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BY

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Abstract

Silicon nanocrystals (Si NCs) have been drawing increasing attention over the last few decades due to their earth abundance, biocompatibility, and low toxicity. At the nanoscale, surface chemistry can drastically impact the electronic and optical properties of nanomaterials. Therefore, tailoring the surface of nanocrystals via surface functionalization reactions is crucial in enabling their applications. In this thesis, we develop surface functionalization routes specifically for luminescent solar concentrator and bioimaging applications using scalable and cost-effective methods.

Nonthermal plasma synthesis allows for the continuous production of silicon nanocrystals on a large scale. However, post-synthesis steps are necessary for silicon nanocrystals to be suitable for luminescence applications. Therefore, we develop an all-gas-phase synthesis and processing route that integrates nonthermal plasma synthesis, plasma-assisted surface functionalization with alkene ligands, and in-flight annealing within one flow stream. Compared with solution-phase functionalization, the gas-phase functionalization method reduces long reaction times and avoids the use of solvents, which shows potential for large-scale production.

The all-gas-phase synthesized and functionalized Si NCs are excellent candidates as emitters for luminescent solar concentrator devices (LSCs). LSC prototypes consisting of Si NCs uniformly embedded in a polystyrene matrix have been successfully fabricated without using additional solvents. After light irradiation, the Si NCs exhibit a photoluminescence quantum yield (PLQY) of above 40%, comparable to the highest PLQY in Si NCs functionalized by solution-phase methods.

Understanding and controlling the energy transfer between Si NCs is of great importance for the design of efficient Si NC-based optoelectronic devices. We demonstrate that energy transfer can be effectively engineered in Si NC films by varying the length and surface coverage of alkyl ligands for Si NC surface functionalization. Using these samples, we are

also able to carry out a fundamental study of distance-dependent energy transfer in Si NC solids.

Finally, the synthesis of red-emitting and water-soluble Si NCs for bioimaging applications is discussed. Si NCs are promising candidates for biological imaging applications due to their low toxicity and strong biocompatibility. However, the Si NC surfaces are intrinsically hydrophobic, and thus surface functionalization is essential to use them in a biological medium. We demonstrate the successful surface grafting of hydrophilic polyethylene glycol ligand by two distinct reaction schemes. In the first method, we apply the thermal hydrosilylation reaction to synthesize Si NCs that are nearly individually dispersed in water and biological media. In the second method, we develop a two-step surface modification approach coupling gas-phase and liquid-phase methods to synthesize PEGylated acrylic acid grafted Si NCs. Such functionalized Si NCs exhibit efficient red emission in biological media for up to 24 hours.

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Chapter 1

Introduction

1.1 Silicon quantum dots

Quantum-confined nanocrystals (NCs), also known as quantum dots (QDs), are attractive materials because of their highly tunable optical and electronic properties.^{1–3} They are semiconductor nanocrystals with diameters on the order of 2–10 nm, where the quantum confinement effect becomes prominent. When light is absorbed by a semiconductor, a valence electron is promoted to the conduction band, creating an electron-hole pair coupled by Coulombic attraction. This bonded electron-hole pair is called an exciton. The average electron-hole distance in the exciton is described by the Bohr exciton radius. If the size of nanocrystals is small enough to be comparable with the Bohr exciton radius, the excitons will become quantum-mechanically confined. The nanocrystals will exhibit atom-like discrete electronic states, and the band gap can be tuned by varying the NC size. Quantum dots have remarkable advantages, including narrow emission colors, size-tunable emission color, and resistance to photobleaching.^{4,5}

Among a great variety of quantum-dot materials, silicon nanocrystals (Si NCs) are drawing increasing attention due to their earth abundance, biocompatibility, and low toxicity.^{6,7} While bulk silicon generally does not emit light due to the indirect band gap, efficient photoluminescence can be achieved in silicon nanostructures due to the quantum confinement of carriers.^{8,9} For bulk silicon, the absorption or emission process must involve the absorption or emission of phonons to conserve the crystal momentum. At the nanoscale, smaller particle size corresponds to smaller uncertainty in position, and thus the strict condition of momentum conservation is relaxed according to the Heisenberg principle. The emission

from silicon nanocrystals has complex characteristics and depends on the synthesis method and surface properties. Advancing the fundamental understanding of photoluminescence from silicon nanostructures remains an active research area, and efficient and economical synthesis methods of silicon nanocrystals are still being explored.

1.2 Photoluminescence of Si NCs

The early discovery of efficient photoluminescence (PL) from porous silicon dates back to the early 1990s.^{8,9} However, fundamental questions, including the mechanism of the photoluminescence and the influence of surface chemistry, still persist. During the last two decades, researchers mainly focused on establishing an understanding of the complex emission mechanism and on developing efficient methods for the synthesis of high-quality functional silicon quantum dots. It is currently understood that the red to near-infrared (NIR) emission in hydrogen-terminated or alkyl-terminated Si NCs originates from the silicon core. In contrast, the blue-green emission from Si NCs with amine surface moieties is related to surface-state-influenced emission.^{10,11}

Steady-state photoluminescence

The intrinsic core emission, usually in the red to near-infrared, exhibit a steady-state spectrum that is relatively broad. The PL linewidth results from both homogeneous broadening and inhomogeneous broadening, as shown in Figure 1.1. On the one hand, each quantum dot has a peak full-width at half maximum (FWHM) around 150 -200 meV, known as the homogeneous broadening.¹² On the other hand, an ensemble of Si NCs contains inhomogeneously broadened emitters due to their size and shape distribution. The homogeneous broadening in Si NCs is significantly more prominent compared to the direct band gap quantum dot and is considered as a consequence of exciton-photon interactions. Interestingly, low-temperature single-dot spectroscopy measurements reveal that the emission linewidth of Si NCs could be as sharp as direct band gap materials, with FWHMs around 2

meV at the temperature of 35K, with the emission energy at around 1.7 eV.¹³ The narrow emission linewidth observed at low temperatures indicates the atomic-like nature of these low-dimensional entities. When temperature increases, the linewidth rapidly broadens as a result of the exciton–phonon interactions. Because inhomogeneous broadening is a consequence of the size distribution of the individual NCs, the ensemble PL spectra can be reconstructed by assuming a lognormal distribution and considering the PL contribution from individual NCs (Figure 1.1).¹²

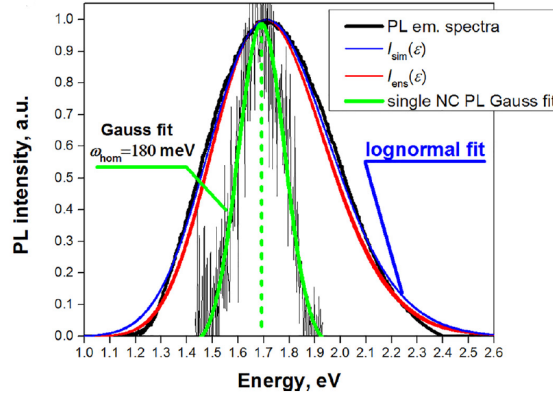


Figure 1.1: PL emission spectra of single and ensemble Si NCs. Figure reprinted with permission from ref 12. Copyright (2017) AIP Publishing.

Time-resolved photoluminescence

Time-resolved photoluminescence reveals the decay dynamics of the excited states and is an essential technique widely used in quantum dot research. In time-resolved photoluminescence measurements, the sample is excited with a pulsed light source, and the photoluminescence from a sample can be subsequently monitored as a function of time t . The decay can be described by the well-known single exponential model if the system has a constant total decay rate k_{tot} . For an exponential decay, the measured intensity I will follow an exponential function

$$I(t) = I_0 \exp(-k_{tot}t), \quad (1.1)$$

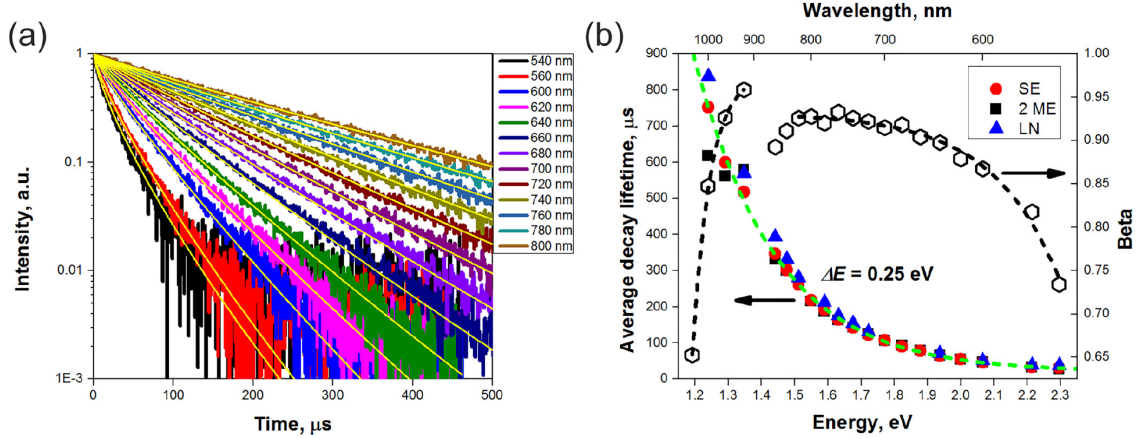


Figure 1.2: (a) Characteristic PL decay curves of Si NCs at different emission wavelengths. (b) Average PL decay lifetimes and dispersion factor β corresponding to stretched-exponential fittings. Figure reprinted with permission from ref 12. Copyright (2017) AIP Publishing.

where I_0 is the intensity at $t = 0$. The measured decay lifetime τ is thus the inverse of the total recombination rate, $\tau = 1/k_{tot}$.

In many cases, the decay curve of quantum dot samples, $I(t)$, deviates from the single-exponential form. This is because a quantum dot sample consists of a large number of single dots with varying decay rates. Specifically, the decay curve in silicon nanostructures has a strong non-exponential characteristic, indicating a broad distribution of individual decay rates. Controversy still remains regarding the origin of this broad distribution. A variety of models have been proposed to explain this lifetime distribution, including distribution of NC size,¹⁴ varying carrier localization,¹⁵ NC blinking,¹⁶ and energy transfer between Si NCs.¹⁷ More recently, it is discovered that size-selected ensembles of colloidal Si NCs have near single-exponential decays, indicating that the NC size distribution is the dominant factor determining the decay shape.¹⁸

For quantitative analysis of a non-exponential decay curve, a commonly adopted method is to fit the decay curve with a stretched-exponential model

$$I(t) = I_0 \exp(-(t/\tau_0)^\beta). \quad (1.2)$$

A time constant τ_0 and a dispersion factor β ($0 < \beta < 1$) can be extracted from the stretched-exponential fitting. The average decay lifetime can then be calculated by

$$\bar{\tau} = \frac{\int_0^{\infty} tI(t)dt}{\int_0^{\infty} I(t)dt}. \quad (1.3)$$

Substitute 1.1 into 1.3, we obtain

$$\bar{\tau} = \frac{\Gamma\left(\frac{2}{\beta}\right)}{\Gamma\left(\frac{1}{\beta}\right)}\tau_0, \quad (1.4)$$

where Γ is the gamma function. In addition to the stretched-exponential model, multi-exponential model¹⁹ and model assuming a lognormal distribution of decay rates^{11,20} can also be applied to fit non-exponential time-resolved PL data.

The average PL lifetime of silicon nanostructures is typically on the order of 10–100 μs .^{21,22} This value is orders of magnitude larger than that of direct band gap materials and is believed to be a consequence of phonon participated radiative recombination. The PL decay curves measured at different detector wavelengths also exhibit different lifetimes. As is shown in Figure 1.2, the average decay lifetime increases exponentially with increasing NC sizes, which is in accordance with the quantum confinement model.¹²

Size dependence

Experimental results indicate that the core emission of Si NCs blueshifts with diminishing NC size.^{23–25} Figure 1.3a plots the PL spectra of Si NCs measured by Yu *et al.* with emission spanning visible to near-infrared wavelengths.²⁶ It is found that the famous effective mass approximation (EMA) model by Brus² well describes the PL peak energy of >3 nm Si NCs, although it overestimates the emission energy at small (2–3 nm) NC diameters (Figure 1.3b).

Briefly, the EMA model describes the optical gap $E(d)$ as a function of NC diameter d :

$$E(d) = E_g + \frac{h^2\pi^2}{2d^2} \left(\frac{1}{m_e^*} + \frac{1}{m_h^*} \right) - \frac{1.786e^2}{\epsilon d}, \quad (1.5)$$

with E_g being the band gap of bulk Si (1.1 eV), m_e^* the electron effective mass, m_h^* the hole effective mass, h the Planck's constant, e the elementary charge, ϵ the semiconductor dielectric constant, respectively.

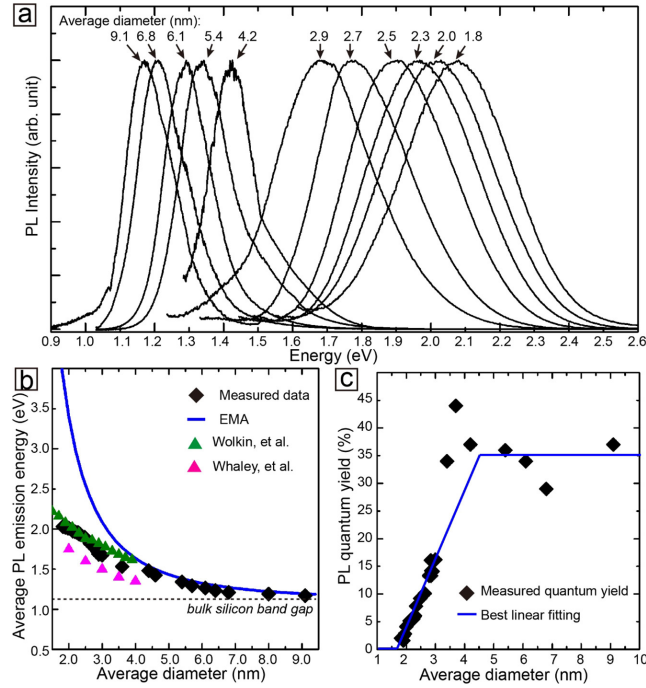


Figure 1.3: (a) PL spectra, (b) PL peak energy, and (c) ensemble PLQY of Si NCs with various diameters. Figure reprinted with permission from ref 26. Copyright (2017) American Chemical Society.

For light-emitting applications, Si NCs with high emission efficiency are desired. Photoluminescence quantum yield (PLQY) is defined as the ratio of the number of photons emitted to the number of photons absorbed. For red-emitting Si NCs, the highest PLQYs (40–50%) are usually found in samples with diameters larger than 3 nm.^{23,26} Si NCs with diameters smaller than 2 nm typically exhibit lower PLQY (<10%) due to defect-related trap states which lead to non-radiative recombination (Figure 1.3c). Using the language

of recombination rates, PLQY also can be viewed as the ensemble average of individual dot internal quantum efficiencies (IQEs), which equals to the ratio of radiative recombination rate k_r to the total recombination rate k_{tot} , where k_{tot} equals to the sum of radiative recombination rate k_r and non-radiative recombination rate k_{nr} :

$$\text{IQE} = k_r / (k_r + k_{nr}). \quad (1.6)$$

It can be observed from this expression that high non-radiative recombination rates (large k_{nr}) due to trap states resulting in shortened PLQY lifetime and reduced PLQY.

1.3 Synthesis of functional Si NCs

The optical properties of Si NCs are highly dependent on both the synthesis method and the Si NC surface chemistry. Size, crystallinity, defect densities, and surface chemistry all have a crucial impact on their optical properties. Depending on the synthesis and surface functionalization method, PLQY of Si NCs can vary from <1% to ~60%.²⁶

1.3.1 Synthesis of hydrogen-terminated Si NCs

The synthesis of freestanding Si NCs with hydrogen-terminated surfaces (H-Si NCs) is usually the first step towards functional Si NCs. The bare particle surfaces allow for controllable and versatile subsequent surface treatments. A variety of approaches have been developed for the synthesis of hydrogen-terminated Si NCs, which can be generally classified as either top-down or bottom-up approaches. Top-down approaches refer to the process of stripping down a larger bulk of silicon matrices into individual small nanocrystals. Typical methods include mechanical grinding,²⁷ chemical etching,^{28–30} electrochemistry synthesis,³¹ and laser ablation.³² These methods are typically time-consuming and have low yields. Bottom-up approaches build nanocrystals atom by atom using small molecular precursors, which has a higher degree of control over particle size. The bottom-up approaches include microwave-assisted synthesis,³³ laser pyrolysis,³⁴ and nonthermal plasma methods.^{35,36}

In this thesis, a nonthermal plasma reactor has been used to synthesize silicon nanocrystals. Compared to other bottom-up methods, the nonthermal plasma method yields high-purity Si NCs with accurate control of size. The as-synthesized Si NCs have relatively narrow size distributions, eliminating the need for subsequent size separation steps. While the current production rates are usually around ~ 50 mg/hour, the potential for industrial scaling may be unlocked through scaling reactor dimensions or parallelizing systems.

In a typical nonthermal plasma reactor, a carrier gas, usually argon, and a precursor gas, such as silane, are flown through a quartz or Pyrex reactor tube. Radiofrequency power at 13.56 MHz with a nominal power of 10–100 W is applied through an impedance matching network connected to a pair of copper electrodes. The formation of nanocrystals is described with a three-stage model. In the first stage, small clusters are formed by the nucleation of the radicals from the electron impact dissociation. In the second stage, these clusters quickly coagulate to form larger nanoparticles. This coagulation continues until the cluster/nanoparticle density has dropped to the ion density level in the plasma. At this point, there are sufficient electrons to charge most particles negatively, and the coagulation is suppressed. Finally, the nanoparticle growth continues mainly through the deposition of remaining radicals onto nanoparticle surfaces. Because coagulation is suppressed at the end of the second stage, the nonthermal plasma method produces nanocrystals with narrow size distributions. Another advantage of the nonthermal plasma method is that it enables the production of nanomaterials with high crystallization temperatures. In a nonthermal plasma, nanoparticles can be heated to several hundred degrees above the gas temperature by gaining energy from recombining electrons and ions, leading to the particles' crystallization.³⁶

By adjusting the synthesis parameters, i.e., gas flow rates, reactor pressure, and the power input, quantum-confined Si NCs with sizes below the exciton Bohr radius (~ 4.9 nm) can be synthesized. As defects contribute nonradiative recombination pathways that compete with light emission, low defect densities are desired in quantum dots. Specifically, Si NCs with extremely low initial defect densities ($7 \times 10^9 \text{ cm}^{-2}$, or 2–5 defects per 1000 Si NCs)

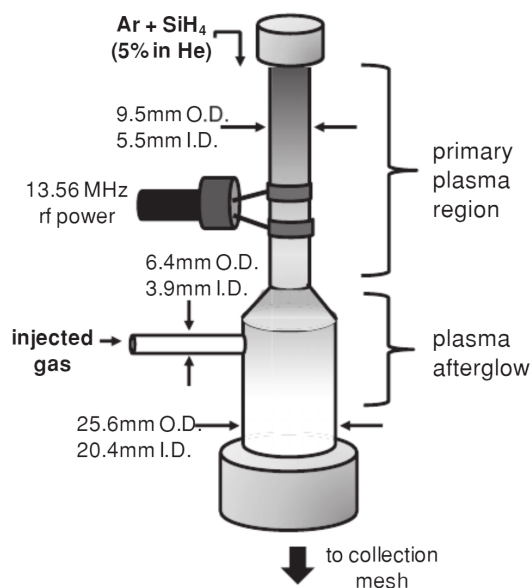


Figure 1.4: Schematic of the nonthermal plasma reactor with an injection point into the plasma afterglow. Figure reprinted with permission from ref 38. Copyright (2011) Wiley.

can be synthesized in a nonthermal plasma reactor, with additional hydrogen injection into the plasma afterglow region.^{37,38} A schematic of this particular type of reactor is shown in Figure 1.4. The hydrogen injection leads to a higher degree of surface hydrogen passivation, presumably because of less surface SiH_x species desorption by faster quenching of the Si NC temperature and increased flux of atomic hydrogen species.

1.3.2 Surface functionalization of Si NCs

At the nanoscale, a large percentage of atoms lie on the nanoparticle surface. Surface functionalization reactions of H-Si NCs are critical to passivate surface defects, enhance optical properties, and modify solubility behaviors of Si NCs. Freestanding hydrogen-terminated Si NCs (H-Si NCs) synthesized from nonthermal plasma methods have relatively high purity and low surface defect density, but they still suffer from low colloidal stability, weak stability towards oxidation, and low PLQYs. Surface functionalization using organic ligands is usually performed to enhance these properties.

Hydrosilylation has been the most commonly used fundamental reaction for Si NC

surface functionalization. Hydrosilylation involves the grafting of ligands to the hydrogen-terminated silicon surfaces through covalent Si-C bonds.³⁹ Hydrosilylation can be initiated either thermally,³⁹ photochemically,^{40–43} by applying a catalyst,⁴⁴ or using bifunctional ligands.⁴⁵ The hydrosilylation reaction utilizing 1-dodecene has been shown to improve the PLQYs up to 60% in freestanding Si NCs.³⁹

Besides passivating defects and enhancing PLQY, surface functionalization through the hydrosilylation reaction also improves the colloidal stability and stability towards oxidation of Si NCs. Hydrogen-terminated Si NCs typically have a tendency towards agglomeration due to the attractive van der Waals force. The grafted polymeric chains can act as a steric barrier to screen the van der Waals attraction force and reduce agglomeration.⁴⁶ The organic layer can also isolate the silicon core from the ambient air, reducing surface oxidation and photoluminescence quenching events from interactions with oxygen and water.⁴⁷

The surface functional group also plays a crucial role in the Si NC PL. Besides the hydrosilylation reaction, Si NCs exhibiting red core-related emission with Si-O, Si-N, and Si-S surface groups have been synthesized with radical-initiated reactions⁴⁸ or thermally promoted reactions.⁴⁹ Such functionalized Si NCs are dispersible in nonpolar solvents with PLQYs in the 10%–20% range. Besides the core-emission component, alkyl-terminated Si NCs after oxidation experience a slight blueshift of the spectra, with an additional nanosecond decay component related to surface states.¹⁰ Green-blue emissions are usually observed in amine-functionalized Si NCs, which are believed to be associated with surface states.⁹

1.3.3 Si NC functionalization for device applications

Silicon nanocrystal-based devices have been developed, including luminescent devices,⁵⁰ light-emitting devices,^{51–54} photodetectors,⁵⁵ and Si NCs have been used in biomedical applications.^{56,57} While high PLQY of Si NCs is desired in most cases, each application can benefit from particular surface characteristics. Therefore, the surface chemistry needs to be specifically designed and tailored for each application.

Luminescent solar concentrators

A luminescent solar concentrator (LSC) is a device acting as a waveguide to concentrate sunlight. An LSC consists of a transparent matrix, usually a flat plate, that is doped with luminophores. Incident sunlight is absorbed and re-emitted by the luminophores embedded in the waveguide material. Part of the re-emitted light is then directed and concentrated to the edges of the plate by total internal reflection, where solar cells are installed. By reducing the areas of solar cells, LSCs can save the cost of solar energy utilization. The main types of luminophores include organic dyes,^{58,59} inorganic phosphors,⁶⁰ and quantum dots.^{61,62} Typically, luminophores are incorporated into a polymer matrix, which can be used to fabricate the waveguide by forming either a thick polymer slab or a thin layer on top of a glass piece.

Silicon quantum dots are excellent luminophores for LSCs because of their high UV absorption, high PLQY, and large Stokes shift.⁵⁰ For LSC applications, Si NCs' surfaces need to be engineered so they can exhibit high PLQY while being able to form a homogeneous dispersion within the selected polymer matrix. The agglomeration of Si NCs is detrimental to the LSC waveguiding efficiency due to scattering losses. A strategy for minimizing agglomeration has been developed by Hill *et al.*⁶³ By selecting an appropriate functionalization ligand with structural similarity to the polymer matrix, Si NC/PMMA nanocomposites can be fabricated with low levels of scattering losses. Apart from matrix compatibility, Si NCs for LSC devices are also desired to have high PLQY, good photostability, and oxidation stability to minimize energy losses.

Light-emitting devices

When Si NCs are used as the active materials in light-emitting devices (LEDs), the length and density of surface ligands are important factors. While ligand functionalization usually prevents oxidation and improves colloidal stability, long and insulating ligands can hinder

charge transport and result in a drop in optoelectronic device efficiencies.⁶⁴ In II-VI and IV-VI quantum dot materials, ligand transfer is typically performed to replace long ligands with shorter ones. While such reactions are challenging to perform due to the covalent nature of the Si-C bond, an alternative functionalization method using organolithium reagents results in a lower surface ligand coverage and higher device performance.⁶⁵

Bioimaging applications

Silicon nanoparticles are desirable for biomedical applications owing to their low cytotoxicity, high biocompatibility, biodegradability, and size-tunable optical properties. Similar to silica or porous silicon, silicon nanoparticles degrade via hydrolytic dissolution into silicic acid ($\text{Si}(\text{OH})_4$), which naturally occurs in human tissues and is easily excreted.^{66,67} For bioimaging applications, the functionalization ligand needs to be either nontoxic or strongly bonded to the Si NCs to avoid the release of toxic components. Moreover, the Si NCs also need to be functionalized with a hydrophilic ligand to be dispersed in water and biological media. Preferably, the silicon nanocrystals also need to exhibit size-tunable emission in the biologically relevant red-to-NIR therapeutic window for deep tissue imaging.⁶⁸

1.4 Scope of Work

In this thesis work, we focus on the surface functionalization of Si NCs synthesized in a nonthermal plasma for luminescent devices and bioimaging applications. By utilizing the plasma-assisted surface functionalization, we are able to synthesize ligand functionalized Si NCs with >20% PLQY entirely in the gas phase. We thereafter develop a solvent-free route for the fabrication of Si NC-based LSCs based on the plasma-assisted functionalization setup. Another advantage of gas-phase functionalization is that it enables the convenient production of Si NCs with controlled ligand coverage. Therefore, by utilizing alkenes with different chain lengths, we conduct a distance-dependent study of energy transfer in Si NC solids. Furthermore, by grafting hydrophilic ligands, we are able to produce Si NCs

compatible with polar solvents, which enables the synthesis of water-soluble Si NCs suitable for bioimaging applications.

- Chapter 2 introduces an all-gas-phase synthesis and functionalization approach for the synthesis of Si NCs. In this approach, alkyl-grafted Si NCs with $\sim 20\%$ PLQY are synthesized continuously in the gas phase on a timescale of ~ 100 ms, which represents an advance towards large-scale production of Si NCs for luminescent applications.
- In Chapter 3, we describe a route to fabricate Si NC-polymer nanocomposites as luminescent solar concentrators without the use of additional solvents. Si NCs functionalized with high electronegativity terminal groups can reach PLQY of 40% – 50% in NC-polystyrene nanocomposites after light irradiation, which provides an environmentally-friendly and cost-effective method for the fabrication of luminescent solar concentrator devices.
- Chapter 4 describes the study of energy transfer in Si NC solids. We measure the energy transfer rates in Si NC solids by time-resolved photoluminescence measurements and simulated the ligand packing structure to estimate interparticle spacing by molecular dynamics simulations. By combining the experimental and simulation results, we obtain the quantitative relationship between energy transfer rates and interparticle distances.
- Chapter 5 discusses the functionalization of Si NCs for bioimaging applications. By exploiting thermal hydrosilylation reaction with PEG acrylate ligand, we synthesize Si NCs with hydrodynamic diameters around 10 nm in water and Tyrode buffer. Alternatively, we use a two-step synthesis method that combines the gas phase grafting of acrylic acid and solution phase grafting of PEG-OH. These synthesized Si NCs have hydrodynamic diameters of 20–30 nm in water and Tyrode buffer.
- Chapter 6 includes the conclusion of this thesis and ideas for future work.

Chapter 2

All-gas-phase synthesis and functionalization of silicon quantum dots

2.1 Introduction

Compared to colloidal methods, nonthermal plasma synthesis of Si NCs eliminates the need for solvents and ligands. Unfortunately, as-produced, plasma-synthesized Si NCs have low PLQY. For applications that rely on high PLQY, it is crucial to apply surface functionalization methods to achieve higher PLQY.^{39,69,70} Previous research has shown that PLQY of Si NCs can be enhanced via alkene/alkyne hydrosilylation, which improves PLQY up to 60% in freestanding Si NCs.³⁹ However, the hydrosilylation reaction needs to be conducted postsynthesis and requires a switch from a gas phase synthesis to a liquid phase postprocessing.

Conducting all synthesis, functionalization, and processing steps in the gas phase is attractive due to the lack of solvents and the presumed speed of an approach that does not require a transition from the gas phase to the liquid phase. An all-gas-phase functionalization approach was proposed by Mangolini *et al.* in which the nanoparticles flow through a second plasma chamber after the main synthesis plasma.⁷¹ Ligands were grafted onto Si NC surfaces in the second plasma and these functionalized nanoparticles formed

*Portions of this chapter have been adapted with permission from Li *et al.*, Chem. Mater. 2019, 31, 20, 8451–8458.

stable solutions in toluene. Anthony *et al.* simplified this scheme by combining synthesis and functionalization in two spatially separated regions of a single plasma.⁷² The NC synthesis was achieved in a higher density upstream synthesis region and functionalizing ligands were injected further downstream into the lower density plasma “afterglow”. This approach has the advantage that nanocrystals never leave the plasma between their synthesis and functionalization, remaining in a negatively charged state that prevents nanocrystal aggregation. However, even though ligands were successfully grafted onto Si NC surfaces, the PLQY remained low at less than 5%. The authors did observe that the PLQY could be improved when the plasma-functionalized Si NCs were heated in mesitylene, but this negated the advantage of the all-gas-phase synthesis and functionalization scheme.

In this chapter, we discuss an all-gas-phase synthesis and functionalization route for producing silicon nanocrystals with >20% PLQY that is higher than previous all-gas-phase approaches. Building on the work of Anthony *et al.*,⁷² Si NCs are synthesized in the intense upstream zone of the plasma and ligands are grafted onto the Si NC surfaces further downstream in the weak plasma “afterglow” where the density of plasma species decays through recombination. The residence time of the NCs in the synthesis and the functionalization zones is just a few milliseconds. However, different from previous work,⁷² Si NCs are then passed through a flow-through furnace, where they are heated in-flight. Such in-flight heating was previously used by Barragan *et al.* to grow carbon shells on silicon crystals for lithium ion batteries.⁷³ The heat capacitance of the 2-4 nm Si NCs is small and the characteristic time for the NC temperature to equilibrate with the gas temperature through conduction is on the order of 0.01 milliseconds, even considering the low-pressure environment at which the Knudsen effect becomes significant.³⁶ By letting the gas stream of Si NCs flow through a tube furnace where the residence time is ~ 100 ms, the temperature of Si NCs will closely follow the gas temperature profile in the furnace. As we discuss below, this in-flight annealing significantly improves the PLQY. Hence, with this all-gas-phase design, highly luminescent Si NCs are synthesized on a timescale of 100 ms, orders of magnitude faster than schemes that require liquid post-synthesis processing.

2.2 Experimental setup

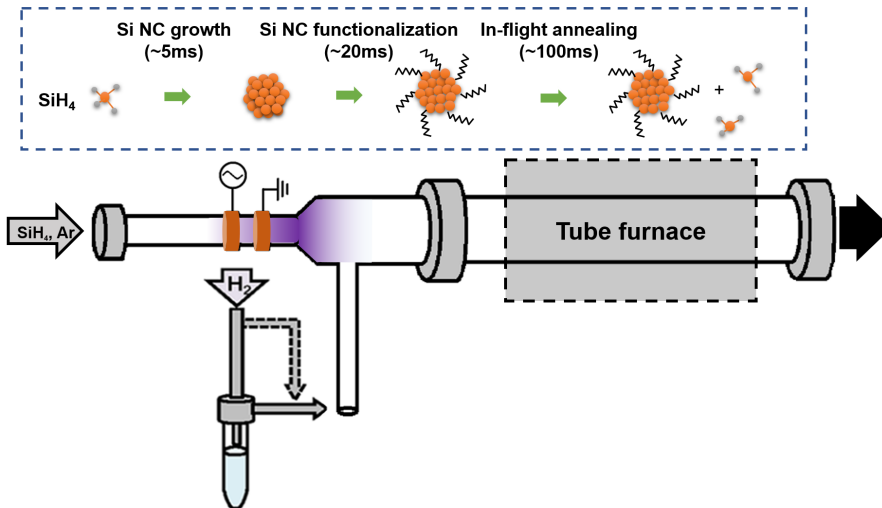


Figure 2.1: Schematic of the reactor used in this study. The three stages of nanocrystals growth and surface modification are: the growth of silicon nanocrystals through dissociation of the SiH_4 precursor and particle nucleation; grafting of organic ligands onto the silicon nanocrystal surfaces; and the desorption of surface silyl species through in-flight annealing.

A schematic of the experimental setup for this study is shown in Figure 2.1. Silicon nanoparticles are synthesized and functionalized in a nonthermal rf plasma reactor as described in ref 72. Argon and silane (5% in helium) enter through a borosilicate glass tube reactor with ligands introduced into the plasma afterglow by flowing hydrogen through a bubbler to carry the ligands. Hydrogen is chosen as the carrier gas since previous studies showed that Si NCs have the lowest defect densities and best photoluminescence quantum yields when hydrogen is injected into the plasma afterglow compared to argon and helium.³⁸ Radiofrequency power at 13.56 MHz and a nominal value of 60 W was applied to a pair of copper ring electrodes placed 2 cm before the afterglow region. The argon flow rate varies between 30 and 100 sccm (Table 2.1), while silane (5% in helium) and hydrogen flow rate were fixed at 14 sccm and 100 sccm, respectively. Ligands used in this study included 1-octene, 1-dodecene, and 1-octadecene (from Alfa Aesar, TCI, and Sigma-Aldrich respectively). The gas pressure in the plasma region was 2.2–2.4 Torr and gas pressure in the

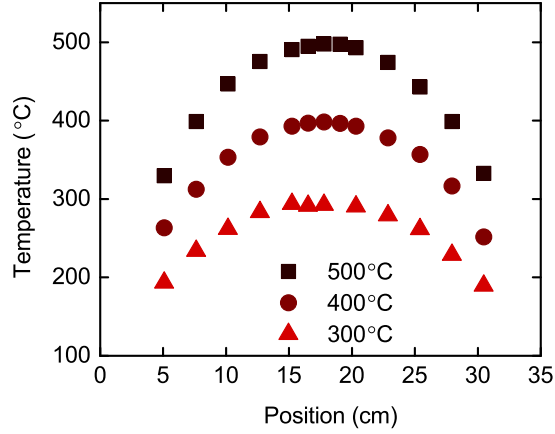


Figure 2.2: Temperature profiles of the tube furnace. Measurements were taken with a sheathed k-type thermocouple. To replicate typical operating conditions, 30 sccm Ar, 100 sccm SiH₄ and 14 sccm He were flown through the furnace.

Table 2.1: Synthesis conditions for silicon nanocrystals. For all samples, SiH₄ (5% in He) and H₂ flow rates are 14 sccm and 100 sccm, respectively

Size (TEM)	Ar flow rate (sccm)	Pressure (Torr)
2.5 nm	80	2.4
3.2 nm	30	2.4
4.5 nm	20	2.2

bubbler was 35–100 Torr. After the plasma region, the gas stream was sent through a tube furnace, with temperature profiles shown in Figure 2.2. The temperature profile was measured by inserting a thermocouple into the gas stream while keeping the typical flow conditions. Si NCs were collected onto glass substrates by inertial impaction using a setup similar to that used in ref 74. The typical collection rate of 3.2 nm, 1-octene functionalized Si NCs was around 10 mg per hour.

2.3 Results and discussion

2.3.1 Si NC characterization

Si NCs with sizes ranging from 2.2 nm to 4.5 nm are prepared using the all-gas-phase setup, schematically shown in Figure 2.1, which is described in detail in the experimental

section. The argon carrier gas flow rate, which affects the residence time of NCs in the plasma region, is adjusted to tune the Si NC size. According to transmission electron micrograph (TEM) images (Figure 2.3a), the average sizes of 1-dodecene functionalized Si NC samples are 2.5 nm, 3.2 nm, and 4.5 nm, not including the ligand shell. This is consistent with crystallite sizes of these Si NCs of 2.2 nm, 3.1 nm, and 3.9 nm based on X-ray diffraction (XRD) pattern and applying Scherrer’s equation (Figure 2.3b). Different from Si NCs that were not functionalized and heated in the gas phase, the Si NCs produced here exhibit photoluminescence in the near-infrared immediately after synthesis and gas phase processing (Figure 2.3c). The emission peak wavelengths of 2.5 nm, 3.2 nm, and 4.5 nm Si NCs are around 750 nm, 820 nm, and 920 nm, respectively, which is in agreement with emission energies predicted by quantum confinement models.⁷⁵

The as-produced Si NCs form stable solutions in common non-polar solvents including toluene and chloroform for furnace temperatures up to 500 °C. No sedimentation is observed over a period of a few months. Dynamic light scattering (DLS) was performed to quantitatively examine the dispersity of Si NCs. Figure 2.3d shows the cumulative size distribution from DLS measurements taken for 3.2 nm Si NCs dispersed in toluene processed at the furnace temperature of 500 °C. The median diameter of the number weighted distribution is 6.8 nm. Considering that Si NCs are capped with dodecyl, which results in a ligand shell of ~1.6 nm thickness, this distribution of hydrodynamic diameters is consistent with singly dispersed Si NCs. When the furnace temperature is raised to higher than 500 °C, a stable solution can no longer be formed, presumably because the high temperature may lead to degradation of the ligands that are required for colloidal stability.

