Quasi-reversible photoluminescence quenching of stable dispersions of silicon nanoparticles

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Optically clear and stable dispersions of brightly photoluminescent Si nanoparticles were obtained by covalent attachment of alkenoic compounds to the particles. Quenching of photoluminescence by ethylamine, diethylamine, triethylamine, pyrazine, and piperazine was investigated. The photoluminescence was quenched by the action of these nitrogenous species, but in some cases could be partially restored by the addition of trifluoroacetic acid. The extent of restoration of photoluminescence, after equilibrium is reached, was independent of the sequence of addition of the amine and the acid. The photoluminescence quenching and recovery are influenced by a combination of basicity, polarity, and steric factors of the quencher molecules. The quenching and subsequent restoration occurs gradually at room temperature and it takes several minutes to reach equilibrium.

Introduction

The discovery of bright luminescence in porous silicon more than a decade ago opened an avenue for possible integration of optoelectronics with traditional silicon technology.[1] Potential applications of luminescent silicon include light emitters for displays or general illumination,[2] photodetectors,[3] solar energy converters,[4] advanced electronic devices[5] and chemical sensor devices.[6] A great deal of attention has been devoted to studying various aspects of the photoluminescence (PL) of porous silicon (PSi).[7] Quantum confinement effects increase the band gap energy in nanocrystalline silicon relative to that of the bulk, and also relax the selection rules that reduce the efficiency of radiative recombination in indirect band gap semiconductors.[8] In general, the physical origin of the luminescence in porous silicon can be attributed both to these effects and to local states introduced by the chemical characteristics of the silicon surface.[9] Luminescent nanocrystalline silicon particles have been prepared by a variety of procedures, including rupturing of porous silicon by ultrasonication,[10] reactive sputtering,[11] ion implantation,[12] inverse micellar growth,[13] laser ablation,[14] and thermal vaporization.[15] However, the PL properties depend on the medium surrounding the PSi or the nanocrystals. Therefore, a clear understanding of the effect of aspects of the surrounding medium on the PL properties is important for potential device applications.

In any nanometric material, the large surface-to-volume ratio implies that the state of the surface will play an important role in determining its optical and electrical properties. There are several unstable or meta-stable bond configurations that leave the surface physico-chemically vulnerable to attack by different chemical species. Furthermore, interaction of various species with the surface can affect the PL differently. For example, quenching of PL from PSi by the action of various organic solvents,[16] acids and bases,[17] amines,[18] aromatic nitro compounds,[19] salt solutions of Cu, Ag, and Au,[20] and metal oxides such as WO_3[21] has been reported. At least one report showed enhancement of PL by the action of cyano compounds.[22] Some detailed studies have been presented by Chandler-Henderson *et al.*[23] on PL quenching by different amines where it was shown that bulkier amines have a weaker quenching ability than the smaller amines. This was attributed to steric hindrance limiting the access of bulkier amines to the emitting surface within the labyrinthine PSi. While a number of published studies have focused on PL quenching in PSi, very few have considered PL quenching in free Si nanoparticles where the ability of the quencher to be transported through the porous matrix cannot be a controlling factor.[18,19] In these studies, the PL quenching phenomenon is attributed to the physico-chemical surface interaction of the quencher molecules with the particles opening new non-radiative pathways to carrier relaxation. In particular, a wide variety of amines have been shown to quench PSi PL. In this context, it is interesting to note that there exist mixed reports about the effects of amines on the PL of other semiconductor nanoparticles. For example, simple amines can be good passivating agents for compound semiconductor nanoparticles, when they adsorb and eliminate surface states through which non-radiative deactivation or red-shifted luminescence could occur. In fact, enhancement of luminescence from CdS, Cd_3As_2 and CdSe has been reported upon exposure to simple amines, leading to increased PL quantum yield.[24] There are, however, also reports of PL quenching in these materials by amines. For example, a study of PL quenching of very small CdSe nanoparticles by butylamine by El-Sayed's group showed that a mechanism of irreversible binding of amines with surface trap states removes them from a radiative recombination pathway.[25]

For Si nanoparticles, the untreated native oxide surface does not allow preparation of stable colloidal dispersions of them in

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many solvents. In many studies, particles were reported to have been ultrasonically suspended in organic solvents, usually toluene or an alcohol, where surface binding of solvent to the particles occurs by physisorption. However, such dispersions are not very stable and over a period of several hours, the particles aggregate into a sediment and have to be resuspended by sonication. The Fendler group[26] reported that by refluxing Si particles with undecanol in an airless procedure, the particle surface can be coated with chemisorbed molecules, yielding a clear dispersion in toluene.

