Surface Morphology Dependent Photoluminescence from Colloidal Silicon Nanocrystals

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Monodisperse 1–2 nm silicon nanocrystals are synthesized in reverse micelles and have their surfaces capped with either allylamine or 1-heptene to produce either hydrophilic or hydrophobic silicon nanocrystals. Optical characterization (absorption, PL, and time-resolved PL) is performed on colloidal solutions with the two types of surface-capped silicon nanocrystals with identical size distributions. Direct evidence is obtained for the modification of the optical properties of silicon nanocrystals by the surface-capping molecule. The two different surface-capped silicon nanocrystals show remarkably different optical properties.

Nanocrystals, also known as quantum dots, offer a unique opportunity to study material science in the regime between the molecular and bulk states.[1,2] The energetic and optical properties of nanoscale materials are influenced by the effect of quantum confinement, and this leads to interesting properties that can be exploited in many electronic and photonic applications.[3–14] Indirect band gap materials, such as silicon, show remarkable changes in their optical properties when the size of a crystallite is reduced to the nanoscale (<10 nm).[15–19] Silicon in its bulk form has become an extremely important semiconductor material for many electronic applications, and the investigation into the properties of nanoscale silicon is critical for its future technological development and understanding.

The indirect band gap in silicon is a phonon-mediated transition and this leads to near-IR photoluminescence with poor efficiency. Quantum confinement in silicon nanocrystals leads to an enhanced photoluminescence efficiency in the visible spectral region. Strong quantum confinement in silicon increases the probability of radiative recombination via direct band gap transitions and reduces phonon-assisted indirect band gap transitions.[15–19] In silicon, this requires the physical dimensions of the nanocrystals to be on the order of or less than the bulk exciton Bohr radius of 4 nm.[15–19]

Silicon nanocrystals with physical dimensions less than 8 nm have a high surface-to-volume ratio, and it is theoretically predicted that the surface morphology drastically affects the electronic charge distribution.[20,21] This leads to modification of the optical properties, which in turn has a major impact on the utilization of silicon nanocrystals in any optoelectronic application. Zhou et al. showed using density function theory (DFT) calculations that surface chemistry can alter the internal electronic structure of silicon nanocrystals and this leads to modifications of the band gap energy and the oscillator strength.[22] Silicon nanocrystals (1–2 nm) with an oxide surface

shell are theoretically predicted to exhibit dipole-forbidden red emission with a long lifetime (10^{-3} s), whereas 1–2 nm silicon nanocrystals with a hydrogen surface termination are predicted to have an electric dipole-allowed direct band gap transition that results in blue emission with short lifetimes (10^{-8} s). Reboredo et al. recently calculated that changing the surface termination of 1–2 nm silicon nanocrystals from hydrogen (Si–H) to alkyl groups (Si–C–R) theoretically resulted in only a small reduction of the energy gap (0.5 eV) as compared to the large reduction observed with an oxide (Si–O) surface termination (2.3 eV).[21] Capping 1–2 nm silicon nanocrystals with alkyl groups is the ideal way to terminate the surface, since a Si–C bond has higher enthalpy than a Si–H bond and minimal change is induced in the optical spectra, unlike the effect of a Si–O surface bond.

Wet chemistry techniques have shown the most promise for synthesizing silicon nanocrystals in the strong confinement regime with relatively monodisperse size distributions.[23] However, to date there exists minimal evidence showing the direct effect and comparisons of different surface-capping ligands on the optical properties of colloidal silicon nanocrystals. The actively debated topic of the origin of the photoluminescence in silicon nanocrystals is facilitated by the lack of systematic studies.

We have recently reported the synthesis of relatively monodisperse 1–2 nm silicon nanocrystals in inverse micelles with strong blue photoluminescence.[23,24] The silicon nanocrystals were capped with either allylamine or 1-heptene, and both surface-capping molecules utilized a Si–C surface bond that differed only in the number of carbon atoms and the termination end group.[23,24] The photoluminescence (PL) from the silicon nanocrystals was in the blue region of the spectrum (400–500 nm), with the PL quantum yields reported to be as high as 10% and attributed to recombination across the direct band gap transition Γ–Γ.[23,24] Before the optical properties of these silicon nanocrystals can be fully exploited in LEDs and as biological chromophores, a full characterization of the steady-state and time-resolved photoluminescence spectra must be performed.