2.3.2 Influence of Annealing Temperature on PLQY

A significant enhancement in PLQY is observed when in-flight annealing is applied, with the furnace temperature profile shown in Figure 2.2. Considering the parabolic temperature profile and assuming 18 cm as the effective heating length, the in-flight annealing time is ~100 ms for the flow rates used here. As is shown in Figure 2.4, for 3.2 nm Si

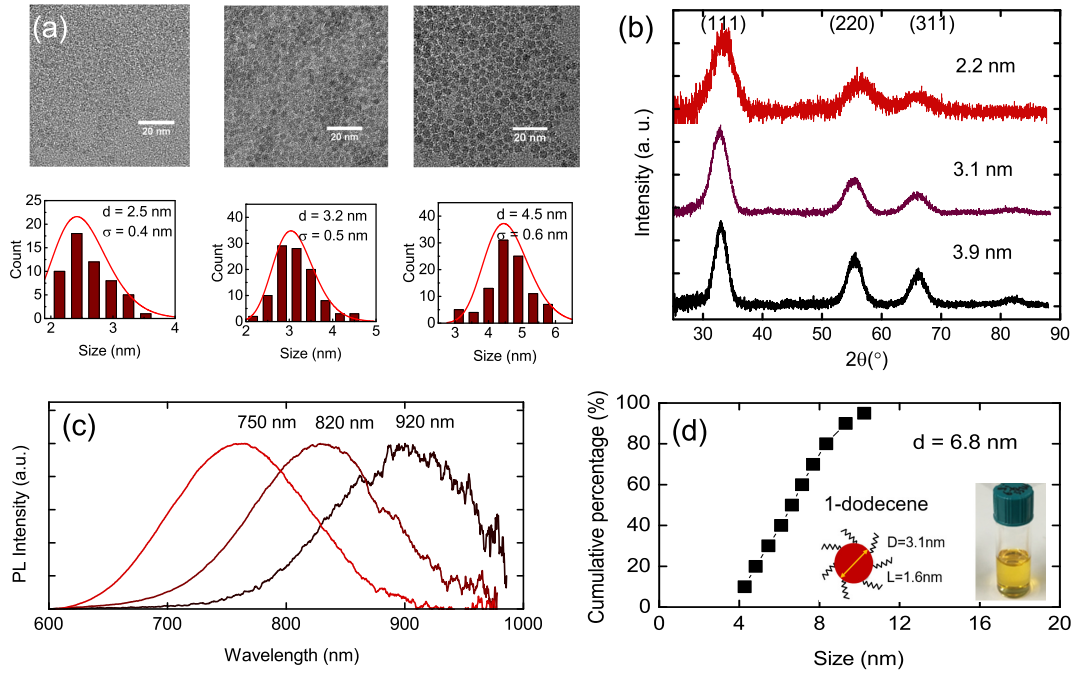


Figure 2.3: (a) TEM images of Si NCs of three sizes prepared by dispersing the as-produced samples in toluene and drop-casting on a TEM grid. The ligand is 1-dodecene and furnace processing temperature is 500 °C. (b) XRD pattern of the 1-dodecene functionalized Si NCs. (c) Photoluminescence spectra of 2.5, 3.2 and 4.5 nm Si NCs that are gas-phase functionalized and in-flight heated at 500 °C, and dispersed in toluene. Spectra are normalized to 1. (d) Cumulative number weighted distribution of as-produced, 1-dodecene functionalized 3.2 nm Si NCs with 500 °C furnace temperature dispersed in toluene determined by DLS. Sample concentration is ~ 1 mg/ml. The inset is a photo of Si NCs dispersed in toluene.

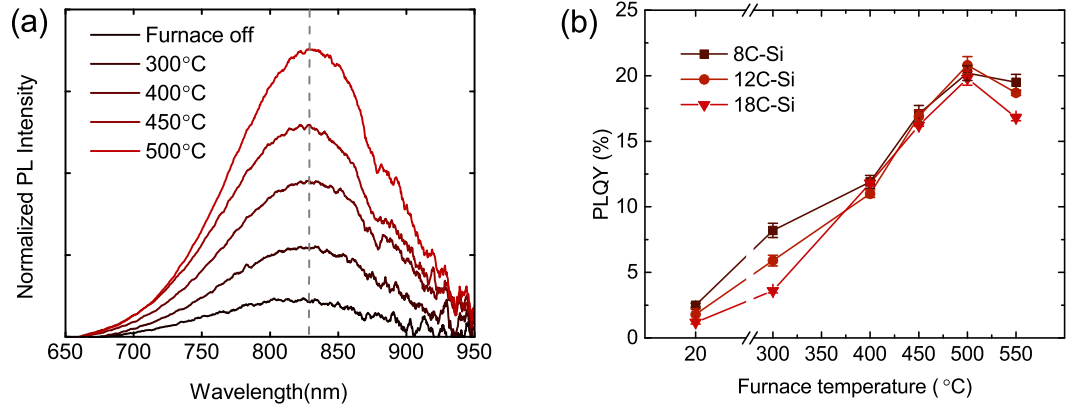


Figure 2.4: (a) PL spectra (excitation $\lambda = 395$ nm) of 3.2 nm, 1-octene functionalized Si NC processed at different furnace temperatures. Spectra are taken with an integrating sphere and PL intensities are normalized by dividing the spectrum by the absorption integral. Measurements were taken for Si NCs dispersed in toluene with concentration of ~ 1 mg/ml. (b) PLQY as a function of furnace annealing temperature for samples functionalized with 1-octene (8C-Si), 1-dodecene (12C-Si), and 1-octadecene (18C-Si).

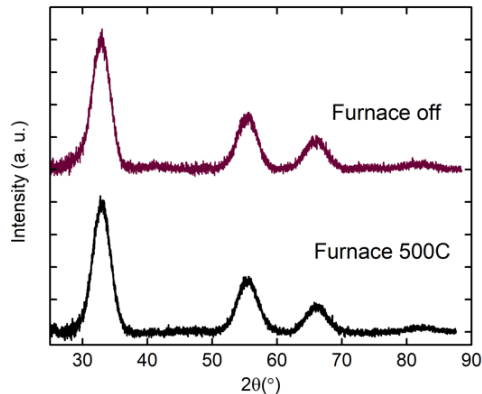


Figure 2.5: X-ray diffraction pattern for Si NCs with different furnace processing temperatures. Sizes from Scherrer fitting are 3.2 nm for both samples, indicating that heating does not affect the Si core size.

NCs functionalized with 1-octene, 1-dodecene, or 1-octadecene, the PLQYs increase with increasing temperature up to 500 °C, reaching a maximum of around 20% (Si NCs of other sizes display similar trends). Note here that the PLQY values need to be taken with caution, due to the low sensitivity of the spectrometer in the NIR region and possible errors from the integrating sphere method.⁷⁶ The PLQY and peak emission wavelength are not affected by ligand length. Similar to the result obtained by Mangolini *et al.*,⁷¹ the PLQY of as-produced Si NCs that are not heated in flight is typically lower than 5%. For all the furnace annealing temperatures shown in Figure 2.4, the emission peaks are located around 828 nm, with some minor sample-to-sample variances. It is believed that red to near-infrared photoluminescence of Si NCs originates from the silicon core states and is subject to quantum confinement effects.^{19,77} The fact that the peak wavelength of the photoluminescence remains constant implies that there is no shrinking of the Si NC core size associated with annealing. Further, size estimations from XRD measurements indicate that crystallite size remains constant during the heat treatment (Figure 2.5). This indicates that the main role of heat treatment is associated with the modification of nanocrystal surfaces.

In order to characterize changes of Si NC surfaces upon in-flight annealing, we performed

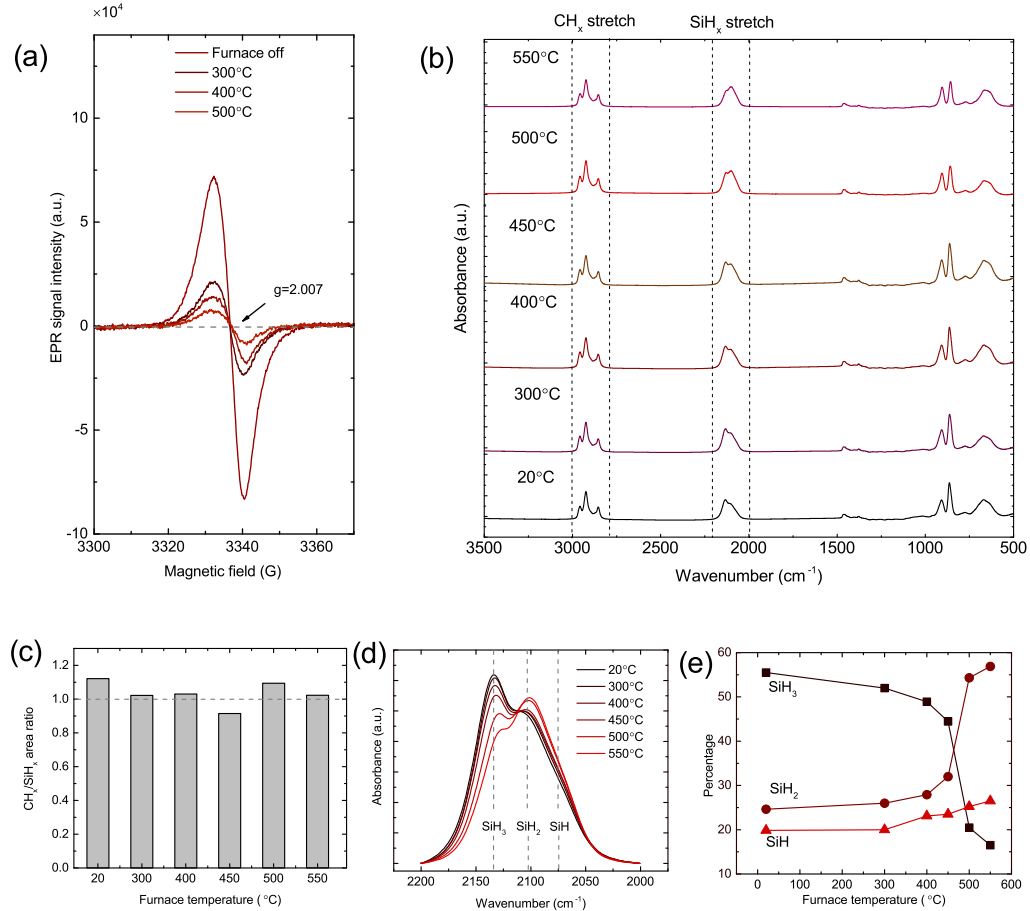


Figure 2.6: (a) EPR spectra of 3.2 nm, 1-dodecene functionalized Si NCs with various furnace operating temperatures. The EPR signal amplitude decreases with increasing furnace temperature for the temperatures studied. (b) FTIR spectra of 3.2 nm, 1-octene functionalized Si NCs with furnace temperature ranging from room temperature to 550 $^{\circ}\text{C}$. (c) Histogram representing the relative area ratio of CH_x/SiH_x obtained from FTIR in (b). (d) FTIR spectral region between 2200 and 2000 cm^{-1} related to Si-H stretch normalized to the signal intensity at 2110 cm^{-1} . (e) Percentage of each SiH_x species obtained by peak deconvolution of the SiH_x stretching region between 2200 and 2000 cm^{-1} .

electron paramagnetic resonance (EPR) measurements and Fourier transform infrared spectroscopy (FTIR) spectroscopy. EPR measurements are capable of identifying paramagnetic defects, including dangling bond centers, which represent an important type of trap state in silicon.⁷⁸ They are believed to be nonradiative centers that contribute to a reduction of the PLQY of silicon nanocrystals.⁷⁹ EPR measurements on 1-dodecene functionalized Si NCs with various furnace heating temperatures were performed while carefully keeping the samples air-free and keeping the sample concentration and volume constant for all samples. The EPR signal centers at 3335 G corresponding to a g-factor of 2.007, which agrees with previous values of silicon nanocrystals functionalized in the gas phase.⁷¹ The broad EPR peak has been previously attributed to a combination of $g_{\parallel}=2.0019$ and $g_{\perp}=2.0086$ from P_b centers at the silicon/silicon oxide interface and $g_D=2.0053$ from dangling bond D centers in a disordered environment^{37,80} for silicon nanocrystals showing some amount of surface oxidation. As is shown in Figure 2.6a, the amplitude of the EPR signal is reduced significantly as Si NCs go through in-flight annealing with furnace temperature at 300 °C. In-flight annealing at higher temperatures leads to a further reduction in the EPR signal. We note that, even for the sample with the 500 °C treatment, there are still EPR-active defects that the heat treatment does not remove. While our annealing time is limited to ~ 0.1 second by the experimental setup, we believe that a longer annealing time in the gas phase might enable more efficient elimination of defects and thus higher PLQY.

FTIR measurements provide valuable information about surface group composition. Figure 2.6b shows the FTIR spectra of 1-octene functionalized Si NCs. The peaks between 2800–3000 cm^{-1} are assigned to CH_x ($x = 1-3$) stretching modes, and the feature between 2000–2200 cm^{-1} ($x = 1-3$) corresponds to SiH_x stretching modes of Si surface atoms that are not functionalized with a ligand. Therefore, the relative area ratio of the CH_x stretching region to the SiH_x stretching region (2000–2200 cm^{-1}) can qualitatively describe the surface ligand coverage (Figure 2.6c). For a set of different furnace temperatures, including room temperature, the CH_x/SiH_x area ratio remains relatively constant, which indicates minor differences in surface ligand coverage. This result indicates that although unreacted ligands

can enter the furnace along with Si NCs, further ligand functionalization does not occur in the furnace. Ligand functionalization is essentially complete once the Si NCs leave the afterglow-plasma functionalization zone.

As the increase of PLQY with increased annealing temperature is presumably not related to the attachment of additional ligands, it is reasonable to investigate the changes of SiH_x surface species caused by the annealing. Previous studies had suggested that thermal desorption of hydrogen^{81,82} and changes of SiH_x species composition^{83–86} can occur at the temperatures used here for in-flight annealing of the SiNCs. Most relevant for this study, Shu *et al.* proposed that the desorption of hypervalent SiH_3 is associated with an improvement in PLQY of plasma produced Si NCs.⁸⁷

Figure 2.6d shows the detailed FTIR spectra of the SiH_x stretching mode region. The dominant peak in the 2000–2200 cm^{-1} range of the sample produced without post-synthesis annealing (20 °C) is centered at $\sim 2141 \text{ cm}^{-1}$, which is attributed to the SiH_3 stretch vibrations.^{81,84} A reduction in the SiH_3 feature is observed at higher furnace temperatures while the feature corresponding to SiH_2 at $\sim 2095 \text{ cm}^{-1}$ becomes more significant. The drop of SiH_3 groups occurs most drastically at around 400–500 °C (Figure 2.6e), which is consistent with the desorption temperatures observed by Holm and Roberts for hydrogen-terminated, plasma-synthesized Si NCs.⁸⁸

The surfaces of Si NCs synthesized from a nonthermal plasma consist of silicon monohydride (SiH), dihydride (SiH_2), and trihydride (SiH_3) groups. In a previous study, it was observed that PLQY of plasma-synthesized Si NCs can be improved by heating them to 160 °C in mesitylene for an hour.⁸⁷ The proposed mechanism is that some of the SiH_3 species, produced as silane fragments in the plasma and not fully consumed during the Si NC growth, are hypervalently bonded to fully coordinated silicon atoms at the Si NC surface, and that the removal of these weakly bonded species by heating leads to a subsequent increase in PLQY. These conclusions were supported by residual gas analysis showing a low desorption temperature of SiH_3 , and quantum chemical calculations showing that such

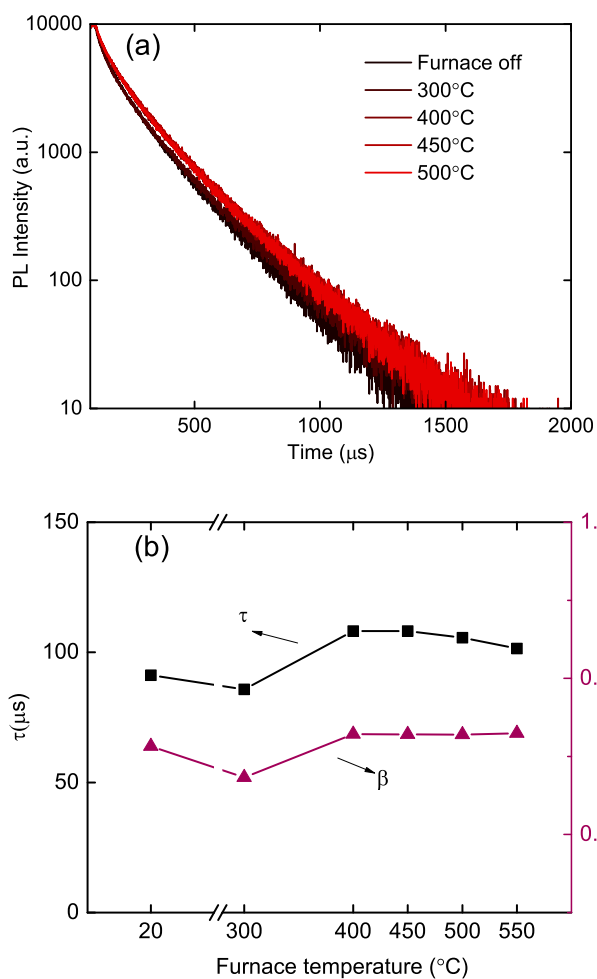


Figure 2.7: (a) Time-resolved decay data for 1-dodecene functionalized, 3.2 nm Si NCs with various furnace temperatures detected at 800 nm. Excitation wavelength is 407 nm and excitation time is $\sim 50 \mu\text{s}$. Si NCs are dispersed in toluene with concentration of $\sim 1 \text{ mg/ml}$. (b) Characteristic times τ (squares) and dispersion factors β (triangles) as a function of furnace processing temperatures.

hypervalently bonded species can act as nonradiative recombination centers. This mechanism is different from the desorption of a hydrogen from covalently bond surface SiH_3 group, which may cause dangling bond formation. Following this previous work, we here also interpret the increase in PLQY and the decrease of SiH_3 in terms of desorption of hypervalently bonded SiH_3 . Compared with the previous solution phase study, the desorption process here occurs at much shorter timescales due to the much higher temperatures enabled by the in-flight heating.

Studying the temporal dynamics of photoluminescence decay provides additional information regarding the nature of the improved PLQY. Figure 2.7 shows the temporal photoluminescence decay of samples emitting at 820 nm, with samples emitting at other peak wavelengths behaving similarly. The time-resolved photoluminescence decay is characterized by a stretched-exponential decay $I = I_0 \exp(-(t/\tau)^\beta)$, with lifetime τ of 100–120 μs and dispersion factor β around 0.7–0.8 (Figure 2.7). This slow radiative decay is characteristic of emission that originates from silicon core states following quantum confinement.⁸⁹ Interestingly, both τ and β change very little with post-synthesis annealing in the furnace, yet the PLQY increases from below 5% to around 20%. This result is consistent with previous reports by Sangghaleh *et al.* that an ensemble of Si NCs is composed of “bright” and “dark” quantum dots.¹⁸ As discussed in that paper, but also pointed out in earlier studies,^{90,91} the ensemble PLQY is often lower than the internal quantum efficiency $\text{IQE} = \Gamma_r / (\Gamma_r + \Gamma_{nr})$ of individual Si NCs, where Γ_r and Γ_{nr} represent the radiative decay rate and nonradiative decay rate of an individual nanocrystal. While the IQE of “bright” dots can approach 100%,^{12,18,91} the ensemble PLQY also accounts for the presence of “dark” Si NCs, which have a very large nonradiative rate, i.e., which absorb but do not emit and have an IQE close to zero. The increase in ensemble PLQY with in-flight annealing at essentially constant τ and β suggests that heating turns some “dark” dots into “bright” dots, while not affecting the intrinsic radiative decay dynamics of the “bright” dots.

2.3.3 Influence of Surface Ligand Coverage

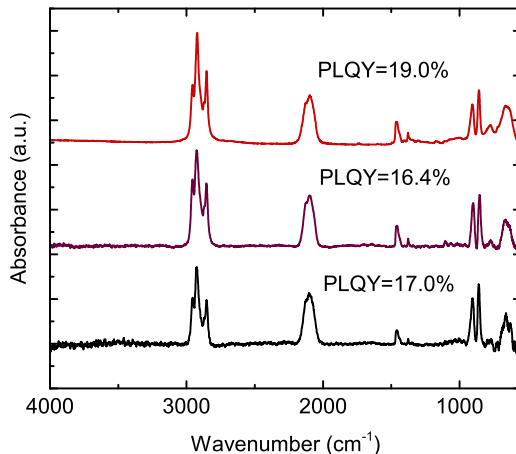


Figure 2.8: FTIR spectra of 1-octene functionalized Si NCs with different surface coverage. The peak between 3000 and 2800 cm^{-1} is attributed to C-H stretching vibration.

Here we investigate the influence of surface ligand coverage on sample PLQY with 1-octene functionalized Si NCs. Surface ligand coverage is conveniently tuned by controlling ligand and injection rate, and values of surface ligand coverage are quantified according to the weight percentage of carbon and hydrogen measured by CHNS/O elemental analysis. By assuming that ligands are covalently bonded to the silicon NC surfaces,⁷² and that ligands remain complete without breaking into fragments or oligomerizing, surface coverage can be estimated using particle size and weight percentage of ligands. Three conditions used for 1-octene functionalization and the corresponding surface ligand coverages are listed in Table 2.2. As expected, surface coverage increases with higher ligand injection rate, which is also qualitatively observed in FTIR spectra (Figure 2.8). While ligand surface coverages range from 25% to 43% for these conditions, the sample PLQY values remain relatively constant when transferred and measured in toluene. This observation clarifies the impact of ligand functionalization of Si NCs on the PLQY. While it is commonly believed that ligand functionalization terminates surface dangling bonds and therefore a higher surface

Table 2.2: Three conditions used to study the relationship between sample PLQY and surface ligand coverage. Furnace processing temperature is 450 °C for all samples, and PLQY measurements are taken for Si NCs in toluene at ~ 1 mg/ml

Bubbler pressure (Torr)	Ligand flow rate (sccm) ^a	Ligand mass fraction	Surface coverage	Sample PLQY	
100	17	23.3%	25%	17.0%	^a
50	35	32.0%	39%	16.4%	
35	50	35.3%	43%	19.0%	

Vapor pressure of 1-octene is 17.4 mmHg at room temperature (20 °C).

ligand coverage should enable higher PLQY, this is not supported by our observations. For our Si NCs produced in a nonthermal plasma, PLQY is primarily determined by surface silyl composition rather than surface ligand coverage, because only an estimated 25–43% of surface Si-H sites are replaced by Si-C bonds, due to steric hindrance of the ligands. Hence, for our plasma-synthesized Si NCs, PLQY is closely related to the post-processing temperature which strongly affects surface SiH_x composition.

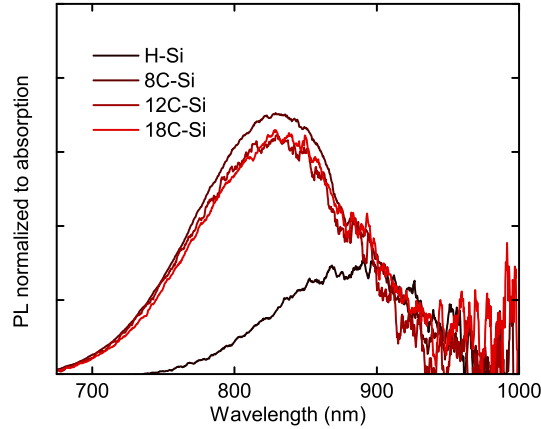


Figure 2.9: Normalized PL spectra of 3.2 nm diameter, non-functionalized, 1-octene, 1-dodecene, and 1-octadecene functionalized Si NCs dispersed in toluene.

However, further reduction of surface ligand coverage will have a negative influence on sample PLQY. We also measure the PLQY value and emission spectrum (Figure 2.9) for non-functionalized Si NCs, which may be of interest for device applications that require

electrical conduction⁹² due to the lack of insulating ligands. At the same 450 °C furnace processing temperature, PLQYs of H-Si NCs are only around 7%. This is likely the result of energy transfer from “bright” to “dark” nanocrystals, as we discussed above that the intrinsic sample PLQY is not primarily determined by ligand coverage. Different from the ligand functionalized samples, the H-Si NCs remain agglomerated in toluene, resulting in much more efficient energy transfer. The interpretation is consistent with the significant redshift of the PL spectrum of H-Si NCs compared to the ligand functionalized samples, consistent with energy transfer from smaller to larger NCs (Figure 2.9).

2.3.4 Light-induced QY enhancement

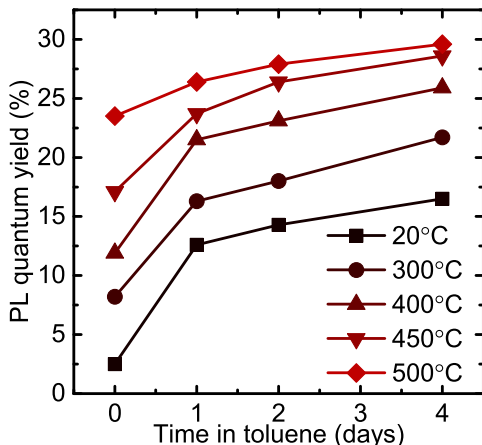


Figure 2.10: The PLQY evolution of 3.2 nm, 1-octene functionalized Si NCs processed at a series of furnace temperatures. Samples are stored under room light and without exposure to air.

Potentially, PLQY of these gas-phase synthesized Si NCs can be even further improved if we let the Si NCs age in an inert environment under room light after synthesis. Figure 2.10 shows the PLQY evolution of samples processed at various furnace temperatures over 4 days. The PLQY enhancement is believed to be relevant to light irradiation, as the control sample of Si NCs covered in aluminum foil has little change in PLQY over time. While the PLQY increase is observed in samples processed at any furnace temperature, the effect of

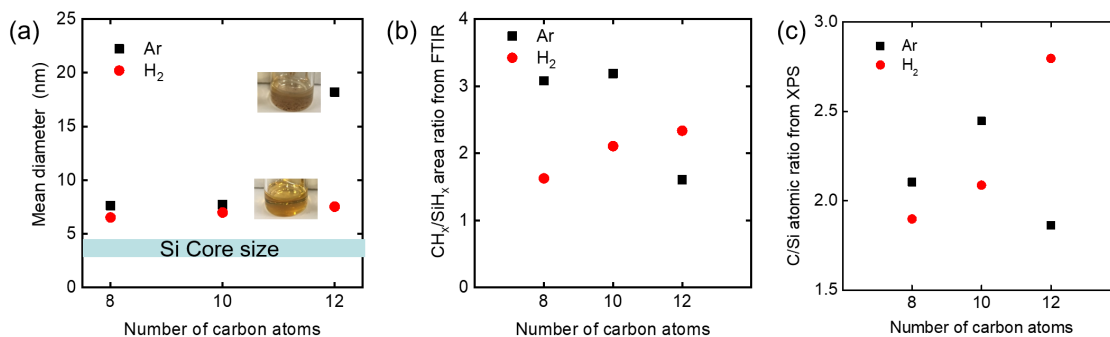


Figure 2.11: Comparison of grafting efficiency between carrier gas of argon for alkenes of different lengths (1-octene, 1-decene, and 1-dodecene) characterized by (a) dynamic light scattering, (b) FTIR, and (c) XPS.

initial PLQY is persistent, with the 500 °C sample constantly having the highest PLQY among all the samples.

2.3.5 Influence of ligand carrier gas on grafting efficiency

During the attempts to produce ligand-grafted Si NCs with high PLQY, we found that the grafting efficiency is dependent on the ligand type, ligand carrier gas, and plasma power. In this section, we discuss the influence of Ar/H₂ as the ligand carrier gas (i.e. Ar/H₂ plasma afterglow) on the ligand grafting efficiency.

In Section 2.3.1, we have demonstrated the successful functionalization of Si NCs by injection 1-dodecene using H₂ as the carrier gas (Figure 2.3d). However, the as-produced Si NCs agglomerate in toluene when we replace the H₂ carrier gas with Ar while keeping other synthesis conditions constant, suggesting that the Ar afterglow leads to lower surface ligand coverages than H₂. This observation in surface coverage variation is confirmed by FTIR and XPS measurements, which show a lower C/Si ratio in the Ar afterglow case (Figure 2.11b, c). Furthermore, we found that this observation of higher reactivity in the H₂ afterglow than Ar is reversed when we replace 1-dodecene with 1-octene or 1-decene (Figure 2.11b, c). For 1-octene and 1-decene, the surface ligand coverage in the Ar afterglow is higher than H₂. The major difference between 1-octene, 1-decene, and 1-dodecene is that their vapor

pressures are 17.4, 1.7, and 0.2 Torr, respectively. As a result, the ligand injection rates are expected to vary by two orders of magnitudes at similar bubbler pressures. Therefore, we conclude that the relative reactivity of alkenes is enhanced in the H₂ afterglow (relative to Ar) at low alkene flow rates but is suppressed by the H₂ afterglow at high alkene flow rates.

We also investigate the ligand grafting efficiency of alkanes and alkynes in the Ar/H₂ plasma afterglow. It has been previously demonstrated that alkenes exhibit higher reactivity than alkanes when Ar is used as the carrier gas.⁷¹ Here, we notice that this grafting efficiency difference between alkane and alkene is more distinct when we replace Ar with H₂. Figure 2.12 plots the FTIR spectra of 1-decene and decane grafted Si NCs, with 100 sccm of hydrogen or argon used as the carrier gas, respectively. For both ligands, higher grafting efficiency is achieved in the argon afterglow, represented by the larger CH_x/SiH_x area ratio. However, the grafting efficiency between 1-decene and decane only varies by a factor of 2.67 (3.2/1.2) when Ar is used as the carrier gas, whereas this ratio is as large as 21 (2.1/0.1) for H₂ as the carrier gas. This finding is significant because it indicates high reaction selectivity in the H₂ afterglow – the surface grafting of alkenes occurs mainly through the carbon double bond and not through the saturated carbons.

Until now, a clear understanding of the ligand grafting mechanism has not yet been established. Nevertheless, the above experiments may provide us with some clue on the possible processes present during the ligand grafting process. When Si NCs meet the ligands in the plasma afterglow, the reaction can be initiated by radicals either on the particle surface or on the ligand itself. Therefore, either of the following two processes may occur:

1. The plasma afterglow provides a reactive environment for the injected ligands to form radical species that can react with the nanoparticle surfaces.
2. There are surface sites available for reactions on the silicon nanoparticle surfaces. In the afterglow region, there are fluxes of hydrogen from and to the nanoparticle surfaces,³⁸ indicating the presence of large numbers of surface radicals.

The fact that the relative grafting efficiency between Ar and H₂ depends on the ligand injection rate and that H₂ suppresses alkane grafting more significantly than alkene indicates

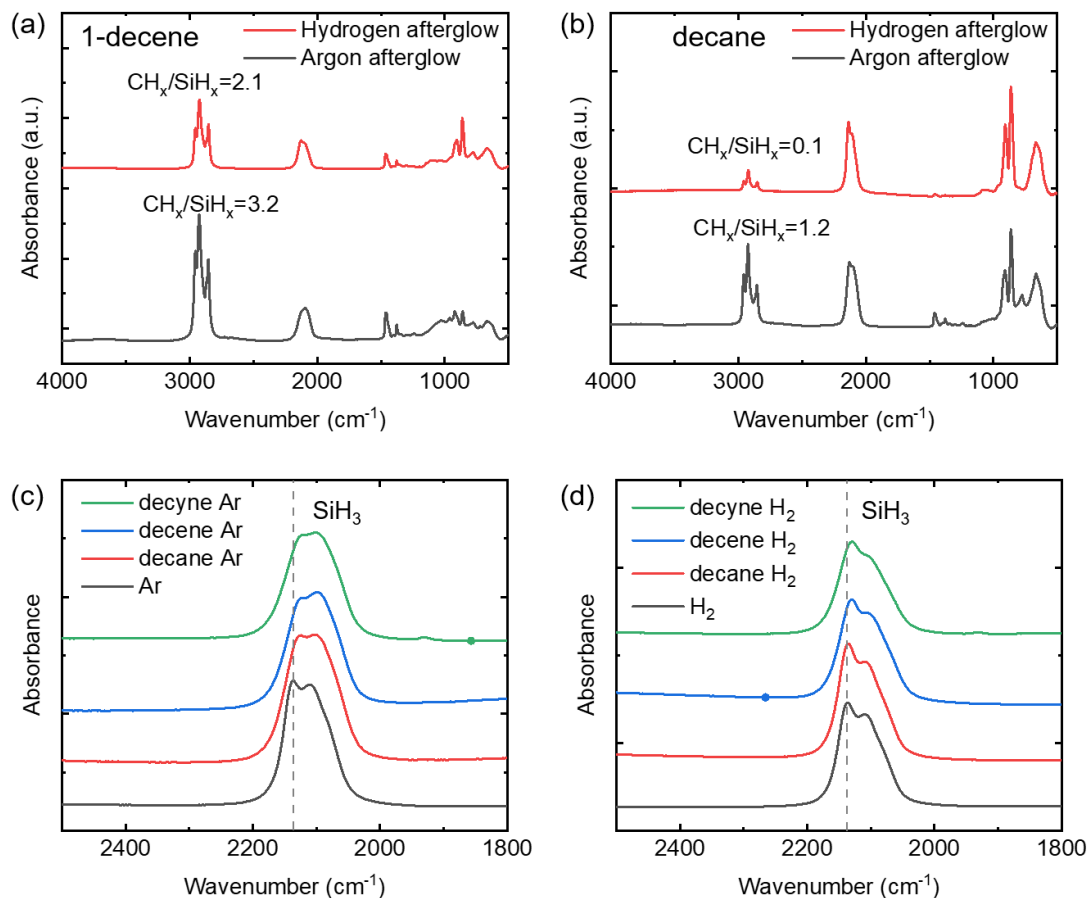
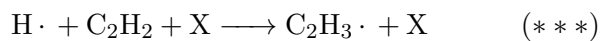
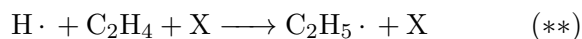
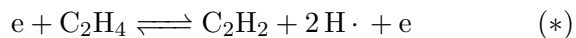


Figure 2.12: (a,b) FTIR spectra of 1-decene and decane capped Si NCs with H₂ and Ar as the carrier gas, respectively. (c,d) FTIR spectra of the Si-H_x stretching vibration region of Si NCs with H₂ and Ar plasma afterglow.

that Process 1 may play a role. If Process 2 is solely responsible for the ligand attachment, the trend of Ar carrier gas having higher grafting efficiency than H₂ should persist regardless of ligand concentration or ligand type. Here, we try to interpret the observed phenomena based on a three-step radical generation mechanism proposed during an early study on plasma polymerization of ethylene⁹³:



According to this proposed mechanism, the creation of alkane/alkene radicals relies on the generation of hydrogen radicals via electron impact dissociation as the first step. The alkane/alkene radicals are subsequently generated via the attachment of these hydrogen radicals across an unsaturated bond. In a hydrogen afterglow, the atomic hydrogen density is expected to be high. These atomic hydrogen radicals may facilitate the generation of radicals via process (**) at low ligand concentrations. Meanwhile, the high atomic hydrogen concentration may also suppress process (*), preventing the formation of unsaturated carbons and radicals from saturated carbons, leading to the low grafting efficiency of alkanes.

