

**FORMATION AND UNDERSTANDING
OF HIGHLY-CONTROLLED 2- AND
3-DIMENSIONAL NANOARCHITECTURES**

by

Mackenzie G. Williams

A dissertation submitted to the Faculty of the University of Delaware in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Chemistry and Biochemistry

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OF HIGHLY-CONTROLLED 2- AND
3-DIMENSIONAL NANOARCHITECTURES**

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ABSTRACT

The controlled covalent attachment of nanostructures to chemically-modified surfaces is necessary for the fabrication of devices for diverse applications including chemical and biological sensing, catalysis, microfluidics, photovoltaics, and spintronics. Just as important as understanding the bonding processes taking place, is the knowledge of how the procedural processes affect the resulting structure. The work outlined in this dissertation focuses on identifying and characterizing the chemical interactions taking place during the coupling of molecular- and nanometer-scale structures to amine- and azide-modified solid substrates. Furthermore, these studies address the importance of tailoring the fabrication process to result in highly-controlled architectures. The emphasis is placed on maintaining control over surface coverage, film thickness, and adsorbate placement. The morphology of the resulting structures is studied using various microscopic techniques and characterization of the attachment chemistry is carried out by utilizing a number of spectroscopic methods. Computational investigations augment the conclusions drawn from the spectroscopic results and provide evidence supporting the newfound understanding of the processes of attachment and their effects on the resulting material.

Chapter 1

INTRODUCTION

Chemical functionalization and modification of surfaces and interfaces has been a major focus of material science for decades. As technology and devices for a myriad of applications approach the micro- and nanoscale, the surface chemistry of these materials plays a larger role defining stability and physical properties of the resulting components. This can be directly observed in examples such as poisoning of chemical sensors [1], adsorbate effects on catalytic activity [2], ramifications of surface defects on charge transfer through electronic components [3,4], or material breakdown of silicon anodes during electrochemical cycling of lithium-ion batteries [5]. As such, a comprehensive understanding of the surface and interfacial interactions taking place in these materials is imperative to producing effective, robust devices.

The formation of well-defined monolayers upon various surfaces is the first step in creating a platform for subsequent controlled chemical modification. Numerous studies have been performed on this topic alone to produce molecular monolayers with finely-tuned dimensional and chemical properties [6–9]. Various systems have been studied on different types of substrates, including silicon, gold, and metal oxides [10–15]. The careful procedures—from cleaning and etching, solution- and vacuum-based deposition, chemical deprotection, and removal of physisorbed species—have been developed and carried out with precision to produce distinct, characterized surfaces [16,17].

These monolayers can serve as a starting point for further modification through subsequent deposition processes or attachment of larger structures such as molecules with interesting photoactive, biological, or electronic properties, including dye molecules, proteins, or carbon nanotubes [9,18,19]. The attachment mechanisms and type of bonding processes taking place at these interfaces must be well-understood for their successful integration into devices aimed toward specific applications. Chapter 3 of this dissertation focuses on the identification and characterization of such attachment processes between carbon nanotubes and molecular monolayers. Molecularly-modified substrates can even serve as the scaffold for the attachment of larger structures such as nanoparticles. Through precise deposition methods, these materials can be built from the bottom up to produce layered nanostructures for devices with predetermined dimensions and physical and chemical properties for applications ranging from catalysis [20,21], solar cells [22], and sensors [23] to micro- or nanoelectromechanical systems (MEMS/NEMS) [24], memory devices [25], and energy storage [26].

Two of the most frequently-utilized approaches for forming layered nanostructures are atomic layer deposition (ALD) and traditional layer-by-layer (LbL) methods. ALD offers an acute level of control over each layer formed and the overall film thickness, with high precision of adsorbate placement at the molecular-level scale [27–29]. Generally, the mechanisms of the chemical processes taking place are known. Additionally, conformal filling over high aspect-ratio features is attainable. However, due to the molecularly-sized (less than 1 nm) building blocks, it is a slow process, especially when thicker films on the order of hundreds of nanometers to microns are desired. ALD processes may also require vacuum conditions to achieve

defect-free films. Nevertheless, the introduction of defects is still possible, which is compounded upon each additional deposition cycle.

On the other hand, traditional LbL techniques such as dip-, spin-, or spray-coating can be used to form much thicker layers in only a few deposition cycles, compared to their ALD counterparts [30–32]. This can also be performed under ambient conditions. Compared to ALD however, the precision over the mono- and multilayers formed is low. In particular, utilizing polymer filler layers may introduce new properties or change the stability of the material. This is complicated by the fact that the term “monolayer” can be deceiving in the context of LbL techniques because the number of deposition cycles usually does not represent a true monolayer in the traditional sense of surface science, in which a single adsorbate is attached to a single binding site of the substrate. Conformal filling over high aspect-ratio features is also problematic with these techniques.