Use of unstable or metastable dispersions, obtained by simple sonication of PSi in alcohols, limits the ability to perform quantitative PL measurements, because the dispersion naturally becomes inhomogeneous over time. In the present work, we have performed all experiments on homogeneous, stable and optically clear dispersions of Si nanoparticles in toluene or ethanol. We have investigated the quenching of PL and the reversibility of PL quenching using polar and non-polar amines as quencher molecules. This study provides insight into the quenching mechanism of amines at the Si particle surface. Such knowledge is potentially of great use in designing both light emitters based on Si nanoparticles, where quenching must be avoided, and chemical detectors, where PL quenching is a potential detection mechanism.

Experimental

Silane (SiH_4), (electronic grade, Scott Gases), undecylenic acid (Aldrich, 98%), octadecene (Aldrich, 90%), ethylamine (Aldrich, 97%), diethylamine (Aldrich, 99.5%), triethylamine (Aldrich, 99.5%), trifluoroacetic acid (Aldrich, 99%), pyrazine (Aldrich, 99%), and piperazine (Aldrich, 99%) were used as received. The Si nanoparticles were synthesized, as described in detail previously,[27] by dissociating silane (SiH_4) *via* heating with a CO_2 laser beam (Coherent, Model 42, 60 Watts) in an aerosol reactor. The resulting particles were collected on cellulose nitrate membrane filters. They did not exhibit photoluminescence. The particles were then dispersed in methanol at about 10 mg mL^{-1}, and etched using a mixture of 3% HF and 32% HNO_3 (by weight). This reduces the particle size and passivates the particle surface such that the particles exhibit bright, visible photoluminescence. Finally, the particles were washed with a 5% HF solution, which increases the hydrogen coverage on the surface. After etching, the particles were collected on a polyvinylidene fluoride membrane filter and washed with distilled water and methanol. In order to obtain a good dispersion of Si nanoparticles, the method of Lie *et al.* for producing alkylated silicon quantum dots[28] was followed with some modifications, as described in more detail by Li *et al.*[29] The dispersions were produced in two different batches, one in toluene and the other in ethanol, with octadecene and undecylenic acid used as the respective surfactants. In the first case, the etched powder and octadecene were taken (40 mg Si powder and 2 mL octadecene) and suspended in 15 mL dry toluene to be refluxed for 6 h at 110 °C in an argon atmosphere. This resulted in a fairly clear light yellow dispersion that was subsequently filtered through a fine pore Whatman paper to obtain a clear filtrate. The resulting toluene dispersion was useful for studies involving triethylamine, but the solubility in toluene for the other amines considered here is too low for this dispersion to be useful. So, an ethanolic dispersion was prepared with undecylenic acid as the surfactant by refluxing the particles and the surfactant in 190 proof ethanol at 78 °C for 3 h under anaerobic conditions. We note that similar procedures have been used to modify PSi surfaces.[30] A light yellow dispersion was obtained that was subsequently filtered to obtain a clear filtrate. The filtrate was dialyzed against pure ethanol at least four times using a 12–14 kD cut-off cellulose membrane (Spectrum Laboratories, Inc., USA) for 24 h, in order to remove excess unbound undecylenic acid. The resulting clear sample in ethanol was miscible with all amine solutions considered here.

Samples were prepared for transmission electron micrography (TEM) imaging by evaporating multiple drops of a clear dispersion of octadecene-coated particles onto a copper grid with an ultrathin amorphous carbon support film. The dispersion was subjected to multiple precipitation, vacuum sublimation, and re-suspension steps for the high-resolution images. TEM images were obtained using a JEOL 2010F microscope at an acceleration voltage of 200 kV.