The FTIR spectra of the Si-H_x stretching vibration region in 2200–2000 cm⁻¹ support this assumption (Figure 2.12c, d). As a result of hydrogen consumption through reaction (**) and (***), there is a significant reduction of SiH₃ peak intensity during 1-decene and 1-decyne injection in the Ar afterglow. In the H₂ afterglow, the reduction is less distinct due to the abundance of atomic hydrogen. However, this hypothesis still needs to be verified by more explicit evidence. Comparing the atomic hydrogen concentration at various ligand injection rates in the Ar/H₂ afterglow may be the first step to clarifying whether these proposed mechanisms are responsible for the ligand grafting reaction.

2.3.6 Ligand grafting with a dual-plasma system

The above experiments were performed with a single plasma source, with ligands injected into the spacial plasma afterglow. We also explored the ligand grafting behavior using a dual-plasma setup, with the second plasma power applied downstream the ligand (1-octene) injection point (Figure 2.13). The as-synthesized materials were characterized by FTIR (Figure 2.14), and different behaviors were observed where H₂ and Ar were used as the carrier gas. In the case of H₂ injection, the surface coverage characterized by the CH_x/SiH_x area ratio decreases as the second plasma power increases. In the case of Ar injection, the second plasma source increases the degree of ligand coverage at low plasma power (1W). At higher powers, however, the synthesized materials start to exhibit a band in the 750–950 cm⁻¹ region, which is assigned to Si–C stretching vibration in silicon carbide.

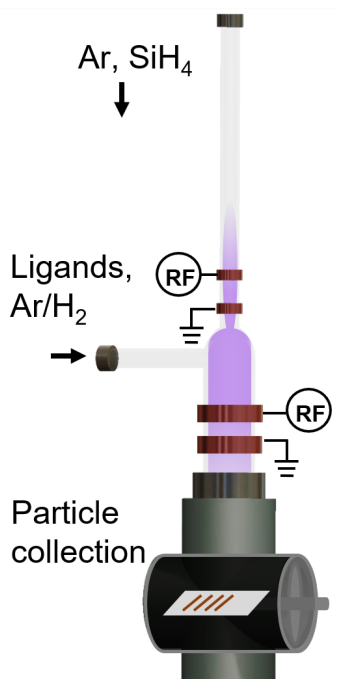


Figure 2.13: Schematic of the dual-plasma setup for ligand grafting.

The sample produced with argon injection and 20W second plasma power was further characterized with TEM and XRD. The samples are readily dispersible in toluene (Figure 2.15a), presumably due to the attachment of undissociated 1-octene onto particle surfaces. The samples also exhibit green/blue photoluminescence under 400 nm irradiation. Green/blue PL has been previously observed in SiC nanoparticles prepared from other methods and is believed to be originated from surface states.^{94,95} TEM confirms that the as-synthesized materials are spherical nanoparticles with diameters around 3–5 nm. XRD indicates that the as-synthesized materials appear to be a mixture of Si and 3C–SiC (β -SiC). This cubic crystal structure is consistent with previous studies, where 3C–SiC nanocrystals are produced with a nonthermal plasma process with CH_4 or C_2H_2 as the carbon source.^{96–98} By replacing the carbon source with 1-octene, we are able to synthesize nanocrystals with similar structures but enhanced solubility in nonpolar solvents.

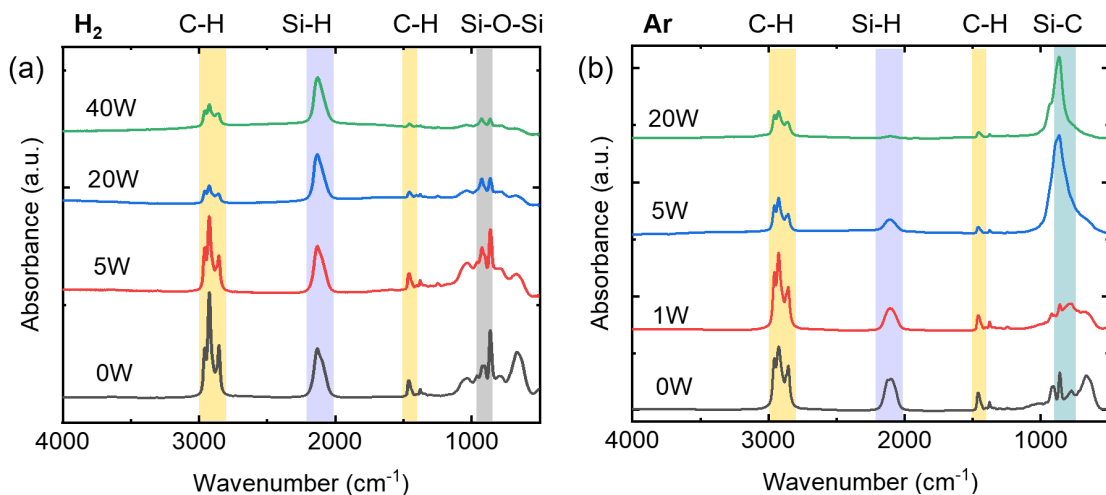


Figure 2.14: FTIR of as-synthesized nanoparticles with varying second plasma power, with (a) hydrogen and (b) argon as the carrier gas for 1-octene, respectively.

2.4 Future work

Ligand grafting mechanism. The aforementioned experimental work in Section 2.3.5 shows that the generation of ligand radicals may be a dominant step towards surface functionalization. Simulation work can also shed light on the ligand grafting mechanism. Our preliminary results from ReaxFF molecular dynamic simulations show that the radical density on a silicon surface can dominant the ligand grafting efficiency as opposed to the ligand type. Briefly, the reactivity of each species with a silicon surface is tested by placing a molecule (octane, octane 1-radical, octane 2-radical, and 1-octene) in the proximity of a silicon slab and run microcanonical ensemble (NVE) molecular dynamics simulations to observe whether the molecule leaves or attaches to the silicon surface. It is found that when the silicon surface is fully terminated with hydrogen, all the above molecules have low attaching probabilities ($<10\%$), whereas, for a partially terminated silicon surface, octane 1- and 2- radicals and 1-octene all have high attaching probability (approaching 100% when the radical is placed next to the Si radical site). We can qualitatively conclude that the radicals on the silicon surface are a dominant factor affecting the ligand grafting reactivity.

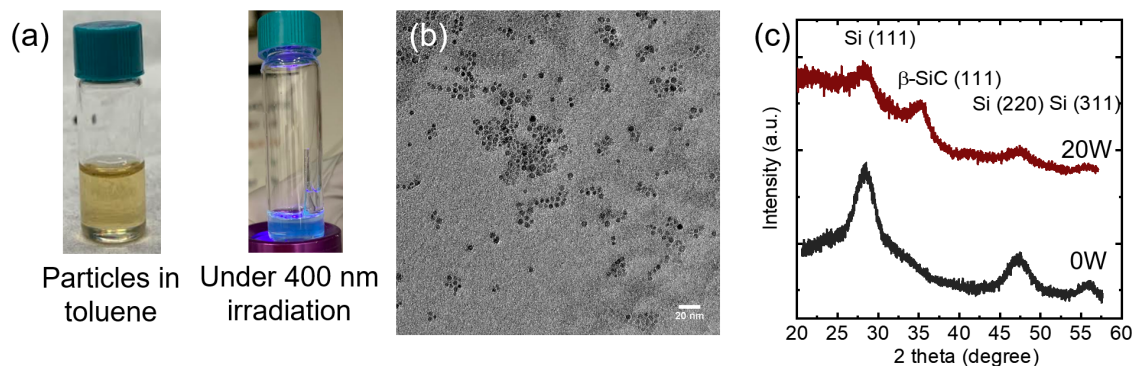


Figure 2.15: (a) As-synthesized Si/SiC NCs dispersed in toluene under ambient and UV light irradiation. (b) TEM of Si/SiC NCs dropcast from toluene. (c) XRD of Si/SiC NCs in comparison with Si NCs.

To gain a thorough understanding of the ligand grafting process through experiments, more detailed sample characterization, especially *in situ* measurement, needs to be performed. Therefore, we propose a reactor setup that may allow us to gain more information on the ligand grafting mechanism (Figure 2.16). Here, hydrogen-terminated Si NCs are first synthesized and then placed onto an ATR crystal inside the reaction chamber. This reactor design allows the *in situ* FTIR characterization of large quantities of Si NCs in a variety of plasma environments. The following experiments may be performed:

a. Surface hydrogen coverage of Si NCs during Ar/H₂ plasma treatment. As discussed above, the reactivity difference of Ar/H₂ could be originated from the different densities of silicon surface radicals. FTIR measurements of Si NC surface hydrogen coverage in an Ar/H₂ plasma can verify whether Ar/H₂ plasmas lead to different surface radical densities. If the difference in silicon surface radical densities exists, a relationship between ligand grafting efficiency and surface radical can be established by varying the plasma power.

b. Ligand grafting efficiency as a function of substrate temperature. Even without a plasma, gas-phase grafting of alkene ligands can proceed at elevated temperatures.⁸⁵ Combined with the *in situ* monitoring of the SiH_x densities as a function of temperature, we can establish the relationship between the ligand grafting efficiency and the surface hydrogen coverage outside a plasma.

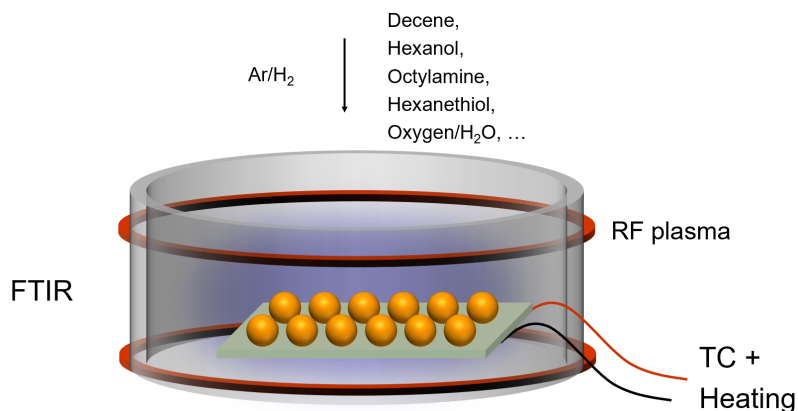


Figure 2.16: Proposed reactor setup for the study of ligand grafting mechanism.

Comparing the results from experiments a and b may help us understand whether the radical density of ligand or surface silicon dominates the reactivity.

Application of 3C–SiC nanoparticles. We successfully synthesized solution-processable nanocrystals consisting of Si and 3C–SiC using a dual-plasma reactor with 1-octene as the carbon source. 3C–SiC nanoparticles have shown their potential in various applications as single-photon emission sources,⁹⁹ bioimaging labels,⁹⁴ and photocatalysts.¹⁰⁰ The 3C–SiC NCs synthesized with 1-octene as the carbon source are readily dispersible in nonpolar solvents and do not need further surface functionalization. Therefore, further work needs to focus on optimization of the synthesis conditions to yield phase-pure 3C–SiC nanoparticles without Si. After that, we may continue to explore the application of these solution-processable 3C–SiC nanoparticles in various fields.

2.5 Conclusions

Si NCs with $\sim 20\%$ PLQY and very good solubility in non-polar solvents have been synthesized via a one-step, all-gas-phase approach. The nanoparticles are synthesized in a nonthermal plasma and functionalized in the plasma afterglow, followed by an in-flight heat treatment in a furnace. The plasma grafting produces a ligand-functionalized surface, which grants the Si NCs solubility in common nonpolar solvents. While the heat treatment does

not affect surface ligand coverage, it has a strong influence on the silicon-hydride groups at the Si NC surface. A significant increase in the ensemble photoluminescence quantum yield is observed, which is presumably associated with the desorption of hypervalently bonded SiH₃ groups at the surface.

The fact that Si NCs with respectable, though not record-breaking PLQY can be synthesized, functionalized, and heat-treated entirely in the gas phase on time scales of ~ 100 ms represents an advance that may enable the practical application of Si NCs for many luminescent applications. A scale-up of this technology is also possible through scaling reactor dimensions and/or parallelizing systems. While equipment limitations did not allow us to study longer annealing times in the gas phase, it is possible that these may enable even higher PLQY.

2.6 Experimental methods

Photoluminescence spectra were recorded with an Ocean Optics USB 2000 spectrometer in an integrating sphere setup as described in ref 101. The excitation source is a 395 nm LED and absolute quantum yields were calculated quantitatively using the absorption and emission intensities. The spectrometer was calibrated with an Ocean Optics LS-1-CAL tungsten halogen light source. Immediately after synthesis, Si NCs were transferred air-free into a nitrogen-filled glovebox via a pushrod assembly, where they were dispersed in 1 ml toluene at the concentration of ~ 1 mg/ml and sealed in a borosilicate glass vial for PLQY measurements. The PLQY measurements were then immediately performed, while the Si NCs were kept in the nitrogen-filled glass vials during the measurements. The spectrum of the glass vial containing 1 ml toluene under the illumination of the excitation source is first recorded as the baseline. The spectrum is divided into the excitation region and the luminescence region. Once the sample is inserted, the signal from the excitation region will decrease and the signal from the luminescence region will appear. The PLQY is calculated by $\text{PLQY} = \frac{P_s - P_b}{-(L_s - L_b)}$, where $L_{s,b} = \int_{\text{excitation}} \lambda I(\lambda) d\lambda$ and $P_{s,b} = \int_{\text{luminescence}} \lambda I(\lambda) d\lambda$ are

integrals of the spectral regions of excitation and emission, respectively, with the subscript s indicating the sample and b the baseline measurements. Unless specified otherwise, the spectra appearing in figures are normalized to the integral $-(L_s - L_b)$ which represents how much of the excitation signal is absorbed by the sample. For Si NCs having the same size and thus having identical absorption properties, this normalization guarantees that the luminescence spectra represent the emission from the same amount of Si NCs.

For structural and surface characterization, X-ray diffraction (XRD) data were recorded with a Bruker D8 Discover diffractometer with a Co X-ray source. Scherrer fitting was applied to determine the nanocrystal sizes using the MDI JADE software with shape factor $K = 0.89$. Bright field transmission electron microscopy (TEM) images were taken using a Tecnai T12 microscope with an accelerating voltage of 120 kV. For TEM measurements, Si NCs dispersed in toluene were drop cast onto a carbon-coated TEM grid and measurements were taken after the solvent evaporated. Fourier transform infrared (FTIR) spectra were recorded with Bruker ALPHA FT-IR spectrometer using under Diffuse Reflectance (DRIFTS) mode in a nitrogen-filled glovebox. FTIR samples were deposited on aluminum-coated silicon substrates with an impactor described in ref 74. 20 scans were taken for each measurement at 2 cm^{-1} resolution. Electron paramagnetic resonance (EPR) measurements were performed at ambient temperature in a Bruker Continuous Wave EleXsys E500 EPR spectrometer equipped with X-band (9GHz) microwave bridge and spherical SHQ resonator. 5 mg Si NCs were dispersed in 0.1 ml toluene for all samples. EPR grade quartz tubes with 5 mm diameter were used for the measurements and the tubes were sealed in nitrogen to avoid air exposure during measurements. The surface ligand coverages were measured with a 2400 Series II CHNS/O Elemental Analyzer performed by Atlantic Microlab, Inc. Weight percentages of carbon and hydrogen are within $\pm 0.3\%$ error limits. The surface coverage values are estimated by calculating the ratio of the number of ligands per NC to the number of surface Si atoms per NC.

To measure the size of silicon nanocrystals suspended in solution, dynamic light scattering (DLS) measurements were taken with a Nanotracs Flex In-situ Analyzer using volume

distribution mode. The equipment was calibrated with NIST-traceable particle size standards and the mean diameter measured has accuracy of within 5%. Solvents (toluene, from Fisher Scientific) used for characterization were dried over 4Å molecular sieves and degassed by bubbling nitrogen through the solvent.

Chapter 3

Gas-phase functionalization of silicon quantum dots for solvent-less luminescent solar concentrator fabrication

3.1 Introduction

A promising application for the gas-phase synthesized Si NCs described in Chapter 2 is to use them as luminophores in LSCs. The conventional method for preparing Si NCs for LSC applications involves solution-phase surface functionalization reactions to enhance PLQY and offer compatibility with the polymer matrix. These processing steps are time-consuming and require the use of excess solvents that need to be removed through evaporation after the reaction. Replacing the solution-phase functionalization with a gas-phase method can significantly reduce solvent and energy costs. However, the current PLQY achieved by all-gas-phase methods is still relatively low. In Chapter 2, we described an approach that enhanced the PLQY of as-synthesized Si NCs compared to previous gas-phase methods by a factor of 4–5, but the highest PLQY ($\sim 20\%$) is still significantly lower than the highest PLQY (50–60%) exhibited in solution-phase functionalized Si NCs.

In this chapter, we expand the gas-phase functionalization method to a broader variety of ligands and investigate the influence of functionalization ligand on Si NC photoluminescence. Ligands including alkene, alcohol, amine, and thiol have been successfully grafted onto the Si NC surface by plasma-assisted surface functionalization. We find that replacing the alkene with alcohol or amine leads to higher PLQY in as-synthesized Si NCs, with typical PLQYs

of 12–15%. Furthermore, the PLQY of as-synthesized Si NCs can be further enhanced under light irradiation at room temperature. Specifically, Si NCs functionalized with 1-hexanol and 1-octylamine exhibit PLQY values 40–50% after near-UV or visible light irradiation, approaching the highest PLQY reported for freestanding Si NCs prepared with solution-phase hydrosilylation.

Herein, we demonstrate the application of gas-phase synthesized for solvent-less LSC fabrication. The gas-phase ligand grafting of Si NCs offers enhanced solubility in nonpolar monomers, enabling the formation of homogeneous NC/polymer nanocomposites after polymerization. Polystyrene (PS) is a naturally transparent thermoplastic with a wide variety of applications. PS can be synthesized through the radical initiated polymerization of styrene, which is nonpolar and has excellent compatibility with gas-phase functionalized Si NCs. The UV stability and mechanical strength of polystyrene can be further enhanced by adding one or more other monomers to the styrene monomer during polymerization to form copolymers. Here, we use the copolymer poly(styrene-methyl methacrylate) (PS-PMMA) for the fabrication of Si NC/PS-PMMA films for LSC applications. Bulk Si NC/PS-PMMA nanocomposites can be fabricated with thermal polymerization,¹⁰² while films of Si NC/PS-PMMA can be deposited on glass via doctor blading.¹⁰³ The Si NC/PS-PMMA nanocomposites have PLQY of $\sim 40\%$ with low light scattering and are suitable for LSC applications.

3.2 Varying surface ligands

We extend the gas-phase functionalization approach to ligands with four different terminal groups, i.e., 1-decene, 1-hexanol, 1-hexanethiol, and 1-octylamine, to produce Si NCs with different surface chemistries. The reactor setup used in this chapter (Figure 3.1a) is similar to the design in Chapter 2 except with the tube furnace being omitted. The gas flow rates, reactor pressure, and plasma power were identical to the conditions described in Chapter 2 for the synthesis of 3.2 nm Si NCs. For each terminal group, the ligand length is selected,

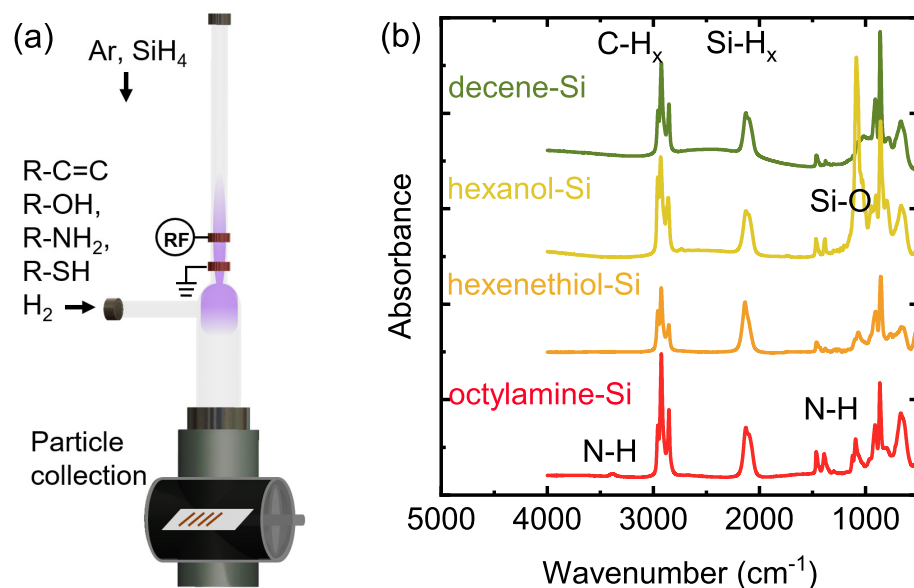


Figure 3.1: (a) Schematic of the reactor setup. (b) FTIR spectra of 1-decene, 1-hexanol, 1-hexanethiol, and 1-octylamine capped Si NCs.

so that all the ligands have similar vapor pressures (0.75–1.5 Torr) at room temperature. The ligands' similar vapor pressures ensure that the ligand injection rates are of the same order of magnitude.

The Si NCs functionalized with the above four ligands are all able to spontaneously form a clear solution when dispersed in toluene, indicating successful surface functionalization. The colloidal stability can last for a few months when samples are stored under nitrogen. In ambient air, all samples except thiol-capped NCs remain colloidally stable. In contrast, the thiol-capped Si NCs are very susceptible to hydrolysis due to the weak Si–S bond, with the solution turning cloudy after exposure to air for a few minutes.

The as-synthesized Si NCs were characterized by FTIR, proton nuclear magnetic resonance (¹H-NMR), and X-ray photoelectron spectroscopy (XPS). Figure 3.1 shows the FTIR spectra of Si NC capped with alkene, alcohol, amine, and thiol ligands, respectively. The spectral region corresponding to Si–H_x stretching vibrations at 2000–2200 cm⁻¹ and C–H_x

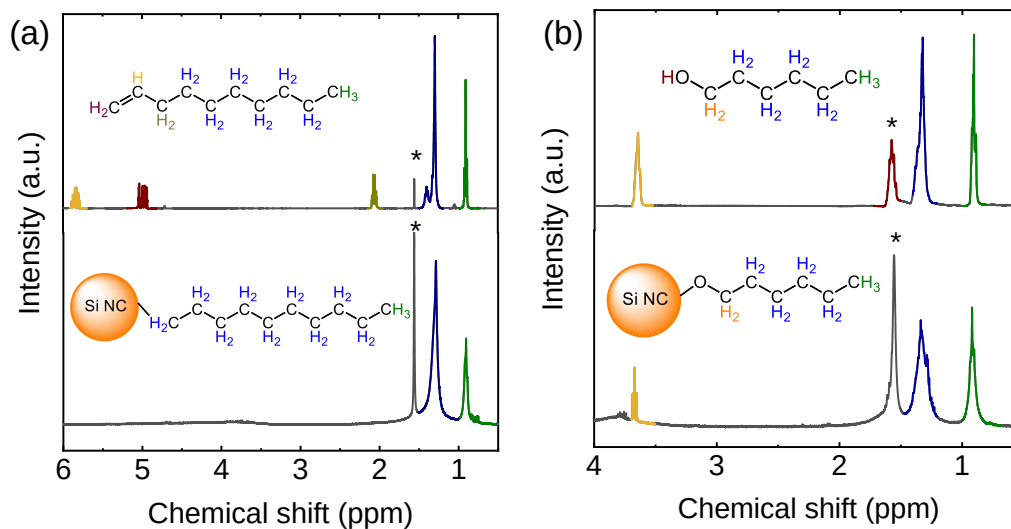


Figure 3.2: ^1H NMR spectra of (a) decene/decene-capped Si NCs and (b) hexanol/hexanol-capped Si NCs.

stretching vibrations at $2800\text{--}3000\text{ cm}^{-1}$ are present in all the samples. The Si-H_x and C-H_x peaks indicate that the nanoparticle surfaces are partially functionalized with the ligands, which is typically observed in gas-phase and solution-phase functionalized Si NCs due to steric hindrance. While Si-C-R and Si-S-R features have low IR sensitivity, more information regarding the surface bonding of hexanol and octylamine-capped Si NC surfaces can be revealed from FTIR. For hexanol-capped Si NCs, the sharp peak at $\sim 1080\text{ cm}^{-1}$ has been attributed to Si-O-R rather than Si-O-Si bridging bonds,¹⁰⁴ and for octylamine-capped Si NCs, the single peak at $3300\text{--}3400\text{ cm}^{-1}$ corresponds to secondary amine groups.⁴⁸ We can conclude that for both alcohol and amine functionalization, the oxygen and nitrogen atoms are singly bonded to the silicon surfaces rather than bridging between two adjacent Si atoms.

^1H -NMR also confirms the attachment of ligands onto the nanocrystal surfaces (Figure 3.2). As discussed in Chapter 2.3.5, the saturated carbons have low tendencies to

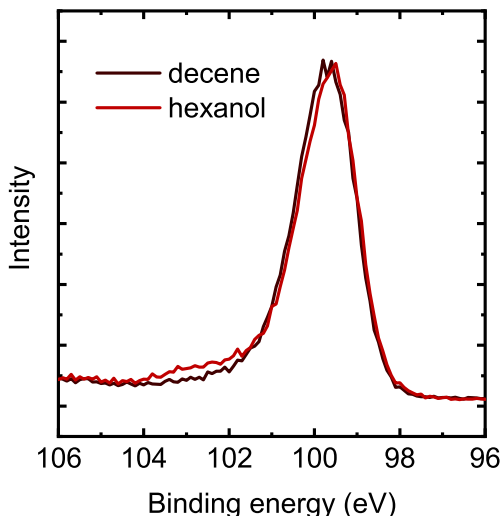


Figure 3.3: XPS spectra of decene and hexanol-capped Si NCs.

attach to the silicon surfaces in a hydrogen afterglow. Therefore, it is likely that the ligands are bonded to the silicon surfaces through the C=C or -OH functional groups. For decene-capped Si NCs, the disappearance of the peaks around 2.0 ppm, 4.8–5.0 ppm, and 5.7–5.9 ppm confirms that decene is attached to the particle surfaces via the C=C bond. For hexanol-capped Si NCs, there are two possible configurations: hexanol can either be grafted through Si–O bonds or through Si–C bonds with the O atom forming Si–O–Si bridging bonds. The latter configuration can be excluded since the area ratio of the yellow peak at ~ 3.7 ppm and the blue peak at ~ 1.3 ppm is similar for 1-hexanol and hexanol-capped Si NCs. The yellow peak corresponds to the hydrogen atom bonded to a carbon next to an oxygen atom and wouldn't be expected in the latter configuration. The most possible configurations for decene and hexanol-capped Si NCs determined from the above information are summarized in Figure 3.2.

X-ray photoelectron spectroscopy (XPS) measurements were also performed to verify the surface properties of gas-phase functionalized Si NCs (Figure 3.3). For XPS measurements, the as-produced decene/hexanol-capped Si NCs are transferred air-free from the reactor to the XPS chamber to avoid oxidation by the ambient air. The shoulder at 103.5 eV

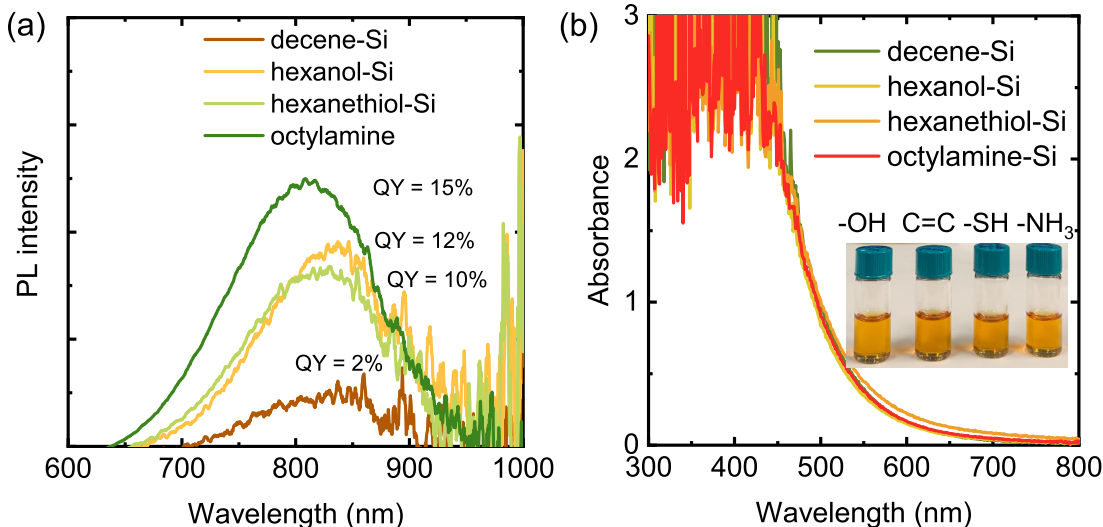


Figure 3.4: (a) PL and (b) UV-vis spectra of as-produced, -CH₂, -O, -NH, and -S function-alized Si NCs.

corresponding to the Si-O feature is slightly higher in the hexanol-capped Si NCs due to the surface bonding with the hexanol ligands. The prominent silicon peaks at 99.4 eV in both samples indicate that neither decene nor hexanol functionalization causes significant surface oxidation.

We measure the PL of as-produced Si NCs and found that both the PL wavelength and the PLQY are dependent on surface ligands. The alkene, alcohol, and thiol-capped Si NCs have similar peak wavelengths, while amine-capped Si NCs exhibit slightly blueshifted (~ 20 nm) PL. Previously, a study on PL from Si NCs with different surface chemistries has been performed by Carroll *et al.* with alkene, alcohol, and amine-capped Si NCs functionalized through radical initiated hydrosilylation.⁴⁸ Even though the preparation method and sample PLQYs are different in our study, the observation that Si NCs with nitrogen surface species exhibiting PL blueshift are consistent with the study by Carroll *et al.*, thus supporting the assumption by Carroll *et al.* that the differences in PL arise from the nature of surface ligands. Presumably, the surface atoms that Si NCs are bonded to may alter the quantum

confinement in Si NCs to some extent, similar to the “confinement softening” observed when Si NCs have varying matrix environments.¹⁰⁵ Regardless of the peak shift observed in PL, the difference in the UV-vis spectra are negligible, presumably due to the fact that the band gap energy only varies by ~ 0.04 eV.

The surface capping ligand also significantly influence PLQY of as-synthesized Si NCs. The amine and alcohol-capped Si NCs exhibit the highest PLQYs at 15% and 12%, respectively, while the alkene and thiol-capped Si NCs exhibit PLQY at 2% and 5% (Figure 3.4a). As Si NCs with these surface ligands functionalized through solution-phase reactions in ref 48 does not exhibit such PLQY differences, the differences in PLQY are presumably related to the plasma synthesis process. The $-OH$ and $-NH_2$ species within the plasma can lead to the higher electronegativity of the plasma, and as a result, the particles tend to be less negatively charged.¹⁰⁶ While the negatively charged nanoparticles tend to discharge when they leave the plasma, the charges may influence the nanoparticle surface growth, resulting in surface trap states responsible for a drop in PLQY.

3.3 Light-induced PLQY enhancement

As is shown in Figure 3.4a, PLQY in as-produced Si NCs are relatively low for LSC applications, even for the alcohol and amine-capped Si NCs whose PLQYs (10–20%) are improved compared to the alkene functionalized ones (2–5%). Interestingly, the PLQY of gas-phase functionalized Si NCs continues to increase upon exposure to light irradiation. Figure 3.5 shows the PLQY evolution of alkene, alcohol, amine, and thiol-capped Si NCs, all dispersed in toluene upon 400 nm near-UV irradiation. For simplicity, the “400 nm irradiation” is also referred to as “UV irradiation” in this chapter. While the PLQY increase is observed in all the samples, the trend that PLQYs in alcohol and amine-capped Si NCs are higher than alkene and thiol-capped Si NCs remain unchanged. After ~ 48 hours, PLQYs of hexanol and octylamine-capped Si NCs reach $\sim 45\%$, approaching the highest PLQY value of 50–60% reported in Si NCs, while PLQYs of alkene and thiol capped Si NCs remain $\sim 10\%$

lower. The errors associated with the PLQY measurements are on the order of 5%.¹⁰⁷ For each sample, the PL peak wavelength remains stable, indicating that the silicon core is unchanged during this UV treatment.

Similar trends are observed when repeating the experiment with a 633 nm visible light source (Figure 3.5b). The hexanol-capped Si NCs can reach PLQY $\sim 45\%$ after ~ 48 hours light irradiation, while the highest PLQY observed in decene-capped Si NCs is around 35%. When we reduce the irradiation intensity to half of the initial value, a slower increase of PLQY is observed. Furthermore, the “dark” control samples exhibit very slow increases in PLQY, which may be associated with the light exposure during PLQY measurements. All of these observations suggest that the PLQY increase is associated with light irradiation.

Time-resolved PL measurements were also performed to provide insight into the carrier dynamics. The lifetime is in the $\sim 100 \mu s$ range both before and after light irradiation, which is on the order of typical intrinsic core Si NC emission. The lifetime values are summarized in Table 3.1. Initially, the decene-capped Si NCs exhibit a shorter lifetime and smaller β value corresponding to larger nonradiative recombination rates and a variety of nonradiative recombination events. The shorter lifetime and the smaller β value are consistent with the lower PLQY of decene-capped Si NCs than hexanol-capped ones. For both samples, the average decay lifetime and dispersion factor β increasing after the light irradiation, corresponding to an increase in PLQY.

Table 3.1: τ , β , and average lifetime values from stretched-exponential fitting of decene and hexanol-capped Si NCs before and after UV irradiation

sample	τ (μs)	β	average lifetime (μs)
decene-Si NC	91	0.65	191
	200	0.85	232
hexanol-Si NC	149	0.85	219
	233	0.89	245

Following the work by Anthony *et al.*,⁸⁷ in our previous work, we attributed the PLQY

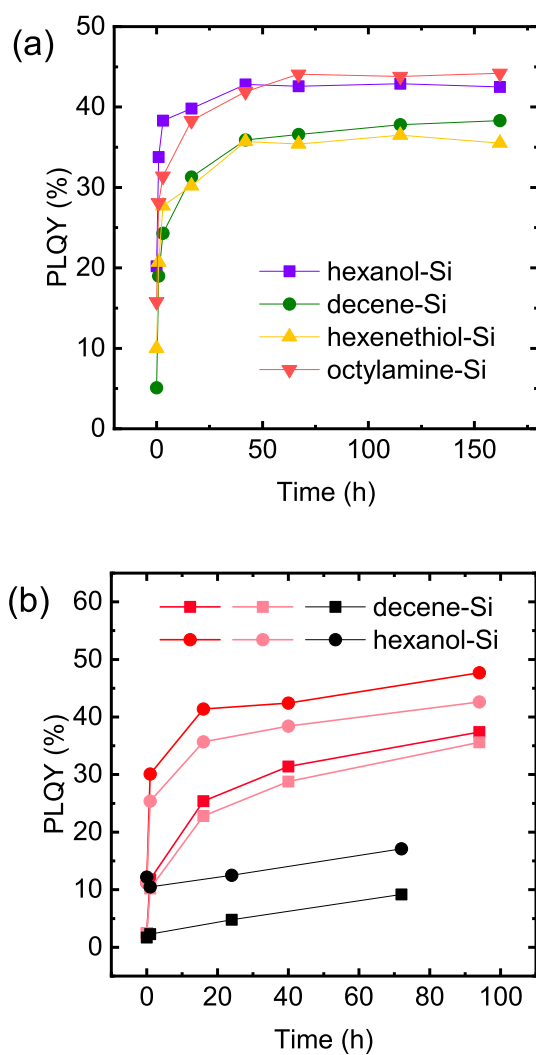


Figure 3.5: (a) The PLQY evolution of decene, hexanol, octylamine, and hexenethiol-capped Si NCs dispersed in toluene and under 400 nm irradiation at $\sim 0.5 \text{ mW/cm}^2$. (b) The PLQY evolution of decene and hexanol-capped Si NCs under 633 nm LED at ~ 0.5 (red), 0.25 (light red), or 0 (black) mW/cm^2 .

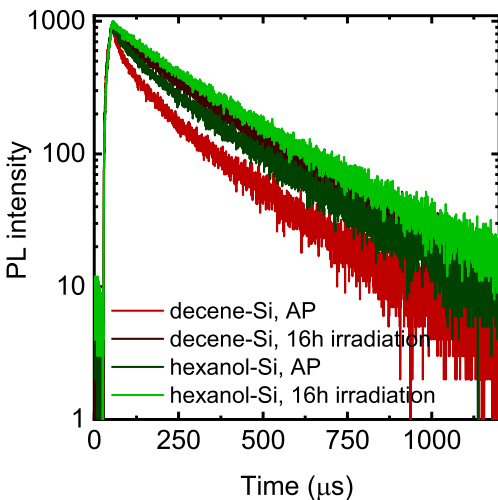


Figure 3.6: Time-resolved PL decays of decene and hexanol-capped Si NCs before and after UV irradiation.

increase upon heating to the surface desorption of weakly bonded SiH_x species.¹⁰⁸ A significant reduction in the SiH_3 signal was observed after heating, which is concurrent with an improvement in PLQY. However, this reduction in SiH_3 intensity is not observed after room-light irradiation. As shown in Figure 3.7, the SiH_x stretching vibration region remains similar for both decene and hexanol-capped Si NCs, although the PLQY increased by a value of $\sim 20\%$ after light irradiation. Using 400 nm light irradiation instead of room light or by substituting chloroform with toluene yielded similar results, with no significant change in SiH_x composition before and after light irradiation. These results contradict our previous conclusion that the improvement in PLQY is associated with the removal of weakly bonded SiH_3 species.

