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Surface Functionalization of Silicon Nanoparticles Produced by Laser-Driven Pyrolysis of Silane followed by HF−HNO$_3$ Etching

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CO$_2$ laser induced pyrolysis of silane was used to produce silicon nanoparticles with an average diameter as small as 5 nm at high rates (up to 200 mg/h). Etching these particles with a mixture of hydrofluoric acid (HF) and nitric acid (HNO$_3$) reduces their size and passivates their surface such that they exhibit bright visible photoluminescence (PL). This paper describes the attachment of organic molecules to hydrogen-terminated and hydroxyl-terminated surfaces of these nanoparticles. Stable particle dispersions in various solvents were obtained by treatment of hydrogen-terminated surfaces with octadecene or undecylenic acid and by treatment of hydroxyl-terminated surfaces with octadecyltrimethoxysilane. Transmission electron microscopy showed that the surface-functionalized particles were well dispersed and crystalline. FTIR spectroscopy confirmed the expected reactions of the organic molecules with the particle surfaces. Photoluminescence measurements showed that surface treatment significantly stabilized the PL properties of the nanoparticles against degradation. Size selective precipitation was applied to particle dispersions and allowed some narrowing and tuning of the PL spectrum.

1. Introduction

Since the first report of bright photoluminescence (PL) at room temperature from porous silicon (PSi) produced by electrochemical etching of crystalline silicon wafers,[1] a tremendous amount of research has been done on the synthesis and surface modification of this material. This was due to many interesting potential applications of luminescent porous silicon for solid-state lighting or displays, photodetectors, solar energy converters, and chemical sensors.[2] Porous silicon is a complex material that consists of crystalline nanowires and silicon nanocrystallites.[3,4] Many researchers have studied the origin and physical aspects of PL from PSi. When the size of silicon crystallites is below about 5 nm, visible PL from them can be explained by widening of the band gap as a result of quantum confinement effects.[4] Si nanoparticles exhibit strong PL in the red when their size is in the range of 3−5 nm and the PL shifts to shorter wavelengths with decreasing size.[5] Because there have not been methods available to reliably produce macroscopic quantities of luminescent silicon nanoparticles that are free of a substrate, studies of the surface chemistry of such nanoparticles in colloidal dispersion have been quite limited. In a recent paper, we reported a novel method of producing macroscopic quantities of silicon nanoparticles by laser-driven pyrolysis of silane followed by an HF−HNO$_3$ etching treatment.[6] With the availability of macroscopic quantities of silicon nanoparticles, it is possible to systematically explore their surface reactivity and compare it with that of single-crystal silicon wafers and porous silicon. Initial results of such studies are reported here.

Lack of stability of the PL from porous silicon has been a major barrier to its commercial application. Surface modification of porous silicon surfaces with different functional groups provides an attractive means of stabilizing the PL. It also has the potential to provide a controlled interface with other semiconductors, polymers, and biological molecules for various applications. Several strategies have been used for functionalizing porous silicon surfaces for the purpose of stabilizing the PL or for providing controlled surface properties for further applications. The functionalization of flat single-crystalline silicon wafers has also been extensively studied, since silicon wafers provide a low-cost, almost atomically smooth, and very well characterized surface for preparing self-assembled monolayers and for studying bound species by atomic force microscopy and other scanning probe microscopies. High-quality alkyl monolayers on hydrogen-terminated Si(111) were prepared by Linford et al.[7] These monolayers were produced by reaction of 1-alkenes and alkynes with the surface upon free-radical initiation with diacyl peroxides. Similar work was done by Sieval et al.[8] to prepare stable Si−C linked functionalized monolayers on the hydrogen-terminated Si(100) surface. Derivatization of PSi by Grignard reagents at room temperature was done by Kim and co-workers,[9] where the PSi surface was functionalized with aryllithium reagents to form Si−C bonds. Buriak and co-workers and Boukherroub and co-workers each published a series of papers on surface modification of Si and PSi. They coated nonoxidized hydride-terminated PSi surfaces and the Si(111) surface with alkenyl and alkyl functionalities in the presence of

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Lewis acid catalysts[10,11] and studied the photoluminescence properties of the treated PSi.[12] They produced stable PSi covered with 1-decene that had both oxidized and alkylated regions, and they studied the PL stabilization.[11,13] Stewart and co-workers applied white-light-promoted reactions for hydrosilylation of alkenes and alkynes on luminescent Si nanocrystals. They achieved stable PL without significant loss of the photoemissive qualities of the materials.[14,15] They also conducted thermal reactions of alcohols and aldehydes with Si(111)−H to form Si−OH_2R films,[16] and used UV irradiation to link ethyl undecylenate to Si(111)−H to form a Si(111)−$C_{10}H_{20}$-CO_2Et surface.[17] In another paper,[18] they modified PSi surfaces with ethyl undecylenate to achieve greatly enhanced PL and structural stability of the PSi. The resulting PSi was stable in boiling CCl_4, in water, and against corrosion when exposed to 100% humidity in air. They also linked activated esters of undecylenic acid covalently to PSi.[19] Choi and Buriak[20] studied the effects of organic monolayers attached to the surface of PSi on its electrochemiluminescence characteristics. Gole et al.[21] reported enhancement and stabilization effects of chloride salts on the PL of PSi. Liquid-phase synthesis of alkyl-capped nanocrystalline Si by reaction of $SiCl_4$ with Mg_2Si in ethylene glycol dimethyl ether was conducted by Yang and co-workers.[22] Reaction of luminescent PSi with lithium reagents to form Si−C bound surface species was conducted by Song and co-workers.[23,24] Kim et al.[25] and Swerda-Krawiec et al.[26] explored surface modification of PSi with various alcohols. The PL of these alcohol-capped particles was completely quenched initially but partially recovered after heating. Fabre and co-workers[27] derivatized the Si(111) surface with a thiophene-terminated alkyl monolayer for preparing a conducting film. Pavlovic and co-workers coated an oxidized silicon surface with (3-mercaptopropyl)silane.[28] Li et al.[29] presented an amine-catalyzed method for carrying out silane chemistry on porous silicon without pretreating the surface with an oxidizer to form Si−OH groups on the surface. Schmeltzer and co-workers prepared alkenyl- and alkyl-terminated surfaces by hydride abstraction with triphenylcarbenium cations in the presence of terminal alkynes and alkenes.[30] The preparation of the Si(111 or 100)−H surfaces, the reactions involved in formation of Si−C and Si−O bonds, and the functionalization of monolayers were reviewed by Wayner et al.[31] Organometallic chemistry on silicon and germanium surfaces was recently reviewed by Buriak.[32] Surface functionalization of free silicon nanoparticles prepared by methods other than sonication of PSi has only recently been explored. Korgel and co-workers[33,34] recently published a novel method to prepare brightly luminescent, surface-capped silicon nanoparticles in supercritical organic solvents at high temperature and pressure. Further studies of the electrochemistry and electrogenerated chemiluminescence of these particles were conducted by Ding et al.[35]