These limitations of ALD and LbL methods are perfectly acceptable for the fabrication of devices for selected applications, but it is important to understand them and recognize when these limitations will pose an issue to the functionality of the device. One of the challenges addressed in this dissertation is the development of an approach to form layered structures that combine the merits of ALD and LbL methods. This was attained in the process developed for nanoparticle layer deposition and is discussed in detail in Chapters 4 and 5.

The selectivity of this procedure is based on “click chemistry”, which is an umbrella term used to describe an array of modular reactions that meet a number of requirements. These reactions must be fast, simple, selective, and high-yielding [33–35]. They are stereospecific, proceed under mild conditions, and generate few or no

byproducts that can be isolated by means other than chromatography. The best known “click” reaction is the dipolar cycloaddition of azide and alkyne functional groups, resulting in a triazole ring. The reaction scheme for this cycloaddition process is presented in Figure 1.1. It has been widely utilized in various applications, including bioconjugation, materials development, and drug discovery [34,36–43]. While this reaction proceeds thermally to produce multiple regioisomer products, it was reported simultaneously and independently by the groups of Meldal and Sharpless in 2002 that the presence of a copper (I) catalyst forms the 1,4-regioisomer exclusively at room temperature and at a much faster rate [44,45]. This is often carried out practically by the *in situ* reduction of copper (II) in the presence of a reducing agent, but can also be performed directly with copper (I)-containing reagents or by the oxidation of copper metal [46]. The *in situ* reduction by sodium ascorbate is performed in the procedures followed for Chapters 4 and 5. An alternative indirect reduction method in a light-mediated reaction was utilized to form the spatially-controlled organic monolayers in Chapter 6.

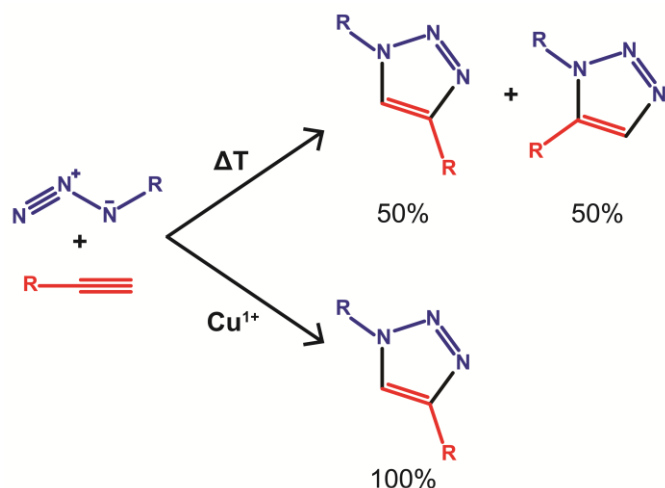


Figure 1.1: Reaction scheme for the azide-alkyne dipolar cycloaddition “click” reaction

In addition to developing the procedure to combine the precision of ALD and the scalability of LbL techniques, it is highly useful to determine the underlying parameters within the procedure that affect the characteristics of the resulting material. Chapter 4 investigates how precise control over the film thickness is maintained and Chapter 5 focuses on the consequences of the substrate and nanoparticle surface functionalization schemes on resulting surface coverage. The knowledge obtained from these conclusions allows for the judicious design of the fabrication procedure to result in structured materials tailored for specific applications. The improved level of control over height precision and surface coverage in nanostructure layers facilitated by “click chemistry” was extended further to include spatial and temporal control of adsorbate placement on a solid substrate. Described in Chapter 6, this procedure presents a gentler substrate modification approach compared to traditional photolithographic methods to result in patterned surfaces.

Nanoparticles and carbon nanotubes are already being integrated into devices, which makes understanding the nature of the chemical bonding paramount to their successful applications. The processes and linkers used to tether these nanostructures to substrates have a profound effect on the stability and electronic structure of the resulting device. Therefore, the overarching goal of the research outlined here was to investigate the covalent attachment of nanostructures to support materials in an effort to control the variables that affect the stability of the resulting interface. This was realized in the development of attachment methods that provide a thorough understanding of the chemistry involved and offer a greater degree of control over coverage, precision, and placement of the adsorbates.

Chapter 2

EXPERIMENTAL PROCEDURES AND INSTRUMENTATION

2.1 Introduction

This section describes the experimental methods that were used to obtain the results for the projects described in subsequent chapters. Respectively, sections 2.2.1 – 2.2.4 provide the procedures for the work outlined in Chapter 3-6. Section 2.3 describes the working principles, instrumentation, and type of information provided of the analytical techniques used in Chapters 3-6. The instrumental parameters used for these projects follow the description of each characterization method in Section 2.3.