We hypothesize two different explanations for this unexpected light-induced PLQY enhancement:

1. The PLQY enhancement is still related to adsorbed surface SiH_x species. Instead of desorbing from the surface, the adsorbed SiH_3 species may undergo a light-induced mechanism that allows them to convert to covalent bonds. Presumably, similar to the light-mediated hydrosilylation reaction,^{40,41,109,110} the generation of positively charged holes may

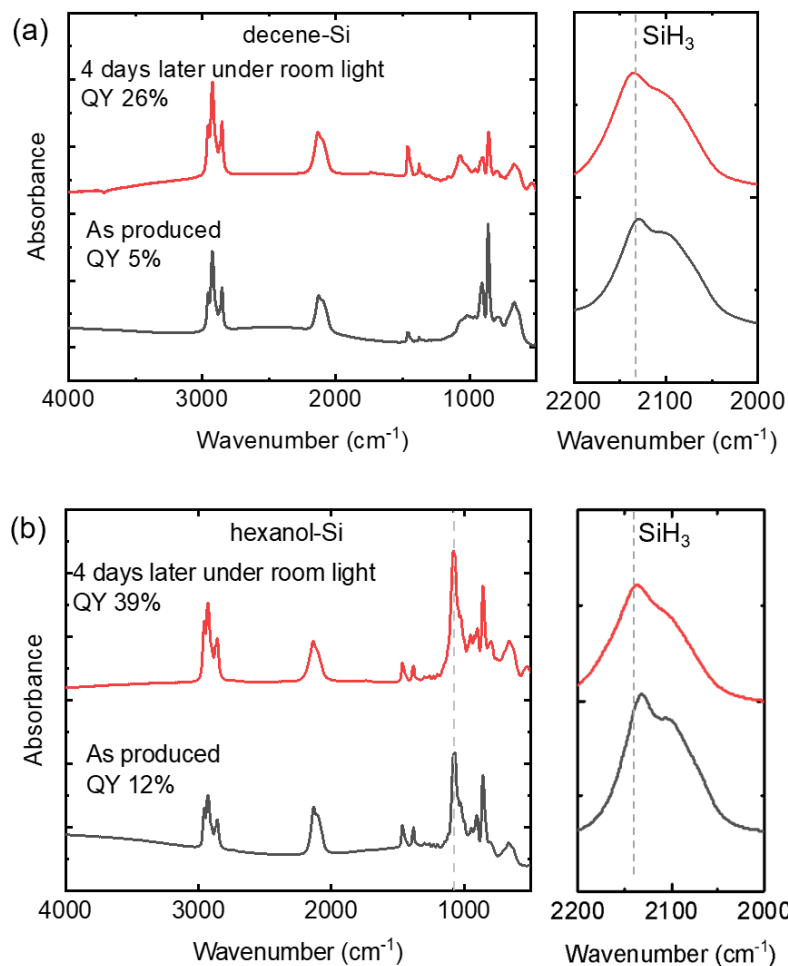


Figure 3.7: FTIR of decene and hexanol-capped Si NCs before and after room light irradiation.

drive the transition of the SiH_x species from physisorption to chemisorption.

2. The SiH_3 desorption and the physical or chemical process leading to PLQY enhancement are two uncorrelated processes. The PLQY enhancement can occur provided a source of energy input, which can be either heat or light irradiation. Coincidentally, the heating temperature leading to PLQY enhancement is similar to the adsorbed SiH_3 desorption temperature.

To verify these two hypotheses, we heated the as-produced Si NCs and UV-treated Si NCs in mesitylene at 160 °C and measured their FTIR before and after heating. If the

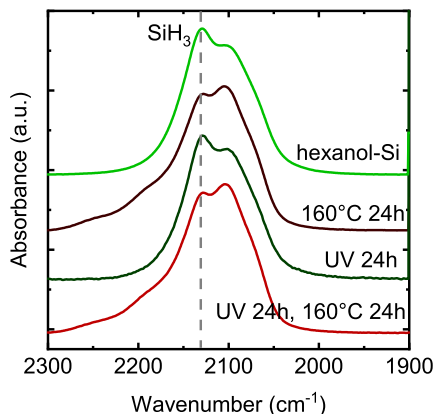


Figure 3.8: FTIR spectra of the Si-H_x stretching vibration region of as-produced and UV-treated hexanol-capped Si NCs before and after heating in mesitylene at 160 °C for 24 hours.

adsorbed SiH₃ groups convert to covalent bonding after light irradiation, they would be expected to exhibit a higher dissociation temperature since the Si-Si bond (2.2 eV) is more stable than the dissociation energy of adsorbed SiH₃ (0.7 eV⁸⁷). As shown in Figure 3.8, heating the Si NCs at 160 °C leads to the desorption of SiH₃ species, regardless of whether former UV treatment is performed. We conclude that Hypothesis 2 is more likely to be true – there are other mechanisms responsible for the PLQY enhancement upon heating or UV/visible light irradiation rather than SiH_x desorption. While there is no current experimental evidence to verify this assumption, it is possible that the charging of Si NCs plays a role. In a recent study, it is predicted that Si NCs collected from a nonthermal plasma reactor are aggregates consisting of both positively and negatively charged particles.¹¹¹ NC charging has long been associated with their blinking behavior and PL quenching through a longer “off” state.^{112,113} The PLQY enhancement upon UV irradiation may be interpreted as a result of NC decharging through interaction with the solvent through exciton-mediated reactions.^{40,41,109,110}

The PLQY enhancement overtime under UV irradiation is also dependent on the solvent. Figure 3.9 shows the PLQY evolution of decene and hexanol-capped Si NCs dispersed in mesitylene, toluene, chloroform, and styrene under 400 nm irradiation. It can be observed

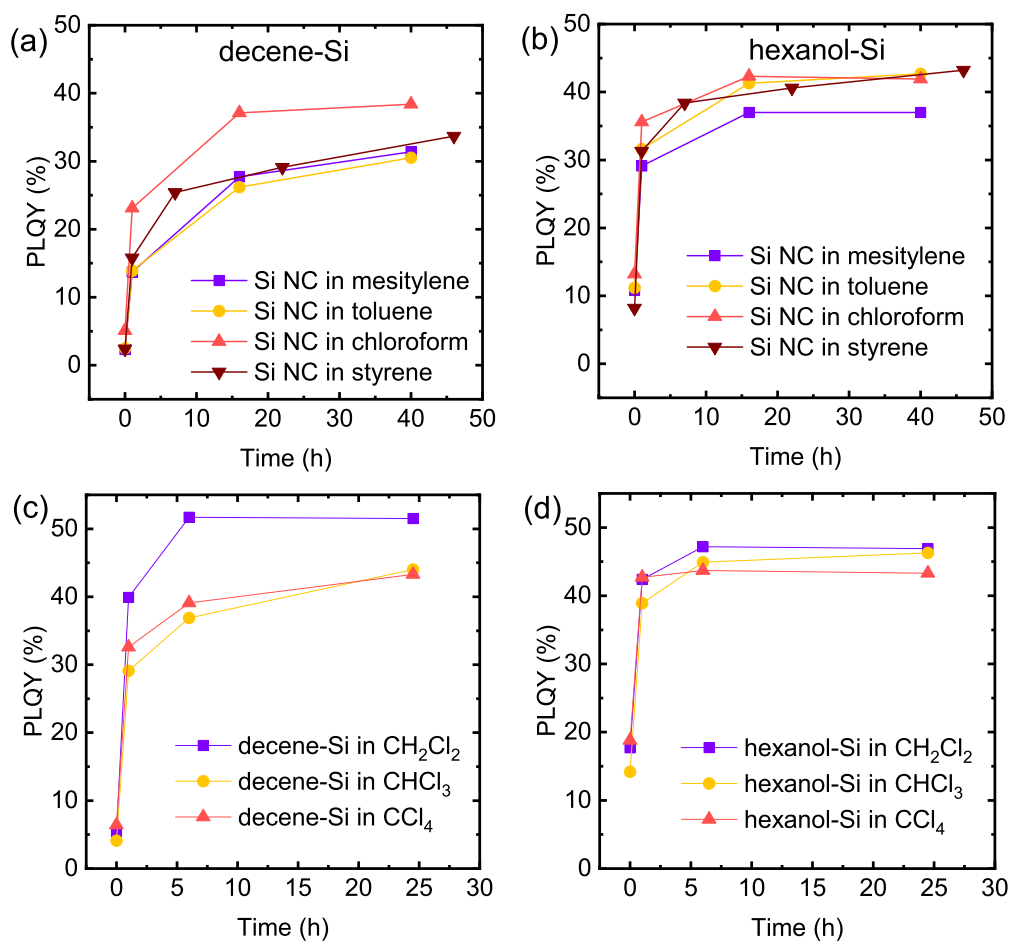


Figure 3.9: (a,b) PLQY evolution of decene and hexanol-capped Si NCs dispersed in mesitylene, toluene, chloroform, and styrene. (c,d) PLQY evolution of decene and hexanol-capped Si NCs dissolved in dichloromethane, chloroform, and carbon tetrachloride.

in Figure 3.9a that PLQY of decene-capped Si NCs in chloroform is distinctly higher than Si NCs in other solvents. For hexanol-capped Si NCs, the PLQY increase in chloroform occurs the fastest, even though the PLQY in toluene and styrene also reach >40% after 20 hours (Figure 3.9b).

The solvent dependence may be attributed to the different electron-accepting abilities of the solvent molecules. Following the NC charging discussion, good electron acceptors may temporarily trap an electron from the NC in their excited state, facilitating the neutralization of negatively and positively charged NCs. The different behaviors in decene and hexanol-capped Si NCs may originate from their distinct band structures. A previous computational study indicates that amine and alcohol-surface functionalization can raise the band edges compared to alkene and thiol.¹¹⁴ As a result of the higher conductor band edge, the trapping of electrons may be more likely to occur in hexanol-capped Si NCs, contributing to the faster increase of PLQY.

Based on the unusual behavior of decene-capped Si NCs dispersed in chloroform, we also measured the PLQY evolution of decene and hexanol-capped Si NCs dispersed in dichloromethane, chloroform, and carbon tetrachloride under 400 nm light irradiation. For hexanol-capped Si NCs, the PLQY in all the above solvents exhibits similar trends, with their PLQY reaching around 45% after 24 hours (Figure 3.9d). For decene-capped Si NCs, the samples in CHCl_3 and CCl_4 both reach PLQY of $\sim 40\%$ after 24 hours (Figure 3.9c). Interestingly, the sample in CH_2Cl_2 was accidentally stored in a vial with a slightly leaky cap, so the sample was briefly exposed to air before the start of light irradiation. This sample turned out to exhibit the highest PLQY, with the PLQY exceeding 50% after 24 hours. The slight blueshift of emission peak (~ 25 nm) during 24 hours of irradiation confirms that this distinct behavior is likely related to the exposure of oxygen. As oxygen is a good electron acceptor, a small concentration of oxygen may facilitate the surface transformation reaction of SiH_x species. Further work is required to study the PLQY evolution of Si NCs at various oxygen concentrations to find the optimal conditions that may enable higher PLQY.

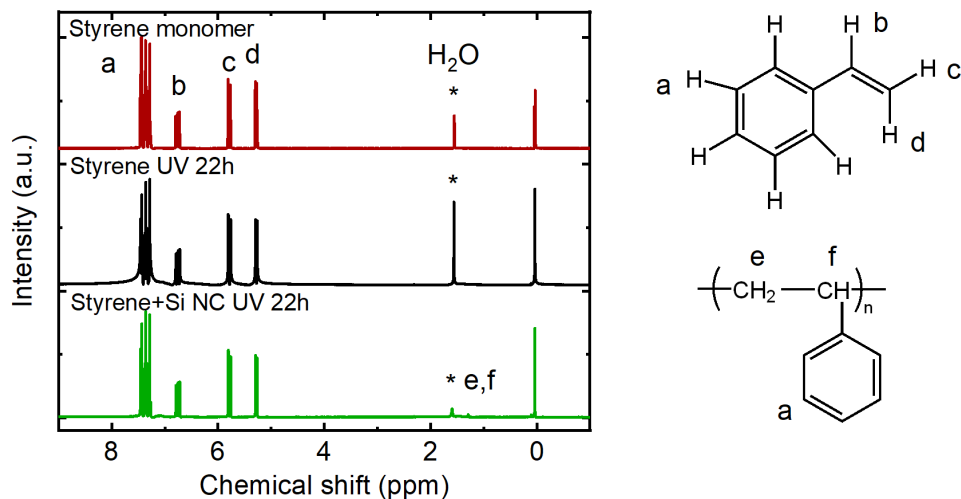


Figure 3.10: ^1H NMR spectra of styrene monomer, styrene after 400 nm irradiation for 22 hours, and Si NC/styrene mixture after 400 nm irradiation for 22 hours.

3.4 Solvent-less LSC fabrication

Si NC accelerated UV polymerization. For solvent-less fabrication of LSCs, we first disperse hexanol-capped Si NCs in styrene monomer and use UV irradiation (400 nm) to activate their PL. As shown in Figure 3.9, a PLQY of 40% is reached when Si NCs are dispersed in styrene and UV-irradiated for 24 hours. Meanwhile, we notice that the Si NC/styrene solution became viscous, indicating that the monomer is undergoing polymerization. While styrene is known to undergo self-polymerization at room temperature through a Diels-Alder type of reaction without an additional initiator,¹⁰² the presence of Si NCs greatly accelerates the polymerization reaction. After 22 hours of UV irradiation, only the styrene + Si NC mixture becomes apparently viscous, while the styrene reference group looks similar to the naked eye. Similar NC-accelerated polymerization has been observed in the photocuring of acrylate systems with silica nanoparticles, where silica nanoparticles accelerate the UV curing of acrylate due to synergistic effect.¹¹⁵

NMR characterization (Figure 3.10) confirms this difference in the degree of polymerization with or without the Si NCs. After UV irradiation for 22 hours, a peak at ~ 1.6

Table 3.2: PLQY values of Si NC/polymer composites

method	polymer	PLQY, as-produced	PLQY, 24 hours in air
UV polymerization	PS	40%	13%
	PS-PMMA	39%	10%
thermal polymerization	PS	44%	28%
	PS-PMMA	46%	39%

ppm emerges in the Si NC + styrene sample, which corresponds to aliphatic hydrogens and indicates the polymerization of styrene monomers. The monomer conversion fraction is estimated to be $\sim 10\%$ by comparing the area ratios corresponding to the aliphatic and aromatic protons. This monomer conversion fraction allows for the convenient fabrication of thick polymer films via doctor-blading.¹⁰³

Thermal polymerization. Besides UV-initiated polymerization, styrene can undergo thermal polymerization at elevated temperatures of 200–230 °C, even without thermal initiators.¹⁰² Previous experiments have shown that PLQY of gas-phase functionalized Si NCs can be enhanced via heating to ~ 160 °C.^{71,108} Therefore, the Si NCs are expected to have 40–50% PLQY after thermally initiated polymerization.

Fabrication of nanocomposites and their PLQYs. The fabrication process using either UV polymerization or thermal polymerization is described in Figure 3.11. In both methods, visibly clear Si NC/PS nanocomposites with low NC agglomeration and high visible transmission are fabricated. As polystyrene has relatively weak mechanical strength, we also study the PLQY properties of Si NC/PS as well as Si NC/PS-PMMA nanocomposites. For PS-PMMA polymer fabrication, a monomer volume ratio of styrene: methyl methacrylate (MMA) = 1 : 1 is used. Unfortunately, the addition of MMA during thermal polymerization leads to a hazy polymer. The polymerization conditions need to be further optimized to synthesize high-quality copolymers with low haze. The PLQY values of as-synthesized Si NC/PS and Si NC/PS-PMMA nanocomposites are summarized in Table 3.2. For both UV and thermal polymerization, PLQY of Si NCs in the nanocomposite are consistent with the values measured in styrene monomer. However,

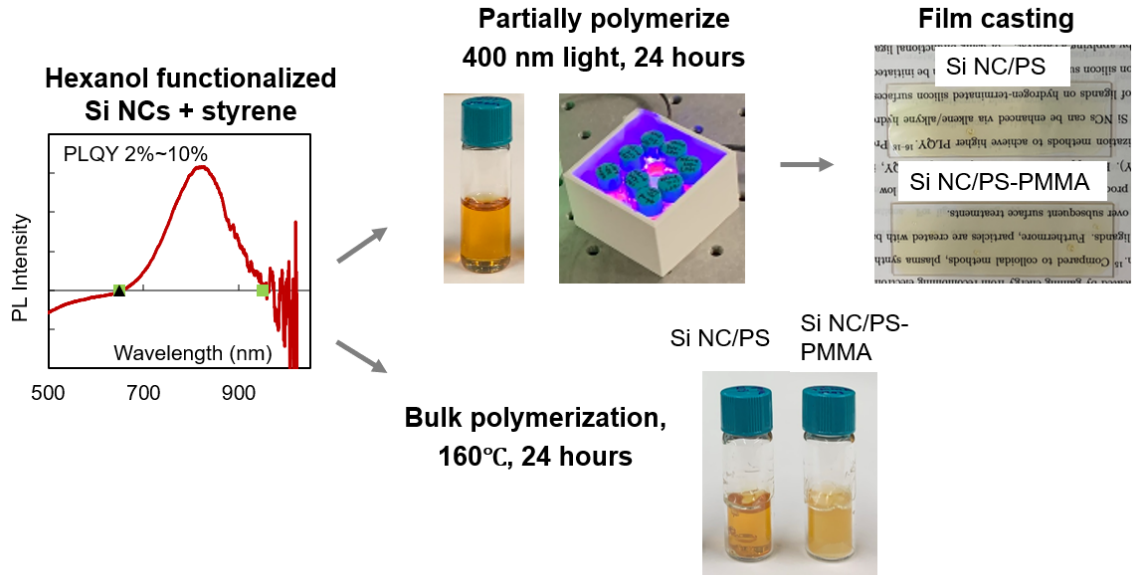


Figure 3.11: Schematic of the LSC fabrication process by UV polymerization and thermal polymerization.

the PLQY drops drastically after 24-hour exposure to air in the UV-polymerized samples.

There are two main differences in the UV and thermal polymerized Si NC/polystyrene nanocomposites that may lead to their different air stabilities. First, in the UV polymerized samples, styrene is only partially polymerized to form a prepolymer solution, which is subsequently used for film casting, while in thermal polymerization, styrene is more completely polymerized to yield solid bulk polystyrene. Upon air exposure, the remaining styrene in the partially polymerized samples may continue to polymerize through a radical-based mechanism in the presence of oxygen.¹¹⁶ The generated radical species in the partially UV-polymerized samples may contribute to the PL quenching of Si NCs. Second, as the heating temperature for thermal polymerization (200 °C) is high enough for SiH₃ desorption, the Si NCs prepared by two methods have different SiH_x compositions. As the SiH₃ species are weakly bonded to the Si surfaces, they may be more susceptible to oxidation.

To verify whether the UV-treated and heat-treated Si NCs have different air stabilities, we performed the experiment by comparing the PLQY of Si NCs in the air before and

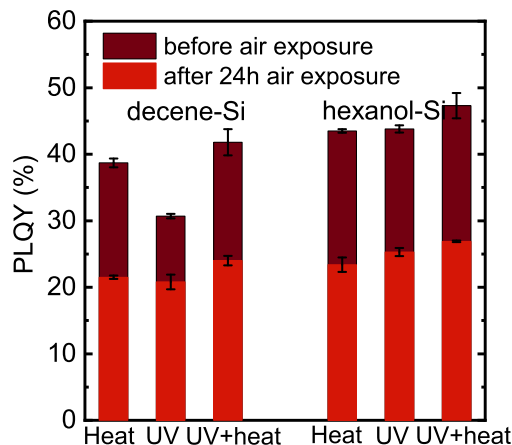


Figure 3.12: Air stability of 1-decene/1-hexanol grafted Si NCs after the treatment of 24h 400nm irradiation, 18h 160 °C heating, or 24h 400nm irradiation + 18h 160 °C heating, respectively.

after UV, heat, or UV+heat treatments, all in the form of a toluene solution. As shown in Figure 3.12, all these samples exhibit similar PLQY reduction after 24 hours of air exposure. Therefore, it can be concluded that the use of partially polymerized styrene may be detrimental to the air stability of Si NCs. Unless the air stability of Si NCs can be improved through other surface passivation methods, thermal polymerization of styrene into bulk polymer slabs is the preferred method for LSC fabrication.

3.5 Discussion and future work

PLQY enhancement mechanism. The PLQY of Si NCs functionalized with 1-hexanol and 1-octylamine can reach 40–50% after UV or room light irradiation, which is among the highest reported values of Si NC PLQY. However, the mechanism leading to the PLQY enhancement is still not fully understood. Contrary to our previous hypothesis that a high PLQY can only be achieved with the desorption of SiH_3 , our results indicate that other mechanisms may play a more important role. Time-resolved PL measurements indicate that the PLQY enhancement is possibly related to the reduction of NCs in “dark”

states. Understanding the origin of this “dark” NC reduction by characterizing NC charges or exploring the PL blinking behavior at high illumination intensity should be a topic of future studies.

LSC fabrication. Prototypes of LSC consisting of Si NC/polystyrene nanocomposites have been fabricated using either UV-mediated polymerization or thermal polymerization. Homogeneous nanocomposites can be produced with both methods while maintaining Si NCs’ high PLQY of around 40% before air exposure. The UV-mediated polymerization method has the advantage that additional heating is not required. However, the partially polymerized styrene accelerates the drop of Si NC PLQY after air exposure. While thermal polymerization avoids this problem due to a higher degree of polymerization, initial attempts to thermally polymerize styrene/MMA without any thermal initiators lead to high haze polymers. In the future, the thermal polymerization conditions, including temperature, pressure, and thermal initiators, need to be optimized to fabricate highly transparent Si NC/PS-PMMA nanocomposites. Alternatively, Si NC/PS-PMMA nanocomposites slabs with a high degree of polymerization may also be fabricated by UV polymerization using a UV initiator.

3.6 Conclusions

In this work, we demonstrate the fabrication of luminescent solar concentrator devices based on gas-phase functionalized Si NCs. Owing to the gas-phase ligand grafting, the as-produced silicon nanocrystals are readily dispersible in styrene monomers. This NC/monomer mixture can be directly used for subsequent polymerization, thus eliminating the need for excess solvents. The uniform dispersion of silicon nanocrystals in nonpolar solvents allows for the fabrication of homogeneous and low light scattering nanocomposites. This cost-effective method with green chemistries is a step forward towards practical uses of Si NC-based LSCs.

3.7 Experimental methods

Si NC synthesis. For Si NC synthesis, the reactor setup is similar to the one shown in Figure 2.1 without the use of the furnace. 14 sccm of silane (5% in helium) and 30 sccm of argon were flown through the reactor inlet. For ligand injection, 100 sccm of hydrogen as the carrier gas was flown through the bubbler containing 1-decene, 1-hexanol, 1-octylamine, and 1-hexenethiol. The bubbler pressure was kept at ~ 50 Torr.

Light irradiation. Light irradiation experiments were performed by placing the Si NC samples inside a custom-built chamber with UV/400 nm or red/633 nm LED strips as the light source. The light intensity was on the order of 0.5 mW/cm^2 measured by a powermeter.

Materials characterization. FTIR, PLQY, and TRPL measurements were performed using similar methods as described in Chapter 2.5. ^1H NMR measurements were performed with an AX-400 Bruker spectrometer. For Si NC characterization, ~ 5 mg Si NC were dissolved in 0.75 ml chloroform-d. For the determination of styrene monomer conversion fraction, 10 μl partially polymerized solution was dissolved in 0.75 ml chloroform-d. Sixteen scans were taken for each sample.

Chapter 4

Energy transfer in Si NC solids

4.1 Background

We have demonstrated in Chapter 2 and 3 that the PLQY of Si NCs from all-gas-phase approaches can be as high as $\sim 20\%$, or even $>40\%$ after light irradiation. Therefore, it is promising to integrate the gas-phase functionalization approach with previously developed gas-phase device fabrication methods, e.g., LEDs by Anthony *et al.*,⁷² to fabricate high-efficiency Si NC-based devices entirely in the gas phase. To achieve high-efficiency LEDs, high PLQYs of Si NCs in the form of gas-phase deposited nanocrystal films are necessary. However, we found that the gas-phase deposited Si NC films typically have lower PLQY values than Si NCs measured in toluene. Depending on the film density and the ligand length, the film PLQYs vary from $<2\%$ to $\sim 10\%$, while these Si NCs all have PLQYs of $\sim 20\%$ when dissolved in toluene. This PLQY drop in NC films is consistent with PL quenching due to inter-NC energy transfer, which has been commonly observed during LED fabrication using II-VI quantum dots.⁶⁴ Still, this phenomenon caught our attention because energy transfer in Si NCs is considered inefficient and rarely observed in ligand-functionalized Si NCs. Based on the above discussion, we decide to perform a thorough study on the energy transfer in Si NC solids.

4.2 Introduction

Understanding the charge and energy transfer processes in quantum dot (QD), or nanocrystal (NC) solids is essential for the design of high-performance optoelectronic devices. Controlling the exciton diffusion length and rates is crucial for achieving optimal device efficiency. For instance, effective exciton diffusion to the charge separating interface is desired in the design of solar cells.¹¹⁷ On the contrary, in light-emitting devices, exciton diffusion is unfavorable as the goal is for exciton to recombine radiatively to emit photons. Therefore, long-chain interparticle linkers are employed to prevent exciton migration to “dark” dots and minimize photoluminescence quenching.⁶⁴

PL quenching experiment is a common and effective strategy for probing energy transfer dynamics in NC solids. By placing acceptor NCs in the proximity of donor NCs, excitons can migrate to an acceptor NC.^{118,119} As a result, the PL intensity from the donor NC will be reduced and the exciton lifetime will decrease due to the extra non-radiative recombination channel.^{118,119} Optical techniques, including steady-state, time-resolved, temperature-dependent photoluminescence, transient absorption, or transient PL quenching, can all provide information regarding the energy transfer rate and efficiency from different perspectives.¹²⁰

The major mechanisms describing the energy transfer in NC solids include Förster, Dexter, and Tandem processes. Förster mechanism describes the resonant coupling between two point dipoles,¹²¹ whereas Dexter and Tandem mechanisms rely on the direct tunneling of electrons.^{122,123} For ligand-functionalized quantum dot solids, the energy transfer is mainly described with the Förster mechanism since there is no direct overlap of the wave functions between donors and acceptors due to the presence of long carbon chains. In the literature, several experimental studies have been conducted to validate the distance dependence of Förster mechanism in other nanocrystal systems, where inter-dot distances are varied by altering ligand lengths¹²⁴ or by constructing a bilayer structure.¹²⁵ For silicon nanocrystals, however, only a few experimental studies have been reported in the literature.^{126–128} The

lack of studies on silicon nanocrystals is partially due to the difficulty of synthesizing closely packed silicon quantum dots with sufficiently narrow size distribution and controlled interdot distances. Due to the nature of the indirect bandgap, the energy transfer is not efficient. Moreover, theoretical and computational work has shown that the Förster mechanism only applies when NCs are separated at relatively large distances.^{129,130} The dipolar transitions in Si nanocrystals are relatively weak due to the indirect gap, and multipole interactions play an important role when particles are in closer contact.

In this work, we prepare Si NCs surface-functionalized with a series of 1-alkenes with their lengths ranging from 8C to 18C. For each alkene length, Si NCs with two surface ligand coverages were synthesized using either solution-phase or gas-phase ligand grafting. Apparent differences of PL spectra and PL lifetime in Si NC films with varying ligand lengths and ligand coverages provide evidence for interparticle energy transfer. Through ReaxFF molecular dynamic simulations, we modeled the ligand packing structures on a spherical silicon nanoparticle to estimate the surface-to-surface spacing for each ligand length. By varying the ligand length and ligand coverage, we obtained the relationship of energy transfer rate as a function of interparticle distance. The results indicate that in Si NC films, the energy transfer rates as a function of donor-acceptor distances may exhibit a faster decay than predicted by the Förster mechanism.

4.3 Results and discussion

4.3.1 Evidence of energy transfer in Si NC solids

We prepared alkyl-terminated Si NCs with ligand lengths varying from 8C to 18C using thermal hydrosilylation. Briefly, a mixture of 1-octene, 1-decene, 1-dodecene, or 1-octadecene, 5 mg Si NCs and 1 ml mesitylene was heated to 160 °C for 96 hours. The number of ligands were calculated so that the ratio of ligand: Si NC surface sites = 1 : 2.5. After the hydrosilylation reaction, mesitylene was evaporated, and the functionalized Si NCs were redispersed in 0.5 ml toluene. 20 μ l of the Si NC/toluene solution were then drop-cast onto

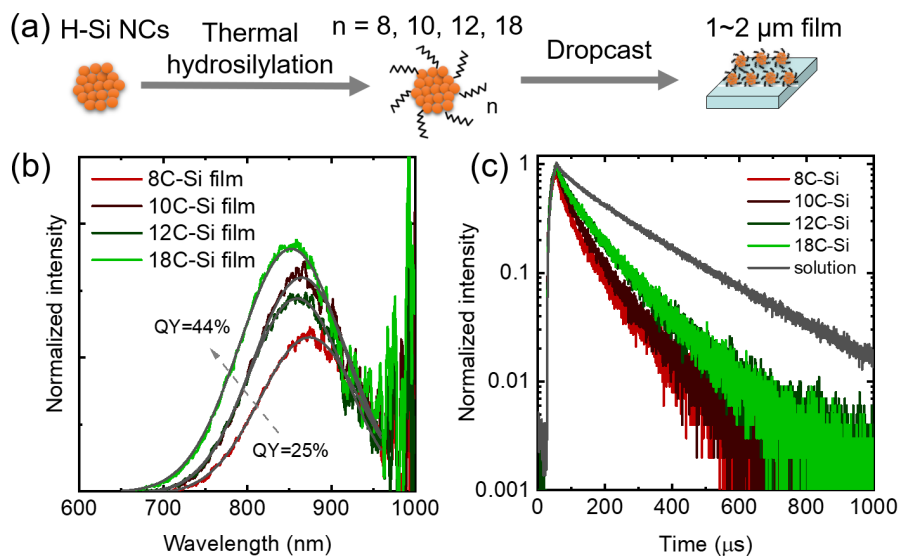


Figure 4.1: (a) Schematic of sample preparation for the energy transport study. (b) Steady-state PL spectra and (c) time-resolved PL decays from solution-phase functionalized Si NC films.

glass substrates to yield $1\sim 2\ \mu\text{m}$ of solid films (Figure 4.1a).

The Si NCs functionalized with different-length ligands exhibit the same PLQY and steady-state PL spectrum when measured in toluene. However, the PLQYs and PL spectra of Si NC films show a drastically different trend, as shown in Figure 4.1b. Films with short ligands (8C-Si) show lower PLQYs than films with longer ligands (18C-Si), consistent with the expected trend due to energy transfer to “dark” NCs. Specifically, for the longest ligand of 1-octadecene the maximum PLQY is about 44%, equaling that of the solution phase measurements. Along with the degradation of PLQY, the redshift of the PL spectrum is also observed as ligand length becomes shorter. Time-resolved PL decay confirms the trend of energy transfer (Figure 4.1c). The films exhibit faster decays than the solution samples, with decreasing lifetime as the ligand length becomes shorter.

Time-resolved PL spectra of Si NCs in the form of solution and films also exhibit different characteristics. For Si NCs dispersed in toluene where energy transfer is negligible, the emission exhibits an intrinsic redshift as delay time increases (Figure 4.2a). The intrinsic redshift is presumably due to the NC size distribution within the ensemble. As larger NCs

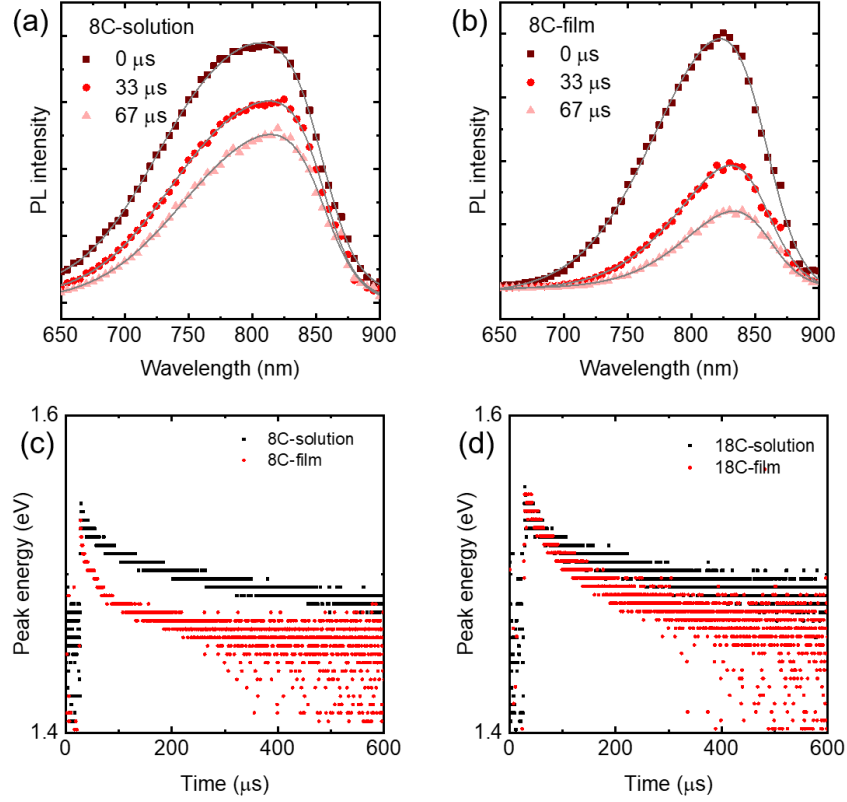


Figure 4.2: (a,b) Time-resolved PL spectra of 8C-Si NC films at 0, 33, and 67 μ s in the form of solution and film. The grey lines represent fitting results from an asymmetric double sigmoidal function. (c,d) Peak energies of time-resolved PL spectra of 8C-Si film/solution and 18C-Si film/solution plotted against time, exhibiting dynamic redshift.

with smaller emission energies exhibit faster decays, the detected PL at longer wavelengths is relatively weaker at longer delay times. In NC films, the time-resolved PL spectra exhibit a narrower linewidth compared to the solution-phase counterparts. The redshift becomes more pronounced as the delay time increases, with a rapid reduction in the time-resolved PL intensity. The redshift is an indication of exciton migration to larger NCs.¹¹⁹ By plotting the peak energies against delay time, we obtain the temporal evolution of PL peak energy, which exhibits a “dynamic redshift” (Figure 4.2c, d). As shown in Figure 4.2c and d, the 8C-Si film data exhibit a notably faster redshift, while the 18C-Si film differentiates little compared to the solution data. All these characteristics of time-resolved PL confirm that the energy transfer becomes more pronounced when ligand length decreases.

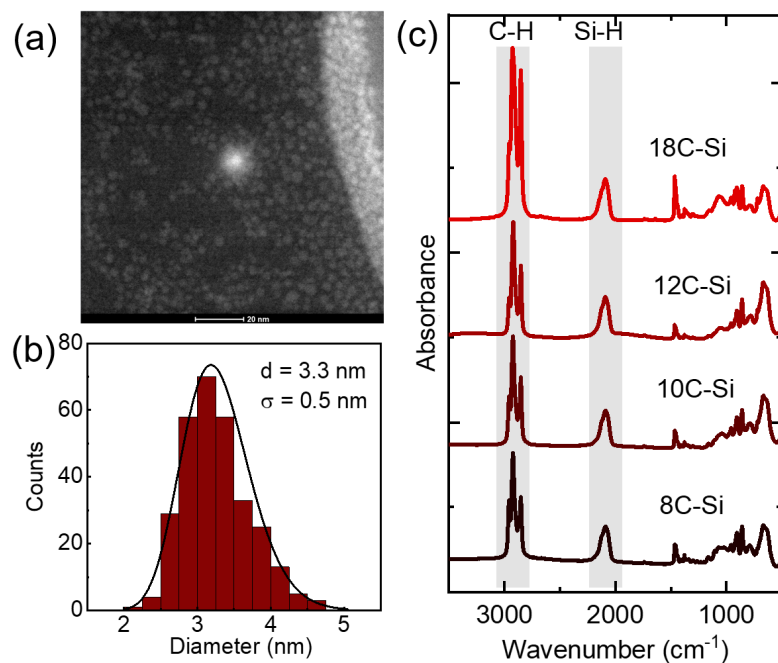


Figure 4.3: (a) HAADF TEM images of 1-octene functionalized Si NCs drop-cast from toluene. (b) Size distribution obtained from the TEM image. (c) FTIR characterization of Si NCs with varying ligand lengths.

