ZERO AND TWO DIMENSIONAL NANOMATERIALS FOR BIOLOGICAL
AND ELECTRONIC APPLICATIONS

AN ABSTRACT

SUBMITTED ON THE THIRD DAY OF JANUARY 2022 TO THE DEPARTMENT
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SCHOOL OF SCIENCE AND ENGINEERING OF TULANE UNIVERSITY FOR THE

DEGREE OF

DOCTOR OF PHILOSOPHY

BY

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Abstract

Silicon nanomaterials exhibit unique properties from those of bulk silicon based on quantum confinement effects created by the reduction in size to the nanoscale. These properties include a tunable band gap, elevated brightness, increased chemical stability and, resistance to photobleaching. The compatibility with organisms makes silicon nanoparticles model candidates for use in many biological applications, while the exploitation of the size-dependent quantum confinement effects has led to the development of a range of electronic applications for both silicon nanoparticles and nanosheets. The preparation and characterization of zero-dimensional silicon nanoparticles and two-dimensional silicon nanosheets and their relevance to biological and electronic applications is described in the proceeding dissertation.

TEGylated silicon nanoparticles were produced in one step from the reactive high-energy ball milling of silicon wafers with synthesized triethylene glycol monomethyl monopropargyl ether. A new approach for purifying the functionalized silicon nanoparticles using a silica-gel column was developed. Surface characterizations and optical properties of the silicon nanoparticles were accomplished through various analytical methods. Nanoparticle size and size distribution were determined using TEM and DLS while confirmation of ligand attachment to the silicon surface was confirmed through XPS and FTIR.

Multilayer silicene nanosheets were generated from the oxidation of calcium silicide with synthesized ferrocenium tetrafluoroborate. The two-dimensional nanosheets were produced via a redox assisted chemical exfoliation reaction in which silicon polyanion layers were exfoliated from calcium silicide. A visual color change from dark
blue to bright orange aided in the recognition of the culmination of the synthesis reaction. Interplanar spacing values for the silicene sheets were detected by XRD, crystal lattice parameters found from SAED images, and nanosheet composition revealed by EDS.

Finally, the synthesized triethylene glycol monomethyl monopropargyl ether was used to attempt to produce electronically conductive silicon nanoparticles containing 4-ethynylaniline. TEG and 4-ethynylaniline were ball milled with silicon wafers to produce functionalized nanoparticles; however, separation limitations were met during the processing of the nanoparticles prior to characterization.
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DEDICATION

TO LOCHLAN

A TRUE KNIGHT IN A WORLD OF MONSTERS

TU ES MA RAISON D’ÊTRE
ACKNOWLEDGEMENTS

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To my parents, Michael and Karen Armstrong, thank you. You have never doubted my ability to succeed, even when I doubted myself. To you I owe my life.

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Chapter 1: Background, Theory, and Significance

1.1. Introduction

Silicon is one of the most plentiful elements found on the Earth, second only to oxygen. However, due to its reactive nature, especially with oxygen, silica-based clays, sands, and stone constitute the major forms in which silicon is observed naturally. Silicon, along with selenium and tellurium, was one of the first semiconductor materials discovered to amplify electronic signals. It has played a major role in the modern technological industry, leading to the late 20th century being dubbed the Silicon Age with the invention of the first working silicon transistor by Tanenbaum of Bell Labs in 1954.\(^1\)

Because of the relatively low costs associated with purification, and relative earth abundance, as well as its ease of modification, silicon has made its mark on the electronics industry in the form of computer chips, solar cells, and most notably semiconductors devices. Reduced to the size of 1-100 nanometers, nanocrystalline silicon materials will exhibit unique optical and electronic properties quite different from their bulk counterparts, especially those arising from quantum confinement effects.\(^2\) Further surface modification of the nano silicon surface renders it with targeted functionality and stability according to the requirements of the environment. Of particular interest are the impacts from surface functionalization of silicon nanomaterials on the solubility characteristics and optoelectronic properties, particularly the effects observed from the addition of water-soluble ligands. These surface modified nanoparticle semiconductors, with their characteristic size-dependent attributes have great potential for uses in
numerous biological applications such as biosensing, intracellular delivery of biological agents, and treatment of cancerous cell lines.

Along with silicon nanoparticles, silicon nanosheets have been increasingly studied in recent decades in hopes of bridging the gap between the quantum and bulk material worlds. Current research focuses on multi-layered materials or those grown on substrates, as the challenges associated with characterizing single layer, and ultra-thin layer, 2D nanosheets often require their own examination. Silicon nanosheets, much like silicon nanoparticles, also exhibit tunable optoelectronic characteristics which makes them highly desirable research candidates in the fields of light sensing, energy storage, and tumor treatment.

This thesis describes the synthesis, functionalization, and characterization of silicon nanoparticles and their applications in the nanobiotechnology field along with a synthesis of silicon nanosheets and their applications in the area of electronic devices. This work focuses in-particular on the production of passivated silicon nanoparticles via a mechanochemical approach, and a new method for separation of the nanoparticles. In addition, an original procedure yielding single-layer silicon nanosheets, absent the need of growth substrates and harsh chemicals, is presented.

1.2. Silicon Nanomaterials

Silicon in bulk form can be an incredibly useful material in the building of semiconductor devices; however, it is not favored in the production of optics or optoelectronics due to a low light emission efficiency at room temperature. This inability to fluoresce or luminesce at normal operating temperatures can be attributed to the small,
indirect band gap of 1.1 eV found in silicon.\textsuperscript{10,11} Indirect band gap materials require the production of phonons, quantized vibrations in the crystal lattice, in order to facilitate the radiative recombination necessary to release photons. This phonon requirement makes it more likely that an electron in an indirect band gap will undergo a nonradiative process in which no light is produced rather than a radiative recombination in which light is emitted.\textsuperscript{12} Photon emission is both material and band gap dependent as the size of the material will determine the size of the band gap.\textsuperscript{13} Silicon nanomaterials have been the focus of numerous studies due to the large band gap associated with the nanomaterials and recently there have been a variety of synthetic approaches developed to produced silicon nanomaterials with emissions at normal working temperatures.\textsuperscript{14} Thus, silicon nanomaterials show great potential for applications in the fields of nanobiotechnology, energy storage, and optoelectronic devices.

1.3. A Brief History of Nanomaterials

Richard Feynman’s 1959 Caltech lecture “There’s Plenty of Room at the Bottom: An Invitation to Enter a New Field of Physics”\textsuperscript{15} went largely unnoticed at the time; however, it has since been considered as the defining moment of the dawn of nanotechnology. In his speech, Feynman discussed the direct manipulation of individual atoms in synthetic chemistry along with computer circuitry design and electron microscope development. He theorized that we could “swallow the doctor”, a concept involving the manufacture of nanoscale robots that could be ingested by the user. Feynman also suggested that it should be possible, in principle, to "arrange the atoms the way we want" and perform chemical synthesis via mechanical manipulation. His theories,
along with the dedication of numerous researchers, has led us to where we are today; living in a world that can write much more than the entire 24 volumes of the *Encyclopaedia Brittanica* on the head of a pin.

In the 5th century BC, Democritus developed his atomic theory in which he questioned whether continuous matter can be divided into distinct pieces or particles called atoms, thus developing the study of nanoscience. The Latin prefix ‘nano’ is derived from the Greek word ‘nanos’ meaning dwarf and when used as a unit of measurement for length, such as in nanometer, is equal to one billionth (10^-9) of a meter. Nanomaterials can be organized into three distinct categories based on the magnitude of one or more dimensions (x, y, or z) of the material. These are known as zero, one, and two-dimensional structures as seen in Figure 1.1. If all three dimensions (x, y, and z) of a

![Figure 1.1. Comparison of 0D, 1D, and 2D nanomaterials.](image-url)
material are less than 100 nm, it is considered a zero-dimensional (0D) material, and more commonly referred to as a nanoparticle, quantum dot, or spherical fullerenes, in the case of carbon. When two dimensions of a material are less than 100 nm (x and y), and the other dimension (z, or length, L) is much larger, the structure is then considered to be a one-dimensional (1D) material generally referred to as nanowires, nanotubes, and nanorods. Two-dimensional (2D) nanomaterials are larger than 100 nm in two dimensions (x and y), but their overall thickness (z) is less than 100 nm. Examples of 2D include nanosheets, nanofilms, and nanocoatings. If the material does not have any dimensions less than 100 nm, it is considered a 3D bulk material.

The use of nanomaterials can be traced back to the 4th century AD with the introduction of dichroic glass used by the Romans in the famous Lycurgus cup\textsuperscript{16} as seen in Figure 1.2.\textsuperscript{17} The silver and gold 0D nanoparticle colloids present in the manufactured glass give rise to the two distinct colors, which can be manipulated by the use of reflected

![Figure 1.2. Lycurgus cup demonstrating dichromic features of gold and silver nanoparticle infused glass. Reprinted/adapted with permission.](image)
light as when it is shining from in front of the cup (green) or transmitted light as when it is shone from behind (red).

By utilizing transmission electron microscopy in 2006, Reibold discovered that 1D cementite nanowires and carbon nanotubes were incorporated into “Damascus” saber steel blades manufactured between the 13th and 18th centuries. He found that these nanostructures were responsible for the incredibly sharp edge, increased mechanical strength, and wavy banding pattern (Figure 1.3) absent in other steel blades.

2D graphite, also referred to as plumbago, has been exploited since the beginning of time in ceramic paints, pottery, lubricants, and most famously pencils. It was not until 1778 that the term ‘graphite’ was coined by Abraham Gottlob Werner from the Greek word graphein for ‘write’ while attempting to clarify the confusion between molybdena, plumbago, and black lead after Carl Wilhelm Scheele showed that the three
minerals contained distinct chemical formulae. Two hundred years passed before the expression graphene would be approved by the International Committee for Characterization and Terminology of Carbon and Graphite to describe, “a single carbon layer of the graphitic structure [with the] ending -ene [that contains] fused polycyclic aromatic hydrocarbons. The term graphene layer should be used for such a single carbon layer.” Almost twenty years after this, Geim et al. showed that it was possible to extract few-layer graphene (FLG) 2D nanomaterials from bulk graphite (Figure 1.4) with a simple mechanical exfoliation process utilizing sticky tape and in 2010 silicon nanoribbons with hexagonal symmetry were synthesize on a Ag (110) substrate by Aufray leading the way for the production of silicene, a silicon analog of graphene.

1.4. Optical Properties of Silicon Nanoparticles

![Crystal structure of graphite](image)
All materials can be classified as conductors, semiconductors, or insulators due to the disposition of energy bands created by the extensive overlap of atomic orbitals. When two atoms join together, their atomic orbitals overlap. However, due to the Pauli exclusion principle, which states that no two electrons in a molecule may have the same quantum number, each atomic orbital splits into two molecular orbitals of differing energy allowing the electrons to exist in the new structure without having the same quantum value. Similarly, when a large number of atoms come together to form a solid, such as a crystal lattice, the resulting energy difference of the molecular orbitals is so small that the orbitals can be considered as continuous, forming a band of energy levels. The conduction band is a collection of the energetically lowest vacant atomic orbitals and occurs above the band gap while the valence band is the highest range of orbitals in which electrons are normally present at absolute zero temperature. The valence band derives its name from the valence orbitals that occupy the band region.

1.4.1. The Band Gap

An energy band gap ($E_g$) is the energy difference between the highest occupied energy state of the valence band and lowest unoccupied energy state of the conduction band in a material. It is essentially the energy difference required to excite an electron from the valence band to the conduction band. Several optical properties of a material, and in turn nanomaterial, are determined by the size of said energy band gap. For a conductor there is no band gap, and the electrons, along with their subsequent holes, are free to move between the overlapping atomic orbitals as needed as seen in Figure 1.5.
The Fermi level ($E_f$) is the thermodynamic quantity of work (or amount of energy) that must be added to the material in order to add one electron to the conduction band, or conversely the work produced when the electron is removed from the valence band. This work can then be measured in the units of volts, indicating the chemical and electronic potential existing between the two bands. In an insulator, the Fermi level is arbitrary as the band gap is energetically too large to allow electrons to travel between the occupied and unoccupied valence and conduction bands respectively. For semiconductors, the band gap is relatively small, and therefore if the electrons are energized by an external source, they can transition between the valence and conduction band, producing an empty space or a ‘hole.’ An electron from a neighboring atom can then fill the empty space creating a new ‘hole’ in the neighboring atom which can then be filled by third electron, and so on. This is analogous to a bowler removing their bowling
ball from the middle of a fully occupied return mechanism, which leaves a hole between two other balls. An additional ball is then automatically returned, while the other balls move forward, filling the empty space left behind by the ball that was removed. This traveling of the ‘hole’ is viewed as the movement of a positively charged particle through the material. Thus, the electrons and holes in a semiconductor can be regarded as mobile charge carriers as they both participate in the conduction process. In addition, semiconductors can be p or n doped by introducing chemical impurities, causing the Fermi level to shift and in turn decreasing the amount of energy required to excite an electron from the valence to the conduction band.

Semiconductors can possess either of two basic types of band gaps, the direct or indirect band gap. For direct band gaps, the momentum of the maximum energy state of the valence band matches the momentum of the minimum energy state of the conduction band. This momentum is termed the $k$-vector and describes the sinusoidal oscillations of the electrons within the crystal lattice. An electron must be able to transition with no changes in the $k$-vector from the valence band to the conduction band in a direct band gap. However, if the $k$-vector of the valence band and the conduction bands is not equivalent, as when the transition is dipole forbidden, a phonon must induce a change in the momentum ($k$-vector) and an indirect band gap arises as seen in Figure 1.6.

When an electron in the valence band is excited by an amount of radiative energy $h\nu$ that is greater in magnitude than $E_g$, the electron will be promoted to the conduction band, leaving behind a hole’ with a positive charge in the valence band. The distance created between the electron and its corresponding hole, termed the Bohr exciton radius,
is dependent upon the dielectric constant of the respective material. For bulk silicon, this radius is found to be 4.2 nm. These excited electrons will remain only for a short time in the conduction band before falling back down to the valence band and repopulating their normal valence energy level. When an electron from the conduction band eliminates a ‘hole’ in the valence band upon its return, excess energy in the form of a photon will be released. This process is known as radiative recombination and produces the phenomena known as photoluminescence. Recombination also produces non-radiative heat energy by internal conversion, which is a crossover of a charge carrier between two states with the same multiplicity meaning singlet-to-singlet or triplet-to-triplet states.

The relative rates of radiative and non-radiative recombinations will determine the quantum efficiency of the semiconductor. By decreasing the size of the semiconductor...
material from the bulk to the nanoscale, quantum confinement effects can be introduced to the system, transferring the semiconducting material from the indirect band gap state to the direct band gap state. For nanoscale semiconductors (quantum dots), these effects alter the size of the band gap, resulting in the production of photons with differing wavelengths. As the size of the nanocrystal decreases, the band gap increases due to the quantization of the energy levels that arises when the radius of the quantum dot is smaller.

Figure 1.7. Size effects of quantum dots on optical properties.
than the Bohr exciton radius. This increase in the band gap results in a blue shift in the absorbance and emission wavelengths as more energy is required to bridge the gap between the valence and conduction bands as seen in Figure 1.7.

1.4.2. Optical Effects of Surface Passivation and Defects

Surface defects and surface functionalization can also play an important role in the modification of the optical properties of silicon nanomaterials. During the synthesis process, surface defects, or dangling bonds (DB) can form on the outer surfaces of the nanomaterial. Often termed an “immobilized free radical,” dangling bonds are highly reactive and unstable; however, they do gain some stability from the existence of steric strain and limited mobility, often exhibiting a longer life span than typical free radicals. DB occur when the anchored, external silicon atoms experience an unfilled valence, as

![Dangling bonds on the surface of silicon nanomaterials.](image)

*Figure 1.8. Dangling bonds (red) on the surface of silicon nanomaterials.*
seen in Figure 1.8. The unpaired valence electrons on the silicon surface are unable to form covalent bonds, creating a disruption in the crystal lattice. Through density functional theory (DFT) calculations, Scherpelz and Galli\textsuperscript{30} showed that dangling bonds create trap states in the band gap region in which electrons are prevented from further participating in charge transport until recombination occurs. By effectively decreasing the band gap energy of the quantum dot (Figure 1.9.), the trap states have been found to increase the frequency of competitive nonradiative recombinations, diminishing the luminescent efficiency of the nanomaterial.\textsuperscript{12,31} Bhatt \textit{et al.} have shown

\textbf{Figure 1.9.} Illustration showing how electronic trap states created from dangling bonds prevent luminescence of the nanomaterial.
that the electronic position of the DB in the band gap region is dependent on the thickness of the material, and in turn, the size of the quantum dot.\textsuperscript{32} Therefore, it is possible to tune the optical properties of materials by adjusting the number of the dangling bonds on the surface of the nanomaterial via functionalization or passivation.\textsuperscript{33}

Surface passivation of silicon nanoparticles by hydrogen, oxygen, and carbon appears to have a dramatic effect on the optical properties of the small-scale substances. Hydrogen is a well-established substitution of the dangling bonds that occur on the silicon surface during synthesis.\textsuperscript{34–37} The functionalization of the silicon surface with hydrogen induces changes in the electronic as well as optical properties of the silicon nanomaterial by lowering the density of the electron states band gap created by the localized dangling bonds. \textsuperscript{38} Girginoudi and Thanailakis showed via electron spin resonance (ESR) and photoluminescence (PL) studies that as the hydrogen content (by percentage) on the surface of silicon-carbide films increased, the band gap size increased from 1.74 eV to 2.22 eV, photoconductivity increased, and PL intensity increased.

Density functional theory (DFT) calculations performed by Hikita, Padama, and Rittiruam\textsuperscript{39} demonstrate that functionalization of terminated silicon atoms with hydrogen atoms enlarges the band gap from the bulk state to the semiconductor state due to the passivation of the dangling bonds. However, silicon hydrogen bonds are considered unstable due to their reductive nature and as such are subject to oxidation to form silicon oxygen double bonds.\textsuperscript{40} Oxygen passivation produces deep trap states which create a red shift in the photoluminescence of the nanomaterial as demonstrated by Biteen \textit{et al.}\textsuperscript{41} Silicon carbon bonds on the surface of nanomaterial have shown to generate similar
optical effects as Si-H bonds\textsuperscript{42} and are considered to be more stable than the Si-H bonds due to a larger difference in electronegativity.

\textbf{1.5. Silicon Nanoparticle Synthesis}

There are two main routes for the synthesis of silicon nanomaterials that have been developed in the last few decades: top-down and bottom-up. For the bottom-up approach, molecular precursors such as halosilanes or silicates are assembled into nanosized silicon materials. These processes can be more cost efficient than top-down approaches and are able to be scaled up for mass production. In the top-down processes, nanomaterials are formed from the reduction of bulk silicon into nanosized fragments. Even so, the top-down approach can be slow, not suitable for narrow size distribution, and is not cost effective. Most synthetic processes focus on producing oxygen free silicon surfaces via passivation with ligands containing carbon backbones; however, the overall routes to achieve this goal can greatly differ.

\textbf{1.5.1 Bottom-Up Synthesis Methods}

Bottom-up synthesis methods are generally carried out using silicon-containing precursors such as halosilanes or silicates. The silicon nanomaterials prepared by bottom-up methods are commonly hydride or halogen terminated, and thus additional surface passivation with carbon-based molecules is required to stabilize the reactive surface and prevent oxidation.
1.5.1.1. Halosilane Reduction

The reduction of halosilanes has shown to be an effective mode of producing organically capped silicon nanoparticles. In 2001, Mayeri reacted silicon tetrachloride with the Zintl salt sodium silicide and dimethoxyethane (DME) to produce chloride capped silicon nanoparticles as seen in Scheme 1.1.

Scheme 1.1. Production of chloride capped silicon nanoparticles via the reduction of silicon tetrachloride.

The reduction of halosilanes has shown to be an effective mode of producing organically capped silicon nanoparticles. In 2001, Mayeri reacted silicon tetrachloride with the Zintl salt sodium silicide and dimethoxyethane (DME) to produce chloride capped silicon nanoparticles as seen in Scheme 1.1. The chloro-terminated

Scheme 1.2. Maeryi method for alkylation of chloride capped silicon nanoparticles.
nanoparticles were then stirred with 2.5 molar n-butyllithium in DME and hexane to produce n-butyl passivated silicon nanoclusters as shown in Scheme 1.2.

1.5.1.2. Halogenation of Metal Silicides

Neiner and Kauzlarich have reported a synthetic method to produce hydrogen functionalized silicon nanoparticles from metal silicides, specifically sodium silicide. Ammonium bromide, sodium bromide, and sodium silicide (1:1:2 molar ratio) were ball milled in an agate mortar then pressed into pellets before being annealed at 200$^\circ$C for seventeen hours in an argon atmosphere while under dynamic vacuum as seen in Scheme 1.3.

\[
\text{NaSi + NH}_4\text{Br + NaBr} \xrightarrow{17\text{hr}, 200^\circ\text{C, Ar}} \text{Si H + NaBr + NH}_3 (g)
\]

Scheme 1.3. Synthesis of hydrogen capped silicon nanoparticles from metal silicides.

Reaction completion was indicated by the cessation of ammonia gas production and the resultant nanoparticles were washed with an aqueous 2\% HF solution to remove any residual sodium bromide salts. Particle sizes varied from 4 nm to 60nm. The 60 nm and 5 nm particles were found to be crystalline, as evidenced by XRD spectra containing Si [111], [220], and [311] indices at 28.7$^\circ$, 47.5$^\circ$, and 56.5$^\circ$, respectively, while the 10 nm and 4 nm particles were amorphous. FTIR data showed Si-H stretches in the 2000 cm$^{-1}$ region along with Si-H$_2$ scissoring at 900 cm$^{-1}$ and 1900-2100 cm$^{-1}$ along with silicon lattice vibrations around 600-700 cm$^{-1}$. Na solid state NMR data indicates that the 60 nm and 10 nm particles contain 20\% unreacted sodium silicide, while the 5 nm particles
contain 12% unreacted sodium silicide, however, proton NMR shows agreement with FTIR spectra with a Si-H shift at 0-1.3 ppm and a Si-H2 shift at 4.29 ppm.

1.5.1.3. Reverse Micelle Formation

In 1993 Wilcoxon, Williamson, and Baughman designed a water-free, inverse micelle synthesis method for the production of gold colloids with a demonstrated resonance blue shift from 520 nm to 480 nm.45 Utilizing this successful synthetic route, six years later the group was able to design silicon nanoparticles with direct band gap transitions noted at 3.2 eV (380 nm) and 3.4 eV (365 nm).46 In this process a halosilane, SiX4 (X = Cl, Br, or I) is initially dissolved in the hydrophilic interior of a solution of micelles such as nonionic aliphatic polyethers or quaternary ammonium surfactants with each micelle having an interior volume range of 1-10 nm. The micelle solution, containing the halosilane, is then dissolved in a hydrophobic medium such as octane, thus forcing the hydrophilic silicon to aggregate, forming nanoclusters. The absence of water ensures no Si-H bonds are oxidized to Si-OH or SiO2 bonds, which would quench any luminescent properties. The Si (IV) is then reduced to Si (0) using a metal hydride such

![Scheme 1.4. Synthesis of hydrogen functionalized silicon nanoparticles using surfactants to form inverse micelles.](Image)
as LiAlH$_4$ in dry THF, producing hydrogen gas and lithium salts (Scheme 1.4.). Upon exposure to oxygen, the silicon clusters formed a yellow precipitate that fell out of the octane solution, leading Wilcoxon to believe that the silicon nanoparticles were hydrogen functionalized as a hydrogen terminated silicon surface is hydrophobic and more likely to remain suspended in the octane medium. Control over the final nanocluster size of 1.8-10 nm was achieved by the variation of micelle size, inter-micellar interactions, and reaction chemistry along with further purification steps such as high-performance liquid chromatography (HPLC). In-addition, supplemental passivation steps were necessary in order to render the surface chemically stable as demonstrated by the reaction of the solution with atmospheric oxygen and water.

Following in the footsteps of Wilcoxon, the Tilley group was able to synthesize silicon nanoparticles in micelles with smaller particle size distributions than previously reported by using powerful hydride reducing agents. Silicon tetrachloride was dissolved in either of two surfactants, tetraoctyl ammonium bromide (TOAB) in toluene or pentaethylene glycol monododecyl ether (C12E5) in hexane then reacted with the

\[
\text{SiCl}_4 + \text{LiAlH}_4 \rightarrow \text{Si} + \text{H}_2
\]

\text{TOAB/toluene (or)}
\text{C12E5/hexane}
3h, RT, Ar

Scheme 1.5. Solution-phase synthesis of hydrophobic silicon nanoparticles
reducing agent lithium aluminum hydride (LiAlH₄) for three hours under argon atmosphere at room temperature as seen in Scheme 1.5.

TEM data indicates that the nanoparticles produced from TOAB are the most uniform in size with an average diameter of 1.8 nm and a nominal distribution of ±0.2 nm, illustrating the large amount of control achievable by using micelles. In addition, atomic-resolution images show that the particles are crystalline and faceted. The Si-H surface bond can then be treated with both a compound containing a carbon-carbon double bond and a platinum catalyst, such as H₂PtCl₆, to produce hydrophilic or hydrophobic particles through the formation of a Si-C surface bond as seen in Figure 1.10.⁴⁸

![Figure 1.10. Schematic diagram of the procedure used to change the surface chemistry of the silicon quantum dots from hydrogen to allylamine. Reprinted/adapted with permission.](image)

The resultant allylamine-capped silicon quantum dots, with an average size of 1.4 nm, were found to be stable for several months with no signs of photo bleaching. UV-Visible and photoluminescence data showed a direct band gap absorbance at 320 nm and a strong emission at 480 nm. FTIR spectra indicated that the presence of Si-CH₂
vibrational scissoring at 1460 cm\(^{-1}\) and symmetric bending at 1260 cm\(^{-1}\) along with C-CH\(_2\) and C-NH\(_3\) vibrations in the 2500-3500 cm\(^{-1}\) region. XRD data is limited due to the small dimensions of the silicon quantum dots; therefore, no conclusive data has been obtained by this method.

1.5.1.4. Spray Pyrolysis

Spray pyrolysis is a process in which reagents dispersed in a solution are deposited in a thin film onto a heated substrate, where the constituents react to form a chemical compound. Products aside from the desired compound become volatile at the deposition temperature and will remain in the gaseous phase where they may be removed by a vacuum or flow of gas. The shape and size of the film or particles formed can be controlled by adjusting the concentration of the initial solution, volume of the droplet dispersed, or the deposition temperature of the substrate.\(^{49}\) Particles produced by spray pyrolysis experience a spherical morphology, narrow particle distribution, and relatively homogeneous composition.\(^{50}\)

During the spray pyrolysis procedure, a precursor solution is prepared by dissolving, typically, the metal salt of the desired product in a suitable solvent. The starting solution is then fed through an atomizer and subsequently a spray nozzle (Figure 1.11\(^{51}\)), where droplets of a desired size are formed. Once released, the droplets are transported throughout a furnace to the heated substrate surface, where the solvent solution evaporates, and the metal remains deposited. Drying, reactions between
precursor and surrounding gas, pyrolysis, or sintering may occur inside the furnace to form the final product.

Ng et al. have produced carbon-coated silicon nanocomposites from a spray pyrolysis method that employs lower temperatures than what is typically required for silicon or silica nanoparticle production. Nanocrystalline silicon powder was combined with citric acid in absolute ethanol and heated to 300 °C, 400 °C, or 500 °C in air as seen in Scheme 1. Air stable, spherical, homogeneously dispersed silicon nanocomposites
were obtained, as evidenced by x-ray diffraction patterns and scanning electron microscopy images along with high-resolution transmission electron microscopy images.

1.5.1.5. Chemical Vapor Deposition

There are a variety of different types of chemical vapor deposition (CVD) processes, however, they are all similar in that volatile, or gas phase, precursors react with a heated substrate to form a solid material. Most modern methods are either low

![Figure 1.12. High resolution electron microscopy image of Zavorin silicon nanocomposites. Reprinted/adapted with permission.](image)

\[
\text{Si} + \text{C}_6\text{H}_8\text{O}_7/\text{C}_2\text{H}_6\text{O} \xrightarrow{T^\circ\text{C}} \text{Si} - \text{C} + \text{CO}_2 \uparrow + \text{H}_2\text{O} \uparrow + \text{energy} \uparrow
\]

\textbf{Scheme 1.6.} Synthesis of silicon nanocomposites via spray pyrolysis.
pressure chemical vapor deposition (LPCVD) or ultrahigh vacuum chemical vapor
deposition (UHV CVD) as reduced chamber pressures tend to reduce unwanted gas-phase
reactions and improve product purity. CVD is most commonly used to deposit conformal
films and augment surfaces in order to increase their functionality.\textsuperscript{53}

Recently silicon nanoparticles were inserted onto multi-walled carbon nanotubes
(MWCNT) via CVD in order to determine the electrochemical properties of the
nanocomposites.\textsuperscript{54} Zavorin and colleagues deposited silicon nanoparticles on MWCNT
(Figure 1.12\textsuperscript{54}) via a fluidized bed reactor. Each 5-6 g MWCNT batch was exposed to a
mixture of argon and monosilane (no more than 5 vol.\%) at 500 °C for 2.5-5 hours. The
quantity of silicon nanoparticles added onto the MWCNT could be controlled by the time
of processing with the reaction mixture. The method produced Si-MWCNT composites
with high amounts of amorphous silicon nanoparticles containing crystalline silicon
particles of 2-3 nm in diameter.

1.5.1.6. Thermal Annealing

Thermal annealing refers to a procedure in which a material is heated to an
elevated temperature for an extended period of time, sometimes for many hours, then
slowly cooled in order to prevent thermal shock. During the prolonged heating period,
atoms migrate inside the crystal lattice, decreasing the number of defects found within the
crystal structure. During the heating phase of the annealing process, a disproportionation
reaction occurs, in which silicon suboxide, SiO\textsubscript{x} (Si\textsuperscript{2+}), is oxidized to SiO\textsubscript{2} (Si\textsuperscript{4+}) and
reduced to Si°. The neutrally charged atoms then congregate together to form nanoparticle clusters.

A simple, two-step process involving the thermal annealing of silicon suboxide (SiOx, X = 0.4, 1.0, 1.6) powder has been reported by Liu, Sato, and Kimura. The precursor was annealed in a ceramic crucible at 900 °C under the flow of argon for one hour at normal atmospheric pressure (Scheme 1.7). The resulting powder was then etched with a 1-5% aqueous hydrofluoric acid solution to dissolve any silicon dioxide produced, yielding hydrogen capped silicon nanoparticles with an average diameter of 4.2 nm. The particles also demonstrated a photoluminescent peak maximum at 487 nm (2.55 eV) and were soluble in multiple organic solvents including octanol, toluene, methanol, chloroform, acetonitrile, dimethylformamide (DMF), and hexane.

In 2006, the Veinot group demonstrated a reductive thermal annealing method for the production of silicon nanocrystals from hydrogen silsesquioxane (HSQ), capable of being fully scaled to bulk proportions. During the process, commercially available

\[
\text{SiO}_x \xrightarrow{\text{Ar, 900°C, 1h, atm}} \text{Si} \xrightarrow{1-5\% \text{ HF}} \quad \text{Scheme 1.7. Synthesis of hydrogen functionalized silicon nanoparticles via thermal annealing.}
\]
HSQ, a white powder, was annealed in a quartz crucible at various temperatures ranging from 500° to 1100 °C under mixed atmosphere for one hour producing a dark glassy solid consisting of Si nanocrystals embedded in SiO\textsubscript{2} as seen in Figure 1.13. XRD data indicated powders annealed above 900 °C contained a prominent Si (111) reflection, with powders yielding a Scherrer relationship to the diffraction pattern of 4 nm for particle size, which is in agreement with TEM images (d = 3.41 nm).

FTIR spectra show a loss of the Si-H stretch at 2251 cm\textsuperscript{-1} for samples annealed above 900 °C, suggesting a collapse of the HSQ cage structure; however, the Si-O-Si bend remains around ≤ 1400 cm\textsuperscript{-1} for all samples, indicating incomplete liberation of the Si-O bond. The nanocrystals expressed no luminescent tendencies until etched in an acidic ethanol-water solution, which produced luminescent maximum dependent upon etching times (Figure 1.14).56
1.5.1.7. The Role of Chemical Etching

Due to its high surface reactivity, silicon is highly vulnerable to oxidation by water and elemental oxygen from the environment, which then form thin layers of silicon oxides with distinct composition and structure. Unfortunately, the surface oxides such as SiO$_2$ and SiO cannot be removed during subsequent passivation or functionalization processes due to their inherent stability. In addition, oxygen at the silicon surface may introduce states within the band gap that lead to loss of emission or a red-shifted emission along with a decrease the bandgap up to 1 eV.$^{57}$ Therefore it is imperative to remove any surface oxygen contamination in order to avoid undesired negative effects and render the silicon surface available for functionalization.

Figure 1.14. Photoluminescence spectra of pentane solutions of 10 (red), 11 (orange), 12 (yellow), and 13 (green). Inset: Photographs of photoluminescence observed from pentane suspensions of 10-13 upon exposure to a standard handheld UV light. Reprinted/adapted with permission.
Chemical etching by hydrofluoric acid has proven to be an effective route to remove surface oxygen species from silicon materials. In 1771, Scheele first prepared hydrofluoric acid and found that it etched his silicate glassware. More than 50 years later, Berzelius found the reaction products of the reaction between SiO$_2$ and HF to be tetrafluorosilane and water. Today HF etching is a widely utilized process in the microelectronics and micromachining fields allowing for the preparation of integrated circuits and semiconductors.

In 1999 Hoshino and Nishioka used ab initio theoretical computations to reveal the mechanism of the hydrofluoric acid etching reaction of silicon dioxide. Their calculations showed that there is a probable reaction path, in which the etching process proceeds through four sequential steps to remove a single fragment of silicon dioxide for each separate reaction (Scheme 1.8). In every step, the insertion of an HF molecule into an Si-O bond leads to the dissociation of the Si-O bond via elongation and ultimately breakage. The potential energy barriers evaluated along the reaction steps suggest that the HF molecule has the ability to etch the silicon dioxide surface. However, polymer like formations caused by the linking of HF molecules is thought to impede the progress of the etching procedure as demonstrated by XPS measurements. Ubara demonstrated with numerous IR spectra that the SiF$_3$ intermediate further reacts with the hydrofluoric acid.

\[
\text{HO(HO)-(SiO}_2\text{)}_n + 4\text{HF} \rightarrow \text{HO(HO)-(SiO}_2\text{)}_{n-1} + \text{SiF}_4 (g) + 2\text{H}_2\text{O}
\]

**Scheme 1.8.** Hoshino mechanism for chemical etching of silicon dioxide with concentrated HF.
molecules in solution to produce various silicon-hydrogen bonding motifs on the surface of the substrate as seen in Figure 1.15.  