2.2 Experimental Procedures

2.2.1 Carbon Nanotube Attachment to Amine-Modified Gold and Silicon

Chapter 3 describes the covalent attachment of carbon nanotubes (CNTs) directly to amino-terminated solid substrates directly through the carbon cage [47]. To prepare the amine-modified gold substrate, a pre-fabricated gold-coated wafer (1000 Å gold supported on silicon with a titanium adhesion layer, Sigma Aldrich) was annealed for 2 hours at 400 K and 10^{-5} Torr. It was immersed in a solution containing 2 mg cysteamine hydrochloride (98%, Acros Organics) in 10 mL *N,N*-dimethylformamide (DMF) (certified ACS, Fisher) for 24 hours followed by rinsing with DMF to remove physisorbed species and drying in a stream of N_2 . To prepare the amine-modified silicon substrate, a phosphorous-doped, n-type, double-side-polished Si(111) wafer

(Virginia Semiconductor Inc., $>0.1 \text{ } \Omega \cdot \text{cm}$ resistivity, $500 \text{ } \mu\text{m}$ thickness) was cleaned using a modified RCA (Radio Corporation of America) procedure [17,48,49]. The hydrogen-terminated silicon wafer was immersed in a 5 mL solution of *tert*-butyloxycarbonyl (t-BOC)-protected 11-amino-1-undecene (AUD) synthesized from a published procedure [50,51]. The solution was fitted with a condenser and deoxygenated and backfilled with dry N_2 for at least one hour. It was maintained under N_2 flow at $110 \text{ } ^\circ\text{C}$ in an oil bath for two hours. Following removal from the solution, the wafer was cleaned with petroleum ether ($40\text{-}60 \text{ } ^\circ\text{C}$) (Certified ACS, Fisher), methanol ($\geq 99.8\%$, Fisher), and dichloromethane (DCM) (99.9% , Fisher). The t-BOC protecting groups were removed by treating the surface with 25% trifluoroacetic acid (99% , Aldrich) in dichloromethane for one hour, followed by rinsing in 10% ammonium hydroxide (29% certified ACS plus, Fisher) for five minutes. It was then rinsed with Milli-Q water ($18 \text{ M}\Omega \cdot \text{cm}$) and dried with N_2 .

A 50% w/v solution of either single-walled non-functionalized carbon nanotubes (NF-CNTs) ($>90\%$, $1\text{-}4 \text{ nm}$ diameter, cheaptubes.com) or carboxylic acid-functionalized carbon nanotubes (COOH-CNTs) (95% , $1\text{-}2 \text{ nm}$ diameter, Nanostructured & Amorphous Materials, Inc.) was prepared in DMF and sonicated (40kHz , Branson 1510) in ice-cold water for at least one hour to achieve a well-dispersed solution. Carbon nanotube attachment was promoted by sonicating an amino-terminated wafer in the CNT solution in an ice-cold water bath for 3 hours, followed by rinsing with methanol and Milli-Q water to remove physisorbed species and drying in a stream of N_2 .

To confirm that the sonication-assisted process does not induce attachment with a chemically-inert monolayer, the procedure was also performed with the t-BOC-

protected AUD-modified silicon. To prove that bonding occurs between the surface amine groups and the CNT cage, a gold wafer was prepared with a monolayer of tertiary amine-modified tail groups before reaction with the CNTs as a control sample. This was prepared by immersing the cleaned substrate in a solution of 2-dimethylamino ethanethiol hydrochloride (95%, Acros Organics) in ethanol (200 proof, Decon Laboratories, Inc.).

To prove that the carbon nanotubes were present on the surface following the rinsing steps, scanning electron microscopy and atomic force microscopy were utilized. Transmission electron microscopy was used to determine the average diameter of the nanotubes to confirm that individual carbon nanotubes were attached to the surface. To investigate the binding processes taking place between the modified substrates and carbon nanotubes and compare attachment between functionalized and non-functionalized carbon nanotubes, X-ray photoelectron spectroscopy and time-of-flight secondary ion mass spectrometry were used. The spectroscopic results were supplemented with computationally-predicted spectra; computational methods were also used to compare the relative energies of attachment products.

2.2.2 Nanoparticle Layer Deposition for Highly-Controlled Mono- and Multilayers

Chapter 4 focuses on a procedure for the formation of nanoparticle mono- and multilayers exhibiting a large degree of control over surface coverage and film thickness [52]. To prepare the azide-modified gold substrate, a gold-coated silicon wafer (with titanium adhesion layer) was cleaned with piranha solution to remove organic contaminants. The wafer was immersed in a 3:1 (v/v) sulfuric acid (98%, Fisher): hydrogen peroxide (30%, Fisher) solution for five minutes, followed by

immersion in Milli-Q water for five minutes. They were then rinsed in hydrochloric acid (37%, Fisher), and Milli-Q water, and dried in a stream of nitrogen gas. The wafer was finally immersed for 24-36 hours in a 7 mM ethanolic solution containing 1-azidoundecan-11-thiol (96%, Krackeler Scientific Inc. or synthesized following a previously-published procedure [53]). The wafer was then removed and rinsed twice with ethanol, once with each DCM and Milli-Q water, and dried in N₂ gas.