The alkyl-functionalized Si NCs were characterized with TEM, FTIR, carbon hydrogen and nitrogen (CHN) elemental analysis, and DLS. Figure 4.3a and b show the dark field TEM image of 8C-Si NCs and the size distribution obtained from TEM. The average diameter obtained from TEM images is 3.3 nm with a standard deviation of 0.5 nm. The size distribution shown in Figure 4.3b reflects the Si NC core size since the surface ligands dissociate drastically under beam irradiation. The size distribution also agrees with the size from XRD measurements and previous work by our group.⁶³ FTIR measurements confirm that the CH_x/SiH_x area ratios increase with increasing ligand length. The surface ligand coverages are determined by elemental analysis, and the values are listed in Table 4.1. The surface ligand coverages are all around 40%, which agrees with the 1 : 2.5 ligand-to-surface site ratio used for functionalization. The solvodynamic diameters in toluene are all around 10 nm, indicating that the nanoparticles are nearly singly-dispersed, and the NC films are expected to be free of agglomerates.

Table 4.1: Surface ligand coverages and solvodynamic diameters of solution-phase and gas-phase functionalized Si NCs

	solution functionalization		gas-phase functionalization	
	surface coverage	solvodynamic diameter	surface coverage	solvodynamic diameter
8C	37%	9.6 nm	25%	7.1 nm
10C	38%	10.5 nm	23%	8.1 nm
12C	37%	9.5 nm	26%	8.0 nm
18C	44%	11.9 nm	28%	8.9 nm

We also synthesized samples using the gas-phase functionalization method with the same ligand series. For each ligand length, the bubbler pressure and temperature were carefully selected to ensure similar surface ligand coverages. As indicated in Table 4.1, the gas-phase ligand grafting method leads to surface ligand coverages of around 25% for each ligand. Even though the ligand coverages are lower than those from solution-phase functionalization, the resulting solvodynamic diameters also indicate good dispersibility before film deposition. It is noteworthy that the solvodynamic diameters of solution-phase functionalized Si NCs are slightly larger than the gas-phase functionalized Si NCs, presumably due to larger viscous drag in Si NCs with higher surface ligand coverages.

Similar to the solution-phase functionalized samples, the gas-phase functionalized Si NCs were drop-cast into films for time-resolved PL measurements. Prior to film deposition, the gas-phase functionalized Si NCs were refluxed in mesitylene for 4 hours to ensure that their PLQYs are similar to the solution-phase functionalized samples (Figure 4.4a). The PL decay curves exhibit similar trends to the solution-phase functionalized samples, with the shorter ligand film exhibiting faster decay. Moreover, for each ligand length, the decay lifetimes in gas-phase functionalized samples are shorter than their solution-phase functionalized counterparts, indicating more efficient energy transfer due to lower surface ligand coverages.

4.3.2 Analysis of PL decay

Fitting of the decay curve. The decay curves from Si NCs exhibit a stretched-exponential behavior due to the dispersion of decay rates. Specifically, for NC films, the

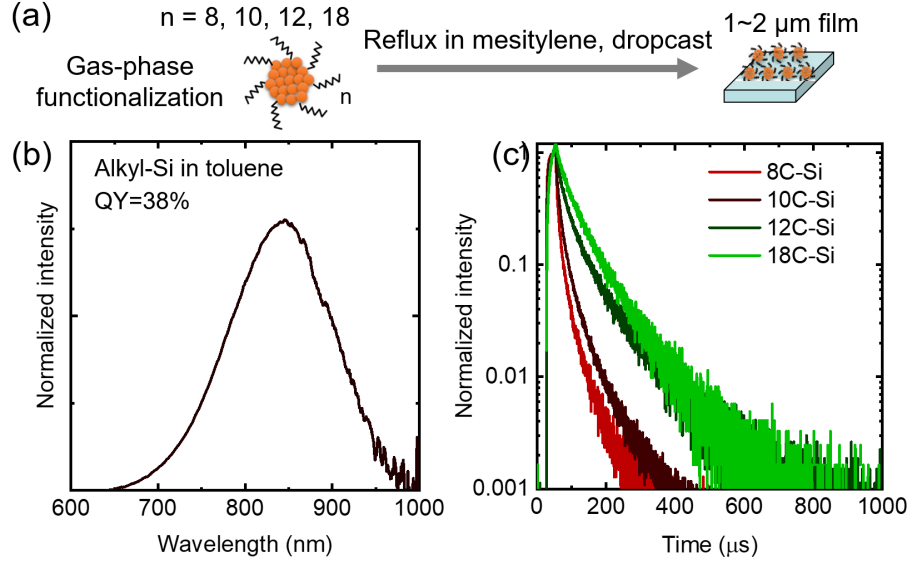


Figure 4.4: (a) Schematic of sample preparation of gas-phase functionalized Si NCs for the energy transfer study. (b) Steady-state PL spectra of gas-phase functionalized Si NCs measured in toluene. (c) Time-resolved PL decays from gas-phase functionalized Si NC films.

decay-rate dispersion results from both the distribution of intrinsic radiative and nonradiative decay rates of individual NCs and the variation of energy transfer rates. As discussed in Section 1.2, the decay curve can be fitted with a stretched-exponential function:

$$I(t) = I_0 \exp(-(t/\tau_0)^\beta), \quad (4.1)$$

where I_0 is the intensity at $t = 0$, τ_0 is the time constant, and β ($0 < \beta < 1$) is the dispersion factor. A stretched exponential decay can be viewed as the weighted average of single exponential decays with continuously varying decay lifetimes:

$$\exp\left[-\left(\frac{t}{\tau_0}\right)^\beta\right] = \int_0^\infty \exp\left(-\frac{t}{\tau}\right) \rho(\tau) d\tau, \quad (4.2)$$

where $\rho(\tau)$ is the distribution function of single decay lifetime. However, the expression $\rho(\tau)$ for a given set of τ_0 and β is not trivial. To explicitly obtain the distribution of decay rates, we adapt the method by van Driel *et al.*²⁰ and fit the decay curve assuming a continuous

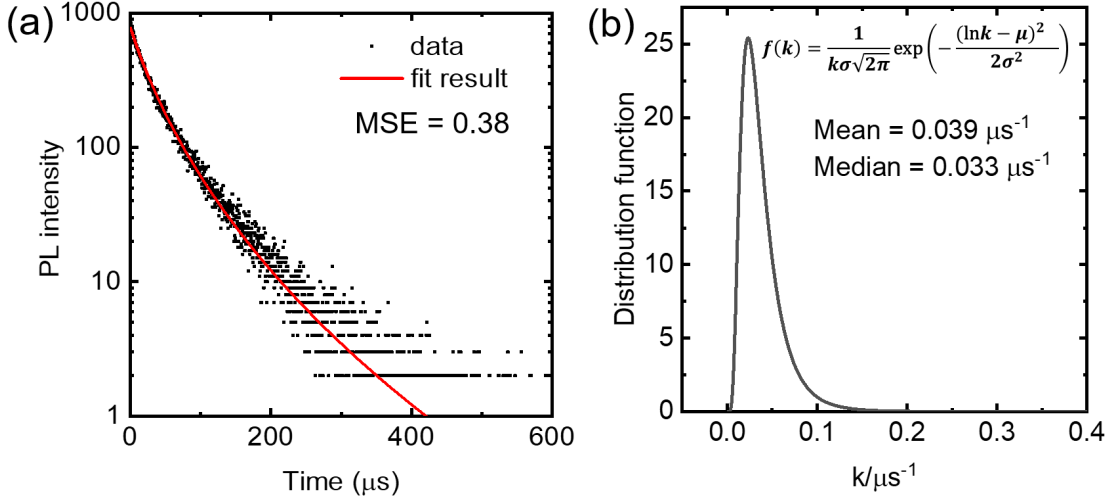


Figure 4.5: Fitting of the PL decay of solution-functionalized 8C-Si film. (a) Original data and the fit result assuming a lognormal distribution of total recombination rate k_{tot} . (b) The distribution of k_{tot} obtained from the fitting.

distribution $\sigma(k_{tot})$ of total decay rates $\bar{k}_{tot}$. The decay curve thus has the following form:

$$f(t) = \int_0^\infty \sigma(k_{tot}) \exp(-k_{tot}t) dk_{tot}, \quad (4.3)$$

with the distribution of $\bar{k}_{tot}$ following a lognormal distribution:

$$\sigma(k_{tot}) = \frac{1}{k_{tot}\sigma\sqrt{2\pi}} \exp\left(-\frac{(\ln k_{tot} - \mu)^2}{2\sigma^2}\right), \quad (4.4)$$

where σ and μ are parameters to be determined. Figure 4.5 demonstrates the fitting of solution functionalized 8C-Si film. As is shown in Figure 4.5a, this method fits our experimental data well with a mean squared error (MSE) of 0.38. Figure 4.5b plots the distribution of $\bar{k}_{tot}$ obtained from the fitting, with $\mu = -3.4$ and $\sigma = 0.57$. The average total decay rate $\bar{k}_{tot}$, or the arithmetic mean of $\bar{k}_{tot}$, can thus be deduced:

$$\bar{k}_{tot} = \exp\left(\mu + \frac{\sigma^2}{2}\right) = 0.039 \mu s^{-1}. \quad (4.5)$$

The $\bar{k}_{tot}$ values will later be used for the calculation of the average ET rate $\bar{k}_{ET}$.

The effect of dielectric environment. It is well known that the local dielectric environment of an emitter can affect its emission properties significantly. The radiative transition probability γ_r is governed by Fermi's golden rule¹³¹:

$$\gamma_r = \frac{2\pi}{\hbar} \rho(\hbar\omega) |M|^2, \quad (4.6)$$

where $\rho(\hbar\omega)$ is the density of states (DOS) at the final state with frequency ω , which can be modified by the dielectric medium and is thus a function of the refractive index n and M is the matrix element of the Hamiltonian between the final and initial states.

Different theoretical models have been developed to predict the radiative recombination rate for emitters embedded in an environment with a refractive index n . The most prominent models include virtual cavity model (VC), empty cavity model (EC), and fully microscopic model (FM). The expressions of the radiative recombination rate k_r as a function of refractive index n and vacuum radiative rate k_{r0} are

$$k_r = \left(\frac{\bar{n}^2 + 2}{3} \right)^2 \bar{n} k_{r0}, \quad (4.7)$$

$$k_r = \left(\frac{3\bar{n}^2}{2\bar{n}^2 + 1} \right)^2 \bar{n} k_{r0}, \quad (4.8)$$

$$k_r = \left(\frac{\bar{n}^2 + 2}{3} \right) k_{r0}, \quad (4.9)$$

for VC, EC, and FM models, respectively.¹³²

In the literature, a few experimental studies have been conducted in CdSe and CdSe/ZnS NC systems to test these theories.^{132–134} While the FM model agrees well with the experimental data in some studies,¹³³ the VC model is more successful for others.^{132,134} In these studies, NCs with near-unity quantum efficiency are the perfect candidates to eliminate complications arising from changes in nonradiative recombination rates. In this case, the radiative recombination rate k_r is equal to the measured total recombination rate $\bar{k}_{tot}$, since

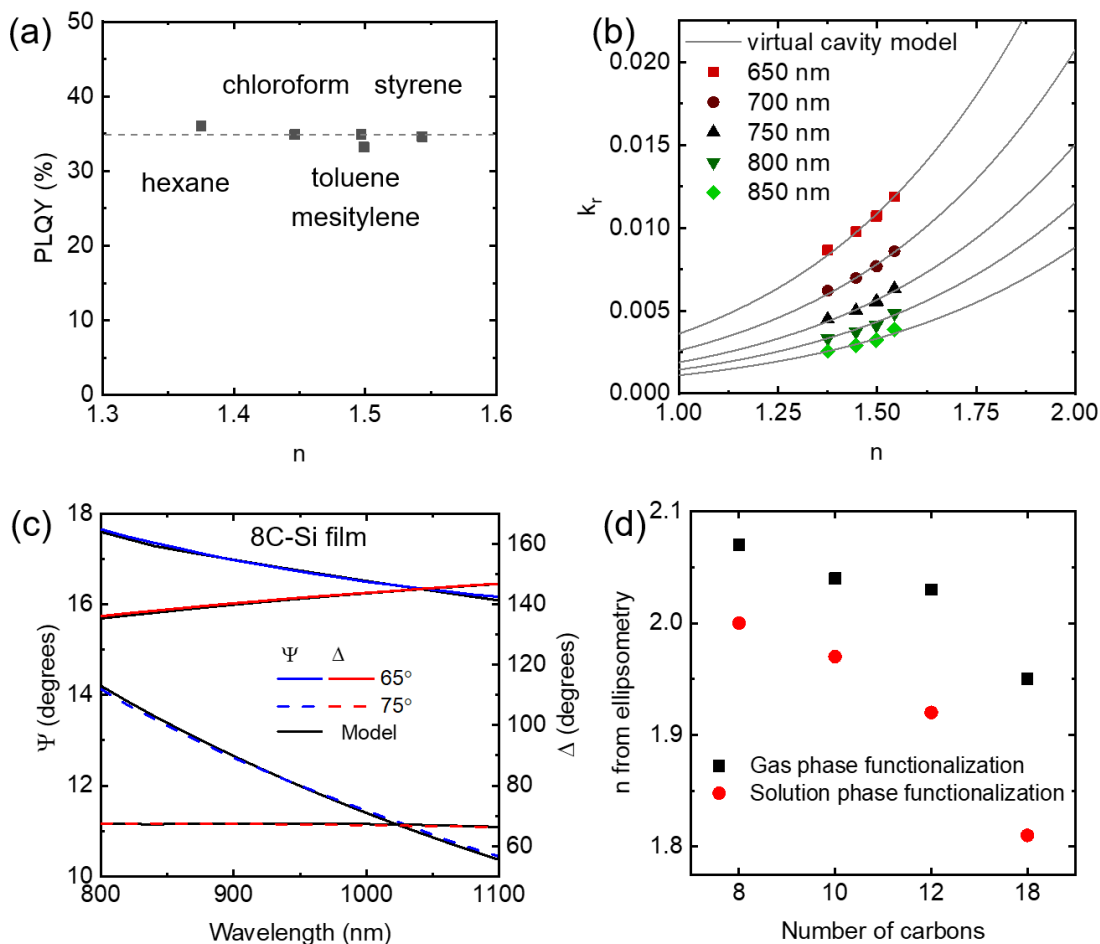


Figure 4.6: (a) PLQY of Si NCs dispersed in solvents spanning a range of refractive indices n . (b) Experimentally measured average k_r as a function of n and the predictions from the virtual cavity model. (c) Ellipsometry measurement of 8C-Si film with the data fitted assuming a Cauchy layer. (d) Refractive indices of nanocrystal films obtained by ellipsometry.

“bright” NCs with no nonradiative recombination pathways dominate the measured PL. According to previous studies pointing out that Si NCs with $\sim 50\%$ QY are likely to have near-unity quantum efficiency,^{18,135} similar experiments can be performed for Si NCs.

To establish a relationship between the radiative recombination rate of Si NCs and the local refractive index, we measured the PL lifetime of Si NCs dispersed in solvents spanning a range of refractive indices. The solvents where Si NCs all form a clear and uniform solution and have refractive indices ranging from 1.375 (hexane) to 1.516 (styrene). The measured PLQY of Si NCs in these solvents are all around 35% (Figure 4.6a). As the PL emission of Si NCs features a broad spectrum, the PL lifetime is measured across the PL spectrum at detector wavelengths of 650, 700, 750, 800, and 850 nm. As shown in Figure 4.6b, the VC model well describes the experimental data, while the other models underestimate the influence of the refractive index.

As Si NCs in the form of solutions and films are expected to have different dielectric environments, the influence of the refractive index needs to be taken into consideration when calculating ET rates based on solution and film recombination rates. Therefore, we experimentally measure the refractive indices of the NC films with ellipsometry. For ellipsometry measurements, Si NCs dissolved in toluene at ~ 20 mg/ml are spin-cast onto silicon substrates at 600 rpm. As shown in Figure 4.6c, modeling the 8C-Si film using a Cauchy layer provides good fits, with $n = 2.08$ and film thickness of 39 nm. Figure 4.6d shows the measured refractive indices of the solution-phase and gas-phase functionalized nanoparticle films. A decrease in measured refractive index with increasing ligand length is observed in both series of samples.

Energy transfer rates. Assuming the measured PL is dominated by “bright” NCs showing radiative recombination in both the solutions and films, the total recombination rate measured in solution $k_{tot,s}$ can be written as

$$k_{tot,s} = k_{rad,s}, \quad (4.10)$$

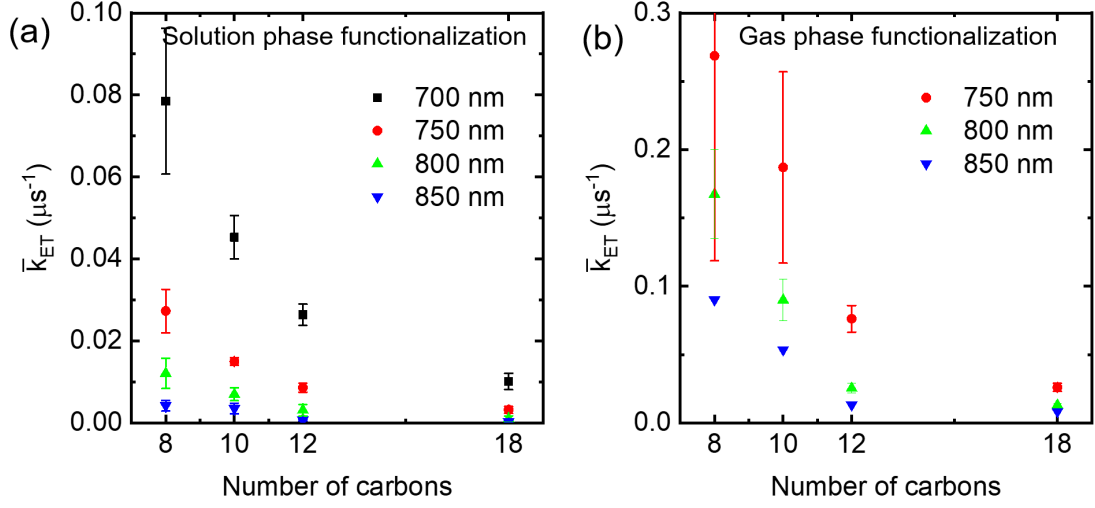


Figure 4.7: Experimentally measured average ET rates $\bar{k}_{ET}$ in (a) solution-phase functionalized Si NC films and (b) gas-phase functionalized Si NC films.

and the total recombination rate in film $k_{tot,f}$ will be

$$k_{tot,f} = k_{rad,f} + k_{ET}, \quad (4.11)$$

where $k_{tot,f}$ can be calculated based on $k_{tot,s}$ and the measured refractive indices through Equation 4.7. Within an ensemble, $k_{tot,s}$ and $k_{tot,f}$ are assumed to follow lognormal distributions described Equation 4.4. Therefore, we fit the solution and film PL decay curves to obtain the distribution and then calculate their average values according to Equation 4.5 to substitute into Equation 4.11.

In Figure 4.7a and b, the calculated average ET rates, $\bar{k}_{ET}$, are plotted as a function of alkyl chain length for solution-phase and gas-phase functionalized samples, respectively. For each sample series, $\bar{k}_{ET}$ over a few detector wavelengths are measured, corresponding to the ET rates of donors emitting at these wavelengths. For each ligand length, the measured ET rates increase with decreasing wavelengths, as exciton in smaller NCs has a higher probability of transferring energy to nearby larger NCs with smaller bandgaps. At each wavelength, the ET rates decrease as the ligand lengths increase due to the larger interdot

separation by the alkyl chains.

4.3.3 Ligand packing of alkane-grafted Si NCs

To establish a relationship between the average ET rate $\bar{k}_{ET}$ and the donor-acceptor distance, measuring inter-NC distances at each alkyl chain length is necessary. However, it is difficult to directly measure the inter-NC distance in TEM due to the dissociation of ligands under electron beam irradiation. Therefore, we perform ReaxFF molecular dynamics simulation with parameters developed in ref. 136 and the LAMMPS software package¹³⁷ to simulate the ligand packing structure and to extract the particle surface distances for each ligand length.

A schematic of the simulation process for generating a ligand-grafted Si NC surface is summarized in Figure 4.8a. We used a Si NC with partial hydrogen termination as the starting configuration and deposited ligands successively to take into consideration the effect of steric hindrance. The Si NC was modeled to be a 3.2 nm diameter half-sphere consisting of 523 silicon atoms. The surface silicon atoms were passivated by a layer of 152 surface H atoms, corresponding to a 60% hydrogen surface coverage. For ligand deposition, 1-radicals of octane, decane, dodecane, and octadecane were placed adjacent to the Si surface with a random position. Microcanonical ensemble (NVE) MD simulation was performed for 10 ps to simulate the gas-phase grafting (1 ps to simulate the solution-phase grafting). The resulting structure was then either accepted or rejected depending on whether or not the deposition was successful. After each cycle, the next radical was randomly deposited. The above process was repeated until the desired surface coverage was reached. 11 and 17 ligands were deposited on a 5.5 nm² spherical cap to represent the coverages of 25% and 40%, corresponding to ligand densities of 2 and 3.2 ligands/nm² for gas-phase and solution-phase functionalization, respectively. The ligand-grafted structures were equilibrated at 300 K for 500 ps. A Berendsen thermostat was used with a 0.1 fs timestep and temperature-damping factor of 10 ps to simulate the gas-phase grafting (0.01 ps to simulate the solution-phase grafting).

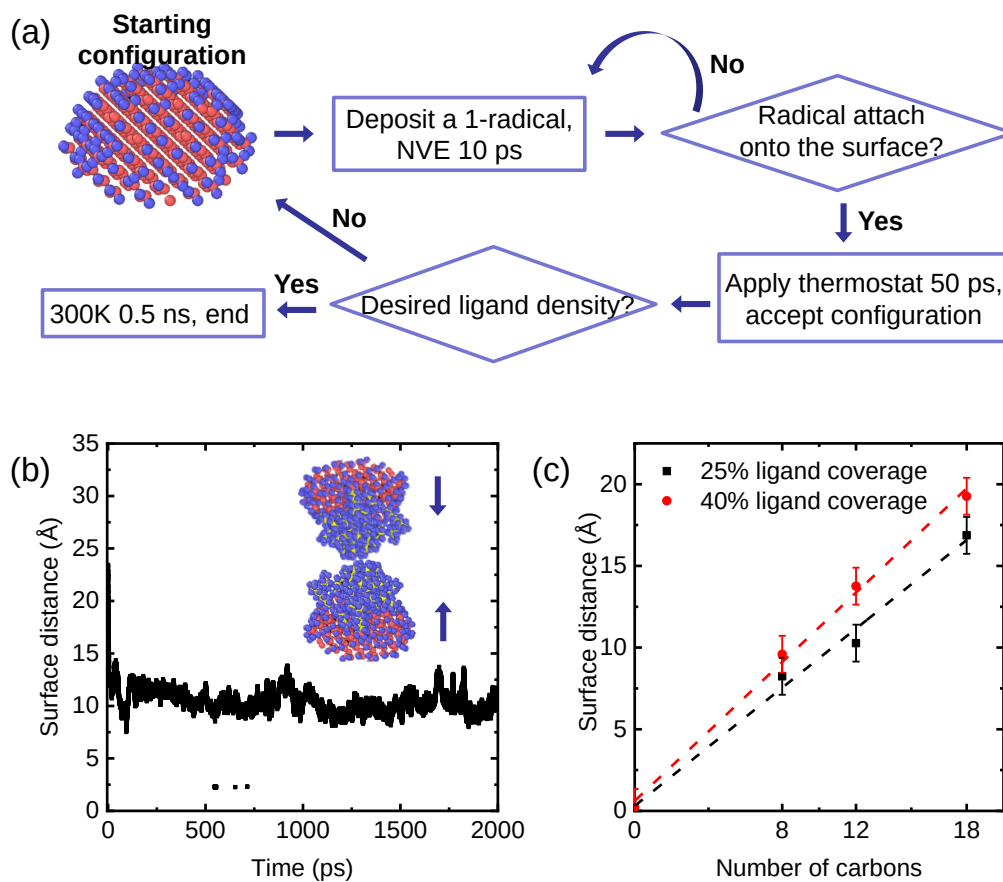


Figure 4.8: MD simulation for ligand packing structure. (a) Flowchart of the MD simulation for generating the ligand-covered nanoparticle structure. (b) The evolution of distance *vs* time for 12C-Si with 25% surface coverage. (c) Simulated surface distance *vs* alkyl chain length. The error bars indicate the standard deviation of surface distances.

To simulate the surface distance separated by each ligand, we used two ligand-grafted surfaces with initial velocities facing towards each other. The MD simulations were performed for 500 ps with the temperatures controlled by a Berendsen thermostat. For each ligand length, the last 200 ps was used for surface distance estimation.

As shown in Figure 4.8b, the surface distances first drastically decrease due to the opposite movement and then oscillate around an average value. The average distances for 8C, 12C, 18C ligands with 25% or 40% ligand coverages are plotted in Figure 4.8c. For each surface ligand coverage, the average surface distances roughly follow a linear relationship as a function of ligand length. The ligand tilting angles calculated from Figure 4.8c are 22° and 29° for 25% or 40% ligand coverage, respectively. These tilting angles appear to be very small due to the interlacing between ligands when two ligand-terminated surfaces interact with each other.

4.3.4 Distance-dependent energy transfer rates

By combining the results in Section 4.3.2 and 4.3.3, we obtain the relationship between ET rate and donor-acceptor distances. To model the scattered size distribution of donor-acceptor distances within the Si NC ensemble, the donor-acceptor distance is estimated using a linear relationship $R = x + \bar{d}/2$, where x is the sum of donor radius (1.6 nm for 800 nm emitting Si NCs) and surface spacing obtained in Section 4.3.3 and is dependent on ligand length. To compare the distance dependence with the Förster formulation, we compare $\bar{k}_{ET} \cdot n^4$ and donor-acceptor distance $R = x + \bar{d}/2$ on a log scale (Figure 4.9). The expression for the Förster radius R_0 is given by

$$R_0^6 = \frac{9\eta_{PL}\kappa^2}{128\pi^5n^4} \int \lambda^4 F_D(\lambda) \sigma_A(\lambda) d\lambda, \quad (4.12)$$

where η_{PL} is the quantum efficiency of the donor, κ is the dipole orientation factor between donor and acceptor and typically assumed to be 2/3 for randomly oriented dipoles, n is the refractive index of the sample, $F_D(\lambda)$ is the normalized donor PL, and $\sigma_A(\lambda)$ is the

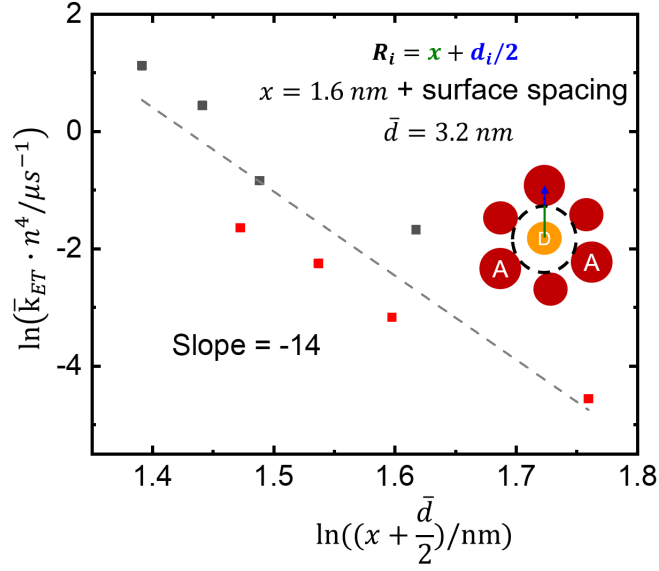


Figure 4.9: The product of average ET rate $\bar{k}_{ET}$ and the fourth power of refractive index n plotted as a function of average donor-acceptor distance for both gas-phase and solution-phase functionalized Si NCs.

acceptor absorption coefficient. According to the Förster expression, $k_{ET} = 1/\tau_D \cdot (R_0/R)^6$, where τ_D is the donor lifetime and R is the donor-acceptor separation, the product of k_{ET} and n^4 should be proportional to R^{-6} for a given sample. However, applying a linear fit in Figure 4.9 yields a slope of -14, indicating deviation from the Förster expression.

Typically, NC films consisting of monodispersed particles are considered as ideal candidates for energy transport studies. For interacting NCs with an identical size, the donor-acceptor distance will simply be the NC diameter. As our Si NC sample consists of a distribution of NC sizes, deviation from the inverse sixth-power distance dependence may arise. Therefore, we generalize the traditional Förster formulation and take into consideration the NC size distribution. The main assumptions are as follows:

- For each donor, the number of nearest acceptors N is a fixed number regardless of ligand length.
- The donor-acceptor distance R_i for a donor with each adjacent acceptor is described by $R_i = x + d_i/2$, where x is the sum of donor radius and NC surface distance and is

thus a function of ligand length, and d is the diameter of the acceptor.

- The diameter d is described by a distribution $f(d)$ with a mean value $\bar{d}$.
- The total energy transfer rate measured for the donor k_{ET} is the sum of ET rates of each possible acceptors $k_{ET,i}$. According to the traditional Förster formulation, each $k_{ET,i}$ has the same expression $k_{ET,i} = (R_0/R_i)^6/\tau_D$, where R_0 is the Förster radius and τ_D is the donor lifetime. Because of the expected $1/d^6$ scaling, only the nearest neighbors have substantial contributions, and thus $k_{ET} = \sum_{i=1}^N k_{ET,i}$.

Based on the above assumptions, k_{ET} is a function of d with a known distribution $f(d)$, with its mean value $\bar{k}_{ET}$ calculated by

$$\bar{k}_{ET} = \sum_{i=1}^N \bar{k}_{ET,i} = N\bar{k}_{ET,i}, \quad (4.13)$$

with

$$\bar{k}_{ET,i} = \int_{-\infty}^{\infty} \left(\frac{R_0}{x + d/2} \right)^6 \cdot \frac{1}{\tau_D} f(d) dd. \quad (4.14)$$

The integral in Equation 4.14 does not have an analytical solution. To verify the deviation from the traditional Förster expression due to the influence of NC diameter distribution $f(d)$, we plot the numerically calculated values of $\ln \bar{k}_{ET}$ vs $\ln(2x + \bar{d})$. Assuming constant R_0 and τ_D and a normal distribution of d ($f(d) \sim \mathcal{N}(\mu, \sigma^2)$), the calculated values are plotted in Figure 4.10, with $\mu = 2$, $\sigma = 0.1, 0.75$, and 5 . For $\sigma = 0.1$ representing a narrow distribution of d , the slope of $\ln \bar{k}_{ET}$ versus $\ln(2x + \bar{d})$ approaches -6, which is the limit of a uniform size sample described by the Förster model. As σ increases, corresponding to broader size distribution, the slope gradually deviates from -6. It is noteworthy that for typical size distributions, represented by the $\sigma = 0.75$ case, the deviation of slope shown in Figure 4.10b from -6 is not significant. In other words, the relationship between average ET rate and average NC distance can be roughly described with $\bar{k}_{ET} \propto 1/(2x + \bar{d})^6$, even in a non-size-purified NC sample if the energy transfer process follows the Förster model.

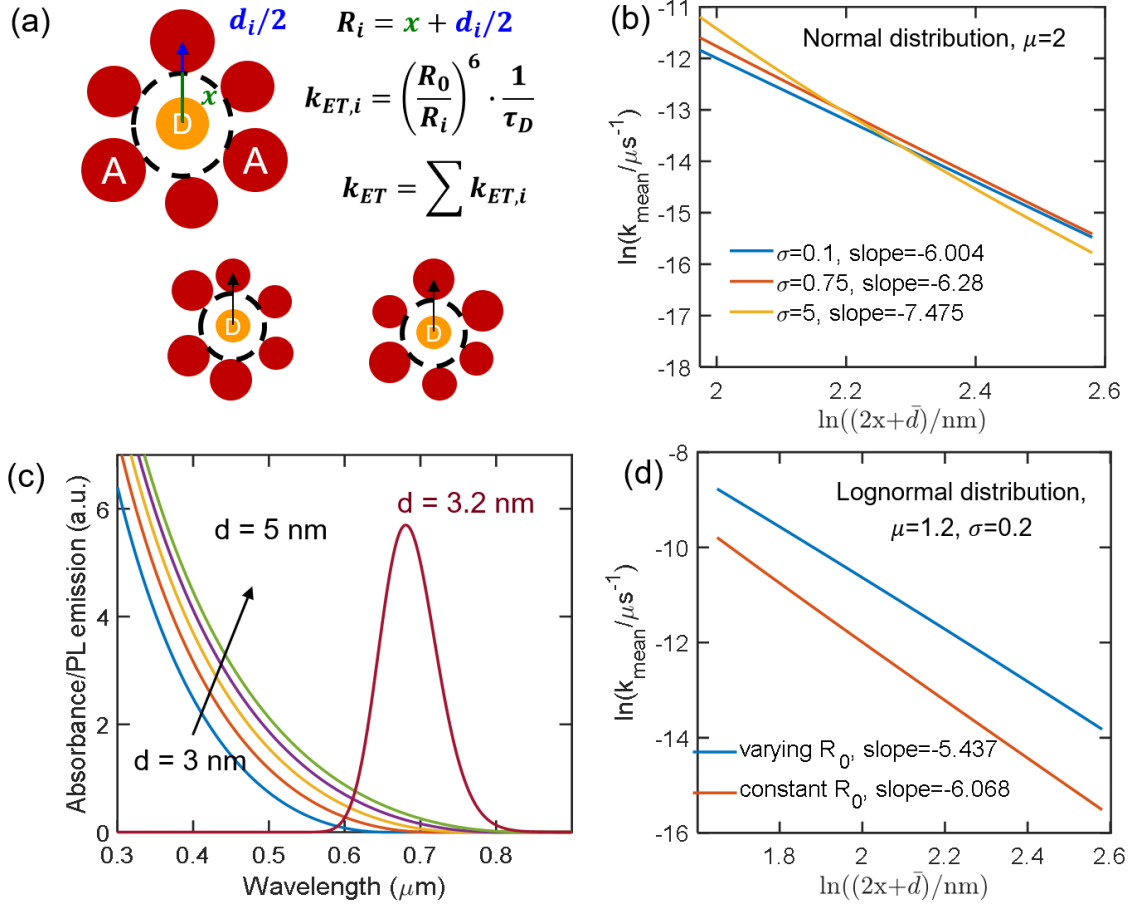


Figure 4.10: Influence of particle size distribution on the traditional Förster formulation. (a) Schematic of the distances considered in the Förster model. (b) Modified relationship between mean ET rate and average donor-acceptor distance $\ln(2x + \bar{d})$ assuming three NC size distributions. (c) Modeled donor emission spectrum corresponding to 3.2 nm diameter NP and acceptor absorption coefficients corresponding to 3–5 nm diameter NPs used in the calculation of overlap integral. (d) Modified relationship between mean ET rate and $\ln(2x + \bar{d})$ taking into consideration the overlap integral as a function of acceptor sizes.

The above analysis is based on the assumption of a constant Förster radius R_0 . From Equation 4.12, R_0 is, in fact, proportional to the overlap integral of donor emission and acceptor absorption spectra. As the acceptor absorption varies with the acceptor diameter d , the actual R_0 is also a function of d . Here, we use the emission and absorption models from ref. 138 to quantify the effect of varying R_0 . The PL spectrum and absorption coefficient are predicted by

$$F_{NC}(\hbar\omega, E_g, \Delta E) \propto \frac{1}{\Delta E \sqrt{2\pi}} \exp\left(-\frac{(\hbar\omega - E_g)^2}{(2\Delta E)^2}\right), \quad (4.15)$$

and

$$\alpha(\hbar\omega, E_g) \propto \omega^{-1}(\hbar\omega - E_g)^2, \quad (4.16)$$

where $E_g(\text{eV}) = 1.081(\text{eV}) + 3.73/d(\text{nm})^{1.39}$ is the bandgap using a linear combination of atomic orbitals (LCAO) model,⁷⁹ and ΔE is the spectral width with a typical value $\Delta E = 70$ meV at room temperature.

