

Surface Modification of Silicon Nanocrystallites by Alcohols

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Room-temperature addition of 1-undecanol (UD-OH), 1-hexadecanol (HD-OH), 1-octanol (OC-OH), and 1,12-dodecanediol DD-(OH)₂ completely quenched the photoluminescence of silicon nanocrystallites, Si-nc. Heating Si-nc with UD-OH, HD-OH, and OC-OH resulted in the partial recovery of the photoluminescence and in the formation of 1–10 nm diameter alcohol capped Si-nc: Si-nc-O-UD, Si-nc-O-HD, and Si-nc-O-OC. Heating Si-nc with DD-(OH)₂ also restored partially the photoluminescence and TEM and AFM images indicated the formation of diol interconnected, 100–800 nm diameter silicon nanoparticle agglomerates, Si-nc-O-DD-O-nc-Si.

Introduction

The desirability of constructing optoelectronic¹ and fluorescence² display devices and sensors^{3,4} based entirely on silicon has prompted the exponentially growing interest in the preparation and characterization of light-emitting porous silicon (PS)⁵ materials.⁶ Photoluminescence of PS is discussed in terms of a modified quantum-confined mechanism, where the observed light emission is attributed to the presence of silicon nanocrystallites (generally, 1–5 nm in diameter, created during the etching of silicon wafers), which are believed to remain buried in the PS layer.^{7–9} Despite the general consensus that quantum confinement is involved in luminescence, contribution of the silicon surface states cannot be entirely ruled out.^{10–12} Extensive recent investigations of the PS surface and the factors which modify it are hardly surprising therefore.^{13–15} It is well-known that exposure of PS to various solvents or to small organic molecules affects the intensity of PS photoluminescence due to noncovalent interaction between the chromophore and usually the quencher.^{16–19} The silicon porous layer can also be permanently derivatized through a number of processes including free radical initiation to form densely packed alkyl monolayers,^{20,21} derivatization with alcohols²² and halogens,²³ photoelectrochemical esterification,^{24,25} and reaction with chlorosilanes.²⁶

Crystalline silicon has been functionalized by alkyl groups by a two-step reaction with PCl₅ and Grignard reagent at elevated temperature,²⁷ or alternatively by an electrochemical treatment in ether solution of either CH₃Li or CH₃MgCl.²⁸ More recently, the PS surface has been functionalized by aryllithium reagents, benzoquinone,²⁹ and alkyllithium reagents³⁰ and the chemistry of PS and crystalline silicon functionalization has been reviewed.¹⁵ Only recently, the effect of the surface layer composition (with regard to Si–O and/or Si–H bonds) on the fine structure of UV/vis spectra of Si nanocrystallites (Si-nc) was studied.³¹ There is, however, no report dealing with capping the surface of Si-nc, dispersed in an organic solvent. Such dispersion can be conveniently prepared by the extraction of Si-nc from an anodically etched PS layer by ultrasonication.³² Si-nc undergo photoluminescence, essentially analogously to substrate supported PS.

Functionalization of Si-nc by 1-undecanol (UD-OH), 1-hexadecanol (HD-OH), 1-octanol (OC-OH), and 1,12-dodecanediol (DD-(OH)₂) is the subject of the present report. We have shown

that Si-nc react with UD-OH, HD-OH, OC-OH, and DD-(OH)₂ to form alcohol capped Si-nc: Si-nc-O-UD, Si-nc-O-HD, Si-nc-O-OC, and Si-nc-O-DD-O-nc-Si.⁵ The photoluminescence (PL) of the Si-nc-O-UD, Si-nc-O-HD, and Si-nc-O-OC has been observed to increase with time in contrast to that observed for underivatized Si-nc.

Experimental Section

Materials. 1-undecanol (99%), 1-hexadecanol (99%), 1-octanol (99+%, HPLC grade), and 1,12-dodecanediol (99%) were purchased at Aldrich and used as received. Toluene was used as purchased from Fisher Scientific Company to prepare a colloidal dispersion of Si-nc. Silicon wafers (CZ 4" boron doped <100>, 6–8 Ω·cm, 500–550 μm, test grade) were obtained from Silicon Sense, Inc. Silver two part conductive adhesive was purchased from Alfa Aesar and was used to attach nickel wire (99.8%, 0.38 mm diameter, Alfa Aesar) to the silicon wafers. After drying, the contact was painted using colloidal silver liquid paint purchased from Electron Microscopy Science. The anodic etching of silicon wafers was performed in (1:1) HF (48.0–51.0%, J. T. Baker) and ethyl alcohol (anhydrous, Pharmco Products).