Alkyne-modified nanoparticles were prepared based on a previously-established procedure [54]. Equal volumes (218 μ L) of 4-pentyn-1-ol (97%, Aldrich) and tetramethyl orthosilicate (98%, Aldrich) were stirred in 10 mL of toluene (>99%, Fisher) at room temperature for 24 hours. Silica nanoparticles (40 mg, 80 nm diameter, dried, Nanocomposix) were dispersed in 2 mL toluene and added to the solution. The solution was stirred for 24 hours at 80 °C, then cooled to room temperature. The nanoparticles were collected by centrifugation and underwent five cycles of washing in methanol and collection by centrifugation. They were then dispersed in methanol for further use.

To prepare azide-modified nanoparticles, silica nanoparticles (50 nm diameter, 10 mg/mL in water, Nanocomposix) were transferred to ethanol by dispersion into a series of ethanol/water solutions of varying ratios (1:1, 3:2, 1:0 and 1:0) [55]. The nanoparticles were then transferred to toluene by dispersion in a series of toluene/ethanol solutions of varying ratios (1:1, 3:2, 1:0 and 1:0). Tetramethyl orthosilicate (218 μ L) and 2-azidoethanol (36 μ L, 95%, MolPort) were stirred in 10 mL toluene at 80 °C for 24 hours. The nanoparticles dispersed in toluene (2 mL) were added to the solution and refluxed under nitrogen for 24 hours. The solution was cooled to room temperature and the nanoparticles were washed five times with

methanol and collected by centrifugation. They were dispersed in methanol for further use.

To form the first nanoparticle layer, the alkyne-modified 80 nm nanoparticles (~3 mg/mL) were added to a methanol:water (4:1 by volume) solution. The azide-modified substrate was added to the solution with catalytic amounts of copper sulfate pentahydrate (>99%, Fisher) and sodium ascorbate (>99%, Fisher). The solution was sonicated for 24 hours. The wafer was then rinsed in ethanol (twice), DCM, and ethanol (twice more). The wafer was then sonicated in ethanol for 30 minutes to remove physisorbed nanoparticles, followed by rinsing in ethanol (twice) and drying in a stream of nitrogen.

To create the second layer of nanoparticles, a solution containing the 50 nm azide-modified nanoparticles in methanol:water (4:1 by volume) was drop cast onto the sample supporting the nanoparticle monolayer. The system was incubated until dried, then rinsed with ethanol, DCM, water, and ethanol. The wafer was sonicated for 30 minutes in ethanol to remove physisorbed nanoparticles and dried in a stream of nitrogen. The third layer of nanoparticles was created by incubating the wafer containing the double layer of nanoparticles covered by a drop of solution containing 80 nm alkyne-modified nanoparticles and trace amounts of copper sulfate and sodium ascorbate in 4:1 methanol:water (by volume). The sample was rinsed with ethanol, DCM, water, and ethanol, and sonicated for 30 minutes in ethanol, followed by drying in a stream of nitrogen.

A titration control experiment was independently performed by sonicating the azide-modified gold substrate or nanoparticle monolayer sample for 24 hours in a solution containing 4:1 (by volume) methanol:water, ~ 15 mM 5-hexynoic acid (97%,

Aldrich), and catalytic amounts of copper sulfate and sodium ascorbate. The wafer was then rinsed with ethanol, DCM, water, and ethanol, then dried with N₂ gas.

To determine how effectively this layer-by-layer method forms nanoparticle layers, scanning electron microscopy was used. This technique permits confirmation of surface coverage but does not, by itself, allow for determination of nanoparticle layer height. Atomic force microscopy was used to confirm the formation of a single nanoparticle monolayer. Beyond one layer, a focused ion beam was used to mill through the nanoparticle layers and the resulting surface was observed with scanning electron microscopy to determine film thickness. While microscopy techniques confirm the formation of highly-controlled nanoparticle multilayers, they cannot confirm binding by “click chemistry”. To do so, Fourier transform infrared spectroscopy and X-ray photoelectron spectroscopy (supplemented with computationally-predicted binding energies) were performed.

2.2.3 Formation of High-Coverage Magnetic Nanoparticle Monolayers by “Click Chemistry”

The work on using “click chemistry” to form covalently-bound nanoparticle layers on a modified substrate was expanded to magnetic materials. Chapter 5 describes the work performed to “click” magnetic nanoparticles onto a surface and to understand the reasoning behind the high surface coverage achieved [56]. The azide-modified gold substrate was produced following the same procedure outlined in Section 2.2.2. To produce alkyne-modified magnetic iron oxide nanoparticles, 1 mL of commercially-available 20 nm diameter Fe₃O₄ nanoparticles (5 mg/mL in toluene, Fisher) was sonicated for 20 minutes with 1 mg 10-undecynylphosphonic acid (>95%,

Sikemia). The nanoparticles were washed five times in hexanes (Certified, Fisher) and collected via centrifugation, then dispersed in hexanes for further use.

