Silicon nanoparticles with chemically tailored surfaces

Andrew S. Heintz\textsuperscript{a}, Mark J. Fink\textsuperscript{b} and Brian S. Mitchell\textsuperscript{a}\textsuperscript{*}

Silicon nanoparticles are useful materials for optoelectronic devices, solar cells and biological markers. The synthesis of air-stable nanoparticles with tunable optoelectronic properties is highly desirable. The mechanochemical synthesis of silicon nanoparticles via high-energy ball milling produces a variety of covalently bonded surfaces depending on the nature of the organic liquid used in the milling process. The use of the C\textsubscript{8} reactants including octanoic acid, 1-octanol, 1-octaldehyde and 1-octene results in passivated surfaces characterized by strong Si–C bonds or strong Si–O bonds. The surfaces of the nanoparticles were characterized by infrared spectroscopy and nuclear magnetic resonance spectroscopy. The nanoparticles were soluble in common organic solvents and remarkably stable against agglomeration and air oxidation. The luminescence and optical properties of the nanoparticles were very sensitive to the nature of their passivating surface.

Supporting information may be found in the online version of this article.

Keywords: mechanochemistry; silicon–carbon bonds; silicon nanoparticles; mechanochemical synthesis; organosilicon

Introduction

Silicon nanoparticles have shown immense promise as materials for use in optoelectronic devices,\textsuperscript{[11–3]} solar cells,\textsuperscript{[4]} nanoparticle lasers,\textsuperscript{[5,6]} and as fluorescent biomarkers.\textsuperscript{[7,8]} Quantum confinement of electrons in small silicon nanoparticles (Bohr exciton radius less than 5 nm)\textsuperscript{[9,10]} results in size-dependent bandgaps with high photoluminescent quantum yields in the visible spectrum.\textsuperscript{[11]} The photoluminescence (PL) typically arises from core states which may be influenced by the presence of surface states which depend profoundly on the nature of the passivating surface. For instance, a native oxide surface layer can cause a significant decrease in silicon nanoparticle PL efficiency,\textsuperscript{[12,13]} whereas a nanoparticle surface linked molecularly through covalent Si–C and Si–O bonds has been shown to preserve PL through surface passivation of electronic states.\textsuperscript{[14]}

Although many routes to the synthesis of stable alkyl, alkoxy and siloxy passivated silicon nanoparticles have been developed,\textsuperscript{[15–27]} most require the use of highly reactive and corrosive chemicals and involve the modification of metastable nanoparticles with highly reactive silicon surfaces.\textsuperscript{[28]} An example of direct reactions with pure silicon surfaces include the formation of strong Si–C and Si–X bonds through the mechanical scribing of flat silicon surfaces in the presence of a reactive organic liquid.\textsuperscript{[28–32]} The reactive sites at the scribed surface have been modeled on Si(100) and Si(111) surfaces which contain surface-bound zwitterionic disilene and silyl radicals, respectively.\textsuperscript{[33–35]} Recently, we introduced a new method for the simultaneous production of silicon nanoparticles and the chemical passivation of the particle surface using reactive high-energy ball milling (HEBM).\textsuperscript{[36]}

Experimental

Production of Silicon Nanoparticles

A 1.0 g aliquot of silicon pieces of 99.95% purity obtained from Sigma-Aldrich were placed in a stainless steel milling vial along with two stainless steel milling balls, each with a diameter of 1.2 cm and weighing approximately 8.1 g. In a glovebox under nitrogen atmosphere, the vial was loaded, filled with approximately 25 ml...
of the desired liquid media, and then tightly sealed. For the functionality comparison, 1-octyne of purity ≥98.0%, 1-ocetone of purity ≥98%, octanoic acid of purity ≥98%, 1-octanol of purity ≥99% and 1-octanal of purity ≥99% were all obtained from Sigma Aldrich. After charging and sealing, the milling vial was placed in a SPEX 8000-D Dual Mixer/Mill, and HEBM was performed over various lengths of time.

Characterization

FTIR spectra were obtained at 1 cm⁻¹ resolution with 1000 scans using a Bruker IFS-55 spectrometer. For FTIR analysis, the nanoparticle solutions obtained from centrifugation supernatant were placed in a vacuum oven for solvent removal, and were re-dissolved in carbon disulfide then placed on a salt plate where the carbon disulfide was allowed to evaporate. NMR spectra were obtained on a Bruker Avance 300 MHz high-resolution NMR spectrometer. For NMR analysis, the nanoparticles were placed in a vacuum oven for solvent removal, and were dispersed in methylene chloride-d₂. The excitation–emission spectra and photoluminescence data from the nanoparticles were obtained using a Varian Cary Eclipse spectrofluorimeter. UV–vis spectra of the nanoparticles dissolved in hexane were obtained on a Cary 50 spectrophotometer.