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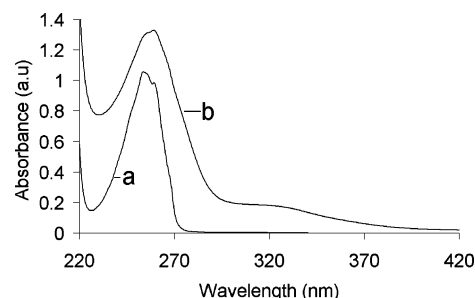*J. Phys. Chem. B, Vol. 109, No. 41, 2005* **19065**
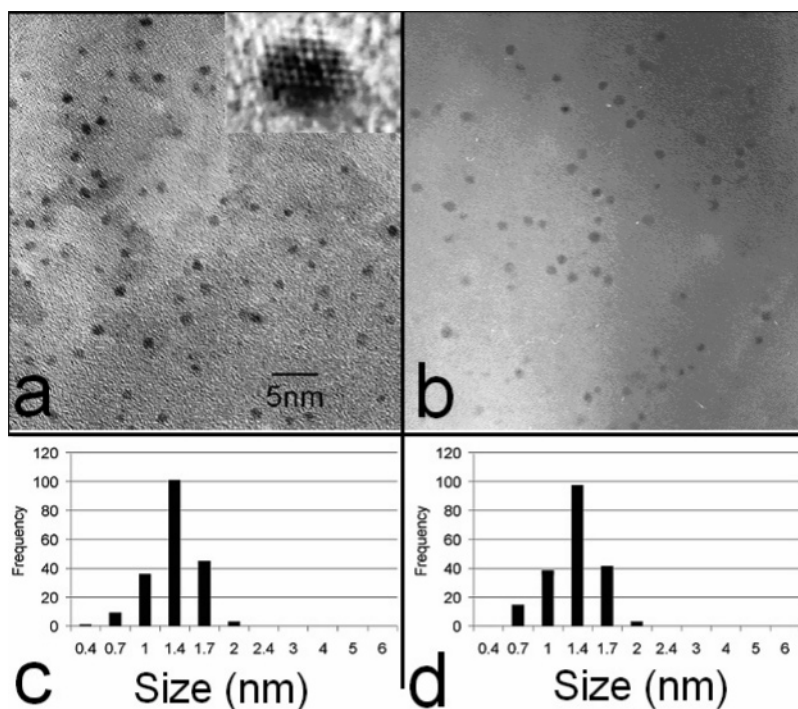
Figure 1. High-resolution transmission electron microscope images of (a) allylamine-capped silicon nanocrystals and (b) 1-heptene-capped silicon nanocrystals. Scale bar is for both images. Inset shows an allylamine-capped silicon nanocrystal with observable lattice fringes. (c) Size histogram of allylamine-capped silicon nanocrystals and (d) size histogram of 1-heptene-capped silicon nanocrystals.

Identical ensembles of silicon nanocrystals capped with allylamine or 1-heptene are prepared, and the differences in the optical properties are examined. Ensuring that the size distribution of the silicon nanocrystals is identical for both types of surface-capping molecules allows us to attribute any change in the optical properties to the modification of the surface and surrounding environment of the silicon nanocrystals.

The silicon nanocrystals were prepared according to a previously reported method.[23,24] Briefly, 92 μL of $SiCl_4$ was added to 100 mL of anhydrous toluene and 1.5 g of tetraocty-lammonium bromide (TOAB). Silicon nanocrystals (1−2 nm) were formed by adding 2 mL of the reducing agent $LiAlH_4$ and letting the reaction run for 3 h under vigorous stirring. After 3 h, the excess reducing agent was quenched with 20 mL of anhydrous methanol. The solution of hydrogen-terminated silicon nanocrystals was then split in half so that the surface-capping procedure could be applied to an identical ensemble of silicon nanocrystals. The surface-capping process was performed on each half by adding 20 μL of 0.05 M H_2PtCl_6 followed by 1 mL of either 1-heptene for hydrophobic nanocrystals or allylamine for hydrophilic nanocrystals. Removing the solvent using a rotary evaporator to form a powder and then dispersing in either hexane (1-heptene-capped) or water (allylamine-capped) performed purification and solvent exchange. The solutions were then filtered twice to remove the TOAB, and clear solutions of silicon nanocrystals in hexane or water were obtained.