Several groups have carried out surface functionalization of silicon for biological applications. Hart et al.[36] recently reported a new method to attach biomolecules to PSi while retaining the PL of the PSi. This surface modification was achieved by Lewis acid catalyzed hydrosilylation with nitrile-terminated alkynes, followed by reduction with $LiAlH_4$. Dahmen et al.[37] studied chemical modification of hydrogenated amorphous Si and Si suboxide surfaces for the purpose of selective cell adhesion. A review of chemical and biological applications of porous silicon was presented by Stewart et al.,[38] in which they considered surface chemistry, Si lithography, sensing in chemical and biological systems, and PSi as a support for biochemical reactions and proteomics.

Although there have been a huge number of papers published on PSi and on the surface chemistry of silica and flat silicon wafer surfaces, very little research has been done on the surface chemistry of luminescent Si nanoparticles that are free of a substrate and that have not been derived from PSi. Information from the literature on silicon wafers and PSi is very helpful in identifying functionalization routes for the free nanoparticles, but chemistry on the free nanoparticles sometimes proceeds much differently than on a bulk surface. For example, when etching silicon nanoparticles with HF/HNO_3 mixtures, we use etching mixtures that etch bulk silicon at more than a 1 μm/min but that etch the nanoparticles at less than 1 nm/min. Our recently published process for preparing free silicon nanoparticles[6] in macroscopic quantities enables us to conduct research directly on free luminescent silicon nanoparticles to achieve different surface functionalities for different potential applications. Here we present studies focusing on the surface modification of these free silicon nanoparticles by uncatalyzed thermal reactions in solution.

2. Experimental Details

As described in detail previously,[6] silicon nanoparticles with bright visible photoluminescence have been prepared by a new

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combined vapor-phase and solution-phase process, using only inexpensive commodity chemicals. CO_2 laser induced pyrolysis of silane was used to produce Si nanoparticles at high rates (20−200 mg/h). Particles with an average diameter as small as 5 nm were prepared directly by this vapor phase (aerosol) synthesis. Etching these particles with mixtures of hydrofluoric acid (HF) and nitric acid (HNO_3) reduced the size and passivated the surface of these particles such that after etching they exhibited bright visible photoluminescence at room temperature. However, these particles are not well dispersed in most solvents. The long-term stability of their photoluminescence (PL) is also unsatisfactory. The PL intensity tends to decay with time, and the peak of the PL intensity tends to shift, especially if the particles are dispersed in water or alcohols. To produce particles useful for optoelectronic devices, sensors, biological imaging, and other applications, stable PL and good dispersability in a range of solvents are essential.

Here we consider two approaches to surface functionalization of these particles: (1) hydrosilylation of Si−H surfaces and (2) silanization of Si−OH surfaces. There are many published studies applying these approaches, mostly to the porous Si surface generated by electrochemical etching of silicon wafers.[10,11,13,28,39] It has been shown that these methods work quite well for porous silicon. However, there is no guarantee that they will work equally well for the silicon nanoparticles produced by laser pyrolysis of silane followed by acid etching. Surface modification of etched, luminescent silicon nanoparticles offers interesting scientific and technological possibilities because it allows us to form stable colloidal dispersions of these particles that can be handled and manipulated like ordinary chemical reagents.

The PL of the treated particles was visually observed using a handheld UV lamp (Black-Ray ultraviolet lamp, model B100SP) and recorded using a Perkin-Elmer LS 50 fluorescence spectrometer with a 351 nm band-pass filter used to suppress any scattered light from the source. The surface properties of functionalized particles were analyzed by Fourier transform infrared (FTIR) spectroscopy using a Mattson Galaxy series FTIR 5000. Powder samples were mixed with KBr to prepare thin pellets for FTIR measurements. For particle dispersions, membrane dialysis was first performed to remove excess reagents, and then the solvent was evaporated. The resulting oily looking particles were mixed with KBr to make pellets for FTIR measurements. For liquid samples, FTIR measurements were conducted in the horizontal attenuated reflectance mode of the spectrometer by casting a drop on the internal reflection element card. High-resolution transmission electron microscopy (TEM) (JEOL, JEM 2010) and selected area electron diffraction were used to obtain information on crystalline lattice spacing, particle size, and degree of agglomeration of the surface-treated particles.

