Organically Capped Silicon Nanoparticles with Blue Photoluminescence Prepared by Hydrosilylation Followed by Oxidation

Fengjun Hua, Folarin Erogbogbo, Mark T. Swihart, and Eli Ruckenstein*

Department of Chemical and Biological Engineering, The University at Buffalo (SUNY), Buffalo, New York 14260-4200

A facile method of preparing stable blue-emitting silicon nanoparticles that are dispersible in common organic solvents is presented. Oxidation of yellow-emitting silicon nanoparticles with an organic monolayer grafted to their surface, using either UV irradiation in solution or heating in air, converted them to blue-emitting particles. The evolution of the PL spectrum and infrared absorption spectrum of the particles was followed during the oxidation process. The PL spectrum showed a decrease in the PL emission peak near 600 nm and the appearance and increase in intensity of a PL emission peak near 460 nm rather than a smooth blue shift of the emission spectrum from yellow to blue. The organic monolayer grafted to the particle surface was not degraded by this oxidation process, as demonstrated by FTIR and NMR spectroscopy. Similar results were achieved for particles with styrene, 1-octene, 1-dodecene, and 1-octadecene grafted to their surface, demonstrating that it is the silicon nanocrystal, and not the organic component, that is essential to this process. The organic monolayer allows the nanoparticles to form stable, clear colloidal dispersions in organic solvents and provides for the possibility of further chemical functionalization of the particles. Combined with previous work on organically grafted silicon nanoparticles with green through near-infrared emission, this enables the efficient and scalable preparation of stable colloidal dispersions of organically grafted silicon nanoparticles with emission spanning the entire visible spectrum.

Introduction

Luminescent silicon nanoparticles have been widely studied in recent years on the basis of their potential use as light emitters in displays or general illumination and as fluorescent probes for bioimaging. Several methods have been developed for preparing them, including fracturing of porous silicon by ultrasonication,[1,2] inverse micellar growth,[3] laser ablation,[4,5] thermal decomposition of organosilane precursors in supercritical solvents,[6,7] solution-phase methods,[8–11] plasma decomposition of silane,[12,13] and vapor-phase thermal decomposition of silane or disilane.[14–16] Si particles ranging from 1 to 5 nm in diameter exhibit PL emission ranging from blue to the near-infrared. The small size of these nanocrystals widens the band gap due to quantum confinement effects, relaxes the selection rules that decrease the efficiency of radiative recombination in indirect band gap materials, and reduces the probability of nonradiative recombination at defects. Both nonradiative and radiative recombination may occur at the nanocrystal surface as well as within the core of the nanoparticle. Therefore, the origin and characteristics of the luminescence are associated with both the crystallite size and with the nature of the crystallite surface. In particular, as Wolkin et al. pointed out, the presence of oxygen at the particle surface can introduce states within the band gap that lead to red-shifted emission.[17] An effective means of stabilizing the silicon surface and photoluminescence properties is to graft an organic monolayer to it through hydrosilylation of a hydrogen-terminated surface[18–22] or through organosilane chemistry on a hydroxyl-terminated surface.[20,23,24] However, this has not generally been possible for blue-emitting silicon nanoparticles (∼1 nm in diameter). The preparation of organically protected silicon nanoparticles with blue emission that remains stable in air has been a persistent challenge that has limited the possibility of using silicon nanoparticles in potential applications such as full-color displays or general illumination where full coverage of the visible spectrum is required. Alkyl-capped silicon nanoparticles prepared in solution have shown UV-to-blue photoluminescence, but in that case the alkyl groups were readily displaced from the surface by

* To whom correspondence should be addressed. E-mail: feaeliru@acsu.buffalo.edu.

(1) Belomoin, G.; Therrien, J.; Smith, A.; Rao, S.; Twesten, R.; Chaieb, S.; Nayfeh, M. H.; Wagner, L.; Mitas, L. *Appl. Phys. Lett.* **2002**, *80*, 841–843.

(2) Yamani, Z.; Ashhab, S.; Nayfeh, A.; Thompson, W. H.; Nayfeh, M. *J. Appl. Phys.* **1998**, *83*, 3929–3931.

(3) Wilcoxon, J. P.; Samara, G. A.; Provencio, P. N. *Phys. Rev. B* **1999**, *60*, 2704–2714.

(4) Carlisle, J. A.; Dongol, M.; Germanenko, I. N.; Pithawalla, Y. B.; El-Shall, M. S. *Chem. Phys. Lett.* **2000**, *326*, 335–340.

(5) Carlisle, J. A.; Germanenko, I. N.; Pithawalla, Y. B.; El-Shall, M. S. *J. Electron Spectrosc.* **2001**, *114–116*, 229–234.

(6) English, D. S.; Pell, L. E.; Yu, Z. H.; Barbara, P. F.; Korgel, B. A. *Nano Lett.* **2002**, *2*, 681–685.

(7) Holmes, J. D.; Ziegler, K. J.; Doty, R. C.; Pell, L. E.; Johnston, K. P.; Korgel, B. A. *J. Am. Chem. Soc.* **2001**, *123*, 3743–3748.

(8) 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.

(9) Baldwin, R. K.; Pettigrew, K. A.; Ratai, E.; Augustine, M. P.; Kauzlarich, S. M. *Chem. Commun.* **2002**, *17*, 1822–1823.

(10) Bley, R. A.; Kauzlarich, S. M. *J. Am. Chem. Soc.* **1996**, *118*, 12461–12462.

(11) Heath, J. R. *Science* **1992**, *258*, 1131–1133.

(12) Bapat, A.; Perrey, C. R.; Campbell, S. A.; Carter, C. B.; Kortshagen, U. R. *J. Appl. Phys.* **2003**, *94*, 1969–1974.

(13) Shen, Z.; Kim, T.; Kortshagen, U. R.; McMurry, P. H.; Campbell, S. A. *J. Appl. Phys.* **2003**, *94*, 2277–2283.

(14) Littau, K. A.; Szajowski, P. J.; Muller, A. J.; Kortan, A. R.; Brus, L. *J. Phys. Chem.* **1993**, *97*, 1224–1230.

(15) Schuppler, S.; Friedman, S. L.; Marcus, M. A.; Adler, D. L.; Xie, Y.-H.; Ross, F. M.; Harris, T. D.; Brown, W. L.; Chabal, Y. J.; Brus, L. E.; Citrin, P. H. *Phys. Rev. Lett.* **1994**, *72*, 2648–2650.

(16) Wilson, W. L.; Szajowski, P. J.; Brus, L. *Science* **1993**, *262*, 1242–1244.

