Charge transfer state emission dynamics in blue-emitting functionalized silicon nanocrystals

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We explore the dynamics of blue emission from dodecylamine and ammonia functionalized silicon nanocrystals (Si NCs) with average diameters of ~3 and ~6 nm using time-resolved photoluminescence (TRPL) spectroscopy. The Si NCs exhibit nanosecond PL decay dynamics that is independent of NC size and uniform across the emission spectrum. The TRPL measurements reveal complete quenching of core state emission by a charge transfer state that is responsible for the blue PL with a radiative recombination rate of \( \sim 5 \times 10^7 \) s\(^{-1}\). A detailed picture of the charge transfer state emission dynamics in these functionalized Si NCs is proposed.

1. Introduction

Nanostructured silicon (Si) has received significant attention owing to its strong tunable visible photoluminescence (PL) that has potential applications in optical devices such as light-emitting diodes\(^1,2\) and silicon-based full color displays,\(^3,4\) as well as luminescent labels for biological imaging,\(^5\) among others. PL from silicon nanocrystals (Si NCs) can be tuned from infrared to the most intriguing because of the relatively small indirect bandgap of bulk Si (1.1 eV) and the wide variety of potential emission mechanisms that have been proposed. Besides QC in Si NCs with diameters \( d < 2 \) nm,\(^15,16\) blue emission has also been discussed in terms of surface oxygen-related defects,\(^17\) amorphous surface layers,\(^18\) and near-interface traps.\(^19\) Recently, blue emission from charge transfer (CT) states in Si NCs has been suggested by Dasog et al. based on solvatochromic studies that showed a dependence of the PL peak emission on the polarity of the solvent.\(^10,20\) To date, a detailed study of the PL dynamics of these materials, which provides insights into the specific nature of the blue emission process, has not been performed.

In this letter, we used time-resolved photoluminescence (TRPL) to probe the emission dynamics in blue-emitting functionalized Si NCs with different NC sizes and surface passivation prepared by reacting dodecylamine with chloride-terminated Si NCs and ammonium bromide with hydride-terminated Si NCs. We show that the blue emission originates from a CT state at the Si/SiO\(_2\)/N\(_2\) interface. Understanding the dynamics of the CT emission process will have an impact on potential applications of such blue-emitting Si NCs in optoelectronics. In particular, since CT is an intermediate step for charge separation, it is important to understand CT dynamics for designing efficient Si NC-based solar cells.

2. Materials and methods

2.1 Synthesis of functionalized Si NCs

The syntheses of the colloidal Si NCs used in this study has been described in detail elsewhere.\(^13,20,21\) Briefly, commercial
hydrogen silsesquioxane was thermally processed in a slightly reducing atmosphere (95% Ar/5% H₂) at 1100 °C (for ~3 nm Si NCs) and 1200 °C (for ~6 nm Si NCs) to yield well-defined Si NCs embedded in a SiO₂-like matrix. Hydride-terminated Si NCs were obtained from the oxide matrix via HF etching. The Si NCs were functionalized using dodecylamine and ammonium bromide to obtain nitrogen-bonded colloidal Si NCs. Details of the functionalization of Si NCs is presented in the (ESI†).

2.2 Characterization

Fourier transformation infrared spectroscopy (FT-IR) was performed using a Nicolet Magna 750 IR spectrometer. Raman spectra were recorded on Renishaw inVia Raman Microscope. Transmission electron microscopy (TEM) and selected area electron diffraction (SAED) analyses were performed using a JOEL-2010 (LaB₆ filament) with an accelerating voltage of 200 keV. TEM samples were prepared by drop coating the Si NC suspension onto a carbon coated copper grid with a 400 µm diameter hole. The NC size was averaged over 200 particles determined using ImageJ software (version 1.45).

2.3 Time-integrated and time-resolved PL spectroscopies

TRPL spectroscopy measurements on sub-nanosecond (sub-ns), nanosecond (ns), and microsecond (µs) time scales were carried out at room temperature on functionalized Si NCs dissolved in toluene. Si NC solutions were placed in 10 mm quartz cuvettes for PL measurements. For nanosecond-TRPL (referred to here as ns-TRPL) measurements, samples were excited using 400 nm, 70 fs excitation pulses from the second harmonic output of an ultrafast amplified Ti:sapphire laser source (Coherent RegA) with a repetition rate of 250 kHz. The PL was detected using an avalanche photodiode coupled to a monochromator, and analyzed using time-correlated single photon counting unit (PicoQuant, PicoHarp 300) with a temporal resolution of 50 ± 4 ps. The excitation spot size was ~20 µm at the center of the solution, and the average excitation fluence was varied from 0.02 to 2.94 mJ cm⁻². The time-integrated PL (TIPL) spectra were detected by a thermoelectrically-cooled CCD coupled to a monochromator. For comparison, steady-state PL (SSPL) measurements were also carried out using a continuous-wave 406 nm laser diode with average excitation power of 4.8 mW. All the PL spectra were corrected to the spectral response of the system.