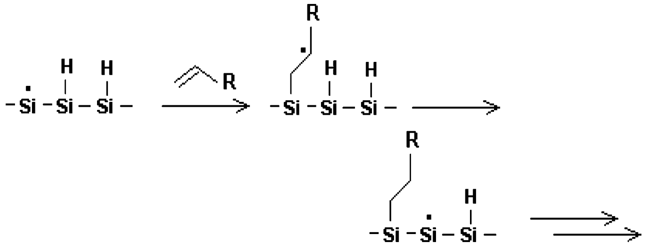
Particle treatment following surface functionalization included dialysis using a 12−14 kDa cutoff regenerated cellulose membrane (Spectrum Laboratories, Inc., USA) against an appropriate solvent to remove excess reagents. The solution outside the dialysis membrane usually showed weak PL under UV illumination, indicating that some small particles could pass through this membrane. We also removed unreacted alkenes by size exclusion chromatography of surface-treated particles in a column (9 in. × $^{3}/_{4}$ in.) packed with Bio-beads S-X1 from Bio-Rad. These beads have a molecular cutoff limit of ~14 kDa. Small molecules such as octadecene, with a molecular mass of 252 Da, enter the pores of the beads and move through the column more slowly than the particles, which cannot enter the pores. Under continuous flow of solvent, particles can be tracked through the glass column by illuminating it with a UV lamp. It took about 30 to 40 min for typical red to orange emitting particles to pass through the column.

Chemicals used in these experiments were as follows: sulfuric acid (H_2SO_4), Aldrich, 95−97%; hydrogen fluoride (HF), 48.0−51.0%, A.C.S. reagent grade; nitric acid (HNO_3), 68.0−70.0%, EMD chemicals, GR grade; methanol (MeOH), EMD chemicals, HPLC grade; toluene, Aldrich, 99.0%; ethyl alcohol, Pharmco, 200 proof, ACS/USP grade, 190 proof ethyl alcohol and HPLC grade ethyl alcohol were also used for some experiments; octadecene, Acros organics, 90%; undecylenic acid, Acros organics, 99%; hydrogen peroxide (H_2O_2), Acros organics, 30%; potassium bromide (KBr), Acros organics, IR grade, 99+%; octadecyltrimethoxysilane, Aldrich, 90%. All chemicals were used without further purification.

2.1. Hydrosilylation of Nanoparticles with a Si−H Surface. Preparation of Si−H terminated nanoparticle surfaces took advantages of the known reactions of aqueous hydrogen fluoride (HF) solution with silicon. On flat silicon wafers, one can readily generate Si−H surfaces with excellent chemical homogeneity (>99% H termination) using aqueous HF solution or degassed 40% aqueous NH_4F solution.[40,41] The strong FTIR stretching modes at ~2100 cm^{-1} provide clear information on the state of the particle surface before and after surface functionalization. We have used the same methods to produce Si−H nanoparticle surfaces. Subsequent surface functionalization of the Si−H surface was based on thermally induced hydrosilylation. At sufficiently high temperature, some Si−H homolytic cleavage occurs

$$\mathrm{Si{-}H} \rightarrow \mathrm{Si}^{\bullet} + \mathrm{H}^{\bullet}$$

These silicon-based radicals (dangling bonds) will then react with alkenes via the following free-radical chain mechanism:[42]



Silicon nanoparticles were produced by laser pyrolysis of silane as described previously. The resulting particles were washed with deionized (DI) water and methanol several times on a polyvinylidene fluoride (PVDF) membrane filter (Millipore) to remove excess HF and HNO_3**.** These particles need to be further surface treated to generate the Si−H terminated surface. An aqueous 5% HF solution was used for this purpose. Particles, still deposited on the filter paper, were transferred to a container containing 5% HF solution and were then sonicated for 5 min to remove particles from the filter paper, break up agglomerates, and promote mixing. The resulting particles were then filtered and again washed thoroughly with DI water and methanol. For most experiments (typically starting from 100 mg of original unetched particles), about 20−50% of the original mass of unetched particles was recovered after the entire etching and HF wash process. Particles were then transferred to a small flask and dispersed in the solvent to be used for the functionalization reaction. All solvents were bubbled with pure nitrogen for at least 30 min to remove dissolved oxygen. A sonicator (Branson 2510) was used to disperse particles from the filter paper. A small fraction of the particles was always left untreated, for comparison to the treated particles. The particle solution was mixed with additional solvent to yield a final volume of about 15 mL. The dilute particle solution was transferred into a flat bottom flask. For preparing octadecene-coated particles, 2 mL of octadecene was added to the solution and it was sonicated for 15 min. The solution was then refluxed with stirring at the solvent boiling point (~110 °C for toluene) overnight. After some time, the particle dispersion became less turbid. The solution typically became completely clear in a few hours to 20 h. The clear, well-dispersed particle solution can pass through filter paper with 0.1 μm pore size without significant loss of photoluminescence, indicating that surface modification effectively changed the dispersability of particles in the solvent used. When the etched particles were treated with undecylenic acid, the solvent was changed to 190

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proof ethanol. The surface treatment process otherwise proceeded in the same way as described above for octadecene in toluene.

2.2. Silanization of Si−OH Surface. This surface functionalization method uses silane coupling agent chemistry and requires a Si−OH terminated surface. The general formula for an organosilane is $R_nSiX_{(4-n)}$, where X is a hydrolyzable group that is typically alkoxy, acyloxy, amine, or chlorine. When reacted with the Si−OH surface, each Si−X bond is replaced by a Si−O bond to the surface or to another organosilane molecule. In the work presented here, X is methoxy, which gives methanol as the byproduct when reacted with the silicon surface. Silanes are available with a wide variety of functional groups (R), which makes this a potentially versatile route for particle functionalization.

To generate Si−OH terminated surfaces, we applied two different methods. The simplest method was to wash the etched particles directly with 20% nitric acid for a few minutes and then wash them thoroughly with DI water. The second one was to reflux the etched particles in a mixture of concentrated sulfuric acid and 30% hydrogen peroxide (7:3 by volume, also called "piranha etch"). Note that extreme care should be taken with this reagent mixture since there is high risk of explosion or fire if it comes in contact with reducing agents, and it is also highly corrosive. The second method can generate a more uniform Si−OH surface, but if the first method is also effective, then it is preferable because it avoids the use of the hazardous sulfuric acid/hydrogen peroxide mixture.