Equipment. Anodic etching of silicon wafers was performed using a Princeton Applied Research model 273 galvanostat. A Branson 2200 Ultrasonic cleaning apparatus was used to prepare crystalline suspensions. Steady-state photoluminescence spectra (PL) were obtained using a Spex Fluorolog 0.22 m double spectrometer with a 475 cutoff filter. The excitation wavelength was the 375 nm emission line from a Xe lamp. Transmission electron microscopy images were obtained by using a JEOL 1200 EXII microscope operating at 120 kV. Absorption spectra were recorded on a Hewlett-Packard 8452A diode array spectrophotometer. AFM images were taken by a Topometrix Explorer 2000 scanning probe microscope in the noncontact mode using standard silicon nitride tips (force constant of 0.12 N/m). FTIR spectra were collected using a Mattson Instruments model 2020 Galaxy Series FTIR.

Methods. Preparation of Porous Silicon (PS). Rectangular pieces (~6 mm × ~16 mm) of *p*-type, <100>, Czochralski zone (CZ)-grown, boron-doped Si (5–10 Ω·cm resistivity) were employed in a lateral anodic etch process. These samples were prepared by galvanostatically etching Si wafers at 10.4 mA/

cm² in a 1:1 solution of 48% HF/95% ethanol for 90 or 200 min. After etching, the wafers were rinsed with ethanol and dried under nitrogen.

Preparation of Colloidal Suspension of Si Nanocrystallites (Si-nc). Colloidal solutions of Si-nc were derived from PS. The PS wafers were suspended in 5 mL of degassed toluene and sonicated for 60–90 min in closed vials. During sonication, crystallites leached out from the porous Si network and the toluene suspension became pale yellow. Each wafer was sonicated in a separate vial.

Derivatization of Si-nc. To a reaction chamber containing 0.2 mL of an alcohol dissolved in 5 mL of toluene, 5 mL of a freshly prepared colloidal dispersion of Si-nc was added. The reaction was then carried out in a water bath at 95–100 °C under a stream of nitrogen for different time periods (5, 15, 45, 120 min). After the completion of the reaction, the excess solvent was evaporated by heating (to about 200–250 °C) under a stream of nitrogen. After cooling to room temperature, 5 mL of toluene was added to disperse the Si-nc powder and the photoluminescence of the dispersion was measured. In the case of solid alcohols, the equivalent amount was dissolved in toluene prior to starting the reaction and the solution was introduced into the reaction chamber. For atomic force microscopy (AFM) measurements one drop of a colloidal dispersion of Si-nc after heating with a given alcohol was spread on polished Si wafer and scanned in noncontact mode.

Sample Preparation for FTIR Measurements. Crystalline Si wafer is transparent in the infrared wavelength region (4000–1000 cm⁻¹), and FTIR spectra can be conveniently taken through the Si wafer.²⁵ Small pieces of Si wafers were cleaned in freshly prepared piranha solution (3H₂SO₄:1H₂O₂), washed with ethanol and water, and dried under a stream of nitrogen. Few drops of the Si-nc suspension were cast onto the cleaned Si wafer. The sample was dried, and the infrared absorption spectra were collected. In the case of Si-nc-O-R, the suspension was washed a few times with toluene, to eliminate the free alcohol. It is important to notice that all IR spectra were taken for qualitative analyzes because it is difficult to control the concentration of Si-nc in suspension and on the supporting Si-wafer. All samples were exposed to ambient atmosphere during data collection and all samples exhibited the presence of SiO₂ on the surface of Si-nc.

Results and Discussions

Derivatization of Si-nc by alcohols is the most significant accomplishment of the present work. Our derivatization method involved three steps: (i) preparation of toluene dispersions of silicon nanocrystallites, Si-nc; (ii) exposure of Si-nc to alcohols in toluene at room temperature; (iii) subsequent heating of the alcohol containing toluene dispersions of Si-nc to induce a chemical reaction to form a covalent bond and thereby produce a capped Si-nc (Si-nc-O-R, where R = UD, HD, OC).

We have prepared colloidal dispersions of Si-nc by exposure of electrochemically etched Si wafers to ultrasonic irradiation in degassed toluene. It should be pointed out that this method leads to high purity Si-nc since the preparation is carried out in the absence of oxygen, which precludes the formation of Si–O–Si bonds and the formation of a SiO₂ shell.³² Furthermore, the obtained Si-nc can be transferred onto carbon coated copper grids for electron microscopy. Typical transmission electron microscopy (TEM) images of Si-nc dispersions in toluene showed the presence of particles, predominantly with diameters in the range of 1–10 nm (Figure 1a) and some larger (up to 80 nm, not shown) agglomerates. Dispersions of Si-nc with similar size distributions have been reported previously.^{32–34}