All photoluminescence spectra were recorded using a Spex Fluorolog-3 spectrofluorometer with a 420 nm long-pass emission cutoff filter. To study the quenching by each individual amine and subsequent recovery with trifluoroacetic acid, a 2.5 mL aliquot of sample was placed in a quartz cuvette and excited at 300 nm. Prior to the experiment, the sample had been refluxed with undecylenic acid and dialyzed in ethanol, as described above. For each amine, the PL of the original sample was measured. Then 100 μL of a 2 M ethanolic solution of the amine was mixed into the cuvette. After waiting for 30 min to allow the system to reach equilibrium, the PL spectrum was recorded. Following this, 400 μL of neat trifluoroacetic acid (TFA) was added, again by mixing directly into the cuvette, and the PL was again measured after 30 min. We observed that the addition of these small amounts of pure ethanol to an original sample aliquot caused negligible decreases in the measured PL spectrum. Also, we observed that the addition of only TFA to an original sample aliquot causes a similarly negligible decrease in the PL.

Results and discussions

In previously published work,[29] the covalent attachment of octadecene and undecylenic acid, by the methods used here, was clearly demonstrated using FTIR spectroscopy. While we do not repeat that demonstration here, the FTIR spectra as a whole support the model that undecylenic acid covalently binds to the Si particle surface through the ethylenic end. Consequently, the carboxyl group remains free on the surface and renders the coated particle somewhat polar and, hence, dispersible in ethanol. The ethanolic dispersion of undecylenic acid coated nanoparticles was found to be totally stable and homogeneous. After storage under ambient conditions over the course of two months, no visible signs of particle agglomeration or precipitation were observed, and the PL was qualitatively retained (based on visual inspection under an ultraviolet lamp).

TEM images of octadecene-coated particles cast from a toluene dispersion are shown in Fig. 1. It was noted that particles cast on the grid from a toluene dispersion gave clearer and better-separated images than those cast from an ethanol dispersion. Thus, it was easier to estimate the sizes. Many of the particles in Fig. 1(a) may be doublets, triplets, or larger groups of individual particles, but there are no large agglomerates present. The high-resolution images in Fig. 1(b) and (c) show that the particles are somewhat polydispersed in size and shape.

The PL of the neat sample shows a broad peak at about 650 nm. This PL was gradually quenched by the addition of various amines (Fig. 2). Among ethylamine (EA), diethylamine (DEA), and triethylamine (TEA), it was found that the quenching efficiencies of EA and DEA were higher than that of TEA. This observation is consistent with earlier studies on PSi samples.[23] Addition of trifluoroacetic acid (TFA), a strong organic acid, leads to a gradual partial recovery of the PL, with a much greater fraction of the PL recovered in the case of TEA (~80% recovery) than in that of EA and DEA (~50%). Also, for each amine, the addition of excess TFA never results in total recovery of the PL, even after accounting for sample dilution effects. Therefore, the restoration of PL by the addition of TFA can be called quasi-reversible. The PL quenching of octadecene-treated samples in toluene by TEA (Fig. 3) was qualitatively similar to that for the undecylenic acid-treated samples in ethanol. That the same PL quenching and recovery trends are observed for both toluene and ethanol dispersions suggests that the solvent and surfactant molecules

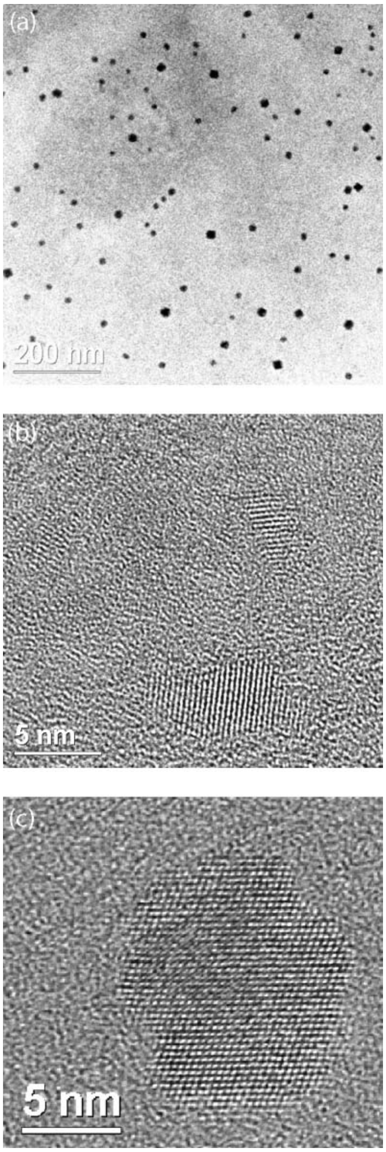

Fig. 1 TEM images of silicon nanoparticles cast from toluene dispersions: (a) low-resolution overview, (b) HRTEM showing the variability of particle size and shape, and (c) HRTEM of a single, relatively large particle.

