Advances in Silicon Nanocrystals

by

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A thesis submitted in conformity with the requirements for the degree of Doctor of Philosophy in Chemistry

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Abstract

Silicon nanocrystals (ncSi), which are considered as greener alternatives to traditional nanocrystals like CdSe and PbS, offer the benefits of being earth abundant, potentially inexpensive, purportedly less toxic and compatible with silicon electronics. The work presented in this thesis focuses on the contributions in the advances in silicon nanocrystals. This would include developing new synthesis methods for ncSi with simpler precursors and higher yields, exploring new design strategies to enhance the stability and photoluminescence (PL) absolute quantum yield (AQY) of the ncSi, and probing other surface reactions, such as the reduction of gaseous carbon dioxide by the nanosilicon surface hydrides (ncSi:H). Specifically, a batch synthesis based on the thermal solid-state disproportionation of SiO was developed. We managed to pinpoint an optimal temperature range of 850-1100 °C, in which the nucleation and growth of ncSi in a SiO₂ matrix were observed. More importantly, by implementing this synthetic route, we were able to prepare ncSi with a wider size range and observe directly the size-dependent PL AQY of these ncSi. For the first time we observed optically the both upper and lower critical size at which the quantum size effects (QSE) begin to switch on and switch off, respectively. Apart from this, a major step was taken towards the synthesis of a more stable ncSi ensemble against oxidation by capping the surface with perfluorocarbon chains. Lower rates of oxide shell forming on the ncSi surface was observed and a higher PL AQY was measured for
these ensembles. On the other hand, by utilizing the reducing ability of the ncSi surface hydrides, we were able to convert gaseous CO$_2$ selectively to CO, and the observation was unprecedented. The work presented in this thesis has pushed the boundaries of ncSi research, towards a more thorough understanding in the fundamentals and surface chemistry of ncSi.
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Chapter 1
Introduction

This chapter has been compiled using excerpts from previously published work:


(† contributed equally)

1 Introduction

1.1 Quantum Confinement in Silicon Nanostructures

1.1.1 First Light from Silicon

As early as 1950s, Haynes and Briggs had reported the existence of radiation from the recombination of electrons and holes in silicon at room temperature.\textsuperscript{1,2} The maximum intensity was found to be at 1.1 microns. They did experiments to prove that this radiation was an intrinsic property of silicon. At that time they used current pulses to generate the carriers in the immediate vicinity of the junction. They explained it was due to the indirect transition with phonon cooperation. The fact that this process must be phonon assisted determines bulk silicon is a poor light emitter.

Then everything started with Canham’s exciting discovery published in 1990 that electrochemical or chemical fabricated mesoporous silicon layers of high porosity would exhibit visible (red) and bright photoluminescence at room temperature.\textsuperscript{3} This seminal paper has now been cited more than 10,000 times.
When the silicon is made mesoporous and the pore size gets 20-500 Å, it’s essentially locally crystalline. By decreasing the spatial confinement of excitons within the nanocrystalline silicon particles, the probability of radiative recombination is increased. When excitons are confined to a dimension (or particle) that compares to its Bohr exciton radius (≈5nm for Si), they behave more like waves and their energy levels becomes quantized. With decreasing particle size, the energy gap between the ground and excited state (Eg) increases and the emission wavelength is blue-shifted. For nanocrystalline silicon, the theory that the quantum size effect gives optical transitions and then consequently visible luminescence gains support from the emission wavelength dependence on porosity. This model was later supported by the data of X-ray absorption fine structure (XAFS) spectra studied by Sham and his coworkers. It also excluded the possibility that the photoluminescence was coming from the silicon surface oxide.

1.1.2 Further Studies and Developments

Quantum size effects are known in semiconductor nanocrystals such as CdSe and PbS and have been well studied in the past two decades. The researchers are also naming these semiconductor clusters and nanocrystals as quantum dots. That opens up a whole new era with opportunities for numerous fundamental as well as applied research in this field. The possibility of tuning the emission wavelength by tuning the size of these quantum dots allows optimization and customization in various applications. For example, CdSe and PbS quantum dots based optoelectronic and biomedical devices have shown outstanding performance and great promises. Silicon nanocrystals (ncSi), which are considered as greener alternatives to traditional CdSe and PbS quantum dots containing heavy metals, offer the benefits of being earth abundant, potentially inexpensive, purportedly less toxic and compatible with silicon electronics. Compared to bulk Si crystals, nanoscale silicon crystals have new properties and functionalities and are expected to have new and exciting applications in microelectronic, photonic, photovoltaic and nanobiotech industries. The details of several examples will be given in Part 1.3.
1.2 Synthesis and Size Separation of Silicon Nanocrystals

To date a number of different methods for the synthesis of silicon nanocrystals have been developed, including top-down methods and bottom-up methods such as the sol-gel synthesis. Two examples of the top-down approaches are laser ablation and electrochemical etching. Laser ablation of Si in vacuum or in He is considered a clean technique because of less production of waste.\(^\text{17}\) Later development of laser ablation and its use has enabled a one-pot synthesis of ligand capped ncSi:R but with a low yield.\(^\text{18}\) The electrochemical etching of Si wafers with HF is the most common top-down method for preparing porous Si, which can then be deconstructed and dispersed via ultrasonication into solvents.\(^\text{19}\) However, the ncSi are polydispersed with irregular shapes and usually range in size from the micrometer to the nanometer scale.

Compared to the top-down methods, the bottom-up methods allow better control of size and shape, including oxidation/reduction reactions in solutions, pyrolysis of silane, and thermolysis of silicon suboxides. The solution reduction of halide salts (e.g., SiCl\(_4\)) is a versatile method for synthesizing freestanding ncSi:H in which the nanocrystal size can be tuned using different surfactants or reducing agents.\(^\text{20-23}\) The reaction of alkali silicides (MSi, M = Na, K or Mg) with SiCl\(_4\) has also been commonly used to synthesize freestanding ncSi with chlorine termination. The Kauzlarich group has extensively studied these solution phase routes.\(^\text{24,25}\) In one case, magnesium silicide was oxidized with bromine and the ncSi was subsequently terminated by means of alkyllithium reagents.\(^\text{26}\) The solution phase PL of the synthesized ncSi was usually within the UV region. The gas phase pyrolysis of silane precursors have been reported using several methods including thermal decomposition in flow reactors\(^\text{27}\), through irradiation with laser light,\(^\text{28}\) and through microwave plasma.\(^\text{29}\) The non-thermal plasma method which uses unconventional heating through electron-ion recombination, was reported to form non-agglomerated ncSi with high yields.\(^\text{30}\) Finally, the thermolysis of silicon sub-oxide is a feasible route to prepare silicon nanodomains in SiO\(_2\), where the size of ncSi mainly depends on the heating temperature and time. The high temperature thermal treatment of commercially available hydrogen silsesquioxane (HSQ)\(^\text{31}\) or sol-gel polymers derived from trichlorosilane (HSiCl\(_3\))\(^\text{32}\) produces ncSi embedded in SiO\(_2\), which can subsequently be liberated as ncSi:H with HF etching. HSQ was originally introduced by the Veinot group in 2006.\(^\text{33}\) The Veinot group also pioneered in the surface functionalization of silicon nanocrystals and investigated the properties (such as optical) of silicon nanocrystals of different sizes and terminal groups.\(^\text{34-36}\)
The work presented in Chapter 3 mainly follows the route from HSiCl₃. The general route is illustrated in Figure 1.

Recently, we developed a new synthesis method based on the commercially available SiO powder. We observed the nucleation and growth of silicon nanocrystals from SiO and optimized the reaction conditions. *The work presented in Chapter 2 and Chapter 4 mainly follows the route from SiO.*

![Figure 1. Illustration of the sol-gel synthesis using precursor HSiCl₃.](image)

A problem that has always impeded research and development on silicon nanocrystals since their discovery around 30 years ago, when Canham discovered that silicon becomes brightly fluorescent when made nanoporous, has been their poly-disperse nature. Even though the average size can be usually varied via tuning the synthesis conditions, within the same batch the deviation in particle size can still be large. Recently this situation has improved a lot with the discovery of various means of separating silicon nanocrystal poly-dispersions into mono-dispersions with a much narrower size distribution. This breakthrough facilitates more precise size tuning than simply modifying the synthesis parameters and has enabled more in-depth studies of their size dependent chemical, physical and biological properties.
Conventional chromatography is one approach that has been used for size separation of ncSi, but the separation is still coarse, resulting in broad size distribution in each fraction. Today the two common methods are density gradient ultracentrifugation (DGU) and size-selective precipitation (SSP).

Density gradient ultracentrifugation (DGU) was originally used as a size-separation technique in the field of biochemistry since the 1950s. DGU has been demonstrated as a promising technique to separate single wall carbon nanotubes (SWNTs) by diameter. The criteria for successful separations using DGU is that the materials to be separated must have different effective densities that fall within the density extrema of the gradient medium. Because there is a difference between the density of the silicon core (bulk 2.329 g/cm$^3$) and the density of organic ligands on the surface (generally less than 1 g/cm$^3$), as the surface area to volume ratio decreases for particles of increasing size, the effective density will vary, enabling surface functionalized ncSi to be separated by this method. DGU to generate size-separated fractions of ncSi capped with decyl group (ncSi:C$_{10}$) has been described by our group.

Briefly, ncSi:C$_{10}$ was placed on top of 2,4,6-tribromotoluene (TBT) in chlorobenzene (the density gradient medium), and centrifuged for 18-20h with acceleration of ~103,000g and ~140,000g at the middle and bottom of the centrifuge tube. Fractions of about 150 μL, collected by carefully puncturing the tube at the top and bottom, yielded uniform size distributions, confirmed by high resolution transmission electron microscopy (HRTEM).

Size-selective precipitation (SSP) does not need the ultracentrifugation instrumentation. The processing is easy but needs a lot of repetitive experimentation. It is a technique commonly used to purify and narrow the size-distribution of nanomaterials, requiring sequential addition of an antisolvent into the colloidal dispersion of nanomaterials. For a system where the nanocrystals are capped with organic ligands, the addition of a polar solvent as the antisolvent into the original organic solvent will disrupt the solvation of the nanocrystals. Larger particles with the smaller surface to volume ratio and higher surface ligand density tend to aggregate and precipitate first, as the attractive van der Waals potential dominates. Again a specific case has been reported by our group, where ncSi were made colloidally stable in toluene with capping with allylbenzene, denoted ncSi:AB. Methanol was repeatedly added into the supernatant as the antisolvent, and precipitates were collected after centrifugation. The PL of the resultant fractions monotonically shifted with ncSi size and the PL absolute quantum yield (AQY) could be
evaluated as a function of size. The work presented in Chapter 2 in this thesis uses SSP as one of the key techniques.

1.3 Applications of Silicon Nanocrystals

The burgeoning research activity on new kinds of nanostructured silicon, made from one of the most abundant and green materials on earth, is striking. This activity transcends the utilization of top-down nanofabricated silicon for integration in the incredible shrinking world of more powerful and faster microelectronics. What is remarkable is the notable intensification of research on bottom-up synthesized forms of nanostructured silicon for everything other than microelectronics. Nanometer scale silicon materials and structures fashioned into almost every conceivable size and shape, chemically functionalized surface and overall form, are beginning to play a prominent role in the assembly of chemical and biological sensors, fluidic field effect transistors and flow monitors, printed-ink backplane thin film transistors, thermoelectric membranes, computer memories, radio frequency identification tags, proton conducting membranes for hydrogen-oxygen fuel cells, high capacity lithium ion battery anodes, solar fuels photo-catalysts, solar cells, solid state lighting, optical interconnects, ultrahigh frequency oscillators, photonic crystal optical cavities and waveguides, electronic eyes, bio-inspired self-cleaning anti-reflection coatings, nutrients in functional foods and beverages to enhance bone health, biodegradable luminescent porous drug delivery systems, immuno-fluorescent cellular imaging, and biocompatible implantable medical devices. Moreover, the purported non-toxicity and biocompatibility of nanometer scale silicon allows it to be marketed as a “Green” material in the emerging field of medical theranostics. This overly long list just highlights a few prominent reports for nanometer scale silicon that one can easily search in the recent literature.

In this introduction to the applications of silicon nanocrystals one major field would be highlighted – silicon nanocrystals based biological in vivo applications. The work presented in Chapter 3 in this thesis is directly related to this topic, since that project was designed to tackle one of the major issues in the field – enhance the stability against irreversible oxidation with the presence of water.
Semiconductor nanomaterials show great promise for use in in-vivo targeting, probing, and imaging applications. Traditionally used fluorescent labels include the commonly seen organic dyes. However, they can easily undergo irreversible photoinduced reactions such as photooxidation and lose their optical activity, which is known as photobleaching. One advantage of semiconductor nanomaterials (such as CdSe quantum dots) over the traditional organic dyes as fluorescent probes is their resistance to photobleaching. Another important characteristic of these quantum dots (e.g., CdSe) is their longer fluorescence lifetime so that their emission is slow enough for time-resolved fluorescence bioimaging to eliminate the interference of autofluorescence signal from the samples themselves. However, while these quantum dots have excellent optical properties in terms of performance and lifetime, their toxicity remains a concern to the research community, especially when they are used for biological testing, or considered for industrial scaling. In contrast, the purported non-toxicity and biocompatibility of nanometer scale silicon allows it to be considered as a green material in the emerging fields of biological applications. Before applied to biological systems researchers have been investigating the stability of silicon nanoparticles. Swihart and coworkers demonstrated that with surface treatment by silanization, the photoluminescent properties were significantly stabilized against degradation. Kauzlarich and coworkers also employed the method of silanization to enhance the photochemical stability of silicon nanoparticles in organic solvents. Compared to common fluorophores these silicon nanoparticles did not shown any significant photobleaching over 4000s. Then hydrosilylation was used by many to modify the silicon nanoparticle surface to reach water solubility and biocompatibility.