1.5.1.8. Sonochemistry Reactions

![Sonochemistry Reactions Diagram](image)

**Figure 1.15.** Ubara\(^64\) mechanism for etching of silicon dioxide from silicon metal in HF. Reprinted/adapted with permission.

Sonochemical synthesis is another popular technique that is utilized for the production of silicon nanomaterials. During the ultrasonication process, acoustic cavitation produces the rapid formation and collapse of bubbles in a solution, causing erosion of a material’s shell. The method can be used to remove the surface oxides of many silicon nanomaterial precursors. Sato and Swihart exploited this principle in 2006 by ultrasonicating suboxide (SiO\(_{0.6}\)) in a mixture of methanol, concentrated hydrochloric...
acid, and concentrated nitric acid for up to eighteen minutes to form hydrogen functionalized silicon nanoparticles as seen in Scheme 1.65 The resultant particles underwent photoinitiated hydrosilylation to produce water-soluble, air stable propionic acid capped silicon nanoparticles varying in size from < 1.5 to 2.4 nm, depending on sonication time, and a direct band gap value of 2.52 eV.

![Scheme 1.9. Ultrasonication of suboxide to form hydrogen functionalized silicon nanoparticles.](image)

1.5.1.9. Solution Pyrolysis of Silanes

Pyrolysis is the chemical decomposition of a substance brought about by high temperatures; therefore, solution pyrolysis is a process that can used to alter the chemical structure of silanes in order to produce silicon nanomaterials. In 2004 the Korgel group synthesized amorphous silicon colloids simply by exposing trisilane to elevated temperatures and pressures.66 Trisilane was heated to 400-500 °C in supercritical hexanes under a nitrogen atmosphere at 345 bar for 10-20 minutes producing amorphous silicon particles ranging in size from 50 nm to 500 nm as seen in Scheme 1.10. The authors state
that particle size could be controlled by altering the concentration of the precursor, the temperature of the reaction vessel, and the pressure at which the reaction occurred. A high product yield, ranging from 93.7 to 91.9%, assuming 0 and 20% hydrogenation, respectively, was also reported.

1.5.2. Top-Down Synthesis Methods

Top-down synthesis methods are most commonly conducted on silicon encompassing bulk scale materials such as wafers, powders, or ingots. The silicon nanomaterials prepared by top-down methods can be created with dangling bonds or exposed reactive surfaces, rendering them water and oxygen sensitive. Thus, as with bottom-up methods, surface passivation with carbon-based ligands is required to stabilize the reactive surface and prevent oxidation as shown by the groundbreaking work of Lindford and Chidsey in 1993\(^6\)\(^7\) in which silicon surfaces were first covalently linked with alkyl monolayers.

\[ \text{Si}_3\text{H}_8 \xrightarrow{\text{hexane, } \text{N}_2} \Delta, 345\text{bar, 10-20min} \rightarrow \alpha\text{-Si colloids} \]

*Scheme 1.10. Synthesis of silicon colloids by solution pyrolysis.*
1.5.2.1. Anodic Reduction

Electrochemical anodization of single crystalline silicon wafers in a hydrofluoric acid electrolyte solution is useful for the production of porous silicon. The mechanism of pore formation is thought to involve a combination of electronic and chemical factors including electric current density, type (p- or n-) and concentration of dopant, wafer crystal orientation, and concentration of electrolyte.\textsuperscript{68} The reaction is typically carried out as an electrochemical process, using a two-electrode configuration under galvanostatic control. The Si wafer acts as the anode, and in the presence of fluoride ion, the oxidized Si atoms are removed from the surface as either SiF\textsubscript{4} or SiF\textsubscript{6}\textsuperscript{2-}.\textsuperscript{69,70} (Scheme 1.11.)

\textbf{Scheme 1.11.} Mechanism of silicon oxidation during the formation of porous Si. Reprinted/adapted with permission.
Nychyporuk found that during the first 100 ms of anodization of boron doped silicon (100) wafer, the nanopores are nucleated, start to enlarge, coalesce, then form large conglomerations. The ability to easily tune the pore sizes and volumes is a unique property of the material. While pores form only at the Si/porous-Si interface the porosity of a growing layer can change according to the current applied, which allows for the construction of chemically tailored nanostructures. Large pore sizes can accommodate sizable molecules or drugs while smaller pores provide more surface area and expose more sites for attack of aqueous media, providing a convenient means to control degradation rates of the porous silicon host.

During the electrochemical anodization process, silicon oxide nanoparticles are often formed on the surface of the silicon wafer, which can then be segregated by sonication methods for further uses such as in drug delivery devices. At the beginning of anodization, Si$^{4+}$ interacts with O$^2$- and OH$^-$ found in the acidic electrolyte solution form an initial oxide layer on the surface of the silicon wafer. These ions migrate, under an applied external field, through the oxide layer to the metal/oxide interface where they react with the crystalline silicon wafer, causing subsequent Si$^{4+}$ ions to quickly migrate from the metal/oxide interface to the oxide/electrolyte interface. Si-O bonds are then weakened under the electric field promoting the disbanding of the metal ions at the oxide/electrolyte interface, thereby releasing a suspension of Si$^{4+}$ into the electrolyte solution and promoting a subsequent reaction with the free O$^2$- forming silicon oxide nanoparticles.
1.5.2.2. Laser Ablation

There are various categories of ablation used to create silicon nanomaterials including laser and microwave ablation, however the basic principle is still similar for each process. Ablation is the removal of material from a solid by vaporization, chipping, or other erosive processes. Laser ablation is the usage of a high powered laser beam to irradiate the surface of a material in order to remove a thin layer of the solid, producing smaller particles as seen in Figure 1.16.

![Figure 1.16](image.png)

**Figure 1.16.** Laser ablation of solid material in liquid to produce nanoparticles. Reprinted/adapted with permission.

Semaltianos *et al.* used a femtosecond laser with a wavelength of 365 nm to surface ablate a 9.5 x 9.5 x 0.25 mm undoped silicon wafer in deionized water. The wafer was exposed to a laser beam exhibiting 3.5 µJ of pulse energy for 70 min intervals.
producing a colloidal solution containing 15 µg of silicon nanoparticles ranging in size from five to two hundred nanometers with a median diameter of twenty nanometers. The nanoparticles also showed a blue shift of 0.08 eV from the bulk silicon band gap energy value.

Kuzmin produced spherical polycrystalline silicon nanoparticles via laser ablation of an undoped silicon wafer in 95% ethanol. The 2.5 mJ single pulse laser with a wavelength of 800 nm and 1 KHz repetition rate was exposed to the wafer surface in 35-900 femtosecond pulse rates for a duration of ten minutes. TEM and PL analyses showed a range of particle sizes from less than three nanometers to more than two hundred nanometers (Figure 1.17.77) and an emission band of 635 nm.

Figure 1.17. Silicon nanoparticles produced by laser ablation. Reprinted/adapted with permission.
1.5.2.3. Sonochemical Synthesis - Reactive Cavitation Erosion

Cavitation occurs when a fluid's operational pressure drops below its vapor pressure causing bubbles to form and eventually collapse. This can occur in a somewhat explosive manner, which can then lead to dramatic pressure drops ultimately causing erosion on the surface of any substrate in the fluid. The Mitchell group recently developed a new one-step sonochemical approach for the production of organically passivated silicon nanoparticles. The method calls for 10 grams of acid etched crystalline silicon wafer to be suspended in a 20% Hexyne/THF solution in a glass reaction vessel. The vessel is placed in an ice bath and argon is bubbled into the mixture for the duration of the reaction. An ultrasonic probe (Figure 1.18) is placed 1 cm into the solution and allowed to sonicate for 60-100 mins with a production rate of 6 mg of

\[\text{Figure 1.18. Diagram of Mitchell's cavitation erosion method. Reprinted/adapted with permission.}\]
nanoparticles per hr. The alkyl passivated silicon nanoparticles are then further purified and characterized showing particle sizes less than one nanometer and strong blue green photoluminescent emissions at 370 nm, 390 nm, and 395 nm.

1.5.2.4. Mechanochemical Synthesis – Reactive High Energy Ball Milling

Ostwald first coined the term “mechanochemistry” in 1891 to describe various methods in which to stimulate chemical processes. More recently, IUPAC has defined the phrase to mean a “chemical reaction, that is induced by mechanical energy.”

Mechanical synthesis is a bridge between the world of mechanics and chemistry. It can involve the cutting, breaking, stress cracking, grinding, or erosion of a bulk solid and the interaction of reagents at the molecular level. Reactions occur not in the bulk of the sample, but at the interfaces between the phases (solid + liquid, solid + gas, liquid + gas, etc.). The mechanical action can break or stretch chemical bonds directly, increasing the likelihood of contact between the reagents due to mixing, decreasing particle size, and generating a reactive surface for the interaction of the components. Initial instillation and materials are low cost, the procedure can generate large scale amounts of product, as well as eliminate the need for multiple solvents or harsh oxidizers and in turn is more environmentally friendly.

Reactive High Energy Ball Milling (RHEBM) is a type of mechanochemical synthesis that consists of a high energy ball miller, a mixing vial, and milling media such as stainless-steel balls as seen in Figure 1.19. The mixing vial and milling balls are typically made of stainless steel as it is durable, generally non-reactive, resists corrosion, and is easily separated from the desired product. The internal cascading effect of the
milling media in the mixing vial reduces a solid to a fine powder, whose particle size can be adjusted by varying the size of the milling balls. Various materials of differing hardness can be used in either continuous milling or closed batch runs. Milling vials also allow for the control of oxygen and water free environments in the case of air sensitive synthesis routes such as those involving silicon.

Figure 1.19. Ball miller (a), mixing vial with milling balls (b), interactions inside mixing vial (c). Reprinted/adapted with permissions.
Heintz demonstrated a one-step synthetic route utilizing RHEBM to produce alkylated silicon nanoparticles in 2011 as seen in Figure 1.20.\textsuperscript{85} One gram of pure silicon, along with two 1.2 cm stainless steel milling balls, were combined with 25 mL of various organic solvents in a stainless steel milling vial surrounded by a nitrogen environment and milled for twenty-four hours. Most notable is the reaction of the silicon pieces with 1-octyne as silicon nanoparticles with a blue luminescence at room temperature and a 435 nm photoluminescence emission maximum were produced. FTIR data supports the suggestion of a reduction of the carbon-carbon triple bond in octyne to a

\textbf{Figure 1.20.} Schematic of the RHEBM of a silicon wafer with alkyl (alkyne or alkene) ligands. Reprinted/adapted with permission.
carbon-carbon double bond by the appearance of a C=C stretching vibration at ~1600 cm$^{-1}$ and the lack of any alkyne stretching vibrations, supporting the idea that the octyne has formed a covalent bond with the highly reactive Si=Si formed during the milling process. This claim was also corroborated with $^{13}$C and $^1$H nuclear magnetic resonance (NMR) spectra.

1.6. Surface Functionalization and Passivation of Silicon Nanoparticles

Size, shape, crystal structure, and surface chemistry all influence nanomaterial properties. However, it can be argued that the surface atoms of the nanomaterials play the most important role in determining the properties of the substance, and given that roughly 43% of the 280 silicon atoms found in a 2 nm nanoparticle reside at the surface\textsuperscript{57}, it is paramount that the surface chemistry of the nanomaterial be carefully evaluated.

As silicon is a highly reactive material, all synthetic approaches to produce silicon nanomaterials require passivation or functionalization steps in order to protect the silicon surface from undesired reactions and/or oxidation. Passivation is the act of rendering the surface of a solid as chemically nonreactive or inert so that there is no change in the solid’s chemical or electrical properties when exposed to air or other substances. Organic passivation is useful not only for protection from undesired surface oxidation, but also for increased solubility in an array of solvents. On the other hand, functionalization aims to give a solid different attributes by applying a single layer of reactive species, ultimately changing the chemical or electrical characteristics of the solid. Functionalization of
silicon nanomaterials can lead to an increase in hydrophilicity, biocompatibility, and allow the material to be utilized in the biosensing and electronic fields. A visual

![Figure 1](image1.png)

**Figure 1.21.** Visual summary of nanoparticle surface modification methods: Alkylation of halide surfaces (a), "Click" chemistry (b), and Hydrosilylation (c). Reprinted/adapted with permissions.
summary of some of the many surface modification methods available for silicon nanomaterials is shown in Figure 1.21. Typically there is a primary passivation/functionalization of the silicon surface, generally with hydrogen or halogens, followed by a secondary reaction in order to stabilize the material against oxygen and water reactivity as demonstrated in Figure 1.21. a and b.

1.6.1 Alkylation of Halide Capped Silicon Surfaces

Alkyl lithium (RLi) and alkyl Grignard (RMgX) reagents can be used to passivate or further functionalize chemically reactive halide-terminated silicon nanomaterials. Dasog showed that halide-capped silicon nanoparticles did not exhibit photoluminescence in the visible region under ultra-violet irradiation, however after reacting the nanoparticles with hexyl-magnesium chloride or hexyl-magnesium bromide, the nanoparticles displayed a blue and red visible photoluminescence respectively. In addition, it was found that bromide terminated silicon nanoparticles functionalized with RMgBr displayed size-dependent luminescence; however, those modified using RMgCl exhibited blue photoluminescence, verifying the proposed halide exchange mechanism that occurs during alkylation of the bromide terminated silicon nanoparticles. Pettigrew et al. produced shelf-stable, alkyl terminated silicon nanoparticles from bromine-capped silicon nanoclusters originally synthesized in n-octane as seen in Scheme 1.12. The

\[
\text{Si}_m\text{Br} + n\text{-BuLi} \rightarrow n\text{-BuSi}_m + \text{LiBr}
\]

silicon-bromide surface was reacted with $n$-butyllithium in octane to produce nanoparticles with an average size of 3-6 nm, a photoluminescent maximum at 390 nm, and a 10.9% yield.

1.6.2. Hydrosilylation

As the majority of synthetic routes to produce silicon nanoparticles result in the generation of hydrogen capped surfaces (Figure 1.22. shows examples of common types of hydrogen terminated silicon surfaces), further functionalization must be performed in order to passivate the surface of the nanoparticle. The highly reactive Si-H bonds are especially susceptible to oxidation by water and oxygen, which often means handling of the particles under inert atmosphere. However, it is this reactivity that makes hydrosilylation a simple and effective means to stabilize and protect the silicon nanoparticle surface. The hydrogen-terminated surface undergoes hydrosilylation with unsaturated ligands (such as alkenes and alkynes), to form a secure monolayer on the nanoparticle. The resulting layer, which is stable and chemically resistant, inhibits oxidation of the silicon surface.
Hydrosilylation reactions can be initiated with heat, irradiation from light, or a catalyst, which can stimulate the production of radicals (dangling bonds) on the silicon surface by way of removal of a hydrogen atom. This activation step is followed by addition of the olefin to the silicon dangling bond to form a surface-bonded, secondary carbon radical. The secondary radical can then abstract another hydrogen from the allylic position of an unreacted olefin, or from the Si-H surface. (See Scheme 1.13.)
Scheme 1.13. Proposed mechanism for the hydrosilylation of a terminal olefin and the Si-H surface.
Linford and Chidsey were the first to report on radical initiated covalent linkages of densely packed, long alkyl chains formed on a silicon surface. The authors report that alkyl monolayers were covalently bound to Si (111) and Si (100) surfaces. Pyrolysis of diacetyl peroxides (\([\text{CH}_3(\text{CH}_2)_n\text{C(O)O}]_2\)) and Si-H films were heated to 100 °C under argon for one hour, or until gas production ceased. The mechanism was theorized to proceed via the formation of a radical at the silicon surface, formation of alkyl radicals from thermal decomposition of the peroxides, and subsequent bond formation that occurs when the two radicals interact. IR-ATR data confirms both the Si-CH\(_2\)- formation as well as the Si-O-C(O)-CH\(_2\) linked chain, supporting the radical mechanism hypothesis. Subsequent hydrolysis reactions indicated that sites bonded with alkyl chains were not removed under harsh conditions; however, the Si-O-C(O)-CH\(_2\) linkage was easily eliminated.

Two years later, Linford et al. expanded their research to include the formation of a stable monolayer from the reaction of terminal alkenes/alkynes and hydrogen capped Si (111) surfaces. The chemically etched, silicon-hydride surface was heated with the appropriate olefin to 100-200 °C for one hour under argon atmosphere, then rinsed with ethanol, hexanes, and dichloromethane. The resultant alkyl-capped silicon surfaces were found to inhibit oxidation of the silicon substrate, and to be stable in hot solvents, acids, and bases.

In 1998 Stewart and Buriak described the functionalization of a porous silicon surface through white light promoted hydrosilylation of unsaturated C-C bonds at room temperature as seen in Figure 1.23. The light source was a typical tungsten halogen (ELH) lamp operating at an intensity of 22.4 mW/cm\(^2\). It was found that the degree of
substitution on the silicon surface by the ligand was directly related to the light intensity along with wavelength as monochromatic light promoted hydrosilylation of 1-dodecyne at 450, 550, and 650 nm (1h, 1.8x10^15 photons cm^-1 s^-1) showed decreasing substitution with increasing wavelength. The proposed mechanism was supported by the use of [D8]styrene as a substrate, a molecule with no C-H bonds. Hydrosilylation was observed by the appearance of methylene (CD-H) vibrations at 2917 and 2846 cm^-1 in the IR spectrum, which indicated the transfer of a surface hydride to the perdeuterated structure. The preceding work was further validated in 2001 by a proposed exciton driven mechanism where in silicon-centered positive charges are intermediates.  

Figure 1.23. White light promoted hydrosilylation on porous Si. By using a mask (black line) to protect part of the surface, the remaining surface can be functionalized with alkynes (a) or alkenes (b). Reprinted/adapted with permission.
It has also been reported that hydrogen capped silicon nanoparticles can be further functionalized with even more complex ligands such as aryl compounds, biocompatible moieties, and bifunctional terminal alkenes. In 2004 Stewart described the activation of aryl diazonium salts to assemble covalently bound conjugated monolayers on hydride-passivated silicon surfaces. The salts were reacted with the Si-H surfaces for two hours, protected from the exposure of light, under nitrogen atmosphere, producing covalently bound multilayers. IR reflectance spectra with p-polarized light at angles of incidence greater than Brewster’s angle on dielectric surfaces yielded negative absorbance peaks and vibrational modes with components perpendicular to the substrate surface, indicating the aryl compounds adopt an upright orientation rather than lying parallel to the substrate surface.

In 2008 Sudeep, Page, and Emrick utilized the exciton mediated reaction to add alkene terminated PEG-1100 to Si-H surfaces to form water soluble PEGylated silicon nanoparticles. Successful nanoparticle PEGylation was suggested from the optically clear solutions obtained by dissolving the particles in solvents suitable for PEG, including water, methanol, and chloroform. Covalent attachment of PEG to the nanoparticle surface, by the formation of C–Si bonds, was also confirmed by FTIR spectroscopy data. Observed peaks at 1467 and 1280 cm\(^{-1}\) were attributed to vibrational scissoring and symmetric bending, respectively, of the Si–CH\(_2\) group. And in 2013 the Korgel group reported the addition of bifunctional alkenes with distal polar moieties, ethyl ester, methyl ester, or carboxylic acids, without the aid of light or added catalyst to the surface of hydrogen capped silicon nanocrystals. The respective ligands were stirred with the Si-H nanocrystals for 24 hours under nitrogen atmosphere at room temperature producing
ω-ester/ω-acid terminated, luminescent nanoparticles capable of being dispersed in polar solvents, including water. It was found that the ethyl 10-undecenoate provided the most effective room temperature passivation, and the smallest nanocrystals were found to be most reactive as shown by Figure 1.24. 100

1.6.3. “Click” Reactions

What once started as a way to mimic nature’s preference to create carbon-heteroatom bonds over carbon-carbon bonds has evolved into a group of powerful, highly reliable, and selective reactions for the rapid synthesis of new compounds through heteroatom links (C-X-C). In 2001 Kolb, Finn, and Sharpless defined a set of stringent criteria that a synthetic method must meet in order for the process to be deemed “Click Chemistry.” The reaction must be modular, wide in scope, give very high yields, generate only inoffensive byproducts that can be removed by nonchromatographic methods, and be stereospecific (but not necessarily enantioselective). The required process characteristics include simple reaction conditions unaffected by water and oxygen,
readily available starting materials and reagents, the use of no solvent or a solvent that is benign (such as water) or easily removed, and simple product isolation. Due to their high thermodynamic driving force, the resultant reactions usually proceed to completion quickly, often yielding a single product. Two of the major click reactions are the azide-alkyne Huisgen cycloaddition, a copper catalyzed 1,3-dipolar cycloaddition between an azide and a terminal or internal alkyne to give a 1,2,3-triazole, and the thiol-ene reaction, which is an organic reaction between a thiol and an alkene to form a thioether.

1.6.4. Cycloadditions with Silicon Surfaces

Cycloadditions are the combination of two π-electron systems to create a ring of atoms having two new σ bonds and two fewer π bonds; for example, when two or more unsaturated molecules (or parts of the same molecule) come together to generate a cyclic product. The Diels-Alder [4+2 cycloaddition], a chemical reaction between a conjugated diene and a substituted alkene to form a substituted cyclohexene product, is the most common of the cycloadditions. The exact mechanism of the Diels Alder reaction, whether by a concerted pericyclic single step or by a two-step addition involving an intermediate, has been heavily contested; however, the predominantly accepted opinion is that the addition occurs in one step due to the stereospecific syn addition of the two substrates. [2+2] cycloadditions are also possible, yet less favorable as the [4+2] cycloaddition produces a six-membered ring that is less strained than the four-membered ring produced by the [2+2] cycloaddition. Therefore, the [4+2] products are expected to be thermodynamically more stable than the [2+2] products. The [2+2] cycloaddition is
also considered to be symmetry forbidden for carbon based olefins, and thus extremely slow at room temperature; however, the reaction of ethylene with the Si=Si dimers of the Si (001) surface has been known to be successful at room temperature\(^\text{109}\) as in \textbf{Figure 1.25}.\(^\text{110}\) Yoshinobu proposed that acetylene is di-sigma bonded to an adjacent Si adatom and Si rest atom, saturating the Si dangling bonds of the Si (111) (7X7) surface,\(^\text{111}\) forming two new Si-C sigma bonds.

The Bent group was the first to observe experimental evidence indicating the creation of a Diels-Alder adduct formed between either 1,3-butadiene or 2,3-dimethyl-1,3-butadiene and a Si (100) surface.\(^\text{112}\) FTIR studies showed that after exposing the hydrogen terminated Si (100) surface to 1,3-butadiene, there was a prominent C-H stretch at 2989 cm\(^{-1}\) and a CH\(_2\) mode near 2895 cm\(^{-1}\), however, no terminal vinylic modes were observed above 3080 cm\(^{-1}\) indicating that the CH\(_2\) stretches are of an alkane nature. The spectrum obtained following the passivation with butadiene was inconsistent with
the [2+2] bonded adduct, which would be expected to show a distinctive signature of the terminal CH₂ modes. When the Si (100) surface was reacted with 2,3-dimethyl-1,3-butadiene only CH₂ and CH₃ modes, at 2916 cm⁻¹ and 2976 cm⁻¹ respectively, were detected. These observations led to the realization that the [4+2] process was indeed the prominent pathway; however, considerable quantities of the [2+2] product were also formed as evidenced by the Hamers group in 2000.¹¹⁰

Schwartz employed deuterated styrene (C₆D₅CH=CH₂) to study the binding modes of π-conjugated organic molecules and the Si (100) surface (Figure 1.26).¹¹³ Vibrational data indicated C-H alkane stretches similar to those found in non-deuterated styrene at 2874 cm⁻¹ and 2916 cm⁻¹, C-D stretches from the aromatic ring at 2276 cm⁻¹, and a stretch at 2060 cm⁻¹ signifying partial dissociation on the silicon surface. When comparing the FTIR spectra of the liquid styrene and the passivated Si (100) surface, the authors concluded that new vibrational modes in the 2800-3000 cm⁻¹ region arise as a consequence of bonding to the surface. The preservation of the aromatic stretches along

Figure 1.26. (a) Styrene in [2+2] geometry bonding through the vinyl group; (b) styrene in “tight bridge” geometry bonding through the aromatic ring; and (c) styrene in [4+2] geometry bonding through the aromatic ring. Reprinted/adapted with permission.
with the absence of the vinylic modes indicate that styrene prefers to bond through the external vinyl group in a [2+2] process. This is contrary to that of benzene, which bonds to the Si (100) surface via the aromatic ring system, producing FTIR alkyl stretches at 2899 cm\(^{-1}\) and 2944 cm\(^{-1}\) with no indication of the retention of aromaticity.\(^{114}\)

1.7. Applications of Silicon Nanoparticles

1.7.1 Biological Applications

The low toxicity of \textit{in vitro} and \textit{in vivo} applications, high biocompatibility, and ease of degradation in organisms of silicon nanoparticles makes them ideal candidates for use in many biological applications.\(^{115}\) Furthermore, the water solubility and extensive surface area of functionalized silicon nanoparticles render them suitable for the use in biomedical technology applications such as molecular imaging,\(^{116}\) drug delivery\(^{117}\), and photodynamic therapy.\(^{118}\)

1.7.1.1. Bioimaging

Intracellular organelles are commonly labeled using organic dyes; however, these compounds will suffer from photobleaching when exposed to continuous light exposure.\(^{119}\) Photobleaching occurs when a fluorophore loses its fluorescence due to damage induced by light. This can lead to signal loss while imaging a sample. Therefore, it is important that the compound used to stain the cell have good photostability.

Fan and coworkers have designed an optically stable, biocompatible, water-soluble, highly fluorescent silicon quantum dot capped with polyacrylic acid that emits
blue and green light. The cytotoxicity and uptake abilities of the silicon quantum dots were demonstrated *in vitro* on mouse blood monocytes and *in vivo* zebrafish embryo. Aqueous solutions containing monocytes and the quantum dots were incubated for 6-72 hours depending on the specified method, then analyzed. The zebrafish embryos were injected with either the green or blue quantum dots, hatched 72 hours after fertilization, and then imaged.

The authors reported that, when compared to a traditional dye such as 4′,6-diamidino-2-phenylindole (DAPI), the monocytes injected with the green silicon quantum dots glowed at a similar intensity as seen in Figure 1.27. Upon exposure to a 100W UV (254 nm) lamp for 2 hours, there was no indication of photobleaching as was noted with fluorescein isothiocyanate, indicating the photostability of the quantum dots (Figure 1.28). The authors also stated that blue- and green-emitting Si QDs exhibit a concentration-dependent behavior on the survival rates of the zebrafish as yolk sac

![Figure 1.27. Confocal laser scanning microscopic images of green Si QDs’ internalized monocytes compared with DAPI dye. Reprinted/adapted with permission.](image)
edema, head edema, and tail truncation were the most frequently observed abnormalities found in the fish treated with the quantum dots, suggesting that concentrations of the quantum dots could be tailored in order to decrease unwanted affects.

1.7.1.2. Drug Delivery

Silicon displays a number of qualities that make it an appealing material for controlled drug delivery applications. Synthesis methods allow for the management of material size, while chemical tailoring of the surface controls for the amount, the identity, as well as the release rate of drugs. And finally, optical properties derived from quantum confinement effects of the materials contribute to in vivo self-reporting.

*Figure 1.28. Photostabilities of blue- and green-emitting silicon quantum dots upon comparison with fluorescein isothiocyanate (FITC) dye under exposure of 100 W Hg lamps for 2 hrs. Reprinted/adapted with permission.*
In 2019 Maximchik et al. synthesized porous silicon nanoparticles (PSi-NPs) loaded with the chemotherapy drug doxorubicin (DOX) while studying the ability of the nanoparticles to fully biodegrade along with their ability to regulate cancer cell death pathways. The authors found that after 24 hours of incubation, there was no increase in caspase-3 (a cell apoptosis indicator) for the nonfunctionalized nanoparticles compared to the control group, indicating the low cytotoxicity of the particles. It was also found that the DOX functionalized nanoparticles penetrated cell membranes within 12 hours of introduction and then localized within the cytoplasm. In addition, Western blot results indicated that the DOX-PSi-NPs were more efficient at initiating cell death than simply adding DOX in all cell lines. Degradation studies also showed the full release of DOX after 12 hours (Figure 1.29) and complete degradation of the nanoparticles within two weeks.

![Figure 1.29. Schematic representation of the DOX release and degradation timeline for the DOX-PSi NPs. Reprinted/adapted with permission.](image)

1.7.1.3. Photodynamic Therapy
Photodynamic therapy (PDT) is an effective, noninvasive therapeutic treatment against localized, malignant tumors that are accessible to the source of light, or close to the surface of the skin. It involves the use of light and photosensitizers (PS), molecules that can transfer energy from the triplet excited state to neighboring oxygen molecules when activated by a specific wavelength of light,\textsuperscript{118} that accumulate in the tumor tissue as shown in Figure 1.30.\textsuperscript{121} The ideal photosensitizer would exhibit chemical stability despite repeated interactions with light, water solubility, low cytotoxicity until a light beam has been applied, a strong absorption in the red region which allows for deeper tissue penetration, little to no photobleaching, and would preferentially accumulate only in diseased tissue.\textsuperscript{122}
In 2007 the Prasad group synthesized water soluble, highly stable, organically modified silica nanoparticles (ORMO-SIL), encapsulating hydrophobic 2-devinyl-2-(1-hexyloxyethyl)pyropheophorbide (HPPH), which can generate singlet oxygen upon photo activation. Colon-26 cells were incubated overnight with the selected nanoparticle mixture, then imaged and characterized for cellular uptake, phototoxicity, and singlet oxygen production studies. Absorption data for 9,10-anthracenedipropionic acid, disodium salt (ADPA) dissolved in an aqueous environment containing the ORMO-SIL showed a decrease in the ADPA concentration over time, indicating the production of singlet oxygen inside the nanoparticle, which diffused across the nanoparticle membrane, ultimately oxidizing the ADPA. Further singlet oxygen studies found that decay times in methanol were 4.5-5 µs, which is similar enough to that of singlet oxygen in water (4 µs) that the HPPH moieties inside the nanoparticles retain their functionality as photosensitizers for PDT. Finally, confocal imaging shows uptake of the ORMO-SIL by

Figure 1.31. Colon-26 cells treated overnight with ORMO-SIL. Transmission (left) and fluorescence (right) channels are shown. Reprinted/adapted with permission.
the colon-26 tumor cells, while indicating phototoxicity in treated cells upon irradiation with light as seen in Figure 1.31.123

1.7.2 Electronic Applications

In recent decades there has been a great amount of focus in the electronics industry on the synthesis and application of various silicon nanomaterials including nanoparticles. Exploitation of the size-dependent quantum confinement effects of silicon nanoparticles (SiNPs) has led to the development of a variety of electronic applications including semiconductors,13 solar cells,124 nanoparticle lasers,125 and various optoelectronic devices such as light-emitting diodes126 and optical fibers.127

1.7.2.1. Energy Storage

Early generation anodes for lithium-ion batteries have largely consisted of graphite or other carbon-based materials. However, up to 3.75 moles of lithium per mole of silicon can be absorbed by the silicon surface (for Li$_{15}$S$_4$), producing a theoretical gravimetric current capacity of 3580 mAh$^{-1}$, which is far greater than the 372 mAh$^{-1}$ for graphite based electrolytic systems.128 Nanostructured silicon can offer added benefits such as reducing the lithium cation diffusion length resulting in more rapid charge and discharge rates.129,130

1.7.2.2. Photovoltaics
Photovoltaic (PV) systems convert sunlight directly to electricity by means of PV cells made of semiconductor materials such as silicon nanoparticles. The photovoltaic cells exploit a property known as the photoelectric effect that causes a material, such as a semiconductor, to absorb photons of light and release electrons. The electrons can be captured, stored, and ultimately connected together into arrays of cells known as modules or panels.\(^{131}\) When the size and shape of quantum dots is controlled, it is possible to regulate which wavelengths of light the photovoltaic cell will absorb.\(^ {132}\) Smaller quantum dots (2.3 nm) are able to absorb smaller wavelengths of light (505 nm), while larger quantum dots (3.7 nm) will absorb longer wavelengths (580 nm), improving the overall efficiency of the solar cell. In addition, while bulk semiconductors only produce one electron-hole pair for every photon absorbed, quantum dot based photovoltaics can produce multiple charge carriers when absorbing photons in the visible and near IR regions.

Chowdhury has investigated the enhanced performance of amorphous silicon based photovoltaic cells when covered in a thin film of 2.85 nm diameter hydrogen capped silicon nanoparticles (Figure 1.32).\(^ {124}\) It was discovered that the addition of the thin film of silicon nanoparticles reduced the reflectivity of light, improving the couple of the light with the solar cell, increasing external quantum efficiency (EQE). There was also an enhancement of the internal quantum efficiency (IQE) of the photovoltaic cell of 31% at 445 nm due to the charge separation of the nanoparticles. Furthermore, the thin film of nanoparticles increased the current density 13.4% from 4.70 mA/cm\(^2\) for
reference cell devoid of nanoparticles to 5.33mA/cm\(^2\) for the cell containing the thin film of nanoparticles.

1.8. History and Introduction of 2D Silicon Nanostructures

In 1863 Wöhler observed that the Zintl salt calcium silicide (CaSi\(_2\)) reacted with concentrated hydrochloric acid, producing hydrogen gas and an insoluble yellow solid with the composition of Si\(_6\)O\(_4\)H\(_6\). However, in 1979 Weiss found that without water, in the case of water free acids, the reaction would not proceed.\(^{133}\) He also demonstrated a similar topochemical reaction with calcium silicide crystals etched in 37% aqueous hydrochloric acid that would produce yellow 2D nanosheets composed of repeating

\[
\text{Bulk CaSi}_2 + \text{HCl/H}_2\text{O} \rightarrow \text{Si}_6\text{H}_3(\text{OH})_3 \text{ (2D siloxene sheets)} + \text{H}_2 (\text{g}) + \text{CaCl}_2 \text{ (aq)}
\]

**Scheme 1.14.** Strong acid etching of Zintl salt to produce 2D silicon nanosheets.
silicon hexagonal units with the formula Si$_6$H$_3$(OH)$_3$ (Scheme 1.14.), also known as Kautsky’s siloxene. Weiss’s complex showed x-ray data indicative of a hexagonal unit cell with $(0 0 l)$ and $(h k 0)$ reflections signifying the retention of the original silicon lattice found in calcium silicide. Thus, the study of 2D silicon nanosheets was born.