Microsecond-TRPL (referred to here as µs-TRPL) was performed using 400 nm, 50 fs excitation pulses from a frequency-doubled amplified Ti:sapphire laser source (Coherent Legend Elite) operating at a repetition rate of 1 kHz. The average excitation power was 4.5 mW focused to a spot size of ~500 µm, resulting in a fluence of 2.29 mJ cm⁻². The PL was collected by a fast silicon photodiode and amplifier (rise time of ~45 ns, fall time <µs) connected to a 300 MHz oscilloscope. Bandpass filters with 10 nm bandwidth were used to select emission wavelengths between 450 nm and 760 nm. A 435 nm longpass filter was used in all the PL measurements to block scattered excitation light. The transmission of the longpass filter was 86% at 450 nm, followed by a sharp decrease in transmission at shorter wavelengths, as shown in Fig. S1 (ESI†). The filter cut-off region is shown as a blue shaded area in all the PL spectral plots.

3. Results and discussion

The schemes for ammonia and dodecylamine functionalized Si NCs are shown in Fig. 1(a) and (c), respectively. Both samples exhibit visible blue PL when excited by 365 nm UV lamp, as shown in Fig. 1(b) and (d). Selected-area electron diffraction (Fig. S2, ESI†) shows high crystallinity for the ammonia and dodecylamine functionalized Si NCs. Typical TEM images of the functionalized Si NCs are shown in Fig. 1(e), (f) and Fig. S3(a) and (c) (ESI†). Two different sizes of dodecylamine and ammonia functionalized Si NCs were prepared to determine the effect of NC size on the PL emission dynamics for this particular set of functionalized Si NCs. Analysis of TEM micrographs shows that ammonia functionalized Si NCs have average diameters of 3.4 ± 0.4 nm and 5.7 ± 0.6 nm (Fig. 1(g) and S3(b), ESI†) while dodecylamine functionalized Si NCs have average diameters of 3.1 ± 0.4 nm and 5.8 ± 0.7 nm average diameters (Fig. 1(h) and Fig. S2(d), ESI†).

Surface passivation was verified using FTIR and Raman spectroscopies, as shown in Fig. 2. FTIR measurements revealed that the functionalized Si NCs exhibit partial surface oxidation, as evidenced by a Si–O–Si stretching mode (Fig. S2, ESI†). Analysis of TEM micrographs shows that ammonia functionalized Si NCs show strong N–H absorptions at 3000–3100 cm⁻¹, consistent with ammonia passivation of the Si surface. On the other hand, Fig. 2(b) shows a characteristic N–H stretch at ca. 3300 cm⁻¹ in neat dodecylamine, which is absent from the Si NC spectrum, consistent with an amine group attaching to the Si surface. Features attributable to C–H stretches of the alkyl chain are observed at ca. 2900 and 1470 cm⁻¹ in neat dodecylamine and functionalized Si NCs. Si–N vibrational modes at ca. 840 cm⁻¹ for both ammonia functionalized Si NCs and dodecylamine functionalized Si NCs were observed in Raman spectra (Fig. 2(c) and (d)) further confirming the nitrogen bonding to the Si surface. Si–Si vibrational modes were also observed at ca. 520 cm⁻¹.

Fig. 3(a) and (b) show the TIPL of the ammonia and dodecylamine functionalized Si NCs, respectively. The high-energy shoulder of the PL is truncated by the transmittance of the optical filter (Fig. S1, ESI†). Interestingly, the TIPL spectra show size-independent PL spectral profiles, with peak emission at ~493 nm for ammonia functionalized Si NCs and at ~479 nm for dodecylamine functionalized Si NCs. Size-independent PL emission is incompatible with quantum confined core state emission. In addition, the measured PL spectra are significantly blue shifted with respect to QC Si core bandgap transitions reported elsewhere for Si NCs with similar diameters (i.e., QC emission at ~700 nm for 3.1 nm and ~795 nm for 5.8 nm Si NCs). It is therefore unlikely that the observed size-independent blue PL in these functionalized Si NCs arises as a result of core state recombination.
Fig. 3(c) and (d) show the ns-TRPL emission dynamics for ~3 nm and ~6 nm ammonia and dodecylamine functionalized Si NCs, respectively, measured at 470 nm. The PL lifetime exhibits a bi-exponential decay,