The predicted PL spectrum for 3.2 nm donor NC and absorption spectra for 3–5 nm NCs are plotted in Figure 4.10c. As the acceptor size increases, their absorption edges redshift, and the overlap between donor-emission and acceptor-absorption increases. Here, our Si NC size can be described with a lognormal NC size distribution

$$f(d) = \frac{1}{d\sigma\sqrt{2\pi}} \exp\left(-\frac{(\ln d - \mu)^2}{2\sigma^2}\right) \quad (4.17)$$

with $\mu = 1.2$, $\sigma = 0.2$ by fitting the data in Figure 4.3b. Substituting $f(d)$ to Equation 4.14, with R_0 either as a constant or following Equation 4.12, slight differences of slopes can be observed. With the constant R_0 assumption, the average ET rate roughly follows the inverse sixth-power donor-acceptor distance dependence. After taking into consideration the varying R_0 , the index of the power-law relationship is modified to 5.4.

The above analysis indicates that in the modified Förster expression where the influence of NC size distribution is taking into consideration, the index of the power-law may be

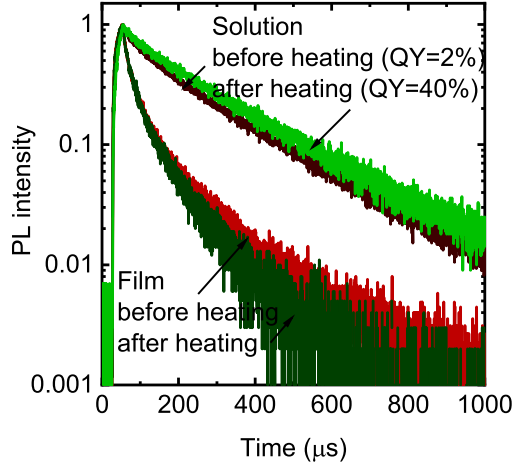


Figure 4.11: PL decay curves of gas-phase functionalized Si NCs before and after heating.

slightly modified to $-(5-7)$. Still, this range contradicts the slope of -14 obtained from the experimental data. Therefore, our experimental data shows that the inverse sixth-power donor-acceptor distance dependence relationship predicted by the Förster model does not accurately describe the distance-dependent energy transfer in Si NC films.

4.3.5 Influence of PLQY on energy transfer

According to the expression of the Förster radius (Equation 4.12), the quantum efficiency of the donor η_{PL} proportionally influences the ET rate. When preparing the gas-phase functionalized Si NCs, we perform heating at 160 °C on these samples, during which their PLQYs are improved from 2% to 35–40%, to make sure that their PLQYs are similar to the solution-phase functionalized Si NCs. It is noteworthy that the ET rates of 3.2 nm Si NCs before and after heating in fact have no significant difference (Figure 4.11). This constant ET rate supports our previous conclusion that heating increases PLQY by reducing the “dark” NC fraction within the ensemble without influencing the IQE of NCs.¹⁰⁸ The ET rates of the “bright” donor NCs contributing to the measured PL remain constant regardless of ensemble PLQY, and thus the measured PL remains unchanged.

We also performed the ET rate measurements on smaller-sized Si NC samples with

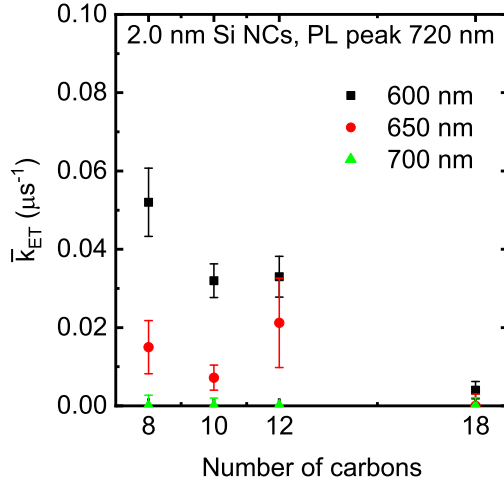


Figure 4.12: Experimentally measured average ET rates $\bar{k}_{ET}$ in solution-phase functionalized, 2.0 nm Si NC films.

an average NC diameter of 2.0 nm and a PL peak wavelength of 720 nm (Figure 4.12). Contrary to the $\sim 40\%$ PLQY in 3.2 nm Si NC samples, the smaller NCs only have a PLQY of around 6%. At around peak wavelengths, the measured ET rates are already negligible, suggesting that the Förster radius in the 2.0 nm Si NCs samples are significantly smaller than the 3.2 nm Si NC case. The smaller Förster radius indicates that these smaller NCs likely have IQEs less than 1. Therefore, the excitons have a larger probability of being trapped by trap states before migration to another nanoparticle.

4.4 Conclusions and future work

We demonstrate tunable energy transfer in Si NC films by varying the alkyl ligand lengths used for Si NC functionalization. Steady-state and time-resolved PL measurements confirm that the energy transfer becomes more efficient when ligand length becomes shorter. Specifically, surface functionalization by the plasma-assisted gas-phase method can lead to surface coverages small enough to exhibit efficient energy transfer but large enough to grant the Si NC solubility. To quantitatively measure the energy transfer rates, the influence of

the local dielectric environment needs to be taken into consideration. It is found that the radiative recombination rates in Si NCs can be well described with the virtual cavity model.

To obtain the NC spacing at the presence of surface alkyl ligands, we model the ligand packing structure using ReaxFF molecular dynamics simulation. The combined analysis of experimental ET rate measurements and the MD simulation revealed that the distance-dependent ET rates in Si NCs decay faster than that predicted by the Förster formulation, even with the NC size distribution effect taken into consideration.

Due to the size distribution within the ensemble, the measured average energy transfer rates are slightly modified from predictions of the traditional Förster energy transfer formulation. Instead of the inverse sixth-power relationship between the average ET rate and the average donor-acceptor distance, the index of the power-law may only be slightly modified (5–7 for a moderate size distribution). This suggests that a NC sample with a moderate size distribution can be used for distance-dependence studies and verification of the Förster mechanism. However, size-selective samples are still ideal for energy transfer studies, especially for Si NCs where there is significant homogeneous broadening. In future work, efficient size-purification methods need to be developed to produce monodispersed Si NCs with sufficient quantities for PL measurements. Low-temperature measurements are also needed since they can provide clear evidence for energy transfer and shed light on the energy transfer mechanism.

Chapter 5

Water-soluble, red-emitting Si NCs

5.1 Introduction

Inorganic nanocrystals have garnered increasing interest in biomedical applications, such as drug and gene delivery,¹³⁹ biosensing,¹⁴⁰ and bioimaging.^{141,142} Specifically, silicon nanocrystals (Si NCs) are desirable for biomedical applications owing to their low cytotoxicity,^{143,144} biocompatibility,¹⁴⁵ biodegradability,¹⁴⁶ and size-tunable optical properties.^{147,148} Similar to silica or porous silicon, Si NCs are hydrolytically unstable and dissolve over time into water-soluble silicic acid ($\text{Si}(\text{OH})_4$) which is a composition in human tissues and can be excreted through renal clearance.^{66,67} In addition, their size-tunable emissions in the biologically relevant red-to-NIR window and high photostability make Si NCs a potential alternative for heavy metal-based quantum dots.⁵⁷

Various strategies have been applied to synthesize luminescent water-dispersible Si NCs, which can be mainly categorized into steric stabilization and electrostatic stabilization. The use of polymers such as polyethylene glycol derivatives typically provides steric stabilization.^{57,149,150} Poly(ethylene glycol) (PEG), being safe and non-toxic, is one of the most popular and most effective molecules for coating the surface of nanoparticles.^{151–154} Surface PEGylation of inorganic nanoparticles can be achieved through direct adsorption, covalent attachment, or entrapment.^{155,156} Electrostatic stabilization approaches typically rely on ionic ligands, including olefinic ligands with terminal carboxylic acid,^{33,157,158} or amine functional groups.^{159–161} The colloidal stability of such surface-functionalized Si NCs in water or high ionic strength buffer solutions greatly depends on the type of stabilization

strategy. Compared to steric stabilization, the stability achieved by electrostatic repulsion is more strongly affected by pH or ionic strength.^{162–164} The electrostatic stabilization method is also considered as a kinetic stabilization method, where temporary aggregates are difficult to be redispersed.²⁵

In this chapter, we demonstrate two separate reaction routes to synthesize water-soluble and red-emitting Si NCs relevant for bioimaging applications. In these two methods, we focus on two important metrics: hydrodynamic diameter and PL stability. Si NCs with hydrodynamic diameters <20 nm are able to cross the blood-brain barrier, which opens up the potential for brain imaging applications. In contrast, for general cell-imaging applications, it is essential for Si NCs to exhibit stable photoluminescence in biological media for at least a few hours. In the first method, we utilize thermal hydrosilylation reaction with PEG acrylate. The PEGylated Si NCs (PEG-Si NCs) are nearly singly dispersed in water or Tyrode buffer with mean hydrodynamic diameters of ~ 10 nm. To our knowledge, this is the smallest size reported hydrodynamic diameter of Si NCs in water. This type of NC is ideal for brain imaging applications but does not have long-term photoluminescence stability in Tyrode buffer. In the second method, we explore a two-step synthetic procedure coupling plasma-assisted acrylic acid grafting and solution-phase room temperature reaction with PEG-OH. Relatively high PL stability in water and Tyrode buffer is achieved due to an oxide shell formed during the functionalization reaction. These Si NCs have slightly larger hydrodynamic diameters (20–30 nm in water and Tyrode buffer) but can exhibit PL in Tyrode buffer for >1 day at moderate concentrations.

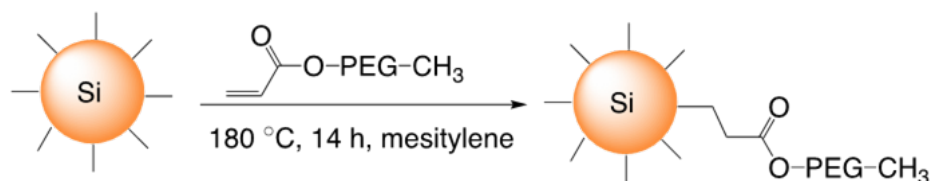


Figure 5.1: Schematic of the thermal hydrosilylation reaction.

5.2 PEG thermal hydrosilylation

5.2.1 PEG-Si synthesis and characterization

Hydrogen-terminated Si NCs with diameters around 3.2 nm were synthesized in a nonthermal plasma reactor using parameters similar to those described in ref 38. For the thermal hydrosilylation reaction, 0.15 ml of Poly(ethylene glycol) methyl ether acrylate (PEG-acrylate) and 5 mg of Si NCs were refluxed in 5 ml mesitylene for 14 hours (Figure 5.1). After the reaction, the solvents were evaporated, and PEG-Si NCs were redispersed into water or Tyrode buffer.

As shown in Figure 5.2, the hydrodynamic diameters in water and Tyrode buffer are 9.9 ± 1.8 nm and 11.2 ± 2.0 nm measured from dynamic light scattering (DLS), respectively. However, the longer-term stability of PEG-Si NCs suffer from oxidation or dissolution. The Si NC/water solution's yellow-brown color turns significantly lighter after a few hours, indicating that most Si NCs are either oxidized or dissolved. This degradation occurs especially fast in Tyrode buffer, with the solution turning colorless within a few hours.

5.2.2 PL in water and Tyrode buffer

After the hydrosilylation reaction, Si NCs exhibit photoluminescence (PL) centered at 812 nm with a PLQY of $\sim 7\%$ in mesitylene. However, their PLQY drastically drops to $\sim 0.03\%$ after dispersion in water, with the PL peak wavelength blueshifted to ~ 700 nm (Figure 5.3a). The drastic PL drop and peak blueshift indicate that water has a significant quenching effect for all Si NCs, but this quenching effect is especially strong for larger particles emitting at

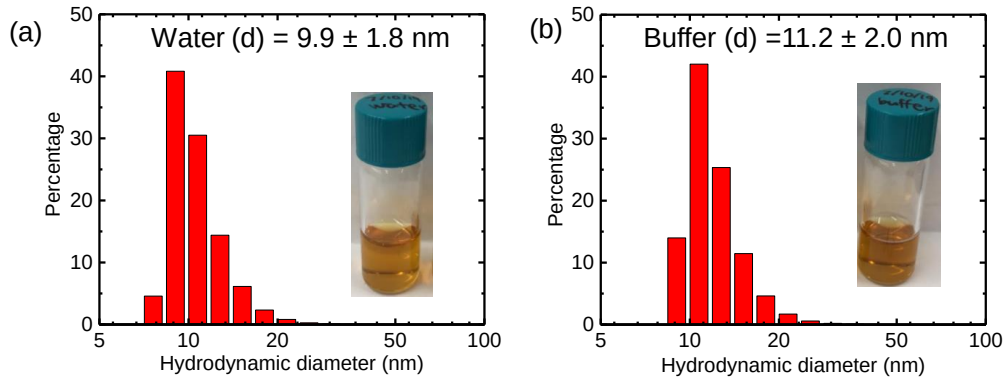


Figure 5.2: Hydrodynamic diameters of functionalized Si NCs dispersed in (a) water and (b) Tyrode buffer. Photo insets are for Si NCs dissolved in water/Tyrode buffer at ~ 2 mg/ml.

longer wavelengths. Figure 5.3b shows that the PL peak wavelength redshifts back to around 800 nm after 1-day dispersion in water, accompanied by the recovery of PLQY to 6%. Si NCs in mesitylene and after 1-day dispersion in water have similar PL wavelengths, which indicates that the physical process causing the PL quenching is limited to the NC surface during this timescale. The PL quenching and recovery both occur faster for larger NCs, resulting in the initial blueshift and subsequent redshift of PL wavelength.

After the temporary spectral redshift from day 0 to day 1, the PL spectrum continues to blueshift after longer-time dispersion in water (Figure 5.3b). Figure 5.4c–e show the long-time evolution of PLQY, PL peak wavelength, and PL full width half maximum (FWHM) for Si NCs dispersed in DI water from 0 to 35 days. The continued PLQY increase, peak blueshift, and peak broadening are consistent with surface oxidation by water, which has been previously observed in porous silicon samples.¹⁴⁶ The oxide layer passivates surface defects, which reduces nonradiative states and meanwhile leads to shrinking the nanocrystal core size and raising of band gap. After 35 days, the PLQY approaches 40% at the peak wavelength of 748 nm. We attribute this high PLQY to the high crystallinity of the silicon core and the high quality of the oxide passivation layer.

Figure 5.4d shows the evolution of average lifetime measured across the PL spectrum.

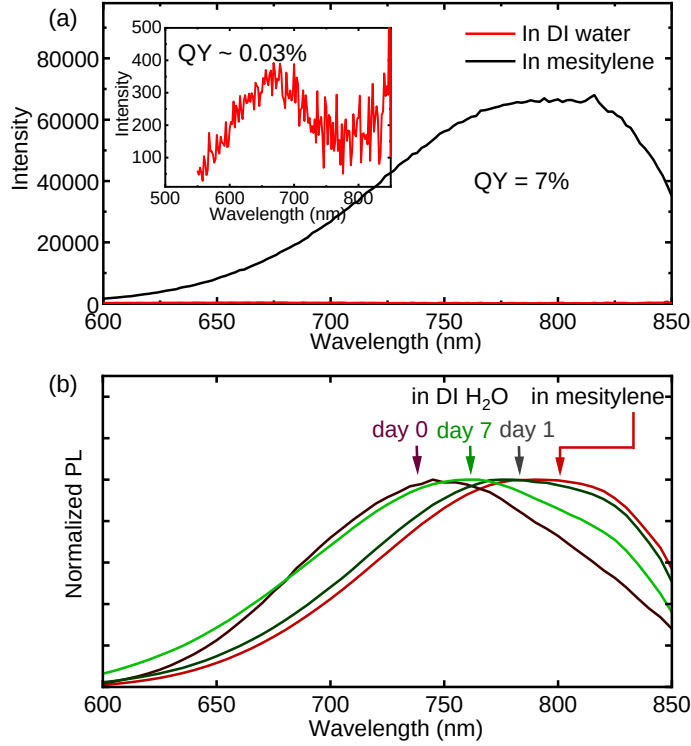


Figure 5.3: (a) Photoluminescence spectra ($\lambda_{ex} = 407$ nm) of PEG-Si NCs dispersed in mesitylene and DI water, respectively. The inset is the spectrum in DI water with a different vertical scale. (b) Normalized photoluminescence spectra of PEG-Si NCs dispersed in mesitylene and in water for 0, 1, and 7 days.

The PL lifetimes remain in the μs range, corresponding to emissions originating from the nanocrystal core. The PL lifetimes are also consistent with the spectral blueshift and redshift from day 0 to day 1. Compared between the lifetime values of Si NCs in mesitylene and in water at day 0, the lifetime drop is more significant at longer wavelengths, corresponding to the PL blueshift observed in Figure 5.3b. Consistent with PLQY measurements, the PL lifetime continues to increase at longer timescales.

Similar steady-state and time-resolved PL measurements were performed for PEG-Si NCs dispersed in Tyrode buffer. The initial PL spectrum is centered at 740 nm, similar to that in DI water. Different from the case in DI water, the PL experiences a continuous blueshift. The PLQY also remains lower than 1% over the period of 24 hours. The low

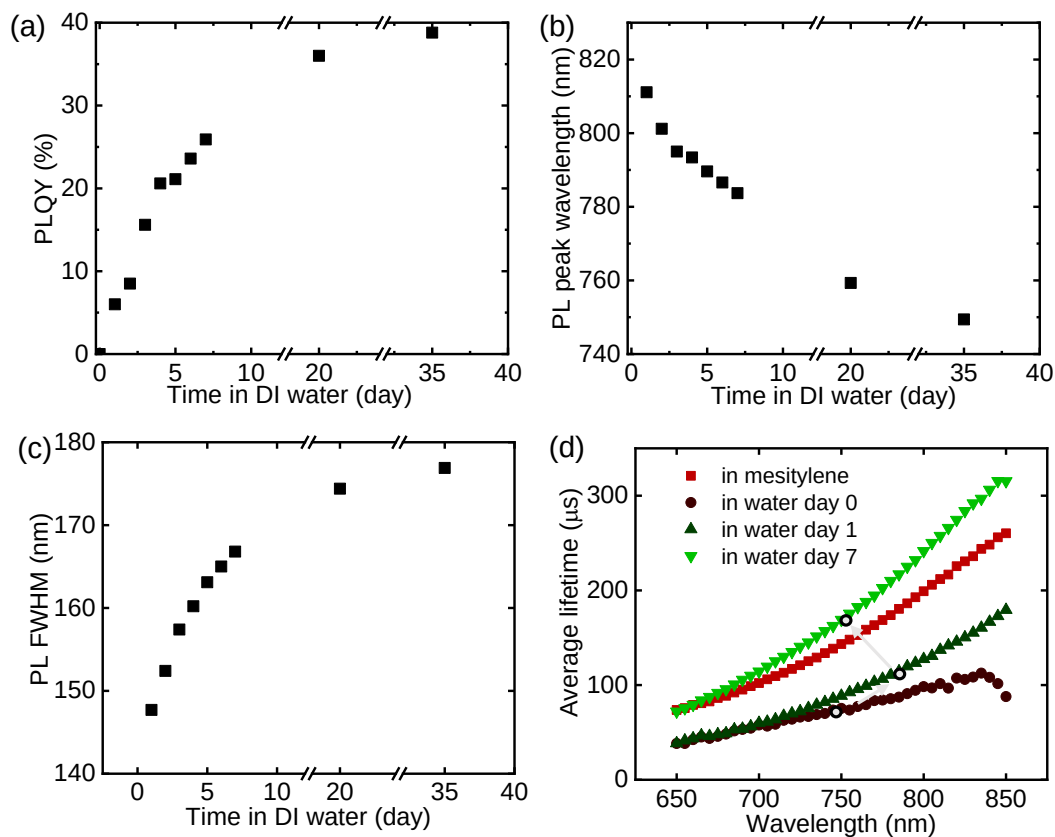


Figure 5.4: (a–c) The evolution of PLQY, PL peak wavelength, and PL FWHM for PEG-Si NCs dispersed in water. (d) Average lifetimes over the wavelength range of 650 to 850 nm for Si NCs dispersed in mesitylene and in water after 0, 1, and 7 days.

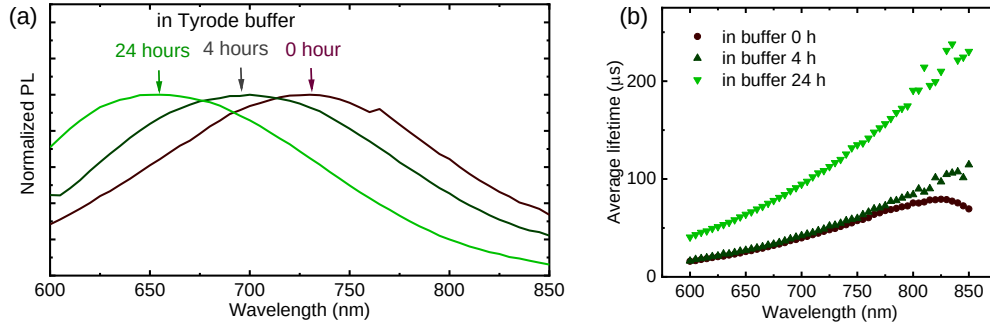


Figure 5.5: (a) Normalized photoluminescence spectra and (b) average lifetime of PEG-Si NCs dispersed in Tyrode buffer at 22 °C after 0, 4, and 24 hours, respectively.

PLQY in Tyrode buffer indicates that the ions in Tyrode buffer prevent the growth of a high-quality surface passivation layer. Here, the time range being studied is also shorter, as the particles oxidize or dissolve at a faster rate in the buffer. After 24 hours, the PL intensity continues to drop and soon becomes negligible.

A few previous studies focus on the PL quenching mechanism of silicon nanostructures by liquid water. Several models have been proposed in the literature to explain the PL quenching of silicon by water, including non-radiative recombination from trap states created from oxidation¹⁶⁵ or induced stress,^{166,167} the dielectric effect,¹⁶⁸ and solvent polarity.¹⁶⁹ Meanwhile, the long-time oxidation-induced PLQY enhancement is believed to be associated with the formation of an oxide passivation layer. Letting silicon nanostructures oxidize in liquid-phase water has been previously employed to “activate” PL from porous silicon.¹⁴⁶ The PL quenching from oxygen molecules also plays an important role here due to the exposure of PEG-Si NCs in ambient air and the dissolved oxygen in DI water.

5.2.3 Time-resolved PL analysis

A complete understanding of the PL quenching behavior also enables applications of Si NCs in PL-based sensing.^{170,171} Photoluminescence quenching processes can be classified into two categories – dynamic quenching and static quenching.

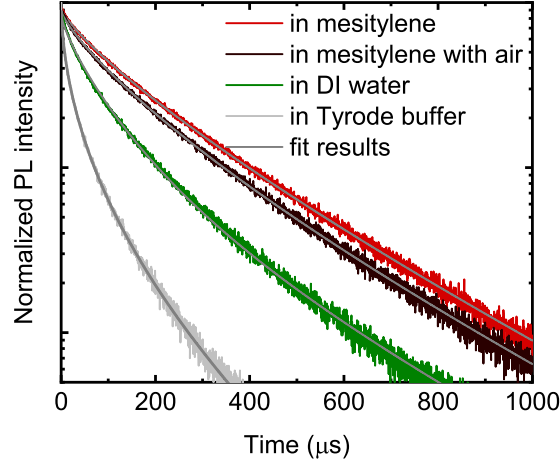


Figure 5.6: Fitted decay curves for PEG-Si NCs measured in the three solvents. The decay in mesitylene was fitted with a stretched-exponential fitting, and the decays in mesitylene with air and in DI water were fitted with the procedure described above. The decay in Tyrode buffer with the stretched-exponential fitting is also plotted for comparison.

Dynamic quenching refers to the process where the luminophore in its excited state interacts with a quencher and undergoes non-radiative recombination. The interaction between the luminophore and the quencher can be FRET, Dexter electron transfer, or exciplex formation processes.¹⁶⁵ The intensity of dynamic quenching can be described with the Stern-Volmer equation:

$$\frac{I}{I_0} = \frac{QY}{QY_0} = \frac{\tau}{\tau_0} = \frac{k_r + k_{nr}}{k_r + k_{nr} + k_q[Q]}, \quad (5.1)$$

where k_q is the quencher rate coefficient, $[Q]$ is the quencher concentration, and I_0 and I , τ_0 and τ , QY_0 and QY represent the intensity, PL lifetime, and PLQY before and after quenching, respectively. In Equation 5.1, τ_0/τ and QY_0/QY are both linearly dependent on the quencher concentration $[Q]$.

In contrast, static quenching refers to quenching due to the formation of a non-luminescent complex between the quencher and the luminophore in the ground state. In this scenario, the measured PL lifetime will remain unchanged.

Table 5.1: PLQY, τ and β values from stretched-exponential fittings (measured at 800 nm), and the fitted relative concentrations of PEG-Si NCs in mesitylene without air exposure, mesitylene that is exposed to air, and DI water, respectively

	stretched exponential fitting			fitted concentrations		
	PLQY (%)	τ (μ s)	β	ϕ_1 (bright)	ϕ_2 (quenched)	ϕ_3 (dark)
mesitylene (m)	7	149	0.80	100%	0	0
mesitylene + air (ma)	4	123	0.76	44%	21%	35%
DI water + air (wa)	0.03	58	0.64	0.2%	0.6%	99%

The type of quenching process is usually classified by measuring the PL lifetime at a series of quencher concentrations. While we currently do not have the experimental setup to vary quencher concentrations, a combined analysis of PLQY and lifetime before and after PL quenching provides insight into the PL quenching mechanism. Table 5.1 shows the measured PLQY, τ and β values from the stretched exponential fitting of the same PEG-Si NC sample dispersed in mesitylene without quenching (m), mesitylene that is exposed to air (ma), and water (wa). If the quenching is purely dynamic, we would expect

$$\frac{\tau_m}{\tau_{ma}} = \frac{QY_m}{QY_{ma}}, \quad (5.2)$$

$$\frac{\tau_m}{\tau_{wa}} = \frac{QY_m}{QY_{wa}}. \quad (5.3)$$

As can be observed from Table 5.1,

$$\frac{QY_m}{QY_{ma}} < \frac{\tau_m}{\tau_{ma}} < 1, \quad (5.4)$$

$$\frac{QY_m}{QY_{wa}} < \frac{\tau_m}{\tau_{wa}} < 1. \quad (5.5)$$

Therefore, the PL quenching from air and water exhibits both dynamic and static characteristics.

We further analyze the decay data to determine the impact of each effect. For PL decay from an ensemble composed of emission from two components with different radiative lifetimes, the intensity $I(t)$ can be expressed as a sum of both decays weighted by their

concentrations and radiative lifetimes²⁰:

$$I = \frac{\phi_1}{\tau_{1R}} \exp\left(-\frac{t}{\tau_1}\right) + \frac{\phi_2}{\tau_{2R}} \exp\left(-\frac{t}{\tau_2}\right), \quad (5.6)$$

where ϕ_1 and ϕ_2 are the concentrations, and τ_1 and τ_2 are the lifetimes, respectively. Similarly, the PL decay from a quenched sample (either mesitylene + air or water + air) can be treated as a sum of three components: NCs that behave the same as in mesitylene (lifetime denoted by τ_1), NCs with a quenched lifetime τ_2 ($\tau_2 < \tau_1$), and NCs that no longer emits. We denote the relative concentrations of the above three types as ϕ_1 , ϕ_2 , and ϕ_3 , where

$$\phi_1 + \phi_2 + \phi_3 = 1. \quad (5.7)$$

As the decay from Si NCs has a stretched exponential characteristic, we modify the above equation to

$$I = \frac{\phi_1}{\tau_{1R}} \exp\left[-\left(\frac{t}{\tau_1}\right)^\beta\right] + \frac{\phi_2}{\tau_{2R}} \exp\left[-\left(\frac{t}{\tau_2}\right)^\beta\right], \quad (5.8)$$

assuming that the altered lifetime follows the same shape factor β as before quenching for simplicity. As the PLQY can also be described as a sum of each component, we have:

$$\text{PLQY} = \phi_1 \frac{\tau_1}{\tau_{1R}} + \phi_2 \frac{\tau_2}{\tau_{2R}}. \quad (5.9)$$

For Si NCs with the same sizes, the intrinsic radiative lifetimes should be equal:

$$\tau_{1R} = \tau_{2R}. \quad (5.10)$$

Therefore, ϕ_1 and ϕ_2 can be obtained by fitting the decay curve from Equation 5.8 while satisfying Equation 5.7 and 5.9. The fitted results are plotted in Figure 5.6 and the ϕ_1 , ϕ_2 , and ϕ_3 values are summarized in Table 5.1. It can be concluded that the PL quenching from the air has both static and characteristics, while the PL quenching from the water almost has a static nature.

From the literature, PL quenching of silicon nanostructures by molecular oxygen occurs through the energy transfer to oxygen molecules and exhibits a dynamic nature.^{172,173} Assuming our Si NCs have the same characteristics, the PL quenching by air can be view as a combined result of oxygen and water. Although the PL quenching by water has a static nature, it is unlikely a result of the formation of a non-luminescent ground-state complex. Instead, similar to the discussion in Chapter 2.3.2, the creation of “dark” NCs due to fast non-radiative recombination events can also lead to PL quenching without altering the observed lifetime, exhibiting a similar characteristic to the static quenching.^{18,90}

5.2.4 Discussion

PEG-Si NCs functionalized by thermal hydrosilylation reaction have excellent dispersibility in water and Tyrode buffer due to steric stabilization imparted by PEG ligands. However, severe PL quenching is observed when Si NCs are dispersed into water. From the combined analysis of PL lifetime and PLQY, we conclude that more than 99% of the Si NCs turn into dark NCs in water, leading to a PLQY of $\sim 0.03\%$. This PL quenching by water is much more significant compared to the previously reported data in the literature, where PLQY of 10–20% can be measured for Si NCs in water after functionalization with PEG molecules.^{174,175}

Several factors may contribute to this differentiation. First, our PEG-Si NCs have a highly hydrophilic surface, evidenced by the small hydrodynamic diameters in water measured by DLS. Therefore, there is a higher chance of water molecules reaching the proximity of surface Si atoms, leading to more significant PL quenching.¹⁷⁶ Second, we perform the thermal hydrosilylation reaction air-free, so the Si NCs are barely oxidized. Other reported functionalization schemes usually involve steps such as washing the Si NCs in methanol or water, which may potentially lead to their surface oxidation. As can be observed from the PLQY evolution in water (Figure 5.4), the formation of an oxide passivation layer can significantly reduce the PL quenching effect. In fact, by letting the PEG-Si NCs oxidize in the air for a few days and then measure the PLQY in water, we were able to get PLQY of

1–2% in water. Finally, another possibility is that the plasma-synthesized Si NCs may have different surface structures from HF-etched Si NCs used in other studies.^{174,175} A recent study by solid-state NMR and XPS reveals that the H-Si NCs produced by HF etching have disordered surface structures.¹⁷⁷ It is possible that the surface structures of Si NCs have a potential influence on their interaction with the outer environment.

5.3 Room temperature PEGylation of acrylic acid grafted Si NCs

5.3.1 Synthesis and characterization

The gas-phase functionalization approach described in Chapter 2 is appealing because it avoids high temperatures that have been typically used and requires a minimal amount of solvents. To apply the gas-phase functionalization to synthesize Si NCs for bioimaging applications, we explored a two-step synthetic procedure coupling steric and electrostatic repulsions to achieve colloidal stability of Si NCs in both water and high ionic strength buffer that is similar to biological media.

First, we synthesized acrylic acid grafted Si NCs using an all-gas-phase approach on a millisecond timescale without any post-synthetic processing. Plasma-assisted surface functionalization with alkene ligands to produce luminescent Si NCs has been demonstrated earlier, and a similar approach was employed to synthesize acrylic acid grafted Si NCs by adjusting the plasma power and gas flow rates.^{71,108} Acrylic acid or poly(acrylic acid) coating of Si NCs has been extensively studied in the solution phase to generate a hydrophilic surface and to reduce nanoparticle agglomeration in water or biological media.^{33,157,158,178,179} Acrylic acid ligands with a terminal carboxylic acid group stabilize particles through a combination of steric stabilization and electrostatic repulsion, thus the colloidal stability can be affected by the presence of electrolytes and pH of the medium.^{162,163,179–181} Hence,

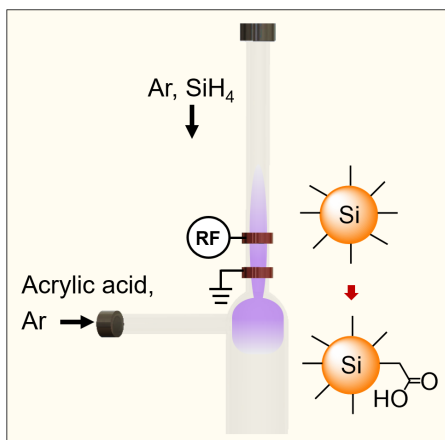


Figure 5.7: Schematic of the synthesis of acrylic acid grafted Si NCs.

even though acrylic acid grafting improves the nanocrystal dispersibility in water, the functionalized nanoparticles are typically slightly agglomerated with hydrodynamic diameters around 100 nm.

In the second step, the acrylic acid grafted Si NCs were reacted with polyethylene glycol (PEG) to achieve steric stabilization. PEG, being safe, non-toxic, with nearly neutral surface charges, is one of the most popular and most effective molecules for coating the surface of nanocrystals.^{151–154} Surface PEGylation of Si NCs has been achieved by utilizing covalent Si–C bonds,^{174,182} Si–O linkage,¹⁸³ chloride-terminated silicon surfaces,¹⁸⁴ and boron surface sites.¹⁸⁵ As the acrylic acid grafting enables an improved dispersibility in polar solvents that allows for large initial surface areas available for reactions, we can employ the reaction with PEG-OH to form Si–O–R linkages at room temperature.¹⁰⁴

Herein, we report the synthesis of luminescent PEGylated acrylic acid grafted Si NCs combining gas-phase and colloidal approaches under room temperature conditions. The surface-functionalized nanocrystals exhibit excellent dispersibility in both water and a high ionic strength buffer media maintaining colloidal stability for months. Furthermore, after oxidation in DI water, they exhibit photoluminescence quantum yield (PLQY) up to ~30% in DI water and ~13% in Tyrode buffer in NIR emission wavelengths, which is suitable for *in vivo* imaging.

Acrylic acid grafted Si NCs (AA-Si NCs) were synthesized using an all-gas-phase setup as illustrated in Scheme 5.7. Si NCs were synthesized in a higher density upstream plasma region followed by acrylic acid ligand grafting, which occurs at the downstream “after-glow” region or the lower density plasma region. The plasma-induced synthesis and surface functionalization occur on a timescale of 10 ms, which is significantly faster than a typical colloidal synthesis of acrylic acid grafted Si NCs. The AA-Si NCs were transferred into water and Tyrode buffer after ultrasonication.

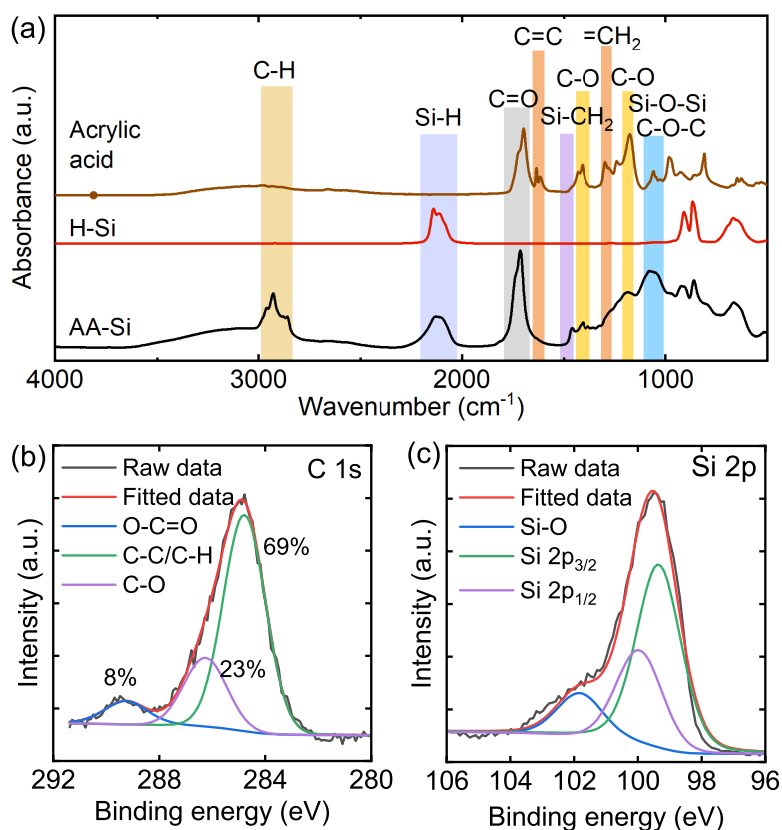


Figure 5.8: Characterization of acrylic acid grafted Si NCs. (a) FTIR spectra of acrylic acid, H-Si NCs and AA-Si NCs. (b,c) XPS high resolution spectra of C 1s peak and Si 2p peaks. The peak corresponding to adventitious carbon is shifted to 284.8 eV as a reference.