Silicon nanostructure based biosensing dates back to the late 1990s when Sailor, Ghadiri and their coworkers developed a porous silicon based optical interferometric biosensor. In the late 2000s Sailor group moved am important step forward into the field of porous silicon nanoparticles for in vivo applications. They demonstrated tumor imaging using dextran-coated porous silicon nanoparticles. In the early 2010s, He and coworkers reported a large-scale synthesis of biocompatible fluorescent silicon nanocrystals used as photostable biological probes. Their facile and rapid synthesis required no tedious and complicated manipulation or harsh conditions. And the products of the aqueous synthesis route were proved to be biocompatible. They also reported a microwave-assisted synthesis of silicon nanocrystals by breaking up silicon nanowires. These
silicon nanocrystals were then grafted with a typical protein, immunoglobulin G, under mild microwave heating. The protein served as a hydrophilic ligand in this case. And more importantly, the as-prepared silicon nanocrystals have strong fluorescence and were biocompatible and stable under tested conditions. It was also demonstrated that they can be directly utilized for immunofluorescent cellular targeting without requiring additional complicated bioconjugation, promising a bright future for high-performance biological probing in various biosensing and bioimaging applications.

1.4 Summary of Chapters

Chapter 2 describes an in-depth investigation of the size-dependent photoluminescent absolute quantum yield of silicon nanocrystals produced from SiO and subsequent hydrosilylation, from synthesis to characterization and finally the discussions on the factors which contribute to the phenomenon of the switching-on and switching-off of quantum size effects.

Chapter 3 presents the synthesis of colloidally-stable, brightly-luminescent perfluorodecyl-capped silicon nanocrystals and how they performed better compared to the perhydrodecyl-capped analogues in terms of photoluminescent properties and stability against oxidation in various conditions.

Chapter 4 outlines the details of the unprecedented observation that CO$_2$ can be reduced to CO by hydride terminated silicon nanocrystals in the gas phase.

Chapter 5 summarizes the results presented in this thesis and proposes some related future work that may help deepen the understanding in fundamentals of silicon nanocrystals.
Chapter 2
Quantum Size Effects in Silicon Nanocrystals Reexamined

This chapter has been compiled using excerpts from previously published work:

(† contributed equally)

Contribution: I conceived and designed the experiments with W.S. I carried out the synthesis of the materials and performed most of the materials characterizations with W.S. L.W. and M.W. also helped in synthesis and characterizations. G.C. conducted the microscopic analysis. M.L.M. and J.B. were involved in some useful discussions. G.A.O. supervised the project. I interpreted the data with W.S., plotted the graphs, and wrote part of the manuscript. All the authors approved the manuscript.

2 Quantum Size Effects in Silicon Nanocrystals Reexamined

2.1 Previous Reports on the Size-Dependent Absolute Quantum Yield of Silicon Nanocrystals

The photoluminescence (PL) peak wavelength is expected to monotonically blue-shift as the size of the silicon nanocrystals (ncSi) decreases, but up to the present time, researchers have observed opposing trends of quantum yield (QY) versus size. For example, Kortshagen’s group\textsuperscript{83} and Ozin’s group\textsuperscript{40} found that the initially high QY of silicon nanocrystals monotonically dropped down as the size decreased, while Korgel’s group\textsuperscript{84} found that the QY increased from a very low value to a slightly higher value as the size decreased. The origin of this discrepancy remains unanswered.

Herein we designed and implemented an experiment to resolve this dichotomy. It permits for the first time a direct measurement of the size at which observable QSE begin to switch-on and
switch-off in silicon nanocrystals, thereby unraveling the mystery mentioned above. It is founded upon the synthesis, size separation and determination of the size dependent PL absolute quantum yield (AQY) of silicon nanocrystals with dimensions in the range of 2-7 nm using SiO as the precursor. The detailed experimental and characterization techniques are described in Appendix A. This study provided a unique insight into the optimum PL efficiency versus emission wavelength, as well as guidance on the tuning of size distributions through the choice of the synthetic conditions to target a specific range of PL wavelengths.

Bulk silicon is an indirect bandgap semiconductor, and nearly non-emissive in the near infrared (NIR) spectral region in the vicinity of its electronic bandgap, unless special materials engineering approaches are applied to increase the probability of escape for photons and suppress surface recombination. By contrast, we have discovered that when the size of silicon decreases, observable PL in silicon nanocrystals emerges, monotonically blue shifts with decreasing size, and the AQY monotonically increases, reaches a maximum and monotonically decreases thereafter to disappearance. These observations allow one to experimentally define the regime in which detectable QSE emerge. Moreover, the observed “volcano” plot of AQY versus size described herein provides a unique insight into the effects that contribute to competitive electron-hole radiative relaxation and non-radiative recombination processes in silicon nanocrystals on passing from a region of weak to strong quantum confinement.

2.2 Preparation of Size-Separated Silicon Nanocrystals

2.2.1 Nucleation and Growth of Silicon Nanocrystals in SiO Powder

Solid SiO (purchased from Sigma-Aldrich, -325 mesh powder) was placed in a quartz reaction boat and transferred to a tube furnace. The samples were typically heated at a rate of 18 °C/min under a flow of 95% Ar/5% H₂ to a peak processing temperature between 850 °C and 1100 °C, then held at that temperature for 1 h before the furnace was allowed to cool to room temperature. For the processing temperature of 920 °C and 925 °C in the optimum PL study, the holding times were 35 min and 30 min respectively instead of 1 h. For a typical batch synthesis, 0.3 g of thermally treated SiO powder was transferred to a Teflon beaker containing a mixture of 10 ml of 95% ethanol (aq. Sigma Aldrich) and 20 ml of 48% HF (aq. Caledon). Personnel should be
well trained in the handling of HF. The mixture was stirred for at least 1 h 30 min to fully etch away the silicon oxide matrix. The hydride-terminated ncSi were then extracted from the aqueous solution into 20 mL 1-decene (Sigma Aldrich, 94%) for surface functionalization by hydrosilylation. The scale of the batch could be enlarged as long as the volume of the beakers and flasks are sufficient for safe handling of chemicals, for example, starting with 2 g of SiO powder instead of 0.3 g.

Silicon monoxide (SiO) has a nearly 1:1 macroscopic stoichiometry ratio, but is not a single phase material comprising only Si(II). Amorphous SiO contains extremely small amorphous Si(0) clusters and amorphous SiO₂ clusters with angstrom-scale sizes, as well as significant amounts of interface silicon sub-oxide regions with variable Si oxidation states between (0-IV). Upon heating, the amorphous Si crystallizes, and grows by accreting the Si(0) from disproportionation of the surrounding sub-oxide portions. The composition and structure of commercially available SiO from different suppliers might slightly vary, but here we use a powder product, which appears amorphous initially before heating, confirmed by Powder X-ray diffraction (PXRD) in Figure 2. The size of the ncSi formed in the temperature range 875-1100 °C, estimated by inserting PXRD line widths into the Scherrer line broadening equation are plotted in Figure 3a together with the extracted silicon diamondoid lattice unit cell dimensions obtained from the Si (111) diffraction peak, which are graphed in Figure 3b. In comparison, the lattice parameter for bulk Si is 5.431 Å.
The progress of the crystallization and growth of the as-supplied SiO, can be conveniently monitored and analyzed by employing ex situ variable temperature PXRD. This method defines the nucleation temperature for the observation of ncSi in a SiO$_2$ matrix to begin around 875 °C. From 900 °C to 1100 °C the Scherrer equation shows that the size of ncSi monotonically increases, accompanied by a corresponding increase in the cubic unit cell dimension. The former effect is expected for a growth process whereby a ncSi seed crystallizes and gradually accretes increasing amounts of Si atoms generated from SiO disproportionation at higher temperatures. The latter phenomenon is anticipated from the decreasing S/V ratio of ncSi as its size increases, reducing the number of lower coordination number surface sites with a shorter bond length relative to the number of higher coordination sites in the core.
Figure 3. Plot of ncSi (a) size and (b) unit cell dimension determined by fitting the Si (111) diffraction peak.

As the broad diffraction peak at ~21 degrees seemed slightly shifted to lower angles as the heating temperature was elevated,\textsuperscript{88} approaching the position for amorphous SiO\textsubscript{2}, the redistribution of the structure towards ncSi in SiO\textsubscript{2} matrix is conceivable. Therefore, we investigated the characteristic peak assigned to Si-O-Si in the IR spectra, which reflects the bond angle information.

As can be seen in Figure 4 as the temperature increases, the Si-O-Si stretching mode appeared sharper and the peak center shifted to higher wavenumbers, from 1028 cm\textsuperscript{-1} for the unheated sample to 1098 cm\textsuperscript{-1} for a sample thermally processed at 1100 °C. The position of the peak has
been correlated with the angle $2\theta$ between the two Si atoms separated by a bridging O atom in Fitch’s work: $^89\nu = \nu_0 \sin \theta$

![ATR-FTIR spectra of SiO thermally processed at different temperatures.](image)

where $\nu_0$ was 1116.5 cm$^{-1}$ when $\theta$ was 75° for a SiO$_2$ grown at 1150 °C in this work. The blue shifting and sharpening of the Si-O-Si stretching frequency observed during the disproportionation SiO $\rightarrow$ Si + SiO$_2$ reaction indicates the formation of a more well-defined SiO$_2$ phase$^{90,91}$ from a poorly ordered SiO phase with a range of Si-O-Si bond angles.$^{92}$ With the change of the structure, we also observed an accompanying colour change of the matrix from reddish-brown to dark brown, which is manifest as changes in the reflectance spectra especially at longer wavelengths that begins above 850 °C, and plateaus above 950 °C, as shown in Figure 5.
2.2.2 Size Separation of the Silicon Nanocrystal Ensembles

To enhance the credibility of our data on the size-dependent photoluminescence properties, we performed size separation to several ensemble dispersions obtained from SiO processed at different temperatures using the size selective precipitation (SSP) method.

The SSP procedure has been described in the previous work done by our group. Briefly, methanol:ethanol 2:3 (v/v) as anti-solvent was added dropwise into 10 ml clear dispersion until it just turned turbid, and then the dispersion was centrifuged for 10 min at 6461g. The solid precipitated was dried in air and redispersed in hexane for decyl-capped ncSi, while the process was repeated with the supernatant. For larger fraction numbers, more anti-solvent and longer centrifuge time were required.
2.3 Reexamining the Size-Dependent Absolute Quantum Yield: Results

The thermally generated ncSi made from SiO can subsequently be liberated from the SiO$_2$ matrix as the hydride-capped silicon nanocrystals (ncSi:H) by etching in dilute hydrofluoric acid (HF).$^{32,38}$ The insoluble ncSi:H can then be made soluble by hydrosilylation of the surface Si-H bonds with terminal olefins to form organic-capped silicon nanocrystals (ncSi:R). Organic-capping groups with hydrophobic termini provide solubility to ncSi:R in non-polar solvents,$^{74}$ while ncSi:R with hydrophilic termini dissolve in polar solvents.$^{74}$

The amorphous SiO used in this study is commercially available in bulk quantities and only shows crystallized Si upon heating. This approach not only affords a viable strategy for synthesizing large amounts of ncSi:R but also provides in a single batch preparation of the entire size range required for addressing the main questions raised in this study. These include, (i) when do observable QSE switch-on to render Si an efficient light emitter, and (ii) when does the increasing rate of non-radiative recombination dominate over that of radiative relaxation?

Atomic resolution images define the crystalline nature of the lattice of the colloidally stable ncSi capped with decyl groups (ncSi:C$_{10}$, IR spectrum shown in Figure 6)$^{94}$ and an analysis of a statistically meaningful population of ncSi provides a histogram of the size distribution measured in bright-field images, a representative case being shown in Figure 7a.
Figure 6. FTIR spectra of the ncSi before (ncSi:H) and after capping with 1-decene (ncSi:C_{10}).
Figure 7. (a) BF STEM image of ncSi:C \textsubscript{10} produced by 1h 50 minute aqueous HF etching from SiO heated at 900\degree C. Some ncSi with Si lattice fringes are circled. (b) Histogram of the core size distribution of ncSi.

Counts: 137
Mean: 3.5 nm
Std dev: 1.2 nm
The red-shifting of the optical absorption edge in UV-Vis spectra (Figure 8) and the wavelength of emission in photoluminescence spectra (PL) (Figure 9) confirm the sizes of the ncSi:C$_{10}$ ensemble, produced from the ncSi formed by thermal treatment of SiO at 900 °C. These ncSi:C$_{10}$ samples are larger than those with visible PL emission we previously synthesized and reported using HSiO$_{1.5}$ as precursor heated at 1100 °C.$^{94}$

![Normalized UV-Vis absorption spectra of the ncSi:C$_{10}$ colloidal dispersions in chloroform produced from thermally annealed (HSiO$_{1.5}$)$_n$ (brown powder) and SiO as the precursors.](image)

Figure 8. Normalized UV-Vis absorption spectra of the ncSi:C$_{10}$ colloidal dispersions in chloroform produced from thermally annealed (HSiO$_{1.5}$)$_n$ (brown powder) and SiO as the precursors.

The ncSi:C$_{10}$ with a PL wavelength around 834 nm, corresponds to an average size of 3.5-4.0 nm$^{95}$ with an associated AQY of 13.7% determined by Kortshagen’s method$^{96}$ and 12.0% determined by Friend’s method$^{97}$. 
The size-selective precipitation (SSP) technique was successfully employed to separate the as-synthesized ncSi:C\textsubscript{10} polydispersion into more monodispersed fractions with different mean sizes. Figure 10a shows several PL spectra of representative size-sorted fractions of ncSi:C\textsubscript{10} normalized to the intensity of the excitation light source. All the spectra are within our photodetector’s range and interesting variations in PL peak wavelength and intensity are both observed.
Figure 10. (a) PL spectra of representative ncSi:C_{10} fractions #2, 4, 6, 8, 10. (b) PL wavelength maxima for size-sorted ncSi:C_{10} fractions, and the fractions for size measurement are marked in red. (c) Correspondence between the measured size and the volume of anti-solvent used in the SSP method. (d) AQY versus volume of anti-solvent used which corresponds to the size of ncSi:C_{10} shown in the inset.
The PL wavelength maximum blue-shifted monotonically from ~900 nm to ~740 nm, Figure 10b, consistent with the QSE expected on decreasing the size of the ncSi:C\textsubscript{10} from the largest to the smallest. For the first 6 fractions, both the PL peak position and the size versus the volume of the anti-solvent used for SSP displayed approximately linear behavior, while the rest of the fractions contain very small ncSi which were particularly insusceptible to precipitation, requiring increasingly more anti-solvent. Of special interest is the a monotonic trend observed for the AQY, which switches on from the lowest detectable value for ncSi:C\textsubscript{10} around 5 nm, increases monotonically to reach a maximum around 3.9 nm and then decreases monotonically to the smallest studied below 3 nm, Figure 10c and d.