(17) Wolkin, M. V.; Jorne, J.; Fauchet, P. M.; Allan, G.; Delarue, C. *Phys. Rev. Lett.* **1999**, *82*, 197–200.

(18) Hua, F.; Swihart, M. T.; Ruckenstein, E. *Langmuir* **2005**, *21*, 6054–6062.

(19) Li, Z. F.; Ruckenstein, E. *Nano Lett.* **2004**, *4*, 1463–1467.

(20) Li, X.; He, Y.; Swihart, M. T. *Langmuir* **2004**, *20*, 4720–4727.

(21) Buriak, J. M. *Chem. Rev.* **2002**, *102*, 1271–1308.

(22) Buriak, J. M.; Allen, M. J. *J. Lumin.* **1999**, *80*, 29–35.

(23) Ruckenstein, E.; Li, Z. F. *Adv. Colloid Interface Sci.* **2005**, *113*, 43–63.

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

reaction with air.[25] More recently, siloxane-coated silicon nanoparticles with blue emission were prepared in solution and shown to be very stable against further reaction or degradation.[26] Silicon nanoparticles with blue emission have also been prepared from porous silicon.[1]

We developed a method for preparing macroscopic quantities of luminescent H-passivated silicon nanoparticles with emission ranging from red to green by CO_2 laser-driven decomposition of SiH_4-H_2-He mixtures, followed by etching with a concentrated HF/HNO$_3$ mixture as described previously.[18,20,27] These H-terminated luminescent silicon particles were reacted with double-bond-terminated molecules including 1-pentene, 1-hexene, 1-octene, 1-decene, 1-octadecene, styrene, vinyl acetate, ethyl undecylenate, 1-hexen-5-ol, and 10-undecen-1-ol by photoinitiated hydrosilylation.[18] This yielded organic monolayer-protected silicon particles with high surface coverage of the grafted organic molecule. We also demonstrated previously that blue-emitting silicon particles could be generated by the rapid oxidation of yellow-emitting particles, without any organic molecules attached to their surface, at 400 °C for 1 min.[27] However, oxidized particles prepared in that manner did not readily disperse in any solvent and had poor processability. Furthermore, the rapid thermal process is relatively difficult to control.

Here we demonstrate that organically grafted blue-emitting silicon nanoparticles can be prepared by the slow oxidation of silicon nanoparticles that, prior to oxidation, emitted in the yellow region of the visible spectrum. This oxidation can be driven by UV irradiation at 254 nm or by heating to ~140 °C in air. These organically grafted particles resisted oxidation when heated at lower temperatures or when exposed to longer-wavelength UV excitation.[18] In contrast, when these same particles were oxidized without first having an organic monolayer grafted to their surface, their PL diminished in intensity. If the untreated particles (without the organic monolayer) initially emitted in the red, then their PL blue shifted upon oxidation, but if they initially emitted green or yellow, then their PL red shifted upon oxidation. This was also the case when the grafting was carried out without removing dissolved oxygen from the organic reagent. This behavior is consistent with the explanations put forward by Wolkin et al.[17] that reduction in the size of the silicon core by oxidation increases the band gap energy due to increased quantum confinement but that the blue shift of the emission is limited by the formation of oxygen-related states within the band gap. If the oxide-free particles emit at an energy higher than that associated with these oxygen-related states, then oxidation will lead to a red shift in the PL via introduction of the new oxygen-related states.

Experimental Section

Materials. Silane (SiH_4), (electronic grade, Scott Gases), 1-octene (Acros, 99+ wt %), 1-dodecene (Acros, 94 wt %), 1-octadecene (Acros, tech, 90 wt %), and styrene (Aldrich, 99 wt %, 15 ppm 4-*tert*-butylcatechol), were used as received. The Si nanoparticles were prepared by dissociating silane (SiH_4) via heating with a CO_2 laser beam (Coherent, model 42, 60 W) in an aerosol reactor, as described in detail previously.[25] The resulting particles, ranging from 5 to 10 nm in diameter, were collected on cellulose nitrate membrane filters. They did not exhibit photoluminescence and were not readily dispersed in common solvents.

Etching Procedure. The etching protocol used here was optimized to produce hydrogen-terminated particles with very little oxygen on their surface and has been described in detail previously.[18] The particles were etched with an acid mixture of HF (48 wt %) and HNO$_3$ (69 wt %) (10/1, v/v). In a typical experiment, 20 to 50 mg of silicon nanoparticles was dispersed via sonication into 2 to 6 mL of methanol. The acid mixture (11 mL) was added to the resulting dispersion. The particle sizes decreased and the particle surfaces were passivated during this etching process. As a result, the particles exhibited bright, visible photoluminescence. The color of the photoluminescence changed from red to yellow to green as the etching proceeded. The etching rate decreased with increasing amounts of methanol used to disperse the particles initially. When the desired emission color was reached, the etching was slowed by adding about 10 mL of methanol or a methanol/water mixture (1/3, v/v). The particles were collected on a polyvinylidene fluoride (PVDF) membrane filter (pore size 100 nm) and washed with a large amount of the water/methanol mixture to remove any adsorbed acid mixture. Finally, the particles were rinsed with pure methanol. The etching time required to obtain yellow-emitting particles was typically from 4 to 12 min. This time varies significantly with the initial particle size, age of the unetched particles, and exact composition of the etching solution.

Photoinitiated Hydrosilylation. The freshly etched hydrogen-terminated silicon nanoparticles were transferred into a 25 mL Aldrich Schlenk-type reactor containing a magnetic stirrer and 2 to 3 mL of the compound that was to be grafted to the particles via photoinitiated hydrosilylation. In the present work, styrene, 1-octene, 1-dodecene, and 1-octadecene were grafted to the hydrogen-terminated nanoparticles, but a variety of other compounds with a terminal double bond can be grafted to the particles by the same basic procedure.[18] Sonication was used to disperse the particles, but a stable colloidal dispersion was not formed, and the reactor contents remained cloudy in all cases. The reactor was attached to a high-vacuum line, and the contents were degassed using at least three freeze−thaw cycles. A Rayonet photochemical reactor (Southern New England Ultraviolet Co.) equipped with 10 RPR-2537 Å UV tubes was used to initiate the hydrosilylation reaction. The reaction time required varied substantially depending on the compound being attached to the particles and the particle size, as described previously.[18] Typical reaction times were 5 min for styrene, 45 min for 1-octene or 1-dodecene, and 60 min for 1-octadecene. After reaction, a clear dispersion was obtained. It was drawn through a PTFE syringe filter (pore size 0.45 μm).[28] Excess styrene or 1-octene was evaporated under vacuum at room temperature. Excess 1-dodecene was removed under vacuum at 60 °C, and 1-octadecene was removed in a vacuum oven at 90 °C. After the photoinitiated hydrosilylation, some unreacted hydrogen always remained on the nanoparticle surface, as evidenced by FTIR spectroscopy.