To deposit a layer of nanoparticles on the functionalized substrate, a solution of 0.5 mL of alkyne-modified iron oxide nanoparticles and 4:1 (by volume) dimethyl sulfoxide (>99%, Fisher):Milli-Q water was created. Catalytic amounts of copper sulfate pentahydrate and sodium ascorbate were added to this solution. The azide-modified gold substrate was either sonicated or stirred for 48 hours [57] in this solution, followed by rinsing with ethanol, DCM, and ethanol. It was then sonicated for 30 minutes in ethanol to remove physisorbed species.

The formation of a high-coverage nanoparticle monolayer was confirmed using scanning electron microscopy and atomic force microscopy. Fourier transform infrared spectroscopy and X-ray photoelectron spectroscopy were used to confirm the presence of the nanoparticles on the surface and to confirm attachment by “click chemistry”. To explain the extraordinarily high surface coverage achieved, density functional theory calculations were performed to compare the relative energies of the reaction intermediate structures.

2.2.4 Patterning of Self-Assembled Monolayers by “Click Chemistry”

Chapter 6 describes a method for achieving spatial control of fluorinated monolayers on azide-modified gold substrates facilitated by indirect copper (II) photo-reduction [58]. To produce the azide-terminated self-assembled monolayer on gold, a pre-fabricated gold-coated silicon wafer was prepared using the same procedure described in Section 2.2.2. In this case, the 1-azidoundecan-11-thiol was synthesized following a modified procedure [53]. The details of the modified procedure are described in Section 2.2.4.1.

To 1 mL of methanol, 5 μ L 3,4,5-trifluorophenylacetylene (Aldrich^{CPR}, Aldrich), 4.3 mg Irgacure 819 photoinitiator (BASF), and 5.3 mg copper sulfate pentahydrate were added. The solution was mixed thoroughly and stored in the dark for no more than six hours prior to the irradiation process described below. Following the substrate modification and washing process, the alkyne solution was drop cast onto the wafer which was then covered with a coverslip and photomask. The sample was irradiated between glass slides for five minutes using an Omnicure S2000 lamp with 365 nm light at an intensity of 30 mW/cm². The wafer was then immediately rinsed with ethanol (twice), DCM, ethanol (twice) and dried in a stream of nitrogen.

Confirmation of successful surface patterning was achieved by X-ray photoelectron spectroscopy in mapping mode. The surface species of the irradiated and masked regions of the sample were compared using high-resolution X-ray photoelectron spectroscopy. Computationally-predicted binding energies were compared to the high-resolution spectra to confirm attachment by “click chemistry.” Mapping mode was also performed on a control series to conclude that indirect copper reduction was the mechanism by which patterning occurred.

2.2.4.1 Modified 1-Azidoundecan-11-thiol Synthesis Procedure

1-Azidoundecan-11-thiol (**1**) was synthesized with high purity according to the previously-published literature precedent [53] with optimization (Scheme 2.1). Alternative storage methods of **1** were explored to decrease the future oxidation and disulfide formation of the product, which is not shelf-stable. The thioacetate intermediate (**2**) produced in this synthesis is much more stable and was chosen as the optimal intermediate for long-term shelf storage. Therefore, only a small amount of 1-

azidoundecan-11-thiol (**1**) could be synthesized at a time to avoid compound degradation.

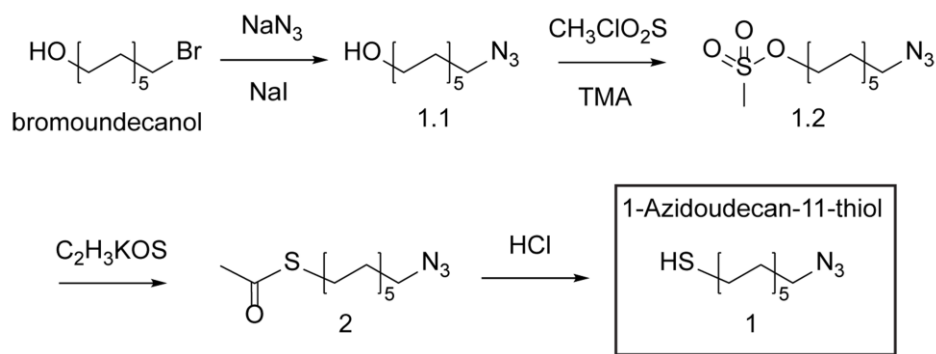


Figure 2.1: Reaction scheme for the synthesis of 1-azidoundecan-11-thiol

To synthesize 1-azidoundecan-11-ol (**1.1**), 1 molar equivalent (eq.) bromoundecanol (97%, Acros), 2 molar eq. sodium azide (99.99%, Aldrich), and 0.5 molar eq. sodium iodide (Certified, Fisher) were combined in anhydrous DMF. The flask was evacuated and backfilled with N_2 and the solution was heated at 60°C while stirring for 24 h. Vacuum was pulled on the DMF for 15 minutes prior to its use to remove volatile degradation products. The reaction was quenched with water. The aqueous layer was extracted with diethyl ether (Lab grade, Fisher) three times. The organic phase was washed with water (twice), then brine, then dried over MgSO_4 (Certified, Fisher) and collected via rotary evaporator. Characterization of **1.1** was performed with proton nuclear magnetic resonance (^1H NMR) spectroscopy at 400 MHz with CDCl_3 as the solvent. The results were consistent with those reported in the literature [53].