2.4 Towards a Better Understanding in Switching-On Quantum Size Effects in Silicon Nanocrystals: Discussions

In this study we have discovered that the temperature controlled thermally treated commercially available SiO, followed by aqueous HF extraction to form ncSi:H and hydrosilylation with 1-decene to make ncSi:C\textsubscript{10}, is a facile and practical synthetic pathway for making gram scale batches of decyl-capped hexane-soluble silicon nanocrystals. The size-distribution is sufficiently broad to permit size-separation of ncSi:C\textsubscript{10} into fractions in the size range 2-7 nm which allows the observation of size-dependent QSE on the PL spectra and AQY in the NIR wavelength range just below the bandgap of bulk Si, Figure 10.

Pertinent to the main question posed in this study is the observed ‘volcano’ plot of the PL AQY of ncSi:C\textsubscript{10} as a function of size. It can be discerned that PL appears to switch-on with a measurable AQY of 4-5% for ncSi:C\textsubscript{10} sizes around 5 nm which emit around 900 nm. With diminishing size of ncSi:C\textsubscript{10} the AQY begins around 5%, continues to rise to about 20% for the 3.9-3.7 nm fraction and thereafter gradually falls to approximately 5% for the smallest fraction with a barely discernible PL peak profile.

To understand the origin of this ‘volcano’ like behavior of the size dependent PL AQY of ncSi:C\textsubscript{10} displayed in Figure 10, one has to consider how radiative and non-radiative contributions to photo-excited electron-hole recombination emission are affected by the size of the ncSi:C\textsubscript{10}. In an earlier study from our laboratory\textsuperscript{40} that focused on size separated ncSi:AB
with smaller sizes below 2 nm and allylbenzene capping groups, PL was observed in the visible spectral range and showed a trend of monotonically diminishing AQY, which tended to fade away around a nanocrystal size of 1 nm. This corresponds well with the decreasing trend of the smaller-size side of the ‘volcano’ plot, explained in terms of increasing contributions of organic-capping group vibrations and defects which favored non-radiative recombination.

An earlier paper reported that the NIR PL QYs for silicon nanocrystals monotonically increased from a very low value of 0.4% to a higher value of 8.0% in the size range 12.8 to 3.1 nm (determined from TEM results). This corresponds well with the trend of the larger-size side of the “volcano” plot (larger than ~3.4 nm in our case), where the increasing spatial confinement of photo-generated electron-hole pairs enhances radiative recombination, and the decreasing nanocrystal volume favors the escape of photons. This study notably employed relative rather than absolute PL QYs and applied them to as-synthesized silicon nanocrystal polydispersions with polydispersity in the range 18-33% rather than monodispersions. It is likely that the large breadth of the silicon nanocrystal size distribution and the use of relative rather than absolute PL QY in this study together resulted in the observation of the very weak QY value for ncSi larger than 5 nm.

Both the earlier works mentioned above were unable to determine when the antagonistic effects of radiative and non-radiative electron-hole recombination counterbalance each other, a key question that we have been able to answer in our investigation of size-separated silicon nanocrystals.

To further confirm the credibility of this volcano-shaped plot, we also performed size separation to several ensemble dispersions obtained from SiO processed at different temperatures using the size selective precipitation method. In the top plot of Figure 11 it can be seen from the right to the left that the PL wavelength maximum of ncSi:C\textsubscript{10} blue-shifted monotonically from ~900 nm to ~740 nm, consistent with the quantum size effect (QSE) expected on decreasing the size of ncSi:C\textsubscript{10} from the largest to the smallest. Since the measurements were conducted at room temperature and the ncSi are freestanding, temperature and interface effects are excluded. Of special interest is the amonotonic trend observed for the AQY, which switches on from essentially zero for ncSi:C\textsubscript{10} at the wavelength of ~900 nm, corresponding to the size around 5
nm, increases monotonically to reach a maximum around 820 nm and then decreases monotonically to the smallest studied approaching 725 nm, with a value again close to zero.

![Diagram showing absolute quantum yield of photoluminescence as a function of peak center wavelength.](image)

Figure 11. Absolute quantum yield of photoluminescence as a function of peak center wavelength. The SiO powder was processed at 900, 920, 925 °C for 1 h, 35 min, and 30 min, and etched for 2 h 50 min, 2 h 50 min, and 2 h 30 min, respectively. The dashed column indicates the samples where the absolute quantum yield was maximum.

The volcano tops at 820-830 nm in Figure 11 effectively pinpoints where the opposing factors of radiative recombination and non-radiative recombination balance each other. Although the ncSi were produced under different conditions, the position of the maximum in the volcano-shaped plots are very close, thus confirming the credibility of such behaviour, excluding the possibility of artefacts originated from a specific synthetic condition. Therefore, at this wavelength, the PL
of ncSi is most efficient. However, the most complete profile of the volcano-shaped plot was only observed for the ncSi from the SiO processed at 900 °C. The temperature of 920 °C and 925 °C only yielded part of the volcano-shape, without showing the point where the AQY switched on. Therefore, the optimum processing temperature to produce colloidally-stable ncSi with PL spanning the whole efficient luminescence wavelength range should be exactly 900 °C. Nevertheless, if one aims at obtaining PL within the NIR range, 920 °C could be optimum, as shown in Figure 12, in which the most concentrated fractions exhibit longer PL emission wavelength over 800 nm, corresponding with the results in Figure 11.

![Concentrated](image)

Figure 12. Photos of size separated ncSi:C₁₀ fractions under room light (upper) and under UV light (lower).

### 2.5 Summary

It is claimed that around 5 nm, the size of the Bohr exciton in bulk silicon, QSE emerge, however no optical measurement of the transition from bulk to quantum confined silicon has
been reported. Herein it is found that the size-dependence of the absolute luminescence quantum yield of size-separated organic-capped silicon nanocrystals (ncSi:R) reveals a ‘volcano’ behavior, which switches on around 5 nm, peaks near 3.7-3.9 nm and monotonically decreases thereafter. These three regions of the volcano plot respectively define the (i) transition from bulk non-emissive silicon to quantum confined emissive silicon, (ii) increasing spatial confinement of electron-hole pairs enhancing radiative recombination, and (iii) increasing contributions of organic-capping group vibrations and defects favoring non-radiative recombination. Possible future work would include exploring the effect of changing the capping ligand vibrations.
Chapter 3
Non-wettable and Oxidation-Stable Silicon Nanocrystal Film

This chapter has been compiled using excerpts from previously published work:


Contributions: I conceived and designed the experiments. I carried out the synthesis of the materials and performed most of the materials characterizations with some help from W.S. and L.W. K.L. performed the XPS test. J.J., C.C. and G.C. helped with the microscopy. Water contact angle measurement would be impossible without the help of B.D.H. and his setup. M.K. and C.M.Y. conducted the AFM imaging and helped in analyzing the data. W.W. and M.L.M. provoked some useful discussions. G.A.O. supervised the project. I interpreted the data, plotted the graphs, and wrote the paper. All the authors discussed the results and commented on the manuscript.

3 Non-wettable and Oxidation-Stable Silicon Nanocrystal Film

3.1 Background: Surface Chemistry of Silicon Nanocrystals

The size, shape, surface and defects in nanomaterials are the key factors in determining their physical, chemical and biological properties. The work presented in the last chapter mainly focuses on the size-dependent properties (PL AQY) and this chapter would continue and cover the other half of the story about the ncSi surface. In the case of ncSi, the surface capping groups do play an important role. They serve as a chemist’s toolbox to finely tune the nanosilicon-based materials’ properties, for example, the electrical and optical properties, and ultimately, to achieve his goal – certain desired functions and utilities.
3.1.1 Hydrosilylation of Silicon Nanocrystals

As commonly seen in the sol-gel synthesis of ncSi, upon the liberation of ncSi from the oxide matrix by HF etching, they are capped by surface hydrides (represented as ncSi:H). Those ncSi:H are easily oxidized and due to weak interactions with the solvent molecules, they tend to aggregate, which results in poor colloidal stability. Meanwhile these surface hydride groups are well-known platforms for chemically anchoring organic capping ligands to ncSi in a convenient and efficient way. Various methods have been developed, including halide substitution reactions,\textsuperscript{25,98} alkoxy-functionalization of the silicon surface,\textsuperscript{99} and the classical hydrosilylation reactions with terminal alkene or alkyne ligands.\textsuperscript{74,100,101} Among them, classical hydrosilylation reactions (thermal, photochemical, or metal catalyzed) are still regarded as the most facile routes. The original work presented in this thesis has mainly made use of thermal hydrosilylation reactions (via either traditional heating or microwave heating).

After hydrosilylation, the ncSi surface is covalently bonded with organic capping groups. The surface Si-C bonds are strong and this surface passivation allows minimal oxidation of the silicon surface.\textsuperscript{102} Of equal importance is the fact that the surface passivation made colloidal stability of the dispersion possible. This allows for solution processing in different film fabrication techniques (e.g., spin-coating, dip-coating and drop-casting) for state-of-the-art device applications.

Nearly two decades has passed since the first few studies of the hydrosilylation reaction on ncSi or pSi surface were reported. The mechanism and kinetics have been investigated by Huck, Buriak\textsuperscript{103} and then by us\textsuperscript{94} recently. Hydrosilylation of silicon nanocrystals with terminal alkenes in the liquid phase usually requires a reaction temperature above 150 °C, if without catalysts. In our paper, we presented the results of performing hydrosilylation reactions in a microwave reactor as an alternative to the traditional thermal hydrosilylation in a heating medium such as oil baths. In the literature of organic synthesis, hydrosilylation using microwave heating has been reported to have higher rates than the traditional oil bath heating. However, on the contrary, our results show little difference between these two heating methods. We were also able to elucidate the mechanism of the hydrosilylation reaction studied in our system (ncSi:H with 1-decene), which is depicted in Figure 13. This agrees with the currently well-accepted mechanism.
Nevertheless, the seemingly perfect means of hydrosilylation for surface passivation has two intrinsic problems.

First of all, the vibrational modes of the chemically anchored long organic ligands would open pathways for non-radiative vibrational relaxations. This phenomenon is known in other quantum dot systems as well. According to a study by Guyot-Sionnest et al, in CdSe nanocrystals, the energy transfer to the ligand vibrations may be sufficiently effective to account for the intraband relaxation rate. Different ligands would have different effects on the intraband relaxation rates. Recently it has been reported that a side reaction of oligomerization of ligands would take place at the nanocrystals surface during a thermal hydrosilylation. It is also conceivable that the chain length of the ligand could play a role in effecting the rates of non-radiative vibrational relaxations, assuming that ligand density remains comparably constant on the silicon surface. Collectively, with these factors, we anticipate that upon surface passivation by organic ligands, the PL AQY would decrease due to new pathways for non-radiative vibrational relaxations.

Secondly, it is difficult to fully cap the surface by the organic olefins to achieve a 100% coverage. Though some studies have claimed that it is possible to synthesize batches of ncSi with oxide-free surface, it is well recognized that the remaining surface hydrides that are not consumed in the process of hydrosilylation are susceptible to further oxidation in the later storage of the sample, either in solution or in solid state. A recent study performed by our group has investigated in detail the chemical reactivity of allylbenzene-capped silicon.
nanocrystals (ncSi:AB) with oxygen and water. It was made clear that both O\textsubscript{2} and H\textsubscript{2}O and mixtures thereof can oxidize the silicon core in ncSi:AB. And the exposure in O\textsubscript{2}, H\textsubscript{2}O and their mixtures irreversibly changed the photoluminescence properties. For example, O\textsubscript{2} would quench and blue shift the PL. AQY would drop drastically accordingly.

Details about the oxidation of a silicon surface will be discussed in the next part (3.1.2) and details about hydrosilylation reaction used in this thesis work (hydrosilylation of 1H,1H,2H-perfluoro-1-decene on ncSi surface) will be described later in this chapter (3.2).

### 3.1.2 Oxidation of the Silicon Surface

The remnant terminal hydrides of the post-hydrosilylation silicon nanocrystals would undergo oxidation to (possibly hydroxide and then) oxide in the presence of ambient oxygen and water. It is well-recognized that the oxidation of silicon nanocrystals usually follows the Cabrera-Mott mechanism,\textsuperscript{107,108} as supported by previous investigations.\textsuperscript{109-111} The Cabrera-Mott mechanism describes how a silicon crystal surface is oxidized by the simultaneous presence of water and oxygen molecules in ambient air.

Specifically, the polar water molecules approach the surface silanol preferentially and aid in the cleavage of Si–Si bonds adjacent to the silanol groups. Then an electron is transferred from the broken bond to an absorbed oxygen molecule. So it can be speculated that the presence of ambient water accelerates the oxidation process. This process is regarded as the induction period of the oxidation, which is illustrated in Step 1-4 in Figure 14. Studies of bulk-Si surfaces indicate that the duration of the induction period is inversely proportional to the atmospheric humidity and density of Si–OH groups.
3.2 Perfluorodecyl-Capped Silicon Nanocrystal Films

3.2.1 Preparation of Perfluorodecyl-Capped Silicon Nanocrystals

3.2.1.1 Preparation of Hydride Terminated Freestanding ncSi

**Reagents and Materials:**

Trichlorosilane (HSiCl₃, 99%) was obtained from Sigma Aldrich, stored in a refrigerator (2-8 °C), and used as received. Reagent grade hydrofluoric acid (48% aqueous solution, Caledon Laboratory Chemicals) and ethanol (95%, Sigma Aldrich) were used as received.