Oxidation of Grafted Silicon Particles under UV Radiation in Air. Dry-grafted silicon particles were dispersed in 3 mL of chloroform or toluene, and the solution was capped (to prevent solvent evaporation) and subjected to UV radiation in a Rayonet photochemical reactor equipped with 10×RPR-2537 Å UV tubes in the presence of air. In this case, the solvent was not degassed and presumably remained saturated with dissolved oxygen. During the oxidation, the PL and FTIR spectra were followed as described below. The time required for the emission to shift from yellow to blue varied from as little as 2 h for some styrene-grafted samples to more than 12 h for some samples with long-chain alkanes grafted to their surface. Details of the time course of the reaction are given in subsequent sections of this article. After reaction, the particle dispersion was passed through a PTFE syringe filter (pore size 0.45 μm), and the solvent was evaporated. The resulting sample was readily redispersed in chloroform or toluene.

Thermal Oxidation of Grafted Silicon Particles at 140 °C in Air. Dry, grafted silicon particles were introduced into a 3 mL vial and placed into an oven at 140 °C. The oven contained room air and

(25) Yang, C.-S.; Bley, R. A.; Kauzlarich, S. M.; Lee, H. W. H.; Delgado, G. R. *J. Am. Chem. Soc.* **1999**, *121*, 5191−5195.

(26) Zou, J.; Baldwin, R. K.; Pettigrew, K. A.; Kauzlarich, S. M. *Nano Lett.* **2004**, *4*, 1181−1186.

(27) Li, X.; He, Y.; Talukdar, S. S.; Swihart, M. T. *Langmuir* **2003**, *19*, 8490−8496.

(28) In ref 18 the pore size of this filter was incorrectly written at 0.45 nm. The correct pore size is 0.45 μm, or 450 nm.

was not purged. After 1 day, the solid sample was cooled to room temperature and dispersed in 3 mL of chloroform or toluene. The resulting dispersion emitted blue under a handheld UV lamp (355 nm). For futher characterization, the dispersion was passed through a PTFE syringe filter (pore size 0.45 μm), and then the solvent was removed using a rotary evaporator.

Characterization. Fourier transform infrared (FTIR) spectra were obtained using a Mattson Galaxy Series 5000 FTIR spectrometer. The spectra for grafted silicon particles were determined in the horizontal attenuated total reflectance (ATR) mode of the spectrometer by casting a drop (chloroform or toluene dispersion) on the internal reflection element card and allowing the solvent to evaporate. ^{1}H and ^{13}C NMR spectra were obtained using a 400 MHz INOVA-400 NMR. Photoluminescence (PL) spectra were recorded using a Perkin-Elmer model LS-50 fluorescence spectrometer with a 390 nm emission cutoff filter. The excitation wavelength was set at 355 nm, and emission scanning was carried out from 400 to 900 nm. For each PL measurement made during the course of the oxidation process, 50 μL of the silicon nanoparticle dispersion was added to 2 mL of toluene in a quartz cuvette. Quantum yield (QY) measurements were made under illumination from a 404 nm LED using an integrating sphere to collect emission. The QY was determined by reference to two standard dyes, coumarin 102 and coumarin 522B. High-resolution transmission electron microscopy (HRTEM) and electron diffraction were carried out using a JEOL model JEM 2010 microscope at an acceleration voltage of 200 kV.

Results and Discussion

When carrying out photoinitiated hydrosilylation of green-emitting particles with styrene, we observed that the PL emission red shifted if exposure to 254 nm UV light was continued after the hydrosilylation was complete. This appeared to result from partial surface oxidation of the silicon particles by traces of oxygen still present in solution after the styrene had been degassed by multiple freeze–thaw cycles on the basis of the appearance of Si–O–Si stretching vibrations at 1050 cm^{-1} in the FTIR spectrum of the particles after 3 min of reaction. This oxidation could introduce states within the band gap leading to red-shifted emission or loss of emission. Furthermore, after the particles were dried at 70 °C for 100 h in air, the emission red shifted further from light green to yellow while the intensity of the Si–H stretching vibration decreased because of the further oxidation of remaining Si–H$_x$ on the silicon particle surface. Thus, styrene-grafted particles that initially had green emission showed a red shift of their PL and a decrease in PL intensity when they were oxidized. This is qualitatively the same change seen by others and seen by us for particles without organic molecules grafted to their surfaces. However, styrene-grafted silicon particles that had yellow or orange emission before oxidation exhibited qualitatively different behavior. The remainder of this section describes only experiments starting from particles that had been etched for a shorter time to produce samples with orange or yellow emission. Styrene was grafted to the surface of these particles as described above. When the styrene-grafted yellow-emitting particles were dispersed in chloroform or toluene, from which dissolved oxygen had not been removed, and were further treated with UV radiation at 254 nm, a change in their emission from yellow to blue was observed as shown in Figure 1.

This oxidation process and transformation from yellow to blue emission was followed using photoluminescence spectroscopy and FTIR spectroscopy as shown in Figure 2. Initially, the emission peak near 580 nm decreased in intensity and slightly red shifted with increasing irradiation time, as shown in Figure 2a. All PL spectra in Figure 2a were measured under identical conditions and were normalized to the peak intensity of the initial spectrum before irradiation. Thus, the intensities are directly
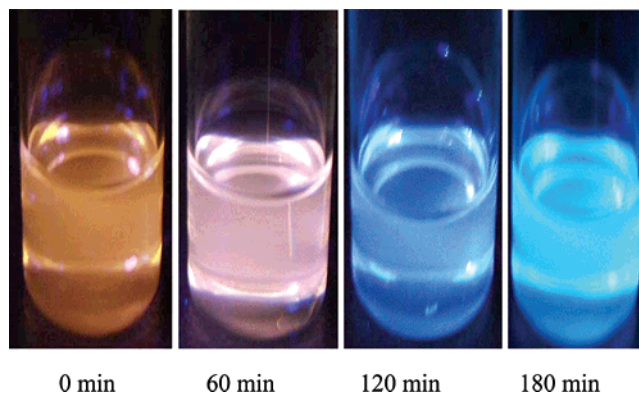

Figure 1. Photographs showing photoluminescence from styrene-grafted silicon nanoparticles after different periods of time under 254 nm UV illumination. For the photographs, the particles were illuminated with a 355 nm handheld UV lamp.