As-synthesized AA-Si NCs have crystalline cores of ~ 3 nm determined by Scherrer analysis (Figure 5.9a). We performed Fourier-transform infrared (FT-IR) spectroscopy and X-ray photoelectron spectroscopy (XPS) measurements to characterize the surface composition of

the AA-Si NCs. Figure 5.8a shows the FT-IR spectra of acrylic acid, hydrogen-terminated Si NCs (H-Si NCs), and AA-Si NCs. The H-Si NCs were produced under the same synthesis conditions, but without acrylic acid injection to the flow stream. The FT-IR spectrum of AA-Si NCs exhibits features at 2200–2100 cm^{-1} , $\sim 1100 \text{ cm}^{-1}$, 1700–1800 cm^{-1} , and 2800–3000 cm^{-1} which were assigned to Si–H stretching, Si–O–Si asymmetric stretching, C=O stretching, and C–H stretching modes. The disappearance of C=C stretching peak at 1640 cm^{-1} and the emergence of Si–CH₂ peaks at 1460 cm^{-1} suggests that hydrosilylation reaction proceeds as expected, replacing C=C and Si–H bonds with Si–C bonds.

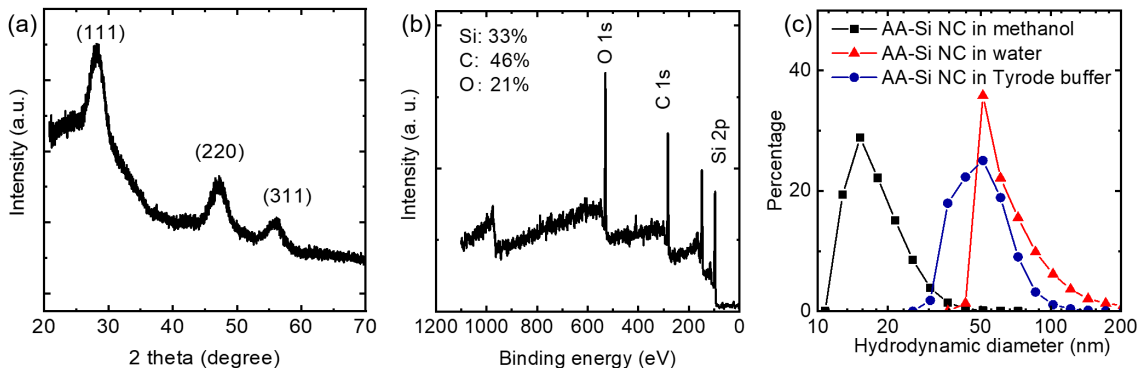


Figure 5.9: (a) XRD and (b) XPS survey scan of the as-synthesized AA-Si NCs and (c) their hydrodynamic diameters in methanol, water and Tyrode buffer.

As shown in Figure 5.8b and c, XPS data further confirm the effective surface functionalization of AA-Si NCs. The survey XPS spectrum (Figure 5.9b) confirms the presence of Si, C, and O with atomic concentrations of 33%, 46%, and 21%, respectively. C 1s high resolution spectrum exhibits a peak at 288.8 eV, which is consistent with the COOH/COOR functionalities indicating the retention of carbonyl groups in acrylic acid grafted Si NCs. The COOH/COOR concentration is around 8%, which is typical among the other studies of acrylic acid plasma coatings.^{186,187} According to the Si 2p high resolution spectrum, the peak at 99.4 eV corresponds to the Si(0) component and two shoulders located at 100.1 and 101.9 eV indicate the oxidized Si species.

The hydrophilic nature of AA-Si NCs enables the dispersibility of functionalized particles

in polar organic solvents and water.^{157,158} The improved dispersibility of AA-Si NCs can be attributed to a combination of steric stabilization and electrostatic stabilization induced by negative surface charges.^{178,179} Similarly, plasma synthesized AA-Si NCs are able to spontaneously form a clear and stable solution in methanol and are readily dispersible in both water and Tyrode buffer. Hydrodynamic diameters of AA-Si NCs in both water and Tyrode buffer were evaluated using DLS measurements. AA-Si NCs have hydrodynamic diameters of 67 ± 20 nm in water and 48 ± 12 nm in the Tyrode buffer (Figure 5.9c). However, AA-Si NCs in the Tyrode buffer degrade completely within 2 h. Furthermore, they do not exhibit photoluminescence when introduced to either water or Tyrode buffer.

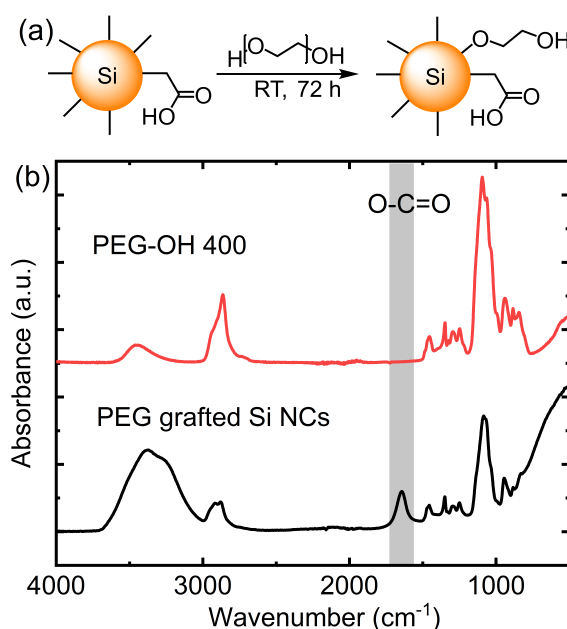


Figure 5.10: (a) Schematic of the PEGylation reaction and (b) FT-IR spectra of PEG-OH 400 and PEGylated AA-Si NCs.

Having demonstrated that AA-Si NCs exhibit improved dispersibility in water and Tyrode buffer but with low stability and negligible PL properties, we carried out a room temperature colloidal PEGylation reaction to achieve enhanced photoluminescence along with

long-term stable dispersions. Briefly, AA-Si NCs were dispersed in a mixture of methanol and PEG-OH (MW = 400), and methanol was subsequently evaporated. Then, AA-Si NCs and PEG-400 were allowed to react under room temperature for 72 h.

We carried out FT-IR analysis of PEGylated acrylic acid grafted Si NCs (PEG-AA-Si NCs) to gain further surface information. As shown in Figure 5.10b, the FT-IR spectrum of the PEGylated AA-Si NCs is mainly dominated by the PEG ligand features. While the characteristic Si-H peaks diminished in the spectrum, the peak at 1700 cm^{-1} confirms the existence of C=O species. This observation confirms the presence of PEG-400 grafted AA-Si NCs.

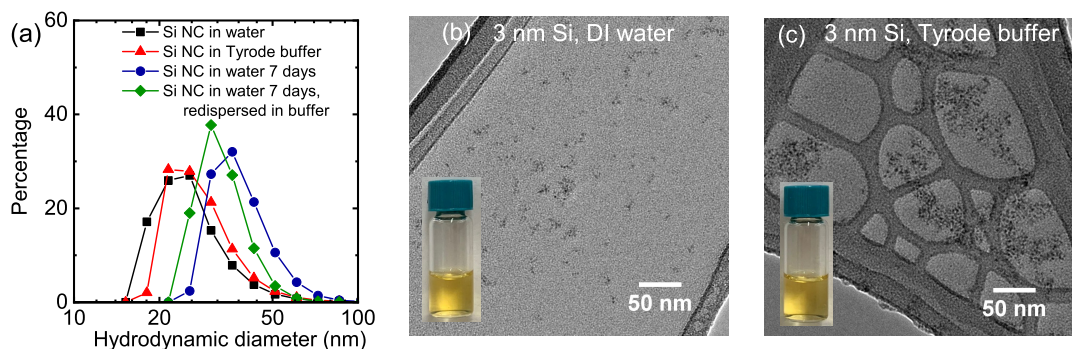


Figure 5.11: (a) DLS of PEG-Si NCs dispersed in water, buffer, water after 7 days, and redispersed in Tyrode buffer after dispersed in water for 7 days, each at 0.5 mg/ml. (b)(c) TEM of PEG grafted Si NCs dispersed in water (b) and buffer (c).

Purified PEGylated AA-Si NCs form a clear dispersion when introduced into water or Tyrode buffer, and these dispersions remain colloidally stable for months without any visible precipitation. Hydrodynamic diameters of PEGylated AA-Si NCs in both water and Tyrode buffer were evaluated using dynamic light scattering (DLS). The hydrodynamic diameter in water and Tyrode buffer were both measured to be $24 \pm 6\text{ nm}$ (Figure 5.11a). The hydrodynamic diameters increased from $24 \pm 6\text{ nm}$ to $36 \pm 7\text{ nm}$ after 7 days of dispersion in water, indicating minor agglomeration during this period.

The hydrodynamic diameters were confirmed by transmission electron microscopy (TEM)

measurements (Figure 5.11b, c). For TEM characterization, PEGylated AA-Si NCs were dispersed in water or Tyrode buffer at 0.5 mg/ml concentration and drop-cast onto the TEM grid. TEM images from both water and Tyrode buffer dispersible PEGylated AA-Si NCs appear as small agglomerates within the size range of 20–30 nm. These results imply that PEGylated AA-Si NCs are not individually passivated but structures of PEG encapsulated nanocrystals.

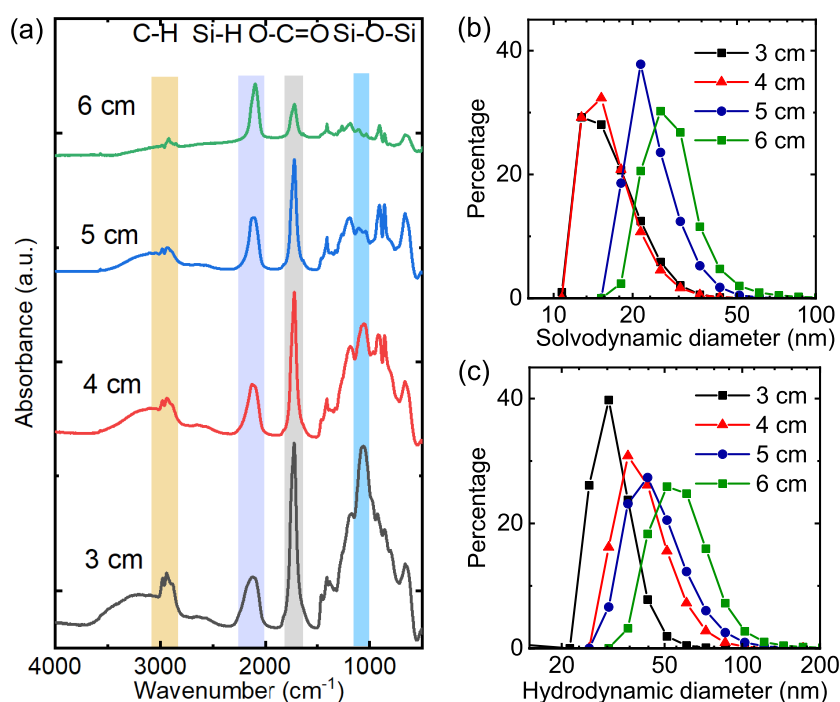


Figure 5.12: The effect of varying the electrode-to-ligand injection distances at 3cm, 4cm, 5cm, and 6cm. (a) FTIR spectra of as-synthesized, acrylic acid grafted Si NCs. (b) Solvodynamic diameters of samples dispersed in methanol at 1 mg/ml. (c) Hydrodynamic diameters of these samples after PEGylation and dispersed in water, each at 0.5 mg/ml.

5.3.2 Tuning agglomerate size

To study the effect of having an acrylic acid grafted surface prior to PEGylation, we carried out a control experiment with pristine H-terminated Si NCs. The reaction was carried out under identical experimental conditions with hydrophobic Si NCs. We observed instant precipitation of PEGylated H-terminated Si NCs when introduced into water or Tyrode buffer without forming a stable dispersion. This result suggests that the acrylic acid surface is vital for effective surface functionalization with PEG-400 ligands, yielding stable dispersions in water and Tyrode buffer.

Based on the above observations, we postulate that the hydrophilic nature of acrylic acid grafted surface enables better dispersibility in methanol, allowing large initial surface areas available for PEGylation reaction. To test our assumption, AA-Si NCs with varying surface ligand coverages were synthesized by adjusting the distance between the powered electrode and the acrylic acid injection point. This distance has been fixed at 3–4 cm for our typical experiments. Varying the distance between the electrode and the injection point affects the electron density where the ligands meet the nanoparticles, which ultimately influences the ligand grafting reactivity. As a result, the surface ligand coverage decreases as the distance from the electrode to the injection point increases (Figure 5.12a). As shown in Figure 5.12b, there is a clear trend between the electrode-to-injection distance and solvodynamic diameters in methanol. We observed that the solvodynamic diameters of AA-Si NCs increased when the electrode-to-injection distance increased, which suggests a varying degree of acrylic acid surface functionalization. Furthermore, these results directly correlate with the hydrodynamic diameters in water after the PEGylation reaction (Figure 5.12c). As the solvodynamic diameters in methanol range from 16 ± 4 nm for the 3 cm sample to 27 ± 6 nm for the 6 cm sample, the hydrodynamic diameters in water after PEG functionalization vary from 24 ± 6 nm to 56 ± 14 nm. These results confirm that acrylic acid grafting enables a better dispersion in methanol, which will directly affect the PEGylation reaction and hydrodynamic diameters in water.

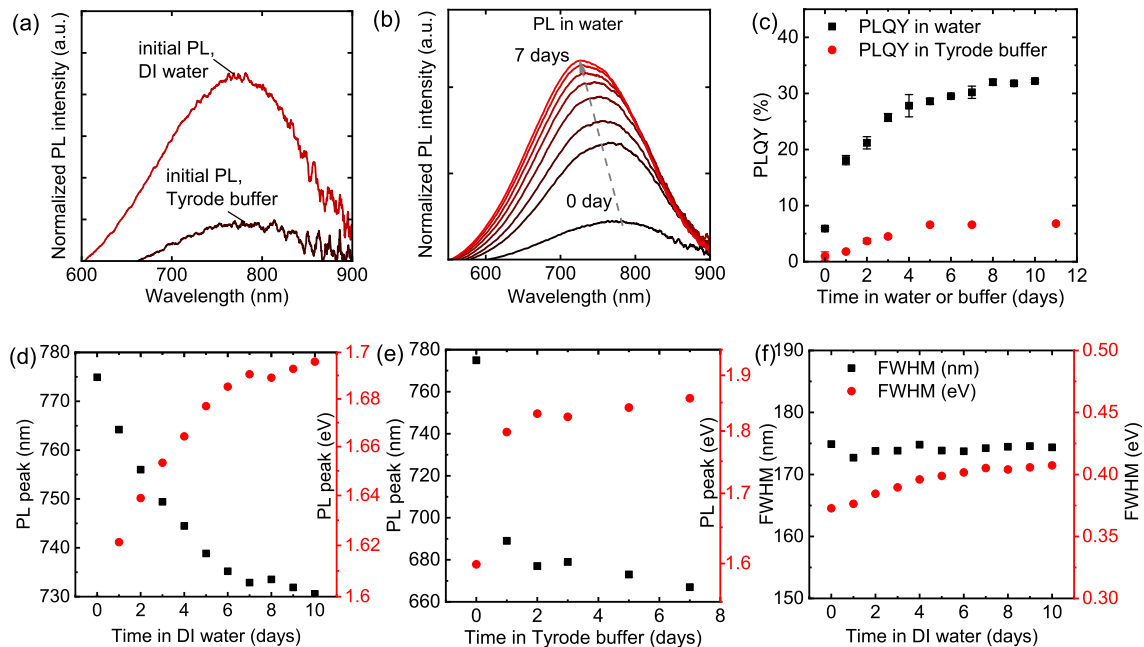


Figure 5.13: (a) Initial photoluminescence spectra of PEGylated AA-Si NCs in water and Tyrode buffer. (b) Photoluminescence spectra of PEG-Si NCs dispersed in water for 0 to 7 days. The spectra are normalized with respect to the absorption measured in an integrating sphere. (c–e) Photoluminescence quantum yield and peak wavelength of PEGylated AA-Si NCs dispersed in water or buffer for 0 to 10 days. (f) Evolution of the PL full width at half maximum (FWHM) in water.

5.3.3 PL in water and Tyrode buffer

Near-infrared (NIR) optical imaging offers improved contrast and depth of tissue penetration by reducing photon scattering, lowering tissue absorption, and minimizing autofluorescence in the NIR window.⁶⁸ We examined the optical properties of PEGylated AA-Si NCs for their potential viability as bioimaging molecules. While PEGylated Si NCs in water exhibit PL centered at 775 nm with a photoluminescence quantum yield (PLQY) of 6% (Figure 5.13a), they exhibit PL at 775 nm with a PLQY of $\sim 1\%$ in Tyrode buffer. Figure 5.13b–e show the evolution of PL, PLQY, and peak wavelength of PEGylated AA-Si NCs in water (Figure 5.13b–d) and Tyrode buffer (Figure 5.13e). As shown in Figure 5.13d

and e, the PL wavelength maxima blueshifts and the PLQY increase over time in both water and Tyrode buffer. The continued PLQY increase coupled with PL maxima blue shift indicates surface oxidation and effective passivation of the Si NCs with an oxide layer. However, PLQYs of PEGylated AA-Si NCs are significantly different in water and Tyrode buffer as they exhibit a 30% PLQY in water after 7 days and only 6% PLQY in Tyrode buffer. In addition, discoloration was observed in PEGylated AA-Si NC dispersion in Tyrode buffer, indicating a significant degradation of the Si NCs due to particle oxidation or dissolution. The degraded PLQY is presumed to originate from charge transfer processes to the ions present in the buffer.¹⁸⁸ Electrolytes are also known to accelerate the dissolution of silicon oxide,^{189,190} and thus remove the passivating oxide shell and create defects. As can be observed in Figure 5.13d and e, the PL maxima blueshift occurs much faster in Tyrode buffer than in water, indicating more rapid oxidation in the buffer.

The PL spectra of PEGylated AA-Si NCs in water exhibit Gaussian profiles with the FWHMs remaining relatively constant at ~ 175 nm (Figure 5.13f). However, typically PL broadening has been observed in the past during the surface oxidation of Si nanostructures.¹⁹¹ Here, we interpret this phenomenon to be consistent with the observation that PL from oxidized Si NCs can be viewed as the summation of core-related and shell-related emission,¹⁹² and PL broadening is related to the shell-related emission. As the Si NCs have been exposed to the air during the functionalization process, the shell-related emission component is already present before being introduced into water. Therefore, PL FWHM remains relatively constant throughout the time period.

Aged PEGylated AA-Si NCs in water exhibit relatively higher PLQY that can be ascribed to the formation of a protective oxide shell that develops enhanced stability against PL quenching and oxidation. In order to explore the colloidal stability and PL behavior of aged and oxidized PEGylated AA-Si NCs in Tyrode buffer, we took a dried sample of PEGylated AA-Si NCs that was oxidized in water for 7 days and then redispersed in Tyrode buffer. These aged particles have a hydrodynamic diameter of 36 ± 7 nm in water and show 30% PLQY at 713 nm. Upon redispersing these aged particles in Tyrode buffer, the

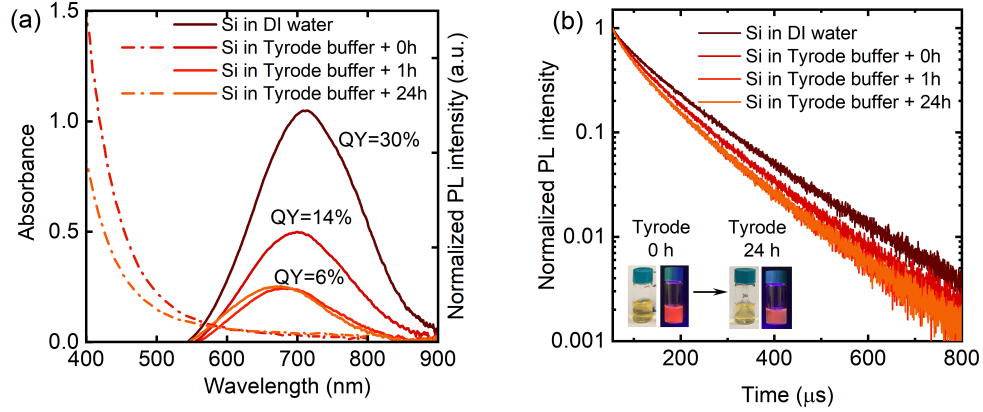


Figure 5.14: Degradation of 7-day oxidized PEG-Si NCs in Tyrode buffer at 22°C. (a) Absorption and photoluminescence spectra and (b) Time-resolved photoluminescence of PEG-Si NCs before and after dispersion in Tyrode buffer for 0h, 1h, and 24h respectively. The inset shows a picture of Si NCs in Tyrode buffer under ambient light and UV irradiation.

particles form a clear dispersion with a hydrodynamic diameter of 31 ± 6 nm (Figure 5.11a). The PLQY dropped to 14%, which is a 53% reduction compared to that in water, while the emission peak and shape remain similar (Figure 5.14a). This result indicates that PL quenching from ions is still substantial regardless of a surface oxide layer. After an hour of dispersion, the PLQY is further reduced to 6%, and this value remained constant until 24 h after dispersion. While the PLQY remains similar during the 1 h to 24 h period, the total number of effective Si NC emitters decreased, as reflected by the reduced absorbance in Figure 5.14a and the solution color shown in the Figure 5.14b inset. However, the concentration of emitters is still substantial as indicated from the absorbance after 24 hours. Time-resolved photoluminescence (TRPL) measurements also support that the quenching of PL occurs at a relatively fast timescale, while the number of effective emitters continues to drop after 1 hour. The decay lifetime τ and dispersion factor β reduced from $\tau = 91\mu s$, $\beta = 0.82$ in water to $\tau = 75\mu s$, $\beta = 0.79$ upon dispersion into Tyrode buffer, while the parameters after 1 hour and 24 hours remains similar, being $\tau = 64.7\mu s$, $\beta = 0.77$ and $\tau = 64.5\mu s$, $\beta = 0.77$, respectively. The DLS, PLQY, UV-vis and TRPL measurements suggest that these PEG-Si NCs remain colloiddally stable and emitting for at least 24 hours,

which is attractive for bioimaging applications.

The above-described synthesis and functionalization scheme can be conveniently adjusted to achieve size-tuning. While Si NCs with 3 nm crystalline core were primarily characterized, Si NCs with a 4 nm core size were also synthesized and investigated. Similarly, a transparent solution can be formed in water and buffer, with hydrodynamic diameters of 23 ± 6 nm and 31 ± 7 nm, respectively. During seven days of dispersion in water, the PLQY increased from 2% at 870 nm to 26% at 838 nm (Figure 5.15).

5.3.4 Conclusion

We have successfully prepared NIR emitting, water and Tyrode buffer dispersible Si NCs through a combination of gas-phase and colloidal synthesis. Compared to other synthetic approaches, our entire synthetic process occurs at room temperature with a minimal amount of solvent and without additional post-synthetic steps or catalysts, reducing energy cost and environmental impact. While we demonstrate that acrylic acid grafted Si NCs can be synthesized in an all-gas-phase setup on a timescale of 10 ms, these particles exhibit low stability and negligible PL in biological buffer. Nevertheless, the acrylic acid grafted Si NCs enable better dispersibility in methanol and undergo PEGylation under room temperature to form stable dispersions in water and Tyrode buffer with NIR emission, which makes them a worthy candidate for biological imaging.

5.4 Discussion and future work

If we compare the results by the two functionalization methods described in Section 5.2 and 5.3, it seems that the Si NC hydrodynamic diameter and their water stability has a negative correlation. Presumably, the interaction of Si NCs with the surrounding water molecules is stronger when Si NCs have a more hydrophilic surface. A systematic study of water stability vs. agglomerate size needs to be carried out in the future to verify this assumption. This can be performed by making a series of samples with various agglomerate

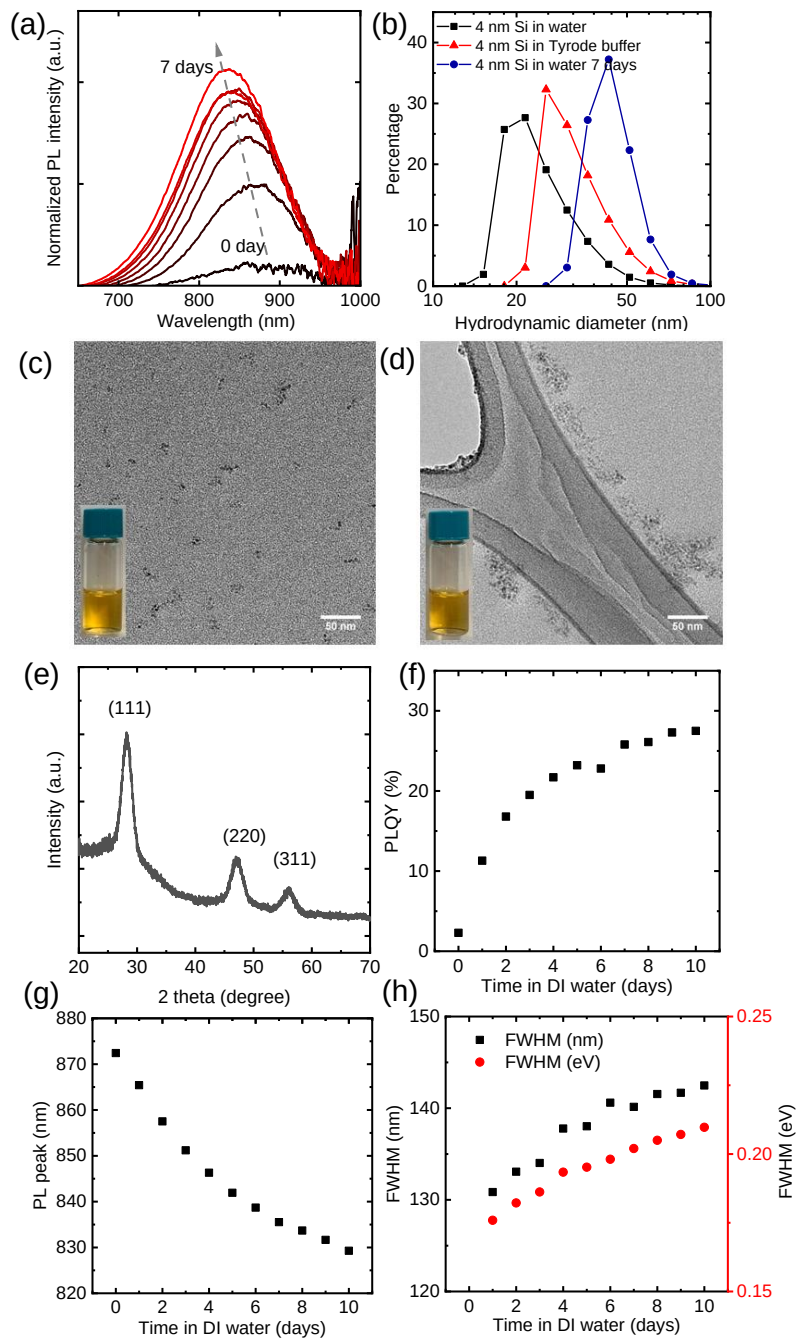


Figure 5.15: Characterization of PEG-Si NCs with 4 nm core size: (a) XRD, (b) DLS, (c,d) TEM in DI water and Tyrode buffer, (e) evolution of PL, (f) quantum yield, (g) peak wavelength, and (h) PL full width at half maximum (FWHM) for the 4 nm, PEG-Si NCs.

sizes using the method described in Section 5.3.2 and compare their stability in water. Another mechanism that remains unclear is the degradation mechanism. Si NCs may degrade into silicic acid or oxidize into silica in water, both transparent and cannot be distinguished only by looking at them by eye. Analyzing the residual product may clarify the process responsible for the Si NC degradation.

As discussed in Section 5.2 and 5.3, Si NCs are still prone to photoluminescence quenching from air and oxygen after surface functionalization. Due to steric hindrance, only a percentage of Si atoms are attached to ligands, while the remaining Si atoms are still hydrogen-terminated and prone to interactions with the outer environment. The PLQY evolution of Si NCs in water shows that a high-quality oxide shell can protect the particles and isolate them from the environment. Previous studies have shown that silicon nanocrystals with PLQY values of 40–50% can be made by oxidizing them in ambient air for a few months. As natural oxidation is time-consuming, synthesizing Si NCs with an oxide shell in the gas phase would be appealing.

We carried out a preliminary experiment of plasma-assisted oxidation using a setup similar to the reactor described in Chapter 3. Briefly, water (5 sccm) or oxygen (2 sccm), together with 100 sccm of hydrogen or argon as the carrier gas, was injected into the plasma afterglow to create an oxidized surface. The as-synthesized particles were characterized by FTIR (Figure 5.16). In both cases, the argon injection leads to a higher degree of oxide passivation, indicated by the weaker Si–H stretching vibration at 2200–2000 cm^{-1} .

However, only the samples with hydrogen injection show measurable PLQY as-synthesized. PLQY is further improved by annealing these particles at 160°C for 24 hours. The PLQY values before and after annealing at 160°C are summarized in Table 5.2. In the future, the gas flow rates, power, and reactor geometry need to be further optimized for the synthesis of high-quality Si/SiO₂ core/shell nanoparticles. The Si/SiO₂ may be further functionalized based on organosilane-based surface chemistries to grant them water-solubility characteristics.¹⁹³ With proper surface functionalization, the Si/SiO₂ core/shell nanoparticles are promising for achieving both small hydrodynamic diameter and high PL stability at the

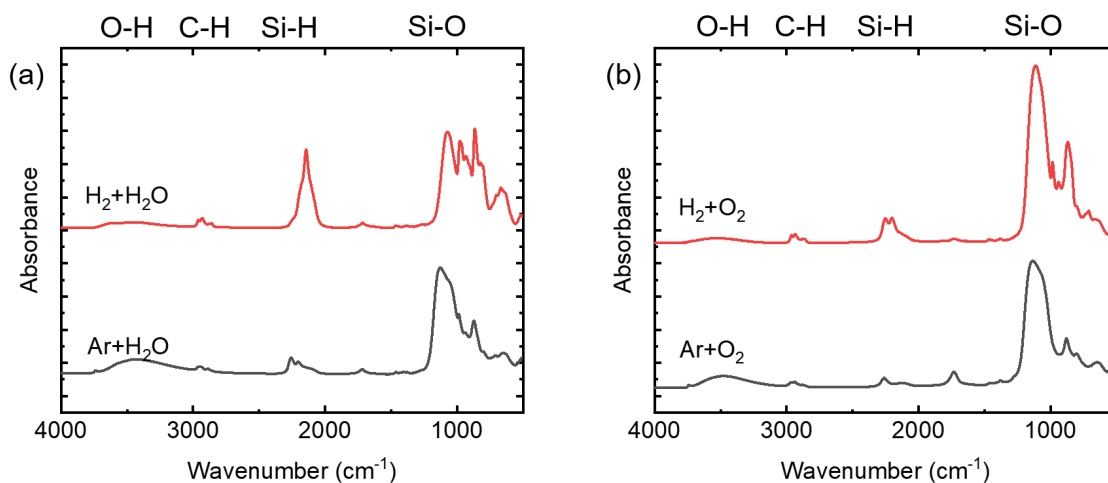


Figure 5.16: FTIR spectra of surface-oxidized Si NCs with (a) water and (b) oxygen as the oxidizing agent. 100 sccm of argon or hydrogen were used as the carrier gas.

same time.

Table 5.2: PLQY values from plasma-oxidized Si NCs with hydrogen as the carrier gas

Oxidizing agent	PLQY, as-produced	PLQY, after annealing
O ₂	< 1%	10%
H ₂ O	4%	10%
TEOS	4%	8%

5.5 Experimental details

Synthesis of acrylic acid grafted Si NCs. Acrylic acid functionalized Si NCs were synthesized in a nonthermal plasma reactor similar to the ones in previous work.^{72,108} The reactor consists of a 1/4 inch outer diameter borosilicate tube which expands to 3/8 inch. 10 to 30 standard cubic centimeters per minute (sccm) of argon and 14 sccm of silane (5% in helium) mixture were flowed through the tube, while the acrylic acid was injected as vapor through a bubbler into the plasma afterglow. 50 sccm of argon was used as the carrier gas for the bubbler, and the bubbler pressure was held at ~ 25 Torr. The plasma was generated by applying radio frequency (13.65 MHz) power to a pair of copper ring electrodes with a

nominal power of 60W. The powered electrode was fixed at 3–4 cm upstream of the acrylic acid injection port unless specified otherwise. The pressure in the plasma region was held at ~ 1.4 Torr. Particles were collected downstream of the plasma using a fine stainless steel mesh.

PEGylation of acrylic acid grafted Si NCs. Acrylic acid functionalized Si NCs collected for 30 minutes were dispersed in a mixture of 0.5 ml polyethylene glycol (PEG-OH) 400 (BioChemica, molecular weight 380–420) and 5 ml methanol. By bypassing acrylic acid injection during the synthesis, we estimated the mass of the core Si NCs to be ~ 5 mg. The nanoparticles formed a clear dispersion in the PEG-OH/methanol mixture by briefly shaking the container by hand. Methanol was then evaporated by flowing nitrogen over the solution, and the AA-Si NCs and PEG-OH mixture (5 mg Si NCs: 0.5 ml PEG-OH) were kept at room temperature for 72 hours. For purification, 1 mg Si NCs was dispersed in 0.5 ml DI water, and excess PEG was removed using an Amicon 3 kDa MWCO centrifuge filtration unit (Sigma Aldrich, Z677094) at 4500 rpm for 30 minutes. The nanoparticles were then redispersed in 0.2 ml methanol prior to FT-IR measurements.

Materials characterization. The nanoparticles were characterized with FT-IR, XPS, Zeta potential measurements, DLS, and TEM. FT-IR was performed with a Bruker Alpha spectrometer with the attenuated total reflection (ATR) single reflective module in a nitrogen-filled glovebox. Samples dissolved in methanol were drop-cast and allowed to dry on the ATR crystal and 20 scans were taken for each measurement at 2 cm^{-1} resolution. XPS was taken with a PHI Versa Probe III XPS and ultraviolet photoelectron spectroscopy (UPS) system. Nanoparticles were drop-cast and allowed to dry to form a film. Zeta potential measurements were taken with a Stabino Zeta potential analyzer.

PLQY was measured with an integrating sphere setup previously described in ref 101. The excitation source is a LED centered at 395 nm and the PL spectra were collected by an OceanOptics USB2000 spectrometer calibrated to an OceanOptics HL-3 Plus lamp. TRPL measurements were taken with a Horiba DeltaFlex TCSPC Lifetime Fluorometer. The excitation source is a 407 nm laser with a delay time of 13 μs .

UV-vis measurements were carried out with a Cary 7000 UV-Vis spectrophotometer.

Chapter 6

Conclusion and future work

In this thesis, we have demonstrated that the plasma-assisted surface functionalization approach successfully enables the production of colloidally-stable Si NCs with high PLQYs and Si NCs suitable for bioimaging applications. Here, the plasma-assisted functionalization method implements the injection of ligands into the spacial afterglow region of a nonthermal plasma. The plasma afterglow is a highly reactive environment with the presence of many molecular or radical species and a variety of reaction pathways. Further investigations into the species reactivity and the ligand grafting mechanism should be performed. These studies are not only for understanding the fundamental mechanisms but will also provide guidance for the design of reaction conditions that enable species selectivity.

The proposed solvent-less LSC fabrication scheme represents a big step towards practical applications. Two main advantages benefit large-scale production. First, Si NCs are continuously produced through the flow-through process without a transition to the solution-phase reactions. Second, Si NCs are spontaneously dissolved into styrene monomers, so the NC/styrene mixture can be directly used for subsequent polymerization reactions. However, the current limitation of these Si NCs is that they still suffer from low air stability. Typically, PLQY drops by 10–20% after prolonged air exposure, causing a drop in LSC devices' overall efficiency. Synthesizing high-PLQY, air-stable Si NCs through the formation of an inorganic shell for LSC application would be an important future direction.