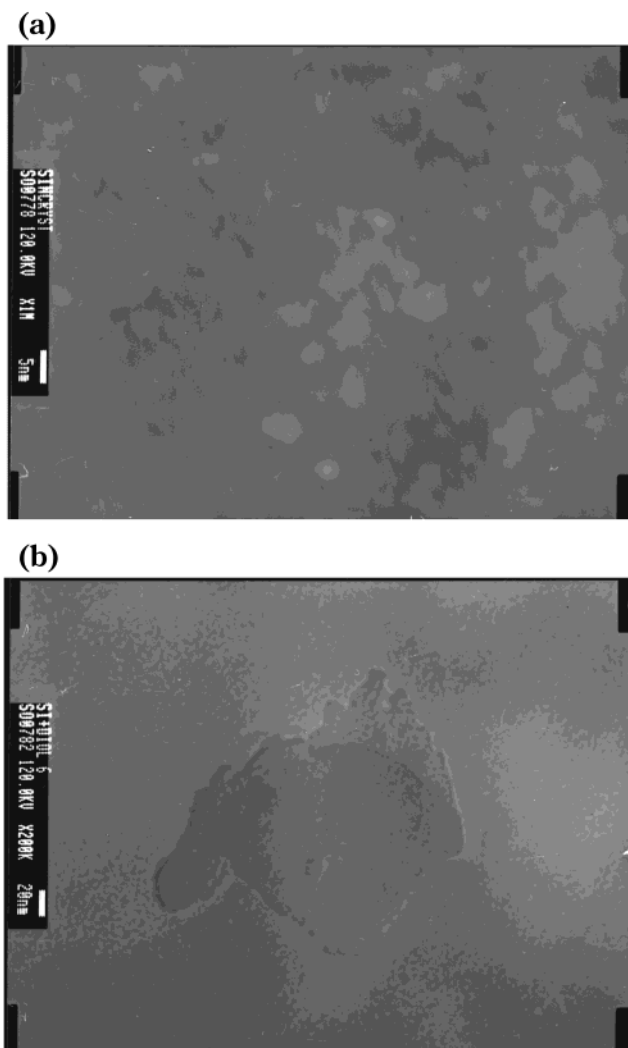


Figure 1. TEM images of a freshly prepared Si-nc (a) and the three-dimensional network of a silicon nanoparticle agglomerates formed from Si-nc-O-DD-O-nc-Si moieties (b).

Exposure to alcohols has quenched the PL of Si-nc. For example, 90–95% of the integrated PL intensity of a 3 mL Si-nc dispersion was found to be quenched immediately after addition of few drops of UD-OH at ambient temperature (compare the PL spectra of 1 and 2 in Figure 2). In isolated Si-nc, the exciton recombines radiatively and the PL emanates from this recombination. However, Si-nc possess large surface areas which can provide good nonradiative recombination centers (dangling bonds or any surface atoms). Exposure of Si-nc to various organic molecules can lead to PL quenching via trapping of the charge carriers at the surface states.^{11,12,19} Diminished PL intensity of Si-nc upon exposure to alkyl alcohols is likely to be the consequence of UD-OH physisorption and concomitant polarization of the charge carriers by alkyl alcohols at the surface states.

These results indicated that the LUMO level of the alcohols was located within the band gap of Si-nc, between 3.6 and 5.8 eV below the vacuum level,³⁵ and is in agreement with the fact that alkyl alcohols exhibit redox potential at 0.4–0.9 V vs Ag/Ag⁺ (5.1 eV to 5.6 eV, above the valence band edge of Si-nc).

Formation of Si-nc-O-R, on the other hand, resulted in the partial recovery of the Si-nc PL. For example, heating a toluene dispersion of Si-nc containing the UD-OH in an inert atmosphere on a water bath (~100 °C) for 30 min resulted in the recovery of 36% of the PL intensity observed for a freshly prepared Si-

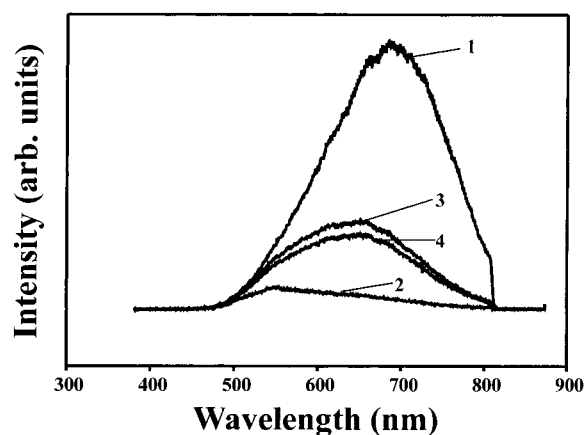


Figure 2. PL of a freshly prepared Si-nc dispersion in toluene prior (1) and after the addition of UD-OH at room temperature (2), after heating for 30 min at 100 °C (3), and after the further addition of UD-OH (4).

nc (see spectra 3 in Figure 2). The extent of PL recovery depended on the type of alcohol used, the temperature, and the duration of heating. In contrast, the PL intensities of Si-nc-O-HD and Si-nc-O-OC were only 10–30% of that observed for Si-nc. Generally, 10–50% of the original PL intensity of Si-nc could be recovered after derivatization with alcohols. The best results were observed in the case of UD-OH.