\[ I(t) = A_1 e^{-t/t_1} + A_2 e^{-t/t_2} + C, \]

where \( t_1 \) and \( t_2 \) are the decay times and \( C \) is a constant offset much smaller than \( A_1 \) and \( A_2 \). As shown in Fig. 3(c) and (d), the PL dynamics of both functionalized Si NCs at an emission wavelength of 470 nm is independent of nanocrystal size. As summarized in Table S1 (ESI†), ammonia functionalized Si NCs have lifetimes of \( t_1 = 1.81 \) ns and \( t_2 = 6.12 \) ns for \( d = 3.4 \) nm and \( t_1 = 1.81 \) ns and \( t_2 = 6.10 \) ns for \( d = 5.7 \) nm. Dodecylamine functionalized Si NCs exhibit slightly shorter PL lifetimes of \( t_1 = 1.46 \) ns and \( t_2 = 5.76 \) ns for \( d = 3.1 \) nm and \( t_1 = 1.64 \) ns and \( t_2 = 5.86 \) ns for \( d = 5.8 \) nm. We also explored the dependence of the PL lifetimes on emission wavelength (Table S1 and Fig. S4, ESI†). All the samples exhibit very fast PL lifetimes shorter than 7 ns. In addition, the PL lifetimes of all the samples do not vary significantly with emission wavelength (the difference is \( \leq 11\% \) between 470 nm to 620 nm, as seen in Table S1, ESI†). Bi-exponential PL decays are typically observed as a result of energy transfer either from core/band edge states to surface states or from smaller to larger NCs.27–29 However, the PL red-shift upon energy transfer predicted by these mechanisms is not observed here. μs-TRPL measurements performed from 450 to 760 nm did not exhibit any long-lived PL lifetime, as shown in Fig. S5 (ESI†), in stark contrast with QC emission of NCs of similar size (3–6 nm) that is known to exhibit a μs-PL decay in the range of 20–130 μs.30,31 In addition, it was recently shown that excitation wavelength-dependent PL measurements on these samples revealed a PL red-shift with excitation wavelength from 300 nm to 380 nm and a saturation in the PL peak position (~485 nm for ammonia and ~473 nm for dodecylamine functionalized Si NCs) at 390 nm excitation wavelength.10,20 Based on these results, we can rule out recombination from the core states as the origin of the observed size-independent blue PL since this process is highly dependent on the size of the NC.31–33
We estimate the radiative recombination lifetime, $t_R$ using the relative PL quantum yield, $QY$ and the weighted average lifetime, $\langle \tau \rangle$ given by

$$QY = \frac{\langle \tau \rangle}{t_R}$$

(2)

$$\langle \tau \rangle = \sum_{i=1}^{n} A_i \tau_i^2$$

(3)

The radiative recombination rate is then given by $k_R = 1/t_R$. The relative PL, $QY$, for dodecylamine and ammonia functionalized Si NCs have recently been reported by Dasog et al. Ammonia functionalized Si NCs have a $QY$ of 22%, while dodecylamine functionalized Si NCs exhibit a $QY$ of 32%. Using the PL lifetimes at the peak emission wavelengths, radiative recombination rates of $k_R = 0.45 \times 10^8$ s$^{-1}$ and $0.72 \times 10^8$ s$^{-1}$ are obtained for ammonia and dodecylamine functionalized Si NCs, respectively. These fast radiative recombination rates suggest dipole-allowed transitions, such as observed in CdSe NCs. This result further confirms that the observed radiative process is unlikely due to emission from the Si core, since radiative recombination rates from QC states in similar size Si NCs is expected to be in the range of $10^3$ to $10^5$ s$^{-1}$. The nonradiative decay rate $k_{NR}$ can be computed using $QY = k_R/k_{NR} + k_{NN}$. The non-radiative processes for both functionalized Si NCs are slightly faster ($k_{NR} = 1.50 \times 10^8$ s$^{-1}$ for dodecylamine and $k_{NR} = 1.59 \times 10^8$ s$^{-1}$ for ammonia) than the radiative process. These efficient recombination processes lead to the observed ns-PL decay.

