Photo-Assisted Hydrosilylation of Silicon Nanoparticles: Dependence of Particle Size on Grafting Chemistry

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ABSTRACT: Silicon nanoparticles between 2.5 nm and 30 nm in diameter were functionalized by means of photoassisted hydrosilylation reactions in the aerosol phase with terminal alkenes of varying chain length. Using infrared spectroscopy and nuclear magnetic resonance, the chemical composition of the alkyl layer was determined for each combination of particle size and alkyln chain length. The spectroscopic techniques were used to determine that smaller particles functionalized with short chains in the aerosol phase tend to attach to the interior (β) alkenyl carbon atom, whereas particles >10 nm in diameter exhibit attachment primarily with the exterior (α) alkenyl carbon atom, regardless of chain length.

KEYWORDS: silicon nanoparticles, aerosol, hydrosilylation, FTIR, NMR

INTRODUCTION

Silicon nanoparticles have potential applications in numerous technologies, including photoluminescent devices,1,2 photovoltaic devices,3 and biophotonic applications.4 In order to alter chemical functionality5 or tailor nanoparticle physical properties,6 there is a need for robust methods of surface functionalization. Silicon nanoparticles are commonly synthesized by methods that result in hydrogen termination, allowing the process of hydrosilylation to take place on the nanoparticle surface. Hydrosilylation has been explored as a method for chemically attaching organic layers to the surfaces of hydrogen-terminated silicon nanoparticles;7,8 however, little work has been performed to fully understand how parameters such as nanoparticle size and choice of precursor affect the chemical structure of the layers bound to the silicon nanoparticle surface after the reaction.

Surface hydrosilylation of terminal alkenes (1-alkenes), as shown schematically in Figure 1, occurs when the alkene reacts with a Si—H bond, replacing the Si—H bond with a Si—C bond and reducing the alkene to an alkyl ligand, forming a new C—H bond. Thermal, catalytic, and photochemical hydrosilylation methods have been employed to modify silicon surfaces,9,10 porous silicon,11,12 and silicon nanoparticles.13–15 Thermally induced hydrosilylation on silicon surfaces16 and silicon nanoparticles13 is known to result exclusively in the α-bonded, linear alkyl chain. Photoassisted hydrosilylation on flat silicon surfaces has also resulted in the exclusive result of α-bonded alkyl chains;17 however, when photoassisted hydrosilylation was performed on silicon nanoparticles using a solution method, the resulting ligands exhibited a bonding structure with a combination of α- and β-bonding.18,19 This evidence has influenced the current work with the concept that the nanoparticle size may have an effect on the bonding structure of the alkyl ligands.

In this research, the products of silicon nanoparticles reacted with terminal alkenes in the presence of ultraviolet (UV) light were characterized spectroscopically. Aerosol silicon nanoparticles were produced by means of a nonthermal radio-frequency (rf) plasma and were functionalized without leaving the aerosol stream by means of photoassisted hydrosilylation. Performing experiments in the aerosol phase has several advantages over solution-based techniques. First, various uniform sizes of silicon nanoparticles can be produced by simply altering the parameters (e.g., precursor flow rates, residence times, etc.) of the plasma synthesis method, and the variety allows for an in-depth analysis of the initial nanoparticle size on the photoassisted hydrosilylation reaction. Also, particles can be functionalized without...
removal from an inert environment, eliminating concerns over whether ambient oxidation or the solvent affect the surface reactions. Finally, aerosol processing allows continuous production and requires no harmful solvents. In this work, infrared (IR) spectroscopy, proton nuclear magnetic resonance (NMR), and tandem differential mobility analysis (TDMA) were used to determine the effects of nanoparticle size and precursor chain length on the chemical attachment of the resulting alkyl layer.

**EXPERIMENTAL SECTION**

A schematic of the experimental apparatus for synthesis, followed by functionalization in the aerosol, is shown in Figure 2. Silicon nanoparticles were synthesized by means of a gas-to-particle conversion in a nonthermal rf plasma reactor that is similar to that described elsewhere. Measured amounts of silane gas (0.5% in argon, Boc Edwards) and argon were introduced into a quartz reactor with mass flow controllers (MFCs). An rf power of 40–70 W at 13.56 MHz was sent to an electrode wrapped around the quartz cell, with a grounded electrode wrapped 1 in. downstream. The nanoparticle sizes were altered by controlling the gas flow rates, reactor diameters, and pressures, and they were determined by differential mobility analysis or transmission electron microscopy (TEM) from previous studies.