To properly examine the properties of the silicon nanocrystals requires the removal of the surfactant (TOAB) and other byproducts of the reaction. TOAB and other reaction byproducts prevent a simple interpretation of the optical spectra, especially in the UV region, and also prevent TEM analysis because of the reduced contrast. Capping the surface of the silicon nanocrystals with allylamine or 1-heptene allows them to be purified and the surfactant and byproducts removed from the analyzed solutions.[23,24] For this reason, it is difficult to compare
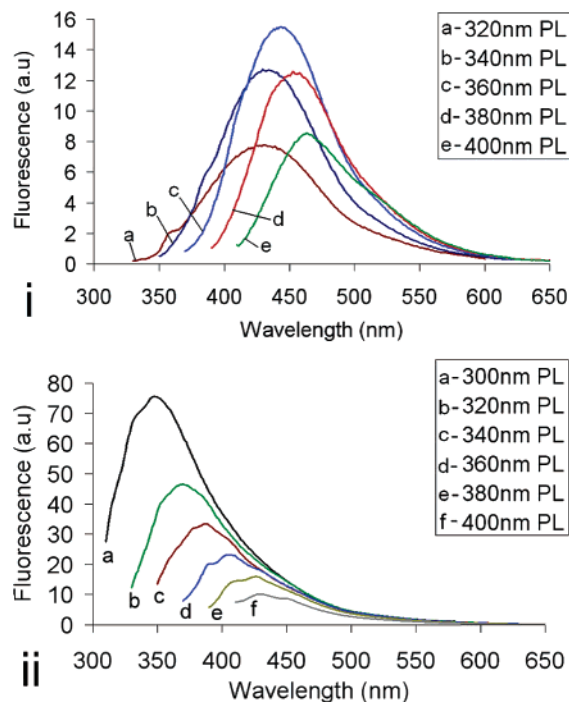

Figure 2. Absorption spectra of (a) 1-heptene-capped silicon nanocrystals in hexane and (b) allylamine-capped silicon nanocrystals in water.

the optical properties of the silicon nanocrystals before and after surface modification.

Figure 1 shows a high-resolution transmission electron microscope (HRTEM) image of (a) allylamine-capped silicon nanocrystals and (b) 1-heptene-capped silicon nanocrystals. The size of the silicon nanocrystals are between 1 and 2 nm, and this agrees well with our previous reports.[23,24] The silicon nanocrystals were highly crystalline and showed no signs of aggregation. The inset of Figure 1a shows a particle with clearly observable lattice fringes. The images in Figure 1 confirm that the size and the size distribution of both the allylamine- and 1-heptene-capped silicon nanocrystals are equivalent. This is further supported by size histograms, shown in Figure 1c and d, obtained by analyzing 200 individual nanocrystals using TEM images of allylamine-capped silicon nanocrystals and 1-heptene-capped silicon nanocrystals. Energy-dispersive X-ray spectroscopy confirmed the presence of silicon and showed no signs of platinum.