The PL intensity of Si-nc-O-R dispersion did not change upon further addition of free alcohol, in contrast to that observed for freshly prepared Si-nc. This confirms our assumption that the interaction of freshly prepared Si-nc with alcohols at room temperature is based on physisorption of organic groups at the surface. Heating, on the other hand, leads to chemisorption and formation of covalent bonds between Si and the alkoxy groups (Si-nc-O-R) and partial recovery of the Si-nc PL. Apparently, derivatized Si-nc (Si-nc-O-R) are less susceptible to quenching than their underivatized counterparts (compare spectra 3 and 4 in Figure 2). One explanation lies in steric hindrance of the Si-nc surface due to insulating capping by alkyl chains in the case of Si-nc-O-R. Alternatively, the behavior of Si-nc-O-R toward quenching is explicable in terms of a tunneling barrier. The presence of oxides on aged PS has been suggested to increase the energy barrier for carrier tunneling by non-radiative pathways, which manifests itself in a more modest quenching of the PL of oxidized PS as compared to freshly prepared PS.^{17,19,34} By analogy with the oxide layer on PS, we may assume that the presence of an alkoxy layer on the surface of Si-nc-O-R increases the energy barrier for carriers tunneling.

The nature of alkoxy groups at the surface of Si-nc (chemisorption vs physisorption) was studied by FTIR spectroscopy. Transmission FTIR data were collected for freshly prepared Si-nc prior to and after heating with undecanol for 1 h (Figure 3). The spectra exhibited typical features observed for PS^{24,25,29,36} and Si-nc^{8,33} samples. The presented spectra consist of absorption modes near 1100 cm^{-1} assigned to $\nu(\text{Si}-\text{O})$ stretching modes and around 620 cm^{-1} corresponding to Si-Si deformation modes.^{26,36} However, there are no hydrogen related modes $\nu\text{Si}-\text{H}_x$ around 2100 cm^{-1} so typical for freshly prepared or partially oxidized PS.^{24,25,29,36} It should be noted that the few IR spectra of Si-nc reported in the literature do not depict Si-H_x stretching modes for Si-nc.^{8,33} The absence of $\nu\text{Si}-\text{H}_x$ can be explained by the oxidation of the surface of Si-nc upon inevitable exposure to air during the preparation or the spectroscopic studies.

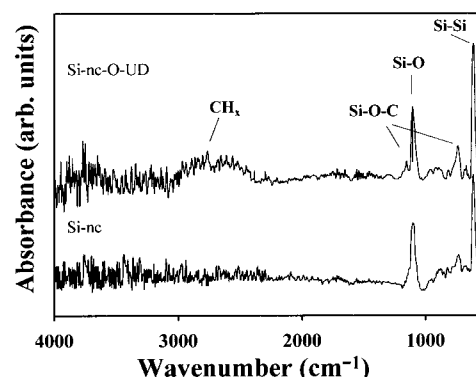


Figure 3. Transmission FTIR spectra of Si-nc and derivatized Si-nc with 1-undecanol. Notice the appearance of new bands with maxima at 2800 cm^{-1} $\nu(\text{C}-\text{H}_x)$ and 1157 cm^{-1} $\nu_{\text{as}}(\text{Si}-\text{O}-\text{C})$, and increased absorption around 800 cm^{-1} $\nu_{\text{s}}(\text{Si}-\text{O}-\text{C})$.

The absorption around 800 cm^{-1} (slightly increased with respect to underivatized Si-nc) and the new band at 1157 cm^{-1} in the FTIR spectrum of Si-nc-UD (Figure 3) is assigned respectively to the $\nu_{\text{s}}(\text{Si}-\text{O}-\text{C})$ and $\nu_{\text{as}}(\text{Si}-\text{O}-\text{C})$ stretching modes,³⁷ substantiating the presence of alkoxy groups on the surface of Si-nc.^{24,25,29} The presence of Si-O-R species on the surface of Si-nc is further evidenced by the broad band around 3000 cm^{-1} (Figure 3) which is very characteristic of alkyl groups $\nu(\text{C}-\text{H}_x)$. The maximum of this broad peak lies around 2800 cm^{-1} and is in agreement with published data for PS derivatized with long chain alkyl alcohols.^{22,32} The presence of physisorbed (free) undecanol on the surface can be ruled out, since no $\nu(\text{OH})$ vibration appears at 3400–3500 cm^{-1} . Thus, the $\nu(\text{C}-\text{H}_x)$ vibrations cannot be assigned to the presence of free alcohol on the surface of Si-nc but to the presence of alkoxy moieties. It is also important to notice the difference in oxidation level of Si-nc and Si-O-R by comparing peak intensities at 1100 cm^{-1} (Si-O stretching mode) and at 620 cm^{-1} (Si-Si deformation mode) for both samples. The difference may be due to incomplete subtraction of the Si-Si mode at 620 cm^{-1} due to the use of Si wafer as a “sample holder”. However, the persistent observations of a larger peak area for the 620 cm^{-1} stretching mode in the case of derivatized Si-nc demonstrated that the freshly prepared Si-nc were much more oxidized than derivatized Si-nc kept in the same conditions. It proves, once again, that chemical functionalization of Si-nc after heating with alcohols was achieved. The potential better stability of the surface of Si-nc toward oxidation due to the presence of alkoxy groups makes derivatized Si-nc more desirable for many applications.