There are several methods of depositing organosilanes on hydroxyl-terminated silicon surfaces. In the work described here, the organosilane was deposited from aqueous alcohol. This approach is appropriate for alkoxysilanes such as that used here. For the more reactive chlorosilanes, a dry nonpolar solvent such as toluene is used. For coating the particles with octadecyltrimethoxysilane, a 5% water in ethanol solution (190 proof ethanol) was first adjusted to pH 4.5−5.5 with acetic acid. Octadecyltrimethoxysilane was added with stirring to yield ∼2 wt % final solution. At least 5 min was allowed for hydrolysis and silanol formation. The etched particles, treated as described above to give an −OH terminated surface, were sonicated in ethanol separately, then mixed with the above 2% silane solution, and sonicated again to promote dispersion of the particles. The resulting solution was refluxed in a flask with a condenser for about 1 h. Then the solvent in the flask was evaporated until the volume was reduced to about half of the original volume. A volume of toluene equal to one to two times the volume of the remaining solution was added, and the mixture was refluxed with vigorous stirring for an additional 10−20 h. The result was a clear yellow dispersion that emitted brightly under illumination by a handheld UV lamp. The final particle dispersion could pass through a piece of 0.1 μm filter paper with minimal loss of PL intensity and no change in color. Removal of excess organosilane was again achieved by membrane dialysis.

3. Results and Discussion

3.1. Surface Functionalization of Silicon Nanoparticles with Octadecene. To make a truly stable dispersion of the etched Si nanoparticles, their surface must be adequately passivated. The hydrogen-terminated Si particle surface is unstable, both toward slow oxidation by air and toward particle agglomeration in most solvents. Oxide-passivated surfaces are similarly unstable to agglomeration in most solvents and can suffer from further oxidation, which alters the photoluminescence spectrum. The approach described in recent work on surface alkylation by Lie et al.[43] has proven to be an effective method of rendering stability to the particles in nonpolar solvents such as toluene. These authors reacted different alkenes with the surface of luminescent silicon nanoparticles (produced by sonication of porous silicon) by refluxing the nanoparticles in toluene solutions of the alkenes. Such hydrosilylation reactions on porous silicon and on hydrogen-terminated silicon wafers are well-known and are described in the review by Buriak.[32]

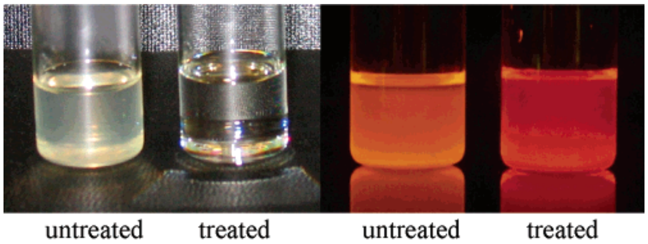

Figure 1. Untreated and octadecene-treated samples under room illumination (two pictures on the left) and UV illumination (two pictures on the right).

Following the methods described above, powder samples and octadecene were refluxed in toluene. This gave yellowish but clear and photoluminescent dispersions of silicon particles in toluene that remain clear after several months to 1 year of storage. Figure 1 shows octadecene-treated and untreated samples under room illumination and UV illumination. It is clear from Figure 1 that before octadecene surface treatment, the particle dispersion was cloudy. After surface treatment, the particle solution was clear and emitted very evenly. The color difference between the two emitting samples results from the fact that these pictures were taken about 6 weeks after the surface treatment was carried out, and the PL from untreated samples blue shifts over time, while that from the treated samples does not. Figure 2 shows TEM images of octadecene-treated silicon nanoparticles. The TEM images show individual particles less than 10 nm in diameter, as well as some larger particles that may be clusters of two, three, or four primary particles. The particles are well separated, indicating that particles in this dispersion do not agglomerate significantly, even during solvent evaporation from the TEM grid. From the high-resolution picture in Figure 2, we see that the etched particles kept their crystalline structure, with a crystal lattice spacing of ∼3.2 Å, roughly the same as that of bulk silicon. The shape of the particles is somewhat irregular.

The hydrosilylation reaction between the double bond in octadecene and the Si−H surface bond is evidenced by the FTIR absorption spectrum of the etched particles compared with the alkylated particles. For these measurements, excess octadecene was removed by dialysis after refluxing. Curves A−C of Figure 3 show FTIR spectra for untreated, etched particles, particles that were surface treated by octadecene and pure octadecene, respectively. Before surface treatment, there is strong peak at 2109 cm^{-1} that arises from Si−H bonds, indicating that particles were mostly Si−H terminated. There are also strong peaks at 1070−1080 cm^{-1}, which can be assigned to Si−O, indicating that this surface is not free of oxygen. After the sample was refluxed with octadecene, the FTIR spectrum for these particles has peaks characteristic of alkyl $C-H_x$ bonds at 2923, 2852, 1657, and 1468 cm^{-1} that are not present in the untreated sample. The intensity of the Si−H feature (2108 cm^{-1}) decreased significantly in the coated sample. Comparing the treated sample (curve B) to neat octadecene (curve C), we see that the C═C features (991, 908 cm^{-1}) have almost disappeared, while all other spectral features are retained. The above results confirm that the silicon particle surfaces have been coated covalently and Si−C bonds are formed (which should appear at ∼1083 cm^{-1}, overlapping with features due to Si−O bonds that are inevitably present). When particles were treated with octadecene, there was little or no shift in the PL spectrum from before to after treatment.