For aerosol-based hydrosilylation, the particles were evacuated from the low-pressure system with a nitrogen-powered Venturi pump immediately downstream from the plasma. To this stream, the alkene precursor was introduced. Propene (99.97%, Valley National Gases) was added by means of a MFC. 1-Hexene (99%, Sigma–Aldrich) and 1-octene (98%, Sigma–Aldrich) (hereafter referred to as hexene and octene, respectively), distilled prior to use, were added by means of flowing nitrogen through a bubbler filled with the precursor after the liquid had been degassed by means of several freeze–pump–thaw cycles. The required flow rates of the alkenes were determined by TDMA experiments, with experimental descriptions detailed elsewhere. The mixed stream of particles and alkenes was then sent through a quartz chamber surrounded by 12 UV lamps (254 nm), with a residence time of ~2 s. After the UV reactor, the stream was sent through an altered IR gas cell in which a stainless steel mesh was placed perpendicular to the aerosol stream. After a sufficient number of particles had deposited on the mesh, the flow of nanoparticles and alkene precursor was ceased and nitrogen was allowed to flow over the collection mesh to purge the sample of unreacted precursors. The IR spectrum was obtained while the sample remained in the nitrogen atmosphere. After the IR spectrum was obtained, the collection chamber was pressurized with nitrogen and taken off the aerosol line and placed into a glovebag filled with argon. The mesh was removed from the collection cell and added to a small vial of deuterated dimethyl sulfoxide (DMSO-d6, 99.9%, Cambridge Isotope Laboratories) and agitated to disperse the particles. The dispersion was pipetted from the vial to a clean NMR tube and capped prior to removing it from the glovebag. This process was repeated for all samples produced in this study.

For TDMA experiments, pristine nanoparticles were mobility selected with a DMA (TSI Model No. 3085) at the statistical modes of the size distribution. A known flow of alkene was then added to the stream of mobility-selected nanoparticles and the combined flow passed through the irradiation chamber. After irradiation, a second DMA scanned over a range of mobility diameters and a particle counter (TSI Model No. 3025A) was used to find the distribution over the range of diameters. The resulting particle diameter was determined from the center of the Gaussian distribution fit to the data collected. The reported change in mobility diameter (ΔDP) was found by subtracting the mobility diameter of the pristine particles from the mobility diameter after the particles and alkenes pass through the irradiation chamber. Each data point represents the average of three independent trials.

All IR spectra were taken on a Nicolet Magna 560 IR spectrometer at 2 cm⁻¹ resolution and averaged over 64 scans. All NMR spectra were taken on a Varian Mercury 300 MHz spectrometer and averaged over 512 scans. The residual proton of the solvent at 2.50 ppm was used as the reference.

**RESULTS**

Figure 3 shows results of TDMA experiments using different flow rates of hexene and octene with two initial diameters of nanoparticles. The particle growth plateaus above flow rates of ca. 80 sccm for all particle sizes and precursors that were examined, so a flow rate of 100 sccm was chosen for all subsequent measurements.

Figure 4 shows the IR spectra of neat, gas-phase octene, hexene, and propene (Figures 4a, 4b, and 4c, respectively); 6-nm silicon nanoparticles after functionalization with propene, hexene, and octene (Figures 4d, 4e, and 4f, respectively); and pristine 6-nm silicon nanoparticles (Figure 4g). Table 1 lists the key features identified in the IR spectra. Important observations to be taken from these spectra are that, upon hydrosilylation, the peaks associated with the C–H stretching of sp² hybridized carbon of vinyl moieties (3095–3075 cm⁻¹), as well as the alkynyl C≡C stretch (1680–1620 cm⁻¹), are nonexistent in the spectra for functionalized nanoparticles, confirming that the photoassisted hydrosilylation reaction occurs in the same...
manner as previously observed for thermally induced hydrosilylation of terminal alkenes.\textsuperscript{13} The presence of silicon-hydride stretching (2160–2040 cm\textsuperscript{-1}) and deformation modes (doublet between 950 and 800 cm\textsuperscript{-1}) is a result of incomplete passivation of the nanoparticle surface by the alkyl group.