comparable among the different spectra in this Figure. It should be noted that the red shift in the overall yellow emission peak cannot necessarily be associated with a red shift in the emission from a given particle. A more likely explanation is that the largest particles, which emit at longer wavelengths, are somewhat less reactive toward oxidation. If that is the case, then the emission intensity from the large particles would decrease more slowly than that from the smaller particles, resulting in a red shift of the spectrum from the ensemble of particles. At any given wavelength outside of the blue peak, the emission intensity decreases monotonically with time. Note that Figure 2 presents results for a different sample than that shown in the photographs in Figure 1. The time required for oxidation and change of the PL emission color varied somewhat from sample to sample. The sample shown in Figure 1 oxidized faster than the sample for which data are shown in Figure 2. Although the quantum yield (QY) for a single sample was not followed during the course of the oxidation process, the QY was measured for two styrene-grafted samples after oxidation. Under 404 nm excitation, those two samples had peak emission wavelengths of 485 and 487 nm and QYs of 6.6 ± 1.5 and 7.1 ± 1.5%, respectively. This is roughly the same as the typical QY measured for yellow-emitting styrene-grafted particles, which ranges from 2 to 10% for samples prepared in our laboratory by the methods used here. In cases such as that shown in Figure 2 where the peak intensity of the blue emission was lower than that of the initial yellow emission, changes in the absorption cross section of the particles are also occurring, so this intensity decrease cannot directly be interpreted as a decrease in QY. Once the UV oxidation was ended, the blue emission was quite stable. Samples stored as dispersions in toluene under room illumination and the ambient atmosphere have thus far maintained their blue luminescence, as well as their colloidal stability, for at least 8 months.

The infrared spectrum of the particles was measured during the course of this photooxidation by extracting ~200 μL of the silicon particle dispersion, dropping it on the internal reflection element of the spectrometer's attenuated total reflectance (ATR) accessory, and allowing the solvent to evaporate. The IR spectrum of the particle film was then measured in the horizontal ATR mode of the FTIR spectrometer. Figure 2b shows the FTIR spectra from the same sample whose PL spectra are shown in Figure 2a. During the first hour of irradiation, the primary change in the PL spectrum is the decrease in intensity and slight red shift of the yellow emission. The most notable change in the IR spectrum during this time is the appearance of a broad absorption peak near 1050 cm^{-1} that corresponds to Si–O stretching. During this time, there is no dramatic change in the absorption peak near
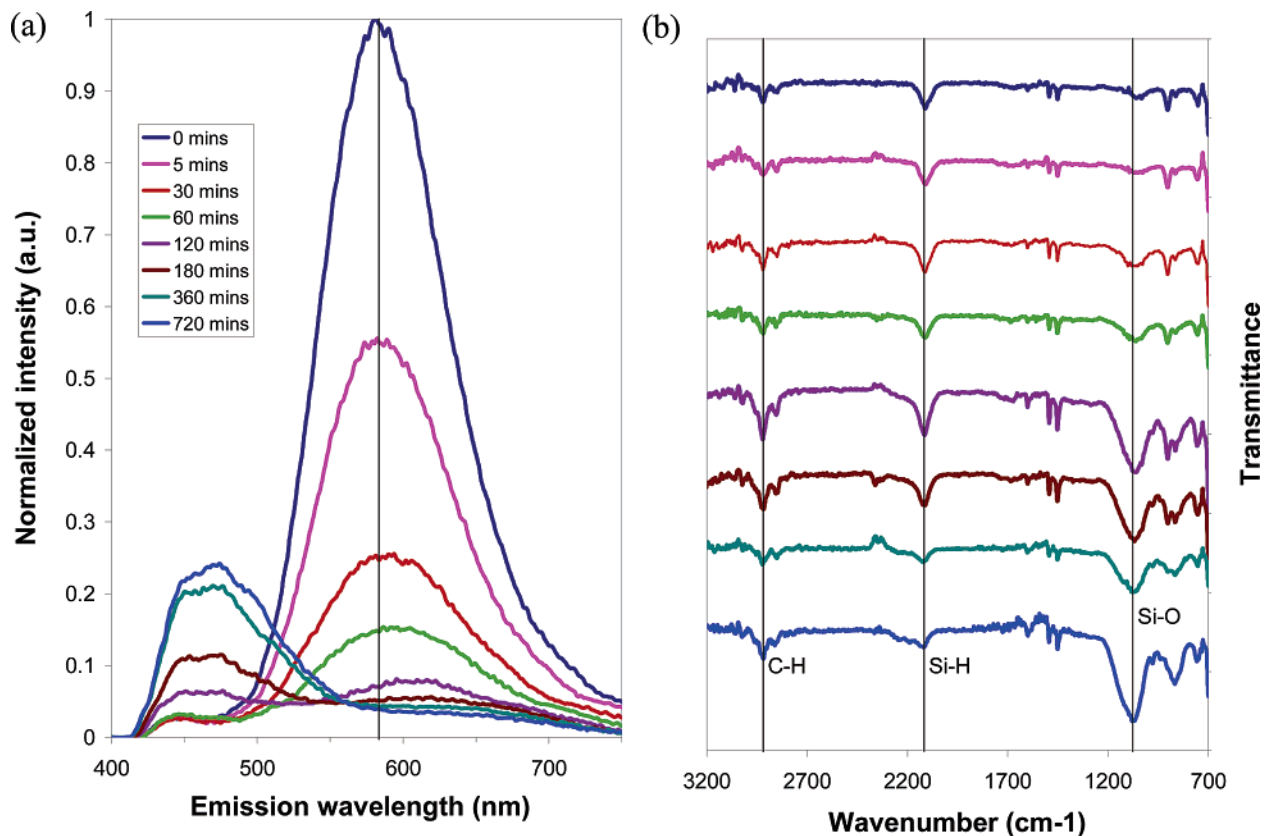
Figure 2. (a) PL spectra and (b) FTIR spectra of styrene-grafted silicon particles after different periods of time under 254 nm UV illumination in toluene. All PL spectra are normalized to the initial spectrum so that relative intensities can be compared between them. PL and FTIR spectra are from the same experiment at corresponding times, as indicated by the line colors.
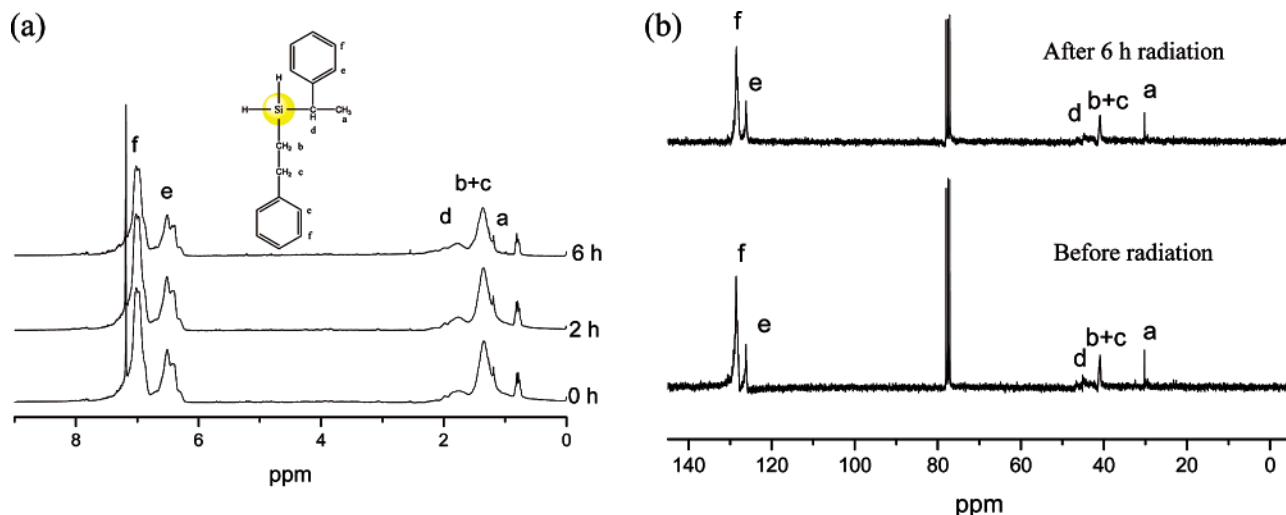