Results and Discussion

Infrared and NMR Characterization

Figure 1 shows FTIR spectra obtained for thin films of passivated silicon nanoparticles milled in various organic solvents (reactants). Because of the solubility of the nanoparticles in organic solvents, it is possible to corroborate the structures of the surface-bound organic monolayer by using ¹³C(¹H) and ¹H nuclear magnetic resonance spectroscopy and a series of multipulse DEPT tests. It is important to note that, for all functionalities, the ¹³C(¹H) spectrum shows a single methyl resonance and a distinct number of methylene carbons, indicating a uniform alkyl carbon chain. However, for the point of brevity, only the peaks of interest found during the NMR experiments are discussed. Full NMR spectra are included in the supplementary materials.

All of the FTIR spectra, irrespective of the reactive liquid used in the milling, indicate the formation of a tenacious organic surface layer on the silicon nanoparticle. The prominent ν₁(C−H) stretching vibrations in the 2800–3000 cm⁻¹ range and the weaker scissoring vibrations (δ, C−H) around 1460 cm⁻¹ are totally consistent with the alkyl backbone of the surface-bound molecules.[37] In the case of the polar substrates: 1-octanol, 1-octaldehyde and 1-octanoic acid (Fig. 1c–e), there is also a broad feature in the range of 3200–3500 cm⁻¹ which is attributed to the O−H stretch of a surface-bound silanol group. A peak near 1050 cm⁻¹ of moderate intensity accompanies the O−H stretch and is attributed to the Si−O stretching vibration of the surface-bound silanol.

The FTIR spectrum obtained on passivated silicon nanoparticles produced by milling for 24 h in (a) 1-octyne, (b) 1-octene, (c) 1-octanol, (d) 1-octaldehyde and (e) octanoic acid.

Spectrum (a) is the FTIR spectrum of a thin film of 1-octyne. A previous version of this spectrum has been published. The lack of alkynic C−H and C≡C stretching vibrations and the appearance of weak C≡C stretching vibrations (~1600 cm⁻¹) is particularly noteworthy. A weak vibration at ~3050 cm⁻¹ appears as a broad shoulder to a much stronger alkyl ν₂(CH) vibration and is probably the ν₂(CH) of the vinylic hydrogens. This clearly indicates that the C≡C triple bond has been reduced to a C≡C double bond at the surface of the silicon nanoparticle. This is corroborated in the ¹³C(¹H)NMR spectrum by olefinic resonances at 125, 129 and 142 ppm. On this basis, two predominate structures were proposed, a surface-bound disilacyclobutene from [2+2] cycloaddition, and a surface-bound vinyl silane. The linear vinyl silane product originates from the reaction of a surface silyl radical with the triple bond of the octyne followed by hydrogen abstraction by the vinyl radical from the surrounding solvent (octyne). Figure 2 shows the structure of these products as well as the products derived from all of the organic liquids studied.

The FTIR spectrum obtained on passivated silicon nanoparticles formed by milling in 1-octene for 24 h is shown in spectrum (b). The nanoparticle spectrum shows clear evidence of an organic layer as shown by the CH peaks in the 2800–3000 cm⁻¹ range, and that the surface is protected from oxidation, as evidenced by the lack of a significant peak in the SiO region from ~1000–1200 cm⁻¹. Three peaks present in the pure 1-octene spectrum at 3076, 1641 and 908 cm⁻¹, attributable to the carbon−carbon double bond, are non-existent in the nanoparticle spectrum, indicating that the C≡C is responsible for the surface reaction. Weak vibrations attributable to the Si−C bond are probably obscured by the broad and slightly overlapping bands at 864 and 1060 cm⁻¹. In analogy to the reaction with 1-octyne, a [2+2] cycloadduct and a linear alkylylsilane structure are proposed.

Spectrum (c) shows a FTIR spectrum obtained for silicon nanoparticles passivated with 1-octanol. Again, the nanoparticle spectrum shows clear evidence of an organic layer as shown by the peaks in the 2800–3000 cm⁻¹ range. The 1-octanol reacys O−H addition to silicon atoms on the surface generating two surface
Scheme 1. Oxidation of unstable Si–H bonds on nanoparticle surface.

Scheme 2. Hydrolysis of the cycloaddition product formed during milling with 1-octaldehyde.