Bending modes of the alkyl groups can provide a qualitative analysis of the structural isomers of the functionalized nanoparticles. Figure 5 shows the IR spectra between 1500 cm\textsuperscript{-1} and 1300 cm\textsuperscript{-1} for nanoparticles functionalized with propyl groups. The area between 1475 and 1425 cm\textsuperscript{-1} contains both the asymmetric deformation mode of the methyl (CH\textsubscript{3}) moiety and methylene (CH\textsubscript{2}) scissor modes. The peaks between 1385 cm\textsuperscript{-1} and 1365 cm\textsuperscript{-1} can be assigned exclusively to the symmetric bending modes of methylv groups. For linear alkyl groups (i.e., \(\alpha\)-bonded), the terminal methyl group can be observed as a singlet in this region, whereas an isopropyl moiety (i.e., \(\beta\)-bonded) exists as a doublet in this region. By examining the ratio of the intensities between the regions of higher to lower wavenumbers, the ratio of methylene to methyl moieties can be estimated, where a higher ratio represents a greater proportion of methylene. Since all nanoparticles in this example were functionalized with propene, it is assumed that a greater relative amount of methylene moiety represents a greater relative amount of \(\alpha\)-bonded alkyl groups. It can be seen that, as the initial nanoparticle size increases, the ratio of intensities of modes at higher to lower wavenumbers also increases, and, therefore, larger particles appear to have a greater propensity for \(\alpha\)-bonding. Also observed is the splitting of the singlet at ca. 1375 cm\textsuperscript{-1} into the doublet as the initial nanoparticle size decreases, representing an increase in \(\beta\)-bonding, as the particle size decreases. Similar plots can be made with all other data collected, but the reaction with propene shows the most disparate spectra in this region. Because of the substantial overlaps in this region, quantification was not attempted.

To estimate the relative amounts of \(\alpha\)- and \(\beta\)-bonded alkyl groups, the C–H stretching region of the IR spectrum can be analyzed. Figure 6 shows the C–H stretching region for nanoparticles functionalized with propyl groups. The integrated areas in this region for all spectra were normalized to aid the eye. The five peaks that exist in this region are the methyl asymmetric, methylene asymmetric, methine (CH), methyl symmetric, and methylene symmetric stretches, at ca. 2954, 2921, 2894, 2867, and 2851 cm\textsuperscript{-1}, respectively. By fitting five Lorentzian functions
in this region for each spectrum, the intensity representing each vibrational mode can be determined. Using the Beer–Lambert law, the intensities of the stretching modes can be directly related to the relative concentration of each moiety. A requirement for using the Beer–Lambert law is that the extinction coefficient of each vibrational mode must be known. Because organic groups bound to the surface of nanoparticles do not share properties with the bulk material, the extinction coefficients were determined by examining the IR spectra of particles functionalized solely with linear alkyl groups. Previous studies have shown that flat silicon surfaces, as well as large nanoparticles, exhibit unbranched chains upon functionalization, which is also observed in the NMR spectra that are discussed later. In this light, 30-nm nanoparticles were produced and functionalized with propyl, hexyl, and octyl groups. A calibration curve was fit to the relative intensities of each vibrational mode versus the relative concentration (assuming all α-bonding) to obtain relative Beer–Lambert constants for each vibrational mode examined. Since they are the simplest to segregate, the methyl and methylene asymmetric stretches were used to quantify all spectra taken in this study.

The NMR spectra of functionalized nanoparticle dispersions can also provide detailed information about the chemical structure of the organic layer bound to the silicon surface. By utilizing the chemical shifts and splitting patterns customarily used in the analysis of organic compounds, the structure of the alkyl group can be determined. Figure 7 shows NMR spectra of particles functionalized with propyl groups. The peaks can be assigned based on the chemical shifts, with methyl, methylene, and methine at ca. 0.85, 1.2, and 1.85 ppm, respectively. The peaks are much broader than would be expected from typical solution-based NMR, because of the constrained motion of the alkyl chains bound to the nanoparticle surface. Although the methyl peaks are broad, splitting patterns can still be observed. From the $n + 1$ rule, a triplet peak, as is present in the spectra of larger particles, signifies that the methyl moieties are directly bound to methylene moieties, whereas the doublet peak, present in the spectra of smaller particles, indicates a direct bond to a methine moiety. While the signal splitting can provide a qualitative assessment of the chemical structure of the ligands, to quantify the prevalence of the structural isomers, peak integration must be performed. The methine peak is too broad and buried in the baseline to obtain a reasonable integral; therefore, the ratio between the integrated area of methylene and methyl peaks was assessed to determine the structure of the bound ligands, specifically

$$R = \frac{A_{\text{methylene}}}{A_{\text{methyl}}} = \frac{2(L - 1)x + 2(L - 3)(1 - x)}{3x + 6(1 - x)}$$