To further confirm that the recovery of PL of Si-nc was due to the reaction of alkyl alcohols with Si-nc, the following control experiment was performed. A toluene dispersion of Si-nc was prepared and one part was heated without adding any alcohol, whereas the second part was heated in the presence of alcohol, in both cases under nitrogen atmosphere. The luminescence of the blank sample heated for 30 min was completely quenched, while the luminescence of the alcohol containing sample was found to be incompletely quenched.

A thin alkoxy layer is assumed to constitute the capping in Si-nc-O-R. This capping is believed to be responsible for preventing the oxidation and PL quenching of the Si-nc and thereby stabilizing the charge carriers at the nanoparticle surface. Covalent capping of semiconductor nanoparticles by thiols and other nucleophilic reagents has been shown to result in analogous altered surface states and PL.³⁸

Another important observation is the blue shift of the emission maximum of the Si-nc-O-R with respect to Si-nc. The magnitude

of the blue shift, in the range of 50–100 nm, was found to depend strongly on the sample and heating conditions, but it is in the range of that associated with size quantization.^{7,8,10}

The mechanism of Si-nc-O-R formation is not entirely clear. On the basis of our observation we assumed that hydroxy groups of alkyl alcohols could interact with Si atoms at the surface defect. The presence of dangling bonds on the surface of freshly prepared Si-nc can slightly polarize a typical covalent Si–Si bond and facilitates its cleavage leading to the formation of alkoxy groups on the surface of Si-nc. Upon derivatization, the surface of Si-nc inevitably changes by elimination of surface defects and leads to a stabilization of the PL. Kim and Laibinis²² suggested that during the reaction of PS with different alcohols the alkoxy group can replace silicon atoms via the cleavage of Si–Si bonds. Longer reaction times (3 h, for example) and higher temperatures are known to result, however, in the dissolution of the porous silicon layer.²² If one deliberately oxidizes Si-nc, the presence of hydroxide and oxide at the surface of Si-nc can polarize back-bonds, allowing alcohols to react with the Si-nc surface. The reaction of oxidized Si-nc with alcohols will be discussed below.

We investigated the blue shift in the absorption spectra upon derivatization of differently sized Si-nc particles by varying the anodization time used for the formation of PS. The size distribution of the Si-nc was monitored from the wavelength of the emission maximum.^{7,8} Two different populations of Si-nc were selected for reacting with UD-OH: one set with an emission maximum at 702 nm and a second with a maximum at 630 nm (obtained by anodic etching of silicon wafer for 90 and 200 min and subsequent sonication under the described conditions). Both samples were allowed to react with UD-OH for 30 min in a water bath at 95–100 °C. The PL spectra of the resulting Si-nc-O-UD dispersions exhibited emission maximum at 640 nm (Figure 4a) and 630 nm (Figure 4b), respectively. Apparently, the emission maximum of the more orange Si-nc sample (630 nm) did not shift after reaction with UD-OH (Figure 4b). A shift of the emission maximum for *both* samples would have occurred if silicon dissolution had taken place. These results indicated that the shift in the PL maximum was not the consequence of the dissolution of Si nanocrystallites, but rather the result of a surface modification (i.e., capping). Additional heating of these two Si-nc-O-UD samples with UD-OH (twice for 15 min) finally shifted the emission maximum, however, into lower energy (red shift between 10 and 20 nm), indicating some dissolution of smaller Si-nc.