An extensive ns-TRPL study was conducted to further probe the nature of the blue-emitting state in this set of functionalized Si NCs (Fig. 4). By monitoring the temporal evolution of the PL spectral profile it is possible to determine the light-emitting states responsible for the observed PL since they will exhibit unique PL spectral profiles and lifetimes. Fig. 4(a) and (b) show the ns-TRPL intensity for the 3 nm ammonia and dodecylamine functionalized Si NCs, respectively, as a function of emission wavelength and time after photoexcitation. From these plots, the temporal evolution of the PL after photoexcitation was extracted, as presented in Fig. 4(c) and (d). Interestingly, the spectral profile of both functionalized Si NCs does not change with time while the peak position is consistent with the TIPL results (Fig. 3(a) and (b)). Notably, excellent agreement between the normalized temporally-resolved PL and the SSPL (Fig. 4(e) and (f)) is observed. A PL peak that is independent of time is consistent with the absence of a μs-PL component in these Si NCs. Furthermore, the time-independent spectral profile also implies that a single emitting state is responsible for the observed ns-PL.

Based on the results of the TIPL (Fig. 3) and TRPL (Fig. 4) measurements, we conclude that the observed ns-blue PL is not from core emission. We can also rule out no-phonon hot carrier recombination described by de Boer et al., since the observed PL does not exhibit a PL red-shift when the size of the NCs is...
decreased, as shown in Fig. 3. It has been shown that Auger recombination could result in a PL blue-shift where carriers are promoted to higher energy levels.\textsuperscript{38} Although the time resolution of our setup prevents us from observing Auger recombination, which normally occurs on time scales $<100$ ps,\textsuperscript{39} excitation-fluence-dependent PL emission and PL dynamics measurements can elucidate whether non-radiative Auger processes give rise to the observed fast blue PL. Fig. 5(a) and (b) show the excitation-fluence-dependent TIPL and ns-TRPL dynamics, respectively of the $\approx 6$ nm ammonia functionalized Si NCs. The TIPL of ammonia-functionalized Si NCs increases linearly with excitation pump fluence, inconsistent with Auger processes. The spectrally-resolved PL lifetimes are also independent of excitation fluence ($\approx 1\%$ variation over the fluence range used here), as shown in the inset of Fig. 5(b). In addition, the absence of PL red-shift (Fig. 4(c) and (d)) at early times after photoexcitation rules out multiple carrier generation that could result in Auger recombination processes.\textsuperscript{40} Recently, Hannah \textit{et al.} suggested that fast PL from Si NCs in the 400–600 nm emission bands is due to a surface layer of amorphous Si.\textsuperscript{41} This is unlikely the case for our samples as we do not observe any amorphous Si–Si peak at $\approx 480$ cm$^{-1}$ in our Raman spectra,\textsuperscript{42} as seen in Fig. 2(c) and (d).

Our results suggest that the observed ns-blue emission is due to radiative recombination at interface-related states by ultrafast carrier trapping or charge transfer (CT).\textsuperscript{34,43} The complete quenching of the Si core emission indicates that carrier trapping/CT depopulates the Si core at a rate much faster than intraband thermalization. Trojanek \textit{et al.} showed that the carrier trapping/CT process occurs in $\approx 400$ fs, approximately two orders of magnitude faster than the intraband relaxation time ($\approx 1$–10 ps) in quantum confined materials.\textsuperscript{44} Hence, we propose that the observed ns-blue PL is related to surface passivation. The FTIR and Raman spectra in Fig. 2 show both Si–O and Si–N surface bonds are present. However, the fast blue emission cannot be attributed to either one of these bonds. Wolkin \textit{et al.}\textsuperscript{45} and Dohnalova \textit{et al.}\textsuperscript{46} show that when the surface of Si NCs is terminated by oxygen, a PL red-shift is observed followed by an increase in the PL lifetime from ns to $\mu$s time scales. Also, computational studies reveal that the same PL red-shift was observed when oxygen-free Si NC surfaces were passivated by nitrogen.\textsuperscript{37} On the other hand, Fuzell \textit{et al.} suggested that blue emission from nitrogen-bonded Si NCs is due to CT to low lying nitrogen traps while oxygen impurities generate deeper traps.\textsuperscript{48} Here, however, we associate the fast blue PL emission to silicon oxynitride (SiO$_x$N$_y$) species at the surface of the nanocrystals, as confirmed by XPS.\textsuperscript{10,20} Wang \textit{et al.}\textsuperscript{49} proposed that both organic ligands and surface oxidation are necessary to form a novel surface state that is responsible for the ultrabright PL and that the structure of the ligand is crucial in determining whether such a state can dominate the entire process. However, it is unlikely that the emission is due to direct excitation of the SiO$_x$N$_y$ surface group since its bandgap is between 4.5–8.0 eV\textsuperscript{50} while the excitation energy used here is only 3.1 eV. Furthermore, absorption measurements shown in Fig. S6 (ESI$^\ddagger$) exhibit size-dependent absorption edges commonly observed for nanostructured Si.\textsuperscript{10}