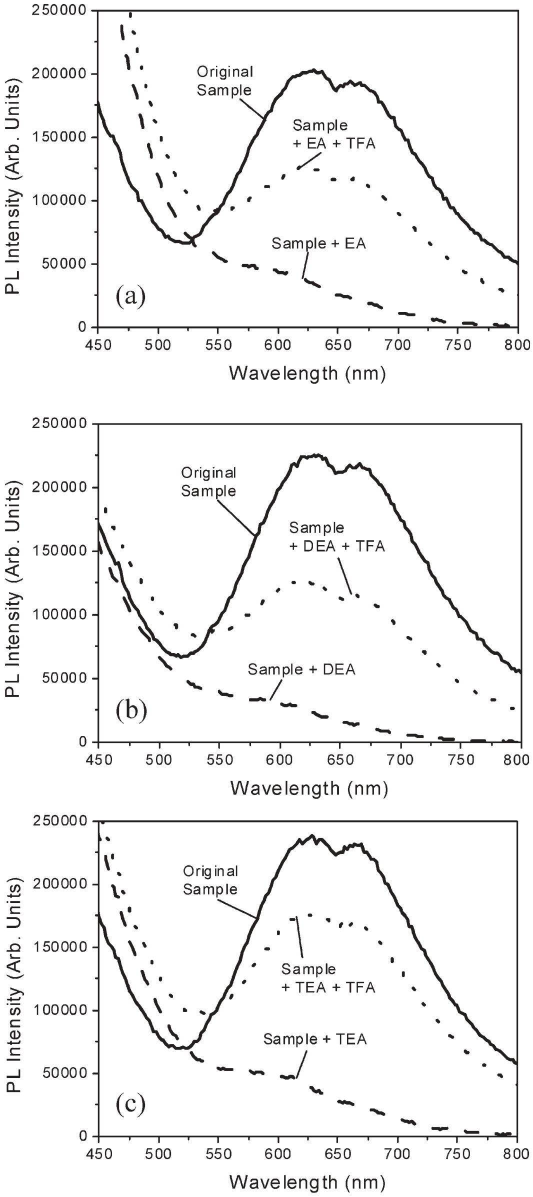

Fig. 2 PL quenching by (a) ethylamine, (b) diethylamine, and (c) triethylamine, and subsequent PL recovery with trifluoroacetic acid. The data have not been corrected for the response of the spectrofluorometer system.

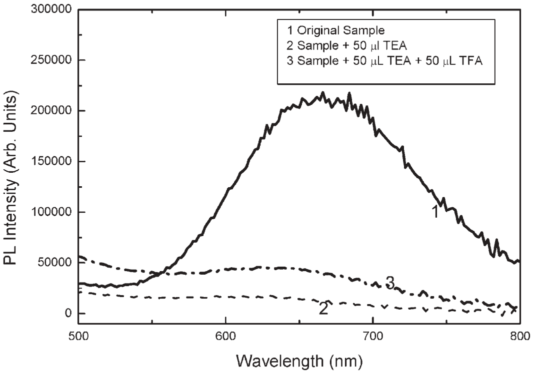

Fig. 3 PL quenching and recovery by the action of TEA and TFA respectively on a toluene dispersion of Si nanocrystallites. The data have been corrected for the response of the spectrofluorometer system.

do not play an important role in the process. We note that the optical absorption of the amine solutions is insignificant from 300 to 700 nm. Therefore, the quenching observed is a real effect caused by a physico-chemical interaction of these amines with the surface of the luminescent Si nanoparticles.

It was also noted that the order of adding the amine and TFA significantly affects the results for some time (several minutes to hours) after the addition, as shown in Fig. 4. In one case, 150 µL of TEA was added to 2.5 mL of the nanoparticle dispersion, followed by 500 µL of TFA. In another measurement the order was reversed, *i.e.* 500 µL of TFA followed by 150 µL of TEA. When addition of TFA followed TEA, the PL started slowly recovering. When the order was reversed (*i.e.* when TFA is added first followed by TEA), the PL slowly decreased. Fig. 5 shows this continued increase and decrease over a period of 30 min. After 24 h, the PL converged to the same equilibrium spectrum in both the experiments, independent of the order of addition of the TEA and TFA.