Figure 2. Summary of the surface structures of silicon nanoparticles passivated by 1-octyne (previously presented), 1-octene, 1-octaldehyde, octanoic acid and 1-octanol. The silanol structures (Si–OH) are the result of ambient oxidation of Si–H groups or hydrolysis of strained Si–O rings.

moieties: an alkoxy silane and an Si–H species. Surface-bound Si–H groups, however, are highly susceptible to air oxidation and are readily converted to a surface-bound silanol (Si–O–H).[38,39] A strong peak can be observed at 1090 cm$^{-1}$ in the Si–O region and is ascribed to the strong Si–O–C linkage that is formed at the surface. An O–H band over the 3200–3500 cm$^{-1}$ range shows the involvement of a silanol group from the insertion of oxygen into a Si–H bond upon air oxidation (Scheme 1). The $^{13}$C(NMR spectrum obtained on the 1-octanol passivated silicon nanoparticles exhibits a resonance peak at 63 ppm indicating an alkoxy carbon. A broad resonance in the $^{1}$H NMR spectrum at 3.5 ppm is attributed to the methylene hydrogens alpha to the oxygen atom. A partially overlapping resonance at 3.6 ppm which is approximately half the area of the previous peak is ascribed to the surface-bound silanol.

Spectrum (d) was obtained on passivated silicon nanoparticles formed by milling in 1-octaldehyde for 24 h. It also exhibits well-defined peaks in the 2800–3000 cm$^{-1}$ range. A broad absorption at 1100 cm$^{-1}$, indicative of a Si–O stretching vibration, and a broad OH band covering the range 3200–3500 cm$^{-1}$ is also observed. The diminished peak (relative to the pure octaldehyde) at ~1733 cm$^{-1}$ is assigned as a carbonyl vibration typical of normal unconjugated alkyl aldehydes.[40] It is not clear if this residual carbonyl group is the result of a physisorbed species or the product of an unknown chemical reaction at the surface. The $^{13}$C($^{1}$H) shows two distinct resonances at 64 and 72 ppm, which suggests that there are two different surface-bound structures. While both peaks are assigned to a carbon bound to an oxygen atom, the slight difference in chemical shift implies two unique chemical environments. A set of three broad resonances centered at ~3.8 ppm corresponds to an oxygen-bound CH group as well as the silanol group. The cyclic 1,2-disilaoloxetane structure is attributed to the [2 + 2] cycloaddition of the aldehyde to silicon dimer pairs at the surface. The 1,2-disilaoloxetane structure has been proposed for the reaction of acetone[41] and aldehydes[42] with clean silicon surfaces. Upon exposure to air, the cycloadduct product undergoes partial hydrolysis as shown in Scheme 2, which accounts for the surface-bound silanol and for the secondary alcohol which together contributes to the broad OH band observed in the FTIR spectrum. Although no analogous reactions have been reported for the reaction with molecular 1,2-disilaoloxetanes with water, the methanolysis of the strained Si–O–C in siloxetanes has been reported.[43]

Spectrum (e) was obtained on passivated silicon nanoparticles formed by milling in octanoic acid for 24 h. The presence of strong peaks at 1530 and 1591 cm$^{-1}$ and at 1441 cm$^{-1}$ is characteristic of the carbonyl vibrations of a bidentate carboxylate group.[44] These IR peaks correspond to the asymmetric and symmetric vibrational combinations, respectively.[45] It is not likely that the octanoic acid is bound predominately to the surface via a bridging bidentate COO$^{-}$ structure. Such structures have been observed for the reaction of carboxylic acids on a Ge(100) 2 × 1 surface.[46] Although no comparable structures have been unambiguously identified on a comparable silicon surface, theoretical calculations suggest that a bidentate structure should be more stable than a monodentate
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Table 1. PL data obtained on luminescent silicon nanoparticles produced by milling in various organic solvents for 24 h

<table>
<thead>
<tr>
<th>Passivating molecule functional group</th>
<th>Excitation wavelength of maximum observed emission intensity (nm)</th>
<th>Wavelength of maximum observed emission (nm)</th>
<th>Stokes shift (nm)</th>
<th>Intensity of maximum emission (a.u.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-Octyne</td>
<td>360</td>
<td>~435</td>
<td>75</td>
<td>~210</td>
</tr>
<tr>
<td>1-Octene</td>
<td>320</td>
<td>~394</td>
<td>74</td>
<td>~72</td>
</tr>
<tr>
<td>1-Octaldehyde</td>
<td>440</td>
<td>~522</td>
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<td>~48</td>
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<tr>
<td>Octanoic acid</td>
<td>440</td>
<td>~518</td>
<td>78</td>
<td>~21</td>
</tr>
<tr>
<td>1-Octanol</td>
<td>290</td>
<td>~406</td>
<td>116</td>
<td>~12</td>
</tr>
</tbody>
</table>

A small peak at 1708 cm$^{-1}$ is assigned to the $\nu_1(\text{C}=\text{O})$ of a carboxylic acid bound, indicating that a small fraction binds in a monodentate fashion.