Silicane and silicene are two dimensional (2D) nanomaterials containing either $sp^3$ or $sp^2$ hybridized silicon atoms, respectively, and can be produced on a substrate such as Ag (111)$^{134}$ or via methods yielding freestanding sheets.$^{135}$ Silicane is a 2D, crystalline solid consisting of a single layer of atoms, made of two or more elements, mainly silicon and hydrogen. In contrast, silicene is a 2D allotrope of pure crystalline silicon in which the atoms are assembled in a continuously repeating hexagonal honeycomb structure similar to that of graphene and graphite as shown in Figure 1.4. Silicene bond lengths are

![Figure 1.33. Calculated energy versus hexagonal lattice constants of 2D Si and Ge for various honeycomb structures. Reprinted/adapted with permission.](image-url)
predicted to be shorter (2.24 Å) compared to those found in cubic silicon (2.35 Å), but longer than those found in disilenes (2.14 Å)\textsuperscript{136}, giving rise to a mixed $sp^2$-$sp^3$ type of hybridization. However, unlike graphene, silicon atoms in the silicene sheet can exhibit out of plane buckling, dubbed the silicon buckling distance and noted by $\Delta_z$, due to the mixture of hybridization caused by the shortened Si-Si bond lengths. These various buckling configurations are known as high buckling (HB), low buckling (LB), or planar (PL) structures as seen in Figure 1.33.\textsuperscript{137} It is theorized that the $sp^3$ low buckled state is preferred due to pseudo-Jahn Teller distortions caused by energetic instability of the planar form,\textsuperscript{137} silicon adatom adsorption behaviors,\textsuperscript{138} and weak silicon-silicon $\pi$-bonds.\textsuperscript{139}

1.9. Optical Properties of 2D Silicon

1.9.1. The Band Gap

Silicene is a 2D nanomaterial with predicted Dirac cones and a hexagonal Brillouin zone; however, the electronic and physical characteristics of the nanosized material are comparatively unknown as most studies are theoretical, and almost all are based on first-principles density functional theory (DFT) calculations.\textsuperscript{137,140–147} Most calculations on silicene, either in a flat or a low-buckled configuration, generally agree on the fact that the honeycomb structure should be stable, with an electronic structure similar
to that of graphene. In other words, the π and π* bands of silicene also cross at the K points, giving rise to a zero gap band state (see Figure 1.34).148

![Figure 1.34. The band structure of silicene calculated with DFT. Reprinted/adapted with permission.](image)

Although it is theorized that crystalline silicene possesses a zero-energy band gap state, multiple studies have indicated that the band gap can be tuned. Kim et al.149 showed that nanosheets with a thickness of less than 2 nm excited by a 325 nm source emitted a 435 nm (2.85 eV) maximum photoluminescent peak that matches the optical band gap well for a direct transmission (E_d of 2.80 eV). Nakano et al.150 also revealed that nanosheets produced via the Yamanaka151 method, in which calcium silicide was reacted with concentrated hydrochloric acid at -30°C to produce hexagonally structured polysilanes (Si₆H₆)ₙ, emitted a 2.7 eV photoluminescent peak indicative of a radiative recombination center. And in 2016 Du et al. demonstrated that the band gap of epitaxial
silicene on a Ag (111) substrate could be adjusted by the oxidation of silicene with an oxygen dose of 60 Langmuir. The authors produced $\sqrt{13} \times \sqrt{13}$, $2\sqrt{3} \times 2\sqrt{3}$, and $4 \times 4$ silicene structures with band gaps of 0.18 eV, 0.22 eV, and 0.9 eV respectively. These studies imply that although the 2D material is larger than 100nm in one direction, it can still perform electronically similar to quantum dots due to the minute thickness of the film.

1.9.2. Effects of Point Defects and Surface Passivation

Contrary to the negative effects caused by surface defects on silicon nanoparticles, point defects in silicene may actually induce band gaps in the silicon nanosheets, ultimately increasing the metallic nature of the 2D substrate. It is theorized that silicene sheets possess Dirac cones (Figure 1.35), similar to that of graphene where massless fermions possess an ultrahigh Fermi velocity of about $10^6$ ms$^{-1}$ allowing transitions of charge carriers from the highest valence band to the lowest conduction

*Figure 1.35. Theorized electronic band structure of single layer graphene/silicene with an inset showing a Dirac cone. Reprinted/adapted with permission.*
The existence of Dirac cones allows for the tuning of the electronic properties of the silicene sheet in such that if a small voltage were to be applied to the sheet, the band gap would increase and an electric current could flow through the material. The unique shape of the Dirac point also allows for greater electron mobility within the 2D sheet as well as photon absorption.

DFT calculations performed by Gao et al. indicated that Stone Wales rotation defects can induce a small band gap opening of 33 meV, while single vacancy defects (Figure 1.36a) cause the silicene to take on a more metallic nature, devoid of magnetic tendencies. The group also showed that double vacancies (Figure 1.36b) can create a band gap of 161 meV while also maintaining the non-magnetic behavior. In contrast, silicon adatoms created a magnetic moment by inducing dangling bonds.

Figure 1.36. Examples of (a) single vacancy and (b) double vacancy defects in single layer silicene. Reprinted/adapted with permission.
perpendicular to the surface of the silicene sheet, leading to the possibility of purely silicon magnetic semiconductors.

_Ab initio_ calculations performed by the Yang group indicate that surface functionalization of the silicene sheet plays a major role in the size of the band gap. DFT computations focused on four hydrogenation schemes (hydrosilylation, alkoxylation, aminization, and phenylation) with experimentally demonstrated surface coverage of 33%. Data indicated that in contrast to the 0 eV band gap of pure semi-metal silicene, hydrogen-capped polysilanes in the chair configuration contain an indirect band gap of 2.2 eV, while aminated polysilanes exhibits a direct band gap of 1.7 eV. In addition, when the coverage of propylene derived ligands increased from 5% to 44%, the bandgap of hydrosilylated polysilanes varied from 1.6 eV to 1.9 eV with either a direct bandgap or indirect bandgap environment.

Experimental photoluminescence studies performed on hydrogen terminated silicon nanosheets derived from calcium silicide by Ryan and colleagues in 2020 are in agreement with DFT calculations performed by earlier researchers. Results indicated a maximum peak centered at 500 nm (2.48 eV) with two distributions occurring at 498 nm.

*Figure 1.37. Si-NSs dispersed in methanol under ambient light (left) and exposed to UV light (right). Reprinted/adapted with permission.*
and 543.9 nm. The absorption onset was in closer agreement with the Tauc plot estimate of a direct band gap transition (2.53 eV) than the indirect band gap transition (2.66 eV) theorized by prior calculations. Ultra-violet illumination of the hydrogen functionalized Si-NSs resulted a blue-green luminescence as seen in Figure 1.37.157

1.10. Synthesis of 2D Silicon Nanosheets

As with nanoparticles, there are two main synthetic routes to the manufacture of silicon nanosheets; bottom-up and top-down. Bottom-up methods include those involving vaporized molecular silicon deposited onto metal substrates such as silver or even graphite. These methods require high temperatures, ultra-high vacuum (UHV), and are often slow to produce large surface area sheets; however, the guarantee of an oxygen free reaction environment is of enormous appeal. In contrast, top-down synthetic methods can be more cost effective and do not require metal substrates or ultra-high vacuum, however, they do require corrosive chemicals such as concentrated acids. Also, there is no assurance of a water free, oxygen free environment, often leading to oxidation of the silicene surface. This subsequent oxidation has prevented the successful manufacture and characterization of 2D crystalline silicon nanosheets; however, the production and manipulation of air stable silicenes has turn out to be a major step forward in the desired direction.

1.10.1. Bottom-Up Synthesis – Chemical Vapor Epitaxy
Because the synthesis of 2D silicon is a relatively new field of study, the vast majority of bottom-up methods are quite similar. Most involve the epitaxial growth of molecular silicon deposited under ultra-high vacuum (UHV) onto a heated metal substrate such as Ag (110), Ag (111), ZrB$_2$ (0001), and even highly oriented pyrolytic graphite (HOPG).\textsuperscript{158–162} In 2012 De Padova produced silicene nanoribbons in which a Si (100) sample was flashed at 1400 K, then evaporated onto a Ag (110) surface heated to 470 K.\textsuperscript{162} The author attributes the two distinct 1s→σ* and 1s→π* transitions to the sp$^2$-like hybridization associated with the honeycomb structure. In the same year, Vogt deposited vaporized silicon atoms onto an annealed Ag (111) substrate under UHV to produce silicene with a buckling distance of 0.1 nm, Si-Si bond distance of 0.22 nm, and a band gap of 0.6 eV, which was theorized to be produced from interactions of the silicene layer with the Ag (111) surface.\textsuperscript{163} Du \textit{et al.} produced quasi-freestanding silicene on a Ag (111) surface via the intercalation of oxygen into a buffer layer between the surface silicene and the silver substrate.\textsuperscript{134} The group deposited vaporized silicon from a crystalline wafer onto an annealed Ag (111) surface maintained at 220 °C while introducing oxygen molecules into the preparation chamber at a temperature of 200 °C, producing pristine $\sqrt{3} \times \sqrt{3}$ silicene that was formed on a $\sqrt{13} \times \sqrt{13}/4 \times 4$ buffer layer as seen in Figure 1.38.\textsuperscript{134}
Figure 1.38. (A to C) Atomic structures of an $O_2$ molecule adsorbed on $4 \times 4$ buffer layer (A), top layer silicene (B), and $4 \times 4$ buffer layer underneath $\sqrt{3} \times \sqrt{3}$ silicene (C); Atomic structure of silicene/SiO$_x$/Ag(111) from ab initio molecular dynamics (AIMD) simulation: side view (D). Reprinted/adapted with permission.

1.10.2. Top-Down Synthesis Methods
Since 1996, various kinds of nanosheets have been prepared and their unique properties demonstrated.\textsuperscript{164–166} Multiple top-down methods including micromechanical exfoliation,\textsuperscript{23} shear force exfoliation,\textsuperscript{167} sonication assisted exfoliation,\textsuperscript{168} and lithium intercalation\textsuperscript{169} have shown to produce inorganic 2D nanosheets; however, techniques to generate two-dimensional crystal silicon nanomaterials, i.e. silicenes, have not been widely established and single layer silicene has yet to be effectively characterized. The predominant top-down synthetic route utilized to produce 2D silicon sheets has been chemical exfoliation,\textsuperscript{170} most notably from Zintl-phase calcium silicide (CaSi\textsubscript{2}), generating layered silicane (Si\textsubscript{6}H\textsubscript{6}) or siloxene (Si\textsubscript{6}H\textsubscript{3}(OH)\textsubscript{3}) substituents.\textsuperscript{170}

1.10.2.1 Silicon Nanosheets by Chemical Exfoliation

Zintl salts, also termed Zintl phases, are compounds formed between a strongly electropositive metal, such as group I alkali metals and group II alkaline earth metals along with a somewhat less electropositive group 13-16 post transition metalloid.\textsuperscript{171} For calcium silicide, silicon fulfills the anionic role. Each silicon atom achieves an octet shell with covalent bonds and lone-pair electrons according to the 8-N rule.\textsuperscript{147} CaSi\textsubscript{2} has a 2D silicon sub-network resembling buckled Si (111) planes, in which the 6-member hexagonal rings are interconnected with $sp^3$ bonds. The slightly buckled silicon layers are separated by planar monolayers of positively charged calcium as seen in Figure 1.39., creating a trigonal crystal structure with unit cell measurements of $a = 3.855$ Å, $c = 30.62$ Å and $a = 3.829$ Å, $c = 15.90$ Å for the tr\textsubscript{6} and tr\textsubscript{3} types, respectively.\textsuperscript{172}
Reacting calcium silicide with concentrated hydrochloric acid causes a topotactic chemical reaction producing hydrogen gas and a yellow-green solid with the formula Si₆H₃(OH)₃, also known as layered siloxene.\textsuperscript{133} Dahn showed via powder x-ray diffraction that the layered siloxene sheets retain the hexagonal silicon pattern found in calcium silicide, with no evidence of oxygen incorporation into the silicon product layers.\textsuperscript{173} The group also demonstrated the first synthesis of layered silicanes by reducing the exfoliation temperature from 80 °C (Scheme 1.15. a) to 0 °C (Scheme 1.15. b), which was confirmed by Yamanaka \textit{et al} in 1996. In addition, when carried out at -30 °C, Yamanaka’s synthetic method produced very little hydrogen gas (Scheme 1.15. c) and generated air stable silicane sheets that retained the in-plane hexagonal lattice constant (a = 3.83 Å) similar to that of calcium silicide.\textsuperscript{151} When reacted with aqueous sodium dodecylsulfate surfactant in a 6/1 ratio, respectively, the silicanes are liberated into
individual silicon nanosheets (SiNOSs) with a photoluminescent emission of 2.7 eV.\textsuperscript{150} The transmission electron microscopy (TEM) images also showed that the sheets had a lateral dimension of less than 200 nm.

\subsection*{1.10.2.2. Free-standing vs Supported Silicene}

Producing a 2D graphene sheet is relatively simple as it has a naturally occurring 3D layered parent material, graphite, composed of graphene layers weakly bound to each other by van der Waals interactions.\textsuperscript{174} However, silicene does not have a naturally occurring 3D parent material since it exhibits highly unstable $sp^2$ hybridization and ultimately prefers to rearrange to the energetically more favorable $sp^3$ configuration. This makes the synthesis of free-standing silicene sheets incredibly difficult. Hoffman even goes as far as to say that, “a pristine free-standing single layer sheet of silicene (or a Si nanotube) will not be made. Silicene exists and will be made only on a support of some sort, metal or semiconductor.”\textsuperscript{175}
During the production of free-standing silicene sheets, the energetic and kinetic instability of Si=Si double bonds forces the atoms to rearrange so as to increase their stability. In 2012, Vogt showed that the addition of a stabilizing metallic substrate such as Ag (111) made it possible to form supported silicene sheets.\textsuperscript{163} If silicene is grown on a substrate it becomes doped due to charge transfer from the substrate, owing to the addition of excess surface charges.\textsuperscript{176} Therefore, an understanding of the doping effects in silicene is highly desirable. Silicene is also highly reactive and therefore may bond with other chemical species, such as oxygen or hydrogen, as it attempts to rebalance the coordination lost.\textsuperscript{147} In addition, free-standing silicene can also be reacted with different carbon based substrates such as benzaldehyde\textsuperscript{177} or hexyl groups;\textsuperscript{178} however, upon covalent bonding, the sp\textsuperscript{2} hybridization is shifted to sp\textsuperscript{3}.

Most DFT calculations for silicene assume a hexagonal lattice allowing atoms either to be planar\textsuperscript{179} (D\textsubscript{6h}) or buckled\textsuperscript{180} (D\textsubscript{3d}), with the freedom to arrange themselves into energetically favorable positions.\textsuperscript{140,142,181} Takeda and Shiraishi were the first to investigate the possibility of planar silicene by DFT in 1994.\textsuperscript{140} Results produced a lattice constant of 3.855 Å, consistent with that of calcium silicide, for both the planar and buckled structure along with bond lengths of 2.247 Å and 2.226 Å for the buckled and planar structures, respectively, indicating that the puckering deformation induces elongation of the Si-Si bonds. It was also found that there is a large hybridization of the calcium 3d and silicon 3p orbitals, leading to a significant charge transport (CT), altering the nature of the silicene sheets from semi-metallic to metallic. Cahangirov’s DFT calculations were consistent with that of Takeda and Shiraishi,\textsuperscript{137} however he went on to add that low buckled silicene (Δ\textsubscript{z} = 0.44 Å) is more energetically favored than the high
buckled configuration ($\Delta z = 2 \text{ Å}$). Yin and Cohen theorized that since the graphitic bond length of Si has a smaller contraction than that of C, the graphitic $\pi$ bonding for Si is not as strong as for C. Also, the graphitic phase of Si is unstable against its diamond phase by 0.71 eV/atom. This confirms the suggestion that $\pi$ bonds are relatively weaker than $\sigma$ bonds rendering graphitic silicon as metastable.

The Vogt group was the first to epitaxially grow silicene on a Ag (111) surface via a thermal annealing process. Vaporized silicon from a wafer was deposited onto a Ag (111) surface maintained at 220-260 °C forming a silicon cell with (4 X 4) symmetry. STM images revealed a silicon adlayer of 0.1 nm (possibly underestimated) with a honeycomb structure, giving rise to triangular structures, each consisting of three bright protrusions separated by 0.38 nm with respect to each other. The triangles are arranged hexagonally around dark centers, which are separated by four Ag lattice constants. ARPES data showed only a single dispersing branch of the ‘Dirac cone’ associated with the $\pi$ band 0.3 eV below the Fermi level. The $\pi^*$ cone could not be detected, leading the authors to assume the band gap opening of 0.6 eV is attributed to the interaction of the silicene sheet with the Ag (111) surface, similar to an effect observed for graphene. Si-Si bonds were found to be 0.22 nm (±0.01 nm) along with varying bond angles for atoms found either directly above Ag atoms (orange balls in Figure 1.40), or those found between Ag atoms (yellow balls in Figure 1.40). For the silicon atoms found directly above Ag atoms, a bond angle of approximately 110 degrees ($\alpha$ angle) was reported; however, for the Si atoms found between the Ag atoms, six are purely 120 degrees
(signifying $sp^2$ hybridization) while the other six vary from 112-118 degrees ($\beta$ angle) indicating a $sp^2-sp^3$ mixture. The authors attributed this to a displacement of the silicon atoms in the $z$ direction, caused by an interaction with the Ag (111) surface. A buckling distance ($\Delta_z$) for the silicene was found to be 0.075 nm, almost twice that found by Cahangirov for theoretical freestanding silicene (0.44 Å).

In 2018 Liu et al. synthesized few-layer silicene nanosheets from the oxidation of calcium silicide with iodine in acetonitrile. The authors report that the resultant sheets are dispersible in N-methylpyrrolidone (NMP), which allows the authors to characterize the sheets via high resolution transmission electron microscopy (HRTEM) and Raman spectroscopy along with other key methods. HRTEM images indicate a honeycomb lattice with a $d_{(100)}$ (interplanar distance) value of 0.34 nm (Figure 1.41), which is significantly smaller than the value for bulk silicon (0.54 nm). The parameters of the simple hexagonal unit cell were found to be $a = b = 3.91$ Å, in similar agreement with the
lattice constant of silicene $1 \times 1$ (3.85 Å) calculated by Takeda and Shiaishi.\textsuperscript{140} Raman spectroscopy data revealed a symmetric Si-Si $E_{2g}$ stretching mode at 517 cm$^{-1}$, indicating the presence of planar hexagonal rings; however, there was also a shoulder region present from 450-500 cm$^{-1}$ assigned to the $A_{1g}$ breathing mode produced by the vertical buckling of the sheet. Powder x-ray diffraction studies showed the disappearance of characteristic calcium silicide peaks along with a new diffraction peak at $2\theta = 24.5^\circ$ attributed to the (001) stacking with a calculated distance of 3.62 Å via Bragg’s formula, which was significantly lower than that found in bulk silicon (5.43 Å), calcium silicide (30.6 Å), and

\textbf{Figure 1.41.} a) SEM images of silicene nanosheets and a single silicene sheet (inset), respectively. b) TEM image of silicene sheets with the inset showing the photograph of a stable dispersion of silicene in NMP (5 µg ml$^{-1}$). c) HRTEM image of silicene matching with AA stacking model. d) SAED pattern of a silicene sheet. Reprinted/adapted with permission.
amorphous silicon oxide (5.52 Å). No bond angles or hybridizations were reported by the authors.

In 2013 Wang et al. used DFT to calculate the effects of atmospheric oxygen and water on silicene sheets. The authors found that when atmospheric oxygen was added to the sheet, two symmetric Si-O-Si bonds on opposite sides on the hexagonal ring formed, with single-side over-bridging oxygen as the most likely oxygen configuration as seen in Figure 1.42 e. Si-Si-Si bond angles increased from 116° up to 122° leading to distortion of the honeycomb lattice and the Si-Si bond length increased from 2.28 Å for silicene to up to 2.34 Å for the single-side over-bridging configuration. Theoretical buckling for the silicene sheet decreased from 0.45 Å to 0 Å in some instances. The addition of oxygen in the quasi in-plane bridging configuration opened the band gap to 6.6 eV, making the oxidized silicon an insulator. However, the single-side over-bridging arrangement contained an optimal band gap of 0.6 eV, giving rise to semi-conductor properties. With the addition of hydroxyl units from water, the boat-like (Figure 1.42 h) and umbrella-like (Figure 1.42 g) configurations were found to be most desirable. Si-Si-Si bond angles did not vary significantly from that found in silicene and the Si-Si bond lengths differed from 2.06 Å to 2.34 Å. Theoretical buckling values ranged from 0.03 Å to 1.14 Å, while band gap values varied from 0 eV to 0.4 eV depending on hydroxyl arrangement.
Figure 1.42. (a) silicene, (b) quasi in-plane bridging, (c) double bridging, (d) overbridging both sides, (e) over-bridging single side, (f) top like, (g) umbrella like, (h) boat like, (i) armchair like bonding. Reprinted/adapted with permission.
1.11. Functionalization and Passivation of 2D Silicon Nanosheets

The main principle behind the functionalization of silicon nanosheets is the conversion of the $sp^2$ hybridized silicene to the saturated $sp^3$ silicane, which is typically isolatable and therefore much easier to be characterized. Passivation of layered 2D crystalline silicon compounds with organic ligands can also promote single sheet exfoliation, assist in control of the interlayer spacing, and theoretically allow for the creation and subsequent modification of the band gap.\textsuperscript{187} The sheets become highly dispersive in organic solvents such as hexane, chloroform, ether, or acetone\textsuperscript{188} while their stability with respect to oxidation and hydrolysis increases due to the formation of a hydrophobic surface.\textsuperscript{147} Silicon is less electronegative than hydrogen; therefore, $\equiv$Si−H bonds are polarized opposite the usual sense, as $\equiv$Si$^{\delta^+}$−H$^{\delta^-}$ causing nucleophilic attack at the silicon centers. Therefore, the introduction of organic functional groups onto silicanes through the $\equiv$Si−C or $\equiv$Si−N bonds is one approach to obtain passivated 2D silicon nanosheets.

Yamanaka’s exfoliation of calcium silicide with 37% hydrochloric acid at -30 $^\circ$C\textsuperscript{151} is the predominant method utilized by researchers when preparing air-stable, multilayered silicanes. It has been shown that an intermediate halogenation step is typically needed for the introduction of organic groups using the Grignard reagent on bulk Si (111), however, Sugiyama demonstrated that direct modification of silicanes with phenyl magnesium bromide is possible.\textsuperscript{189} In 2015 Okamoto produced amino-passivated silicon nanosheets via the reaction of silicanes and n-alkylamines, $\alpha,\omega$-diaminoalkanes, and $\omega$-aminocarboxylic acids.\textsuperscript{190} Oshita has reported the synthesis of silicon nanosheets...
bearing benzyl, naphthylmethyl, or carbazolylmethylamino substituents and in 2014 Ohashi utilized mechanochemical methods to produce lithiated silicane.

1.11.1. Hydrosilylation of Silicane

In 2012 Nakano generated silicane prepared by the Yamanaka method functionalized with hexyl chains using a platinum-catalyzed hydrosilylation reaction with 1-hexene in toluene under argon atmosphere to produce a light-brown stable colloidal suspension (Scheme 1.16.). The acquired alkyl passivated single layer silane sheets are soluble in organic solvents such as hexane, chloroform, acetone, and ether, and insoluble in water and ethanol (Figure 1.43.). Fourier Transform Infrared Spectroscopy showed alkyl stretching and bending absorptions at 2856-2954 cm\(^{-1}\) and 1259-1459 cm\(^{-1}\), respectively with minimal Si-OR stretching vibrations. The author also reported that the absorption associated with the bandgap transition occurred at 4.2 eV, which is in a shorter wavelength region than that for bulk silicon (1.1 eV).

Scheme 1.16. Platinum catalyzed alkylation of polysilanes.
1.11.2. Alkylation of Silicane via Grignard Reagents

Silicanes can also be directly functionalized with phenyl groups using a phenyl Grignard (PhMgBr) reagent without the need of an intermediate halogenation step usually required with Si (111) surfaces. In 2010 Sugiyama et al. reported the synthesis of oxygen-free, phenyl-modified organosilicon nanosheets with atomic thickness, demonstrating the higher reactivity of silicanes as compared to bulk silicon.\textsuperscript{189} The resultant colorless paste was found to be soluble in hexane, chloroform, acetone, and ether, and produced a photoluminescent emission of 3.0 eV when dissolved in 1,4-dioxane. IR data taken in the ATR mode showed Si-Ph vibrations at 1150-1410 cm\textsuperscript{-1},
C=C stretches corresponding to the phenyl aromatic carbon double bonds at 1700-2000 cm\(^{-1}\), and Si-H asymmetric vibrations at 2100 cm\(^{-1}\). Proton NMR confirmed the presence of the Si-H and Si-Ph bonds with resonances at 2.5-3.0 ppm and 7.1-7.7 ppm, respectively. And the extent of substitution on the silicon surface was determined to be approximately -H-:Ph = 2:1. From this result, the composition of the organosilicon nanosheet was determined by the authors to be \(\text{Si}_6\text{H}_4\text{Ph}_2\) (Scheme 1.17\(^{189}\)).

1.11.3. Reactions of Silicanes with Amines

\[ \text{Si}_6\text{H}_6 + \text{PhMgBr} \xrightarrow{\text{diethyl ether}} \text{Si}_6\text{H}_4\text{Ph}_2 \]

\(\text{THF, 70°C, 2 days}\)

*Scheme 1.17. Phenyl modified silicon nanosheets via Grignard reagent. Reprinted/adapted with permission.*

In 2015 Okamoto *et al.*\(^{190}\) reported the synthesis of several types of n-alkylamine-modified layered silicanes (\(C_m\text{-Si}_n\), where \(m\) indicates the number of carbon atoms included in the amines), the reaction of silicane with \(\alpha,\omega\)-diaminoalkanes, which have amino groups at both ends of alkyl chains (\(\text{DiC}_m\text{-Si}_n\)), and finally the modification of silicane with \(\omega\)-aminocarboxylic acids, which is expected to provide versatile reactive
sites on the layer surface ($C_m$COOH-$Si_n$). To generate the red $C_m$-$Si_n$ and yellow $DiC_m$-$Si_n$ sheets, silicanes manufactured by the Yamanka method were reacted with various n-alkylamines including n-butylamine, n-hexylamine, n-decylamine, n-hexadecylamine, and $\alpha,\omega$-diaminooalkanes including 1,2-diaminoethane, 1,6-diaminohexane, and 1,12-diaminododecane in chloroform for 12 hours under a nitrogen atmosphere to produce amino functionalized silicon nanosheets as seen in Scheme 1.18. The author noted that the $\omega$-aminocarboxylic acid precursors were not soluble in chloroform, therefore other polar solvent such as pyridine, DMSO, or N-methylpyrrolidone (NMP) were used to partially dissolve the acids in order to generate colorless silicon nanosheets with a terminating carboxy functional group ($C_m$COOH-$Si_n$).

IR data was consistent for the $C_m$-$Si_n$ and $DiC_m$-$Si_n$ products with Si-N-Si stretches at 930-1150 cm$^{-1}$ and C-H stretching vibrations at 2800-3000 cm$^{-1}$ indicating the presence of organic groups. For the $DiC_m$-$Si_n$ sheets, a primary N-H stretch at 3265 cm$^{-1}$ indicated that only one end of the ligand reacted with the silicon surface, leaving the other free to be further utilized. Also, the use of shorter diamines was likely to leave a
larger amount of unreacted Si-H bonds in DiC\textsubscript{m}-Si\textsubscript{n}, as suggested by the decrease in the Si-O-Si peak intensity with increasing \( m \) as seen in Figure 1.44. (b).\textsuperscript{190}

![Figure 1.44](image)

**Figure 1.44.** (a) Photographs of \( n \)-butyl- \((C_4)\), \( n \)-hexyl- \((C_6)\), \( n \)-dodecyl- \((C_{12})\), and \( n \)-hexadecyl- \((C_{16})\) amine in chloroform, (b) FTIR spectra of DiC\textsubscript{m}-Si\textsubscript{n} sheets \((m = 2, 3, 6, \text{ and } 12)\). Reprinted/adapted with permission.

XRD results showed a large number of silicon layers (roughly 100 nm thick) regularly stacked parallel to the glass plate surface, suggesting that individual sheets self-assemble during evaporation of the solvent on plate. For the \((C_m\text{COOH-Si}_n)\) synthesis,
XRD also indicated that only functionalization of C_{12}COOH was successful and IR peaks differed when compared to the C_{m}-Si_{n} counterpart; however, a C=O stretch at 1640-1730 cm\(^{-1}\) was present, indicating successful functionalization with the carboxylic acid ligand.

In addition to silicon nanosheets passivated with straight-chain amine groups, 2D nanosheets functionalized with aromatic groups were created by Ohshita et al. in 2016.\(^{191}\) Silicanes suspended in chloroform were reacted with benzyamine (NS-Ph), 1-napthylmethylamine (NS-Np), or N-(n-butylcarbazolyl)methylamine (NS-Cz) at 60°C for 24 hours to 3 days to produce aromatic passivated silicon nanosheets as seen in Scheme 1.\(^{191}\)

\begin{center}
\includegraphics[width=\textwidth]{Scheme_1.png}
\end{center}

\textit{Scheme 1.19. Preparation of silicon nanosheets with various aromatic substituents. Reprinted/adapted with permission.}

IR data was consistent for each amino ligand used, showing Si-N-Si stretches at 920 cm\(^{-1}\), and Si-H stretches at 2100 cm\(^{-1}\), however there was no indication of N-H groups present. AFM data indicated that differences of 1.6 and 3.2 nm, which seemed to correspond to single and double-layered nanosheets, agrees with the sheet width of a NS-Ph model with benzylamino substituents on both sides of the silicon nanosheet. XRD spectra showed a peak at 13.3 Å indicative of stacked layers for NS-Np, however, no clear peaks were obtained for NS-Ph or NS-Cz. The PL spectra of NS-Ph and NS-Np
showed different profiles depending on the excitation wavelengths. When excited at 250 nm, NS-Ph emitted a photon at 370 nm, which may be due to possible intrasheet π-stacking. On the other hand, excitation of the NS-Ph nanosheet at 350 nm produced a band at 433 nm. NS-Np showed a broad band also likely ascribed to π stacking indicating a tendency to form stacked layers. For NS-Cz, only bands for carbazolylmethylamino groups and silicon catenation were observed.

1.11.4. Mechanochemical Lithiation of Silicane

Electrochemical and co-melting procedures are commonly used to create Si-Li composites from bulk silicon;\(^{193}\) however, these methods are not adequate for use with silicanes as \(\text{Si}_6\text{H}_6\) undergoes structural deterioration during melting and no composite can be made with melted lithium due to the high surface tension associated with liquid lithium. In order to overcome this limitation, Ohashi \textit{et al.} have designed a

![Figure 1.45. Color of the obtained composites from milling: (a) \(\text{Si}_6\text{H}_6\), (b) \(\text{Si}_6\text{H}_6/1\text{Li}\), (c) \(\text{Si}_6\text{H}_6/3\text{Li}\), and (d) \(\text{Si}_6\text{H}_6/6\text{Li}\). Reprinted/adapted with permission.](image-url)

mechanochemical method to produce lithium functionalized layered silicanes.\(^{192}\) \(\text{Si}_6\text{H}_6\), a
yellow powder, was prepared according to the Yamanaka method, which was then, placed in a mortar with a thin lithium plate and milled using a pestle under an argon atmosphere for 30 minutes until all lithium fragments disappeared and a dark green powder was obtained as seen in Figure 1.45.192

The X-ray diffraction peaks attributed to the layered structure planes [(001), \(2\theta = 14.81^\circ\) and (002), \(2\theta = 29.9^\circ\)] and crystal silicon framework planes [(100), \(2\theta = 27.1^\circ\) and (110), \(2\theta = 47.2^\circ\)] varied depending on the amount of lithium metal added (Figure 1.46.192), which indicated that the mechanical milling of \(\text{Si}_6\text{H}_6\) and lithium resulted in the distortion of the Si framework and breakdown of the original silicane layered structure. In
addition, no diffraction peak assigned to lithium metal was observed. The diffraction peaks of the (001) and (002) planes decreased dramatically and disappeared completely for Si_{6}H_{6}/6Li, while the peak of the (110) plane also decreased. The peak of the (100) plane shifted slightly to a smaller diffraction angle (or a higher d value) suggesting that the obtained Si–Li composites were formed and are not simply a mixture of silanes and lithium. FTIR taken with an attenuated total reflection (ATR) unit, indicated a decrease in the Si-OH, Si-O-Si, and Si-H bands of Si_{6}H_{6}/ nLi when compared to Si_{6}H_{6}, while a new Si-Li stretch at 450 cm\(^{-1}\) was recorded. Solid state diffuse reflectance UV-Vis showed a strong absorption band for Si_{6}H_{6} in the UV region with an edge at 576 nm, indicating a bandgap energy of 2.2 eV, while the absorption band for Si_{6}Li_{6} was shifted to a longer wavelength producing a lower bandgap energy of 0.85 eV. Si_{6}H_{6}/3Li showed two absorption peaks credited to band gaps of 2.2 eV and 0.85 eV suggesting that both Si_{6}H_{6} and Si_{6}Li_{6}-like moieties coexist in the dark green composite.

### 1.11.5. Chemical Vapor Deposition

In 2011 2D silicon nanosheets (NSs) deposited on various substrates were also produced via CVD by the Kim group.\(^{149}\) After the substrate was placed on a quartz tray in a hot-wall horizontal reactor, pure hydrogen and argon gases were introduced and the temperature of the reactor increased to 1000 °C at a rate of 30 °C/min. Once the reaction temperature was reached, silicon tetrachloride was bubbled in at a flow rate of 20 sccm for 30 minutes as seen in Scheme 1.20. After the designed reaction time, the reactor was
allowed to cool to room temperature under the same hydrogen and argon atmosphere. The technique produced nanosheets with an estimated 2 nm thickness as a determination of thickness via high contrast transmission electron microscopy is difficult for such thin films. The nanosheets also exhibited a photoluminescent maximum peak at 435 nm, indicative of an optical band gap with a direct transition of 2.8 eV.

1.12. Applications of Silicon Nanosheets

There may be possible applications of biological sensors; however, due to the recentness of the field and the high reactivity of silicene, these applications are far in the future. Even so, there are electronic applications, such as FET transistors and silicon anodes, that have been developed recently.

1.12.1 Electronic Applications

The fabrication of silicon nanosheets (SiNSs) is being utilized to transform various applications including photovoltaic solar cells, digital data storage, and thin film display devices. In addition, silicon nanomaterials are predicted to reform the ways in which energy is stored and used. The theoretical low buckled $sp^3$ hybridized structure of silicene is thought to give rise to a stronger spin orbit coupling effect when compared to graphene, which results in the electronic quantum states no longer being purely singlet,
doublet, or triplet in nature. As a consequence, radiative transitions and intersystem crossings become energetically allowed, creating the possibility of fluorescent and phosphorescent emissions.