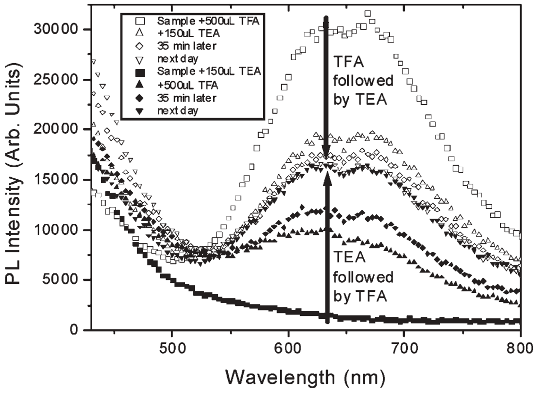

Fig. 4 Effect of the order of addition of TEA and TFA to an ethanol dispersion of Si nanocrystals. The open symbols show evolution of the PL when the addition of 500 uL of TFA to the sample is followed by that of 150 uL of TEA, while the closed symbols show the result when the order of addition is reversed. In each case, the squares show the PL after only the first compound has been added, the upwards triangles show the PL immediately after addition of the second compound, the diamonds show the PL 35 min later, and the downward triangles show the PL the following day. The data have not been corrected for the spectrofluorometer response.

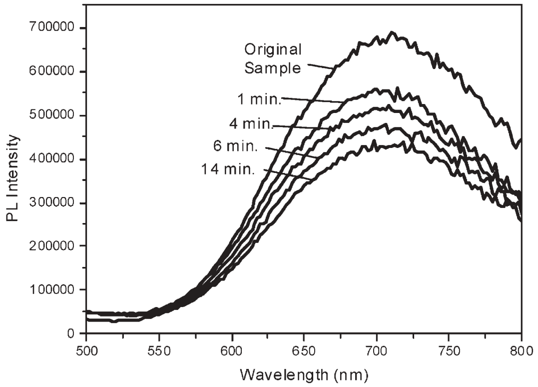

Fig. 5 PL spectra at various times after adding a mixture containing 25 uL of TEA and 100 uL of TFA to a 500 µL ethanol dispersion of Si nanocrystals. The data have been corrected for the spectrofluorometer response.

This result suggests that amines are initially adsorbed on the surface of the particles and decrease the probability of radiative recombination in the particles. Addition of acid leads to an acid–base reaction with the amines that results in displacement of the amines from the surface of the particles, causing restoration of PL. It also appears that the affinity of the amines to the particles surface is considerable, for otherwise in the reverse sequence of adding acid first and amine next, the latter should combine with the acid and hence not be able to quench the PL. The final state of the particles is identical in both cases, but we see that the kinetics of the competitive interaction of TEA and TFA with the particle surface are slow at room temperature. This indicates that the PL recovery observed when TFA is added to the nanoparticle solution is not due simply to the change in acidity of the solution or to the protonation of TEA in solution, since such acid–base reactions would be essentially instantaneous. Rather, a heterogeneous process appears likely.

The kinetics of competitive interaction of TEA and TFA with the particle surface was investigated in a simple manner. 25 µL of TEA and 100 µL of TFA were first mixed and then this mixture was mixed into a cuvette containing 500 µL of an ethanolic particle dispersion. This also resulted in quenching, as shown in Fig. 5. This can happen if binding of TEA to the surface is competitive with its reaction with TFA, or if the TEA–TFA salt (amine–acid addition salt) can also cause PL quenching, as has been seen in the case of other salts on PSi, mentioned above.

Besides the three small alkylamines listed above, experiments were also performed with 2 M ethanolic solutions of two selected symmetric nitrogen containing molecules, namely pyrazine and piperazine. It was found that the PL was quenched by the addition of these molecules, and little or no PL recovery was observed upon subsequent addition of TFA. In the case of piperazine, the addition of TFA resulted in precipitation of the corresponding amine–acid salt and the supernatant did not show any PL.