The broadened absorbance at 3300 cm$^{-1}$ is assigned as an OH stretching vibration of a surface-bound silanol. A broad peak at 1080 cm$^{-1}$ corresponds to the SiO stretch of the silanol. This silanol is probably the result of surface oxidation of the Si–H bond formed from the polar addition of the OH bond of the carboxylic acid group (COOH) across the silicon surface.

A combination of $^{13}\text{C}$(H) NMR and DEPT spectroscopy shows two methylene carbons at 63 and 65 ppm. These peaks were attributed to the methylene carbons adjacent to the carboxylate group on the basis of their downfield chemical shifts. The carboxylate carbons could not be observed, probably due to their long relaxation. Although only one general bonding structure is present, the peak shifts of 63 and 65 ppm were attributed to conformational differences resulting from multiple reaction sites. The bidentate carboxylate can span between adjacent silicon atoms within a dimer row or alternatively between different rows of silicon dimers. This results in cyclic structures containing two and three silicon atoms, respectively, each with a slightly different shift in the $^{13}\text{C}$(H) NMR spectrum. Finally, a peak at 4.1 ppm is found in the $^1\text{H}$ spectrum, which can be attributed to the silanol proton.

### Photoluminescence and UV–Vis Spectra

Table 1 lists a summary of photoluminescence (PL) data obtained on silicon nanoparticles produced by milling in various organic solvents for 24 h. All of the nanoparticles display an observable blue luminescence at room temperature typical of nanoparticles with alkyl or alkoxy surfaces. In addition, all of the particles show the characteristic bathochromic shift of the emission wavelength with increasing excitation wavelength consistent with a polydisperse ensemble of nanoparticles. Selective excitation of a population of larger nanoparticles at longer wavelength results in an emission at corresponding longer wavelengths due to their wider bandgaps.

The positions of the emission bands for 1-octyne ($\lambda_{em} = 435$ nm) and 1-octene ($\lambda_{em} = 394$ nm) are fairly similar but the longer wavelength in the 1-octyne species suggests possible conjugation of the C=C bond to the silicon nanoparticle. The PL from nanoparticles with surfaces of the more polar 1-octaldehyde ($\lambda_{em} = 522$ nm) and 1-octanoic acid ($\lambda_{em} = 518$ nm) exhibit a significant bathochromic shift. In contrast, 1-octanol gives a maximum of $\lambda_{em} = 406$ nm which is more reminiscent of particles derived from the non-polar 1-octene and 1-octyne.

With the exception of the silicon nanoparticles produced in 1-octanol, the Stokes shifts at maximum emission are relatively consistent (within ~8 nm). It is well established that, for quantum dots, decreasing particle size results in an increase in the size-dependent Stokes shift (due to the widening bandgap). Because the Stokes shifts are relatively constant, this indicates that the particle size distributions between the samples are similar, and that the differences in emissions are more likely to result from effects due to the different passivating molecules. Passivated silicon nanoparticles produced in 1-octanol display a slightly different behavior, which seems to indicate a more narrow size distribution. This can be explained through a more limited solubility of the nanoparticles in the milling solution, which only allows nanoparticles of very small sizes to remain in solution.

In contrast to the photoluminescence behavior, the absorption spectra of the different nanoparticles are more variable. Figure 3 is a summary of different UV–vis spectra. Most show no discernable wavelength maximum greater than 200 nm but exhibit an absorbance tailing into the visible. This behavior is highly characteristic of an indirect semiconductor such as silicon. Exceptions to this behavior are octanoic acid, which shows a small peak with a maximum at 275 nm, and octaldehyde, which shows a major absorption with $\lambda_{max} = 290$ nm. This difference in optical absorption behavior is unusual and is more reminiscent of direct band gap semiconductors. The effect of these absorptions on the composition of the surface is currently being investigated.

### Conclusions

We have demonstrated that a mechanochemical method for the simultaneous production and passivation of silicon nanoparticles is not limited merely to $n$-alkynes, but in fact is also effective with normal alkenes, aldehydes, carboxylic acids and alcohols.
scope of this process should be expanded to other functional groups to give nanoparticles with unique optical properties. The facile one-step generation of silicon nanoparticles with diverse surfaces, and their corresponding unique optical properties, should greatly augment their use as materials in optoelectronic applications.

Acknowledgments

The authors acknowledge the financial assistance of NSF (CMMI-0726943) and of NASA (NNX08AP04A), administered by the Tulane Institute of Macromolecular Engineering and Science. The assistance of Steffen Hallmann, Li Kuang and Ted Shaner in the preparation of selected spectroscopic data is also greatly appreciated.

Supporting information

Supporting information may be found in the online version of this article.

References