Figure 2 shows the UV−vis absorption spectra for (a) 1-heptene-capped silicon nanocrystals in hexane and (b) allylamine-capped silicon nanocrystals in water. The allylamine-capped silicon nanocrystals (NCs) exhibit absorption over a much greater spectral range (240−400 nm) than the 1-heptene-
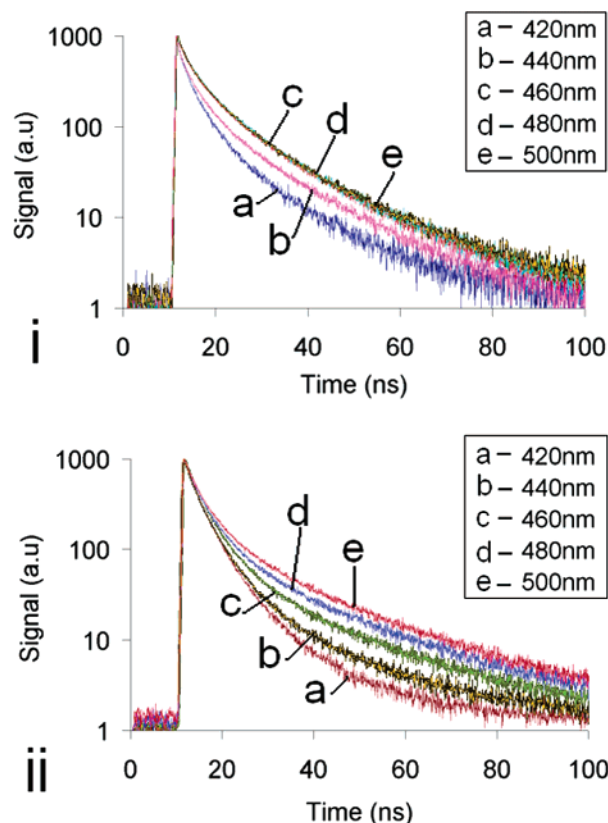
Figure 3. Photoluminescence spectra of (i) allylamine-capped silicon nanocrystals in water and (ii) 1-heptene-capped silicon nanocrystals in hexane.

Figure 4. Time-resolved photoluminescence spectra of (a) allylamine-capped silicon nanocrystals in water and (b) 1-heptene-capped silicon nanocrystals in hexane.

capped silicon NCs (280−240 nm). The peak at 260 nm in the absorption spectra in Figure 2 agrees relatively well with previous reports for 1-2 nm silicon nanocrystals and also alkyl-terminated silicon nanocrystals.[17,25] The allylamine-capped silicon nanocrystal sample exhibits a shoulder at 340 nm, which is attributed to absorption from the $\Gamma-\Gamma$ direct band gap transition.[17,23,24] This transition is also observed in the absorption spectrum of the 1-heptene-capped silicon nanocrystal solution, but it is small in comparison to the absorption between 250 and 290 nm.

Figure 3 shows the photoluminescence spectra of (i) ally-lamine-capped silicon nanocrystals in water and (ii) 1-heptene-capped silicon nanocrystals in hexane. Photoluminescence spectra were obtained using excitation wavelengths ranging from 300 to 400 nm in 20 nm intervals. Clearly, there exists a stark difference in the optical response of the two differently capped silicon nanocrystal solutions. The photoluminescence of the allylamine-capped silicon nanocrystal solution has a peak that ranges from 430 nm for the 320 nm excitation to 465 nm for the 400 nm excitation. This gives only a 35 nm red shift in the PL peak position, as the excitation wavelength is increased 80 nm from 320 to 400 nm. On the contrary, the photoluminescence of the 1-heptene-capped silicon nanocrystal solution has a peak that ranges from 350 nm for the 300 nm excitation to 450 nm for the 400 nm excitation. This corresponds to a 100 nm red shift in the PL peak position, as the excitation wavelength is increased 100 nm from 300 to 400 nm.

The photoluminescence spectra of the 1-heptene-capped silicon nanocrystals also display small features within the main peak that are not observed in the allylamine-capped silicon nanocrystal PL spectra. The 1-heptene-capped silicon nano-crystal solution also displays emission with higher energy than the allylamine-capped silicon nanocrystal solution for the same excitation wavelength. Since both solutions contained an identical size distribution of silicon nanocrystals, the vast difference in the PL spectra must be attributed to the effect of the surface-capping molecule and environment. This result provides direct

evidence that the surface-capping molecule plays an important role in the radiative recombination mechanisms in 1−2 nm silicon nanocrystals.