1.12.1.1. Thin Film Transistors

Transistors are semiconductor devices used to either amplify electrical voltage or act as an electrical switch, opening or closing a circuit. Thin film transistors (TFT) are a type of field-effect transistors that utilize thin film metal-oxide semiconductor materials deposited onto non-conductive substrates, such as glass, along with an insulating material and metal electrode. As the primary application of TFTs are in liquid crystal displays, it is imperative that the building materials be transparent. In order to achieve this transparency, low temperature synthetic procedures such as chemical vapor deposition are employed to avoid the breakdown of the substrate at higher temperatures.

In 2015 Tao and coworkers designed a back-gated silicene field-effect transistor which demonstrated the capability to operate at room temperatures (20 °C). Thin-film silicene was deposited on a Ag (111)/mica substrate via chemical vapor deposition, capped with aluminum oxide, inverted and placed onto a silicon dioxide layer, then etched forming a field-effect transistor containing recycled Ag(111) substrate electrodes as seen in Figure 1.47. Initial electrical characterizations suggest that the substantially lower residual carrier density of the thin-film silicene \(8 \times 10^9 \text{ cm}^{-2}\) compared to graphene \(1.5 \times 10^{11} \text{ cm}^{-2}\) results in a small bandgap of 0.21 eV. The carrier mobility for the
fabricated devices was found to be around $100 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, well within the estimated range of $10–1,000 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ for supported silicene electronic devices.

**Figure 1.47.** Epitaxial growth of silicene on crystallized Ag(111) thin film, in situ Al$_2$O$_3$ capping, encapsulated delamination transfer of silicene, and native contact electrode formation to enable back-gated silicene transistors. Reprinted/adapted with permission.

### 1.12.1.2. Energy Storage / Lithium-Ion Batteries

In 2018 Liu and colleagues designed a process to exfoliate single and double layer silicene sheets from calcium silicide using iodine in acetonitrile in order to study their energy storage abilities in lithium ion battery anodes. DFT calculations were also performed to evaluate the theoretical lithium-ion storage capability of the single and few (double) layer silicene sheets. Calculations showed that for single layer silicene sheets, lithium prefers to adsorb at two sites: the hollow center of the hexagonal ring, or directly above a silicon atom. For single layer sheets, the hollow sites were preferred for lithium adsorption. For multilayer sheets, the lithium ions found the silicon atoms to be energetically more favorable. The authors also found that lithium prefers to adsorb on
differing sides on the silicene layer due to repulsion forces between the lithium atoms. Theoretical capacities were calculated to be 954 mAh/g and 715 mAh/g for single and multi-layer sheets, respectively.

Cyclic voltammetry was used to evaluate the electrical performance of the silicene, which was assembled into a half-cell utilizing one molar lithium hexafluorophosphate (LiPF₆) as the electrolyte. The first negative scan showed some irreversible reactions due to the formation of a solid electrolyte interface (SEI) on the surface of the silicene, however, coulombic efficiency was found to be 61.6%. The silicene anode achieved a high reversible capacity of 721 mAh g⁻¹ after 100 cycles and experienced no decay over 100 cycles at 0.1 A/g. In addition, the silicene nanosheets demonstrated a remarkable stability with the capacity retention surprisingly increased to 107% (553 mAh g⁻¹ vs 596 mAh g⁻¹) after 1800 charge/discharge cycles at 1.0 A g⁻¹ (Figure 1.48).²⁸⁴

Figure 1.48. Cycling performance of silicene up to 1800 cycles at 1.0 A g⁻¹. Reprinted/adapted with permission.

1.13. Motivation and Summary
The primary goal of this dissertation is to investigate the synthesis, characterization of the surface structure, optical properties, and solubility of TEGylated silicon nanoparticles produced by reactive high energy ball milling (RHEBM) as well as the preparation of free-standing, single layer, high-quality silicene nanosheets via a liquid oxidation/exfoliation reaction involving the Zintl salt calcium silicide (CaSi$_2$).

Top-down methods such as RHEBM have the advantage of producing high yields of passivated silicon nanoparticles in a one-step synthetic procedure. Nanoparticles can be transformed from the hydrophobic Si bulk surface to the hydrophilic Si-passivated surface in a relatively efficient manner, increasing their water solubility or enhance their function as drug delivery devices. Silicon nanosheets, specifically silicene, occupy a relatively new field of study. Even today, the basic structure of the sheet is heavily contested. It is essential that the hybridization scheme, and thus the symmetry of the freestanding sheet, be assessed so that functionalization of the surface can be investigated.

Chapter 2 presents the mechanochemical synthesis of TEGylated silicon nanoparticles based on a method established by Heintz and further developed by Xu. Optical and structural properties of the water soluble nanoparticles are thoroughly characterized and analyzed. Methods for purification and separation are presented followed by a focus on a newly developed method involving silica gel chromatography.

Chapter 3 introduces a synthetic method for the production of free-standing single layer silicene sheets derived from calcium silicide. As there are relatively few studies on true freestanding silicene sheets, it is necessary to discuss the fundamental properties of the sheets. Data and results from multiple characterization methods including
transmission electron microscopy, powder x-ray diffraction, energy dispersive x-ray spectroscopy, raman spectroscopy, and photoluminescence are discussed in detail.

Chapter 4 provides a summary of work and suggestions for future experimentation.

In all cases, the main work was carried out by the candidate under the guidance of the advisor Mark J. Fink, Professor in the Department of Chemistry at Tulane University, along with the co-advisor Brian S. Mitchell, Professor in the Department of Chemical and Biomolecular Engineering at Tulane University.
Chapter 2: Luminescent, Water Soluble, TEGylated Silicon Nanoparticles

2.1. Introduction

In the last few decades numerous studies of passivated silicon nanoparticles have been reported. Silicon nanoparticles have been synthesized from various methods, including reduction of halosilanes,\textsuperscript{43} chemical etching of bulk silicon,\textsuperscript{124} reverse micelle formation,\textsuperscript{46} chemical vapor deposition,\textsuperscript{54} and laser ablation.\textsuperscript{76} However, many of these methods require high temperatures, the use of highly corrosive or reactive chemicals such as hydrofluoric acid, and further modification of the unstable hydrogen-terminated silicon surface. The production of passivated silicon nanoparticles by reactive high energy ball milling (RHEBM), initially reported by Heintz \textit{et al.} in 2007,\textsuperscript{200} is an efficient, one-step method devoid of harsh chemicals or high temperatures.

RHEBM allows for a wide range of passivating ligands to be covalently attached to the silicon nanoparticle surface,\textsuperscript{198,200,202,203} which permits several different surface functionalities to be employed, simply by altering the liquid milling medium. The process of RHEBM combines bulk silicon wafer pieces with an unsaturated organic liquid such as an alkyne or an alkene, and a pair of milling balls in a stainless-steel milling vial. The procedure is carried out in a dry box under nitrogen atmosphere, to prevent the formation of silicon oxides from oxygen or water contaminants, then the milling vial is tightly sealed and milled for the desired amount of time. The resultant suspension is removed from the milling vial, diluted, separated by centrifugation, concentrated via evaporation, then purified by means of chromatography. This one-step method results in the formation of a stable covalent bond between the organic milling medium and the silicon surface of the nanoparticle.
During the RHEBM, the mechanical energy provided by the mill causes the silicon wafer pieces to break apart, exposing highly reactive silicon surfaces containing silicon-silicon double bonds and silicon surface radicals. The newly exposed surfaces are free from the oxidation layer found on the bulk wafer, allowing for a subsequent [2+2] cycloaddition of the reactive, unsaturated organic ligand to the exposed double bonds. Alternatively, reactions between newly formed Si surface radicals and the unsaturated ligand result in vinyl radical intermediates followed by subsequent proton abstraction from the solvent (assumed to be the unsaturated organic milling medium) to yield a Si surface bound alkene. As a result, highly stable, covalent Si-C bonds are formed, producing passivated silicon surfaces as seen in Scheme 2.1.

Scheme 2.1. (a) [2+2] cycloaddition of alkyne with a silicon surface to form cyclobutene (b) radical process for the functionalization of a silicon surface.
The ability to transform hydrophilic bulk silicon into stable, water soluble nanoparticles is of the utmost importance when considering their use in biological applications. Bioimaging,\textsuperscript{116,120} drug delivery,\textsuperscript{4,117} photodynamic therapy,\textsuperscript{118,121,123} and biological molecular recognition techniques\textsuperscript{204} require that the nanoparticles be biologically pH compatible as well as able to tolerate the aqueous media of \textit{in vitro} and \textit{in vivo} environments.\textsuperscript{115} In order to meet this need, researchers have employed various surface ligands including poly(acrylic acid),\textsuperscript{205} folic acid,\textsuperscript{206} carboxylic acid,\textsuperscript{207} cell peptides,\textsuperscript{208} amines,\textsuperscript{209} glycerol,\textsuperscript{210} dextran,\textsuperscript{115} and polyethylene glycol (PEG).\textsuperscript{99,201}

PEG, an FDA approved molecule, is often used to aid in the treatment of various medical conditions such as ovarian cancer,\textsuperscript{211} leukemia,\textsuperscript{212} and hemophilia.\textsuperscript{213} It has also proven to be ideal for biological uses due to its inherent biocompatibility,\textsuperscript{214} low intrinsic toxicity,\textsuperscript{215} and water solubility.\textsuperscript{216} PEG is also currently utilized in biological applications as biosensors; however, one of the critical issues limiting sensitivity of the protein sensors is the non-specific adsorption of proteins onto the silicon surface.\textsuperscript{217–219} Protein adsorption is the first step of inflammatory responses leading to the failure of various types of embedded devices.\textsuperscript{220}

PEGylated water soluble nanoparticles with covalently bonded Si-C surfaces have been prepared by Sudeep \textit{et al.} through the hydrosilylation of hydrogen terminated silicon nanoparticles with alkenyl terminated PEG-1100 groups.\textsuperscript{221} Alkyl capped silicon quantum dots encapsulated within phospholipid micelles terminated with DSPE-PEG(2000) were also prepared by Erogbogbo \textit{et al.}\textsuperscript{116} The PEG passivation allowed for a range of biomolecules to be attached, including peptides, amines, and carboxylic acids in order to assess the \textit{in vivo} cytotoxicity of the quantum dots as well as imaging of tumor
cells. Recently, Xu and coworkers utilized the RHEBM technique to synthesize ω-chloroalkyl capped silicon nanoparticles, which were then converted to ω-azido groups in order to graft mono-alkynyl PEG polymers to the surface via a CuAAC reaction, resulting in core-shell silicon nanoparticles along with nanoparticle arrays. In 2013 Zuilhof and colleagues produced PEGylated silicon nanoparticles that were revealed to generate no discernable reactive oxygen species or elevated caspase-3 enzyme activity in rat lung or human colon cells after 24 hours of exposure, reducing the likelihood of inflammatory responses and self-programmed cell death. In fact, the PEG passivated nanoparticles did not show any toxicity up to 100 µg/mL, while the coating alone reduced the relatively enhanced toxicity of iron doped silicon nanoparticles to nearly nil.

Additionally, PEG and its oligomer derivatives are being used in electronic applications as ionic charge carriers. For silicon electrodes, the main hinderance is the development of an unstable, insulating solid electrolyte interface (SEI) generated from the volume expansion and contraction that occurs in the course of electric cycling. The SEI is mainly deposited during the first lithiation process, but will grow throughout subsequent cracking episodes brought on by repetitive volume variations in the silicon anode. Growth of the SEI consumes Li⁺ in the form of Li₂O or Li₄SiO₄ resulting in a short life cycle for the silicon electrode. Studies show that the structure of solid electrolyte interface (SEI) film formed on the surface of Si nanoparticles depends greatly on the surface modification. Adding a monolayer of low molecular weight, hydrophilic PEG oligomers onto the surface of silicon nanoparticles aids in solvent dispersibility and colloidal stability of the silicon nanoparticles allows for the accommodation of the large volumetric changes necessary during charging and discharging, reduces the
production of a solid electrolyte interface (SEI), in-turn increasing coulombic efficiency, and increases the gravimetric current capacities of lithium ion anodes.

PEG oligomers such as triethylene/tetraethylene glycol monomethyl ether (Figure 2.1. compounds 1, 2) can be covalently attached to the surface of silicon nanoparticles in a one-step RHEBM reaction of silicon bulk wafers with the oligomer material. The addition of an alkynyl moiety on the triethylene/tetraethylene glycol, achieved via a well-established Williamson ether synthesis producing triethylene/tetraethylene glycol monomethyl monopropargyl ether (TEG/TTEG) (Figure 2.1. compounds 3, 4), results in an unsaturated organic functional group that undergoes a cycloaddition reaction with the highly reactive silicon surface during the RHEBM. When bulk silicon is milled in an excess of compounds 3 or 4, the alkyne group of the molecule attaches covalently to the exposed silicon surface generating water-soluble, luminescent silicon nanoparticles. To this date, a one-step synthesis of silicon nanoparticles with a TEGylated surface has not yet been reported.

Figure 2.1. Compounds 1-4.

2.2. Results and Discussion
Compounds 3 and 4 were synthesized and covalently bonded onto the surface of silicon nanoparticles via reactive high energy ball milling as seen in Scheme 2.2. Deprotonation of compound 1/2 occurs in the presence of a strong base, such as sodium hydride, forming an alkoxide that undergoes a nucleophilic S\textsubscript{N}2 reaction with an organohalide, in this case propargyl bromide, to form the final 3/4 alkynyl ligand. After the initial precursor synthesis, the 3/4 was combined with crystalline silicon wafer pieces and ball milled for 24 hours. The TEGylated Si NPs were separated from the unreacted starting material via silica gel chromatography then characterized accordingly.

![Scheme 2.2. Synthesis and passivation of TEGylated silicon nanoparticles.](image)

2.2.1. Synthesis and Characterization of Triethylene/Tetraethylene Glycol Monomethyl Monopropargyl Ether (TEG/TTEG)

While compounds 1 and 2 are available commercially, compounds 3 and 4 were obtained through a modified Williamson ether synthesis method reported by Scates in 2008\textsuperscript{232} (Scheme 2.3.) for the subsequent usage as a passivating reagent during the formation of TEGylated silicon nanoparticles.
The proton NMR spectrum of compound 1 in deuterated chloroform (Figure 2.2) shows a multiplet at 3.51 ppm (b) assigned to the three internal ether groups. The singlet at 3.10 ppm (c) is assigned to the hydroxyl group, while the singlet at 3.22 ppm (a) is attributed to the terminal methoxy functionality. For compound 2, (Figure 2.3) the terminal methoxy group (a) appears at 3.32 ppm, the hydroxyl proton (c) at 2.74 ppm, and the internal ether protons (b) occur at 3.61 ppm.

The proton NMR of compound 3 in deuterated chloroform is displayed in Figure 2.4, showing a triplet resonance at 2.40 ppm (d, t, J=2.4Hz), which is assigned to the new terminal alkyne proton. Resonances at 3.33 ppm (a), 3.62 ppm (b), and 4.16 ppm (c, d, J=2.3Hz) are attributed to the methoxy functionality, ether groups, and newly added propargyl methylene protons, respectively. The disappearance of the hydroxyl proton along with the appearance of the propargyl methylene and terminal alkyne protons indicate a successful transformation to the desired nanoparticle ligand precursor.

Conversion to compound 3 is also supported by data shown in the carbon-13 NMR spectra of 3 in deuterated chloroform as shown in Figure 2.5. Carbons c, d, and e appear at 57.84 ppm, 74.22 ppm, and 79.24 ppm, respectively, showing consistency with data previously reported by Scates. The six ether carbons, b, appear as a multiplet centered at 70.00 ppm with additional ether peaks located at 71.44, 70.10, 69.89, 68.58 ppm. A
DEPT135 $^{13}$C NMR was obtained for compound 3 in order to confirm the assignment of the carbon atoms. Figure 2.6. shows that carbons labeled $b$ (70.48 ppm) and $c$ (58.26 ppm) occur as methylene carbons, while $a$ (58.96 ppm) is a methyl carbon, and $d$ (74.46 ppm) appears as a methine carbon.

The proton NMR of compound 4 in deuterated chloroform shows similar chemical shifts as compound 3 as demonstrated in Figure 2.7. A triplet resonance at 2.40 ppm ($d$, t, $J=2.4$Hz), ($c$) a doublet at 4.19 ppm ($e$, d, $J=2.4$Hz), multiplet at 3.64 ppm ($b$), and singlet at 3.36 ppm ($a$) are attributed to the alkyne terminal proton, propargyl methylene protons, ether group protons, and terminal methoxy protons, respectively. A comparative $^{13}$C NMR spectrum for compound 4 is included in Figure 2.8. Carbons $c$, $d$, and $e$ appear at 58.41 ppm, 74.46 ppm, and 79.68 ppm, respectively, while the eight ether carbons, $b$, also appear as a multiplet which is centered at 70.60 ppm with additional peaks at 71.96, 70.63, 70.53, and 70.42 ppm. $a$ is located at 59.03 ppm. The chloroform-d reference triplet peak is again shown at 77.00 ppm. It can be noted that peak appearance for both compounds is relatively consistent, despite the difference in number of ether groups. Table 2.1. gives a summation of the $^1$H NMR and $^{13}$C NMR chemical shifts for compounds 1-4.
Figure 2.2. $^1$H NMR (300MHz, CDCl$_3$), Compound 1, $n = 3$

Figure 2.3. $^1$H NMR (300MHz, CDCl$_3$), Compound 2, $n = 4$
Figure 2.4. $^1$H NMR (300MHz, CDCl$_3$), Compound 3, $n = 3$

Figure 2.5. $^{13}$C NMR (300MHz, CDCl$_3$), Compound 3, $n = 3$
Figure 2.6. DEPT-135 $^13$C NMR (300MHz, CDCl$_3$), Compound 3, $n = 3$

Figure 2.7. $^1$H NMR (300MHz, CDCl$_3$), Compound 4, $n = 4$
Figure 2.8. $^{13}C$ NMR (300MHz, CDCl3), Compound 4, n = 4

Table 2.1. $^1H$ NMR (top) and $^{13}C$ NMR (bottom) chemical shifts for compounds 1-4.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Formula</th>
<th>Chemical Shift (ppm)</th>
<th>a</th>
<th>b</th>
<th>c</th>
<th>d</th>
<th>e</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>CH$_3$(OCH$_2$CH$_2$)$_3$OH</td>
<td>3.22</td>
<td>3.51</td>
<td>3.10</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>CH$_4$(OCH$_2$CH$_2$)$_4$OH</td>
<td>3.32</td>
<td>3.61</td>
<td>2.74</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>CH$_3$(OCH$_2$CH$_2$)$_2$OCH$_2$CCH</td>
<td>3.33</td>
<td>3.62</td>
<td>4.16</td>
<td>2.40</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>CH$_3$(OCH$_2$CH$_2$)$_4$OCH$_2$CCH</td>
<td>3.36</td>
<td>3.64</td>
<td>4.19</td>
<td>2.40</td>
<td>-</td>
<td></td>
</tr>
</tbody>
</table>

| 3        | CH$_3$(OCH$_2$CH$_2$)$_4$OCH$_2$CCH | 58.43 | 70.00, 69.89, 57.84 | 74.22 | 79.24 | 68.58 |
| 4        | CH$_3$(OCH$_2$CH$_2$)$_4$OCH$_2$CCH | 59.03 | 70.60 (2X), 70.53, 58.41 | 74.46 | 79.68 | 70.42 |
The FT-IR (KBr) spectrum for compound 1 (Figure 2.9, red) shows a characteristic broad hydroxyl (O-H) stretching vibration at 3452 cm\(^{-1}\) as well as a strong methyl stretching vibration at 2877 cm\(^{-1}\), weak methylene (CH\(_2\)) bending vibrations in the 1480 cm\(^{-1}\) to 1160 cm\(^{-1}\) region, and a strong ether (C-O) stretch at 1107 cm\(^{-1}\). When comparing the spectrum for compound 3, the disappearance of the hydroxyl mode along with the appearance of a terminal alkyne stretching vibration (≡C-H) at 3250 cm\(^{-1}\) as well as a C≡C vibration at 2110 cm\(^{-1}\) confirms the successful addition of the unsaturated carbon alkyne functionality. The strong methyl stretching vibration at 2868 cm\(^{-1}\), weak methylene (CH\(_2\)) bending vibrations in the 1480 cm\(^{-1}\) to 1160 cm\(^{-1}\) region, and strong ether (C-O) stretch at 1107 cm\(^{-1}\) are maintained as expected. The FT-IR (KBr) spectra for compounds 2 and 4 are shown in Figure 2.10, while FT-IR absorption data for compounds 1-4 is summarized in Table 2.2, for comparison.

**Table 2.2. Summary of FT-IR data for compounds 1-4.**

<table>
<thead>
<tr>
<th>Compound</th>
<th>O-H (v)</th>
<th>C-H (v) methyl</th>
<th>C-H ((\sigma)) methylene</th>
<th>C-O (v)</th>
<th>(\equiv\text{C-H} (v))</th>
<th>C≡C (v)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3452</td>
<td>2877</td>
<td>1480-1160</td>
<td>1107</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>2</td>
<td>3462</td>
<td>2871</td>
<td>1460-1190</td>
<td>1112</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>3</td>
<td>-</td>
<td>2868</td>
<td>1480-1160</td>
<td>1107</td>
<td>3250</td>
<td>2110</td>
</tr>
<tr>
<td>4</td>
<td>-</td>
<td>2871</td>
<td>1460-1190</td>
<td>1103</td>
<td>3244</td>
<td>2115</td>
</tr>
</tbody>
</table>
Figure 2.9. FT-IR comparison of compounds 1 and 3.

Figure 2.10. FT-IR comparison of compounds 2 and 4.
Gas chromatograph data shows a relative retention time of 9.97 mins for compound 1, while compound 3 has a relative retention time of 11.89 mins indicating the larger molecular mass of compound 3 due to the addition of the propargyl group (Figure 2.11. a). Gas chromatograph data for compounds 2 and 4 (Figure 2.12. a) reveal relative retention times of 12.87 min and 14.63 min respectively, similar to the elution order for compounds 1 and 3.

The mass spectrum (Figure 2.11. b) of compound 1 reveals a large amount of relatively intense fragmentation at 45 m/z and 59 m/z, showing the mass distributions with adjacent peaks separated by 14 Da, corresponding to the repeat unit CH₂OCH₃⁺ and CH₂CH₂OCH₃, respectively. There is also fragmentation at 89 m/z and 103 m/z assigned to the CH₂CH₂OCH₂CH₂O and CH₃OCH₂CH₂OCH₂CH₂OCH₂CH₃ moieties. Similar fragmentation occurs for compound 3 (Figure 2.11. c) while the new peak at 73 m/z is attributed to the CH₂CH₂OCH₂CH₂ ether repeat unit. The peak at 113 m/z indicates the addition of the propargyl functionality to the ether, while 133 m/z peak is attributed to the OCH₂CH₂OCH₂CH₂OCH₂CH₃ ether unit. Mass spectroscopy data for compounds 2 and 4 (Figure 2.12. b, c) mirrors that of compounds 1 and 3 with fragmentations at 45 m/z, 59 m/z, 89 m/z, and 103 m/z for compound 2 along with peaks at 43 m/z, 59 m/z, 73 m/z, 113 m/z, and 133 m/z for compound 4 signifying consistency within the synthetic method.
Figure 2.11. GC spectra comparing relative retention times for compounds 1 and 3 (a), Mass spectroscopy for compound 1 (b), and compound 3 (c).
Figure 2.12. GC spectra comparing relative retention times for compounds 2 and 4 (a), Mass spectroscopy for compound 2 (b), and compound 4 (c).
2.2.2. Synthesis of TEGylated Silicon Nanoparticles

Due to the expense of working with compound 4, compound 3 was chosen as a more cost efficient precursor material and the synthesis is now focused on the TEG passivated silicon nanoparticles.

TEGylated Si NPs were successfully synthesized via RHEBM, a method initially developed by Heintz in 2007. The 24hr ball milling time for the silicon nanoparticles was chosen based on past experimental research performed by Hallmann. The group found that nanoparticle formation and subsequent functionalization did not occur initially, but were slower and continued until yield production plateaued after around 20 hours as seen in Figure 2.13. In addition, as milling time increased, the relative concentrations of the impurities created during the milling process decreased to an almost undetectable level. A typical RHEBM run employing 1g of silicon wafer and compound 3 will yield between 0.11g and 0.13g of nanoparticles along with 1.4g of unrecoverable

![Figure 2.13](image_url)

**Figure 2.13.** Total yield of silicon nanoparticles obtained from various milling times. Reprinted/adapted with permission.
gray residue consisting of excess silicon slug material of either bulk size or nanoparticles with insufficient surface passivation to remain solubilized in the milling medium along with chemically bound and physisorbed TEG.

The initial ball milled Si nanoparticle mixture is a dark brown, extremely viscous sludge requiring dilution with dichloromethane for centrifugation as seen in Figure 2.14. After centrifugation, the unrecoverable gray slug is found at the bottom of the centrifuge tube topped by a viscous yellow oil containing the passivated silicon nanoparticles along with any unreacted compound 3. Separation of the nanoparticles from the unreacted TEG was achieved by means of normal phase liquid chromatography (NPLC) employing a silica gel stationary phase.
The high boiling point of compound 3, as well as the high viscosity, made separation of the nanoparticles from the unreacted TEG somewhat of a challenge. Multiple attempted methods, including solvent washes\textsuperscript{234}, phase separation\textsuperscript{235}, dialysis\textsuperscript{236}, and size separations,\textsuperscript{201} proved to be unsuccessful. The use of size exclusion chromatography (SEC) has shown to be useful for past studies;\textsuperscript{201} however, the majority of the TEGylated nanoparticle fractions collected contained a mixture of nanoparticles along with the unreacted milling medium. For example, from a two milliter aliquot of the unseparated ball milling mixture, forty half-dram vials were collected from SEC. From those forty partitions, only fractions nine and ten were free of unreacted compound 3. Fractions eleven through fifteen contained a mixture of nanoparticles and unreacted compound 3, while fractions sixteen onward contained unreacted compound 3 as well as impurities arising from the ball milling process. This has lead to difficulty in the ability to separate and subsequently characterize only the nanoparticles. In 2011 Verdoni\textsuperscript{202} showed that normal phase liquid chromatography (NPLC) could be used to separate silicon nanoparticles synthesized via RHEBM from the unreacted milling medium. A similar methodology was used to develop a new silica gel technique to separate TEGylated silicon nanoparticles from the unreacted TEG.

NPLC was exploited to separate the Si nanoparticles according the differences in polarity between the unreacted TEG and the passivated silicon surface. The covalent bonding of compound 3 to the nanoparticle surface increases the polarity of the silicon quantum dot, leading to the retention of the passivated nanoparticles on the NPLC column. A 1:1 mixture of diethyl ether and ethyl acetate was chosen as the mobile phase due to the polarity index of the two solvents as TEG is soluble in ethyl acetate and
slightly insoluble in diethyl ether. Thin layer chromatography (TLC) studies, along with UV handheld lamp monitoring (365m), were performed on silica gel plates to find the optical solvet mixture and ratio. The unreacted compound 3 was found to exhibit no visible photoluminescence when exposed to the handheld UV lamp (365nm). Mixtures of various solvents with polar indexes higher than 4.4, such as methanol, in combination with ethyl acetate produced relatively no separation of the TEGylated NPs from compound 3 showing retention factors of 0.87 and 0.89 respectively. In contrast, with the 1:1 ethyl ether/ethyl acetate mixture, compound 3 showed a retention factor of 0.75 compared a value of 0.00 for the TEGylated NPs, meaning the nanoparticles were retained on the TLC plate. Intermolecular hydrogen bonding of the solvents with the low molecular weight TEG allowed for a colorless elution of the unreacted ligand prior to the passivated silicon nanoparticles as noted by the retention of a yellow band on the NPLC column during loading of the 1:1 diethyl ether/ethyl acetate mixture.

Upon conversion to a 1:19 mixture of ethyl acetate/methanol mobile phase, movement of the yellow nanoparticle band was noted. The first three retained nanoparticle fractions exhibited strong blue luminescence under handheld UV lamp (365nm) illumination as seen in Figure 2.15. Visible luminescence intensity decreased as elution time elapsed until no longer present after 70mL of sample volume was collected, therefore elution was halted at this point. The TEG passivated Si NPs have been found to be soluble in various organic solvents such as acetone, chloroform, dichloromethane, ethanol, ethyl acetate, diethyl ether, isopropanol, methanol, tetrahydrofuran, and toluene.
2.2.3. Characterization of TEGylated Silicon Nanoparticles

TEGylated silicon nanoparticles were first characterized by proton and carbon-13 nuclear magnetic resonance along with fourier transform infrared spectroscopy. Figure 2.16. shows the proton NMR spectrum of the TEGylated Si NPs after RHEBM and silica gel separation, demonstrating characteristics of the TEG passivated silicon surface. When compared to that of compound 3, the $^1$H-NMR spectrum shows a new broad multiplet from 6.30 ppm to 5.50 ppm (inset d), which corresponds to the protons attached to the newly formed olefin carbons found on the alpha and beta positions attached to the silicon surface. This broadening of the peak in the vinyl region suggests multiple environments for the same proton, in particular the possibility of bimodal ligand bonding to the silicon surface. Retention of the multiplet centered at 3.67 ppm (b) and the singlet at 3.37 ppm (a) are indicative of the preservation of the internal ether protons and the terminal methoxy protons, respectively. The methylene CH$_2$ protons (c) show a small, broad
resonance at 4.30 ppm, which is a downfield shift of 0.14 ppm from 4.16 ppm in 3. The resonances marked with an asterisk at 1.23 ppm, 2.44 ppm, and 4.20 ppm are residual ligand remaining from chromatography separation.

The carbon-13 NMR spectrum (Figure 2.17.) of the TEGylated Si Nps further confirms the passivation of the silicon surface with compound 3. There are four new olefinic carbon peaks in the 165-125 ppm region (inset, d), as well as the disappearance of the alkyne carbon.

**Figure 2.16.** $^1$H NMR spectrum of TEGylated silicon nanoparticles. Residual impurities from the TEG precursor are marked with asterisks.
Figure 2.17. $^{13}$C NMR expanded spectrum of TEGylated silicon nanoparticles. Residual impurity peaks from the TEG precursor are marked with asterisks.

resonances at 79.24 ppm and 74.22 ppm demonstrates the successful reduction of the triple bond of compound 3 with the nanoparticle surface. In addition, there is retention of the methoxy resonance (a) at 58.78 ppm along with the repeating ether carbon peaks (b) in the 73-69 ppm region. Residual impurities from the precursor are marked with asterisks, while the three chloroform-d solvent peaks can be seen centered at 70.00 ppm. A summary of the resonance shifts for compound 3 and the TEGylated Si NPs can be seen in Table 2.3. Most noticeable is the peak shifts of functional groups c and d as well as the disappearance of the propargyl carbon labeled e.
Based on the two possible bonding modes of the alkyne onto the silicon surface shown in Scheme 2.1, two major chain structures can be formed during the RHEBM process as seen in Scheme 2.4.

**Table 2.3.** Comparison of $^1$H-NMR resonance shifts (top) and $^{13}$C-NMR resonance shifts (bottom) for TEG (3) and TEGylated Si NPs.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Functional Group Resonance (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>a</td>
</tr>
<tr>
<td>TEG (3)</td>
<td>3.33</td>
</tr>
<tr>
<td>Si NPs</td>
<td>3.37</td>
</tr>
</tbody>
</table>

<p>| | | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>TEG (3)</td>
<td>58.43</td>
<td>70.00, 69.89</td>
<td>57.84</td>
</tr>
<tr>
<td></td>
<td>72.31, 71.71</td>
<td>68.58</td>
<td></td>
</tr>
<tr>
<td>Si NPs</td>
<td>58.78</td>
<td>71.64, 70.39</td>
<td>61.34</td>
</tr>
</tbody>
</table>

Scheme 2.4. Possible bonding modes of TEG ligand on silicon nanoparticle surface along with NMR spectral assignments. (1) shows attachment via Si radical reaction, while (2) demonstrates covalent bonding through [2+2] cycloaddition.
1) alkynes are bonded to the silicon nanoparticle surface by covalent Si-C bonds through the Si radical reaction,

2) alkynyl group of TEG reacts with the silicon nanoparticle surface through a [2+2] cycloaddition.

Further evidence of the successful passivation of the silicon surface was obtained from FTIR spectra of the purified nanoparticles (Figure 2.18). The TEG ether C-O stretching vibration at 1107 cm\(^{-1}\) is maintained after ball milling, along with the ether methylene (C-H\(_2\)) bending vibrations in the 1480-1160 cm\(^{-1}\) region, and the methyl (C-H) stretch at 2872 cm\(^{-1}\) indicating retention of the TEG backbone structure. In addition, there

![FTIR spectral comparison between compound 3 and TEGylated Si nanoparticles.](image)

**Figure 2.18.** FTIR spectral comparison between compound 3 and TEGylated Si nanoparticles.
is the appearance of a new vinylic carbon stretching vibration at 1721 cm\(^{-1}\) and the disappearance of the alkynyl stretch at 2110 cm\(^{-1}\), verifying the transformation of the propargyl triple bond to a carbon carbon double bond as the alkyne binds to the silicon surface. The small Si-H stretch corresponding to the 5.80 ppm peak in the \(^1\)H-NMR is noted at 2112 cm\(^{-1}\) while a large broad -OH peak can be viewed at 3312 cm\(^{-1}\) due to the atmospheric water absorbed during preparation and characterization caused by the hydrophilicity of the TEG ligand. This assignment is supported by the presence of an additional water peak at 1612 cm\(^{-1}\). Any broad Si-O-Si vibrations, if present, were thought to be concealed underneath the large, sharp C-O stretches in the 1000-1200 cm\(^{-1}\) region.

Transmission Electron Microscopy (TEM) images (Figure 2.20.) show an agglomeration of spherical morphologies varying from 5 nm to 10 nm in size, which is possibly due to the interdigitation of the TEG monomer chains. The population distribution histogram in Figure 2.22. yields an average particle diameter of 6.69 nm, with a minimum diameter of 3.31 nm and maximum observed particle diameter of 9.10 nm. Molecular mechanics calculations yield a surface ligand length of 1.6 nm, yielding a silicon core size of roughly 3.49 nm. When viewing a magnified image the silicon nanoparticles (Figure 2.19.), lattice fringes of the silicon core are unmistakeable, appearing as repeating parallel striations (highlighted in red) occurring at a spacing of 2.38 Å. This measurement is consistent with the Si-Si single bond length, however it signifies a decrease in the mean interatomic Si-Si distance and a theoretical increase in the band gap of the material.\(^{237}\)
Figure 2.19. TEM image of 2 agglomerated TEGylated silicon nanoparticles with lattice fringes indicated (red).

Figure 2.20. TEM images of agglomerated TEGylated Silicon Nanoparticles.
Dynamic light scattering (DLS) data of the TEGylated Si NPs in toluene corroborates the TEM nanoparticle size range of 5-10 nm as seen in Figure 2.21. There is also an occurrence of larger nanoparticles in the 16-21 nm range indicating a bimodal

**Figure 2.21.** Dynamic light scattering data showing bimodal distribution of TEGylated SiNp diameters.
distribution of particle size arising from the RHEBM, which could possibly be due to
dimerization arising from the interdigitation of the surface ligand.