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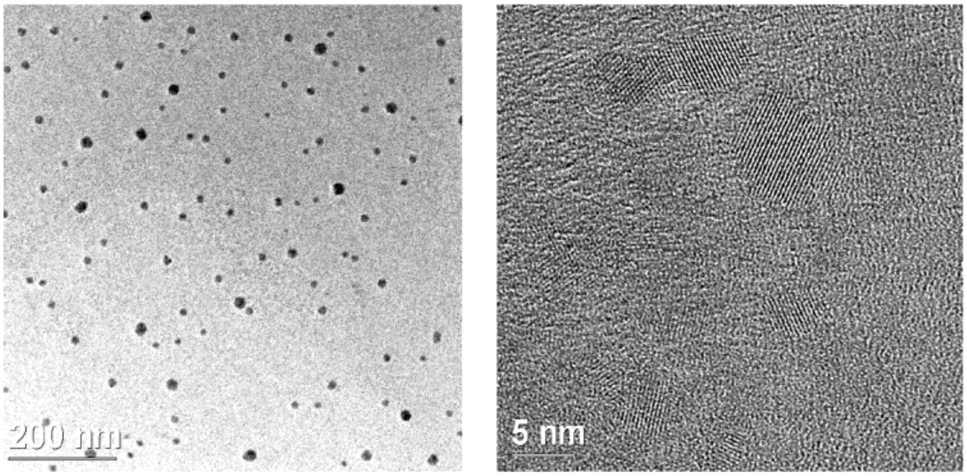

Figure 2. TEM images of particles coated with octadecene.

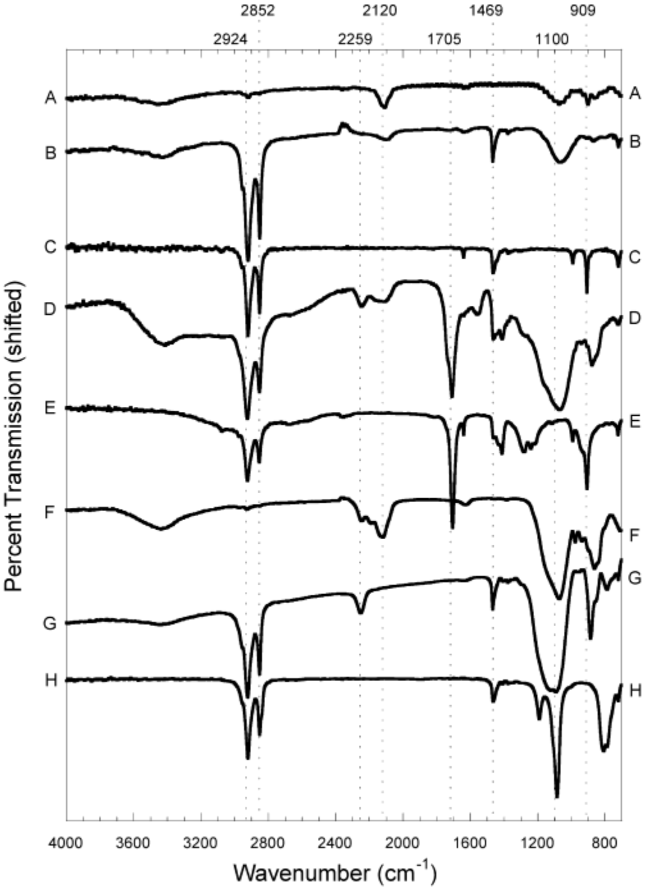

Figure 3. FTIR spectra for etched particles (A), octadecene-treated particles (B), neat octadecene (C), undecylenic acid treated particles (D), neat undecylenic acid (E), etched and HNO_3-washed particles (F), octadecyltrimethoxysilane-treated particles (G), and neat octadecyltrimethoxysilane (H).

3.2. Surface Functionalization of Si Nanoparticles with Undecylenic Acid. By using undecylenic acid instead of octadecene, it was possible to get a clear dispersion of the nanoparticles in a semipolar solvent such as ethanol. After refluxing the particles with undecylenic acid in 95% ethanol, we obtained a clear, yellowish dispersion that could pass through 0.1 μm filter paper without loss of color or photoluminescence. In most cases there was a blue shift in the PL spectrum from before to after surface treatment. This suggests that some oxidation is occurring during surface treatment. With undecylenic acid bound to the surface, it was possible to obtain an aqueous dispersion of the particles, but the clarity lasted only for a few days and eventually some turbidity developed.

Figure 3 shows FTIR spectra for etched (but untreated) particles (curve A), undecylenic acid treated particles (curve D), and pure undecylenic acid (curve E). Strong peaks corresponding to alkyl C$-$H$_x$ bonds at 2922, 2856, and 1467 cm^{-1} appear after treatment with undecylenic acid, along with a peak corresponding to the COOH group at 1704 cm^{-1}. Comparing the treated particles to neat undecylenic acid, we see that the peaks at 908.8 and 994.4 cm^{-1} for C═C double bond vibration are almost completely missing from the treated particles. Similarly, the peaks for Si$-$H bonds at 2119$-$2258 cm^{-1} are much weaker in the treated particles than in the untreated particles. Again, this provides clear evidence of the expected hydrosilylation reaction. The shift of the Si$-$H peak from predominantly a peak at 2120 cm^{-1} to a peak at 2258 cm^{-1} suggests that the remaining Si$-$H bonds are of the O$-$Si$-$H variety. This, in turn, further supports the hypothesis that surface oxidation occurs during the refluxing in 95% ethanol.

3.3. Surface Functionalization of Si Nanoparticles with Organosilanes. Because there are many commercially available organosilanes with various functional groups, surface functionalization of Si nanoparticles by silanization provides an attractive means of preparing the nanoparticles for linking with other materials via these functional groups. After production of etched particles with visible PL, these particles were surface treated to produce a Si$-$OH terminated surface that can react with organosilanes. This was done by washing particles with 20% HNO_3, or by refluxing them with concentrated sulfuric acid and hydrogen peroxide (Pirhana etch). Both methods provided a Si$-$OH terminated surface upon which silanization reactions could be carried out. After refluxing the particles with octadecyltrimethoxysilane in toluene, we obtained a clear, yellowish particle solution that emitted brightly under UV illumination and that passed through 0.1 μm filter paper with minimal loss of color or PL. This particle dispersion was also very stable and remains clear and photoluminescent after several months.