The photoluminescence spectra in Figure 3 show no signs of emission at 600 nm, which is typically associated with defects and Si−O surface bonds.[20−22] This shows that the silicon nanocrystals are well-passivated, robust, and highly crystalline. However, it is unlikely that all the silicon nanocrystal surface atoms are bonded to a surface passivating molecule (allylamine or heptene), and the small number of dangling silicon surface atoms probably form a Si−O surface state. FTIR measurements on the silicon nanocrystals have also been previously performed and showed a small degree of Si−O surface bonds.[23,24] The PL spectra in Figure 3 show minimal emission from Si−O surface bonds leading to the conclusion of a low defect density and a high percentage of surface passivation by the organic capping molecules. Methanol, hydrochloric acid, and sodium hydroxide were each added to separate solutions of silicon nanocrystals, and no obvious shifts in the photoluminescence were detected. This indicates that the solvent does not play a major role in shifting the emission properties of silicon nanocrystals because of their well-passivated surfaces.

Further insights into the optical behavior of the two different types of surface-capped silicon nanocrystals can be obtained by using time-resolved photoluminescence spectroscopy.[26] Time-resolved decays were obtained using a time-correlated single-photon counting spectrometer (Picoquant Fluotime 200) with 380 nm wavelength and 100 fs pulses sourced from a frequency-doubled mode-locked Ti:sapphire laser (Spectra Physics Tsunami). Figure 4 shows the time-resolved PL spectra from (i) allylamine-capped silicon nanocrystals in water and (ii) 1-heptene-capped silicon nanocrystals in hexane. The emission was monitored between 420 and 500 nm in 20 nm

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intervals, using an excitation wavelength of 380 nm. All PL decays required a three-component exponential fit with time constants of approximately 0.6, 4, and 14 ns. This suggests that there exist multiple de-excitation processes in the silicon nanocrystals. The PL lifetimes agree well with our previous reports of PL decay measurements and with other reports from colloidal silicon nanocrystals with direct band gap emission.[17,19,24] The rapid PL decay is consistent with direct band gap recombination in silicon nanocrystals.[22,27] Emission from silicon nanocrystals with an oxygen-passivated surface typically has a long PL decay with a microsecond lifetime.[26]

For the allylamine-capped silicon nanocrystals, the PL decay is fastest for the emission at 420 nm, then slightly longer at 440 nm, and then, it reaches a constant decay rate from 460 to 500 nm. Alternatively for the 1-heptene-capped silicon nanocrystals, the PL decay is fastest for the 420 nm and gradually increases for each interval to 500 nm. The difference in the dynamics of the PL decays provides further evidence for different radiative recombination pathways for the allylamine- and 1-heptene-capped silicon nanocrystals.

The combination of all these optical measurements clearly indicates that the surface-capping molecule and environment strongly affect the optical properties of 1−2 nm silicon nanocrystals. Both the allylamine- and 1-heptene-capped silicon nanocrystals have a Si−C surface bond and have photoluminescence in the blue region of the visible spectrum in agreement with the theoretical predictions of Zhou et al.[22] The difference in the optical spectra of the silicon nanocrystals capped with allylamine as compared to 1-heptene may be related to the difference in the end termination group of the surface capping molecules. Allylamine is a short-chain polar molecule with an NH_2 termination at one end, whereas 1-heptene is a short-chain nonpolar molecule with a CH_3 termination. It is possible that the electronic charge distribution in the allylamine-capped silicon nanocrystals is modified by the polar nature of the allylamine in a similar way to that of a Si−O surface bond in 1−2 nm silicon nanocrystals. This may explain why the band gap of the allylamine-capped silicon nanocrystals is also slightly lower than that of the 1-heptene-capped silicon nanocrystals. Reboredo et al. suggest that the number of bound states in silicon nanocrystals increases as the length of the surface-capping molecule increases.[21] They also suggest that the electronic structure of the 1−2 nm silicon nanocrystals changes because of the large overlap of these new states with the alkyl chains and the little overlap with the valence band wave functions localized in the silicon core, and the energy gap is not modified significantly.[21] However, the fast recombination rate of all silicon nanocrystals with both types of surface capping indicates that the emission is still from an electric dipole-allowed direct band gap transition.[27]

In conclusion, we showed that the optical properties of 1−2 nm colloidal silicon nanocrystals are strongly dependent upon the surface morphology. Apart from providing a detailed characterization of the steady-state and time-resolved optical properties, we also hope these results will stimulate future research into the computational studies of the optical process in colloidal silicon nanocrystals with more complex surface chemistry, such as amine-terminated surface-capping ligands.

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