Studies of PL quenching on PSi have been carried out in the past by exposing it to a variety of chemical species. In one such study by Chun *et al.*,[17] the PL intensity was found to change reversibly by tuning the pH of the medium in which the PSi was immersed, with higher pH quenching the PL and lower pH restoring it. Similarly, in studying the effect of different solvents on PL, Lauerhaas *et al.*[16] found that the quenching efficiency increased with the increasing dipole moment of the polar solvents. They explained the quenching mechanism by a surface trap model where the polar molecules are adsorbed on the surface of PSi and tend to stabilize electrons and holes, thereby causing non-radiative or sub-band gap emission phenomena which dominates the carrier recombination process. Chandler-Henderson *et al.*[23] studied the quenching of PL from PSi by different amines, and found that steric factors play a role in their quenching abilities. There, consistent with our observation with EA, DEA and TEA, a tertiary amine showed reduced quenching efficiency, compared to the secondary and primary amines. The results were explained by the restricted diffusion of a bulky amine through the labyrinthine network of PSi.

The present results shed new light on these previous studies by separating any effects of transport through the porous silicon network from the interactions of quenchers and emitters. Here, we prepared and studied a clear and homogeneous dispersion of Si nanoparticles. As a result, the Si nanoparticles can be considered free standing where the solvation forces dominate attractive interactions among the particles, thus preventing agglomeration. In such a dispersion of free standing individual particles, attack by chemical species from all directions is equally likely. This situation, therefore, is different from their PSi counterpart where the porosity of the wafer hinders the mobility of the bulky species.

It appears that the quenching efficiency of the amines depends on a complex combination of basicity, dipole moment, and steric factors. The amines may bind to the surface of Si nanocrystals by a dative bond, and, despite the surface passivation by undecylenic acid, there may be enough unpassivated surface for TFA to interact with these surface regions. Because of the reactivity of the carboxylic acid with amines, it is probable that some amines can react with the surface-terminal carboxylic acid group. In addition, for these free-standing particles, the surfactant on the particle surface that allows formation of a stable dispersion may also mediate or protect against quenching of the PL. In the experiments described here, similar results were obtained for octadecene-coated and undecylenic acid-coated particles quenched by triethylamine, and the quenching behavior was qualitatively the same as for untreated particles, having just –OH or –H surface termination. Quantitative comparisons cannot readily be made since the –OH and –H terminated particles do not form stable dispersions in solvents compatible with the amines. In other work[31] it was shown that coating the particles using a self-assembled monolayer of bromopropylsilane linked to the –OH terminated particle surface substantially protected the particles against PL quenching by amines.

We estimate that the number of amine molecules added in the experiments substantially exceeds the number that could be bound to the terminal carboxylic groups as explained below. Taking the average size of the Si nanoparticles as 4 nm in diameter, the number density of Si nanoparticles in a dispersion of 1 mg mL^{-1} is $\sim 10^{16}$ mL^{-1}. Allowing a parking area of approximately 20 $Å^2$ per molecule, as often calculated from Langmuir–Blodgett isotherm studies,[32] yields a maximum carboxyl concentration of about 3×10^{18} per mL, whereas the number of amine molecules available from 100 μL of 2 M solution (final $\sim$0.08 M) is $\sim 10^{20}$.

We suggest that the amines are adsorbed (possibly assisted by a hydrocarbon-like layer tethered to the Si surface). After the surface adsorption, the donor character of the amine can stabilize holes, thus preventing radiative recombination. Conceivably, amine–hole interaction would depend on both the basicity and polarity of the amines and on steric factors.

The dipole moments of EA, DEA and TEA are 1.22 D, 0.92 D and 0.66 D, respectively, whereas pyrazine and piperazine, being symmetric molecules, have zero dipole moments.[33] For the three alkyl amines, the decrease of quenching efficiency with decreasing dipole moment is in agreement with earlier studies of mapping quenching efficiencies with molecular dipole moments in the study on PSi.[34] However, the efficient quenching effected by pyrazine and piperazine does not conform to the relationship between molecular dipole moment of the quencher and its quenching efficiency that was observed in the past studies. Thus, we conclude that the amine dipoles do not play a major role in the quenching phenomenon.

As for the recovery of PL by addition of TFA, it is likely that protonation of the nitrogen lone electron pair is responsible for disengaging the amine from the surface of the Si particles. Among the three monodentate amines, because of the higher basicity of TEA (pK_a = 11.01), its protonation is slightly greater than for EA (pK_a = 10.807) or DEA (pK_a = 10.489)[33] and this might be taken as the explanation for the greater PL recovery from TA quenching. In the case of pyrazine (pK_a = 0.65) and piperazine (pK_a = 5.56 and 9.83), the PL recovery is not observed at all; this calls for a different explanation. One possible reason is that the addition salts of pyrazine and piperazine are efficient quenchers themselves. Our observation that addition of premixed TEA and TFA to the ethanol nanoparticle dispersion partially quenched the PL (Fig. 5) suggests that the amine salts are also capable of quenching.