Figure 3. (a) ^{1}H NMR and (b) ^{13}C NMR spectra from styrene-grafted silicon particles before and after UV irradiation at 254 nm.

2100 cm^{-1} that corresponds to Si−H stretching frequencies. This suggests that oxidation is occurring without displacing hydrogen from the surface. After 2 h, the intensity of the Si−H peak relative to the hydrocarbon modes near 2900 cm^{-1} has decreased somewhat. At irradiation times from 2 to 6 h, the primary change in the PL spectrum is an increase in the intensity of the blue emission. The intensity of the Si−O infrared absorption relative to the Si−H features continues to increase during this time, but no new features appear. The Si−H peak continues to decrease during this time. Between 6 and 12 h, there is little further change in the PL spectrum or the FTIR spectrum. Even after 12 h of irradiation, there is still a small amount of Si−H remaining in this sample. The IR absorption peaks characteristic of the styrene

moiety (ν(CH$_3$, CH$_2$, or CH) at 2940−2865 cm^{-1}, ν(C═C, skeletal in-plane vibration of benzene ring) at 1610 and 1495 cm^{-1}, and δ(CH$_2$) at 1449 cm^{-1}), remained stable throughout the 12 h of irradiation. This indicates that oxidation did not displace or oxidize the organic groups grafted to the surface.

To investigate the stability of the organic monolayer under UV irradiation further, in a separate experiment ^{1}H NMR and ^{13}C NMR were performed on a dispersion of the particles in deuterated chloroform, as shown in Figure 3. The proton signals in Figure 3a (δ = 7.15, 6.55 (aromatic protons, m), 2.03 (CH, s), 1.60−1.0 (CH$_2$, m), 0.90 (CH$_3$, m)) can be assigned as shown schematically in the inset. These signals were unchanged by UV radiation and the accompanying oxidation. No new peaks were
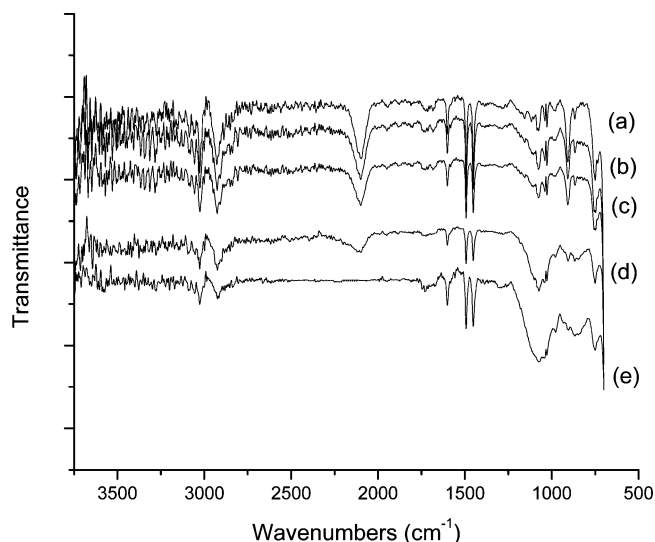
Figure 4. Oxidation of styrene-grafted silicon particles upon heating in air. FTIR spectra are shown for particles after (a) 0, (b) 60, (c) 600, and (d) 6000 min at 70 °C and (e) after 1 day at 140 °C.

observed. Similarly, ^{13}C NMR spectra (Figure 4b) showed that the organic monolayer was not degraded. The treated styrene-grafted silicon particles formed clear, stable colloidal dispersions in chloroform, dichloromethane, toluene, tetrahydrofuran, dimethylformamide, and dimethyl sulfoxide. The lack of change in the NMR spectra and in the organic-related components of the FTIR spectrum, along with the fact that the particles maintained their blue emission in different solvents, provides evidence that the blue emission comes from the silicon nanoparticles and does not arise from the organic monolayer or the solvent. UV illumination of styrene in toluene under the same conditions does not lead to any luminescence. UV illumination of particles without an organic monolayer on their surface, whether as a powder or in a solvent from which dissolved oxygen has not been removed, leads to a reduction in intensity or a complete loss of yellow luminescence but does not lead to blue luminescence from them. Although toluene was used as the solvent in all UV-induced oxidation experiments reported here, similar results were obtained for particles dispersed in chloroform and for dry films of particles without any solvent.

The same oxidation-induced blue shift of the photoluminescence could be achieved by extended heating of the particles in air at 140 °C. After 1 day of heating, oxidation similar to that generated by UV irradiation was observed. However, the particles were quite resistant to oxidation when heated at lower temperatures. Figure 4 shows FTIR spectra for styrene-grafted silicon nanoparticles after different periods of heating at 70 °C and for the same particles after heating for 1 day at 140 °C. Even after more than 4 days at 70 °C, there was residual hydrogen remaining on the particle surface, and the PL emission was not significantly changed. However, after 1 day at 140 °C, substantial oxidation had occurred, and the FTIR spectrum was similar to that of the particles treated with UV irradiation at 254 nm. The photoluminescence from these particles was also very similar to that from the UV-irradiated particles. Because this thermal treatment was performed on dry powders that had to be redispersed in a solvent to make photoluminescence measurements, we did not attempt to follow the course of the oxidation with a series of PL and FTIR measurements as we did for the UV-irradiated particles.