**Synthesis of ncSi:H – details:**

10 mL of HSiCl₃ (13.4 g, 99 mmol) was added to a glass beaker equipped with a magnetic stir bar and stirred while being cooled in a dry ice/acetone bath (-78 °C) to minimize vapor-phase hydrolysis and condensation reactions before the intended reaction. Distilled water (40 mL, 2.22 mol) was added to the cooled HSiCl₃. The clear and colorless HSiCl₃ reacted immediately, followed by the precipitation of a white solid and the evolution of HCl gas. The precipitate remained immersed in the acidic aqueous mixture for 30 min to ensure complete hydrolysis and condensation. The precipitate was then isolated via the removal of the water phase by vacuum filtration and subsequent drying at 100 °C under vacuum overnight. The resulting white solid
(HSiO$_{1.5}$)$_n$ glass was maintained under a nitrogen atmosphere to prevent oxidation, and then was placed in a quartz boat and transferred to a high-temperature tube furnace. Samples were thermally processed in a slightly reducing (5% H$_2$/95% Ar) atmosphere from room temperature to a peak processing temperature of 1100 °C at 18 °C/min and maintained there for 1h. After cooled to room temperature, the resultant light brown solid ncSi/SiO$_2$ composite product was mechanically ground with a mortar and a pestle to yield a very fine powder. The grinding took 20 min. Two equivalent batches of the ground composite (each contains 0.3 g) were added to polypropylene beakers with magnetic stir bars. Subsequently, for each batch, 5 mL of ethanol and 10 mL of 48% HF (aq) as a mixture were added to the solid. The mixture was stirred for 1.5 h to etch away the SiO$_2$ matrix. The ncSi were then extracted from the mixture using 10 mL of decane. The cloudy orange organic layer containing the hydride-terminated ncSi was quickly collected and transferred into two identical 10 mL microwave vials (each with 3 mL of dispersion), with a magnetic stir bar and preserved under a flow of N$_2$ gas.

3.2.1.2 Functionalization of ncSi

![Reaction Scheme](image)

Figure 15. Synthesis of perfluorodecyl-capped silicon nanocrystals.

Our synthesis was performed using a microwave reactor, in a closed vial. The hydrosilylation reaction scheme is shown in Figure 15. It is important to note that this reaction system uniquely guarantees a typical hydrosilylation temperature of 170 °C, which is higher than the boiling point
of the solvent, 1H, 1H, 2H-perfluoro-1-decene. The reaction proceeded for 3 hours to achieve sufficient surface coverage (sufficient degree of hydrosilylation).³⁴

Figure 16. The reaction mixture. The upper layer was decane and the lower layer was 1H,1H,2H-perfluoro-1-decene. (a) Before the reaction the hydride terminated silicon nanocrystals were dispersed in the upper layer, and (b) after the reaction the ncSi:PFD were dispersed in the lower layer.

Reagents and Materials:

1H,1H,2H-perfluoro-1-decene (99%, Sigma Aldrich) and 1-decene (94%, Sigma Aldrich) were used as received.

Synthesis Details of ncSi:PFD:

3 mL of 1H,1H,2H-perfluoro-1-decene was added into the 10 mL microwave vial containing 3 mL dispersion of the hydride-terminated ncSi (The dispersion was in decane). The vials was then closed and put under vacuum to remove any dissolved gasses from the original dispersion, and refilled with nitrogen. The vial with the dispersion was placed into the reaction zone of the Discover SP microwave reactor (CEM Corporation) and heated to 170 °C with 300 W full power. In closed-vessel mode, the reaction temperature could go above the boiling point of 1H,1H,2H-perfluoro-1-decene and reach the typical hydrosilylation temperature of 170 °C. The reaction time was 3 hours. The upper layer was decane and the lower was 1H,1H,2H-perfluoro-
1-decene since they were not miscible. Before the reaction, the hydride terminated silicon nanocrystals were dispersed in the upper layer of decane; after the reaction, they went down to the lower layer of 1H,1H,2H-perfluoro-1-decene (Figure 15 and Figure 16). The dispersion of the product was colloidally stable within 24 hours.

The exact same reaction method was applied to 1-decene. The decyl group capped silicon nanocrystals (ncSi:D) are made from the same batch of ncSi:H ensemble with the same size distribution.

3.2.2 Film Fabrication

We spin coated the ncSi:PFD onto a single crystal silicon wafer (100) surface. The wafer surface was pretreated with 1H, 1H, 2H, 2H-perfluorooctylsilane (PFOTS) to facilitate the anchoring of the perfluorocarbon capped silicon nanocrystals (Figure 17). Through this method, we obtained apparently uniform films with almost full surface coverage by the ncSi:PFD.

Reagents and Materials:

1H,1H,2H,2H-perfluorooctyltrichlorosilane (PFOTS) was used as received. Silicon wafers (P type, with resistivity of 0-100 Ω·cm; orient: <100>; grade: test wafers; supplier: University Wafers) were used as received.

Fabrication Details:

Before coating with ncSi:PFD or ncSi:D, the silicon wafer surface was pretreated with piranha and 1H,1H,2H,2H-perfluorooctyltrichlorosilane (PFOTS), subsequently. Specifically, after the piranha treatment, 50 μL of PFOTS and the silicon wafer substrates were heated together in an airtight jar at 80 °C for 0.5 h. A vapor deposition process was applied and the molecules were assembled on the surface. Then the excess PFOTS deposited on the surface was removed by ethanol rinsing with sonication, leaving only the covalently bonded hydrophobic monolayer of PFOTS. This pretreatment was aimed at an enhanced VDW interaction between the silicon nanocrystals and the substrate surface and facilitated the spin coating process (Figure 17). Then we spin coated the ncSi:PFD onto the treated surface. The silicon substrate was cut into pieces...
with a size about ½ inch by ½ inch. The spin coating speed was 1200-1900 rpm and the process was repeated by 7-10 times to get an apparently uniform film with a high-coverage.

Figure 17. Pretreatment of silicon wafer. Surface covered by a monolayer of perfluorocarbon chains has a significantly enhanced VDW interaction with ncSi:PFD.
3.2.3 Characterization of the Perfluorodecyl-Capped Silicon Nanocrystals and the Fabricated Films

After the hydrosilylation, the surface of the silicon nanocrystal was covalently bonded by tetrahydro-perfluorocarbon chains, which was confirmed by Fourier transform infrared (FTIR) spectroscopy (Figure 18). The large absorption at $\sim$1200 cm$^{-1}$ is due to the CF$_x$ stretching modes. We also observed a small peak at $\sim$2900 cm$^{-1}$ since we still had C-H bonds in ncSi:PFD although the majority were C-F bonds (4 C-H bonds per capped ligand). The peak at $\sim$2100 cm$^{-1}$ assigned to the Si-H bond stretching mode. At $\sim$900 cm$^{-1}$ there is an extra peak assigned to the degenerate deformation mode of SiH$_3$ and wagging mode of SiH$_2$. The lack of a C=C stretching mode indicates that there were olefins left in the system and the nanocrystals were washed thoroughly, and the other absorption peaks in the FTIR spectrum were not from the remnant ligands.

The ncSi:PFD ensembles were further characterized by X-ray photoelectron spectroscopy (XPS) (Figure 19). Figure 19a shows the low resolution XPS spectrum of ncSi:PFD film on an FTO substrate. High resolution Si 2p ionization potentials appeared at 103.49 eV and 100.15 eV and correspond to the surface silicon (oxide) and the core silicon, respectively, as shown in Figure 19b. The existence of F on the silicon surface was further confirmed by XPS (as shown in Figure 19c, the F 1s spectrum). The binding energy of peak A (689.42 eV) confirmed that there was carbon-fluorine bonding. We also did the deconvolution of the high resolution C 1s spectrum. The fitted peaks relating to CF$_x$ bonds at 285.8 eV, 288.8 eV, 292.14 eV, and 294.33 eV are
ascribed to C-Si (surface carbon), C-F, C-F₂, C-F₃, respectively (Figure 19d). The C-F signal is probably coming from impurities introduced when dissolving the surface of Teflon stir bar.

Figure 19. (a) Low resolution XPS spectrum of ncSi:PFD film on an ITO substrate (b) High resolution Si 2p ionization potentials appeared at 103.49 eV and 100.15 eV and correspond to the surface silicon (oxide) and the core silicon, respectively. (c) F 1s spectrum. The binding energy of peak A (689.42 eV) confirmed that there was carbon-fluorine bonding. (d) Deconvoluted high resolution C 1s spectrum. The fitted peaks relating to CFₓ bonds at 285.8 eV, 288.8 eV, 292.14 eV, and 294.33 eV are ascribed to C-Si (surface carbon), C-F, C-F₂, C-F₃, respectively.

The perfluorodecyl capped silicon nanocrystals (ncSi:PFD) were 3-5 nm in diameter, which is supported by the HR-STEM images (Figure 20) and AFM data (Figure 25). Figure 20a shows a high-angle annular dark-field (HAADF) image of the silicon nanocrystals with a large field of view and Figure 20b shows a bright field (BF) image of the silicon nanocrystals with a smaller field of view, where lattice fringes could be clearly seen. Measured lattice spacing of the silicon
(111) planes is 0.31 nm (Figure 20c). A hierarchical structure of the film can be seen through the SEM and AFM images (Figures 21, 25).

Figure 20. HR-STEM images of ncSi:PFD on a Graphene-Cu grid with an ultra-thin support film less than 2 nm: (a) An HAADF image of the silicon nanocrystals with a large field of view; (b) A BF image of the silicon nanocrystals with a smaller field of view, where lattice fringes could be clearly seen; (c) Measured lattice spacing of the silicon (111) planes is 0.31 nm.
Figure 21. Representative top-view (a) and cross-sectional (b) SEM images of the ncSi:PFD film on a silicon wafer surface.

Figure 22. Control experiments showing water droplets on different substrates: (a) PFOTS treated blank silicon wafer (b) ncSi:D coated wafer (c) blank FTO (d) ncSi:D coated FTO
The ncSi:PFD film showed bright photoluminescence (Figures 23a and 26b). The surface of the film as prepared was already superhydrophobic after the facile step of spin coating, without any further treatment (Figure 23b). Water droplets roll off the surface easily. This surface shows a water contact angle (CA) of 168.3 ± 0.5°. The advancing and receding CAs of the surface are 167.7° and 168.8°, respectively (Figure 24). Dynamic contact angles were measured using a continuously adjustable syringe and a digital CCD camera. The volume of each droplet was ~25 µL. When calculating the contact angles, we employed ellipse fitting due to its very small standard deviations compared to circle fitting. The results were shown in Figure 24 and Table 1.

Atomic force microscopy (AFM) showed that the film had different RMS roughness at different length scales (Figure 25). The interplay of the multi-scale hierarchical structure and low surface free energy contributes to the superhydrophobicity. The multi-scale roughness and the cavities suggest the existence of a Cassie–Baxter surface state. A very low sliding angle is also an evidence of such a state. A control experiment showed that a PFOTS treated silicon wafer surface did not exhibit a superhydrophobic character, with a water CA measured at around 117°. Another control experiment was done with a film composed of decyl group capped silicon nanocrystals (ncSi:D), which showed no superhydrophobicity, either (Figure 22). This comparison confirms the superhydrophobic nature is from the ncSi:PFD film itself and the constituent nanocrystals.
Figure 24. Water contact angle measurement: (a) advancing contact angle measurement (b) receding contact angle measurement

<table>
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<th>Theta Left</th>
<th>Theta Right</th>
<th>Theta E</th>
<th>Circle StDev</th>
<th>Ellipse StDev</th>
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<td>12.3</td>
<td>0.255708</td>
<td>0.014782</td>
<td>167.7</td>
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</table>

Table 1. Results of the water contact angle measurement
Figure 25. a) Surface roughness at three spatial scales for thick nanocrystal coating. Rq (RMS roughness) is shown above each panel for 10 um, 3 um and 1 um spatial scales. Note the change in height colour scale for each panel. b) Cross section of nanocrystal features for thin nanocrystal coating. Vertical steps of ~5 nm increments are apparent, which correlates with nanocrystal diameter.
3.3 Results and Discussion: Photoluminescence and Oxidation Stability

3.3.1 Photoluminescence of ncSi:PFD Films

The ncSi:PFD dispersion was brightly photoluminescent and the spectrum shifted to the blue compared to the spectra of ncSi:H and ncSi:D dispersions (Figure 26a). The blue shift can be explained by the lack of aggregation and less electronic coupling compared to ncSi:H dispersions. Due to the lower vibrational levels of ncSi:PFD, they possessed a slightly larger gap and the corresponding spectra shifted further towards the shorter wavelength. The PL spectra of ncSi:PFD and ncSi:D films are shown in Figure 26b. Free from non-radiative solvent relaxations and relaxations via intramolecular rotation, both the ncSi:PFD and ncSi:D films had a higher absolute quantum yield (AQY) than the nanocrystal dispersions.
A few factors contribute to the higher AQY of ncSi:PFD (dispersion or film) comparing with ncSi:D (dispersion or film). Firstly, the lower frequency carbon-fluorine stretching mode disfavor non-radiative relaxation pathways and boosts the absolute photoluminescence quantum yield.\textsuperscript{116,117} Specifically, there is less coupling between lower vibrational levels and the electronic excited states, thus less internal conversions occur and non-radiative relaxations are rarer.

Secondly, due to the ultra-water-repellent nature and decreased energy levels caused by the enhanced electron withdrawing effect of the perfluoroligands, ncSi:PFD are more stable against oxidation and have less oxidation defects (see the details described in 3.4). Previous reports\textsuperscript{118} have shown that the introduction of surface oxidation defects would affect the optical properties of silicon nanocrystals and reduce the photoluminescence quantum yield significantly.

**3.3.2 Oxidation Test: a Comparison between ncSi:PFD and ncSi:D films**

![Figure 27. FTIR spectra showing oxidation trends of silicon nanocrystal films overtime: (a) ncSi:D film in ambient air; (b) ncSi:PFD film in ambient air. (c) ncSi:D film in humid air. (d) ncSi:PFD film in humid air.](image-url)
Since the as-synthesized perfluorodecyl capped silicon nanocrystals still had remnant terminal hydrides (which was confirmed by FTIR, Figure 18), they could undergo oxidation to hydroxide and oxide in the presence of ambient oxygen and water. As stated above, it is well-recognized that the oxidation of silicon nanocrystals usually follows the Cabrera-Mott mechanism, as supported by previous investigations. This mechanism describes how a Si crystal surface is oxidized by the simultaneous presence of water and oxygen molecules in the ambient air. Specifically, the polar water molecules approach the surface silanol groups preferentially and aid in the cleavage of Si-Si bonds adjacent to the silanol groups. Then an electron is transferred from the broken bond to an absorbed oxygen molecule. So it can be speculated that the presence of ambient water accelerates the oxidation process, and a water-repellent perfluorodecane surface, on the other hand, can contribute to slowing such a process.