FTIR spectra were again applied to explore the surface state of the silicon particles before and after surface modification. Figure 3 shows FTIR spectra for etched silicon particles after washing with 20% HNO_3 (curve F), silicon nanoparticles coated by octadecyltrimethoxysilane in toluene (curve G) and pure octadecyltrimethoxysilane (curve H). After surface treatment with octadecyltrimethoxysilane, we expect to have an 18-member hydrocarbon chain attached to the silicon surface by Si−O−Si− bonds. As shown in Figure 3, the surface of the etched, HNO_3 washed silicon particles is a mixture of Si−OH (or Si−O−) and Si−H, as indicated by peaks at 3429, 1102 cm^{-1} (Si−OH and Si−O), and 2133−2253 cm^{-1} (Si−H). After surface treatment, strong peaks corresponding to hydrocarbon chain vibrations at 2879, 2952, and 1467 cm^{-1} appear. The Si−H peak is lower but still present. This indicates that Si−H bonds have been oxidized during this treatment, as one would expect for a Si−H surface heated in the presence of water and ethanol. The Si−OH feature at 3429 cm^{-1} has significantly decreased. This is presumably because most of the Si−OH groups have been converted to Si−O−Si. However, we cannot rule out the possibility that water makes a significant contribution to the 3429 cm^{-1} peak, since measurements were made in KBr pellets in air and KBr is somewhat hygroscopic. The peaks at 1102−1130 cm^{-1} are the joint contribution of Si−O−Si and Si−C. Again, these results suggest that the silane used in this section attached to the silicon surface covalently. Similar experiments were performed using the particles that had been treated with a sulfuric acid/hydrogen peroxide mixture (Pirhana etch). The results were almost identical to those using the HNO_3 treated particles. Although the Pirhana etch appears to create a more uniform −OH terminated surface, vide infra, it did not seem to provide for any greater degree of coating of the surface with octadecyltrimethoxysilane. Though the difference was not dramatic, it seemed that the Pirhana-etch treated particles were slightly less effectively coated with octadecyltrimethoxysilane than the HNO_3-treated particles. In a separate study, we have used the Pirhana-etch treated surface with bromopropyltrichlorosilane and found that it was very effective in that case.[44]

3.4. Study of Dependence of Si−H Coverage on Surface Treatment. Although it is well-known that for silicon wafers, a Si−H terminated surface can be generated easily by treatment with aqueous HF or NH_4F, it is still not clear how aqueous HF affects the surface state of our silicon particles. To optimize our reaction conditions to achieve better Si−H coverage on the silicon particle surface, preliminary experiments were conducted to explore the effects of HF concentration on Si−H coverage. Although it is inevitable that there will be some surface oxidation when we carry out the surface treatments and FTIR measurements in air, we still expect that more complete coverage of Si−H will benefit the reaction of alkenes on the silicon surface and provide for more complete hydrocarbon coverage of the surface.

Figure 4 shows FTIR spectra for particles washed with 3% (curve A), 5% (curve B), and 15% (curve C) aqueous HF solutions. Compared to the original particle surface (for nonluminescent particles before HF/HNO_3 etching), we found that etched particles possess much stronger FTIR peaks.[6] After etching with HF/HNO_3, followed by washing with HF, all silicon surfaces show strong Si−H stretching modes at 2040−2231 cm^{-1} and Si−O vibrations at ∼1070 cm^{-1}. Comparing the relative intensities of Si−H and Si−O, we find that lower HF concentration tends to produce stronger Si−H vibration peaks. The change in Si−H is substantial between 15% and 5% HF, while there is a smaller difference between samples etched with 5% and 3% HF solutions. Another significant change is that the Si−H peak for particles washed with 15% HF is much broader than that of particles washed with 5% and 3% HF solution. This suggests that the Si−H terminated surface generated by 5% and 3% HF is more uniform. The surface produced by 15% HF may contain SiH_2 and SiH_3 groups for which the frequencies are shifted to higher wavenumber.[19] However, O−Si−H would also produce absorption at similar positions. The broad peak at ∼3429 cm^{-1} is assigned to Si−OH or to moisture that has been absorbed by the KBr pellet. The stronger peak at 3429 cm^{-1} for particles washed by 15% HF suggests that this surface also contains more Si−OH than the other samples. This suggests that at high concentrations, HF can catalyze reaction of the surface with water to produce silanol groups. From these results it seems clear that a lower HF concentration is preferable for preparing a uniform Si−H surface on the nanoparticles.

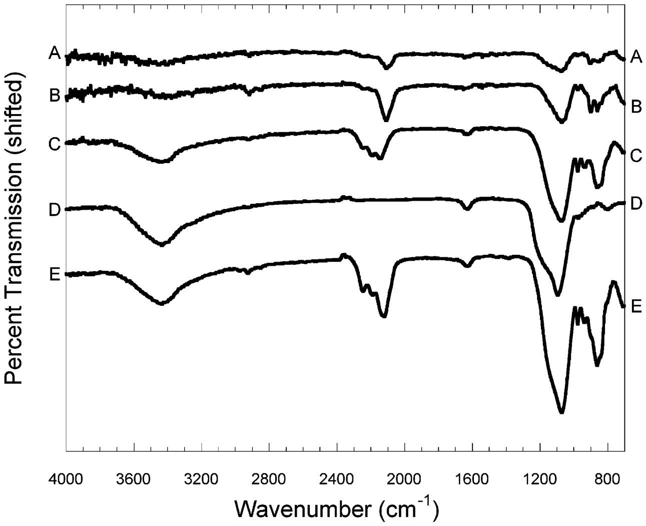

Figure 4. FTIR spectra of particles after HF/HNO_3 etching and subsequent treatment with 3% HF (A), 5% HF (B), 15% HF (C), concentrated H_2SO_4 and H_2O_2 (D), and 20% HNO_3 (E).