The energy dispersive x-ray spectroscopy (EDS) analysis of the TEGylated Si
NPs shows a pronounced signal attributed to silicon at 1.73 KeV, signifying presence of
the silicon nanoparticle core. The oxygen peak at 0.53 KeV and carbon signal at 0.26
KeV confirm successful passivation of the nanoparticle surface with compound \(3\) (Figure
2.23.). However, a portion of the carbon intensity, as well as all of the copper signals, can
be attributed to the copper coated TEM grid used as a sample holder. The absence of an
iron signal at 6.39 KeV also indicates a lack of iron impurities often introduced during
the ball milling process.\(^{203}\)

![Figure 2.23. TEGylated Si nanoparticle EDS spectrum confirming presence of Si, C, O and absence of Fe impurities.](image-url)
The ability of X-ray photoelectron spectroscopy (XPS) to provide information on the bonding environment of a given species makes it an important tool for understanding the surface chemistry of TEG passivated silicon nanoparticles. The XPS survey scan of the silicon nanoparticle sample (Figure 2.24.) shows indications of the TEG ligand covalently bonded to the silicon surface, evidenced by the presence of a Si (2p) peak at around 102 eV, accompanied by a Si 2s peak at 151 eV. In addition, there is a C (1s) peak at 285 eV, and an O (1s) peak at 533 eV. While the Si 2s and 2p regions are

![Figure 2.24. XPS spectrum profiling of the elemental composition across the silicon nanoparticle surface.](image-url)
lower in intensity when compared to the carbon and oxygen regions, due to a large amount of surface coverage by the organic TEG ligand, investigation of the silicon 2p region (Figure 2.25.) indicates the presence of Si-C\textsuperscript{102} and Si-Si\textsuperscript{242} species at 100.2 eV and 98.6/97.2 eV respectively. In addition, there is a Si-O peak found at 102.6 eV, which is attributed to oxidation of the silicon surface. Most noticeable is the lack of SiO\textsubscript{2} peaks around 103.5 eV demonstrating the ability of the TEG ligand to prevent surface oxidation from atmospheric oxygen during and after RHEBM.\textsuperscript{243} The Si 2s region (Figure 2.26.)
also shows a Si-O peak at 155.6 eV, a Si-C peak at 151.2 eV and an elemental Si-Si peak at 148.0 eV, supporting the findings in the Si 2p region. Deconvolution of the carbon 1s survey peak (Figure 2.28.) suggests the existence of a C-O\textsuperscript{102}, C-C and C-Si\textsuperscript{244} species at 286.4 eV, 285.6 eV, and 283.0 eV, respectively while the oxygen 1s region (Figure 2.27.) contains a C-O\textsuperscript{245} peak at 533.4 eV and a Si-O\textsuperscript{246} peak at 531.8 eV, further strengthening the conclusions arising from the Si 2p and Si 2s regions.

Figure 2.26. XPS spectrum (black) and deconvoluted peaks of the Si 2s region of the TEGylated silicon nanoparticles.
Figure 2.27. XPS spectrum (black) and deconvoluted peaks of the O 1s region of the TEGylated silicon nanoparticles.

Figure 2.28. XPS spectrum (black) and the deconvoluted peaks of the C 1s region of the TEGylated silicon nanoparticles.
X-ray Diffraction (XRD) of TEGylated particles obtained after a milling time of 24 hours shows a large, broad peak shifted from $28.5^\circ$ to one centered around $2\theta = 21.08^\circ$ indicating the presence of a sizeable amount of small crystallite material (Figure 2.29. bottom, blue) as well as carbon$^{247-249}$ on the surface of the Si Np. Average crystallite size of the TEGylated Si Nps and silicon slug were found to be 0.9631 nm and 50.50 nm, respectively. The calculated value of the TEGylated Si NPs is more closely related to the surface ligand diameter (1.6 nm) than to the average core size of 3.49 nm found by TEM and DLS measurements.

Figure 2.29. XRD comparison of TEGylated silicon nanoparticles (bottom blue), unrecoverable silicon slug particles (middle red), and crystalline silicon (top black).
Crystallite sizes were computed from the Scherrer equation (Equation 2.1) and the FWHM of the XRD spectral peaks. The instrumental line broadening value ($\beta_{\text{inst}}$) was derived from the K$_{a1}$ peak of the crystalline silicon XRD pattern and found to be 0.0607°, or 0.001 radians, on average. The ($\beta_{\text{inst}}$) for each respective Si Miller plane is as follows: Si (111) 0.0595°, Si (220) 0.05207°, Si (311) 0.0612°, Si (400) 0.06729°, Si (331) 0.06838°. The calculated $\beta_{\text{sample}}$ value used in Equation 2.1 reflects the subtraction of $\beta_{\text{inst}}$ from the total FWHM of the peak ($\beta_{\text{total}}$) observed in Figure 2.29. The large FWHM of the Si NP sample is indicative of line broadening caused by the presence of crystallites containing substantially fewer atoms when compared to a bulk material that is considered to include an infinite number of atoms. These small crystallites prevent the convergence of the lattice point sum to a single diffraction line, creating a large, broad peak.\(^{250}\) The calculated data, along with indexed silicon Miller indices, can be viewed in Table 2.4. Subsequent analysis of the unrecoverable silicon slug confirmed the crystallinity of the unpassivated particles the due to a narrow peak at $2\theta = 28.57^\circ$ (Figure 2.29. middle, red) corresponding to cubic silicon with a [111] orientation, which is the same as the bulk wafer, and is in excellent agreement with diffraction data published in the RRUFF database\(^{251}\) (28.4°, Figure 2.29. top, black) and by Faulkner.\(^{252}\)

\[
D = \frac{K \lambda}{\beta_{\text{sample}}(\cos \theta)} = \frac{K \lambda}{\sqrt{\beta_{\text{total}} - \beta_{\text{inst}}(\cos \theta)}}
\tag{2.1.}
\]

where:

$D$ = diameter of crystallite (nm)
$K$ = shape factor, NPs: 0.9
\[ \lambda = \text{x-ray wavelength, } 0.15406 \text{ nm} \]

\[ \beta_{\text{sample}} = \text{FWHM of sample peak (radians)} \]

\[ \beta_{\text{total}} = \text{FWHM of sample peak + instrumental broadening; taken from sample spectrum} \]

\[ \beta_{\text{inst.}} = \text{FWHM instrumental line broadening, derived from standard reference sample spectrum} \]

\[ \theta = \text{Bragg angle of peak (radians)} \]

**Table 2.4.** Observed and calculated XRD data for silicon slug material (top) and TEGylated Si Nanoparticles (bottom).

<table>
<thead>
<tr>
<th>Miller Indices (hkl)</th>
<th>Peak Position (2(\theta))</th>
<th>(\beta_{\text{inst.}}) (2(\theta))</th>
<th>(\beta_{\text{total}}) (2(\theta))</th>
<th>(\beta_{\text{sample}}) (2(\theta))</th>
<th>Crystallite Size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si (111)</td>
<td>28.5727</td>
<td>0.0595</td>
<td>0.1719</td>
<td>0.1613</td>
<td>50.8181</td>
</tr>
<tr>
<td>Si (200)</td>
<td>47.4015</td>
<td>0.0521</td>
<td>0.1787</td>
<td>0.1709</td>
<td>50.7533</td>
</tr>
<tr>
<td>Si (311)</td>
<td>56.1993</td>
<td>0.0612</td>
<td>0.1905</td>
<td>0.1804</td>
<td>49.9325</td>
</tr>
<tr>
<td>Si (400)</td>
<td>69.1803</td>
<td>0.0673</td>
<td>0.2109</td>
<td>0.1998</td>
<td>48.2878</td>
</tr>
<tr>
<td>Si (331)</td>
<td>76.4032</td>
<td>0.0684</td>
<td>0.2037</td>
<td>0.1918</td>
<td>52.7001</td>
</tr>
<tr>
<td><strong>Average Si Slug Crystallite Size</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>50.4984</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Peak Position (2(\theta))</th>
<th>(\beta_{\text{inst.}}) (2(\theta))</th>
<th>(\beta_{\text{total}}) (2(\theta))</th>
<th>(\beta_{\text{sample}}) (2(\theta))</th>
<th>Crystallite Size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si Nanoparticles</td>
<td>21.0834</td>
<td>0.0607</td>
<td>8.3903</td>
<td>8.3901</td>
</tr>
</tbody>
</table>

The TGA analysis of the TEGylated nanoparticles (Figure 2.30.) shows a small weight loss between ambient room temperature and 185°C, which could be caused by the presence of water or residual chromatography solvent due to incomplete drying. There is a weight loss of roughly 25% from 185°C to 245°C, attributed to the vaporization of
physisorbed TEG ligand. and an additional weight loss of 25% from 257° to 430° caused by the decomposition of the organic ligand shell.\textsuperscript{253,254} The remaining 18% of the sample weight at the culmination of the analysis is attributed to the silicon core. When adjusting the sample weight percentage for loss of water and solvent the silicon core is responsible for 24% of the entire sample. When taking into account the adsorbed TEG ligand in addition to water and solvent, the silicon core accounts for 35% of the total sample. The unrecoverable silicon slug produced during centrifugation showed no weight loss during TGA analysis, maintaining a weight percentage of 100-99.9%.

\textbf{Figure 2.30.} TGA data showing weight percent lost and derivative weight loss for TEGylated silicon nanoparticles.
The most compelling evidence for the formation of silicon nanoparticles comes from the UV-Vis and photoluminescence spectroscopic (PL) data. Figure 2.31. shows similar optical properties as those produced by differing methods,\textsuperscript{79} including a broad continuous UV-Vis absorption tailing at 575nm and a strong PL emission in the range of 340nm to 600nm. PL spectra of the TEGylated silicon nanoparticles were recorded with various excitation wavelengths ranging from 320nm to 420nm in dichloromethane, with a strong emission maximum at 470nm, indicating a blue shift of the silicon nanoparticle.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure2.png}
\caption{UV-Visible absorption spectrum and photoluminescence spectra at various excitation wavelengths of TEGylated silicon nanoparticles.}
\end{figure}

135
maximum in the visible region when compared to bulk silicon. However, the red-shift of the emission maximum with increased excitation wavelength indicates that the TEGylated silicon nanoparticles contain a large broad size distribution. When exposed to UV light (Figure 2.32.) using a compact laboratory lamp (365 nm), the passivated silicon nanoparticles show strong blue luminescence that is visible to the naked eye.

2.3. Conclusion

Luminescent, water-soluble TEGylated silicon nanoparticles via a Williamson Ether synthesis and subsequent Reactive High Energy Ball Milling procedure have been successfully prepared. The one-step, top-down procedure predominately generated small, thermally stable, 5-10nm nanoparticles as demonstrated by TGA, TEM, and DLS studies. The process is also shown to be free of harsh chemicals or high temperatures, often needed to achieve nanoparticles of such small size. Although initial separation techniques presented somewhat of a challenge in characterizing the TEGylated Si NPs, a silica-gel

**Figure 2.32.** TEGylated silicon nanoparticles showing strong luminescence when exposed to a handheld UV lamp.
based method was developed that has proven to be repeatedly successful, evidenced by FTIR and proton NMR findings. XPS and XRD data confirmed the presence of an amorphous organic surface covalently bound to a crystalline silicon core, while the nanoparticles have been shown to emit a strong blue luminescence in the visible region when excited with ultraviolet light.

2.4. Experimental Methods

2.4.1. Materials

Tetraethylene glycol monomethyl ether (95%) and triethylene glycol monomethyl ether (95%) were purchased from Sigma-Aldrich and used after removal of excess water overnight via vacuum. Sodium hydride (60% in mineral oil) was purchased from Sigma-Aldrich and used after washing with dry pentanes. Propargyl bromide (80%) was purchased from Sigma-Aldrich and stored at 1.4°C prior to use. Diethyl ether, dichloromethane, and pentanes were purchased from Fisher Scientific and were used as is unless otherwise stated. Tetrahydrofuran was dried via distillation over a sodium-benzophenone mixture. Silicon wafers (undoped, mirror finish, orientation [111]) were obtained from Silrec Corp of Lexington, KY. Dry box nitrogen atmosphere was maintained at oxygen levels less than 2ppm and water levels less than 1ppm.
2.4.2 Synthesis of Tetra/Triethylene glycol monomethyl monopropargyl ether (TTEG/TEG)

Dried sodium hydride (14.03g, 0.58 mol.) was dissolved in dry tetrahydrofuran inside a 2-neck round bottom reaction flask fitted with a rubber septum under inert nitrogen atmosphere. Nitrogen purged 1 or 2 (20 mL, 0.12 mol.) was added via syringe and allowed to stir until completely dissolved. Propargyl bromide (15.8 mL, 0.18 mol.) was injected into the mixture in small increments via syringe in ten-minute intervals until the entirety of the volume was added in order to reduce the rate of gas production. The solution was then allowed to stir for approximately 12 hours until a dark beige color developed. Upon standing, the mixture separated into two distinct layers, aiding in the filtration process. The reaction mixture was exposed to atmosphere and the top brown, liquid layer was decanted away from the bottom layer, filtered and filtrate collected, while the bottom layer containing the dark beige solids was washed with dichloromethane then filtered and filtrate collected to extract any trapped product. The filtered dark beige solids are quenched with a 1:3 water and ethanol mixture then disposed accordingly. Excess tetrahydrofuran and dichloromethane were removed from the filtrate via rotary evaporation producing a dark brown oil. An aqueous-organic extraction was performed with dichloromethane and distilled water in order to remove any residual sodium salts remaining in the organic product. Dichloromethane was removed from the retained organic phase via rotary evaporation to produce an amber oil, which was then vacuum distilled under nitrogen at 110°C, 0.32Torr to produce a clear oil. The TEG/TTEG (3,4) oil was maintained under nitrogen in a dry box until loading into milling vial.
2.4.3. Synthesis of TEGylated silicon nanoparticles

Gray silicon wafer pieces (1g, 36 mmol) were placed in a stainless-steel milling vial along with two stainless steel milling balls (1.2 cm diameter, approximately 8g) inside a nitrogen-filled dry-box. The milling vial was then filled with 15-20 mL clear TEG/TTEG and tightly sealed. The milling vial was placed in a SPEX 8000-D Dual Mixer/Mill (Figure 2.33.) and high energy ball-milling was performed in 4°C cold room at 1060 cycles per minute for 24 hours. The milling vial was then opened to atmosphere and the resulting brown, viscous, homogeneous slurry was diluted with DCM and centrifuged in glass centrifuge tubes at 3800 rpm for 30 mins to separate larger particles.

Figure 2.33. SPEX8000 ball miller loaded with two stainless steel milling vials. Reprinted/adapted with permission.
and unreacted silicon from the desired transparent nanoparticle layer. The top nanoparticle layer is then slowly decanted away from the brown solids and excess DCM is removed via rotary evaporation producing a transparent oil with yellow tinge, which contains TEGylated silicon nanoparticles that are soluble in water. This oil can also be redispersed organic solvents such as acetone, tetrahydrofuran, chloroform, dimethyl sulfoxide, toluene, methanol, isopropanol, and ethanol.

### 2.4.4. Separation of TEGylated silicon nanoparticles

Any remaining unreacted TEG/TTEG is removed via silica gel chromatography (300g, 60Å, 230-450 mesh) utilizing a 1:1 mixture of diethyl ether and ethyl acetate. Elution of the TEG/TTEG was monitored via thin layer chromatography cospotted with pure TEG/TTEG. Retained silicon nanoparticles are evident via a yellow band that is then eluted with a 1:19 mixture of diethyl ether and methanol. Nanoparticle fractions were collected in 10mL increments, with a total of 70 mL collected including mobile phase solvent. Excess solvent is removed via vacuum concentrator for one hour at 35°C. The resulting separated transparent nanoparticle oil exhibits the solubility in water, acetone, tetrahydrofuran, chloroform, dimethyl sulfoxide, toluene, methanol, isopropanol, and ethanol.
2.4.5. Analytical Characterization Methods

2.4.5.1. Fourier Transform Infrared Spectroscopy (FTIR)

FTIR spectra were obtained at 1 cm⁻¹ resolution with at least 256 scans using a Thermo-Nicolet NEXUS 670 FTIR spectrometer. The nanoparticles were dissolved in dichloromethane then placed on a potassium bromide salt plate, where the dichloromethane was allowed to evaporate, resulting in a thin film. The FTIR sample chamber was purged with dry nitrogen gas before the collection of any data.

2.4.5.2. Nuclear Magnetic Resonance Sample Preparation and Imaging (NMR)

Nuclear Magnetic Resonance samples were prepared by dispersing 0.25mL reagents or 0.1mL nanoparticles in 0.75 mL of either chloroform-d₁ (CDCl₃) or DMSO-d₆ depending on functionality. NMR spectra were obtained on a Bruker Avance 300 MHz high-resolution NMR spectrometer equipped with a 5 mm BBO probe. Chemical shifts are reported in ppm relative to TMS as calibrated by internal TMS for CDCl₃ and by the residual proton signals for other solvents. Carbon-13 spectra in CDCl₃ are referenced to the corrected chloroform signal.

2.4.5.3. Ultra-Violet Visible Absorption and Photoluminescence Spectroscopy (UV-Vis/PL)

The photoluminescence data was obtained as a dichloromethane solution in a quartz cuvette (1cm) using a Varian Cary Eclipse Fluorescence spectrofluorometer from a range of 240 nm to 600 nm with a scan rate of 120 nm per minute. UV-Vis absorption
spectra of silicon nanoparticles were obtained as a dichloromethane solution in a quartz cuvette (1cm) using a Cary 50 spectrophotometer with a recorded absorption range of 200-800 nm and a scan rate of 600 nm per minute. All spectra were corrected for solvent absorption.

2.4.5.4. Transmission Electron Microscopy / Energy Dispersive X-Ray Analysis (TEM/EDS)

Transmission electron spectroscopy data was obtained on a FEI G2 F30 Tecnai TEM utilizing an accelerating voltage of 300 keV. EDS data was obtained in the TEM using an Oxford Inca or Bruker attachment and a XFlash 5010 detector using a 3 nm beam spot. TEM samples were prepared by suspending the nanoparticles in methanol and dropping 0.5 µmL of solution onto a 3 mm, 400 mesh copper grid with formvar.

*Figure 2.34. Tweezers holding TEM grid containing excess sample.*
2.34). Methanol was allowed to evaporate or wicked away with a kimwipe prior to loading into the microscope.

2.4.5.5. Thermogravimetric Analysis (TGA) and Gas chromatography–Mass spectrometry (GC/MS)

TGA data was obtained on a TA Q600 TGA-DSC. The 15 mg sample was loaded into an aluminum pan then heated at a rate of 10°C/min under the flow of nitrogen gas at 50 mL/min from 25-600°C for 2.5 hours. Gas chromatograph/mass spectrometry (GCMS) data was obtained on a Varian 450-GC gas chromatograph followed by a Varian 300-MS SQ mass spectrometer. Samples were prepared by diluting 0.1 mL of reagent in 10 mL methanol and manually injected.

2.4.5.6. X-ray Photoelectron Spectroscopy (XPS)

XPS data was obtained with a VG Scientific MKII system using an Al Kα anode as excitation source (hv = 1486.6 eV) operated at 10 kV and 20 mA emission. The pressure in the chamber during analysis was less than 5x10⁻⁸ mbar with a sampling depth of 3-10 nm.

2.4.5.7. X-Ray Diffraction Analysis Spectroscopy (XRD)

XRD data was obtained with a Scintag SCS2000 x-ray diffractometer using Cu Kα x-rays at a wavelength of 0.15406 nm, equipped with a high-resolution solid-state silicon/lithium detector, over a 2-theta range of three to eighty-three degrees, step size of
0.03 degrees, and a scan rate of one degree per minute. Samples were dried in an oven at 130° C overnight prior to analysis.

2.4.5.8. Dynamic Light Scattering (DLS)

The hydrodynamic diameters of TEGylated silicon nanoparticles in toluene were determined by DLS. All dynamic light scattering measurements were performed on a Nicomp ZLS Z3000 particle size analyzer (Particle Sizing Systems – Port Richey, FL) with a 50 mW laser diode (660 nm wavelength) and an avalanche photodiode (APD) detector. Measurements were performed at 23 C° and scattered light was detected at 90°, in 5min. experiments, with data calculated using a non-negative least squares Nicomp analysis.
Chapter 3: Synthesis of Aniline Functionalized Silicon Nanoparticles

3.1. Aniline Functionalized Silicon Nanoparticles

In recent years, energy storage technology has expanded rapidly, particularly with the extensive usage of lithium-ion batteries (LIBs), which play an ever more vital role in hand-held consumer electronics. Silicon, a promising anode material, can absorb up to 3.75 moles of lithium per mole of silicon (Li$_{1.5}$Si$_{1.4}$). The addition of lithium allows for a theoretical gravimetric current capacity of 3580 mAh g$^{-1}$, compared to 372 mAh g$^{-1}$ for graphite. However, the use of silicon still remains a challenge due to large volume changes during lithiation (300%) that results in cracking of the silicon surface and ultimately pulverization of the silicon anode. These structural changes lead to the production of a solid-electrolyte interphase (SEI) layer, which can cause irreversible capacity loss due to the interruption of electron transport pathways.

The reduction of silicon to the nano scale can decrease the lithium ion diffusion length, resulting in quicker charge and discharge rates. However, the large surface to volume ratio of the nanoparticles results in the continual formation of a SEI on the nanoparticle surface, ultimately reducing the coulombic efficiency of the anode. An added problem is the cracking of the SEI as the particle volume decreases during delithiation. As the initial SEI layer breaks apart, a fresh silicon surface is then exposed to the electrolyte, causing an additional SEI to form. One way to stabilize the SEI is by embedding the silicon nanoparticles in protective carbon matrices. Amorphous carbon coatings were found to increase capacity retention during discharge as well as reduce decomposition of the electrolyte solution on the silicon surface. Unfortunately, these
amorphous carbon layers cannot accommodate the large volumetric changes that occur during lithiation.\textsuperscript{260}

The idea of forming a conformal coating of electrically conductive polymers for silicon nanoparticles was investigated in hopes that it could stabilize the SEI, increase the efficiency of charge and discharge rates, as well as increase gravimetric current capacities of future lithium-ion based anodes. The ultimate goal of our group’s research was to synthesize silicon nanoparticles containing aniline based functional groups alongside polar TEG spacer groups (see

\[
\text{Scheme 3.1. Reactive high energy ball milling of silicon with TEG and 4-ethynylaniline to form electronically conductive silicon nanoparticles.}
\]

.\textsuperscript{)} that would diminish the effects of particle expansion and limited recharge cycles. In the past, nanoparticles containing hydrophobic ligands such as \(\alpha,\omega\)-diynes\textsuperscript{201}, \(\alpha,\omega\)-dienes, or \(\alpha,\omega\)-haloalkenes (ynes)\textsuperscript{201} were synthesized; however, polar terminal groups were not added until after the construction and functionalization of the silicon nanoparticle surface. We have developed a technique to synthesize then ball mill with an aniline based alkyne terminated functional group, which allowed for the reaction of tert-butyl nitrite in water to create a diazonium ion from the surface bound aniline group. The
diazonium ion could then be reacted with multi-walled carbon nanotubes (MWCNT) or graphene, creating a covalent linkage to the silicon nanoparticle. While 4-ethynylaniline was chosen for its electrical conductivity\textsuperscript{261,262} and ability to mediate electron transfer in and out of the nanoparticle,\textsuperscript{263,264} use of the triethylene glycol monomethyl monopropargyl ether (TEG) as a polar spacer ligand ensured compatibility of the nanoparticles with polar or aqueous solvents.

### 3.1.1. Results and Discussion

4-Ethynylaniline (4-EA) was synthesized by a popular Sonogashira coupling mechanism. The Sonogashira reaction employed a palladium (II) chloride catalyst, a copper iodide cocatalyst, and a triethylamine base to combine ethynyltrimethylsilane with 4-iodoaniline under anhydrous and anaerobic conditions producing 4-[(trimethylsilyl)ethynyl]aniline.\textsuperscript{265} Subsequent cleavage of the ethynyl-silicon bonds, freeing 4-ethynylbenzene, was achieved in an alkaline medium\textsuperscript{266,267} as shown in Scheme 3.2. Utilizing the same [2+2] cycloaddition reaction that has proved successful for the synthesis of

![Scheme 3.2. Sonogashira synthesis of 4-ethynylaniline from 4-iodoaniline and ethynyltrimethylsilane.](image-url)
addition of TEG to the surface of Si nanoparticles, 4-ethynylaniline was combined with triethylene glycol monomethyl monopropargyl ether and silicon wafer inside stainless-steel milling vial then subjected to reactive high energy ball milling to yield functionalized SiNPs as seen in Figure 3.1. The SiNPs were separated from the unreacted starting materials via column chromatography then characterized accordingly.

**Figure 3.1. Possible binding modes of aniline functionalized TEGylated Si NPs.**

### 3.1.1.1. Synthesis and Characterization of 4-Ethynylaniline

4-Ethynylaniline was successfully synthesized according to a procedure similar to one published by Flatt, Yao, Maya, and Tour in 2004. The proton NMR spectrum of 4-ethynylaniline in deuterated acetone-d$_6$ (Figure 3.2.) shows a doublet centered at 7.22 ppm (2H, $J = 8.4$ Hz) assigned to the two hydrogen atoms on the benzene ring found in the position meta to the primary amine. The doublet at 6.67 ppm (2H, $J = 8.2$ Hz) is assigned to
Figure 3.2. Proton NMR of 4-ethylnylaniline in acetone-$d_6$. A residual water peak can be seen at 2.84 ppm.

Figure 3.3. Carbon-13 NMR of 4-ethylnylaniline. Acetone-$d_6$ solvent peaks can be seen at 29.84 ppm and 206.08 ppm.
the two hydrogen atoms ortho to the primary amine, while the broad singlet at 5.03 ppm (s, 2H) is attributed to the two hydrogens of the primary amine itself. The sharp singlet at 3.35 ppm (s, 1H) is assigned to the ethynyl hydrogen atom. For the two singlet peaks, these values do not correspond to those reported by Flatt et al., however the change in solvent may be the explanation for the downfield chemical shifts. The peaks at 2.84 ppm and 2.09 ppm are indicative of residual water and the acetone-d₆ solvent, respectively. Synthesis of 4-ethynylaniline is also supported by the ¹³C-NMR spectrum seen in Figure 3.3. The benzyl carbons a, b, c, and d occur at 150.16, 114.74, 133.90, and 110.37 ppm respectively while the two ethynyl carbons, e and f, appear at 85.57 ppm and 75.59 ppm. The two solvent peaks for acetone-d₆ can be viewed at 29.84 ppm and 206.08 ppm.

The FT-IR (KBr) spectrum further confirms successful production of 4-ethynylaniline. Figure 3.4. shows two sharp primary amine N-H stretching vibrations at 3485

![Figure 3.4. FT-IR spectrum of 4-ethynylaniline](image-url)
cm<sup>-1</sup> and 3390 cm<sup>-1</sup> along with two primary amine N-H bending vibrations at 1627 cm<sup>-1</sup> and 1595 cm<sup>-1</sup>. In addition, a strong amine N-H wagging vibration is observed at 832 cm<sup>-1</sup>. A moderate acetylenic C-H stretching vibration is noted at 3265 cm<sup>-1</sup> while the weak acetylenic C-C stretching vibration is found at 2097 cm<sup>-1</sup>. The weak benzyl C-H stretching vibration is observed at 1898 cm<sup>-1</sup> along with a strong benzyl C=C bending vibration at 1513 cm<sup>-1</sup>. The aromatic amine C-N stretching vibration can be found centered at 1297 cm<sup>-1</sup>.<sup>268,269</sup>

Gas chromatography data shows a relative retention time of 11.92 mins for 4-iodoaniline, while 4-ethynylaniline had a relative retention time of 9.88 mins indicating the smaller molecular mass of 4-EA due to the loss of iodine and the addition of the ethynyl group (Figure 3.5. a). The mass spectroscopy data (Figure 3.5. b) of 4-EA reveals an intense peak at m/z 117 representing the stable molecular ion. Fragmentation occurs by elimination of CNH<sub>270</sub> to produce an ion fragment at m/z 89 corresponding to 5-ethynyl-1,3-cyclopentadiene. Scheme 3.3. outlines the elimination of the hydrogen isocyanide HNC

![Gas chromatography data comparing retention times of 4-ethynylaniline and 4-iodoaniline (a) and mass spectroscopy data for 4-ethynylaniline (b).](image)
isomer (m/z 27), which contains a hydrogen and carbon atom originally bonded to the primary amine, resulting in the formation of a cyclopentadiene radical cation. The final step of the mechanism is the loss of a hydrogen radical, creating the stable ethynyl cyclopentadienyl ion (m/z 89). Further fragment elimination of the acetylene group (C₂H₂, m/z 26) leads to the production of the [C₅H₃]⁺ cation (m/z 63).²⁷¹

Scheme 3.3. Fragmentation scheme of 4-ethynylaniline.
4-Ethynylaniline in dichloromethane shows a broad UV-Vis absorption maximum at 270 nm with tailing beginning around 325 nm (Figure 3.6.). The photoluminescence emission spectra in dichloromethane, recorded with various excitation wavelengths ranging from 220 to 320 nm, show a strong, broad absorption between 260nm and 280 nm consistent with the UV-Vis data. The emission maximum at 338 nm indicates a blue shift from published polyaniline PL values.272,273

![Figure 3.6. UV-Vis and photoluminescence spectra of 4-ethynylaniline.](image)

3.1.1.2. Ball Milling of Silicon in a 4-Ethynylaniline/TEG Mixture (1:9 mole/mole)
A homogeneous mixture of 4-ethynylaniline with TEG in a 1:9 (mole/mole) ratio was observed by nuclear magnetic resonance. The $^1$H NMR spectrum of the mixture in chloroform-$d$ (Figure 3.7.) showed that each molecule retained its respective peaks. For the TEG ligand the triplet peak at 2.37 ppm ($t, J=2.3$ Hz, 1H) was assigned to the terminal alkyne proton. The resonances at 3.31 ppm ($s$, 3H), 3.60 ppm ($m$, 12H), and 4.14 ppm ($d$, $J=2.3$ Hz, 2H) were assigned to the methoxy functionality, ether groups, and the propargyl methylene protons respectively. The aniline resonances at 7.21 ppm ($d$, $J = 8.6$ Hz, 2H) 6.53 ppm ($d$, $J = 8.6$ Hz, 2H), and a doublet of doublets, representing the two primary amine hydrogen atoms, centered at 5.38 ppm ($dd$, $J = 8.5$ Hz, 2H) were found further downfield from the TEG resonances. The aniline ethynyl hydrogen peak at around 3.4 ppm is thought to be overshadowed by the large ether peak of the TEG ligand.

*Figure 3.7. $^1$H NMR of 4-ethynylaniline in TEG (1:9 mole/mole) mixture. Inset shows retention of aniline protons.*
The 4-EA/TEG (1:9 mole/mole) reaction mixture was ball milled for 24 hours with 1g of silicon wafer pieces to produce a very viscous brown sludge. However, when attempting to wash and centrifuge the milling oil with dichloromethane, the polypropylene centrifuge tubes typically used during centrifugation shattered or warped until breaking. It was then noted by the manufacturer\textsuperscript{274} that dichloromethane has a severe chemical effect on polypropylene. The incompatibility of the solvent mixture led to the use of glass centrifuge tubes, which solved the issue of breakage, but required longer centrifuge times to achieve separation of the gray unreacted silicon slug from the brown silicon nanoparticle slurry.

3.1.1.3. Separation of Functionalized Silicon Nanoparticles

The brown silicon nanoparticle slurry was initially washed with water with no discernible separation of the unreacted material from the functionalized silicon nanoparticles. A membrane dialysis was performed with a 1kDa cellulose membrane in DCM; however, the nanoparticles crossed the membrane into the solvent system, rendering the waste solution homogeneous with the contents of the membrane. Size exclusion chromatography was then employed in attempts to separate the functionalized nanoparticles from the unreacted 4-EA and TEG. S-X8 resin beads were soaked in THF overnight to allow for adequate solvent absorption. 2 mL of the crude milling vial slurry were pipetted onto the S-X8 beads and eluted with THF. Samples were collected in ½ dram vials and excess solvent was removed via speed-vacuum without use of heat. Three different products were collected: first 0.0267 g of brown sludge, second 0.3879 g of amber oil, and 0.4648 g of yellow oil.
As a result of the chromatographic separation, the brown sludge was shown to be nanoparticle agglomerates coated with reacted TEG as evidenced by the $^1$H-NMR spectrum in acetone-$d_6$ shown in Figure 3.8. With the low surface concentration of the 4-EA ligand, it was impossible to determine the presence of ethynyl aniline as neither the vinyl nor ethynyl peak could be detected. However, there were much less intense benzyl protons resonances centered at 7.18 ppm and 6.65 ppm along with the primary amine proton resonances at 5.44 ppm and 5.03 ppm. The TEG ethynyl triplet at 2.37 ppm was absent along with a reduction in the concentration of the propargyl methylene proton resonances at around 4.14 ppm suggesting successful TEGylation of the silicon surface. By integration, the mole ratio was shown to be 4-EA/TEG 1:4.14. There were also additional impurity peaks noted at 1.31, 0.95, 0.21, 2.26, and 7.43 ppm. A water peak is noted at 2.74 ppm along with the acetone-$d_6$ peak at 2.06 ppm.
The amber oil showed almost the same NMR result as the first elution product. The \(^1\)H NMR spectrum in acetone-d\(_6\) (Figure 3.9.) shows aniline resonances at 7.12, 6.13, 5.30, and 4.91 ppm while the ethynyl peak was suspected to once again be obscured by the TEG ether peak. No new vinyl peaks were detected to give indication of successful addition of the aniline to the silicon surface. For the TEG ligand, reduction in the relative concentration of the methylene protons along with the disappearance of the propargyl proton at 2.37 ppm suggests successful creation of TEGylated silicon nanoparticles. Impurities were noted at 1.28 ppm, 0.87 ppm, 0.45 ppm, and 7.44 ppm. A water peak was seen at 2.81 ppm and the acetone-d\(_6\) peak was noted to be at 2.06 ppm.

![Figure 3.9. \(^1\)H-NMR of size exclusion chromatography elution product 2 (amber oil).]
The third elution product, the yellow oil, proved to be unreacted TEG and 4-EA as evidenced by the $^1$H NMR spectrum in Figure 3.10. The aniline benzyl ppm peaks were noted at 7.19 ppm and 6.64 along with the broad primary amine peak at 4.89 ppm. The ethynyl peak was not noted, for previously stated reasons. All four of the unreacted TEG ligand peaks were present: the methylene doublets at 4.19 ppm, the ether multiplet at 3.58 ppm, the methoxy singlet at 3.30 ppm, and the ethynyl triplet at 2.93 ppm. A water peak was detected at 2.81 ppm and the acetone-$d_6$ peak at 2.06 ppm.