In order to confirm the expected difference between the ncSi:D and ncSi:PFD films in reactivity, we compared the oxidation trends of the two films (ncSi:D and ncSi:PFD) over a period of time by FTIR. Both films were prepared freshly from the same batch of ncSi:H, and were exposed to air under the same ambient conditions (25% R.H.). The relative humidity were controlled by bubbling air through boiled deionized water and monitored using a relative humidity probe (RH-USB, Omega Engineering, Inc.). We investigated the same regions of the FTIR spectra of the ncSi:D and ncSi:PFD, as shown in Figures 27a and 27b, respectively. The Si-O-Si mode is centered at 1070 cm\(^{-1}\). The absolute difference in absorption around this region reflects the extent of oxidation. Since the films were prepared freshly at zero hour when little oxidation occurred, a distinct comparison between the peak height in Figures 27a and 27b would be a fair comparison indicating the extent of oxidation. As expected, the result indicates that under the same ambient conditions, the ncSi:D film was oxidized much faster than the ncSi:PFD film was. We also investigated the oxidation of both films exposed to the same humid air (94% R.H.) and compared their reactivity, in which case the ncSi:D film was also oxidized much faster than the ncSi:PFD film, again as expected (Figures 27c and 27d). It was observed that in a highly humid environment the ncSi:PFD film was still resistant to oxidation.
Figure 28. Comparison of the relative drop in absolute quantum yield (AQY) of two films under different conditions (area of the pies reflect the initial absolute values of AQY, 35% for ncSi:PFD film and 28% for ncSi:D film): top, ncSi:PFD film; bottom, ncSi:D film; left, exposed to air (R.H. 25%) for 8 days; middle, exposed to air (R.H. 92%) for 30 minutes; right, exposed to air (R.H. 68%) for 15 hours.

On the other hand, it is important to further investigate the stability of the films by measuring the absolute quantum yield (AQY) after different time of exposure in air with different ambient relative humidity. Figure 29a shows the AQY evolve under different conditions of the film samples made of ncSi:PFD/ncSi:D prepared with a reaction time of 24 hours. The AQY of the ncSi:D film after exposed to air (R.H. 68%) for 30 minutes dropped significantly, while that of the ncSi:PFD film dropped relatively less. It was the similar case with exposure to air (R.H. 92%) for 15 hours. The comparison of the relative drop in AQY is summarized in Figure 28 as pie charts. In ambient air with lower R.H. (25 %), the relative AQY drop for both films was much slower, measured at 3.92% for ncSi:PFD film and 13.01% for ncSi:D film after 8 days’ exposure (absolute value shown in Figure 29b). This comparison (shown in Figure 28) corresponded well with the difference in oxidation rates indicated by the FTIR mentioned above. Clearly, water assisted the oxidation but at the same time passivated the surface as a protection. These two competing effects could explain why in extremely high R.H. the oxidation was slower for both materials compared to those in humid air with moderate R.H. Information about the
detailed mechanism is planned for a thorough future study. We also observed a much faster intensity drop of ncSi:D film than ncSi:PFD film after being immersed in distilled water for hours (Figure 30). Clearly, it was undisputable that in any case the ncSi:PFD film was always more stable than ncSi:D film in maintaining its photoluminescence absolute quantum yield.

Figure 29. Change in absolute quantum yield (AQY) of two films over time, under different conditions. Left, ncSi:PFD film; right, ncSi:D film. (a) exposed in humid air (b) exposed in ambient air.
3.4 Summary

In summary, freestanding silicon nanocrystals capped by perfluoroalkane chains were synthesized and a higher absolute quantum yield was obtained both for dispersions and films compared to its perhydroalkane analogues. Films of these perfluoroalkane-capped silicon nanocrystals were proven to be superhydrophobic and found to be much more resistant to air oxidation than the perhydroalkane analogue. It is a new, facile and green way of fabricating bi-
functional photoluminescent-superhydrophobic nanocrystal surfaces. Future work may include the synthesis of PEG terminated solid lipid particles composed of these ncSi:PFD for a better biocompatibility and biostability in biomedical applications. Collectively these observations speak well for advanced materials and biomedical uses for these perfluoralkane capped silicon nanocrystals.
Chapter 4  
Heterogeneous Reduction of CO$_2$ by Hydride-Terminated Silicon Nanocrystals

This chapter has been compiled using excerpts from previously published work:


(† contributed equally)

Contributions: I conceived and designed the experiments with W.S., L.H. and G.A.O. I carried out the synthesis of the materials and performed materials characterizations with W.S. The photothermal gas-phase testing was made possible with the help of L.H., A.P.Y.W., J.J., P.G.O.’B., and T.E.W. K.K.G. and C.V.S. performed the DFT simulation. L.M.R. conducted the gas adsorption experiments. A.A.J. performed the XPS test. A.S.H helped evaluate the photothermal effect of Si. C.A.M. and G.A.O. funded and supervised the construction of the gas-phase reactor system. L.H. and G.A.O. supervised the project. I interpreted the data, plotted all the graphs, and wrote the paper with W.S., L.H. and G.A.O. All the authors discussed the results and commented on the manuscript.

4  Heterogeneous Reduction of CO$_2$ by Hydride-Terminated Silicon Nanocrystals

4.1  Background: Silicon Nanostructures for Clean Energy

Silicon, with its earth-abundant, non-toxic and low-cost feature, as well as its unique electrical, optical and thermal properties, has long been crowned as king in the solar energy conversion realm. Within the past many decades, silicon nanostructures, with the benefit of readily tunable chemical and physical properties have been applied to numerous fields in clean energy and
energy storage solutions, including photovoltaics and photoelectrochemical cells,\textsuperscript{119-121} lithium-ion batteries,\textsuperscript{122-125} thermoelectrics,\textsuperscript{126,127} and photocatalysis.\textsuperscript{128}

For clarity, the background introduction would include the recent emerging field of solar fuels, where researchers are working towards the high efficient and convenient conversion of solar energy to chemical energy stored in fuels such as hydrogen, carbon monoxide, methane and other hydrocarbons.

Owing to silicon’s low cost and lack of toxicity, small electronic band gap for near-infrared to visible light absorption, it is scientifically and technologically interesting to introduce silicon nanostructures into different types of solar-to-chemical energy platforms. Silicon nanowires for example, have been employed as electrodes for photoelectrochemical generation of H\textsubscript{2} from H\textsubscript{2}O, photodegradation of dyes, and as anodes in lithium ion batteries.\textsuperscript{122,129-132} Porous silicon and silicon nanocrystals are showing promise for bio-medical and optoelectronic applications.\textsuperscript{63,133}

In the context of CO\textsubscript{2} reduction, it is noteworthy that organo silyl hydrides are well known for their ability to homogeneously reduce CO\textsubscript{2}. In stark contrast, hydride functionalized silicon nanocrystals have not previously been imagined as a reagent for the heterogeneous gas-phase reduction of CO\textsubscript{2}. To amplify on the former, the first step in the solution phase hydrosilylation of Si-H bonds in molecular silyl hydrides with CO\textsubscript{2} has been reported to involve the formation of a formoxysilane SiOCHO group containing a SiO bond.\textsuperscript{134} This insertion reaction is usually enabled using a transition metal or main group homogenous co-catalyst under high temperature and/or pressure conditions. In the case of molecular silyl dihydrides, hydrosilylation of CO\textsubscript{2} has been shown to form di-formoxysilane Si(OCHO)\textsubscript{2} groups.\textsuperscript{135} These formoxysilanes as well as silylacetal groups have been implicated in the reduction of CO\textsubscript{2} to CH\textsubscript{3}OH, and CH\textsubscript{4}.\textsuperscript{134,136-139} There was also a report that by using aqueous Na\textsubscript{2}CO\textsubscript{3} in the presence of silicon quantum dots, both HCHO and HCO\textsubscript{2}H were detected using the Nash reagent.\textsuperscript{140}

Herein we document the unprecedented ability of surface hydride functionalized silicon nanocrystals, denoted ncSi:H, to selectively reduce gaseous CO\textsubscript{2} to CO using the heat and light from the sun. Compared to this gas-phase heterogeneous reduction of CO\textsubscript{2} the aforementioned liquid-phase homogenous hydrogenation of CO\textsubscript{2} has several disadvantages that include: (i) solubility, diffusion and temperature limitations of CO\textsubscript{2} in the liquid-phase, (ii) recovery and
regeneration of catalysts from the liquid-phase, (iii) requirement of a catalyst, and (iv) the scalability of the process. A further advantage of ncSi:H is its ability to harvest light across the near-infrared to visible wavelength range which provides opportunities for photothermal reduction of CO$_2$ using both the heat and light from the sun. If the reducing Si-H surface of ncSi:H could be maintained under reaction conditions the reduction of CO$_2$ could potentially be made catalytic.

### 4.2 Preparation of ncSi:H and Characterization

![Characterization of ncSi:H](image.png)

Figure 31. Characterization of ncSi:H. (a) As-synthesized powder comprised of ncSi:H deposited on a borosilicate glass fiber filter support. (b) Scanning electron microscopy (SEM) image of a film sample made of dried ncSi:H from a pentane dispersion. (c) Powder X-ray diffraction (PXRD) patterns of ncSi:H, showing the main reflections peaks for nanocrystalline Si. (d) Schematic illustration of the reduction of CO$_2$ to CO by ncSi:H.

Hydride terminated silicon nanocrystals, denoted ncSi:H, were obtained through a two-step synthesis reported before.$^{88}$ The source of ncSi:H is silicon monoxide SiO, which is relatively
low cost, commercially available in kilogram quantities. Thermal treatment of SiO in a 5% H₂/Ar environment causes a redox disproportionation reaction in which the formally Si(II) in SiO is simultaneously reduced to Si(0) and oxidized to Si(IV). The so-formed Si(0) undergoes nucleation and growth to form ncSi in a SiO₂ matrix. The size of the produced ncSi is within the range of 2-7 nm. Subsequent extraction of the ncSi from the SiO₂ surrounding matrix is accomplished using aqueous HF (with ethanol), the product of which is a brown powder comprised of ncSi:H (as shown in Figure 31a).

![Figure 32](image)

**Figure 32.** Left: full isotherm of nitrogen adsorption and desorption displaying a type IV behavior with a hysteresis loop indicating disordered (textural) porosity. Middle: linear portion of 1/[W((Pₐ/P) - 1)] vs. relative pressure within the range of 0.5 ≤ P/P₀ ≤ 0.30, used for the determination of BET surface area. Right: pore size distribution determined using NLDFT method – note that observed porosity is textural, due to packing of particles.

Owing to their small sizes, a large surface area of 303 m²/g was determined for ncSi:H by nitrogen gas adsorption. (Figure 32)

Scanning electron microscopy (SEM) investigations of the ncSi:H samples show they consist of aggregates of nanocrystals with textural nanoporosity (Figure 31b), which is consistent with the large surface area measured. If we regard such textural interstices as pores, the mode pore size is 3.5 nm and the pore volume is 0.381 cc/g, determined from the nitrogen gas adsorption experiment (Figure 32). In Figure 31c the powder X-ray diffraction (PXRD) pattern of a typical ncSi:H sample is depicted. All diffraction peaks can be assigned to silicon with no obvious ones, amorphous or crystalline, from SiO or SiO₂ being detected. The surface of the obtained ncSi contains plenty of Si:H bonds, providing the necessary capacity for reducing CO₂ into CO (Figure 31d).
The UV-Vis diffuse reflectance spectra of the brown ncSi:H sample shows strong broad-band optical absorption increasing in absorptivity as it traverses the near infrared to ultraviolet wavelength range arising from a convolution of quantum size effects in the ncSi:H size distribution (Figure 33), rendering ncSi:H a potentially effective photothermal CO₂ reducing agent.

4.3 CO₂ Reduction: Results and Discussion

The reactivity of these ncSi:H samples towards CO₂ was first studied in a batch reactor irradiated with a metal halide lamp which has a similar spectrum to the solar spectrum, in the absence and presence of H₂ at 150 °C, for multiple cycles (Figure 34). The experimental CO₂ reduction measurements are summarized in the Appendix.

To ensure the products of the reactions did not originate from adventitious carbon residues in the ncSi:H samples, isotope labeled ¹³CO₂ was used to authenticate the origin of reduction reaction. In the absence of H₂, we observed a notable initial CO production rate as high as 4.5
micromole/(h\cdot g) for an incident solar intensity of 1 Sun at 150 °C. The rate decreased in the following cycles but the sample was still active over 160 h (Figure 34). It is important to note that $^{13}$CO was found as the dominant product and no other $^{13}$C-containing compounds were detected (except for unreacted $^{13}$CO$_2$). The results of the batch experiments unequivocally demonstrate that ncSi:H itself can heterogeneously reduce CO$_2$:

$$\text{CO}_2 + \text{ncSi:H} \rightarrow \text{CO} + \text{ncSi(O):H},$$

where ncSi(O):H stands for surface oxidized ncSi:H.

With both H$_2$ and CO$_2$ in the reactor, the initial CO production rate is about half of that for the case with the presence of only CO$_2$, as expected because the partial pressure of CO$_2$ is cut by half. This further confirms that CO$_2$ was indeed a reactant. Notably, the rate of subsequent runs decreases much more slowly (Figure 34), showing different kinetics, which suggests H$_2$ likely gets involved in the CO$_2$ reduction process. Unlike the case of only CO$_2$ present in the reactor, where the CO production rate dropped significantly even at the second run, we instead observed an increased CO production rate when we introduced H$_2$ to the reactor (Figure 35). Although the following tests showed the rate was still gradually decreasing, the presence of H$_2$ seemed to aid in retaining more active sites, for example inhibiting the reaction between Si-H and adsorbed/product H$_2$O to yield H$_2$ (Si-H + H$_2$O $\rightarrow$ Si-OH + H$_2$),$^{132}$
according to the simple le Chatelier principle, and similarly inhibiting the hydride loss to released H₂ upon heating (Si-H + H-Si → Si-Si + H₂).\textsuperscript{142} As discussed later, the FTIR spectrum of the ncSi:H after reaction with both H₂ and CO₂ also exhibits less surface Si-O-Si but more Si-OH, compared to that of the ncSi:H reacted with only CO₂ (Figure 36). Importantly, the UV-Vis diffuse reflectance spectrum is less blue-shifted, again indicating lesser amounts of surface oxidation (Figure 33).
Figure 35. Relative CO production rate was recovered when H$_2$ + CO$_2$ are both present in the second run. Each run was also over 20 h at 150 °C. The rate for the first run with the presence of only CO$_2$ is defined as 100%, while the rates for following runs were normalized to it.