Silicon nanoparticles grafted with alkyl chains, including 1-octene, 1-dodecene, and 1-octadecene, were treated with the same methods to generate blue-emitting silicon nanoparticles. Figure 5 shows the evolution of the PL spectrum and the FTIR

spectrum of 1-dodecene-grafted particles during photooxidation. The process proceeded somewhat more slowly in this case than for the styrene-grafted particles, but the results were quite similar otherwise. The dodecene-grafted particles had much less residual hydrogen on their surface after hydrosilylation than the styrene-grafted particles had, and this sample already showed a small amount of surface oxidation prior to irradiation. This experiment was continued for 72 h, but the maximum blue PL intensity was achieved after 12 h. At longer times, the intensity of the entire spectrum decreased slowly. As was the case for the styrene-grafted particles, most of the oxidation seen in the FTIR spectrum occurred during the first 2 h, but the Si−O peak continued to grow slowly over the entire 72 h period. The maximum intensity of the blue emission, relative to the initial yellow emission, was somewhat higher in this case than for the styrene-grafted particles.

Figure 6 shows the FTIR spectra of dodecene-grafted particles heated in air. Like the styrene-grafted particles, the 1-dodecene-grafted particles are quite resistant to oxidation in air at 70 °C. The FTIR spectrum shows that some surface hydrogen is still present after 5 days at 70 °C. However, after 1 day at 140 °C, the FTIR spectrum showed substantial surface oxidation and complete disappearance of the Si−H feature. The particles heated at 140 °C also exhibited blue photoluminescence. Figure 7 shows the ^{1}H NMR spectrum from 1-dodecene-grafted particles before and after oxidation. The FTIR and ^{1}H NMR spectra confirm that the organic monolayer was not significantly degraded by either thermal or UV oxidation.

Similar results were obtained for 1-octene-grafted and 1-octadecene-grafted particles. Figure 8 shows the PL spectra from 1-octadecene-grafted nanoparticles and 1-octene-grafted particles. For the 1-octadecene-grafted particles, the photooxidation was slower than for styrene-grafted or 1-dodecene-grafted particles, but after 24 h of illumination, the particles showed blue photoluminescence. Figure 8a also includes the PL spectrum for 1-octadecene-grafted particles that had been heated in air at 140 °C. The blue component of the photoluminescence is essentially identical to that from the UV-treated particles. For the 1-octadecene-grafted particles, the PL emission after oxidation was slightly narrower and peaked at somewhat shorter wavelength compared to that for styrene-grafted particles and 1-dodecene-grafted particles. For 1-octene-grafted particles, the time scale for the oxidation was similar to that for styrene-grafted particles. The final blue PL emission was at somewhat longer wavelength and was somewhat broader than for styrene-grafted or 1-dodecene-grafted particles. Thus, for these alkyl-capped particles, the oxidation rate seems to decrease with increasing chain length, as might be expected if transport through the alkyl monolayer limits the oxidation rate. The blue-emission peak obtained after oxidation seems to become narrower and more intense with increasing length of the alkyl chains.

Taken together, the results presented here show that controlled oxidation of organically capped yellow-emitting photoluminescent silicon nanoparticles provides a general means of producing blue-emitting silicon nanoparticles. This oxidation can be driven by UV light or by heating with similar results and can be achieved with different organic molecules attached to the nanoparticle surface. The intensity and quantum yield of the blue emission following oxidation are comparable to those of the yellow emission prior to oxidation. The mechanism of the blue photoluminescence from these particles remains a topic for further studies using time-resolved PL and PLE measurements and other techniques that are beyond the scope of the present study. The manner in which the PL spectra shown in Figures 2, 5, and 8 change, with a decrease in the yellow or orange emission
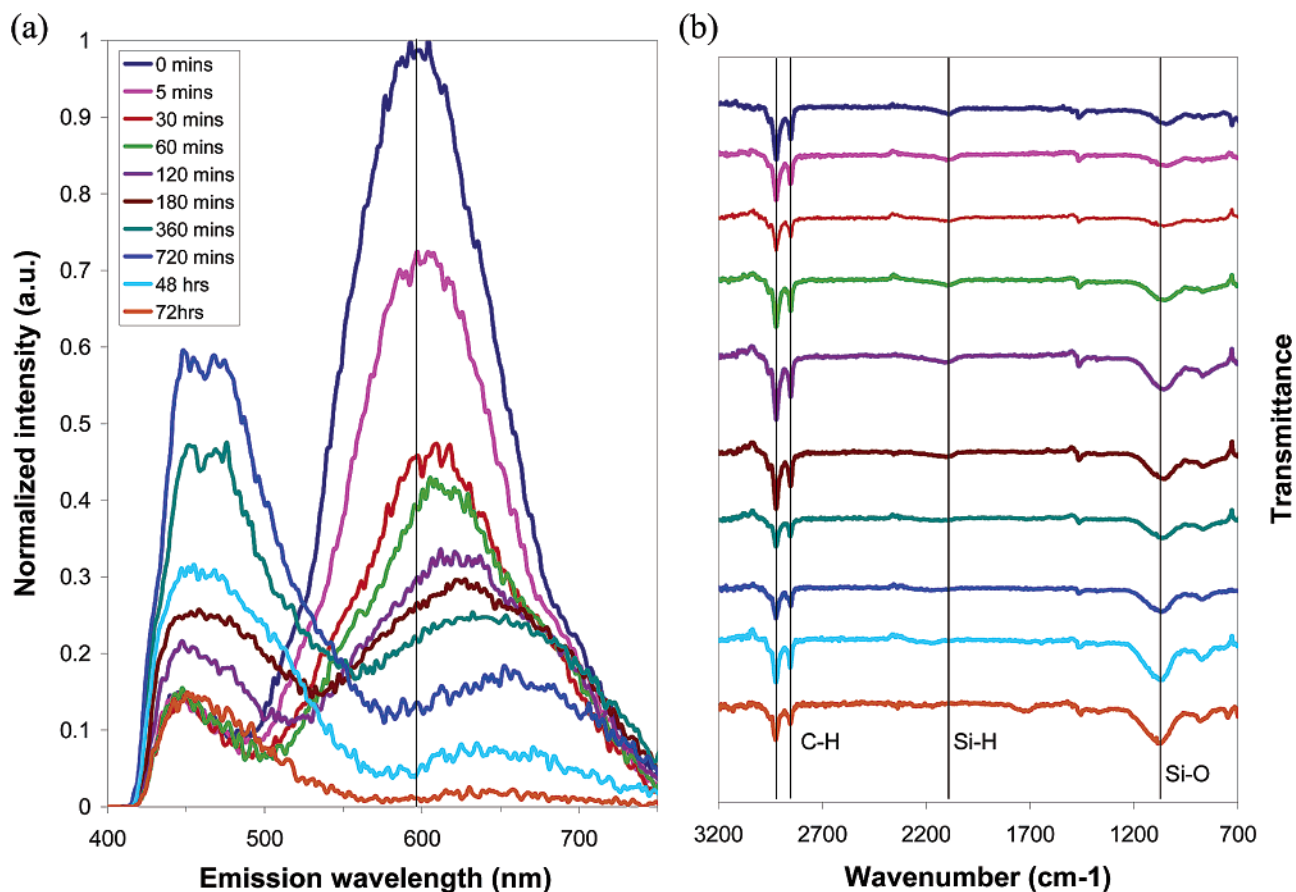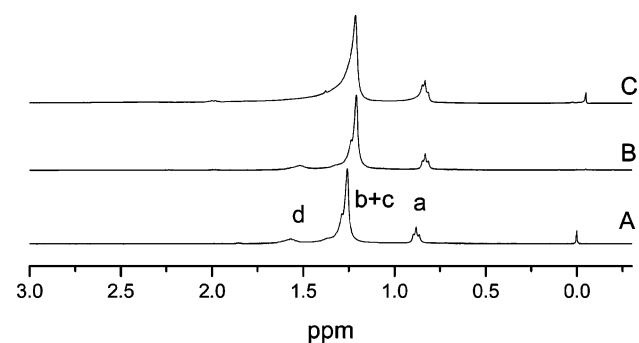
Figure 5. (a) PL spectra and (b) FTIR spectra of dodecene-grafted silicon particles after different periods of time under 254 nm UV illumination in toluene. All PL spectra are normalized to the initial spectrum so that relative intensities can be compared between them. PL and FTIR spectra are from the same experiment at corresponding times, as indicated by the line colors.
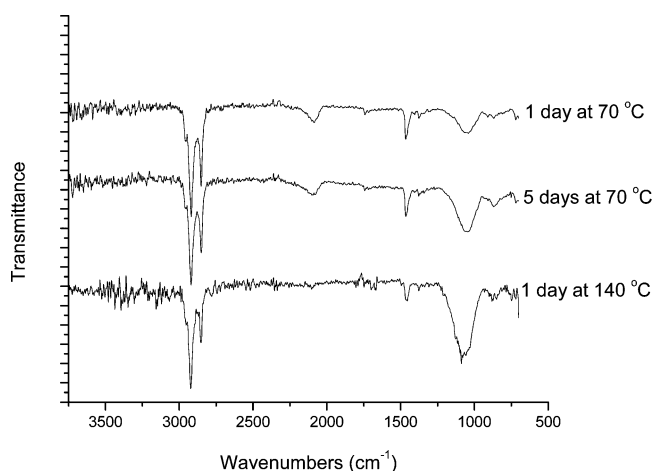
Figure 6. FTIR spectra showing the thermal oxidation of 1-dodecene-grafted silicon particles in air.