In the energy transfer study, a combined study of experiments and simulations is performed. While the molecular dynamics simulations are mainly used to model the surface ligand packing, we can further explore many intriguing questions from molecular dynamics simulations. For example, we found a significant difference in their attaching probability to

a silicon surface between alkanes, alkenes, and 1-radicals. The species attaching probability may be used in conjunction with the ligand grafting mechanism study to shed light on the ligand grafting process. Another intriguing phenomenon is that we have found that the upper-limit for gas-phase deposited ligand density declines with increasing ligand lengths. In vacuum, the average time between NP-ligand collision is on the order of μs , long enough for the deposited ligands to bend towards the NP surface before the next ligand reaches the NP surface. The bending effect is especially pronounced in longer ligands (12–18 carbons). Due to steric hindrance, the bent ligand prevents the next ligand from reaching a surface site, resulting in a smaller achievable ligand coverage. An interesting future direction is to experimentally verify the dependence of surface ligand coverage on ligand length.

The acrylic-acid grafted Si NCs demonstrate that the formation of a good initial NC/solvent dispersion can facilitate further functionalization reactions. The two-step functionalization combining gas-phase and solution-phase reactions opens up the possibility of various surface functionalization schemes. For example, gas-phase grafted Si NCs with initial solubility in nonpolar solvents may be good candidates as the core material for subsequent solution-phase inorganic shell growth. Specifically, gas-phase grafted, thiol-capped Si NCs have the greatest versatility for subsequent ligand-exchange reactions due to the weak Si–S bond.

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Appendix A

Synthesis and characterization of amorphous aluminum oxide nanoparticles

A.1 Introduction

Aluminum oxide (Al_2O_3), commonly known as alumina, is one of the most widely used inorganic ceramic materials due to its superior thermal, chemical, and structural properties. Alumina can exist in both amorphous and crystalline forms. Amorphous alumina is considered to be an excellent candidate for anodic materials, gate insulators in transistors, protective coatings, and catalysts.^{1–5} Various methods have been employed to synthesize amorphous alumina nanoparticles, which include sol-gel processing,^{6,7} solution combustion,^{8–12} precipitation,^{13–15} ultrasonic treatment of porous anodic alumina membranes,¹⁶ energetic pulsed laser ablation,¹⁷ and tragacanth gel synthesis.¹⁸

The structure of amorphous alumina has been studied extensively and found to be comprised of a network of AlO_4 tetrahedra, AlO_5 polyhedra, and small fractions of AlO_6 octahedra.^{19–24} Solid-state ^{27}Al nuclear magnetic resonance (NMR) studies revealed that the existence of a significant fraction of AlO_5 polyhedra, where Al^{3+} ions are penta-coordinated with oxygen ions, creates disorder and hinders the crystallization and growth of crystalline alumina phases.²⁵ Thus, high temperatures ($\sim 800^\circ\text{C}$) are required for the transformation of amorphous to crystalline alumina nanoparticles.²⁶ This process involves a structural

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rearrangement reaction converting AlO_5 polyhedra into AlO_4 and AlO_6 .

Phase transformation of amorphous to crystalline alumina nanoparticles can greatly depend on several parameters such as synthetic route, heating rate, grain size, and chemical composition. Crystalline alumina can exist in various metastable crystalline phases (χ , η , δ , κ , θ , γ , ρ)²⁷⁻²⁹ and corundum or α -alumina is identified as the most thermodynamically stable phase in bulk form. The typical phase transformation sequence in crystalline alumina can be depicted as $\gamma \rightarrow \delta \rightarrow \theta \rightarrow \alpha\text{-Al}_2\text{O}_3$.²⁶ The transformation of $\gamma\text{-Al}_2\text{O}_3$ (density $\rho = 3.56 \text{ g/cm}^3$) to $\alpha\text{-Al}_2\text{O}_3$ ($\rho = 3.98 \text{ g/cm}^3$) is accompanied by a volume reduction of about 10% and proceeds through a meta-phase of $\theta\text{-Al}_2\text{O}_3$.³⁰ Typically, the final transformation to $\alpha\text{-Al}_2\text{O}_3$ requires higher annealing temperature around 1100 °C.²⁶ With superior hardness, low friction, unique heat transfer properties, and excellent wear resistance, $\alpha\text{-Al}_2\text{O}_3$ plays a critical role in the production of advanced ceramic materials and as a core and filler material for nanocomposites.³¹⁻³³ $\gamma\text{-Al}_2\text{O}_3$ nanoparticles themselves also exhibit excellent catalytic properties due to their surface acidity and high surface area.³⁴

In this work, we synthesized amorphous alumina nanoparticles by a nonthermal plasma approach, and studied their crystallization and phase transformation behavior during post-synthetic annealing. Nonthermal plasma synthesis has shown the potential to produce a variety of nanoparticles with high purity and narrow size distributions, and the library of nanoparticle materials has been expanded from group-IV semiconductors to metal oxides and metal sulfides.³⁵⁻⁴⁰ Furthermore, nanoparticles made by this method can be directly deposited into particle films with densities ranging from 20% to 60%.^{41,74} The as-deposited aluminum oxide nanoparticles are annealed at 600 – 1100 °C for the investigation of their phase transformation behavior.

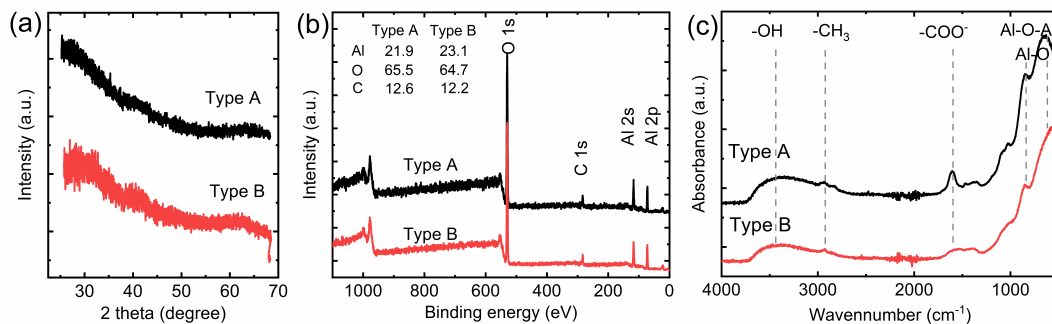


Figure A.1: Characterization of AlO_x nanoparticles synthesized from two types of reactors at $p=3.8$ Torr: (a) θ - 2θ mode out-of-plane XRD patterns of the as-synthesized AlO_x nanoparticles from type A and type B reactors. (b) XPS survey scan of AlO_x nanoparticles from type A and type B reactors. (c) Typical FTIR spectra of AlO_x samples from type A and type B reactors, with major absorption peaks featuring Al-O, $-\text{COO}^-$, $-\text{CH}_3$, and $-\text{OH}$.

A.2 Results and discussion

A.2.1 Synthesis of amorphous alumina nanoparticles

Amorphous alumina (AlO_x) nanoparticles were synthesized using the two reactor geometries shown in the experimental section. Figure A.1 a shows the XRD spectra of as-synthesized AlO_x nanoparticle samples from both type A and B reactors at $p = 3.8$ Torr. The absence of definitive peaks in XRD suggests that as-synthesized AlO_x nanoparticles are amorphous. As shown in a previous study, amorphous alumina nanoparticles are thermodynamically more stable with the lowest surface energy compared to θ - and α phase polymorphs at large surface areas.⁴²

XPS and FTIR measurements were performed to evaluate the surface and atomic composition of AlO_x nanoparticles from both reactor configurations (Figure A.1 b and c). For both samples, XPS survey shows main peaks corresponding to O 1s, C 1s, and Al 2p at 530,

284, and 73 eV respectively, which confirms the elemental composition in AlO_x nanoparticles. Carbon incorporation (5–10 at%) is commonly observed when TMA is used as the aluminum source due to strong Al–C bonds.^{43–45} The carbon content can be partly due to contamination in air, as samples are shortly exposed to air during the transfer, but can also originate from the methyl groups in TMA. Atomic percentage ratios of Al to O are around 1:3 for both A and B type reactor samples, with carbon percentages around 10%–15%. The atomic ratios are in general not affected by the plasma power used for synthesis. FTIR spectra for samples from both reactor types reveal absorption bands related to hydroxyl (–OH), alkyl (C–H), (C–O), and aluminum species (Al–O and Al–O–Al). The peak around $\sim 670\text{ cm}^{-1}$ and the shoulder which is located around $\sim 860\text{ cm}^{-1}$ correspond to the Al–O stretching vibrations in five-fold coordinated AlO_5 and four-fold coordinated AlO_4 , respectively. Features from AlO_6 stretching vibrations could also be present, which according to the literature lie in the $400\text{--}650\text{ cm}^{-1}$ spectral range and overlap with Al–O stretching vibrations and oscillations in AlO_4 and AlO_5 .^{43,46,47}

The average sizes of the AlO_x nanoparticles were determined using transmission electron microscopy (TEM). At $p = 3.8\text{ Torr}$, the average sizes of AlO_x nanoparticles from type A and type B reactors are $11 \pm 3\text{ nm}$ and $6 \pm 1\text{ nm}$, respectively. The different particle sizes can be explained by the different plasma densities at the point of TMA injection. Nanoparticle growth in plasmas proceeds through the nucleation of clusters, many of which are initially neutral⁴⁸. These clusters quickly coagulate to form nanoparticles, leading to a reduction of the overall concentration of clusters and particles. When the cluster/nanoparticle density has dropped to the level of the ion density in the plasma, there are sufficient electrons to charge most particles negatively and suppress further coagulation.⁴⁸ In the type B reactor, the TMA precursor is injected into a higher density plasmas zone than in the type A reactor, where the precursor is injected into the less dense plasma afterglow. Coagulation in the type B reactor is thus suppressed at smaller particle sizes, corresponding to higher particle concentrations, than in the type A reactor. For each type of reactor, size tuning of AlO_x nanoparticles can be achieved by varying the reactor pressure which changes the particle

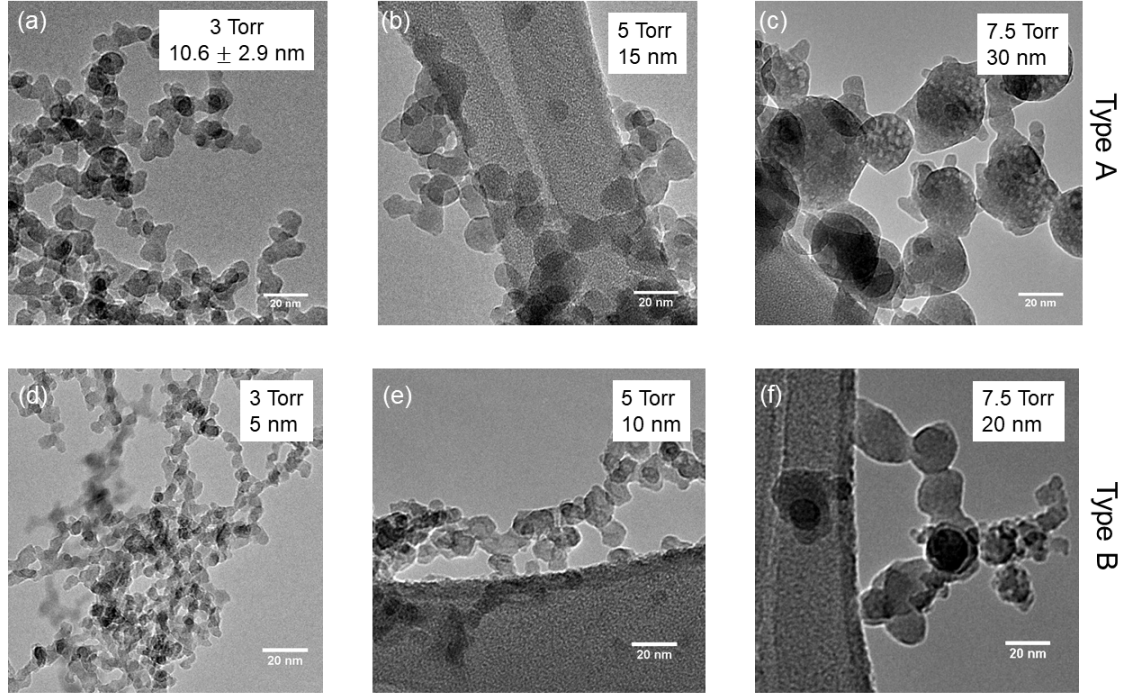


Figure A.2: (a)–(f) TEM images of AlO_x nanoparticles synthesized from type A (a)–(c) and type B (d)–(f) reactors at pressures of 3.8 Torr, 5.2 Torr and 7.5 Torr with mean sizes and standard deviations.

residence time in the plasma, allowing to tune the time of continued surface growth. TEM images of as-synthesized AlO_x nanoparticles from type A and B reactors under three sets of reactor pressures are shown in Figure A.2. At each pressure, the type B reactor produces smaller particles than the type A reactor. For both reactor configurations, the mean particle size increases with increasing pressure. At 3.8 and 5.2 Torr, AlO_x nanoparticles from both reactors are aggregated but nearly spherical in shape and have relatively narrow size distributions. At the relatively high pressure of 7.5 Torr, AlO_x nanoparticles exhibit a bimodal size distribution with both small and large irregular nanoparticles present.

We estimated the process yield of each type of reactor setup by measuring the weight of the AlO_x nanoparticle powders collected at $p = 3.8$ Torr for 10 minutes. With a fixed

substrate position, samples collected from both types of reactor setups were piles of white powders. The sample weights from type A and B reactor are 3.2 mg and 7.0 mg, respectively, which corresponds to yields of 19.2 mg/hour and 42.0 mg/hour. The current production rates are limited by the TMA and oxygen flow rates due to safety considerations.

A.2.2 AlO_x nanoparticle film characterization

We deposited AlO_x nanoparticle films by rastering a substrate beneath the reactor output orifice to study the optical properties of AlO_x nanoparticle films. The films were deposited with 240 raster passes and examined by scanning electron microscopy (SEM) and Mueller matrix measurements. The thicknesses of the AlO_x nanoparticle films were measured to be 7.1 ± 1.1 and 9.1 ± 0.9 μm for type A and type B reactors, respectively. Characteristic cross-sectional SEM images of the nanoparticle films are shown in Figure A.3

Mueller matrix measurements, which allow for the characterization of anisotropic-depolarizing samples, including cross-polarization, were performed to extract the effective (homogenized) complex permittivity of the particle films. The measurements were also used to determine the complex permittivity of the corresponding AlO_x nanoparticles. In both type A and B films, no polarization conversion from p-polarized to s-polarized or vice versa was present. The Mueller matrix data showed only noise for elements mm_{13} , mm_{31} , mm_{22} , mm_{23} , mm_{32} , mm_{41} , and mm_{42} . Furthermore, $mm_{12} = mm_{21}$. This block diagonal structure of the Mueller matrix indicates that the type A and B samples can be treated as macroscopically isotropic. Therefore, the effective permittivity of each sample can be represented by a wavelength-dependent scalar. The nanoparticle films were best homogenized using the Bruggeman mixing formula. This formula has been shown to consistently produce an effective permittivity that accurately models nanoparticle films, including anisotropic-depolarizing effects. Maxwell-Garnett and linear mixing formulas were also explored, but they less accurately modeled the measured data. The permittivity of the individual nanoparticles was modeled using Gaussian oscillators to represent amorphous phonon resonances while satisfying the Kramers-Kronig relations. For the type A film, a sample thickness of

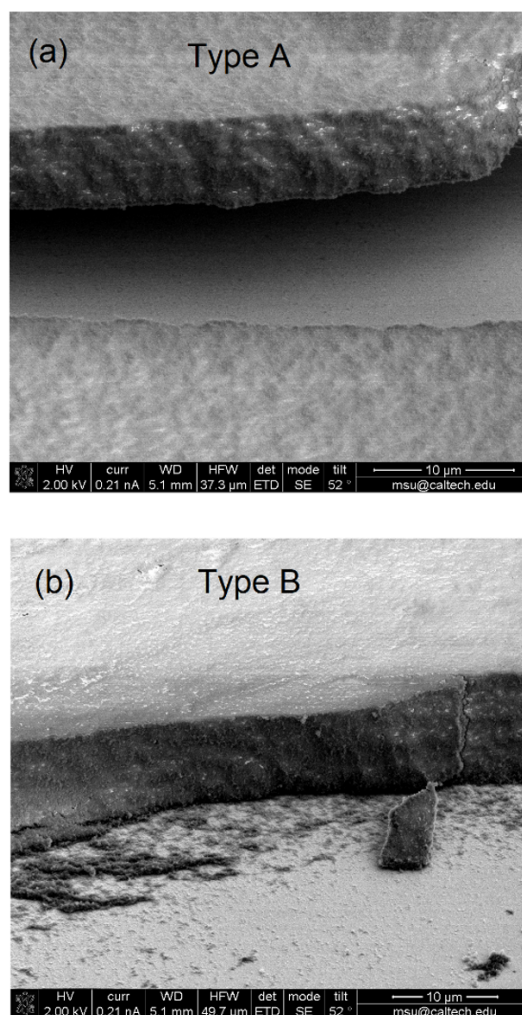


Figure A.3: Cross-sectional SEM images of AlO_x nanoparticle laminate films synthesized from type A (a) and type B reactors (b). A correction factor of $1/\cos(38^\circ)$ is applied in the y-axis to account for the tilt of the setup with respect to the SEM Everhart-Thornley detector.

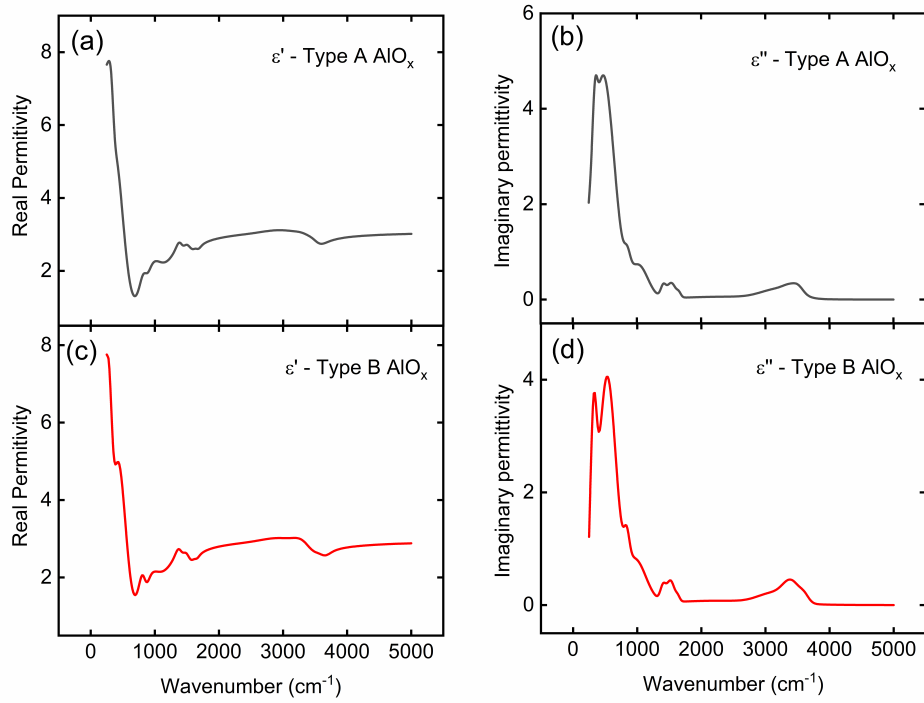


Figure A.4: Real and imaginary parts of the complex AlO_x nanoparticle films' permittivity found in the type A reactor (a,b) and type B reactor (c,d), respectively.

$7.75 \mu\text{m}$ and a particle fill fraction of 22.3% provided the best fit to the optical interference patterns in a nearly lossless region of the amorphous alumina film between 4000 and 6250 cm^{-1} . For the type B film, a thickness of $9.23 \mu\text{m}$ and a fill fraction of 19.4% provided the best fit.

Figure A.4 shows the reconstructed imaginary part of the particle permittivity. Strong oscillators in the $300\text{--}700 \text{ cm}^{-1}$ spectral range correspond to AlO_4 , AlO_5 , and AlO_6 stretching vibrational modes. These values corroborate our results from FTIR as well as the literature.^{46,47} Similar to our findings from XPS and FTIR, the reconstructed permittivity shows that the particles from both types of reactors have a similar chemical composition. The depolarization constant for type A and B reactor films was 0.261 ± 0.005 and 0.407 ± 0.006 , respectively. This indicates predominant scattering of sphere-like inclusions post deposition. All of the above characterizations reveal that particles from type A and type B

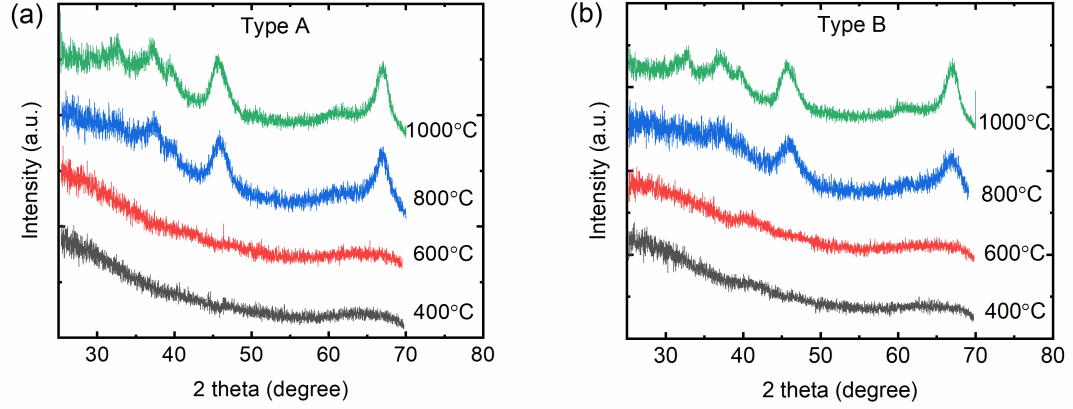


Figure A.5: XRD patterns of the post-synthesis annealed AlO_x nanoparticles from (a) type A and (b) type B reactors, with annealing temperature ranging from 400 °C to 1000 °C and annealing times of 18 h.

reactors have similar compositions but different sizes.

A.2.3 Crystallization behavior of powder samples of amorphous alumina nanoparticles

In a nonthermal plasma, crystallization of nanoparticles can occur through the heat generated by the recombination of electrons and ions on the nanoparticle surfaces.^{49,50} Here, the as-produced AlO_x nanoparticles have amorphous structures, indicating that particle heating from the nonthermal plasma is not sufficient to induce crystallization. Post-synthetic annealing of powder samples of amorphous alumina nanoparticles was explored to induce their crystallization and subsequent phase transformation to networks of crystalline alumina nanoparticles.

To study the crystallization and phase transformation behavior of powder samples of amorphous AlO_x nanoparticles, a pile of AlO_x nanoparticles was collected and annealed in a Thermo Scientific Lindberg Blue furnace at temperatures of 400–1100 °C in the atmosphere. Samples collected in this manner are expected to have porosities > 80% and consist

of loose agglomerates of nanoparticles,⁵¹ some of which may have already been formed in the gas phase before deposition. The typical temperature ramp rate was ~ 50 °C/min. Since the properties of powder samples of small AlO_x nanoparticles are of primary interest, we explored the crystallization behavior of samples synthesized at 3.8 Torr from type A and B reactors, respectively. Phase transformation of amorphous alumina typically proceeds through the amorphous-to- γ and γ -to- α phase transitions,^{52,53} or with an additional transition to the θ -phase between the transformation from the γ - to α -phase,⁵⁴ before reaching the thermodynamically stable α -phase. Our observations reveal that powder samples of AlO_x nanoparticles from both types of reactors begin to crystallize at 800 °C producing a mixture of θ - and γ -phases, as shown in Figure A.5 a and b. The crystallization temperature is consistent with that from the literature.^{9,42}

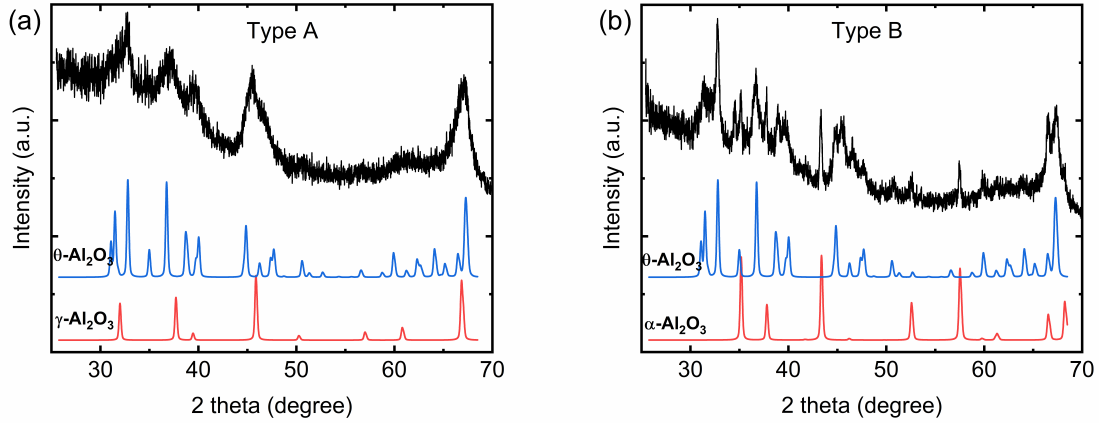


Figure A.6: XRD patterns of the post-heated AlO_x nanoparticles from (a) type A and (b) type B. Both samples were annealed at 1100 °C for 18 h. The bottom columns in both graphs show the reference profile of γ -, θ -, and α -phase aluminum oxides.

As the annealing temperature increased up to 1100 °C, we observed that the powder samples of AlO_x nanoparticles from type A and B reactors form different crystalline phases (Figure A.6). The samples of larger AlO_x nanoparticles from the type A reactor form a mixture of θ - and γ -phase at 1100 °C whereas the samples of smaller AlO_x nanoparticles from

the type B reactor form a mixture of θ - and α -phases. Time of post-synthetic annealing also affects phase transformation of the type B AlO_x nanoparticle powders. When the annealing time increased up to 40 h, type B AlO_x nanoparticle powders form particle networks of phase pure $\alpha\text{-Al}_2\text{O}_3$ nanocrystals (Figure A.7).

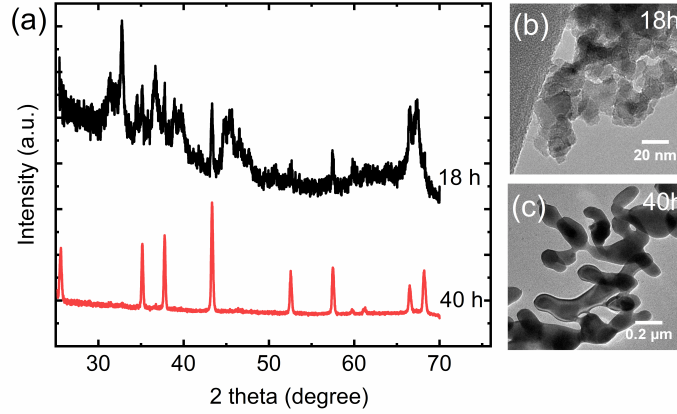


Figure A.7: (a) XRD pattern of type B AlO_x nanoparticles heated at 1100 °C for 18 h and 40h. (b) TEM images of AlO_x nanoparticles annealed at 1100 °C for 18 h and (c) AlO_x nanoparticles annealed at 1100 °C for 40 h.

This transformation is also accompanied with a significant crystal growth. Mean crystallite sizes of crystalline alumina particles after 18 h annealing were estimated using Scherrer fittings. 18 h annealing of ~ 6 nm AlO_x nanoparticle powders at 1100 °C resulted in a particle network consisting of mixture of ~ 30 nm $\theta\text{-Al}_2\text{O}_3$ and >100 nm $\alpha\text{-Al}_2\text{O}_3$ particles. Samples of phase pure $\alpha\text{-Al}_2\text{O}_3$ particles obtained after 40 h are also estimated to be comprised of nanocrystals larger than 100 nm. The crystalline grain sizes are also confirmed by TEM images (Figure A.7b and A.7c). It is interesting to observe that the powders of larger AlO_x nanoparticles from the type A reactor never exhibit $\alpha\text{-Al}_2\text{O}_3$ phase even with longer annealing times.

As the powder samples of AlO_x nanoparticles from both types of reactors have similar composition, we postulated that the difference in their phase transformation behavior is

likely due to the different sizes of their as-synthesized constituent particles. To test this assumption, we investigated the phase transformation behavior of powder samples of the large AlO_x particles with mean sizes around 11 and 15 nm synthesized in the type B reactor with higher reactor pressures. XRD patterns taken after 18 h of annealing time reveal that powders of smaller ~ 6 nm AlO_x nanoparticles form α -phase Al_2O_3 along with θ - Al_2O_3 , while powders of larger ~ 11 and ~ 15 nm AlO_x nanoparticles only forms θ - Al_2O_3 and do not exhibit any α -phase features. These observations support our assumption that powders of initially smaller size AlO_x nanoparticles have a higher tendency to transform to α -phase after annealing.

It has been pointed out that necking and densification of particles starts to occur when annealing amorphous AlO_x nanoparticles, forming nanoporous structures before crystallization.^{42,55,56} It is likely that during the annealing, the rate of densification and neck formation is faster in powder samples of smaller particles compared to larger particles, as the neck growth is dominated by mass transport and is thus enhanced in smaller size particles.⁵⁷ The fact that powder densification can be promoted by a decrease of particle sizes has also been observed in other nanoparticle systems.⁵⁸ After neck growth, the big, interconnected structures tend to transform to α -phase Al_2O_3 as temperature further increases, as it is the thermodynamically stable phase for bulk Al_2O_3 .

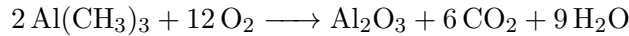
A.3 Conclusion

Amorphous alumina nanoparticles with average sizes ranging from 6 nm to 22 nm were successfully synthesized using a nonthermal plasma approach with two different reactor geometries with typical yields of 19 mg/hour and 42 mg/hour, respectively. Post-thermal annealing of both powder samples of AlO_x particles led to crystallization, forming a mixture of θ - and γ phases at 800 °C. While small powders samples of AlO_x nanoparticles with average diameters of ~ 6 nm were transformed into phase pure α - Al_2O_3 upon annealing at 1100 °C, powder samples of larger AlO_x nanoparticles never formed α - Al_2O_3 .

A.4 Experimental section

A.4.1 Nanoparticle synthesis

For the synthesis of amorphous alumina (AlO_x) nanoparticles via nonthermal plasma, trimethylaluminum (TMA) and oxygen (O_2) gas were used as precursors, with argon as the carrier gas. In the plasma region, TMA is decomposed via electron impact or radical abstraction reactions, forming reactive metal atoms or partially decomposed TMA fragments. The reactive species can subsequently react with oxygen atoms to form Al_2O_3 .⁵⁹ We considered the following chemical equation to control appropriate flow rates:



Based on the stoichiometric molar ratio of TMA and oxygen ($\text{TMA}:\text{O}_2 = 1:6$), over six times more oxygen than TMA should be fed for complete oxidation of TMA to Al_2O_3 and other reaction products (CO_2 and H_2O). We chose an excess oxygen flow rate of 6 standard cubic centimeters per minute (sccm) compared with a TMA flow rate of 0.2 sccm.

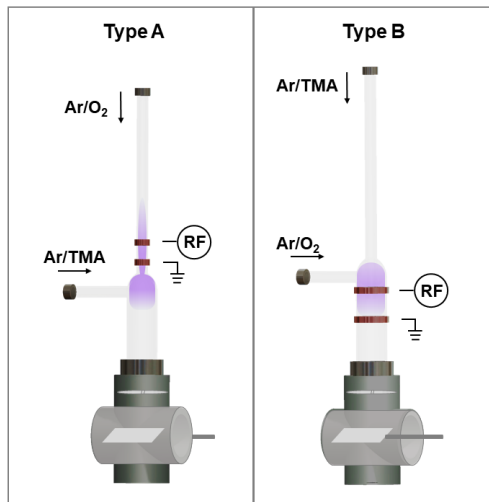


Figure A.8: Schematic of the two types of nonthermal plasma reactors used for AlO_x nanoparticle synthesis and film deposition.

A schematic of the two types of reactors used in this work is shown in Figure A.8. AlO_x nanoparticles were synthesized in a nonthermal, low pressure flow-through reactor equipped

with a 13.56 MHz radio-frequency (RF) capacitively-coupled plasma source similar to that used in our previous work.^{36,37} Because two precursors can spontaneously react with each other to produce uncontrolled products,⁶⁰ we injected both precursor species separately into the plasma for dissociation to occur in the plasma zone. There are two strategies that have been demonstrated before for the successful synthesis of metal oxide nanoparticles.^{36,37} In the first method, denoted as type A, O₂ diluted in Ar gas was injected from the top inlet of the reactor and flowed through the region where RF power was applied. Meanwhile, 0.2 sccm of TMA vapor with 6 sccm of Ar gas were injected from a sidearm tube into the downstream region of the Ar/O₂ plasma. In this afterglow zone, AlO_x nanoparticles nucleated and grew. In the second method, denoted as type B, the TMA vapor diluted in Ar was injected through an inlet tube that extended into the main reactor chamber, while O₂ gas diluted with Ar gas was passed through a sidearm tube and into the space around the upper injection tube. The ring electrodes were placed such that plasma initiated about 1 cm above the end of the top injection tube and the discharge extended downstream of the tube end in order to dissociate TMA and O₂ precursors individually before they mix in the main reactor chamber. As-synthesized AlO_x nanoparticles in both configurations were collected on silicon wafers through a slit-shaped orifice where supersonic nanoparticle impaction produced a curtain of nanoparticles traveling at high speeds.⁴² For each type of reactor, three pressure conditions were studied by using three different orifice sizes (0.3, 0.4, 0.5 mm × 8 mm) while keeping the gas flow rates constant.

A.4.2 Characterization

X-ray diffraction (XRD) was performed with a Bruker D8 Discover 2D X-ray diffractometer equipped with a Co K α radiation point source. Instrument broadening was obtained by measuring a standard LaB₆ crystal powder sample with the same scanning parameters. For XRD analysis, aluminum oxide nanoparticles were directly deposited onto Si wafers to form a pile of powder. The XRD patterns were converted to the wavelength of a Cu source ($\lambda = 1.54\text{\AA}$) for data analysis. Transmission Electron Microscope (TEM) images were taken

from a Tecnai T12 microscope with an accelerating voltage of 120 kV. Nanoparticles were either directly deposited from the gas phase or drop-cast in a methanol dispersion on holey carbon TEM grids for imaging.

Fourier-transform infrared spectroscopy (FTIR) was performed with a Bruker ALPHA FT-IR spectrometer using the attenuated total reflection (ATR) module in a nitrogen-filled glovebox. AlO_x nanoparticles were dispersed in methanol and drop-cast onto the ATR crystal. Nanoparticles were allowed to dry before taking measurements.

X-ray photoelectron spectroscopy (XPS) was performed with a PHI Versa Probe III XPS and UPS system. For XPS analysis, aluminum oxide nanoparticles were deposited onto Si wafers with 30 raster passes to form a film.

Nanoparticle laminate film thicknesses were measured empirically by cross-sectioning the nanoparticle laminate films with a Ga focused ion beam and imaging with a scanning electron microscope (FEI Nova 600 NanoLab DualBeam) at a 52° tilt. The cross-sectioning was performed in two steps: a regular cross-section (30 kV, 1 nA) approximately $2\text{ }\mu\text{m}$ in width was cut first followed by a cleaning cross-section (30 kV, 30 pA). The thickness of the cross-sections was measured with ImageJ with a correction factor of $1/\cos(38^\circ)$ in the y-axis to account for the tilt.

To analyze the film optical properties, the first four columns of the angle- and wavelength-resolved Mueller matrix were measured in the reflection mode. Mueller matrix measurements were performed using an IR-VASE Mark II ellipsometer with an AutoRetarder from the J.A. Woollam Company. The configuration was polarizer-sample-compensator-analyzer. The measurement spectral range extended from 250 to 5000 cm^{-1} with a resolution of 7.7 cm^{-1} . The angular range was 40 to 70° from the surface normal, with an angular resolution of 5° . Data was averaged over 400 measurements – 5 days of continuous measurement per sample under ambient conditions. Once the samples were measured, an oscillator model of the film permittivity was constructed using the software WVASE32 from J.A. Woollam. Model parameters such as the film thickness and particle fill fraction were initialized

based on the empirical measurement averages and constrained by 3 times the measurement standard deviations. Initial values for the particle oscillator model were taken from the literature. All model parameters were simultaneously fitted using the full angle and wavelength-resolved Mueller matrix data.

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