(1)

where $R$ is the ratio of areas corresponding to methylene and methyl hydrogen atoms, $L$ is the chain length of the alkene precursor in units of carbon atoms, and $x$ is the fraction of α-bonded products, with the assumption made that $(1 - x)$ represents the fraction of β-bonded products. Both the numerator and denominator in eq 1 are expressed as the sum of the integrated areas of α- and β-bonded products multiplied by their fraction of occurrence, $x$ or $(1 - x)$, respectively. Rearrangement of this equation yields

$$x = \frac{6(R + 1) - 2L}{3R + 4}$$

(2)

Figure 8 summarizes the results obtained regarding the structural isomers of the alkyl ligands determined from IR and NMR.

**Discussion**

The results expressing the difference in bonding mechanism clearly show a size dependence, where smaller particles are more likely to result in β-bonding, particularly upon reactions with precursors with shorter chains. The most likely reason for this result involves the physical nature of particle surfaces as particles get smaller. Large particles exhibit properties similar to bulk, flat-topped silicon surfaces, whereas smaller particles exhibit extreme curvature. The additional available space above the nanoparticle surface of smaller particles may allow ligands to bond in a branched manner, which possesses a larger “footprint” than linear chains. Larger particles with flatter surfaces require ligands to be linear, because of the smaller accessible area above the nanoparticle surface area available for packing alkyl chains. Along with the curvature, smaller particles have rougher surfaces, because of a greater significance of edge and vertex sites. These “rough” sites provide a different steric environment than the flatter surfaces of bulk materials and larger nanoparticles. Shorter alkyl chains are also significantly more likely to exhibit β-bonding structures. This phenomenon may be caused by the alkyl chains away from the double bond “protecting” the β-site from being involved in the reaction by limiting the interaction of the internal alkenyl carbon atom with the nanoparticle surface.
Another possible reason for the differences in isomerization of the attached ligands is that the initial surface chemistries of the nanoparticles synthesized in the plasma are not able to be controlled, resulting in surfaces exhibiting large variations in monohydride, dihydride, and trihydride, as well as clustered states, dimerized structures, and other polyhydrides.26–28 In order to consistently compare the surface reactions at different particle sizes, the initial surface chemistries should be more consistently similar, which is an aspect of plasma synthesis of nanoparticles that is still uncontrollable. However, the initial particle chemistry does not seem to affect the bonding mechanism, because there is no trend associated with production of particles at a given size with the relative amounts of monohydride, dihydride, and trihydride moieties, while there is a significant trend in attachment chemistry that is related to particle size. Because the alkene flow rates were not changed during the duration of this work, one might assume that the relative concentration of alkene per available surface site was decreased for smaller particles, reducing the total amount of coverage, allowing for the reactions resulting in greater footprints to proceed. Saturation effects were analyzed by observing IR spectra recorded during the particle processing, which exhibited significant peaks associated with the near alkene, suggesting that the irradiation chamber was always saturated with alkene vapor for all trials.

Direct comparison to thermally assisted hydrosilylation in the aerosol phase cannot be made, because heating aerosolized H-terminated silicon nanoparticles leads to the desorption of the hydride layer29 and restructuring of the surface silicon layer30 to a stable crystalline state, forbidding the hydrosilylation reaction.

CONCLUSION

This work provides an in-depth spectroscopic analysis of the products of silicon nanoparticles upon photoassisted hydrosilylation with terminal alkynes in the aerosol phase. Smaller particles and shorter alkyl chains have been shown to exhibit a greater propensity toward β-bonding, resulting in products with branched alkyl groups on the surface, with consistent trends for given particle sizes and precursor chain lengths. Also, the advantages of aerosol techniques for modifying nanoparticles are highlighted by the ease by which particles are continuously functionalized and by the fact that parameters can be adjusted to achieve different sizes of nanoparticles for studying surface modification techniques.

REFERENCES


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ASSOCIATED CONTENT

Supporting Information. Full IR and NMR spectra for all samples investigated. (PDF) This material is available free of charge via the Internet at http://pubs.acs.org.

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