Figure 7. ^{1}H NMR spectra from 1-dodecene-grafted silicon particles (A) before oxidation, (B) after 6 h of irradiation at 254 nm, and (C) after 1 day of heating in air at 140 °C. Peaks a and b + c are assigned to CH_3 and CH + CH_2, respectively. Peak d is attributed to slight H_2O contamination of the $CDCl_3$ solvent.

accompanied by or followed by an increase in the blue emission, suggests that the change is not due to a simple, smooth reduction in the size of the silicon core that would result in a blue shift due to increased quantum confinement. In that case, one would expect a smooth blue shift of the spectrum. Instead, a change in the luminescence mechanism is likely. However, the fact that such similar results are achieved by different treatments and with different organic molecules grafted to the surface suggests that changes in the silicon core or at its surface, rather than changes in the organic component, result in the blue luminescence. It must be noted that all measurements here have been made on an ensemble of particles that presumably contains both lumi-

nescent ("bright") and nonluminescent ("dark") particles. Thus, we cannot conclude from these experiments that a given particle is converted from yellow-emitting to blue-emitting. It may, for example, be that yellow-emitting particles are becoming dark and simultaneously and/or subsequently dark particles are becoming blue-emitting.

Likewise, the molecular-level changes that occur during oxidation remain to be identified in more detail. We cannot, at this time, determine conclusively whether a crystalline silicon core remains after oxidation, but we have not been able to detect crystallinity by HRTEM after oxidation. As shown previously,[18] yellow-emitting samples without organics grafted to their surfaces show some crystallinity in X-ray diffraction, and TEM images of them show crystalline domains with diameters near 2 nm.
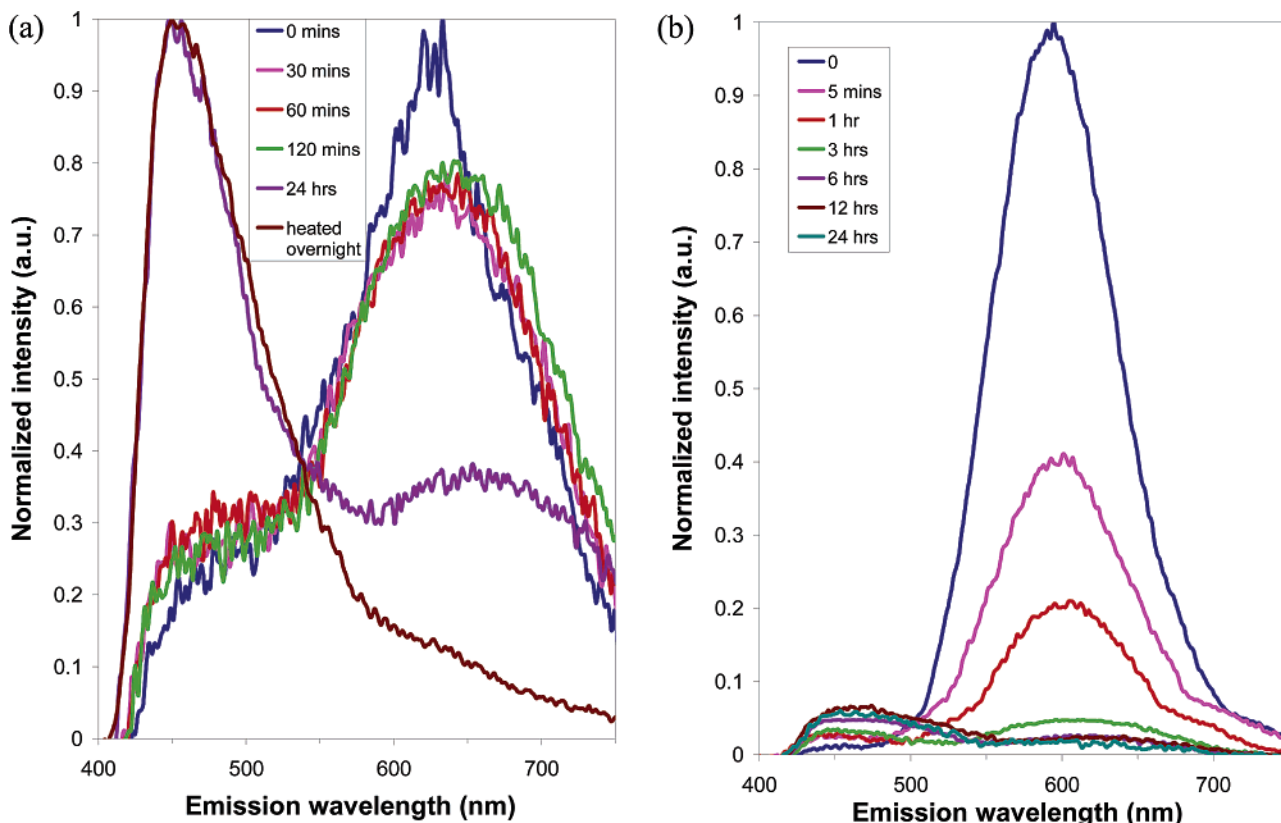
Figure 8. PL spectra from (a) 1-octadecene-grafted silicon particles and (b) 1-octene-grafted silicon particles after different periods of illumination with 254 nm light. For the octadecene-grafted particles, the final spectrum after 24 h of illumination has been separately normalized, and a normalized spectrum from particles that were heated for 24 h in air at 140 °C is included for comparison.
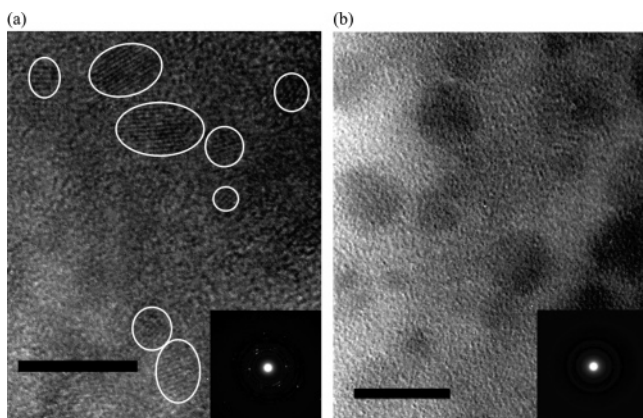
Figure 9. HRTEM images of (a) yellow-emitting nanoparticles before UV-induced oxidation and (b) blue-emitting nanoparticles after UV-induced oxidation. In a, crystalline domains have been outlined for ease of identification. The insets show the corresponding selected-area electron diffraction patterns. In both images, the scale bar is 5 nm.

After grafting a monolayer of an organic molecule to the surface, it may be more difficult to detect crystallinity because of interference from the organic layer. The situation is further complicated by the fact that a distribution of particle sizes is invariably present, so any crystallinity seen in XRD or TEM measurements may correspond to only the largest particles in the distribution and these may not be the particles from which the emission arises. Nonetheless, we have attempted HRTEM imaging of particles before and after oxidation. Typical results are shown in Figure 9. Although it is difficult to identify individual particles in these images, it is clear that some crystalline domains, exhibiting lattice fringes in HRTEM, are visible prior to the