To synthesize 1-azidoundecan-11-methylsulfonate (**1.2**), 1-azidoundecan-11-ol (**1.1**) (1 molar eq.) and methanesulfonyl chloride (3 molar eq.) (99.5%, Acros) were combined in anhydrous tetrahydrofuran (99%, Aldrich) under N₂, which was distilled from sodium/benzophenone. While stirring, 3 molar eq. neat trimethylamine (Peptide synthesis grade, Fisher) was added drop-wise over five minutes. The reaction was allowed to proceed at room temperature while stirring for two hours, after which, ice-cold water was added. The solution was extracted with diethyl ether twice and the organic phase was washed one time each with 1M hydrochloric acid, water, sodium bicarbonate (Certified, Fisher), and water. The resulting 1-azidoundecan-11-methylsulfonate (**1.2**) was dried over MgSO₄, collected via rotary evaporator and immediately carried through to the next reaction. Characterization of **1.2** was performed with ¹HNMR and the results were consistent with those reported in the literature [53].

To synthesize 1-azidoundecan-11-thioacetate (**2**), 1 molar eq. of **1.2** was combined with 2 molar eq. potassium thioacetate (98%, Acros) in methanol. The solution was degassed for one hour, then refluxed under N₂ for three hours. Excess methanol was removed via rotary evaporator and ice-cold water was added to the product. The product was extracted with diethyl ether (three times) and washed with water (two times) and brine (once), then dried over MgSO₄. Solvent removal by rotary evaporation yielded 1-azidoundecan-11-thioacetate (**2**). The product was purified on a Biotage Automated Flash Chromatography instrument with solvent gradient starting at 20% DCM in hexanes and the product was collected by ultraviolet (UV) spectroscopy at 254 nm and 280 nm. The majority of **2** was stored under argon at -80 °C for future synthesis of the thiol product. ¹HNMR analysis revealed that the product obtained

from column chromatography was very clean and characterization of **2** was consistent with the literature [53]. The signals obtained are as follows: 3.25 (t, 2H); 2.85 (t, 2H); 2.32 (s, 3H); 1.51-1.62 (m, 4H); 1.21-1.35 (m, 14H).

To synthesize the final product 1-azidoundecan-11-thiol (**1**), the remaining isolated 1-azidoundecan-11-thioacetate (**2**) (1 molar eq.) was degassed in methanol for 1 hour. The flask was backfilled with N₂ and concentrated hydrochloric acid (40 molar eq.) was added to the flask. The solution was refluxed for five hours then excess methanol was removed via rotary evaporator. The reaction was quenched slowly with ice-cold water and extracted with diethyl ether (twice). The organic phase was washed with water (twice), dried over MgSO₄. Rotary evaporation yielded a clean final product as determined by NMR analysis. Characterization of **1** was performed with ¹HNMR and the results were consistent with those reported in the literature [53]. The signals obtained are as follows: 3.25 (t, 2H); 2.52 (q, 2H); 1.60 (m, 4H); 1.21-1.42 (m, 14H).

To decrease the possibility of degradation of the **1** to oxidized species or disulfide species, the 1-azidoundecan-11-thiol was immediately divided into individual vials containing ethanol to create the 7 mM ethanolic solutions. Each flask was stored under argon gas at -80 °C so that only one flask could be removed, thawed, and used at a time without disturbing the remainder of the product or exposing it to oxygen.

2.3 Instrumentation and Theory

2.3.1 Nuclear Magnetic Resonance Spectroscopy

Nuclear magnetic resonance spectroscopy is an analytical tool for the identification of different types of atoms within compounds. During NMR analysis, the compound to be characterized is placed in a uniform magnetic field so that the spins of the nuclei align with the field. When electromagnetic radiation in the radio frequency range interacts with the nuclei, the spin is flipped. When the nuclei re-align with the magnetic field, electromagnetic radiation is emitted. The process of nuclei in a magnetic field absorbing and emitting radiation is a phenomenon known as nuclear magnetic resonance and the local chemical environments of the nuclei affect the frequency at which they will undergo resonance. NMR spectroscopy can be performed to target a multitude of specific atomic nuclei but one of the most common targets is that for hydrogen. Referred to as proton NMR spectroscopy or ^1H NMR, the radio frequency applied during spectroscopic analysis is specific to induce nuclear resonance within the hydrogen atoms. Different hydrogen nuclei within the compound will undergo resonance at slightly different frequencies due to the local magnetic fields induced by nearby electrons, a process known as shielding, and can therefore be differentiated from one another. On the other hand, nuclei experiencing the same shielding effects will result in signals at the same frequency, which can be integrated to the relative number of equivalent nuclei. The resulting spectra from ^1H NMR reveal the number of equivalent hydrogen atoms at specific chemical shifts which correlate to the molecule being analyzed and can be used to confirm successful formation of intended product and intermediate structures during a synthesis process.