To further analyze the effect of oxygen on the shifting phenomena, another control experiment was performed. A toluene dispersion of Si-nc, with an emission band centered at 700 nm, was prepared and heated *without the addition of any alcohol* for 15 min both in the absence and in the presence of oxygen. The PL spectra were then compared with each other and with that of derivatized Si-nc. The emission maximum of the sample heated under nitrogen did not change significantly (less than 5 nm shift) providing further evidence that the blue shift was due to the presence of alkyl alcohol and its reaction with the surface of Si-nc. The luminescence of the same sample heated for longer time (up to 30 min) under nitrogen was quenched up to 99% of its original value. On the other hand, emission maximum of the sample heated in the presence of oxygen (for 15 min) was found to shift almost to the same extent as samples after derivatization in the absence of oxygen (Si-nc-O-R). In most cases, about 50% of the original PL was still observed after the first heating in the presence of oxygen. Prolonged heating, however, finally quenched the PL, by

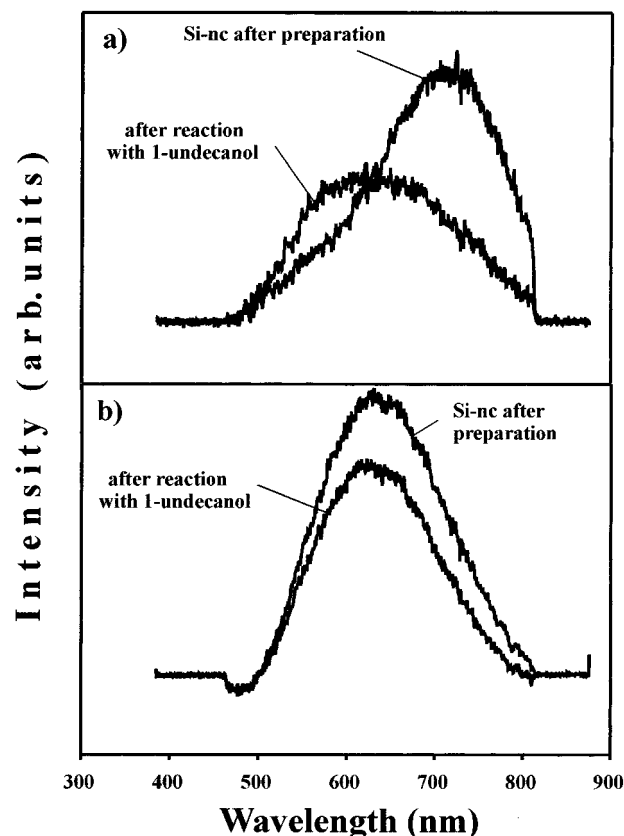


Figure 4. Two different samples of colloidal dispersion of Si nanocrystallites with an emission maximum at 718 nm (a) and at 630 nm (b) prior to and after heating with UD-OH.

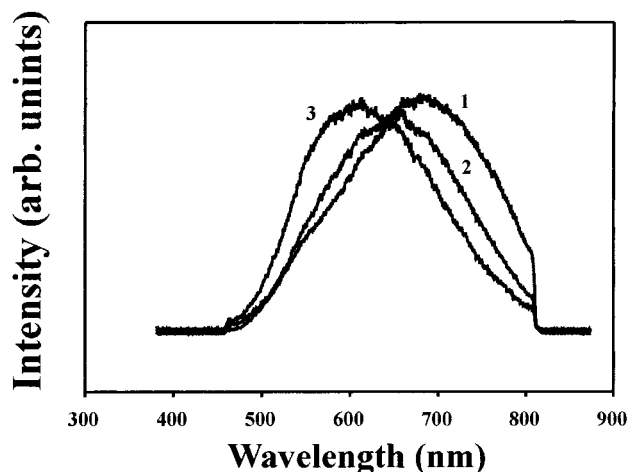


Figure 5. PL of Si-nc dispersions in toluene prior to (1) and after heating in the presence of oxygen ((2), intensity scaled by a factor of 2) and after heating with UD-OH in the absence of oxygen (3), intensity scaled by a factor of 2).

contrast to the Si-nc-O-R samples, which retained their luminescence for months. It can be deduced that the blue shift measured in the PL spectrum can be triggered by oxidation or surface functionalization, but it must be also explained by different phenomena. Indeed, the blue shift during oxidation can be rationalized by a quantum effect associated with the diminishing of the core diameter of Si-nc due to the surface oxidation. In the case of surface derivatization with alcohols, the blue shift could be explained by the stabilization of surface states due to the presence of alkoxy moieties at the surface of Si-nc and should be further studied.

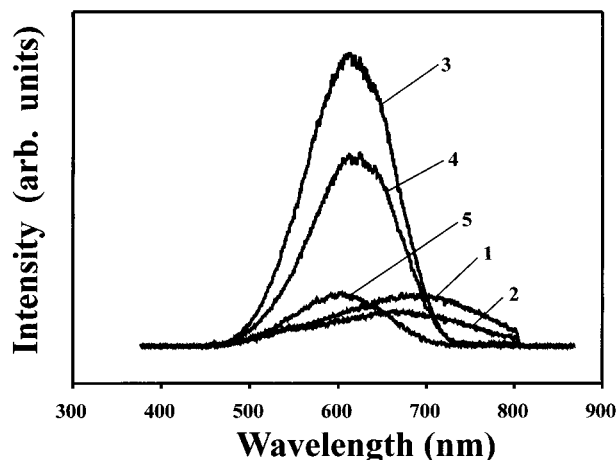


Figure 6. PL of Si-nc with time after reaction with alkyl alcohols: freshly prepared sample (1); sample 1 immediately after reaction with 1-undecanol (2); PL of sample 2 1 month later (3); PL of colloidal dispersion of Si-nc after reaction with 1-hexadecanol observed 1 month later (4); and PL of colloidal dispersion of Si-nc after reaction with 1-octanol observed 1 month later (5).