To further understand the reaction mechanism, all ncSi:H samples were studied by FTIR spectroscopy before and after testing, in order to gain an insight into the surface chemistry responsible for the products formed from the reaction of CO$_2$ and CO$_2$/H$_2$ with ncSi:H, respectively. FTIR studies of the ncSi:H samples subjected to the testing conditions described above, before and after exposure to CO$_2$ or CO$_2$/H$_2$ reactants for many cycles are shown in Figure 36. The FTIR spectra indicate that before the reaction, the characteristic Si-H stretching mode is dominant on the ncSi:H surface, with a little amount of residual CHx species from pentane extraction observed at ~2900 cm$^{-1}$. After reaction with only CO$_2$ for a significant number of cycles, accompanied by the aforementioned decrease of the CO production rate, the surface of ncSi:H was oxidized and Si-O-Si and Si-OH species were formed, which resembles the situation for oxidized Si nanowire surfaces. Interestingly, there was still considerable amounts of OSi-H species remaining on the surface seen at around 2250 cm$^{-1}$. Compared to the
original SiSi-H, the hydride peak shifted from around 2100 cm\(^{-1}\) to larger wavenumbers, which is diagnostic of some surface oxidation.\(^{144}\)

![FTIR spectra](image)

Figure 36. FTIR study of surface properties. FTIR spectra of fresh ncSi:H powder before the reaction, after the reaction with \(^{13}\)CO\(_2\) only for over 160 h, and after the reaction with both \(^{13}\)CO\(_2\) and H\(_2\) for over 200 h.

These results suggest that only the non-oxidized related surface Si-H sites are responsible for the reduction of CO\(_2\) to CO, and the reaction is most likely stoichiometric through O transfer from CO\(_2\) to the surface of ncSi:H. This is supported by the result of a control test, in which a ncSi:H film was oxidized in air and daylight conditions for weeks, and showed no detectable production of CO. In contrast, in the presence of H\(_2\), a higher proportion of surface Si-OH groups are formed after reacting for a similar amount of time, which again implies H\(_2\) may play a role in the CO\(_2\)
reduction process. Nevertheless, with our test condition the presence of H$_2$ could not reinstate the non-oxidized Si-H surface, thus the reaction was still considered not catalytic. Note that the residual organics are being removed during reaction (Figure 36) and are not the source of reducing $^{13}$CO$_2$ to $^{13}$CO. This is further confirmed by a control test where we intentionally grafted a decyl group onto ncSi via hydrosilylation. The $^{13}$CO did not increase but rather dropped significantly proving that the Si-H is the active site.

![Figure 37. EPR Studies. EPR spectra of ncSi:H samples, (a) in N$_2$ (upper, at room temperature; middle, at 170 °C in dark; lower, at 170 °C with 0.5 Sun); microwave frequency, 9.393 GHz, (b) in CO$_2$ (upper, at room temperature; middle, at 170 °C in dark for over half an hour; lower, at 170 °C with 0.5 Sun for another half an hour); microwave frequency, 9.393 GHz](image)

The surface oxidation was further confirmed by probing the dangling bonds on ncSi:H by Electron Paramagnetic Resonance (EPR). We observed split peaks for the sample sealed in CO$_2$ when the temperature was increased to 170 °C both in dark and light (Figure 37b). The small peaks at 3351 G and at 3332 G were hardly seen for the control sample under N$_2$ (Figure 37a).
While the main signals (in all six spectra) are attributed to silicon dangling bonds in a disordered environment (with \( g \approx 2.0081 \)),\textsuperscript{144,145} the new feature that emerged in the presence of CO\(_2\) should originate from the generation of the interface between the ncSi core and the surface oxidation shell. This new feature is similar to the well-known P\(_b\) center in bulk Si/SiO\(_2\) interfaces,\textsuperscript{144,146,147} with an observed \( g \) value \( g_\parallel = 2.0027 \).

Our standard test condition includes irradiation with light, but the same reaction to reduce CO\(_2\) to CO can also be enabled thermally. In the absence of illumination, detectable amounts of CO can be observed after reaction over 20 hours at around 130 °C. The production rate quickly increases to 1 micromole/h·g at 150°C and further exceeds 5 micromole/h·g at 170 °C (Figure 38). In most cases, the samples show higher CO production rates in the light at the same heating temperature except in the case of 170 °C when the sample shows slightly higher CO production rate in the dark.

![Figure 38. Temperature effect. CO production rates of three ncSi:H film samples tested at different heating temperatures (130 °C, 150 °C, and 170 °C), first in the dark (D) and then in the light (L).](image)
The reason is that the studies on the temperature and light effects shown in Figure 38 were conducted using the same sample for each temperature, following the sequence of first in dark then in light, being consistent throughout the whole experiment. Therefore, it is possible there might be less reactive sites for the light test after the dark test was done, showing the same decreasing trend for the consecutive runs shown in Figure 34. Instead, when a fresh ncSi:H sample was directly tested at 170 °C in light, the CO production rate for the first run reaches up to 17 micromole/h·g, roughly three times of that in the dark at the same temperature.

We do not observe new products other than $^{13}$CO and the EPR results show very similar patterns regardless of the irradiation with light (Figure 37). Most importantly with only light irradiation at the intensity of 1 sun but without heating we did not obtain observable amounts of $^{13}$CO. Thus we attribute the enhanced conversion rate to the photo-thermal effect of ncSi:H. In other words, the local temperature at the ncSi:H surface was higher with light irradiation than in the dark under similar thermal heating conditions, which is responsible for the observed light enhancement effect. Significant photothermal effects of Si nanostructure have been well documented in recent years. For example, the CO$_2$ reduction rate of ruthenium nanoparticles was found to be greatly enhanced by the photothermal effect of black Si nanowires.$^{148}$ Porous Si nanoparticles have been used for photothermal therapy.$^{149}$ For Si nanocrystals, laser light could induce intense local heating,$^{150}$ and the photothermal effect of ncSi increases with irradiating energy, consistent with a combination of thermalization of hot carriers under irradiation greater in energy than the bandgap (UV/visible light) and defect-mediated heating processes (induced by both UV/visible light and IR light).$^{151}$ A preliminary Raman study also shows that laser light could significantly heat up Si nanocrystals embedded in SiO$_x$ matrix (Figure 39).
Figure 39. Stokes and Anti-Stokes Raman spectra of the ncSi produced in SiO. We employed a previously reported method\textsuperscript{152-154} to estimate the local temperature.

\[
\frac{I_{\text{AS}}}{{I}_{\text{St}}} = \left(\frac{\omega_L + \omega_V}{\omega_L - \omega_V}\right)^4 e^{-E_R/(kT)}
\]

Here \(I_{\text{St}}\) and \(I_{\text{AS}}\) are the integral intensities of the Stokes (S) and anti-Stokes (AS) Raman scattering; T is the temperature in degrees Kelvin; \(E_R = h\nu_{\text{excitation}} - h\nu_{\text{emission}} = h\nu_V\), where \(\omega_V\) is the wave number of the Raman mode (cm\(^{-1}\)); \(\omega_L\) is the wave number of the exciting laser light. After fitting of the peaks we obtain \(I_{\text{AS}}/I_{\text{St}} = 0.5922\) for the ncSi TO mode at 516.0 cm\(^{-1}\). The estimated local T in this case is 876 K. The actual local T might be lower than the value calculated by this model due to various other physical factors such as heat diffusion, not considered in the model, nevertheless the photothermal heating effect induced by light has been well demonstrated.

As shown in Figure 38, the enhancement effect is more pronounced at 130 °C owing to the largest local temperature difference at the ncSi:H surface between dark and light conditions. Intuitively, the conversion rate could be further improved with more incident photons reaching the ncSi:H surface. To further confirm the light enhancement mechanism, we also performed the reaction in CO\(_2\) and H\(_2\) at 150 °C but with the irradiation of much more intensified light from a Xe lamp (~15 Suns). Amazingly, a 100 times boost of the rate to ~250 micromole/h·g was observed, which is comparable to the best reported CO\(_2\) reduction catalysts (Figure 40).
Figure 40. Light source effect. Enhanced CO production rates of a ncSi:H sample illuminated with ~15 Suns.

It is notable that it is convenient to achieve 15 Suns of light under daily sunlight with the use of a commercial solar concentrator. When illuminated with more concentrated light with the intensity of 20 suns, significant amounts of CO can be produced without providing external heating (Figure 41), but the $^{13}$CO rate was still decreasing over consecutive runs even in the presence of $\text{H}_2$, consistent with the decreasing trend observed under the other reaction conditions (Table in Appendices). While the exact role of $\text{H}_2$ in the reduction process needs further study, it is believed that the presence of $\text{H}_2$ used in these experiments is beneficial for maintaining the reductive atmosphere that minimizes the undesired surface oxidation and dehydrogenation of ncSi:H.$^{33}$
As discussed above, the reductive surface of ncSi:H is crucial for converting CO$_2$ into CO. A common concern would be the stability of ncSi:H against oxidation during storage. One may expect that only freshly prepared samples are active and must be handled under humidity and oxygen free conditions, which may not be convenient for scale-up for industrial applications. Contrary to common belief, our ncSi:H powder is surprisingly stable if stored in air with proper care. For example, throughout an 11-day storage in a dark cabinet, the CO production rate was still as high as the rate shown by the fresh sample (Figure 42). Even after an incredibly long time of two months, the rate only dropped a little to 1.62 micromole/h·g.
Figure 42. Stability of ncSi:H during the storage. CO production rate of ncSi:H film samples after different time spans of storage which demonstrates the stability of the ncSi:H sample in air without the exposure to light.

Our FTIR results also implied very little oxidation with much of the Si-H preserved under such conditions (Figure 43). However, these nanocrystals quickly lost their reducing power stored under similar conditions but exposed to ambient room light. Apparently, the oxidation of the ncSi:H surface can be greatly accelerated even with ambient light.\textsuperscript{155} Therefore, the key to maintain the reductive surface of ncSi:H during the storage in air is away from light.
IR spectra of ncSi:H drop-casted on a KBr plate over oxidation in a dark cabinet. The KBr plate was put in a desiccator open to the air with some drying agent below it. The peak at ~2100 cm\(^{-1}\) assigned to Si-H bond was barely decreased even over a month, while the Si-O-Si peak at ~1100 cm\(^{-1}\) was increased only slightly.

4.4 DFT simulation and Further Discussion on the Mechanism

While this paper reports an important first step in a brand new approach to CO\(_2\) reduction with still much to explore, we have conducted preliminary density functional theory (DFT) calculations to probe the identity, structure and chemical reactivity of the surface species involved in the reaction in more detail. DFT calculations were carried out using Quantum ESPRESSO.\(^{156}\) The plane-wave-pseudopotential approach, together with the Becke-Lee-Yang-Parr (BLYP)\(^{157,158}\) exchange-correlation functional, and norm-conserving pseudopotentials was utilized throughout the analysis. All calculations are spin polarized. The kinetic energy cut-offs of 40 and 400 Ry were used for the smooth part of the electronic wave functions and augmented electron density, respectively. The self-consistent field convergence criterion was set to 1\(\times\)10\(^{-6}\) Ry per Bohr and the structures were relaxed using a Davidson type diagonalization method until the magnitude of the residual Hellmann-Feynman force on each surface atom was less than 10\(^{-3}\).
Ry per Bohr. The Brillouin zone integrations at gamma point were performed for full geometry optimization. To model ncSi:H we choose a spherical region of about 1 nm from the center of bulk diamond cubic silicon lattice and saturated the dangling bonds on the surface with hydrogen. The terminated Si atoms are classified into SiH and SiH$_2$ types leading to a Si$_{35}$H$_{36}$ structure as illustrated in Figure 44. Blue and white spheres in Figure 44 represent the Si and H atoms, respectively. The cluster was located in a $30 \times 30 \times 30$ Å cubic supercell. The relaxed structure is very similar to the previously reported structures.$^{159,160}$ In order to estimate the Si to H ratio in experimental samples that have mean size of about 3.5 nm, we also modeled ncSi:H of size 3.5 nm as shown in Figure 45. The total number of atoms in this model is 1208 with 944 Si and 264 H atoms. However, since it is not feasible to work with such a large size model using DFT, we did not optimize this system and considered only the Si$_{35}$H$_{36}$ model for further DFT analysis.

Figure 44. Three projections of the atomic structure of a Si$_{35}$H$_{36}$ (~1 nm) nanocrystal. Blue and white spheres represent the Si and H atoms, respectively. The H weight percentage is about 3.4% estimated from this model.

We choose ~1 nm Si$_{35}$H$_{36}$ model for this study. Our thermogravimetric analysis (TGA) confirms the H amount is comparable to the estimated amount from such models (Figure 46). The details of the computational method and models are given in the methods section. It is known that surface adsorption can lower the CO$_2$ reduction potential in aqueous systems, making the reaction possible on semiconductors with a conduction band potential lower than the single-electron reduction potential of CO$_2$. $^{161,162}$
Figure 45. The atomic structure of a Si$_{944}$H$_{264}$ (~3.5 nm) nanocrystal. Blue and white spheres represent the Si and H atoms, respectively. This model contains a total number of atoms = 1208, with H weight percentage of about 1% and shows that the amount of surface H relative to the core Si will increase if the nanocrystal size decreases, but not significantly.