oxidation and that none can be observed after oxidation. This is consistent with selected-area electron diffraction patterns (shown as insets) in which clear diffraction spots are visible prior to oxidation but only diffuse rings are present after oxidation. X-ray photoelectron spectroscopy (XPS) was also performed on the samples for which the TEM images are shown in Figure 9. However, no firm conclusions could be drawn from the results. As expected, only peaks corresponding to C, O, and Si were observed. There was an increase in the O/Si ratio after oxidation, but this could not be reliably quantified because of C and O contamination that is invariably introduced into these high surface area samples during sample preparation. There was a slight change in the Si 2p line shape but no change in the position or line shape of the O 1s or C 1s peak.

Despite the evidence of increased oxidation and reduced crystallinity presented above, it is clear that the particles are not fully oxidized to SiO_2 under these conditions. When the particles are heated to much higher temperatures such that they fully oxidize, there is an obvious change in their appearance (from brown to white), and they no longer luminesce. The fact that, as shown for 1-dodecene-grafted particles in Figure 5, the Si−O peak in the FTIR spectrum continues to increase even at very long times for which the blue emission intensity slowly decreases also suggests that emission does not arise from fully oxidized particles. Although it appears that the emission does not arise from the organic monolayer itself, it is clear that the organic monolayer plays a key role in the oxidation process that leads to the blue emission because the oxidation of particles without organic molecules grafted to their surfaces did not result in blue photoluminescence. This suggests that the organic monolayer plays a role in limiting the extent of oxidation and that this partial, but not complete, protection of the particle from oxidation is essential in obtaining the blue emission. Overall, the present

results suggest that the blue luminescence arises neither from quantum-confined states in a smaller silicon core nor from states in fully oxidized SiO_2, and further work will be required to determine the source of the blue luminescence from these particles. Nonetheless, the present work represents a significant technological advance because it allows the convenient production of stable blue-emitting particles, which have been difficult to produce by other means, from yellow-emitting particles, which can be much more easily produced.

Conclusions

A facile method was developed to prepare blue-emitting silicon nanoparticles as colloidal dispersions in a variety of common solvents. The oxidation of yellow-emitting silicon nanoparticles having organic monolayers grafted to their surfaces, using either UV irradiation in solution or the heating of dry particles in air, converted them from yellow-emitting to blue-emitting. The organic monolayer grafted to the particle surface was not affected by this oxidation process. The presence of the organic monolayer allows these nanoparticles to form stable dispersions in a variety of common organic solvents and provides for the possibility of further chemical functionalization of the particles. Combined with previous work on surface-grafted silicon nanoparticles with green through near-infrared emission, this enables the efficient and scalable preparation of stable colloidal dispersions of organically grafted silicon nanoparticles with emission spanning the entire visible spectrum. The mechanism of blue emission from these particles remains an open question to be addressed by further studies using time-resolved PL and PLE measurements and more refined structural characterization of the particles.