Another interesting observation is that oxidized Si-nc after reaction with UD-OH exhibit an additional blue shift (~ 30 nm) of the emission band (Figure 5). This observation indicates that both freshly prepared and surface oxidized Si-nc can interact with alcohols. This result may originate from the fact that Si—O—Si bonds introduced during the oxidation process are neighbored by defects and dangling bonds³⁰ and may serve as good sites for further reaction of alkyl alcohols with the surface.

The effect of different alcohols on the emission maximum of the Si-nc PL was also investigated. The extent of the blue shift observed in PL was independent of the chain length of the capping molecules (for a number of carbons ranging from 8 to 16). The long-term stability of the luminescence of Si-nc was also investigated. It is a very important aspect for future

optoelectronic devices and displays based on silicon. It was reported recently that Si-nc incorporated into a sol-gel matrix can be stabilized for 1 month in the presence of fatty acids, and in the absence of additive it degrades quickly.³⁹ Photoluminescence intensities of the capped Si-nc, Si-nc-O-HD, Si-nc-O-UD, and Si-nc-O-OC, increased with time and then remained stable for months (see curves 3–5 in Figure 6). Of all the alcohols used, the PL of Si-nc derivatized by 1-undecanol (Si-nc-O-UD) is the most intense. After 1 month, 300% of the original intensity of freshly prepared Si-nc was observed for samples derivatized with UD-OH, as compared to 200% with HD-OH and only 50% with OC-OH. Even a 5 month old sample of Si-nc-O-UD was found to luminesce, albeit with a somewhat decreased intensity. The general increase and long-term stability of the PL might be attributed to a more favorable rearrangement of the alkylchains of the organic capping layer, leading to a more efficient insulating barrier.

The stability of the PL intensity can be explained by the fact that Si-nc-O-R exhibited a better resistance to oxidation (from IR observations) and can retain their crystallinity much longer.

Freshly prepared Si-nc require constant mixing to avoid flocculation. After derivatization, the Si-nc-O-R suspension was found to remain stable for months. The photodegradation of PL intensity is also suppressed in Si-nc-O-R suspensions compared to fresh Si-nc. Upon addition of polar solvent (ethanol) to a Si-nc-O-R suspension, the precipitation of nanoparticles was immediately observed. These observations are in accord with the assumption that long chain alkyl alcohols react with Si-nc, changing the surface and optical properties of derivatized Si-nc (Si-nc-O-R). Unfortunately, we do not know the extent of coverage of the Si-nc surface and whether the increase in the observed PL intensity is due to further displacement of the surface oxide or Si—H moieties by alkoxy groups. However, the shift in PL maximum is unambiguously related to the efficient stabilization of the Si-nc surface by alkoxy groups during the derivatization.