Curve D in Figure 4 shows the FTIR spectrum for etched particles refluxed with concentrated H_2SO_4 and 30% H_2O_2 (7:3 by volume, also known as Pirhana etch) for 30 min. As noted elsewhere,[44] the Pirhana etch results in a slight blue shift of the PL but does not lead to significant quenching of the photoluminescence from the particles. Compared to curves A−C, for the HF-treated particles, one significant change is that Si−H features at 2040−2231 cm^{-1} have disappeared almost completely. The large peak at ∼1070 cm^{-1} corresponds to Si−O. The strong, broad peak at ∼3430 cm^{-1} is assigned to Si−OH though some contribution to this peak may also come from H_2O adsorbed by the KBr pellet during measurement. For comparison, curve E in Figure 4 shows the FTIR spectrum for nanoparticles washed with 20% HNO_3. It is clear that the 2040∼2231 cm^{-1} peaks for Si−H_x are still present in this spectrum and thus that some Si−H termination remains. These results confirm that the H_2SO_4/H_2O_2 treatment provides a more uniform Si−OH surface on the nanoparticles than simple washing with HNO_3, and thus this treatment will be preferable if extremely dense coating by an organosilane is required, particularly when the surface will be treated with a chlorosilane rather than an alkoxysilane.[44] However, the OH termination provided by HNO_3 washing was adequate for surface functionalization with octadecyltrimethoxysilane and formation of a stable nanoparticle dispersion in toluene as described in the previous section. As also noted above, for the case of octadecyltrimethoxysilane, the H_2SO_4/H_2O_2 treatment did not provide any improvement in the coating relative to the HNO_3 treatment.

3.5. Stabilization of Photoluminescence by Alkylation. The photoluminescence properties of the alkylated

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(44) Li, Z.; Swihart, M. T.; Ruckenstein, E. *Langmuir* **2004**, *20*, 1963−1971.

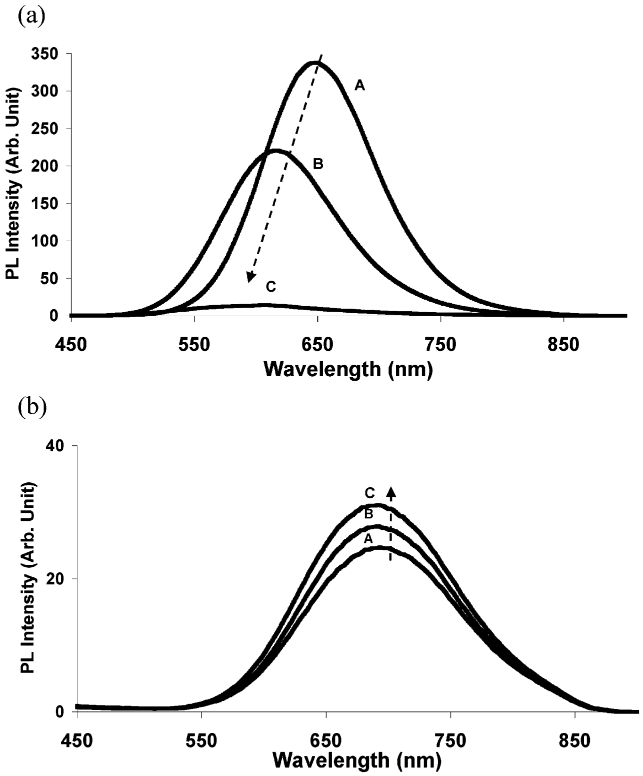

Figure 5. (a) Instability of the PL spectrum of untreated sample. Spectrum immediately after preparation (A) and after 1 day (B) and 12 days (C) of storage in toluene. (b) Stability of PL spectra of treated (alkylated) sample. Spectrum immediately after preparation (A) and after 35 days (B) and 60 days (C) of storage in toluene.

samples were greatly stabilized against degradation compared to untreated particles. Figure 5a shows PL spectra for an untreated, etched sample in toluene at different times after preparation. The peak PL intensity (in arbitrary units, but for identical measurements) dropped by 35% after 1 day. The peak PL intensity dropped further to only 4% of its initial value after 12 days. There is also a substantial blue shift in PL for this sample, with the peak shifting from 649 to 616 nm after 1 day and then to 606 nm after 12 days. It is likely that this is due to oxidation during storage of the particle dispersion in air.

Figure 5b shows the stability of the PL spectrum of a sample that had been treated with octadecene as described above. It was stored in air for 60 days with almost no change in PL intensity and no shift in PL peak position, while the PL spectrum of the untreated sample decreased in intensity by a factor of about 24 and blue-shifted substantially in only 12 days. Both samples were stored in toluene under identical conditions. There is a slight red shift of the PL spectrum for the treated particles compared with untreated, etched particles. However, after surface treatment, the PL did not show any additional changes. The slight increase in PL intensity of the octadecene-coated sample in Figure 5b with storage time could come from a small amount of solvent evaporation during storage in an ordinary sample vial. Note that neither the absorbance nor concentration has been equalized between the untreated and treated sample, so one cannot compare the absolute magnitudes directly between the two samples. However, the change for each sample can be compared quantitatively.

