are similar to those presented for the solids. Energy-dispersive X-ray (EDX) spectroscopy of the samples shows that they contain silicon, and there is no evidence for bromine or sodium. The X-ray powder diffraction pattern for the powder obtained from DME clearly shows peaks consistent with diamond structure, crystalline silicon. The crystallite size based on the diffraction line width is 8 nm. Similar X-ray powder patterns of less than 10 nm particles have been obtained by laser-induced heating of silanes, followed by HF etching.⁴ Calculated scattering with particle size suggests that the diffraction pattern changes to that of diamond structure Si at about 1.7 nm diameter and that once diameters of 6

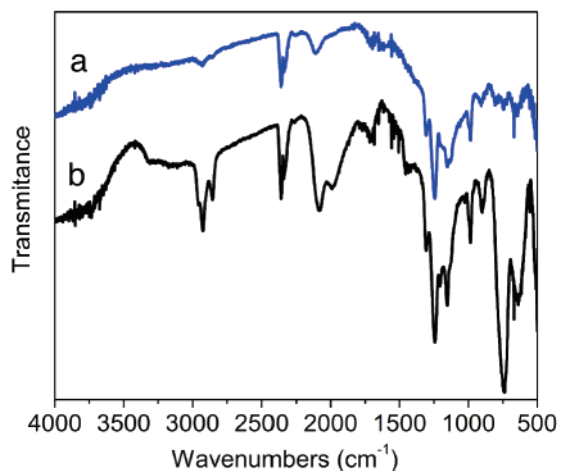


Figure 2. FTIR spectra for Si nanoparticles obtained from (a) DME and (b) DOE, after washing with acidified water.

nm are reached, there is very little change in form factors or line width.¹⁷ Further experimental results are necessary to test this prediction. The X-ray powder diffraction for the product obtained from DOE shows two broad diffraction peaks. These peaks, at about 28° and 49° 2θ , are consistent with what has been observed for amorphous Si.¹⁵ However, recent structure calculations suggest that small nanoparticles (1.0 nm diameter) may also provide a similar diffraction pattern.¹⁷ Because the majority of this sample contains particles that are approximately 4 nm in diameter or larger, the diffraction pattern is best interpreted as due to amorphous Si.

The FTIR data obtained after washing the solid products with acidified water (2% HF in Nanopure deoxygenated water and rinsed with hexane) for the solids prepared in DME and DOE is presented in Figure 2. A broad signal for the Si–H₃ stretches is in the range 2000–2150 cm^{-1} . These signals can be attributed to monohydride, dihydride, or polyhydride species present on the surface of the silicon nanocrystals.¹⁸ Also, the SiH₂ bending mode is present at 900 cm^{-1} . Alkyl C–H stretching modes (aliphatic $\nu(\text{C–H})$ stretching modes at 2800–2900 cm^{-1} , deformation modes at 1300–1400 cm^{-1} , and C–C stretching modes for alkyl chains at 1500–1600 cm^{-1} are also observed due to the solvent. Presumably solvent is adsorbed to the surface of the nanoparticle. The asymmetric stretching modes, Si–O–Si and Si–O–C, are also evident in the 1050–1250 cm^{-1} region.¹⁹ It is likely that the observed stretching modes correspond to silicon–solvent bonds. A comparison of IR spectra before washing with acidified water shows that the Si–H stretches are present before the wash.

The black powder does not have detectable photoluminescence (by eye), but it can be etched in a similar manner as reported by

Swihart⁵ to give rise to luminescence. The yellow and yellow/orange solution can be dried into a powder and redissolved in chloroform. The yellow solution shows a photoluminescence emission maximum at about 420 nm.

In summary, we have developed a simple solution route to hydrogen terminated silicon nanoparticles. Macroscopic amounts of powder can be obtained of either crystalline or amorphous nanoparticles, depending upon solvent and reaction conditions. The hydrogen termination of these nanoparticles provides an ideal surface for further functionalization and application of silicon nanoparticles.

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Supporting Information Available: TEM images, size distributions, EDX spectra, and FTIR data before and after wash of the nanoparticles. Photoluminescence spectra (excitation and emission). This material is available free of charge via the Internet at <http://pubs.acs.org>.

References

- (1) Smith, A.; Yamani, Z. H.; Roberts, N.; Turner, J.; Habbal, S. R.; Granick, S.; Nayfeh, M. H. *Phys. Rev. B: Condens. Matter* **2005**, *72*, 205307/1–205307/5.
- (2) Fojtik, A.; Giersig, M.; Henglein, A. *Ber. Bunsen Ges.* **1993**, *97*, 1493–1496.
- (3) Botti, S.; Celeste, A.; Coppola, R. *Appl. Organomet. Chem.* **1998**, *12*, 361–365.
- (4) Li, X.; He, Y.; Talukdar, S. S.; Swihart, M. T. *Langmuir* **2003**, *19*, 8490–8496.
- (5) Hua, F.; Swihart, M. T.; Ruckenstein, E. *Langmuir* **2005**, *21*, 6054–6062.
- (6) Warner, J. H.; Hoshino, A.; Yamamoto, K.; Tilley, R. D. *Angew. Chem., Int. Ed.* **2005**, *44*, 4550–4554.
- (7) Wilcoxon, J. P.; Samara, G. A.; Provencio, P. N. *Phys. Rev. B: Condens. Matter* **1999**, *60*, 2704–2714.
- (8) Zou, J.; Baldwin, R. K.; Pettigrew, K. A.; Kauzlarich, S. M. *Nano Lett.* **2004**, *4*, 1181–1186.
- (9) Baldwin, R. K.; Zou, J.; Pettigrew, K. A.; Yeagle, G. J.; Britt, R. D.; Kauzlarich, S. M. *Chem. Commun.* **2006**, 658–660.
- (10) Baldwin, R. K.; Pettigrew, K. A.; Garno, J. C.; Power, P. P.; Liu, G.-y.; Kauzlarich, S. M. *J. Am. Chem. Soc.* **2002**, *124*, 1150–1151.
- (11) Bley, R. A.; Kauzlarich, S. M. *J. Am. Chem. Soc.* **1996**, *118*, 12461–12462.
- (12) Yang, C.-S.; Bley, R. A.; Kauzlarich, S. M.; Lee, H. W. H.; Delgado, G. R. *J. Am. Chem. Soc.* **1999**, *121*, 5191–5195.
- (13) Pettigrew, K. A.; Liu, Q.; Power, P. P.; Kauzlarich, S. M. *Chem. Mater.* **2003**, *15*, 4005–4011.
- (14) Lee, S.; Cho, W. J.; Kim, Y. D.; Kim, E. K.; Park, J. G. *Jpn. J. Appl. Phys.* **2005**, *44*, 5843–5846.
- (15) McMillan, P. F.; Gryko, J.; Bull, C.; Arledge, R.; Kenyon, A. J.; Cressey, B. A. *J. Solid State Chem.* **2005**, *178*, 937–949.
- (16) NaSi can also be purchased from Signa Chemistry, LLC, New York, (212) 933–4101, <http://www.signachem.com>.
- (17) Belomoin, G.; Alsalhi, M.; Al Aql, A.; Nayfeh, M. H. *J. Appl. Phys.* **2004**, *95*, 5019–5022.
- (18) Cardona, M. *Phys. Status Solidi B* **1983**, *118*, 463–481.
- (19) Song, J. H.; Sailor, M. J. *Inorg. Chem.* **1998**, *37*, 3355–3360.

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