![Figure 3.10. $^1$H NMR of size exclusion chromatography elution product 3 (yellow oil).](image)

The silica gel separation technique used with the previously synthesized TEGylated SINPs was then attempted due to the limited success of the S-X8 size separation. 2mL of the crude brown nanoparticle slurry was loaded into a 75 g silica gel column (230-450 mesh, 60 Å) and eluted with an ethyl ether/ethyl acetate (1:1) mixture.
A yellow band moved down the silica gel column with the ethyl ether/ethyl acetate which was shown to be unreacted TEG and 4-EA ligands as seen in Figure 3.11. The $^1$H NMR peaks at 7.15, 6.60, and 4.99 ppm are assigned to the unreacted 4-EA (Figure 3.11. inset) while the peaks at 4.16, 3.53, 3.27, and 2.92 ppm are assigned to the unreacted TEG. Water and acetone-d$_6$ were seen at 2.83 ppm and 2.04 ppm respectively.

After elution of the unreacted starting materials, the solvent system was changed to methanol/ethyl acetate (19:1) to elute the functionalized nanoparticles. Samples were collected in ½ dram vials. All collected fractions luminesced when exposed to a handheld UV lamp (365 nm); however, the product collected by the methanol/ethyl acetate elution took on more of a greenish glow compared to the blue glow of the TEGylated nanoparticles and the aniline. Excess solvent was removed by speed vacuum for 1 hour at

*Figure 3.11. $^1$H NMR spectrum of silica gel separation of 4-ethynylaniline in TEG silicon nanoparticle mixture.*
55 °C. The total yield from the 2 mL of separated silicon nanoparticles was 77mg on average. \(^1\)H NMR results (Figure 3.12.) showed that the silicon nanoparticles consisted of reacted TEG ligand and little to no indication of 4-EA aside from two doublet peaks at 7.14 ppm and 6.67 ppm. After review of these results and the absence of the primary amine peak, it was concluded that, given the amount of TEG ligand present, conditions were not conducive for the addition of the aniline to the silicon surface. There was simply too much competition for the aniline to reach the silicon surface.

3.1.2. Experimental Methods

3.1.2.1. Materials
All materials, except when noted, were purchased from Sigma-Aldrich and stored under nitrogen prior to use. Diethyl ether, ethyl acetate, dichloromethane, and hexanes were purchased from Fisher Scientific and were used as is unless otherwise stated. Tetrahydrofuran was dried via distillation over a sodium-benzophenone mixture. Silicon wafers (undoped, mirror finish, orientation [111]) were obtained from Silrec Corp of Lexington, KY. S-X8 size exclusion chromatography beads were purchased from Bio-Rad USA and soaked in tetrahydrofuran overnight prior to use. 60Å, 230 x 450 mesh silica gel was purchased from Fisher Scientific and used as described. Dry box nitrogen atmosphere was maintained at oxygen levels less than 2ppm and water levels less than 1ppm.

3.1.2.2. Synthesis of 4-Ethynylaniline

In a nitrogen filled glovebox, 4-iodoaniline (10 g, 45.7 mmol), bis(triphenyl)palladium (II) dichloride (0.62 g, 0.883 mmol), 60 mL dry THF, and triethylamine (50 mL, 448 mmol) were combined in a two-neck, 250mL round bottom flask equipped with a stir bar then slowly stirred for five minutes to mix producing a yellow solution. Copper iodide (0.9 g, 4.73 mmol) was added, and the solution stirred for one additional minute, turning the mixture from a yellow to burnt orange. Ethynyltrimethylsilane (7.64 mL, 53.7 mmol) was added changing the mixture from a clear orange to a cloudy orange. The flask was stoppered, removed from the glove box, and refluxed at 80°C for fifteen hours under nitrogen, where the mixture turned from a burnt orange to a very dark brown. After cooling to room temperature, the mixture was
filtered over a fritted Buchner funnel, and the solids washed with a minimal amount of room temperature dichloromethane. 

An aqueous wash of the organic layer was then performed. The organic layer was washed three times using 100 mL of distilled water for every 20 mL of DCM present. After the final wash, the bottom organic phase was separated from the aqueous phase then dried with anhydrous magnesium sulfate to remove any residual water. The dried organic phase was filtered over a clean Buchner filter funnel to remove any magnesium sulfate solids then subjected to rotary evaporation to remove excess DCM producing a brownish-yellow oil. The oil (9.9 g) was purified using silica gel chromatography (50:1 silica gel/oil) with a DCM/hexane 1:1 mixture producing orange and brown layers. The desired product was eluted in the bottom orange layer, while the brown layer was not retained. Excess DCM was removed via rotary evaporation producing a white, fluffy solid with a yield of 88% (7.61 g). The temperature sensitive solids were recrystallized with ice chilled hexanes to remove any remaining impurities.

Removal of the trimethylsilane from the 4-ethynylbenzene was accomplished by dissolving the white solids in a 1.5 M potassium hydroxide solution (0.84 g potassium hydroxide in 10 mL methanol for every gram of product) and allowing to stir at room temperature for eight hours. The solution was then transferred to a one-liter Erlenmeyer flask containing 500 mL DCM in order to perform an aqueous/organic separation using a 2:1 distilled water/DCM solvent ratio. The organic phase was collected and dried with anhydrous magnesium sulfate to remove any remaining water, then filtered to remove any solids. Excess DCM was removed via rotary evaporation producing a dark brown oil. The oil was purified by a 30:1 silica gel/oil chromatography column using a
DCM/hexane 1:1 mixture as the mobile phase. As 4-ethynylaniline was the only product to elute, movement was monitored via thin layer chromatography. Excess solvent was then removed via rotary evaporation and pumping under vacuum overnight producing a yellow solid. Product yield is typically around 89% (4.77g) for the overall process.

3.1.2.3. Ball Milling of 4-Ethynylaniline in TEG

4-Ethynylaniline (1.48 g, 13 mmol) was combined with triethylene glycol monomethyl monopropargyl ether (24.5 g, 121 mmol) in a 50 mL Schlenk flask and pumped under vacuum overnight. The flask was then filled with nitrogen gas, sealed, and loaded into a nitrogen glove box where the contents of the flask were transferred to a stainless-steel mixing vial along with silicon wafer pieces (1.03 g, 36.7 mmol) and two stainless steel milling balls (1.2 cm diameter, approximately 8 g). The vial was sealed and milled in a cold room for 24 hours. Milling was performed in a cold room in order to avoid possible exposure to reagents, injury to lab personnel, and the elevated temperatures associated with ball milling.\(^{275}\) The contents of the mixing vial were then diluted with DCM, transferred to glass centrifuge tubes, and centrifuged for 30 mins at 3800 rpm. The supernatant was decanted, collected, and concentrated by rotary evaporation yielding a viscous brown slurry.

3.1.2.4. Separation of Functionalized Silicon Nanoparticles
The brown slurry was divided into functionalized silicon nanoparticles and unreacted starting materials by employing size exclusion chromatography (SEC) or silica gel chromatography. For the SEC, S-X8 beads were soaked overnight in THF prior to loading of the column to allow for adequate expansion of the beads. THF was also used as the mobile phase. For silica gel separation, an ethyl acetate/ethyl ether (1:1) mixture mobile phase separated out any unreacted TEG ligand, while a methanol/ethyl acetate (19:1) mobile phase eluted the functionalized nanoparticles. Samples were collected in ½ dram vials and reduced in a speed vac at 55 °C for 1 hour. For every 2 mL of crude milling oil loaded into a silica gel chromatography column, roughly 40 mg of SiNPs was eluted.

3.1.3. Analytical Characterization Methods

3.1.3.1. Fourier Transform Infrared Spectroscopy (FTIR)

FTIR spectra were obtained at 1cm⁻¹ resolution with at least 256 scans using a Thermo-Nicolet NEXUS 670 FTIR spectrometer. The nanoparticles were dissolved in dichloromethane then placed on a potassium bromide salt plate, where the dichloromethane was allowed to evaporate, resulting in a thin film. The FTIR sample chamber was purged with dry nitrogen gas before the collection of any data.

3.1.3.2. Nuclear Magnetic Resonance Sample Preparation and Imaging (NMR)
Nuclear Magnetic Resonance samples were prepared by dispersing 5 mg of reagents or 5 µL nanoparticles in 0.60 mL of either chloroform-d\textsubscript{1} (CDCl\textsubscript{3}) or acetone-d\textsubscript{6} (CD\textsubscript{3})\textsubscript{2}CO. NMR spectra were obtained on a Bruker Avance 300 MHz high-resolution NMR spectrometer equipped with a 5 mm BBO probe. Chemical shifts are reported in ppm relative to TMS as calibrated by internal TMS for CDCl\textsubscript{3} and by the residual proton signals for other solvents. Carbon-13 spectra in CDCl\textsubscript{3} are referenced to the corrected chloroform signal.

3.1.3.3. Ultra-Violet Visible Absorption and Photoluminescence Spectroscopy (UV-Vis/PL)

The photoluminescence data was obtained as a dichloromethane solution in a quartz cuvette (1cm) using a Varian Cary Eclipse Fluorescence spectrofluorometer from a range of 240 nm to 600 nm with a scan rate of 120 nm per minute. UV-Vis absorption spectra of silicon nanoparticles were obtained as a dichloromethane solution in a quartz cuvette (1cm) using a Cary 50 spectrophotometer with a recorded absorption range of 200-800 nm and a scan rate of 600 nm per minute. All spectra were corrected for solvent absorption.

3.1.3.4. Transmission Electron Microscopy / Energy Dispersive X-Ray Analysis (TEM/EDS)

Transmission electron spectroscopy data was obtained on a FEI G2 F30 Tecnai TEM utilizing an accelerating voltage of 300 keV. EDS data was obtained in the TEM using an Oxford Inca or Bruker attachment and a XFlash 5010 detector using a 3 nm
beam spot. TEM samples were prepared by suspending the nanoparticles in methanol and
dropping 0.5 µmL of solution onto a 3 mm, 400 mesh copper grid with formvar.
Methanol was allowed to evaporate or wicked away with a kimwipe prior to loading into
the microscope.

3.1.3.5. Gas chromatography–Mass spectrometry (GC/MS)

Gas chromatograph/mass spectrometry (GCMS) data was obtained on a Varian
450-GC gas chromatograph followed by a Varian 300-MS SQ mass spectrometer.
Samples were prepared by diluting 7 mg of reagent in 10 mL dichloromethane and
manually injected.

3.1.4. Limitations of the Project

While the TEG ligand easily attaches to the silicon nanoparticle surface, proton
NMR spectra gave no indication of successful addition of the aniline. This could be due
to the competition for binding sites on the silicon surface between the TEG ligand and the
4-ethynylaniline as well as steric hinderance of the aniline ring in 4-EA that retards
binding of the acetylene moiety to the silicon surface. These two issues can be alleviated
by either increasing the 4-ethynylaniline molar concentration in relation to the TEG
ligand concentration or by adding a number of methylene groups between the ethynyl and
arene functionalities of the aniline ligand in order to increase the distance between the
silicon surface and the aniline ring. Unfortunately, the project was halted after the
materials continued to agglomerate and harden over a period of days. Separation and
handling became impossible, while the materials continually solidified and refused to be
removed from the glassware, even after acid treatment and base baths. It was not cost or
time efficient to continue
Chapter 4: Synthesis of Silicene Nanosheets

4.1. Introduction

Silicene is a crystalline two-dimensional (2D) nanomaterial comprised of a single layer of $sp^2$-$sp^3$ mixed-hybridization silicon atoms arranged in a repeating hexagonal, honeycomb pattern with a Si-Si-Si bond angle of 116°. As silicene is considered to be in the early stages of research and production, most studies have been theoretical with what is believed to be the first experimental sheets being grown by the Vogt group in 2012 via evaporation of a silicon wafer and subsequent gradual deposition onto a Ag (111) substrate at 220-260 °C under ultrahigh vacuum conditions. Recently, however, researchers have begun to investigate the effect of substrates and interlayer binding on the geometric and electronic properties of silicene. The presence of a theoretical Dirac cone makes buckled silicene an attractive component for possible applications in electronics, such as field-effect transistors and silicon anodes, whereby its inherent compatibility with the existing silicon technology may lead the way for large-scale, commercial fabrication. Most recently efforts have been made to form freestanding silicene in the absence of substrates and ultrahigh vacuum environments. One example is the exfoliation of Zintl phase calcium silicide, which tends to produce multilayer, bilayer, and free-standing single-layer silicene sheets.

4.1.1 Silicene Theoretical Models

The first geometrical calculations performed by Takeda and Shiraishi in 1994 on freestanding, infinite 2D aromatic silicon structures assumed a hexagonal lattice and a
unit cell analogous to that of graphene. The basis of the unit cell consisted of two Si atoms, A and B, shown in Figure 4.1. and two equivalent lattice constants $A_0$, more commonly known as $a$ and $b$, also shown in Figure 4.1. as yellow arrows along with an angle $\gamma$ between the two lattice constants. As $a$ and $b$ are equal, $a$ is substituted for $b$ for simplicity. To find the optimal geometry of the silicene structure the lattice constant, the length of the unit cell in the crystal lattice, was allowed to vary with changes in the total energy of the silicene. Two separate symmetries were assigned and maintained; either the planar $D_{6h}$ symmetry, comparable to what is seen in graphene, or the corrugated/buckled $D_{3d}$ symmetry observed in the Si (111) plane of bulk silicon. When the $D_{6h}$ symmetry was preserved and the lattice constant was able to fluctuate with changes in energy, the $A_0$
value of 3.855 Å was found to be the most energetically stable, containing Si-Si bonds with lengths ($d$) of 2.226 Å as seen in Figure 4.2. a. The authors also found that when the $D_{3d}$ symmetry was assumed, and no Hellmann-Feynmann z-component forces were acting on $A$ and $B$ of the unit cell, a bond length of 2.247 Å along with a deformation angle ($\theta$) of 9.9° and the same 3.855 Å lattice constant were preferred as seen in Figure 4.2. b. When the deformation angle exceeded 10°, a restoring force that reduced the deformation angle was induced, suggesting that the aromatic sheet favored the puckered $D_{3d}$ symmetry over the flat $D_{6h}$ symmetry. It was theorized that the $D_{3d}$ elongated Si-Si bonds of 2.247 Å arose due to the weakened $\pi$ bond nature between the silicon atoms as seen in Figure 4.3. b.

Figure 4.2. (a) Top view of planar and (b) side view of buckled silicene hexagonal structures proposed by Takeda and Shiraishi.
To find the Si-Si bond lengths from the optimized lattice parameters, the geometry of the hexagonal crystal lattice must be considered. As the silicene crystal lattice is a 2D structure with repeating hexagonal units and 1 atom at each of the six corners of every hexagon, the Si-Si bond length can be found by dividing each hexagon into six equilateral triangles with sides equal to lattice constant $a$ and an angle $\beta = \frac{1}{2} \gamma$ as seen in Figure 4.4. A distance $b$ (Figure 4.4. c, d), representing the Si-Si bond length, is found by utilizing the Pythagorean Theorem in which $\cos(\alpha) = (a/2)/b$, and $\alpha = \frac{1}{2} \beta = \frac{1}{4} \gamma$. (Note that $\alpha$ and $\beta$ in this instance are not equal to the hexagonal lattice parameters $\alpha$ and $\beta$, but are simply used as a means to differentiate between angles in the example calculation.) When considering that $\gamma = 120^\circ$ for a $sp^2$ hybridized system, then $\cos(\alpha) = \cos(30^\circ) = \sqrt{3}/2$. After substituting $\sqrt{3}/2$ for $\cos(\alpha)$ into the original equation, $\sqrt{3}/2 = (a/2)/b$; the Si-Si bond distance ($b$) is found by $b = a/\sqrt{3}$. Given that the optimal...
lattice constant of silicene was calculated to be $a = 3.855$ Å, this yields a planar silicene Si-Si bond distance of 2.226 Å.

Most DFT calculations on freestanding silicene since 1994 have produced very similar buckling heights ($\Delta z$), lattice constants ($a$), and Si-Si bond lengths ($d$) as compared to those of Takeda and Shiraishi. Yin and Cohen found that freestanding graphitic silicon, with flat silicon layers and Si-Si bond lengths of 2.249 Å, is metastable when compared to the diamond arrangement, requiring an extremely large negative pressure (~69 kbar) in order to exist.182 Durgun, Tongay, and Ciraci examined the freestanding 2D silicon honeycomb structure in the xy plane, with repeating units in the z

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**Figure 4.4.** Silicene unit cell (a), single hexagonal cell divided into 6 equilateral triangles (b), singular equilateral triangle with dimensions labeled (c), and triangle used to calculate Si-Si bond distance derived from hexagonal cell.
First-principles DFT calculations revealed the planar structure to be metastable, while the optimized puckered structure contained Si-Si bond lengths of 2.2 Å and a buckling height ($\Delta_z$) of 0.45 Å. Ding and Ni found that for freestanding silicon nanoribbons the buckled ($\Delta_z = 0.53$ Å) silicon hexagonal sheet is semimetal, with electronic structures similar to those of graphene. Cahangirov et al. showed that for single layer silicene, the low buckled structure ($\Delta_z = 0.44$ Å) is more stable than an alternative high buckled ($\Delta_z = 2.13$ Å) structure, even though the high buckled structure has a lower binding energy per unit cell. DFT calculations describing single-layer silicene by Lebègue and Erikkson suggested a buckled structure with a hexagonal lattice constant of 3.860 Å; however, the authors note that $sp^2$-bonded atoms are much less likely to occur in silicene than in graphene, and the synthesis of silicon in a graphene-like structure is expected to produce a metastable material.

Interestingly, a Monte Carlo simulation on the stability of a stand-alone silicene sheet using the Tersoff potential, performed by Bocchetti et al. in 2014 found the planar form of the honeycomb lattice to be the most energetically stable. However, the authors did go on to state that with a Stillinger-Weber potential, the ground state of silicene is buckled, and experimentally observed buckling may arise from interactions with the substrate as further calculations showed that when the planar silicene was deposited on Ag (111), buckling did indeed occur.

### 4.1.2. Properties of Epitaxial Silicene
In 2010 Lalmi et al. published STM images showing that the group had epitaxially grown a low buckled, \((2\sqrt{3} \times 2\sqrt{3})R30^\circ\) silicon sheet superstructure on a Ag (111) substrate by keeping the substrate temperature between 220 and 250 °C and the silicon deposition rate lower than 0.1 monolayer per minute.\(^{290}\) The angle (R30°) represents the angle of rotation between the silicon superstructure and a silicene (1 X 1) unit cell while the one monolayer deposition is considered to be \(1 \times 10^{15}\) atoms/cm\(^2\). A scanning tunneling microscopy (STM) peak-to-peak analysis produced a Si-Si nearest neighbor distance between 0.19 and 0.2 nm, 17% shorter than that for bulk silicon (0.235 nm), which lead the authors to suggest that the Ag substrate may play a facilitator role in the formation and stabilization of the silicene sheet. However, because no other complementary experimental results were presented, the conclusion of the silicene synthesis was regarded as rather speculative\(^{163}\) and insufficient.\(^{160}\)

This changed in 2012 with the publication of low energy electron diffraction (LEED) and scanning tunneling spectroscopy (STM) data by Chen,\(^{291}\) Jamgotchian,\(^{292}\) Enriquez,\(^{158}\) and Vogt.\(^{163}\) Chen et al. found that the growth of silicon superstructures on Ag (111) is very sensitive to the amount of silicon coverage and substrate temperature.\(^{291}\) STM images indicated a buckled honeycomb superstructure with a \((\sqrt{3} \times \sqrt{3})R30^\circ\) LEED pattern, a lattice constant of \(0.64 \pm 0.01\) nm (\(0.64\) nm = \(\sqrt{3} \times 0.385\) nm), and observed Dirac points. DFT calculations performed by the group showed that the \((\sqrt{3} \times \sqrt{3})R30^\circ\) superstructure could not be stabilized in freestanding, fully relaxed silicene, nor was it found to be energetically favorable when incorporated with silver atoms. Further theoretical modeling with the Ag (111) substrate only produced \(4 \times 4\) or \(\sqrt{7} \times \sqrt{7}\) superstructures, contrary to the demonstrated experimental data, which lead the
researchers to state that the Ag (111) substrate may exert some influence on the silicene sheet resulting in the expansion of the silicene lattice. By observing a continuous evolution from \((4 \times 4)\), to \((\sqrt{13} \times \sqrt{13})R13.9^\circ\)\(^{293}\) and \((2\sqrt{3} \times 2\sqrt{3})R30^\circ\) superstructures generated between 150-300 °C, Jamgotchian \textit{et al.}\(^{292}\) confirmed the findings of Lalmi. STM images of the \((2\sqrt{3} \times 2\sqrt{3})R30^\circ\) superstructure deposited at 300 °C showed a honeycomb hexagonal pattern with a lattice constant of 0.6 nm while ball models presented a unit cell with most silicon atoms in three-fold or bridge sites on the silver surface, and only two silicon atoms at the on-top position of the silver atoms as seen in Figure 4.5.\(^{292}\) The raised yellow balls, with an interatomic distance of 0.6 nm, are theorized to be the bright spots that form the hexagonal pattern seen in the inset STM image.

Enriquez \textit{et al.} went a step further by considering the effect of different Ag crystal orientations on the growth of silicene.\(^{158}\) The researchers found that silicon deposited on...
the Ag (110) surface spontaneously produced silicon nanoribbons with a honeycomb structure (Figure 4.6.\textsuperscript{a}), Ag (100) held at 230 °C produced silicon nanoribbons on a p(3 X 3) superstructure, which is a Si monolayer composed of silicon tetramer entities at the on-top positions of the Ag (100) surface\textsuperscript{294} (Figure 4.6.\textsuperscript{b}), while the Ag (111) substrate produced a silicon sheet with a honeycomb structure (Figure 4.6.\textsuperscript{c}) evidenced by a (2\sqrt{3} X 2\sqrt{3})R30° LEED pattern. The group also presented atomistic calculations and simulated STM models indicating a Si-Si lateral distance of 2.0 Å, similar to that presented by Lalmi in 2010.\textsuperscript{290} Chen \textit{et al.} proposed that silicene superstructures will form specific surface reconstruction orientations with respect to the silver crystal lattice.\textsuperscript{280} DFT calculations suggested that weak dispersive interactions between the silicon atoms and the Ag (111) substrate drives the formation of a silicon (\sqrt{3} x \sqrt{3}) superstructure resulting in unusual buckling of the Si atoms and other interface phenomena. In each (\sqrt{3} x \sqrt{3}) silicon unit cell, only one silicon atom was buckled upward, while the other five atoms resided at almost the same height as seen in \textbf{Figure 4.7. right}.\textsuperscript{280} Calculations showed that the \(p_z\) orbitals of the three silicon atoms

\textbf{Figure 4.6.} (a) STM image showing straight, parallel 1D Si NRs after deposition of 0.5 Si ML on Ag (110), (b) STM images on the Ag (001) surface after the deposition of 1.6 Si ML showing the honeycomb structure of the silicon. (c) STM images showing honeycomb structure after the deposition of 1 Si ML on Ag(111). Reprinted/adapted with permission.
surrounding the one highly buckled atom will be filled with electrons transferred from the substrate when silicon is adsorbed onto the Ag (111) surface. As a result, a sigma bond-like interaction between the lower lying five Si atoms and Ag substrate will be formed, which is an important component for the stabilization of the silicon sheet. When the Ag substrate was removed in the calculations, the silicon monolayer superstructure was shown to spontaneously relax back into (1 x 1) phases, indicating that the interactions of the silicon atoms with the Ag surface had an effect on the parameters of the Si unit cell.

Figure 4.7. (left) High resolution STM image of monolayer silicene formed on Ag (111), (right) top and side views of simulated Si $\sqrt{3} \times \sqrt{3}$ structures on Ag (111). Blue spheres are Ag atoms, while red and yellow spheres are Si atoms in the higher and lower layer, respectively. Reprinted/adapted with permission.
Other substrates such as zirconium diboride (0001)\textsuperscript{160,295} and iridium (111)\textsuperscript{281} have also been used to investigate the effects substrates have on epitaxially grown silicene sheets. Fleurence \textit{et al.} grew ZrB\textsubscript{2} layers on Si (111) wafers by UHV chemical epitaxy producing an oxide free, hexagonal-close-packed ZrB\textsubscript{2} (0001)-(2 x 2) thin film.\textsuperscript{160} It was found that a silicene (\(\sqrt{3} \times \sqrt{3}\)) honeycomb mesh, with a lattice parameter of \(a = 3.65 \text{ Å}\), forms spontaneously on the ZrB\textsubscript{2} film, in contrast to DFT calculation results stating that this particular phase would be metastable.\textsuperscript{296} The compression of the silicene unit cell resulted in the formation of an in-plane Si [11-2] || ZrB\textsubscript{2} [11-20] epitaxial relationship such that the silicene unit cell adjusts itself to fit that of the ZrB\textsubscript{2} unit cell. Angle resolved ultraviolet photoelectron spectroscopy (ARUPS) scanning of the Si (2p) region revealed the presence of three different chemical environments assigned to three silicon ad-atoms, Si\textsubscript{A}, Si\textsubscript{B}, and Si\textsubscript{C}. Calculated Si\textsubscript{A}-Si\textsubscript{B} bond lengths were 2.266 Å while

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{silicene_on_zrb2}
\caption{(a) Height profile of silicene on Zr-terminated ZrB\textsubscript{2}(0001) thin film. (b) Model of the Si honeycomb structure on the topmost Zr layer of ZrB\textsubscript{2} (0001). Reprinted/adapted with permission.}
\end{figure}
Si_B-Si_C bond lengths were 2.242 Å, which is smaller than the bond lengths of \( sp^3 \) bonded silicon, and longer than purely \( sp^2 \) bonded silicon, signifying a \( sp^2-sp^3 \) mixed hybridization state. Bond angles of 104.1°, 104.9°, 115.2°, and 117.8° were also noted, indicating that \( sp^2 \) and \( sp^3 \) hybridization varies from one atom to another. For one ZrB_2 (0001)-(2 X 2) unit cell, two Si_A atoms are sitting in hollow sites of the Zr lattice, three Si_B atoms were located at the intermediate positions between top and bridge sites, and one Si_C atom was found on the top of a Zr atom (Figure 4.8. a and b^{160}). Si_B-Si_A total buckling height was observed to be 0.902 Å, twice that of the low-buckled structure proposed by Cahangirov.\(^{277} \) It was assumed that the large degree of buckling, as compared to free silicene, was induced to accommodate the compressive epitaxial strain created by interactions with the ZrB_2 substrate.

Additional density functional theory calculations performed by the Ozaki group investigated three structural variations of the (\( \sqrt{3} \times \sqrt{3} \))-reconstructed silicene, (planar

![Figure 4.9.](image)

**Figure 4.9.** Free-standing (a) planar, (b) planar-like, and (c) regularly buckled silicene structures evaluated by Ozaki. (d) Top view of the unit cell arrangement of the silicon atoms.
Figure 4.9. a, planar-like 4.9. b, and regularly buckled 4.9. c) under the influence of the ZrB$_2$ (0001) substrate and any in-plane compressive strain.\textsuperscript{180} Data suggested that the energetically favored epitaxial silicene ($\sqrt{3} \times \sqrt{3}$) ground state is “planar-like” resembling that of graphene, in which five of the six hexagon atoms reside in the same plane with a nominal buckling height of 0.01 Å, while the sixth silicon atom was found atop a Zr atom with a height of 1.58 Å. Although calculations performed by another group showed the planar-like structure to be meta-stable,\textsuperscript{296} the energy changes brought about by the interactions of the Si $p_z$ orbitals with the ZrB$_2$ $d$ orbitals imply that the substrate plays a crucial role in the stabilization of the epitaxial silicene structure. It was found that the

![Diagram of ZrB$_2$ surface bonding sites occupied by silicene atoms. Zr atoms are colored in blue, the B atoms in black, and the Si atoms in green. The ZrB$_2$ unit cell is shown in orange.](image-url)

\textbf{Figure 4.10.} ZrB$_2$ surface bonding sites occupied by silicene atoms. Zr atoms are colored in blue, the B atoms in black, and the Si atoms in green. The ZrB$_2$ unit cell is shown in orange.
most energetically favored positions for the silicon atoms would be in hollow sites on the ZrB$_2$ substrate (Figure 4.10.) however, this is impossible as the ZrB$_2$ boron sublattice is too small to accommodate the larger silicene honeycomb lattice. With two of the silicon atoms located at hollow sites, three occupying bridge sites, and the sixth found at the on-top position, the planar-like structure can easily be accommodated and is calculated to be the most stable epitaxial structure on the ZrB$_2$ (0001) surface as seen in Figure 4.10. For free-standing silicene, the regularly buckled (√3 x √3)-reconstructed structure was found to be most energetically stable; however, when the silicene lattice constant was increased beyond that of the in-plane lattice constant of the ZrB$_2$ (0001) unit cell, $a > 6.60$ Å, the planar-like phase became more favorable due to the large amount of in-plane compressive stress.

In 2013 Meng et al. fabricated a silicene (√3 x √3) superstructure on Ir (111)$^{281}$ with a buckling conformation and lattice constant value similar to that calculated by the Ozaki group.$^{180}$ LEED patterns confirmed the presence of the Ir (111) surface as well as the epitaxially grown silicon adlayer. STM images revealed bright spots forming a honeycomb-shaped superlattice with lattice constant of 0.72 nm, equivalent to Ir (111) - (√7 x √7), and a buckling height of 0.6 Å, implying that the silicon atoms in the adlayer had differing heights with respect to the underlying iridium substrate (Figure 4.11.$^{281}$ a). DFT calculations were used to simulate the STM findings in order to gain a better understanding of the epitaxial system. It was discovered that the relaxed model, similar to the “planar-like” structure proposed by Ozaki, was the most energetically stable and contained silicon atom protrusions in a hexagonal arrangement, which corresponded to the bright spots that occurred in the STM images (Figure 4.11. b). Consistency between
the experimental STM images and calculated STM simulations revealed the presence of six silicon atoms in one Ir (111) - (√7 x √7) unit cell: one Si atom directly on the top of an Ir atom, two in hollow sites, and three Si atoms located at bridge sites (Figure 4.11. c). These findings indicated that the iridium surface is responsible for the buckled conformation of the silicon layer.

4.1.3. Properties of Freestanding Silicene
In low buckled silicene, the $sp^2-sp^3$ hybridized silicon atoms require an appropriate surface functionalization such as hydrogenation,$^{194}$ oxidation,$^{297}$ or a conductive substrate such as silver$^{163}$ to stabilize the large number of out of plane dangling bonds. However, the evidence of silicene-substrate interactions$^{180,292,295,296}$ makes it desirable to eliminate or minimize substrate effects on the structural and electronic properties of silicene by introducing encapsulation methods$^{298}$ or multilayer silicene$^{299}$ synthetic procedures in which the silicene sheet(s) is sandwiched between protective layers. Although theoretical proposals for quasi- or freestanding silicene sheets have been made,$^{300,301}$ there have been few successful experimental examples.

Motivated by the successful elimination of SiC (0001) substrate interactions with bilayer graphene via the intercalation of hydrogen into the graphene buffer layer,$^{302}$ Du et al. produced bilayer silicene on Ag (111) in which the top silicene layer exhibits the signature $\sqrt3 \times \sqrt3$ (with respect to 1 X 1 silicene) lattice structure of freestanding silicene, independent of the oxidized $\sqrt{13} \times \sqrt{13/4} \times 4$ [with respect to 1 X 1 Ag (111)] silicene buffer layer.$^{134}$

STM images showed that after exposure to 600 Langmuir (L) of oxygen, the $\sqrt3 \times \sqrt3$ layer exhibited islands of higher areas raised by 0.9 Å in which oxygen atoms were intercalated between the $\sqrt3 \times \sqrt3$ silicene top-layer (TL) and the $\sqrt{13} \times \sqrt{13/4} \times 4$ silicene buffer layer (BL) as seen in Figure 4.12.$^{134}$ The raised area was found to form the edge of a $\sqrt3 \times \sqrt3$ silicene flake with weaker structural features than those found in the non-intercalated areas. After a dose of 1200 L, the BL turned into amorphous silicon oxide (SiO$_x$), leading to crumbling of the buffer layer and exposure of the bare Ag (111).
surface, while the \( \sqrt{3} \times \sqrt{3} \) TL remained intact and exhibiting a lattice constant of \( a = 0.64 \) nm. These findings suggested that oxidation weakens the interactions between the top \( \sqrt{3} \times \sqrt{3} \) layer and BL as well as the Ag (111) substrate. The Raman spectra showed a peak at \( 526.3 \) cm\(^{-1}\) representing the doubly degenerate E\(_{2g}\) mode at the Brillouin zone center \( \Gamma \) point, while XPS peaks S\(_1\) and S\(_2\) were assigned to Si-Si bonds in \( \sqrt{3} \times \sqrt{3} \) silicene, and Si\(_3\) and Si\(_4\) were attributed to the \( \sqrt{13} \times \sqrt{13}/4 \times 4 \) silicene buffer layer.

DFT calculations confirmed experimental findings suggesting that the oxygen atoms were intercalated between the top \( \sqrt{3} \times \sqrt{3} \) silicene layer and the BL while weakening interactions between the TL and the Ag (111) surface. Models showed that when an O\(_2\) molecule was adsorbed onto the 4 X 4 BL, the molecule breaks into 2 O atoms, one on top of a Si atom and one in a neighboring bridge site. For the \( \sqrt{3} \times \sqrt{3} \) silicene layer, the O\(_2\) molecule did not decompose, indicating a higher level of resistance.

**Figure 4.12.** (a) Schematic diagrams of oxygen intercalation in silicene layers, in which the oxygen gas diffuses into the underlying silicene BL, breaks the bonds at the buffer layer/Ag(111) interface, and saturates the dangling bonds in the \( \sqrt{13} \times \sqrt{13}/4 \times 4 \) BL, and (b) STM image of \( \sqrt{3} \times \sqrt{3} \) silicene top layer with rhombus indicating \( \sqrt{3} \times \sqrt{3} \) unit cell. Reprinted/adapted with permission.
to oxidation. After constructing a simulated sandwich structure of $\sqrt{3} \times \sqrt{3}$ silicene/SiO$_x$/Ag (111) ($x = 1.909$), it was found that the binding energy between the TL and SiO$_x$ BL (12 meV/Å$^2$) decreased by an order of magnitude when compared to that of the bilayer silicene prior to oxygen intercalation (123 meV/Å$^2$). In addition, the top $\sqrt{3} \times \sqrt{3}$ silicene layer retained its hexagonal honeycomb structure with an average separation distance of 3.09 Å between the $\sqrt{3} \times \sqrt{3}$ silicene layer and the SiO$_x$ buffer layer.