In this work, ^1H NMR was used to characterize the product and intermediates during the synthesis of 1-azidoundecan-11-thiol. The full synthesis procedure is described in Section 2.2.4.1. Characterization was performed at 400 MHz with an AV400 NMR spectrometer. The samples were solvated in deuterated chloroform. Data analysis was performed with MestReNova software (version 11.0).

2.3.2 Scanning Electron Microscopy and Focused Ion Beam

Throughout the various projects outlined in subsequent chapters, scanning electron microscopy (SEM) was used to observe the morphology of the various systems. SEM is a useful technique for observing micro- and nanoscale structures and like its optical microscopy counterparts, it provides topographical information of the surface being probed. Unlike optical microscopes, which focus light upon the sample, SEM relies on electromagnetic lenses to focus a beam of electrons onto the surface of the sample. This usually takes place under high vacuum conditions, but can be performed in low vacuum or at environmental pressures. Upon striking the surface of the sample, the incident beam emits secondary electrons from the material which are detected and, depending on the origin of these electrons and the type of detector utilized, provide different information about the sample. The incident beam is rastered across the surface resulting in the detected signal being assigned to specific pixels which, together, make up an image representing the surface.

Elastically-scattered electrons from the bulk of the material can be detected using an electron backscatter detector and provide both topographical and compositional information, based on the atomic number of the atoms making up the material. Alternatively, inelastically scattered electrons near the surface can be detected by an in-lens detector, which provides very high-resolution detail of the

surface topography at the nanoscale. Features observed using this technique may appear brighter if they are protruding from the surface (“hills”) because there is more surface area from which electrons can escape, while depressions in the surface (“valleys”) appear darker.

A technique that can be used in tandem with SEM is the use of a focused ion beam (FIB) which involves a beam of ions to sputter away the surface. Rather than just the removal of electrons, the FIB removes portions of the surface and allows one to mill through it to create highly-resolved features. This technique is often used to create thin cross-sections for use in transmission electron microscopy. In the work described here, it was used to obtain cross sections of the nanoparticle layers in order to determine the nanoparticle film thickness.

In Chapters 3 – 5, an SEM equipped with FIB capabilities (Zeiss Auriga 60) was used to observe the morphology of the structures covalently-bound to the substrate (carbon nanotubes or nanoparticles). Images were collected with an in-lens detector, with a working distance of 5.0 mm, and an accelerating voltage of 3 kV (Chapter 3, 4) or 5 kV (Chapter 5). Control experiment images in Chapter 4 were collected with a JEOL JSM-7400F SEM with a 8.0 mm working distance and 15 kV accelerating voltage. The cross-sectional images in Chapter 4 were obtained after using a gallium FIB with an energy of 30 kV and current of 120 pA. The sample was tilted at a 65° angle (the limit of the SEM/FIB stage) and images were collected.

2.3.3 Transmission Electron Microscopy

Transmission electron microscopy (TEM) operates on a similar principle to SEM in that an incident electron beam results in detection of ejected electrons from the material. Unlike SEM however, the incident beam is condensed and focused to

transmit *through* the (very thin) sample and are detected on the other side. Both elastic and inelastic scattering of electrons occur and can result in images that are more highly-resolved than those from SEM. Dark areas in the image result from the transmission of electrons through thicker regions of the sample or through components of the material comprised of higher atomic number atoms due to scattering, while bright regions can be observed from thinner or lower atomic number areas. As such, TEM imaging provides information about both sample morphology and composition. In Chapter 3, a JEOL JEM-3010 TEM operating with an incident electron energy of 300 keV was used to determine the average diameter of individual carbon nanotubes within a bundle of nanotubes.

2.3.4 Atomic Force Microscopy

Another method used to characterize the morphology of a material is atomic force microscopy (AFM). AFM is a scanning probe technique that relies on the piezoelectric effect, in which the physical structure of the material changes linearly in response to applied electricity. In AFM, a cantilever with a tip is brought in close proximity to the sample. A laser is reflected off the top of the cantilever onto a photodiode that records a signal proportional to the deflection of the cantilever. A feedback system adjusts the height of the cantilever in response to the deflection. While the cantilever position remains stationary, the sample is moved laterally in relation to the cantilever so that the tip is rastered across the surface of the sample. This results in the measured signal as a function of location on the sample, allowing for the construction of a map.