It is conceivable that CO$_2$ adsorption could similarly facilitate its reduction in gas phase reactions. Thus to explore the interaction of the gaseous CO$_2$ molecule with the ncSi:H sample we also investigated computationally CO$_2$ adsorption on all possible surface sites. We placed the CO$_2$ molecule in the vicinity of SiH$_2$ (Si bonded with 2 H's, Figure 47a), SiH (Si bonded with 1 H, Figure 47c), and Si (Si with dangling bond, Figure 47e) surface sites and optimized each system. This analysis showed that the CO$_2$ molecule will not interact with surface SiH$_2$ and will remain intact (Figure 47b). However, it will interact with the other two sites. At the dangling bond Si site CO$_2$ molecularly adsorbs and bends as shown in Figure 47f. The calculated binding energy of CO$_2$ on the Si site is 0.63 eV. The C-O bond lengths for CO$_2$ molecule increased from 1.16 Å to 1.22 Å and 1.53 Å, and the bond angle reduced from 180° to 121.2°. However, the dangling bond Si site is not able to dissociate CO$_2$. Interestingly, the SiH site managed to dissociate CO$_2$ into CO and Si-OH endothermically (adsorption energy ≈ 0.11 eV) making
surface SiH the most favourable site for CO$_2$ reduction reaction in ncSi:H system (Figure 47d). The C-O and O-H bond lengths of the products are 1.17 Å and 1.01 Å, respectively, the Bader charges on O and C of CO are -1.79e and +1.74e, respectively, and Bader charge on O and H of OH are -2.07e and 0.00e, respectively. The strong bonds and charge distribution shows that products formed by CO$_2$ dissociation on the SiH site are very stable.

Figure 46. Thermal gravimetric analysis (black) and differential thermal gravimetric analysis (green), which has been demonstrated to be an effective way to quantify the surface hydride on ncSi.$^{163}$ In this paper, the weight loss before 350°C under Ar is mainly due to H loss accompanied by some loss of hydrocarbon, shown in Figure 11 in this reference (Chem. Mater., 2010, 22, 487–493). Inspired by this work, we also heated our freshly synthesized ncSi:H to 350 °C under He at a low ramp rate of 0.5 °C/min and with a high gas flow rate of 100 mL/min. In this way, we observed a 3.3% loss above 150 °C where the derivative starts to show significant increase of weight loss, corresponding to non-volatile species including H$_2$ loss. These observations provide an estimate that the surface Si-H accounts for up to ~3% of the total sample weight (this 3% weight loss may still contain a small amount of other non-volatile species), comparable to the models we constructed.
Figure 47. The DFT models. The initial models of CO$_2$ adsorption on (a) SiH$_2$, (c) SiH, and (e) Si surface sites. The final optimized models of CO$_2$ adsorption on (b) SiH$_2$, (d) SiH, and (f) Si surface sites.

In order to examine if H$_2$ can reinstate surface Si-H sites, the interaction of H$_2$ with Si-OH formed after CO$_2$ dissociation was also investigated. We simulated three different configurations.

In the first configuration H$_2$ was placed horizontally about 1.17 Å away from surface SiOH (Figure 48(a)), in the second configuration H$_2$ was placed horizontally about 0.67 Å away from surface SiOH (Figure 48(b)) and the in third configuration H$_2$ was placed vertically about 0.63 Å away from surface SiOH (Figure 48(c)). While optimizing all three configurations, H$_2$ showed
no interaction with the surface OH and remained intact moving away from the ncSi:H surface. This shows that surface hydroxides are very stable as also indicated by bond length and charge distribution discussed above and that H$_2$ cannot easily recover the Si-H. This result is consistent with the literature$^{164}$ and experimentally observed decrease in rate over time.

![Figure 48. The initial configurations considered for H$_2$ adsorption on ncSi:OH.](image)

We propose that unlike the reduction of CO$_2$ by the molecular silanes, which goes through an intermediate species (such as SiOCH$_2$OSi or SiOCHO)$^{165}$ in the case of ncSi:H the product CO directly leaves the surface of ncSi:H after O abstraction from CO$_2$ without the C bonding to H. If our ncSi:H system went the same route as molecular silanes, we might expect to see CH$_x$ surface species and ultimately CH$_4$ and/or CH$_3$OH as the products.

However, we see no $^{13}$C labelled species on the Si surface in the IR spectrum, and no $^{13}$C labelled organic products other than CO. These diagnostics suggest that the reaction might not go through the insertion of CO$_2$ into the Si-H bonds, as found with molecular silanes with added catalysts. Instead, the insertion of O into the Si surface directs this heterogeneous reduction reaction to produce only CO. The Si-H surface of ncSi:H likely facilitates the adsorption/binding of CO$_2$,$^{166}$ and the large surface curvature and large surface to volume ratio likely facilitates the surface reactivity,$^{167}$ features which differentiate ncSi from bulk Si and molecular silanes. It is also important to note that the gas phase reaction temperature, is quite different from that used with molecular silanes. Since the reaction also occurred in the dark, it is likely that the reduction reaction was thermally driven without the need of exciton generation by light. Therefore, we
attribute this unique gas-phase heterogeneous reduction reaction of CO$_2$ by ncSi:H to its very small size, high surface area and highly reactive SiH surface. The impurity of F after HF etching during synthesis was negligible and should play a trivial role for very small Si nanocrystals with high surface curvature,\textsuperscript{168} with only 1.43 at.% F compared to 98.57 at.% Si determined by XPS after heating at 60 °C in vacuum (spectra shown in Figure 49).

![Figure 49](image)

Figure 49. F 1s (a) and Si 2p (b) core-level spectra of the sample. Background lines for atomic percentage analysis are also shown in the graphs, corresponding with the positions of fluoride (rather than Si-F) and Si(0) respectively.\textsuperscript{169}

With such a vacuum thermal treatment, the sample was still active for CO$_2$ reduction (Figure 41). In the presence of H$_2$, the production rate of CO from CO$_2$ was enhanced. Apparently, the presence of H$_2$ is beneficial for maintaining the Si-H surface of ncSi:H in an un-oxidized state. Minimizing adventitious air oxidation especially in the light seems to be another way to preserve activity. Pertinently, light can be helpful in the reduction of CO$_2$ via the oxidation of ncSi:H by the abstracted O from the CO$_2$ itself. The potential of concentrated light to further enhance the CO$_2$ reduction rate is also apparent. By optimizing the photothermal effect in ncSi:H it may prove possible to boost CO$_2$ reduction rates to technologically significant values. If reduced to practice this would make earth abundant low-cost silicon (and potentially low-cost nanosilicon) an attractive material as part of a global CO$_2$ utilization strategy to meet IPCC emission targets by 2035.
4.5 Summary

Almost four decades have passed since the first report that sunlight can power the reduction of CO$_2$ to carbon containing products in aqueous suspensions using semiconductor powder photocatalysts.$^{170}$ Since that time the photoreduction of CO$_2$ by H$_2$O or H$_2$ has been studied in the aqueous and gas phase using almost every conceivable nanostructured composition imaginable.$^{171-175}$ While CO$_2$ conversion rates and efficiencies of reported photocatalysts are still orders of magnitude below those required to inspire technological development,$^{176,177}$ progress towards achieving this objective has been steady and promising. One obstacle along the road to success could prove to be the cost of scaling the photocatalyst to proportions of industrial relevance, because the compositions of the best photocatalysts are invariably comprised of rare and expensive elements. Overcoming this hurdle emphasizes the distinctiveness and significance of the work reported herein. It is indeed a surprising yet welcome discovery that plentiful, inexpensive and benign elemental silicon, synthesized in the form of ncSi:H, made easily and cheaply from commercially available SiO, can exploit the reducing power of surface hydride to chemically reduce CO$_2$ to CO - a synthon for making methanol or hydrocarbons by well-established methods – at scientifically impressive $\sim$millimole/h$\cdot$g$_{cat}$ conversion rates. This advance bodes well for continued improvement by composition variations and doping methods, as well as size, shape and surface variations of ncSi:H, to achieve a higher rate and perhaps even transform the seemingly stoichiometric reaction to catalytic. The ultimate goal is to achieve technologically relevant CO$_2$ utilization rates of mole/h$\cdot$g$_{cat}$ which translates into Gt/y$\cdot$t$_{cat}$.

On a final note, it is worth recalling that the world is currently consuming the equivalent of about 70 billion barrels of oil which translates into about 20 billion ton equivalents of CO$_2$ emitted into the atmosphere per year. The world’s energy needs are projected to double by 2030. If one is to stabilize the expected increasing levels of CO$_2$ in our atmosphere in the next couple of decades then the sum total of all kinds of envisioned CO$_2$ refineries around the globe will have to cope with CO$_2$-to-Fuel conversion rates of 20-40 billions of tons per year.$^{177}$ It might well take something as simple and elegant as CO$_2$ fixation by ncSi:H to solve such a monumental global problem.
Chapter 5
Conclusions and Future Work

5	Conclusions and Future Work

5.1 Conclusions

The work presented in this thesis outlines some of my contributions towards a better understanding of some fundamental attributes of silicon nanocrystals, from their physical properties (size-dependent and surface-dependent photoluminescence and photoluminescence absolute quantum yields, in Chapter 2 and Chapter 3) to surface chemistry (hydrosilylation reactions, stability against oxidation, and gas-phase CO$_2$ reduction, in Chapter 3 and Chapter 4).

In Chapter 2, we focused on the preparation of size-separated silicon nanocrystals and the investigation into the quantum size effects (QSEs) and size-dependent photoluminescence (PL) absolute quantum yields (AQY). We managed to tune the size of silicon nanocrystals through thermal treatment of SiO and size separation of extracted and surface functionalized silicon nanocrystals. Missing links in the story of the size-dependent PL AQY of ncSi:R, are where QSEs begin and end and how AQY really vary with size. The results described in this chapter provide a first step towards answering these questions. It is found that the size-dependence of the absolute luminescence quantum yield of size-separated organic-capped silicon nanocrystals (ncSi:R) reveals a ‘volcano’ behavior, which switches on around 5 nm, peaks near 3.7-3.9 nm and monotonically decreases thereafter. These three regions of the volcano plot respectively define the (i) transition from bulk non-emissive silicon to quantum confined emissive silicon, (ii) increasing spatial confinement of electron-hole pairs enhancing radiative recombination, and (iii) increasing contributions of organic-capping group vibrations and defects favoring non-radiative recombination.

In the work presented in Chapter 3, a new type of ligand, the perfluorodecyl group, was utilized to cap the silicon nanocrystal surface through the classical hydrosilylation reactions. To compare the claimed effects that perfluoro-substituted ligands have on the nanocrystals, the analogues capped by perhydrodecyl groups were also synthesized. One main drawback of silicon nanocrystals for various microelectronic and biomedical applications is the instability against oxidation, which leads to a significant decrease in the absolute quantum yield of
photoluminescence. In this work, we describe for the first time the synthesis of colloidally-stable, brightly-luminescent perfluorodecyl-capped silicon nanocrystals. Through the facile surface engineering, the absolute quantum yield of the photoluminescence is increased and the stability against oxidation is enhanced. Compared with the commonly reported perhydrodecyl-capped analogues, the lower frequency vibrational modes of perfluorodecyl-capped silicon nanocrystals disfavor non-radiative relaxation pathways and boosts the absolute photoluminescence quantum yield. The strong electron withdrawing character lowers the energy levels of the silicon nanocrystals, making them thermodynamically more stable. The superhydrophobic nature of the film repels ambient water and slows down the oxidation process. The method of preparing the perfluorodecyl-capped silicon nanocrystals is also a new, facile and green way of fabricating bi-functional photoluminescent-superhydrophobic nanocrystal surfaces. These observations speak well for advanced materials and biomedical uses for these perfluoralkane capped silicon nanocrystals.

In Chapter 4, we report the unprecedented observation that hydride-terminated silicon nanocrystals, denoted ncSi:H, synthesized from commercially available SiO, can function as a single component heterogeneous reducing agent for converting gaseous CO$_2$ selectively to CO, at an impressive rate of hundreds of micromol/h$\cdot$g. The large surface area, strong broadband visible to near infrared light harvesting and highly reducing Si-H surface sites of ncSi:H play key roles in the conversion of CO$_2$ to CO. It is indeed a surprising yet welcome discovery that plentiful, inexpensive and benign elemental silicon, synthesized in the form of ncSi:H, made easily and cheaply from commercially available SiO, can exploit the reducing power of surface hydride to chemically reduce CO$_2$ to CO - a synthon for making methanol or hydrocarbons by well-established methods – at scientifically impressive $\sim$millimole/h$\cdot$g$_{cat}$ conversion rates. This advance bodes well for continued improvement by composition variations and doping methods, as well as size, shape and surface variations of ncSi:H, to achieve a higher rate and perhaps even transform the seemingly stoichiometric reaction to catalytic. With a scalable synthesis together with the ability to tailor the surface chemical and physical properties of ncSi:H, the future looks brighter for CO$_2$ utilization powered by the light and heat from the sun.
5.2 Future Work

5.2.1 Silicon-Metal Hybrid Nanocrystals

As presented in Chapter 4, we previously reported that hydride-terminated silicon nanocrystals can convert gaseous CO₂ selectively to CO. This conceptually distinct strategy for making fuels directly from sunlight is proven practical by our observation. However, after the stoichiometric reduction reaction, the hydride surface is oxidized and a silica shell forms. In this sense, we would like to do follow-up studies to examine the possibility of going catalytic. We rationally designed a complex silicon nanostructure with modified surface to achieve a full catalytic cycle of CO₂ hydrogenation. In our proposed scheme (Figure 50), the silicon hydrides could be replenished with the assistance of decorated hydrogen spillover reagents such as nanoclusters of noble metals. Mechanistic insights can be provided by techniques such as in-situ FTIR and turnover numbers could then be estimated.

![Figure 50. Illustration of Pd assisted hydrogen spillover on silicon surface.](image-url)
Figure 51. Our proposed synthesis: surface hydrides natively reduce the Pd(II) in solution.

The synthesis of Pd decorated Si is schematized in Figure 51.

5.2.2 Silicon Nanocrystals with Redox-Tunable Surface Ligands

Due to quantum size effects, we could tune the photoluminescence emission wavelength by tuning the size of the silicon nanocrystals, usually between the sizes of 1 to 5 nm. Specifically, with decreasing particle size, the energy gap between the ground and excited state (Eg) increases and the emission wavelength is blue shifted.

Herein we propose another strategy to control the photoluminescence by electrochemically tuning the charge on the silicon surface. In order to achieve this, the surface of the silicon nanocrystals would be grafted with redox-tunable molecules, such as C\textsubscript{60}. A model of a C\textsubscript{60} capped silicon nanocrystal is shown in Figure 52.