Very recently Nie et al. developed a multistep synthesis method for the development of multilayer silicene by chemical vapor deposition (CVD) in which the silicene sheets were sandwiched between graphene layers suspended around spherical Cu nanoparticles formed on the surface of a Cu foil substrate. The graphene served not only as a weakly interacting substrate due to the long-range, nonlocal van der Waals interactions in graphene/silicene stacked structures, but also as a protective barrier against atmospheric oxidation of the silicene layers.

SAED images revealed a polycrystalline, or multiphase, multilayer structure indicated by the ring-like shape of the diffraction spots. The stronger diffraction rings were indexed to the (111), (200), and (220) lattice planes of cubic copper, while HRTEM images showed lattice fringes in the core of the nanoparticle with lattice spacings of 2.1 Å, in agreement with the SAED findings. For the wrapped layers surrounding the Cu nanoparticle, lattice fringes of 3.43 Å and 3.54 Å were thought to originate from the as prepared graphene and silicene layers, respectively. EDX data confirmed the presence of C, Si, Cu, and O with the highest concentration of Cu being at the center of the nanoparticle. Silicon distribution was found to be uniform over the surface of the nanoparticle, while the oxygen signal was believed to be due to the small amount of
surface oxidation from absorption of atmospheric oxygen during exposure of the sample to air. Upon deconvolution of the Si 2p XPS spectrum region, three peaks at around 100.4, 101.6, and 103.0 eV were observed, which were thought to correspond to Si^{x+} (0 < x < 1), Si^{2+}, and Si^{4+}, respectively. The peak at 103.0 eV was attributed to stishovite (102.8 eV), a tetragonal form of silicon dioxide. The 101.6 eV peak was thought to originate from Silic-1O (101.7 eV) and Silic-2O (102.2 eV), which contain one or two oxygen atoms per silicene unit cell, respectively. As the internal layers of the silicene are less susceptible to oxidation than the outer layers, the presence of the 100.4 eV peak confirms the presence of multilayer silicene.

DFT simulations indicated that the multilayer silicene is stable when sandwiched between the protective graphene layers. The modeled multilayer silicene consisted of stacked layers in which each layer is placed directly over the last in an eclipsed or AA stacking motif (Figure 4.13.305 a). The simulation resulted in a silicene-graphene distance of 3.5 Å that agreed with the lattice fringe measurements found by HRTEM (3.54 Å) and

![Figure 4.13. Schematic representation of bilayer silicene configurations showing eclipsed (AA) stacking (a) and staggered (AB) stacking (b) motifs. Reprinted/adapted with permission.](image)
showed that the stable silicene layers maintained their $sp^2$ hybridization when inserted between the graphene layers. Simulated XRD spectra of the graphene/silicene/graphene/Cu structure showed characteristic silicene peaks at $2\theta = 27.5^\circ$ and $46.4^\circ$ corresponding to multilayer silicene, which was in close agreement with the diffraction pattern for silicene/graphene found in the experimental SAED pattern. Oxidized silicene was also considered as it was found to be present in the XPS spectrum. The simulations produced a wide XRD peak at around $2\theta = 32.7^\circ$ and $39.7^\circ$ which were indicative of 2 oxygen atoms in the silicene unit cell (Silic-2O) and 1 oxygen atom in the unit cell (Silic-1O), respectively. These interplanar distances were also found in the experimental SAED pattern, confirming that a small amount of oxidation occurred on the silicene surface. However, the researchers point out that these oxidized layers of silicon atoms are not the same as that in silicene as the oxygen atoms acted as bridges interconnecting the oxidized silicon layers by forming atomic bonds with Si atoms from two adjacent layers simultaneously.

In 2013 Molle et al. investigated the effect of an Al capping layer on the oxidation of multilayer silicene with ultra-pure oxygen and atmospheric oxygen. Molecular beam epitaxy was used to deposit multilayer silicene onto a Ag (111) substrate heated to 250 $^\circ$C. Subsequent Al capping layers were deposited at room temperature, achieving a final Al film thickness of 7 nm.

For the uncapped epitaxial silicene sample, STM images showed the evident multi-phase character of the layered film with predominantly $4 \times 4$ and $(\sqrt{3} + \sqrt{3})$-II type superstructures while in situ XPS monitoring of the Si 2p region revealed an elemental silicene peak at a binding energy of 98.8 eV. In addition, no Si-Al interactions could be
deduced, aside from the Si wetting layer. When the sample was exposed to 1000 L of ultrapure oxygen, the development of a small asymmetric Si-O suboxide peak at a binding energy of 100.3 eV was observed. However, after the multilayer sample was exposed to air for 3 minutes, the XPS spectra showed a double peak profile decomposed into three regions: Si$^{4+}$, Si$^{+}$ and, Si$^{0}$ attributed to SiO$_2$, Si-O suboxide species, and elemental silicene, respectively. Longer exposure times in atmospheric conditions led to complete oxidation and formation of a SiO$_2$ film.

When the silicene layers were capped with a 7 nm thick Al film, XPS data revealed a shift of the Si 2p peak to a lower binding energy due to the interaction of the silicene film with the Al capping layer related to the charge exchange between the Al and silicene layers, similar to that seen with silicene deposited on Ag. Upon exposure to air, the capped sheets developed a new Al$^{+}$ peak at a binding energy of 103.3 eV related to the partial oxidation of the Al layer and corresponding to Al$_2$O$_3$. While pseudo-Voigt function fitting of the XPS spectra resulted in average atomic concentrations of 65% Al and 35% O for the Al$_2$O$_3$ layer, ex-situ atomic force microscopy indicated a conformal morphology of Al$_2$O$_3$/Al/Si on Ag (111).

To simultaneously address the issue of substrate interactions and the oxidation of the silicene sheets in ambient conditions, de Padova et al. produced thick multilayer silicene of roughly 43 layers thick on a Ag (111) substrate. When exposed to air, an ultra-thin oxide layer on the surface region of the film protected the underlying silicene layers for at least 24 hours so that XRD and Raman measurements could be taken.

A comparison sample was produced, consisting of a 16-layer silicene film with a $\sqrt{3} \times \sqrt{3}R30^\circ$ LEED pattern in a single orientation. The sample was then covered in-situ
with an Al layer and exposed to air, creating a protective Al₂O₃ capping layer. XRD data showed a broad peak centered at 2θ = 28.71° with a FWHM of 1.63° attributed to the Al₂O₃ covered silicene multilayer. The peak was shifted about 0.3° from the Si (111) reference sample, ruling out epitaxial Si (111) growth on the Ag (111) substrate. The broad FWHM allowed the authors to use the Scherrer equation (0.9* λ* FWHM₉₀ * cos(θ), λ = 1.5418 Å) to calculate a thickness of ~50 Å for the multilayer silicene film. Utilizing Bragg’s law (2d * sin(θ) = λ = 1.5418 Å), an interplanar distance of about 3 Å was calculated for the spacing between the silicene layers. The authors stress that the FWHM found in the XRD is due to the finite thickness of the multilayer film.

Raman spectral data showed a peak at 523.26 cm⁻¹ attributed to the silicene G (Γ) band, a broad spectral band ranging from 430-500 cm⁻¹ assigned to the silicene D band, and two peaks at 960 and 990 cm⁻¹ credited to the silicene 2D band. It was noted that the G band at 523.26 cm⁻¹ was shifted 2.86 cm⁻¹ away from the reference Si (111) peak at 520.40 cm⁻¹ and upshifted by 7.5 cm⁻¹ from the peak assigned to capped single layer silicene.

To evaluate the ability of multilayer silicene to resist oxidation in air, a 43-layer uncapped silicene multilayer sample was deposited onto a Ag (111) substrate. The silicene film showed the same √3 X √3R30° LEED pattern as the 16-layer film, however upon exposure to air, the thick 43-layer uncapped film developed a thin SiO₂/suboxide film. It was noted that the majority of oxidation occurred within the first seven minutes, however, even after 24 hrs the silicene film remained largely intact, being oxidized only at the surface. Auger electron spectroscopy spectra showed that Si-Si bonds dominated over Si-O bonds, no matter the exposure time while LEED observations revealed...
disappearance of the initial $\sqrt{3} \times \sqrt{3} R30^\circ$ LEED pattern, indicating development of the SiO$_2$ layer. XRD patterns in the $2\theta = 27.5^\circ - 30^\circ$ range displayed a peak occurring at $28.71^\circ$ assigned to the (002) reflection, in perfect agreement with the 16-layer capped silicene film. In addition, the FWHM of the uncapped silicene film decreased from 1.63$^\circ$ to 0.63$^\circ$ yielding a film thickness of 130 Å and a silicene layer stacking distance of 3 Å. Raman spectral data was also consistent with that of the Al$_2$O$_3$ capped silicene film. A peak at 523.26 cm$^{-1}$ and a broad band ranging from 430-500 cm$^{-1}$ assigned to the silicene G and D bands were observed.

Despite the need of single layer silicene to be stabilized by an appropriate surface functionalization such as oxidation or a substrate such as silver to stabilize the large number of out of plane dangling bonds, multilayer silicene exhibits incredible stability when either sandwiched between protective layers or even on its own, as evidenced by de Padova. Freestanding multilayer silicene shows resistance to oxidation up to 24 hours as well as independence from charge exchange effects created by conductive metal substrates.

4.1.4. Properties of Silicon Sheets in Metal Silicides

Calcium silicide also exhibits discernible covalent bonding of the interlayer calcium and silicon atoms resulting in a 2D silicon sub-network resembling low-buckled Si (111) planes, in which the honeycomb Si$_6$ rings are interconnected between $sp^3$ Si atoms.$^{174,308}$ The manufacture of CaSi$_2$ follow the Goldschmidt method in which CaO is
combined with bulk crystalline Si along with fluxes at 1400 °C and stirred with an Al₂O₃ rod until molten CaSi₂ separates onto the surface of the melt. Upon cooling, the mixture disintegrates producing small silicide particles. In order to increase impurity, the resultant CaSi₂ can be combined with additional bulk Si under the flow of H₂ gas at 1000 °C. As a result, Si [111] impurities are often found in commercially sourced CaSi₂. Fe can also occur as a low concentration (up to 5%) impurity in the CaSi₂ received from the manufacturer. Attempts to remove the Fe with concentrated acids yield hydrogen-terminated polysilanes. CaSi₂ consists of two polymorphs, an artificial tr₃ structure and a naturally occurring tr₆ structure, both with the trigonal-rhombohedral R-3m space group. In the tr₆ structure (Figure 4.14. a), the stacking of trigonal Ca layers follows a 6-layer AABBC pattern in which each pair of Ca layers is separated by a Si double layer. The tr₃ structure has a three-layer repeating pattern (Figure 4.14. b), with Ca layers stacked in an ABC sequence. There is a strong tendency for hybridization of the
Ca 3d atomic orbitals and the nearest Si layer 3p orbitals to occur, resulting in greater stability for the compound.\textsuperscript{311} Treatment with oxidizers such as HCl results in single layer Si sheets with hydrogenated surfaces,\textsuperscript{133,151} while deintercalation of the planar calcium layers by cleaving, polishing, and electrochemical oxidation\textsuperscript{286} has shown to produce single layer 2D Si nanosheets possessing Si dangling bonds, also termed immobilized radicals, as seen in Figure 4.15.\textsuperscript{286} Since every Si atom is bound to three additional Si atoms and either three or four equivalent Ca atoms,\textsuperscript{312} upon deintercalation of Ca\textsuperscript{2+} from the Si polyanion surfaces, multiple dangling bonds can be expected to form.\textsuperscript{313} These surface radicals are highly reactive and may readily form Si-O-Si bonds with atmospheric water and oxygen,\textsuperscript{314} therefore inert gas or UHV reaction environments are required to prevent undesired surface passivation.

Following removal of the Ca\textsuperscript{2+} ions, it is theorized that the Si sheets undergo surface relaxation, resulting in subsequent Si-Si buckling. The buckling is thought to be due to the pseudo John-Teller (PJT) effects caused by the Si atomic rearrangements bought about by the reduction in the number of the dangling bonds produced by vibronic

![Figure 4.15. Structural model showing the formation of dangling bonds (b) from the intercalation of calcium from CaSi\textsubscript{2} (a). Shaded parts indicate unpaired electron orbitals (radicals). Reprinted/adapted with permission.](image-url)
coupling of lowest unoccupied molecular orbitals (LUMO) with highest occupied molecular orbitals (HOMO). This surface relaxation increases the Si-Si corrugation height ($\Delta_z$) from 0.183 Å in CaSi$_2$ to a theoretical 0.44 Å for silicene while Si-Si bond lengths are reduced from 2.42 Å in CaSi$_2$ to 2.24 Å in silicene. Interestingly, the lattice constant parameters $a = 3.85$ Å for the hexagonal sheets remain unchanged despite adjustments in Si atom positions. Due to the absence of covalent π-stacking in silicene which prevents the clustering of sheets into stacks, there is no lattice parameter value $c$. Nevertheless, Ponrouch et al. have calculated an overall 29% volume reduction in the $c$, [001] direction for a CaSi$_2$ electrode after the deinsertion of Ca$^{2+}$.

4.2. Project Rationale

The synthesis of silicene without using ultra high vacuum environments and chemical vapor deposition is challenging and is expected to receive significant attention for a wide range of electronic and biological applications. An idea was conceived in which the freestanding silicene can be generated from CaSi$_2$ with an oxidizing agent, which should reduce the Si polyanion layer to generate silicene. Redox assisted chemical exfoliation (RACE) is a synthetic method based on the procedure developed by Nakano et al resulting in the production of 2D silicene sheets by the exfoliation of (Si$_{2n}$)$_{2n-}$ layers from CaSi$_2$. The charge on the silicon layers is decreased in order to weaken the strong electrostatic interactions experienced between the Ca$^{2+}$ and (Si$_{2n}$)$_{2n-}$ layers, however, as silicene is a reactive polydisilene polymer, atmospheric water and oxygen along with reactive reagents and solvents must be avoided. Acetonitrile was chosen as the
optimal solvent as it is nonreactive, can accommodate the Ca\(^{2+}\) generated from the dissolved CaSi\(_2\) layers\(^{321}\) and does not dissolve the silicene product. Ferrocenium tetrafluoroborate, \([\text{FeCp}_2][\text{BF}_4]\), a mild one-electron oxidizing agent\(^{322}\) is able to facilitate the oxidation and subsequent exfoliation of the Si 2D layers found in CaSi\(_2\) \(^{323,324}\). As \([\text{FeCp}_2]^+\) is usually considered an outer-sphere reagent\(^{325}\) no chemical bond is formed between in the Si sheets and the oxidizer during the synthesis reaction, resulting in the retention of the hexagonal lattice of the 2D sheet. As the Si sheets contain highly reactive dangling bonds, care must be taken to avoid exposure to atmospheric water and oxygen; therefore, air sensitive techniques such as the use of a glovebox, a Schlenk line and appropriate Schlenk glassware, as well as purge-and-refill methods are required.

\[
2\text{FeCp}_2 + C_6H_4O_2 + 2H_3OBF_4 \rightarrow 2[\text{FeCp}_2][\text{BF}_4] + C_6H_4(OH)_2
\]

*Scheme 4.1. Synthesis of ferrocenium tetrafluoroborate oxidizer.*

### 4.3. Results and Discussion

Ferrocenium tetrafluoroborate was synthesized and used to exfoliate individual silicon sheets from bulk calcium silicide (CaSi\(_2\)) via oxidative deintercalation of the Ca\(^{2+}\) ions from the Si 2D nanosheet layers. \([\text{FeCp}_2][\text{BF}_4]\) was formed in solution by the reduction of p-benzoquinone to form p-hydroquinone in the presence of aqueous tetrafluoroboric acid as seen in *Scheme 4.1*. \([\text{FeCp}_2][\text{BF}_4]\) was then dissolved in acetonitrile and reacted with CaSi\(_2\) under nitrogen to free the alternately stacked silicene layers without changing the fundamental honeycomb silicene lattice. Acetonitrile was
chosen as a suitable solvent as [FeCp2][BF4], ferrocene, and the byproduct Ca(BF4)2 exhibited excellent solubility in it and acetonitrile was found to be non-reactive\textsuperscript{326} with the silicene surface. A visible color change from dark, navy blue of the ferrocenium salt to the bright orange associated with ferrocene signifies the completion of the reaction. The exfoliated silicon sheets were segregated by filtration under nitrogen from any unreacted CaSi2 then characterized accordingly. The reaction filtrate was also isolated and analyzed for the presence of calcium ions to confirm the release of free calcium ions.

4.3.1. Synthesis and Characterization of Ferrocenium Tetrafluoroborate

There are many methods for the production of ferrocenium salts (Fc\textsuperscript{+}),\textsuperscript{322} however, the method introduced by Hendrickson in 1971\textsuperscript{327} seems to be the most commonly cited and is quite inexpensive to accomplish. A readily apparent color change of the ferrocene (\textbf{Figure 4.16. left})\textsuperscript{328} from a bright orange to dark, navy blue upon oxidation by the yellow p-benzoquinone (\textbf{Figure 4.16. middle}) indicates the successful synthesis of ferrocenium tetrafluoroborate. The [FeCp2][BF4] solid is easily separated by filtration and can be stored in air for extended periods\textsuperscript{329} until ready for use. Transformation of the diamagnetic ferrocene to the paramagnetic Fc\textsuperscript{+} can also be viewed
in the obtained $^1$H-NMR spectra. Figure 4.17. shows that ferrocene exhibits a sharp peak at 4.17 ppm with a full-width-at-half-max of 0.0149 ppm. In addition, water and CD$_3$CN can be seen at 2.13 ppm and 1.93 ppm, respectively. In contrast, the $^1$H-NMR spectrum of [FeCp$_2$][BF$_4$] (Figure 4.18.) shows only a single peak at 5.67 ppm. A full-width-at-half-max of 0.0668 ppm is noted along with a noticeable downfield shift of the
ferrocenium peak indicating a successful loss of one electron. \(^{330}\) \(^{331,332}\) \(^1\)H NMR can be utilized as a means to verify complete conversion of Fc\(^+\) to Fc as peak position and FWHM of the oxidizer can be monitored throughout the reaction.

![Figure 4.18. \(^1\)H-NMR of ferrocenium tetrafluoroborate in acetonitrile-\(d_3\).](image)

4.3.2. Oxidation and Exfoliation of Calcium Silicide
Initial oxidation reactions of CaSi$_2$ with [FeCp$_2$][BF$_4$] (Scheme 4.2.) were carried out at room temperature while stirring under nitrogen for 5 days, or until the [FeCp$_2$][BF$_4$] solution color changed from a dark, navy blue color to brown. At the culmination of the reaction, the solution was allowed to settle yielding a solid, light-brown suspension floating on the surface of the reaction mixture (Figure 4.19. a) and dark brown-black solids at the bottom of the reaction flask. The light brown film, attributed to the exfoliated silicon sheets,$^{147,185,334}$ was separated by decanting into a Schlenk filtration flask under nitrogen, then washed with dry, degassed acetonitrile until the filtrate ran clear. Each wash was reserved and qualitatively tested for calcium ions by adding saturated aqueous ammonium carbonate drop wise to the filtrate. Upon the addition of the (NH$_4$)$_2$CO$_3$ to the filtrate a white, cloudy precipitate formed$^{286,335}$ and the solution immediately changed from brown to bright orange. It is thought that the deintercalated Ca$^{2+}$ ions are stabilized by (BF$_4$)$^-$ to form Ca(BF$_4$)$_2$ in solution, and upon

\begin{equation}
\text{CaSi}_2 + 2[\text{FeCp}_2][\text{BF}_4] \rightarrow (\text{Si}_{2n}) + 2\text{FeCp}_2 + \text{Ca(BF}_4)_2
\end{equation}

\textbf{Scheme 4.2. Synthesis of silicon nanosheets by oxidation and exfoliation of CaSi$_2$.}
addition of the \((\text{NH}_4)_2\text{CO}_3\) insoluble, white calcium carbonate was formed as seen in Figure 4.19. b. The precipitates were separated from the filtrates by a simple filtration step and analyzed by XRD as shown in Figure 4.20. For the brown reaction solvent, it was found that the precipitates formed after addition of ammonium carbonate contained mostly ferrocene and a small amount of ammonium bicarbonate \([(\text{NH}_4)\text{HCO}_3]\). The peaks at \(\theta = 15.22^\circ, 17.45^\circ,\) and \(18.97^\circ\) were assigned to the ferrocene \((-110), (001),\) and \((-111)\) planes, respectively, while the peak at \(\theta = 16.55^\circ\) is attributed to the \((\text{NH}_4)\text{HCO}_3\) \((020)\) plane. For the precipitates collected from the acetonitrile wash, there is a marked absence of ferrocene and an increase in the proportion of ammonium bicarbonate, evidenced by the presence of the peaks at \(\theta = 16.46^\circ, 21.84^\circ, 24.44^\circ,\) and \(29.66^\circ\)
corresponding to the (NH$_4$)$_2$HCO$_3$ (020), (012), (200), and (220) planes, respectively.

There was also a large overlapping peak at $2\theta = 29.53^\circ$ assigned to the CaCO$_3$ (104) plane. The solid precipitates were confirmed to be ammonium bicarbonate and calcium carbonate by comparing the experimental XRD data with the peak positions of pure ferrocene (PDF card 29-1711) and calcium carbonate (PDF card 05-0586) and PDF card 09-0415 for ammonium bicarbonate. It is possible that the brown color of the filtrate is caused by soluble silicene sheets dissolved in the acetonitrile.\textsuperscript{184,188,320} As NH$_4^+$ is acidic and silicene is reactive to acids, the addition of (NH$_4$)$_2$CO$_3$ may account for the color shift from brown to colorless as the sheets become functionalized by hydrogen atoms. The resulting orange color of the filtrate treated with (NH$_4$)$_2$CO$_3$ is due to Fe$^+$ being reduced to ferrocene during the CaSi$_2$ oxidation reaction.

\textbf{Figure 4.20.} XRD analysis of the precipitates formed after addition of (NH$_4$)$_2$CO$_3$ to the brown reaction solvent and the first acetonitrile wash. The precipitates are compared against pure ferrocene and CaCO$_3$. 

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Figure 4.20. XRD analysis of the precipitates formed after addition of (NH$_4$)$_2$CO$_3$ to the brown reaction solvent and the first acetonitrile wash. The precipitates are compared against pure ferrocene and CaCO$_3$.

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4.4. Characterization of Silicene Nanosheets

4.4.1. Silicene Nanosheets from Commercially Supplied CaSi$_2$

Multiple methods of analysis were employed to determine the composition of the suspended silicene flakes. XPS was used to establish the binding energy and surface structure of the sheets. The XPS survey spectrum of the isolated silicon nanosheets is shown in Figure 4.21. and shows the presence of Ca, Si, C, and O groups. Deconvolution of the Si (2p) region results in a Si-O peak found at 102.4 eV, an elemental Si 2p peak at 98.4 eV, and a Si $sp^2$ peak at 93.2 eV as seen in Figure 4.22. The shift of the $sp^2$ peak to a lower binding energy compared to the elemental peak has also been observed in graphitic carbon grown by molecular beam epitaxy$^{336}$ and few-layer supported graphene.$^{337}$ The additional low intensity peak occurring at 93.2 eV is too high in binding energy to be elemental Fe (92.0 eV)$^{338}$ and too low in binding energy to be considered as CaSi$_2$ (97.5 eV).$^{238,338,339}$ Molle et al showed that the oxidation of silicene started after only a 3 min exposure to air,$^{306}$ therefore it is believed that the presence of the Si-O peak is due to exposure of the silicon nanosheets to atmospheric water and oxygen during preparation for characterization. There is a marked absence of iron peaks in the 700-720 eV region (Figure 4.22. top inset), which is indicative of the lack of any residual α-FeSi$_2$ impurities.$^{340,341}$ Ca in the form of Ca 2p$_{1/2}$ and Ca 2p$_{3/2}$ is noted at 347.5 eV and 351.2 eV, respectively$^{342}$ (Figure 4.22. bottom inset) and can be attributed to the inability of
**Figure 4.21.** XPS survey spectrum of isolated Si sheets.

**Figure 4.22.** Si 2p XPS region of isolated Si sheets. Top inset shows focused Fe 2p region absent of any Fe peaks while the Ca 2p focused region (bottom inset) indicates the presence of residual Ca.
Fc+ to fully oxidize the CaSi₂ pieces.

XRD scans were performed on the samples in a sealed plastic dome in order to prevent oxygen contamination during analysis. An initial scan of the manufacturer supplied CaSi₂ revealed characteristic CaSi₂ peaks along with α-FeSi₂ and bulk Si impurities (Figure 4.23. black). A comparison of the isolated Si nanosheets (red) with the commercial CaSi₂ revealed CaSi₂, FeSi₂, and Si-bulk peaks suggesting incomplete removal of Ca²⁺ and retention of the FeSi₂ and Si-bulk impurities; although, there is a noticeable decrease in the intensity of the CaSi₂ and FeSi₂ peaks. Interestingly, there is a clear lack of a Si-O crystalline peak or an amorphous hump in the 20–30° region, which is in stark contrast to the XPS data, supporting the idea that the formation of the Si-O bonds occur during exposure of the sample to atmospheric oxygen. Two new diffraction peaks at 2θ = 18.16° and 28.5° attributed to the silicene (001) and (002) stacking layers, respectively, are also noted. The shifted position, broad asymmetric peak shape, and large peak intensity of the silicene (001) diffraction peak suggests staggered (AB) as well as random stacking of the silicon nanosheets as demonstrated in Figure 4.13. When the 2D materials are stacked in a staggered (AB) as opposed to an eclipsed (AA) motif, an interphase plane shift will generate a change in the XRD peak position, while destructive interference caused by the staggered stacked nanosheets will generate a broad, asymmetric peak shape. The large intensity of the (001) peak compared to the (002) peak can be credited to constructive interference caused by the arbitrarily occurring overlap of Si atoms in the c direction caused by random stacking displacements among the different layers.
Bragg’s law (Equation 4.1.) was employed to calculate the interatomic spacing $(d)$ of each crystallite, and when used along with the 2θ peak positions, was useful in the assignment of a Miller index $(hkl)$ to each peak when compared to PDF cards 75-2192 for CaSi$_2$, 77-2109 for Si, and 65-7295 for α-FeSi$_2$.

\[ 2dsin\theta = n\lambda \]  

(4.1.)

where:

- $d$ (Å) = interplanar spacing
- $\theta$ (radians) = incident angle
- $\lambda$ (Å) = wavelength of x-ray = (1.5406)
- $n$ = diffraction order (1, 2, 3, ...)

Figure 4.23. XRD spectrum of silicon sheets produced from 5-day reaction (red) compared to commercially supplied CaSi$_2$ (black).
Example interplanar spacing calculation for the Si (111) peak:

\[ \theta = 14.165^\circ = 0.247 \text{ rad} \]

Manipulation of equation 4.1. yields:

\[ d = \frac{n\lambda}{2 \sin \theta} \quad (4.2.) \]

therefore,

\[ d = \frac{1 \times 1.5406 \text{ Å}}{2 \sin(0.247)} \]

\[ d = 3.148 \text{ Å} \]

However, Bragg’s equation doesn’t necessarily pertain to 2D nanomaterials as Bragg diffraction requires that the incident light rays be in phase to produce a constructive interference pattern in order to generate an interplanar distance \( d \) between the two atomic planes as seen in Figure 4.24.\textsuperscript{346} When the 2D materials are stacked in staggered (AB) motif as in Figure 4.13.\textsuperscript{b}, XRD peaks corresponding to the in-plane reflection

\[ \text{Figure 4.24. 3D crystal structure demonstrating constructive interference necessary to fulfill Bragg diffraction requirements. Reprinted/adapted with permission.} \]
[(h,k,0)] of a monolayer at several 2θ values can be absent or shifted because of destructive interference.\textsuperscript{345} This staggered and random stacking of the sheets would explain why there is an absence of (100) or (110) 2θ peaks in the above mentioned XRD pattern.

Transmission electron microscopy images showed stacked planar sheets as viewed in Figure 4.25. a. Energy dispersive spectroscopy (EDS) characterization was performed on the area of the sample indicated by the red arrow and revealed traces of Ca and Fe (Figure 4.25. b), supporting the XRD findings suggesting incomplete exfoliation and retention of the Fe impurity; however, the sheet is predominantly silicon. Carbon and copper transmissions can be attributed to the formvar coated, copper TEM grid used to hold the sample during analysis, while oxygen contamination may occur during preparation for characterization. Selected area electron diffraction (SAED) data capture was attempted for the sample; however, analysis of the image is inconclusive due to the lack of any evident diffraction pattern as seen in Figure 4.25. c. Images shown in Figure 4.26. a and b display additional sample regions exhibiting characteristic stacking of the multilayer Si sheets.
Figure 4.25. TEM image of light brown suspension material collected after 5 day oxidation of CaSi$_2$ (a). Red arrow indicates region of EDS data collection (b). SAED pattern shows lack of discernible diffraction pattern (c).
X-ray and microscopic examinations of an alternate region of the same sample revealed a protruding, wire or tube-like structure as noted in Figure 4.27. a. EDS characterization was performed on the area indicated by the white arrow, revealing that the structure contained only Si (b). The presence of pure Si, free of Fe and Ca impurities, suggests that the Si sheets were allowed to move independently in solution after complete oxidation of CaSi$_2$. It is believed that the structure in Figure 4.27. a is a single 2D Si nanosheet curled upon itself to form a tube. Curling of 2D nanomaterials into rods or tubes from compressive stresses has also been noted by numerous other researchers.$^{347-351}$ Carbon, Cu, and O in the EDS spectrum are attributed to the same sources as those of the EDS in Figure 4.25. Upon standing in air for prolonged periods of time, it was noted that the brown flakes developed a white film, possibly indicating the development of an oxidized surface.
XRD, XPS and EDS data shows that the reaction of Fe⁺ with CaSi₂ produced pure Si nanosheets, however partial oxidation occurred due to exposure to the reactive Si sheets to atmospheric water and oxygen during characterization. XPS data indicates that a shift from elemental Si at 98.8 eV to Si-O at 102.4 eV occurs when the sheets are exposed to atmosphere, which is in agreement with previous findings. XRD spectra showed random and staggered sheet stacking patterns evidenced by the shifted, asymmetric peak at 2θ = 18.16° and 28.5° as well as a lack of (100) and (110) peaks, while SAED images were inconclusive due to sample thickness.
4.4.2. Multilayer Silicene Nanosheets from Manually Ground CaSi₂

In order to increase the surface area of CaSi₂, as well as the number of interactions with [FeCp₂][BF₄], the shiny calcium silicide pieces were ground in a quartz mortar and pestle under nitrogen until a dull gray, homogeneous powder was produced prior to oxidation by Fe⁺. The grinding had no chemical effect on the CaSi₂ as evidenced by the obtained XRD and SAED data. The XRD comparison spectra between raw CaSi₂ and the ground CaSi₂ show preservation of the major Miller indices (hkl) of CaSi₂, Si, and α-FeSi₂ as seen in Figure 4.28. It is important to note that the XRD spectra for the raw CaSi₂ and the ground CaSi₂ were taken on different instruments, which accounts for the difference in peak resolution noted between the two spectra. Instrumental

![Figure 4.28: XRD spectra of ground CaSi₂ (top, red) and raw CaSi₂ (bottom, black).](image-url)
specifications are noted in section 3.5. The selected area electron diffraction (SAED) pattern confirms the retention of the polycrystalline CaSi$_2$ structure as suggested by the appearance of ring-like diffraction patterns in Figure 4.29. left. Miller index values (hkl) were found by comparing measured interplanar distances to PDF cards 75-2192 and 65-2795 for calcium silicide and iron silicide, respectively. The TEM image of the ground CaSi$_2$ (Figure 4.29. right) shows the preservation of the initial granular form of CaSi$_2$ indicating that the grinding does itself does not produce sheets.

![SAED of ground CaSi$_2$ (left) showing retention of crystal structure and FeSi$_2$ impurities. Labels are shown to the right of each assigned spot. TEM image of ground CaSi$_2$ crystal showing preservation of initial granular shape.](image)

The interplanar spacing value (d) of the CaSi$_2$ sample was found by employing image-based processing software ImageJ. The software was used to measure the diameter of each polycrystalline ring in reciprocal space (1/nm). Considering that diameter = 2 * radius, Equation 4.3. can be used to find the interplanar spacing (nm) of each polycrystalline ring.
\[ d = \frac{1}{r^*} \quad (4.3. \text{ )} \]

where:

\( d = \text{interplanar spacing in real space} \)

\( r^* = \text{radius of crystalline ring in reciprocal space} \)

Example calculation to find interplanar spacing of CaSi\textsubscript{2} (104) from SAED pattern:

\( \text{diameter of ring in reciprocal space (} 2r^* \text{)} = 6.755 \text{ 1/nm} \)

\( \text{radius of ring in reciprocal space (} r^* \text{)} = 3.378 \text{ 1/nm} \)

\[ \text{interplanar spacing (} d, \text{nm)} = \frac{1}{3.378 \text{ nm}} = 0.296 \]

\[ \text{interplanar spacing (} d, \text{Å)} = 2.96 \]

When compared to PDF card 75-2192 for rhombohedral CaSi\textsubscript{2}, the interplanar spacing most closely matches that of the (104) plane with an established interplanar spacing of 3.0598 Å. For FeSi\textsubscript{2} and Si-bulk, none of the interplanar distances listed on cards 65-2795 and 77-2109 match more closely in terms of interplanar distance than that of CaSi\textsubscript{2} (104), therefore the spot was assigned accordingly. The CaSi\textsubscript{2} (015) plane with an interplanar distance of 2.931 Å was not considered due to the low intensity (4.1%) at which the plane occurs. A comparison of the calculated SAED interplanar distances to the obtained XRD spectrum must also be made in order to confirm the assignment of each ring in the SAED pattern. As the fundamental difference between XRD and SAED is that with XRD measurements the intensities and position of the diffracted beam are observed, but in SAED only the position of the beam is observed, the interplanar spacing and 2θ positions should correlate between the SAED pattern and XRD spectrum.
In contrast to the five days required for the raw CaSi$_2$ reflux reaction to reach completion, the reaction with ground CaSi$_2$ only required 24 hours to change from navy blue to orangish brown. A comparison of the XRD spectra for the brown suspension attributed to the silicon sheets, the residual solids remaining at the bottom of the reaction flask, and ground CaSi$_2$ (Figure 4.30.) reveals an obvious decrease in the number and intensity of the CaSi$_2$ peaks for the silicon sheets, which signals a successful oxidation of the Ca-Si layers. The remaining FeSi$_2$ peaks (2$\theta$ = 37.55°, 48.86°, 55.97°, 50.37°) and the Si-bulk planes suggest a retention of the initial impurities.$^{341}$ There is also no apparent Si (100)/(110) peak at 2$\theta$ = 40.23°, for $d$ = 2.24Å, however, there are new peaks at 2$\theta$ = 17.91°, 27.92° which are assigned to the (001) and (002) planes of the Si nanosheets. The peak at 27.92° is in good agreement with that calculated by Nie et al. for multilayer silicene (2$\theta$ = 27.5°)$^{298}$ as well as the experimental value found by de Padova (2$\theta$ = 28.71°)$^{307}$ The two new peaks are absent in the ground, crystalline CaSi$_2$ and increase in intensity from the residual solids to the isolated Si nanosheets indicating a greater concentration of the nanosheets in the isolated sample versus the residual, partially reacted solids. As with the unaltered CaSi$_2$ oxidation reaction, there is a lack of (hk0) and (h00) planes due to the staggered stacking of the layered sheets in a direction perpendicular to the sample holder. The idea of staggered stacking is supported
Figure 4.30. Comparison of XRD spectra for silicon sheets (top, blue), residual solids (middle, green), and ground CaSi$_2$ (bottom, black).
by the shifted 2θ position of the (001) peak as well as its broad, asymmetric shape.