The CT state, which occurs at the Si/SiO$_x$N$_y$ interface, is therefore responsible for the observed ns-blue PL, as illustrated in Fig. 6.
The Si NC, with bandgap $E_{\text{QC}}$ (1.1 eV bandgap of bulk silicon), is excited by 400 nm (3.1 eV) light creating an electron–hole pair. The photoexcited electron rapidly transfers to the SiO$_x$N$_y$ forming the CT state located at the interface. The CT thermalization process occurs at a much faster rate than the thermalization process within the bands of the Si core resulting in quenching of the QC core emission that typically emits red PL with a lifetime in the $\mu$s time scale, as shown by the red solid downward vertical arrow in Fig. 6. After a fast thermalization within the CT state, the bound electron–hole pair recombines emitting ns-blue PL. Deibel et al. pointed out that when sufficient wavefunction overlap of the electron and hole forming the CT state occurs, significant luminescence can be achieved.\(^5\) In addition, Dasog et al. recently showed that these functionalized Si NCs exhibit solvent-polarity dependent (solvatochromic) PL,\(^13,20\) consistent with a CT state at the interface. The difference in PL spectra and lifetimes of ammonia and dodecylamine functionalized Si NCs can be attributed to the difference in structure of the SiO$_x$N$_y$ species, which affects the CT state. Wang et al.\(^49\) pointed out that for surface-modified Si QDs a modulation in the exciton wave functions is expected due to core–ligand interactions which implies that the emission dynamics will be sensitive to the structure of the capping agents. This explains the difference in the PL quantum yield and radiative recombination rate observed in dodecylamine and ammonia functionalized Si NCs. Indeed, Augustine et al. used various amorphous silicon oxynitride
(a-SiO$_x$N$_y$:H) thin films prepared by PECVD to demonstrate tunable visible PL emission with a characteristic decay of $\sim$10 ns.$^{52}$ While the origin of the bi-exponential nature of the PL decay observed here is still unclear, similar bi-exponential PL emission dynamics due to CT states has been observed in polymer–fullerene systems.$^{53,54}$ Loi et al. attributed the bi-exponential behavior to energy transfer followed by PL emission,$^{53}$ whereas Veldman et al. suggested that bi-exponential decay dynamics could be a result of CT state distribution due to different electron–hole separations.$^{54}$

The CT state emission from our functionalized Si NCs exhibits complete blue PL with no other components attributable to core emission, and is therefore a more efficient blue emitter compared to oxygen-related defects and amorphous surface layers where the blue emission is just a small part of the total PL.$^{17,18}$ Compared to QC blue emission from Si cores, CT state emission is likely to exhibit higher PL QY and faster radiative recombination since it has been shown that a significant decrease in QY is observed when the Si NCs diameter is less than 2 nm.$^{11}$ Mastronardi et al.$^{10}$ observed that as the NC size decreases, the non-radiative recombination rate dominates the radiative rate which results in a decrease in absolute QY. Hence, blue emission from CT states is a promising candidate for applications in Si-based LEDs, as luminescent tags in imaging, and in other applications where efficient emission in the blue region of spectrum is required. Understanding the CT state emission dynamics is also important for Si NC-based photovoltaics, where CT states are the intermediate process necessary for charge dissociation that can results in the generation of photocurrent.$^{50}$ Since recombination from a CT state is considered an energy loss, preventing it to happen by ensuring that charge separation occurs before recombination will result in better performance of solar cells. The key to achieving this is by knowing the characteristic time of the CT state emission.

4. Conclusions

In summary, the PL dynamics of blue-emitting ammonia and dodecylamine functionalized Si NCs with average diameters of $\sim$3 and $\sim$6 nm was investigated. The NC-size-independent blue emission is attributed to CT states at the Si/SiO$_x$N$_y$ interface with a radiative recombination rate of $\sim 5 \times 10^{7}$ s$^{-1}$. In addition, the CT state emission spectral profile is independent of time after excitation. The size-independent PL and the absence of $\mu$s-PL from all of our samples suggest a very efficient electron transfer from the Si NC core excited states to the CT state. Understanding the CT state emission dynamics in blue-emitting Si-NCs will impact their application in optoelectronic devices.

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References