Upon reduction, each C\textsubscript{60} molecule can accept up to 6 electrons. This process is reversible and can be electrochemically controlled. Before the C\textsubscript{60} has its LUMO filled with external electrons, there would be charge transfer between the silicon core and the C\textsubscript{60} ligands, and the photoluminescence might be quenched due to this charge transfer. But with electrochemically reduced C\textsubscript{60} molecules on the surface, we might be able to switch on the photoluminescence again.
Other molecules that can be oxidized or reduced reversibly include ferrocene and tetrathiafulvalene (TTF). An illustration/scheme of the ferrocene terminated and TTF terminated silicon nanocrystals are shown in Figure 53a and 53b, respectively. The research in silicon nanocrystals capped with redox-active ligands may open another gateway towards the promising future for their optoelectrical applications.

Figure 53. Surface of silicon nanocrystals grafted with other redox-tunable molecules: a) ferrocene b) tetrathiafulvalene (TTF).

5.2.3 Pursuing Lower-Cost and Greener Approach to Silicon Nanocrystals for Applications

Despite the fact that silicon is earth abundant and relatively low-cost, silicon nanocrystals we synthesized and documented this thesis has higher cost if the price of the precursors, reaction
time and conditions, yield, and post-treatment methods were taken into account. Also our synthesis involves the usage of hydrofluoric acid, which needs to be handled with special facilities and extreme care. He group reported the biomimetic synthesis of silicon nanoparticles from diatoms\textsuperscript{178} and Veinot group reported synthesis of porous silicon from sand.\textsuperscript{179}

It would be very interesting and important to explore new innovative ways to make silicon nanocrystals and other silicon nanostructures from various sources. It is also of great significance if we could lower the amount of hydrofluoric acid in the synthesis or even avoid using it. That would promise a better future for nanosilicon based advanced materials and biomedical applications.
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Appendices

Appendix A  Details of the Synthesis and Characterization Experimentation in Chapter 2

Synthesis of ncSi in Silicon Oxide Matrix. Solid SiO (purchased from Sigma-Aldrich, -325 mesh powder) was placed in a quartz reaction boat and transferred to a tube furnace. The samples were typically heated at a rate of 18 °C/min under a flow of 95% Ar/5% H₂ to a peak processing temperature of 900 °C, then held at that temperature for 1 h before the furnace was allowed to cool to room temperature.

Liberation of ncSi:H from Silicon Oxide Matrix. For a typical batch synthesis, 0.3 g of 900 °C treated SiO powder was transferred to a Teflon beaker containing a mixture of 10 ml of 95% ethanol (aq. Sigma Aldrich) and 20 ml of 48% HF (aq. Sigma Aldrich. Personnel should be well trained in the handling of HF. The mixture was stirred for 2 h 50 min to fully etch away the silicon oxide matrix. The hydride-terminated ncSi were then extracted from the aqueous solution into pentane. The scale of the batch could be enlarged as long as the volume of the beakers and flasks are sufficient for safe handling of chemicals, for example, starting with 2 g of SiO powder instead of 0.3 g.

Characterization. Powder X-ray diffraction (PXRD) was performed on a Bruker D2-Phaser X-ray diffractometer, using Cu Kα radiation at 30 kV. The nitrogen sorption experiments were performed at 77 K on a Quantachrome Autosob-1-C instrument. Prior to each adsorption measurement the samples were degassed at 60 °C overnight under vacuum. The specific surface area was determined using the Brunauer-Emmett-Teller (BET) equation, applied to the best linear fit within the range of 0.05 ≤ P/P₀ ≤ 0.35. The cumulative pore volume and pore size distribution were determined using non-local density functional theory (NL-DFT). Fourier transform infrared spectroscopy (FT-IR) was performed using a Perkin Elmer Spectrum-One FT-IR fitted with a universal attenuated total reflectance (ATR) sampling accessory with a diamond coated zinc selenide window. For the oxidation study of the ncSi:H on the KBr pellet, the FT-IR spectra were acquired using the transmission mode without the ATR accessory. Diffuse reflectance of the samples was measured using a Lambda 1050 UV/VIS/NIR spectrometer from Perkin Elmer and an integrating sphere with a diameter of 150 mm. The ncSi:H aggregates morphology was characterized by scanning electron microscopy using a QUANTA FEG 250 ESEM. EPR measurements were performed at room temperature and 170 °C using a Bruker
ECS-EMX X-band EPR spectrometer equipped with an ER4119HS cavity. An Oxford ITC503 temperature controller was utilized. Typical operating parameters were as follows: microwave frequency 9.363/9.393 GHz (for N₂/CO₂), microwave power 2.147/2.144 mW (for N₂/CO₂), modulation amplitude 1.000 G, sweep width 100 G centred at 3347.25 G, time constant 0.01 ms, total sweep time 300.00 s, number of scans 4. The EPR analysis was applied to dried ncSi:H samples, which were sealed in the 4 mm EPR tubes in the glove-box under a N₂ gas atmosphere or sealed in CO₂ gas. The thermogravimetric analysis experiments were performed using a Discovery TGA (TA Instruments). XPS was performed in an ultrahigh vacuum chamber with base pressure of 10⁻⁹ Torr. The system used a Thermo Scientific K-Alpha XPS spectrometer, with an Al Kα X-ray source operating at 12 kV, 6 A and X-ray wavelengths of 1486.7 eV. The spectra were obtained with analyzer pass energy of 50 eV with energy spacing of 0.1 eV. The sample for XPS analysis was prepared by drop casting ncSi:H in pentane on GaAs substrates and left in vacuum at 60 °C for several hours. The data analysis was carried out using Thermo Scientific Avantage software.

Appendix B  Details of the Characterization Methods in Chapter 3

Characterization Methods

FTIR Characterization of ncSi:PFD

The as synthesized perfluoro-ligands capped silicon nanocrystals were drop-cast onto an IR transparent KBr substrate for spectroscopy. The substrate was then stored in a desiccator under vacuum, in order to remove the remnant solvent 1H,1H,2H-perfluoro-1-decene. Fourier transform infrared (IR) spectroscopy was performed on a Perkin Elmer Spectrum One FTIR spectrometer. The FTIR spectrum of ncSi:PFD is shown in Figure S3.

XPS

High-resolution XPS spectra of Si 2p, F 1s, C 1s were measured to determine the oxidation states of the constituent elements (Figure S4). The C 1s spectrum was deconvoluted into five well-resolved contributions. The peaks of Si 2p spectrum appeared at 103.49 eV and 100.15 eV, which correspond to the surface silicon (oxide) and the core silicon, respectively. In the F 1s
spectrum, the binding energy of 689.42 eV confirmed that there was carbon-fluorine bonding. For the deconvoluted C 1s spectrum, the absence of a ~284 eV peak indicated that there was no $sp^2$ carbon, which confirmed all the remnant solvent 1H,1H,2H-perfluoro-1-decene was removed. The fitted peaks relating to CF$_x$ bonds at 285.8 eV, 288.8 eV, 292.14 eV, and 294.33 eV are ascribed to C-Si (surface carbon), C-F, C-F$_2$, C-F$_3$, respectively.

**HR-STEM**

STEM images were acquired in a probe-corrected JEOL ARM200F operated at 80 kV equipped with a cold field emission gun and a high resolution pole-piece. Middle angle annular dark field (MAADF) images were acquired with 45 and 180 mrad inner and outer collection angles, respectively, while BF images used 11 mrad collection angles. Both images were recorded with a dwell time of 38 µs, and convergence semi-angle of 25 mrad resulting in a probe current of 40 pA. Samples were drop-casted onto Graphene-Cu grids (Graphene Supermarket) to ensure an ultra-thin support film of less than 2 nm. The STEM images were shown in Figure S5.

**SEM**

The morphologies of the samples were examined by a FEI Quanta FEG 250 environmental scanning electron microscopy (ESEM) at an accelerating voltage of 20 kV. The SEM samples were adhered onto stubs by using carbon tape and reinforced using carbon paste. The top-view and cross-sectional images are shown in Figure S6.

**Water Contact Angle Measurement**

Dynamic contact angles were measured using a continuously adjustable syringe (Hamilton), and a digital CCD camera (DigiCam, Dino-Lite Digital Microscope Pro). The volume of each droplet was ~25 µL. The images were taken by DinoCapture 2.0 and analyzed using ImageJ. The fitting and calculation was done by ImageJ. When calculating the contact angles, we employed ellipse fitting due to its very small standard deviations compared to circle fitting. The results were shown in Figure S8 and Table 1.
AFM

A Digital Instruments (Veeco, now Bruker) MultiMode AFM was used with a Nanoscope IIIa controller and J scanner to image sample surfaces. Tapping mode was used in air with a Bruker TESP tip driven at 345 kHz and using 1-2 Hz scan rate and 512 sampling rate. The setpoint was chosen by backing off the tip after it engaged the surface until contact was lost, and increasing the drive amplitude until the tip engaged the surface again. Nanoscope III software (v5.14r3) was used for acquisition and Nanoscope Analysis (v1.40) software was used to process the images, applying a 0th order flattening and low-pass filter before computing the quadratic (RMS) roughness of the surface. Images and analysis are shown in Figure S9.

Photoluminescence Absolute Quantum Yield (AQY) Measurement

The absolute quantum yield was determined using a previously reported integrating sphere method (Mangolini, L.; Jurbergs, D.; Rogojina, E.; Kortshagen, U. J. Lumin. 2006, 121, 327.). Samples were excited in an integrating sphere (Gigahertz Optik, custom made) with light from a 365nm LED (Thorlabs M365L2), and photoluminescence was collected by a 1 mm diameter optical fibre (Ocean Optics) and detected by an Ocean Optics Maya 2000 spectrometer. The continuous absolute quantum yield was measured by taking appropriate ratios of the excitation and emission peak areas of spectra recorded for the empty sphere and sample holder, and the excitation focused directly onto the sample (Faulkner, D. O.; McDowell, J. J.; Price, A. J.; Perovic, D. D.; Kherani, N. P.; Ozin, G. A. Laser Photon. Rev. 2012, 6, 802.). The accuracy of the system was verified against literature values for rhodamine 6G and MEH-PPV. Solution samples were measured in cuvettes that were filled and sealed in the glove box. Film samples were sealed into a custom made sample holder in the glove box that was then inserted into the integrating sphere.

Appendix C  Gas phase CO₂ Reduction Measurements in Chapter 4
Borosilicate glass microfiber filters were used as a substrate for gas phase reaction measurements to provide increased surface area as well as mechanical stability. A fresh dispersion of ncSi:H in pentane was dropped onto the filters and dried under N₂ flow to yield films containing several mg of ncSi:H. Then the films were further dried under vacuum for at least 0.5 h, before being put into the reactor. A total pressure of ~27 psi and a light intensity of 1 sun were the standard conditions for each run, otherwise the different conditions would be stated in the main text. The details of the reactor are listed as follows. These experiments were conducted in a custom fabricated 1.5-mL stainless steel batch reactor with a fused silica view port sealed with Viton O-rings. The reactors were evacuated using an Alcatel dry pump prior to being purged with the reactant gases H₂ (99.9995%) and CO₂ (99.999%) at a flow rate of 6mL/min and a stoichiometry of 1:1 (stoichiometric for reverse water gas shift reaction). During purging, the reactors were sealed once they had been heated to the desired temperature. The reactor temperatures were controlled by an OMEGA CN616 6-Zone temperature controller combined with a thermocouple placed in contact with the sample. The pressure inside the reactor was monitored during the reaction using an Omega PX309 pressure transducer during the reaction. Reactors were irradiated with a 1000W Hortilux Blue metal halide bulb for a period of ~22 hours. For the test irradiated with concentrated light, the reactor with a volume of 11.8 mL was irradiated with a 300W Xe lamp for a duration of 3 hours. Product gases were analyzed with a flame ionization detector (FID) and thermal conductivity detector (TCD) installed in a SRI-8610 Gas Chromatograph (GC) with a 3’ Mole Sieve 13a and 6’ Haysep D column. Isotope tracing experiments were performed using \(^{13}\)CO₂ (99.9 atomic % Sigma Aldrich). The reactors were evacuated prior to being injected with \(^{13}\)CO₂ followed by H₂. Isotope product gases were measured using an Agilent 7890A gas chromatographic mass spectrometer (GC-MS) with a 60m GS-CarbonPLOT column fed to the mass spectrometer.

### Appendix D  Tables for \(^{13}\)CO Production Rate versus CO Production Rate in Chapter 4

<table>
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<tr>
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<th>CO₂ only</th>
<th>CO₂+H₂</th>
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<tr>
<td>CO rate (nmol/g*h)</td>
<td>$^{13}$CO rate (nmol/gcat*h)</td>
<td>CO rate (nmol/g*h)</td>
<td>$^{13}$CO rate (nmol/gcat*h)</td>
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</table>

**Table in Appendices 1a.** $^{13}$CO production rate of the CO$_2$ only and CO$_2$+H$_2$ tests compared to the total CO production rate ($^{12}$CO and $^{13}$CO combined). The ratio of $^{12}$CO to $^{13}$CO produced were estimated by the ratio of the corresponding GCMS peak areas (mass-to-charge ratios of 28 and 29, respectively). The peaks were fitted assuming that they are Gaussian and areas were determined by the Peak Analyzer tool of OriginPro software. The ratio of $^{12}$CO to $^{13}$CO is then applied to the total CO production rates to obtain the corresponding production rates. The approach used in Table 1a to obtain the $^{12}$CO:$^{13}$CO ratio is the same as that used to obtain the results shown in Table 1b, 1c.
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<th>sample storage time (days)</th>
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<tr>
<td>CO rate (µmol/g*h)</td>
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<tr>
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**Table in Appendices 1b.** 13CO production rate compared to the total CO production rate (12CO and 13CO combined) in the sample stability tests.

<table>
<thead>
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<th>Temperature and Light Conditions</th>
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<th>170 °C</th>
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<td>Dark</td>
<td>Light</td>
<td>Dark</td>
</tr>
<tr>
<td>CO rate (µmol/g*h)</td>
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<td>13CO rate (µmol/gcat*h)</td>
<td>0.026</td>
<td>1.526</td>
<td>0.277</td>
</tr>
</tbody>
</table>

**Table in Appendices 1c.** 13CO production rate compared to the total CO production rate (12CO and 13CO combined) in tests of the effect of temperature and light.
Copyright Acknowledgements

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