Improvement of the diffraction intensity of the (hk0) and (h00) planes can be achieved by transmissive geometry, in which the sample holder is rotated from the flat to the vertical position, placing more nanosheets in the perpendicular position for diffraction.\textsuperscript{345}

TEM images of exfoliated Si nanosheets (Figure 4.31. a, b, c, e) reveal representative flake-like structures observed during characterization. Figure 4.31. a shows a large, slightly transparent region of overlapping Si sheets while Figure 4.31. b clearly shows two randomly stacked Si sheets. Figure 4.31. c displayed a transparent Si sheet with a diameter of 1.9 µm and edges curling inward toward the center of the sheet, similar to that noted by other groups for 2D nanomaterials.\textsuperscript{347,349–351} The related EDS spectrum (Figure 4.31. d) reveals the presence of a Si peak at 1.76 keV and the absence of Ca at 3.69 keV. The low relative ratio of Fe for the structure in c (5.68 %) is similar to that for bulk CaSi\textsubscript{2}, which could possibly be due to the retention of FeSi\textsubscript{2} impurities, while the oxygen peak at 0.54 keV is attributed to water and oxygen absorption during preparation for characterization. Cu at 8.04 keV is due to the copper/formvar grid used to hold the sample during analysis. For Figure 4.31. e, there are multiple transparent, thin sheets overlapping one another along with smaller, darker CaSi\textsubscript{2} fragments. The EDS (f) Si peak occurs at 1.76 keV and there is a noticeable absence of Ca at 3.69 keV. Iron is found at the lowest relative ratio (3.24 %) of the sampled areas while the sheets exhibit no regularly discernible pattern as to a preferred shape.
Figure 4.31. TEM images (left) and corresponding EDS spectra (right) of Si nanosheets exfoliated from CaSi$_2$. 
A Selected Area Electron Diffraction (SAED) image taken of the silicon sheets, assuming that the sheets were lying flat on the sample surface, in the [00l] direction (Figure 4.32.) shows three hexagonal lattice rings, from which the interplanar spacing values \(d\) can be found. Image-based processing software ImageJ was used to measure the diameter of the hexagonal rings in reciprocal space, then converted to the corresponding real space interplanar distance values using Equation 4.3. From the inner-most ring a Si-Si bond distance of 2.12 Å was found, which is only 5% smaller than that

![SAED Image](image-url)

**Figure 4.32.** SAED of silicon nanosheets parallel to [001] direction formed by oxidation and exfoliation of CaSi\(_2\) by Fc\(^+\). Scale bar units are 5 1/nm. Inset shows hexagonal lattice diffraction pattern prior to beam focus.
proposed by Takeda\textsuperscript{140} and experimentally found by Vogt\textsuperscript{163} on Ag (111) substrates. It is also closer to the Si-Si double bond distance of 2.14 Å than the mixed \(sp^2\)-\(sp^3\) Si-Si distance of 2.24 Å found in other studies, signaling the possibility of a planar, honeycomb silicon sheet. Assuming a hexagonal lattice, measurement of the silicene unit cell yields an interplanar distance of \(d = 1.401\) Å giving rise to a lattice constant \(a = 6.47\) Å, which closely coincides with a \(\sqrt{3}a\) (\(\sqrt{3}a = \sqrt{3} \times 3.85\) Å) relationship to that of theoretical freestanding silicene. An example calculation for finding the lattice constant \(a\) from the interplanar spacing value is provided in Equation 4.4. The experimental lattice parameter is identical to the \((\sqrt{3} \times \sqrt{3})R30^\circ\) superstructure observed by Chen,\textsuperscript{291} the \(\sqrt{3} \times \sqrt{3}\) honeycomb superstructure structure grown by Feng,\textsuperscript{283} the \((\sqrt{3} \times \sqrt{3})R30^\circ\) silicene layer detected by Vogt,\textsuperscript{279} and the multilayer \(\sqrt{3} \times \sqrt{3}\) silicene film produced by de Padova \textit{et al.}\textsuperscript{299} It is also similar to the \(\sqrt{3} \times \sqrt{3}\) large honeycomb dumbbell silicene proposed by Cahangirov.\textsuperscript{352} In addition, a Si-Si-Si bond angle (\(\gamma\)) of 120° supports the implication of a potential planar, honeycomb structure. The inset photo shows the hexagonal lattice of the staggered stacked silicon sheets in what is assumed to be a AB pattern\textsuperscript{353} prior to the focusing of the beam for SAED.

To calculate the lattice parameters \(a\) and \(c\) (\(b\) is equal to \(a\) for a hexagonal lattice) from the interplanar spacing values, the formula for the hexagonal crystal lattice (Equation 4.4) is utilized.

\[
\frac{1}{d^2} = \frac{4}{3} \left( \frac{h^2 + hk + k^2}{a^2} \right) + \frac{l^2}{c^2} \tag{4.4.}
\]

where:
\[ d (\text{Å}) = \text{interplanar spacing} \]
\[ a, c (\text{Å}) = \text{lattice constants} \]
\[ h, k, l = \text{miller index values} \]

Example calculation to find lattice constant \( a \) from interplanar spacing value \( (d) \) 1.401 Å:

Prior to outlining the example calculation, some assumptions must be clarified. As the silicene unit cell corresponds with the (400) plane, the values for \( h, k, \) and \( l \) are 4, 0 and 0, respectively. Also, since the lattice constant \( c \) is not being considered at this point, the value zero can be substituted in the formula so that \( c = 0 \), which gives:

\[
\frac{1}{1.401 \text{Å}^2} = \frac{4}{3} \left( \frac{4^2 + 4 \times 0 + 0^2}{a^2} \right) + \frac{0^2}{0^2}
\]

\[
\frac{1}{1.963 \text{Å}^2} = \frac{4}{3} \left( \frac{16}{a^2} \right) + 0
\]

Solving for \( a \) gives:

\[
a = \sqrt{\frac{4 \times 16 \times 1.963 \text{Å}^2}{3}}
\]

\[ a = 6.47 \text{Å} \]
An additional SAED pattern (Figure 4.33.) taken of a different region on the TEM grid of the same sample clearly shows stacking of the multilayer sheets. Calculated interplanar spacing values of 6.11 Å for the $A \rightarrow A$, (001) plane and 3.04 Å for the $A \rightarrow B$, (002) plane corresponding to a lattice constant $c$ equal to 6.11 Å were noted. The value 3.04 Å is in excellent agreement with the (002) plane found by De Padova et al. for thick multilayer silicene stacks. It also matches the value calculated for bilayer silicene grown on a hexagonal-BN monolayer and on a hydrogenated bulk-SiC (0001) surface.

Figure 4.33. SAED of silicon nanosheets parallel to [110] direction Scale bar units are 2 l/nm.
Attenuated Total Reflectance Infrared spectroscopy (AT-IR) allowed for the solid samples to be analyzed directly, without any need for further sample preparation. Initial scans of the ground CaSi$_2$ material (Figure 4.34, bottom, black) reveal no vibrations or bending frequencies, confirming the lack of oxidation caused by grinding as typically only Si-O, Ca-O, or Si-O-Ca stretching modes are noted for CaSi$_2$ oxidized in atmosphere. The AT-IR spectrum for the residual solids (middle, blue) is consistent with unreacted CaSi$_2$ along with possible silicene sheets found on the surface of the characterized sample, evidenced by a small, broad Si-O-Si asymmetric stretching peak, which can be seen centered at 1056 cm$^{-1}$ indicating oxidation of the reactive Si surface. The same broad asymmetric stretching Si-O-Si peak occurs at 1040 cm$^{-1}$, although with a

![AT-IR spectra comparison](image)

**Figure 4.34.** AT-IR spectra comparing ground crystalline CaSi$_2$ (bottom), the residual solids (middle), and Si nanosheets (top).
greater intensity, along with a symmetric Si-O-Si stretching peak at 800 cm\(^{-1}\) for the isolated Si nanosheets (top, red) indicating oxidation of the reactive surface. The increase in peak intensity suggests an increased number of silicon nanosheets while oxidation may occur during preparation and analysis in atmospheric conditions. In addition, the increase in Si-O bonds also signifies an increase in the number of available Si bonding sites on the nanosheet surface as the Ca\(^{2+}\) ions are removed. There are also C=C aromatic stretching frequencies occurring at 1415 cm\(^{-1}\) and 1623 cm\(^{-1}\) suggesting that ferrocene was not completely removed from the surface of the nanosheets during washing of the product.

Raman spectroscopy is a non-destructive optical technique widely used to explore the modification of the Si buckled structure in the presence of metal substrates. In addition, the method has been shown to be an efficient tool for the characterization of the vibrational modes of \(sp^2\) based 2D materials. For CaSi\(_2\) ground in the quartz mortar and pestle (Figure 4.35, bottom/black), the Raman spectrum shows an intense, slightly broadened peak (FWHM = 7.32 cm\(^{-1}\)) centered at 517 cm\(^{-1}\) and a small, broad peak centered at 388 cm\(^{-1}\) which are attributed to the corrugated Si planes in CaSi\(_2\). The small, broad peak at 482 cm\(^{-1}\) is due to the presence of amorphous Si in the sample. When compared to the residual solids (middle/blue) and the Si nanosheets (top/red), it is apparent that the peak at 388 cm\(^{-1}\) is no longer present, signaling a loss of Ca layers and successful oxidation by the Fe\(^+\) indicating that the sheets have retained the honeycomb structure and are no longer composed of CaSi\(_2\). The shift of the Si nanosheet peak to a
slightly lower frequency of 516 cm\(^{-1}\), as compared to the theoretical 530 cm\(^{-1}\) for freestanding silicene,\(^{360}\) is often seen in epitaxial silicene\(^{181,357}\) and may signal the retention of the Fe atoms, which could possibly lead to more \(sp^2\)-like hybridization characteristics.\(^{361}\) In addition to a peak shift, there is also an increase in the FWHM from 7.32 cm\(^{-1}\) for the ground CaSi\(_2\) to 10.73 cm\(^{-1}\) for the Si nanosheets. Theoretical calculations and experimental results have verified that such broadening of the FWHM has a linear relation to the size of the nanostructure,\(^{359,362}\) which is attributed to the size confinement effect in the Si nanosheets. In this case, the increase in FWHM is due to the phonon confinement of the Si nanosheets.

4.5. Conclusion
Layered silicon nanosheets with residual Fe atoms have been successfully prepared via the oxidation of CaSi$_2$ by [FeCp$_2$][BF$_4$]. The one-step, top-down procedure generated small 2 µm or less Si nanosheets stacked in a staggered AB motif as evidenced by TEM, EDS, XRD, Raman, and AT-IR analyses methods. SAED patterns were used to calculate a Si-Si bond distance of 2.12 Å with a lattice constant $a = 6.47$ Å and a stacking distance of 6.11 Å and 3.04 Å for the (001) and (002) planes, respectively. The process has shown to be free of harsh oxidizers such as strong acids or the need for ultra-high vacuum environments as well as epitaxial substrates such as Ag (111) or Ir (111). However, FeSi$_2$ and bulk-Si impurities remain as evidenced by XRD data.

4.6. Experimental Methods

4.6.1. Materials

Calcium silicide was purchased from Sigma Aldrich, stored in a dry box under nitrogen atmosphere, and ground in a quartz mortar and pestle to a fine light gray powder prior to exfoliation by ferrocenium tetrafluoroborate. Ferrocene was purchased from Sigma Aldrich and used as received. p-benzoquinone was purchased from Sigma Aldrich and purified by recrystallization in hot petroleum ether. Aqueous fluoroboric acid (48-50%) was purchased from Spectrum Chemical and used as received. Diethyl ether, petroleum ether, acetonitrile, and tetrahydrofuran were purchased from Fisher Scientific and were used as is unless otherwise stated. Acetonitrile was dried over calcium hydride by distillation, under nitrogen atmosphere prior to use. Tetrahydrofuran was dried by
distillation over a sodium-benzophenone mixture. The dry box nitrogen atmosphere was maintained at oxygen levels less than 2 ppm and water levels less than 1 ppm.

4.6.2 Synthesis of Ferrocenium Tetrafluoroborate \([\text{Fe(C}_5\text{H}_5\text{)}_2]\text{BF}_4\)

Ferrocenium tetrafluoroborate was synthesized according to the method reported by Hendrickson.\(^{327}\) While \([\text{Fe(C}_5\text{H}_5\text{)}_2]\text{BF}_4\) is commercially available, it was found to be more cost efficient to synthesize the compound. In a 1 liter round bottom reaction flask equipped with a stir bar, orange ferrocene (1.93g, 10.4 mmol) was dissolved in 300 mL anhydrous ethyl ether and stirred. In a 500 mL beaker, yellow p-benzoquinone (2.25g, 20.8 mmol) was dissolved in 300 mL anhydrous ethyl ether and manually stirred until dissolved. Tetrafluoroboric acid (7.31 mL, 41.6 mmol, 48%) was added to the p-benzoquinone solution and manually stirred. Once fully dissolved, the yellow p-benzoquinone mixture was added to the orange ferrocene solution, immediately creating a dark blue precipitate that was allowed to stir for 5 minutes. The blue precipitate was filtered and washed thoroughly with anhydrous ethyl ether. The resultant solids were dried and stored in an oven at 125 °C until ready for use. Yield is typically 95%.

4.6.3. Synthesis of Silicene Nanosheets

Inside a nitrogen filled dry box, shiny, gray calcium silicide pieces were ground to a fine dull gray powder with a quartz mortar and pestle. The gray powder (5 g, 52 mmol) was transferred to a 2 liter, 2-neck round bottom flask and sealed with a glass stopper and rubber septum, then removed from the dry box. A separate 2 liter Schlenk flask was evacuated and back filled three times with nitrogen prior to filling with dried acetonitrile.
The acetonitrile was degassed with nitrogen for at least one hour prior to use. In a 2-liter Schlenk flask equipped with a stir bar, the dried ferrocenium tetrafluoroborate (28.38g, 0.104mol) was added, then evacuated and filled three times with nitrogen. 1 liter of dried, purged acetonitrile was then transferred by positive nitrogen gas pressure via cannula to the ferrocenium tetrafluoroborate to create a blue solution. The solution was allowed to stir under nitrogen until fully dissolved. Once homogeneous, the ferrocenium solution was transferred by positive nitrogen gas pressure via 16-gauge cannula to the 2-liter round bottom flask containing the ground calcium silicide. Upon complete addition of the ferrocenium tetrafluoroborate solution, the rubber septum was quickly replaced with a Graham condenser under positive flow of nitrogen gas. Once sealed, the round bottom flask was allowed to reflux under nitrogen atmosphere for 24 hours, at which a brown solution with a thin layer of floating light brown solids, and black solids at the bottom of the reaction flask, was produced.

The resultant brown solution was allowed to cool to room temperature and decanted carefully into a Schlenk vacuum filtration funnel under positive flow of nitrogen gas. The retained light brown solids were washed with dried, degassed acetonitrile until the filtrate ran clear. The solids were then sealed inside the filtration funnel and transferred into a nitrogen dry box for storage. The percent yield for the brown solids/silicene sheets was 2.41%. The acetonitrile wash procedure was repeated for the black solids, which were also retained for analysis.

The brownish-orange filtrate was tested for the presence of calcium ions with saturated aqueous ammonium carbonate solution. 2 mL saturated ammonium carbonate solution was added to 10 mL of filtrate, whereupon the solution immediately turned a
bright orange (the color of ferrocene) and a thick, white precipitate formed indicating the formation of calcium carbonate, which is insoluble in water. The solid precipitate was separated from the filtrate by filtration through a whatman filter membrane and analyzed by XRD.

4.6.4. Analytical Characterization Methods

4.6.4.1. Attenuated Total Reflectance Infrared Spectroscopy (AT-IR)

AT-IR spectra were obtained at 1 cm\(^{-1}\) resolution with at least 256 scans using a Thermo-Nicolet NEXUS 670 FTIR spectrometer and the ATR accessory. The sample solids were placed on the diamond crystal then sandwiched with the pressure anvil to ensure there were no air gaps within the sample. The FTIR sample chamber was purged with dry nitrogen gas before the collection of any data.

4.6.4.2. Nuclear Magnetic Resonance Sample Preparation and Imaging (NMR)

NMR samples were prepared by dispersing 0.25 mL reagent solution in 0.75 mL of acetonitrile-d\(_3\). NMR spectra were obtained on a Bruker Avance 300 MHz high-resolution NMR spectrometer equipped with a 5mm BBO probe. Chemical shifts are reported in ppm relative to TMS as calibrated by internal TMS for CD\(_3\)CN and by the residual proton signals for other solvents.
4.6.4.3. Transmission Electron Microscopy / Energy Dispersive X-Ray / Selected Area Diffraction Analysis (TEM/EDS/SAED)

Transmission electron spectroscopy data was obtained on a FEI G2 F30 Tecnai TEM utilizing an accelerating voltage of 300 kV. TEM samples were prepared by sonicating the powders in acetonitrile and dropping 0.5 µmL of solution onto a 3 mm, 400 mesh copper grid with formvar. Acetonitrile was allowed to evaporate or wicked away with a kimwipe prior to loading into the microscope. EDS data was obtained in the TEM using an Oxford Inca or Bruker attachment and a XFlash 5010 detector using a 3 nm beam spot. SAED data was collected by utilizing the SAED aperture and subsequent beam block attachment.

4.6.4.4. X-ray Photoelectron Spectroscopy (XPS)

XPS data was obtained with a VG Scientific MKII system using an Al Kα anode as excitation source (hv = 1486.6 eV) operated at 10kV and 20 mA emission. The pressure in the chamber during analysis was less than 5x10⁻⁸ mbar with a sampling depth of 3-10nm.

4.6.4.5. Raman Spectroscopy

Raman data was obtained on a Thermo Fisher DXR Raman Microscope with a laser wavelength of 532 nm, laser power of 5 mW, and an aperture slit of 50 µm with a spot size of 2.1 µm. Scan range is 67 – 3500 cm⁻¹ with an estimated resolution of 5.5 – 8.3 cm⁻¹, a grating of 900 lines/mm, and an exposure time of 8 sec for a total of 16
exposures. Solid samples were placed inside nitrogen filled quartz fluorometer cells. Minimal background noise from the quartz cells was subtracted from sample data.

4.6.4.6. X-Ray Diffraction Analysis Spectroscopy (XRD)

XRD data for air sensitive scans was obtained by placing roughly 20 mg of the silicon nanosheet sample inside a Bruker A100B33 “airtight specimen holder” with dome like x-ray transparent cap for environmentally sensitive materials. Sample reception is a diameter of 25 mm and 1 mm depth. The sample was analyzed on a desktop Bruker D2 Phaser system equipped with a Lynxeye 1D detector, a 2-theta range of ten to seventy degrees, and a step size of 0.02 degrees.

Samples exposed to atmospheric conditions were analyzed by a Scintag SCS2000 equipped with a high-resolution solid-state silicon/lithium detector and a 2-theta range of three to eighty-three degrees, step size of 0.03 degrees, and a scan rate of one degree per minute. All samples were stored under nitrogen prior to analysis.
Chapter 5: Future Directions and Conclusions

5.1. Future Directions

5.1.1. Fabrication of coin-cells based on TEGylated Silicon Nanoparticles

In order to evaluate the Coulombic efficiency of the silicon nanoparticles, a coin-cell can be assembled and subjected to galvanostatic cycling experiments to simulate charge and discharge scenarios.\(^{227,247}\) The TEGylated Si nanoparticle active material can be loaded into a coin-type cell, along with an appropriate binder such as polyvinylidene fluoride (PVDF) or carboxymethyl cellulose/styrene butadiene rubber (CMC/SBR), and Super S carbon black as a conduction diluent in order to form the anode.\(^{363,364}\) Weight percentages of coin-cell materials vary according to experimental parameters\(^{258}\) while electrolyte solutions typically consist of 1 mol/L LiPF\(_6\) in a 1:1 mixture of ethylene carbonate/dimethyl carbonate.\(^{365}\) Finally, copper foil can be utilized as the current collector for the anode. Full charge and discharge testing would be performed over the voltage range of 0–2 V while current density could be held stationary to determine capacity retention or increased steadily from 50 mA/g to 1000 mA/g in order to elucidate rate capability.\(^{366}\)

5.1.2. Surface Passivation of Silicon Nanosheets

Due to the highly reactive nature of the silicon nanosheets, they must continuously be handled under inert atmosphere, as evidenced by the oxidation of the SiNSs in atmospheric conditions prior to Raman, EDS, and XRD analysis. It is proposed
that the passivation of the nanosheets with various functional groups including hexene\textsuperscript{188}, octene, octyne, TEG and differing phenyl based ligands\textsuperscript{177,187} will create air stable structures that can be more easily characterized.\textsuperscript{14,194} The introduction of organic groups on silicon nanosheets through \textequivSi–C bonds is a plausible approach to obtaining silicenes capped with organic molecules. Functionalization of layered silicon nanosheets with organic groups is shown to encourage exfoliation and aid in the management of interlayer spacing. The addition of the organic ligands also increases the dispersion of the silicon sheets in organic solvents as well as prevents future hydrolysis and/or oxidation reactions, due to the formation of a hydrophobic surface surrounding the silicon. Figure 5.1 demonstrates the oxidation of CaSi\textsubscript{2} by \([\text{FeCp}_2][\text{BF}_4]\) followed by the viable binding modes of various unsaturated organic ligands on Si nanosheet surface.

\textbf{Figure 5.1.} Oxidation of CaSi\textsubscript{2} by [FeCp\textsubscript{2}][BF\textsubscript{4}] followed by demonstration of possible binding modes of various unsaturated organic ligands on Si nanosheet surface.
mixture can be carried out by a simple filtration and wash process, yielding air stable, functionalized silicon nanosheets. In order to increase the likelihood of Ca\(^{2+}\) and Fe\(^+\) removal, a chelating agent such as tetramethylethlenediamine (TMEDA) can be introduced to bind to the metal ions, preventing further interactions of the metal atoms with the reactive silicon nanosheets.

5.1.3. Oxidation of Silicon Nanosheets

The silicon equivalent of graphene, silicene, has progressively increased its scope of impact due to its programmable electronic properties and its compatibility with the current silicon-based technology. For example, the Dirac cone produced by the low-buckled arrangement of silicene facilitates the opening of a band gap and in the presence of an electric field fulfills the possibility of silicon anodes\(^{184}\) and room temperature field-effect transistors\(^{197}\). Successful synthesis of silicene has been achieved by either the use of a stabilizing substrate or as demonstrated by the oxidative reduction of CaSi\(_2\) with [FeCp\(_2\)][BF\(_4\)].

Silicene, with its repeating system of conjugated double bonds, can be considered a silicon analog to a reactive polyacetylene in 2D and as such can be functionalized or doped in much the same way. Generally, the functionalization of polyacetylene can be achieved by attaching a functional group to one or both sides of the acetylene monomer (mono/di-substituted acetylene), and then transforming the functionalized monomer into the subsequent polymer by employing a heavy metal catalyst.\(^{367-371}\) However, modification of the polyacetylene double bonds does not occur after polymerization is complete. With silicene, this is not the case. Owing to its weak Si-Si \(\pi\) bonds, silicene can
easily be reacted with an assortment of reagents ranging from amines to halides and olefins.

5.1.3.1. Addition of Halogen Atoms to Silicon Nanosheets

It was initially demonstrated by the 2000 Nobel Prize winners Shirakawa, MacDiarmid, and Heeger that whenever polyacetylene was doped with chlorine, bromine, or iodine vapor, uptake of halogen atoms occurred, resulting in an increase in the conductivity of the polyacetylene film at room temperature.\textsuperscript{367,372} This same concept of the halogenation of silicene has been studied via first principle calculations,\textsuperscript{373} however little to no experimental evidence has been produced. Halogen atoms passivate silicene via the unpaired electrons of silicon atoms at the silicene surface. Similar configurations such as the top, chair-like, and boat-like configurations may form just as during the full hydrogenation of silicene. Fully halogenated silicene with these configurations possess negative formation energies, indicating that they may be thermodynamically possible. The formation energy of fully halogenated silicene in the chair-like configuration is the lowest and thus most likely formed.\textsuperscript{297} For fully halogenated silicene with a specific configuration, the formation energy increases from fluorine to iodine meaning that halogenation is less likely to occur as the atomic radius of the halogen atom increases.\textsuperscript{374} Gao, Zheng, and Jiang showed through DFT calculations that, when compared to hydrogenated silicene containing indirect band gaps, the halogenation of silicene produced direct band gap materials with lower band gap energies, which are better suited for semi-conductor usage.\textsuperscript{375}
It is proposed to form a halo-silicane from the silicene sheets with a halogen vapor such as Cl₂, Br₂, or I₂ in order to study the effects of halogenation upon the structure and electronic properties of the silicene sheet. This can be achieved in a relatively simplistic manner. Following the synthesis of the brown silicene sheets, the introduction of the halide vapors must be achieved according to the physical state of the halide reactant. For solid iodine, two reaction flasks can be attached, one containing iodine initially cooled by a liquid nitrogen bath, and the other flask containing the silicene sheets. The flasks can be evacuated, sealed, and pumped under dynamic vacuum for 24 hours. Iodine, when warmed to room temperature, will sublime, exposing the silicene sheets to the reactive halogen. When the reaction is complete, a non-polar solvent such as toluene or hexanes can be used to wash away any excess iodine.

To react silicene with solid iodine or liquid bromine, the silicene sheets can be sealed in a reaction flask, the flask evacuated, then filled with inert atmosphere. Solid iodine or liquid bromine can be dissolved in acetonitrile, which can then be injected by syringe, or transferred via cannula to the reaction flask containing the silicene sheets. Hexanes or acetonitrile can be used as a suitable solvent to remove any remaining iodine or bromine. With gaseous chlorine, the silicene sheets can either be suspended in hexanes under an inert atmosphere while the chlorine gas is bubbled through the mixture, or the chlorine gas can be pumped into the reaction flask reacting with the exposed silicene sheets for 1-2 hours. Again, hexanes or acetonitrile can be used to remove any unreacted chlorine from the silicene surface.
5.1.3.2. Reaction of Silicon Nanosheets with Silver Nitrate

Researchers have used Ag(111) as a support substrate during the synthesis of single layer\textsuperscript{283,292} and multilayer silicene.\textsuperscript{299,376} The Shockley state in the Ag(111) surface leads to charge transfer from the silver substrate to the silicene layer, ultimately aiding in the stabilization of the silicene sheet.\textsuperscript{280} Similarly, preparation of graphene oxide (GO) containing silver nanoparticles (AgNPs) has become a popular research topic in recent years.\textsuperscript{377–381} The addition of silver atoms to the electron rich graphene oxide surface has been achieved via a facile synthetic method based on electrostatic interactions between the oxygen containing functional groups and the silver ions. The silver ions are then reduced by ascorbic acid to form AgNPs anchored to the surface of the GO sheet. The graphene oxide acts as a support system for the growth and stabilization of the silver nanoparticles, while the electron dense oxygen sites anchor the silver nanoparticles to the GO.

It may be possible to synthesize silver loaded silicene sheets derived from the reaction of AgNO\textsubscript{3} and silicene in acetonitrile. The silver does not alloy with the silicon, however the positive charge on the silver ions may stabilize the charge density in the

\textbf{Figure 5.2.} Silicene sheets (brown circles) containing silver nanoparticles derived from AgNO\textsubscript{3}.\textsuperscript{235}
silicene sheets in a manner comparable to the way the silver substrate stabilizes the epitaxial silicene layers. With the addition of ascorbic acid, the silver ions are reduced to silver atoms, which form colloidal AgNps on the surface of the silicene sheet (Figure 2).

It is possible that the AgNPs will prevent the aggregation of silicene flakes into multiple layers, yielding single layer silicene. In addition, the charge transfer from the silver nanoparticles to the silicene sheet may alleviate the buckling often found in free standing silicene.280

Silver/silicene nanomaterials can be prepared by stirring AgNO₃ dissolved in acetonitrile at a low concentration (< 5mM) with a slurry of silicene sheets in acetonitrile (< 1 mg mL⁻¹) under a nitrogen atmosphere.381 Ascorbic acid dissolved in acetonitrile is then slowly added to form the silver nanoparticles. Ultrasonication is suggested to prevent aggregation of the nanoparticles and silicene sheets in solution. The size of the AgNPs can be controlled by varying the AgNO₃ concentration and reaction temperature.380 TEM images obtained by Cobos et al. show AgNPs with mean diameters of 3.1 nm were obtained with 1.5 mM AgNO₃ solutions and temperatures around 60 °C while temperatures of 80 °C and concentrations of 2.0 mM produced AgNPs with a mean diameter of 6.1 nm.380 Characterization methods may include transmission electron microscopy to find the diameters and size distributions of the AgNPs, x-ray photoelectron spectroscopy to identify the Ag₃d₃/2 and Ag₃d₅/2 peaks signifying the metallic character of the AgNPs, x-ray diffraction spectroscopy to show the crystal planes of the AgNPs, and UV-Vis which can show the characteristic surface plasmon resonance band of the AgNPs. Raman spectroscopy may be able to show a shift in the silicene D and G bands to lower wave numbers signifying an increase in the silicene sp² character.
due to the partial reduction of silicene as a consequence of the attachment of AgNPs to the silicene surface. Possible uses of Si/AgNPs nanomaterials include antibacterial properties and electronically conductive pastes.\textsuperscript{382} Ma et al. found that silver nanoparticles attached to graphene oxide exhibited enhanced antibacterial activities in comparison to that of AgNPs.\textsuperscript{377} In addition, AgNPs may improve the electrical conductivity of silicene sheets by creating a charge transport bridge between the silicene layers.\textsuperscript{383–385}

\section*{5.2. Conclusion}

Mechanochemical synthesis via reactive high energy ball milling (RHEBM) is an efficient, top-down approach to the synthesis of TEGylated silicon nanoparticles. These 0D silicon nanoparticles can be further employed as precursors for energy storage devices, solar cells, semiconductors, and light emitting diodes. Along with electronic applications, multiple biocompatible uses including molecular imaging, drug delivery, and photodynamic therapies may be possible with further modification of the silicon surface.

The surface composition and optical properties of the silicon nanoparticles have been methodically characterized to confirm the synthesis of passivated silicon nanoparticles via RHEBM. Due to the polarity of the resultant surface ligand, a normal phase silica gel chromatography column technique has been developed to purify the passivated Si NPs. The hydrodynamic diameters and size distribution of the separated silicon nanoparticles have been characterized by DLS and TEM while NMR, FTIR, XPS and EDS were employed to thoroughly investigate the surface structure of the TEGylated
silicon nanoparticles. UV-Vis and PL results indicate the creation of a direct band gap as evidenced by an absorption in the UV region as well as an accompanying luminescent emission in the visible region.

Water soluble TEGylated silicon nanoparticles were synthesized through the application of [2+2] cycloaddition chemistry using silicon wafers and triethylene glycol monomethyl monopropargyl ether. The attached ligand is ideal for the modification of nanomaterials based on its inherent biocompatibility and water solubility. $^{13}$C-NMR and FTIR results confirmed the formation of covalent Si-C surface bonds while TEM images indicated possible interdigitation of the Si surface bound ligand, creating a bimodal size distribution. In addition, the TEGylated silicon nanoparticles, with an average size of 6.7 nm and a calculated Si core diameter of 3.1 nm, exhibited vastly improved solvent compatibility compared to alkyl passivated nanoparticles while maintaining the strong blue photoluminescence associated with similarly sized unmodified nanoparticles as demonstrated by a visible luminescence at 470 nm.

The oxidation of CaSi$_2$ by [FeCp$_2$][BF$_4$] is another effective one-step method for the production of silicon nanomaterials. Due to their compatibility with existing technology, there is a large focus on the implementation of the Si nanosheets in electronic applications such as lithium-ion batteries, solar cells, and supercapacitors. While there may not be any current biomedical applications of Si nanosheets, 2D silicon is anticipated to be an attractive candidate for future biosensors, as other 2D materials have shown superior performance values when compared to the use of conventional 0D, 1D, and 3D nanostructures.
Employment of a gentle, one-electron oxidizer has allowed for the large-scale solution synthesis of ultrathin silicon nanosheets via liquid oxidation and subsequent exfoliation of Ca\(^{2+}\) from CaSi\(_2\). The Ca\(^{2+}\) ions were shown to be removed from between the Si layers without damage to the original Si framework leading to the separation of thin silicon sheets while the oxidized Ca was isolated the form of Ca(BF\(_4\))\(_2\). The obtained silicon sheets demonstrate varying levels of thickness as well as excellent crystallinity as demonstrated by TEM, EDS, and XRD data while SAED measurements showed a $\sqrt{3} \times \sqrt{3}$ honeycomb structure with a Si-Si bond distance of 2.12 Å.
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Biography

Jamie L. Armstrong was born on May 15, 1983, spending her childhood in the small village of Greensburg, Louisiana, before moving to Baton Rouge then to Walker, Louisiana. She is an alumnus of Walker High School where she was the president of the Walker High School Marching Band and member of the Livingston Parish Honor Band. Upon receiving a full scholarship to attend Louisiana State University, she double majored in chemistry and sociology and was a recipient of the STEP through STEM scholarship, Robert Noyce Scholarship, and member of the Dean’s List for the duration of her studies. After graduation, Jamie spent six years as a Radiochemistry Analyst, Project Manager, and Lead Laboratory Analyst at American Radiation services where she developed synthetic methods to analyze the activity of naturally occurring radioactive materials. She started her graduate studies at Tulane University in August 2013 and joined Prof. Mark J. Fink’s research group in April 2014. Her graduate research involves the synthesis, characterization, and functionalization of zero and two dimensional silicon nanomaterials for biological and electronic applications. Jamie now lives in New Orleans with her son, two dogs, one cat, and a snake named Pork Chop. She is an avid collector of uranium glass, loves to scuba dive, rides her motorcycle, and plays rugby on the weekends. Jamie is currently employed as a visiting assistant professor at Loyola University of New Orleans.