In our experiment, steric factors should be inconsequential in determining transport of quenchers to the particle surface, unlike the case of PSi. Because of the dilute and clear dispersion employed in our study, the amines should have unimpeded access to the particles from all directions. However, the size of the amines could still play a role if the mechanism involves the amines forming a physically adsorbed layer on the surface. Among the monodentate amines, the bulkier tertiary amine could be adsorbed on the surface less efficiently than the smaller ones due to steric effects, and consequently the tertiary TA would have a reduced quenching power. Here again, in our study, the di-amine shows a higher quenching ability, in spite of the fact that because of its ring structure, the adsorption on the modified particle surface should be less favorable on geometric grounds as well as the fact that the incoming quencher molecules have to make their ways through the surfactant layer.

We also performed qualitative checks of the quenching ability of a number of other molecules with electron lone pairs, including trioctylphosphine, trioctylphosphine oxide, urea, thiourea, aminoethanethiol, hydrazine sulfate, hydroxylamine sulfate and tetraoctylammonium bromide. We found that none of the above compounds quenched the PL noticeably. Thus, it appears that phosphorous or oxygen, in spite of their Lewis electron pairs, do not bind to the Si particle surface and/or do not stabilize the holes and lead to quenching in a manner similar to the amines. Urea and thiourea (very weak bases) do not make their lone electron pairs available. It is interesting to compare ethylamine with aminoethanethiol where we find that the presence of a thiol group eliminates the quenching ability of the molecule. Similarly, in the case of tetraoctylammonium bromide, hydrazine sulfate, and hydroxylamine sulfate, the lone pairs of electrons have been protonated and are, therefore, not available for quenching. It should be noted, however, that Canaria *et al.* observed PL quenching on PSi by dodecyltrimethylammonium bromide, a similar molecule, in aqueous solution where it was accompanied by chemical corrosion.[35]

Earlier reports of PL quenching in Si nanoparticles mostly involved particles prepared *via* an electrochemical etching process. The surface properties of nanoparticles depend strongly on their preparation methods. Our aerosol mediated method combined with surface modification is notably different from the existing literature reports. We note that the surfactants that modify the surface and regulate dispersibility of the particles in different solvents does not detectably interfere with the photophysics with regard to PL quenching by molecules (basic, polar, *etc.*) analogous to those studied by different groups. From the detailed work by various authors, especially from the elegant work by Fauchet group[36] on the quenching of PSi by various agents, the relative position of the different molecules in the electrochemical series is important in determining their quenching ability and the quenching mechanisms. They can be classified, by analogy with the results of Fauchet group with nitrogenous species,[36] as valence band quenchers or conduction band quenchers, depending on whether their redox potentials *vs.* hydrogen are positive or negative respectively. Additionally, if the quencher redox level is above the conduction band or below the valence band of that of the Si nanocrystallites, there is an energy barrier to electron transfer and the quenching ability of the molecule is consequently suppressed. Therefore, the relative redox potential of a species could override its acid–base properties that could be operating according to Chun *et al.*'s mechanism,[17] in determining its absolute quenching ability. It appears that amines make suitable conduction band quenchers.

However, Chun *et al.*[17] have shown that the porous Si surface behaves as if the surface has mono-protic sites. This is attributed to the formation of Si–O(H)$^+$–Si., which could be present presumably in the unmodified regions on the surface of our free standing Si particles. Thus, we also cannot rule out the possibility of their proposed mechanism of an acid–base reaction for photoquenching.

Conclusions

We conclude that the amines interact with the exciton of the particles in a complicated manner and provide a ready non-radiative recombination route resulting in PL quenching. The amines have a redox potential relative to that of the Si nanocrystallites that allows energy transfer to occur easily, as opposed to other organic molecules that otherwise have electron donating ability but do not quench PL. We conclude that the availability of electron lone pairs for surface binding plays a more crucial role for quenching phenomena irrespective of the polarity of the molecule.

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