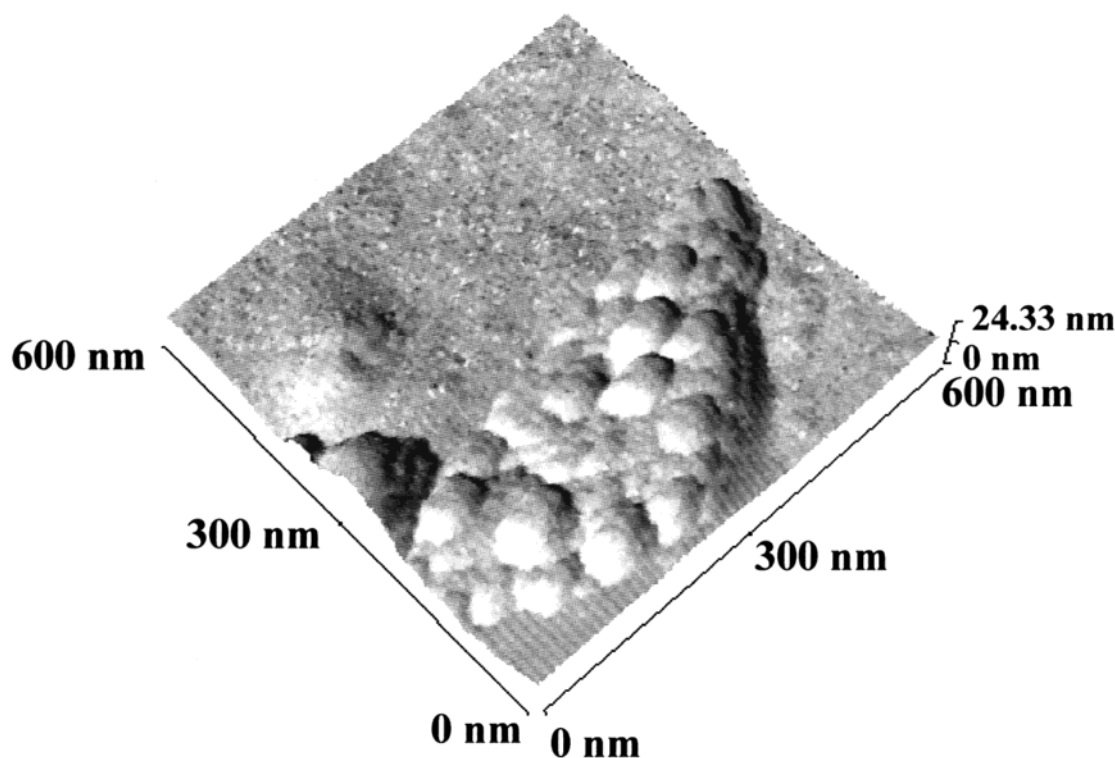


Figure 7. AFM image of interconnected Si-nc-O-DD-O-nc-Si particles. There was also a variation in the PL recovery observed between samples prepared under the same conditions.

Organic molecular wires with high conductivity could, in principle, be used in constructing self-assembled interconnected networks for ultrasmall electronic devices. On the basis of the previous observations with alkyl alcohols, we assumed that a possibility of constructing a network of nanoparticles of Si-nc connected to each other by a molecular linker should exist by using diol molecules. This idea was tested by using 1,12-dodecanediol (DD-(OH)₂). The reaction with Si-nc was carried out under the same conditions as those described for UD-OH. After reaction, toluene was added and a clear transparent yellow or pale-yellow solution was obtained characterized by an absorption band centered at 445 nm and a very weak fluorescence peak at 460 nm (not shown). The dispersion was stable for months, but the addition of small amounts of ethanol could cause a precipitation.

There are three possible reaction pathways for the interaction of Si-nc with diols: (i) only one OH group reacts with Si-nc leaving the second functional group free; (ii) chelation with both OH groups; (iii) connection of different Si-nc with each other via alkyl linkages to form Si-nc-O-DD-O-nc-Si networks which can grow into clusters. TEM and AFM investigations provided evidence in favor of the last alternative. In particular, TEM images of DD-(OH)₂ derivatized Si-nc indicated the presence of three-dimensional networks (with 100–500 nm diameter) in which the capped nanocrystals were connected to each other by diol linkages (see Figure 1b). In contrast, the images obtained with other monoalcoholic Si-nc-OR only showed well separated nanoparticles similarly to that observed for freshly prepared Si-nc (Figure 1a). AFM images of DD-(OH)₂ derivatized Si-nc confirmed the presence of three-dimensional structures. The agglomerates seen were similar to that observed by TEM with diameters ranging from 100 to even 800 nm. Figure 7 shows a typical AFM image of an interconnected 300 nm diameter Si-nc-O-DD-O-nc-Si aggregate with heights ranging from 5 to 7 nm.

On the basis of these observations (blue shift of emission spectra and stability of the PL) it is assumed that freshly prepared (containing, presumably, no significant oxide layer) and oxidized Si-nc (prepared by heating in the presence of oxygen) react with alcohols. Alkoxy groups present at the surface of Si nanocrystallites after reaction stabilize the colloidal suspension and prevent it from the diminishing of PL intensity with time. Reactions of Si-nc with alcohol are significant since they provide stable dispersions of Si-nc with long lasting optical properties and permit the covalent attachment of functional moieties, which may open the door to the formation of two-dimensional networks. Using this approach we have already successfully attached functionalized Si-nc to solid surfaces.³⁵

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- (5) Abbreviations used in this paper: PS = Porous silicon, prepared by the anodic etching of silicon wafer in ethanolic HF; Si-nc = silicon nanoparticles, prepared by the ultrasonic irradiation of PS wafer in toluene; UD-OH = 1-undecanol; HD-OH = 1-hexadecanol; OC-OH = 1-octanol; DD-(OH)₂ = 1,12-dodecanediol; Si-nc-OR = Si-nc derivatized (capped) by alcohols, where R = UD (1-undecanoxo), HD (hexadecanoxo), or OC (octadecanoxo); Si-nc-O-UD = Si-nc derivatized (capped) by UD-OH; Si-nc-O-HD = Si-nc derivatized (capped) by HD-OH; Si-nc-O-OC = Si-nc derivatized (capped) by OC-OH; Si-nc-O-DD-O-nc-Si = Si-nc derivatized (capped) by DD-(OH)₂; PL = photoluminescence.
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