The stabilization of PL by the coating is attributed to the covalent passivation of the surface by the hydrocarbon, which prevents oxidation of the nanoparticle surface. Complete stabilization should require that the density of molecules on the surface is sufficient to block transport of oxidizers to the surface. So, the quality of the coating is important in determining the degree of stabilization that can be achieved. The PL of samples treated with undecylenic acid was also stabilized somewhat, but not to the same extent as for octadecene-treated particles. This could reflect a difference in the quality of the coating produced in the two cases, and improved undecylenic acid coatings may eventually provide the same long-term stabilization as octadecene coatings. As described above, it appears that some surface oxidation occurred during the treatment with undecylenic acid, and therefore we expect that the coating is less complete than for the treatment with octadecene. Solvent effects are also likely to be important. Untreated particles degrade more rapidly when dispersed in ethanol or other alcohols than when dispersed in toluene and degrade even more rapidly in water. More rapid degradation in alcohols than in toluene may be related to the greater solubility of oxygen and water in the alcohols than in toluene, or the alcohols may actually be involved in the degradation reactions. In particular, hydrogen bonding interactions between the solvent and surface hydroxyl groups are possible in ethanol and ethanol/water mixtures, but not in toluene.

3.6. Study on Size Selective Precipitation of Coated Silicon Nanoparticles. Size selective precipitation is a well-known technology that has been applied for size classification of nanoparticle dispersions of materials such as cadmium sulfide and cadmium selenide.[45,46] The ability of a solvent to disperse particles is decreased by the addition of a miscible nonsolvent to the point of particle agglomeration. The larger particles agglomerate first as a result of their greater van der Waals attraction to each other. The agglomerated fraction, rich in larger particles, is precipitated under centrifugation, leaving smaller particles dispersed in the solvent. This process is reversible, so the precipitated fraction can be redispersed into the initial solvent. After surface functionalization with octadecene, size-selective precipitation can be applied to these polydisperse silicon nanoparticle samples. Because the PL of these particles is size-dependent, if there is a way to separate particles of different sizes, then we should be able to tune and narrow the PL spectrum.

For the size-selective precipitation studies, the nanoparticles were coated with octadecene in chloroform rather than in toluene. Dialysis of the clear, well-dispersed particle solution against chloroform was carried out at least twice to remove excess octadecene. Then a few milliliters of this dispersion were transferred to a vial to which methanol was slowly added dropwise. At some point particles started to agglomerate and the solution changed from very clear to slightly cloudy. The solution was then sonicated for 20 min and then centrifuged (VWR Scientific, model V centrifuge) at 8000 rpm for 10 min to separate the deposit. The solid deposit was redispersed in chloroform. The resulting sample was enriched in the larger particles. The process was repeated with the clear solution for further separation of particles of different sizes. A series of samples with different average sizes can be obtained by repeating the above procedure.

Figure 6 shows normalized PL spectra for samples prepared by size-selective precipitation. The peak of the PL spectrum of the original etched sample is 610 nm,

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(45) Murray, C. B.; Norris, D. J.; Bawendi, M. G. *J. Am. Chem. Soc.* **1993**, *115*, 8706−8715.

(46) Murray, C. B.; Kagan, C. R.; Bawendi, M. G. *Annu. Rev. Mater. Sci.* **2000**, *30*, 545−610.

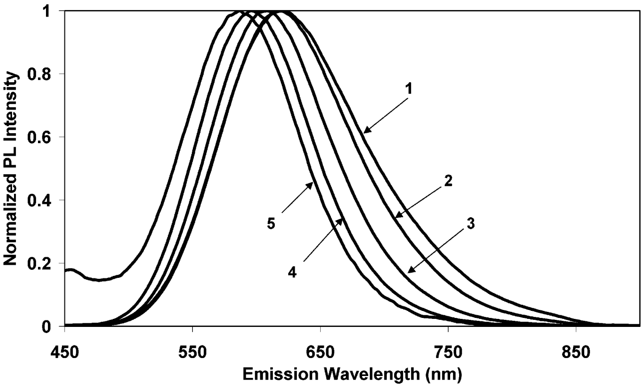

Figure 6. Normalized PL spectra from octadecene-coated particles in chloroform after size selective precipitation. For samples 1−5, which were successively precipitated, the peak of the PL spectrum is at 620, 619, 608, 596, and 588 nm, respectively.

while peaks of samples 1 through 5 are at 620, 619, 608, 596, and 588 nm, shifting toward the blue. For size-dependent PL, shorter PL peak positions should correspond to smaller particle sizes. With increasing addition of methanol, the polarity of the solution increased and the size of the separated particles decreased. Note that the PL spectrum of the first separated particle fraction (sample 1) does not shift much from the PL spectrum of the original etched particles. This suggests that there are some remaining agglomerates that consist of primary particles with a size distribution similar to that of original etched particles and that this fraction of the particles precipitated first. This process provides us with an additional method to control the PL of coated particles.

4 Summary and Conclusions

Surface-treated silicon nanoparticles were prepared by reaction with several reagents. Si−H terminated particle surfaces were generated by washing particles with aqueous HF solution. The relation between Si−H coverage and HF concentration was studied. Alkenes, such as octadecene and undecylenic acid, were attached to the particle surface via hydrosilylation reactions. FTIR spectra confirmed that these reagents were covalently bound to the silicon surface. Si−OH terminated surfaces were generated by washing particles with 20% HNO_3 or with concentrated sulfuric acid and hydrogen peroxide. Commercially available silanes can be attached to this surface, and the FTIR results confirmed that octadecyltrimethoxysilane had been bound to the silicon surface covalently. These coated particle dispersions are very clear and can easily pass through 0.1 μm filter paper. Surface coating of silicon nanoparticles increased the stability of their PL substantially. Dispersions of octadecene-coated particles can be stored in air under fluorescent lighting for months without any measurable change in PL peak position or any decrease in PL intensity. Untreated samples usually experienced significant changes in PL peak position and intensity over a period of a few days. The surface-treated particle dispersions can be purified by dialysis and size exclusion chromatography. These separation technologies provide convenient methods for producing “clean” particle dispersions. It is crucial to remove excess reagents from the particle dispersion in order to obtain high-quality TEM images and to prevent interference with subsequent processing of the particles. TEM imaging confirmed that there are crystalline nanoparticles with size less than 5 nm in the surface−treated, luminescent particle dispersion. Size selective precipitation provided an additional means of tuning and narrowing the PL spectra.

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