AFM is operated in different modes. In contact mode, the tip comes into physical contact with the surface and is dragged along the surface and the measured

signal results from cantilever deflection or adjusted cantilever position based on a feedback loop. A less destructive (to both the sample and the tip), and more commonly-used, method is tapping mode. In tapping mode, the cantilever oscillates at its resonance frequency, which is perturbed upon electrostatic interactions between the tip and the sample. In this case, the perturbation in amplitude of the cantilever oscillation is what drives adjustments to the cantilever height. An image obtained by AFM is a map in which the x-y grid of pixels represents the position on the surface and the color of the pixel indicates the signal obtained, or the height of the sample in that position, resulting in a high-resolution topography map.

In Chapter 3, AFM is used to compare the surfaces before and after addition of the carbon nanotubes. In Chapters 4 and 5, it is used to confirm the presence of a nanoparticle monolayer on the surface. AFM was performed in tapping mode with a Veeco Multimode SPM equipped with either a Nanoscope V controller (Chapters 3, 5) or a Nanoscope Dimension 3100 controller (Chapter 4). In all cases, aluminum-coated tips (Budget Sensors) with a force constant of 40 N/m and a drive frequency of 300 kHz were used. Image analysis was performed with Gwyddion software [59].

2.3.5 X-Ray Photoelectron Spectroscopy

X-ray photoelectron spectroscopy (XPS), otherwise known as electron spectroscopy for chemical analysis is a technique used to analyze the composition of the surface (as opposed to the bulk) of a material. Sensitive only to the top few nanometers of the material (depending on the energy of the X-rays and escaping electrons), XPS can be used to identify the elemental components and oxidative states of the surface. The operating principle is based on the photoelectric effect. X-rays are generated from a source (usually Al or Mg) and upon striking the material, cause the

atoms of the material to emit electrons. These electrons undergo a number of interactions, such as inelastic scattering, excitation, recombination, and trapping within the material, with the result that electrons in the bulk are attenuated and those from only the top few layers are emitted and detected. Electrons originating from near the surface of the material travel through a hemispherical analyzer and are detected. By varying the voltage through the analyzer, it is possible to separate and isolate electrons traveling with different kinetic energies to the detector.

The kinetic energy is directly related to the binding energy of the electron in its original atom and can be calculated from the kinetic energy of the electron, the incident energy of the X-rays, and the work function of the instrument. The binding energy is characteristic of the identity of the element, the orbital from which the electron is ejected, and the chemical environment of the atom. Electrons from specific elements and orbitals are generally known (for example, an electron from the Si 2s orbital has a binding energy of about 150 eV, while one from the 2p orbital is observed around 99 eV). The binding energy shift from the expected binding energy also provides information about the oxidation state of the surface. Electrons from oxidized species typically exhibit a shift to a higher binding energy (for example, the existence of a peak at 103 eV (SiO_x) in addition to one at 99 eV (elemental Si) indicates the presence of oxides on a silicon surface. XPS typically is performed in ultrahigh vacuum (UHV), but some instruments allow for analysis of samples at ambient pressure.

XPS analysis results in a plot of intensity (counts per second) as a function of binding energy. In most cases, a survey spectrum (a lower resolution plot over a large range of binding energies, such as 0-1000 eV) is collected and can be used to provide

a summary of the elements present on the surface. Additionally, high-resolution spectra can be collected for a smaller range of binding energies and can be very useful for identifying the chemical state of a particular element of interest. Another XPS technique, mapping mode, collects information from specific points on the surface in a rastering pattern over the area and constructs a map of the surface showing the elemental composition. XPS can also be used as a quantitative measurement to determine relative surface species concentrations by comparing the intensities of the peaks after taking into account the atomic sensitivity factor for each component, which is a known value related to the detection efficiency of each element and can vary greatly depending on the X-ray source.

In Chapter 3, XPS is used to confirm the changing chemical nature of the nitrogen and carbon species following substrate interactions with carbon nanotubes. Chapters 4 and 5 employ the use of XPS to confirm the disappearance of azide and appearance of triazole ring nitrogen atoms following nanoparticle layer deposition. Chapter 6 relies on XPS for both confirmation of photopatterning and comparison of the surface in masked versus irradiated regions of the sample.

In Chapters 3, 5, and 6, a Thermo Fisher Scientific K-Alpha⁺ instrument with a monochromatic Al K α source ($h\nu = 1486.6$ eV) at a take-off angle normal to the surface and base pressure of 5×10^{-9} mBar was used to collect the data. Survey spectra were collected over a binding energy region of 0-1000 eV with a 100 eV pass energy at 1 eV/step and 10 ms dwell time. High-resolution spectra were collected with pass energy of either 58.7 eV (Chapter 3), 20 eV (Chapter 5), or 60 eV (Chapter 6), with a step size of 0.10 eV, and dwell time of 50 ms. The number of scans ranged from 3 to 50, depending on the spectral region being analyzed to account for differences in

sensitivity. All spectra were calibrated to the Au $4f_{7/2}$ peak at 83.8 eV, except for those collected on silicon (in Chapter 3) which were calibrated to the most intense C 1s peak at 284.6 eV. In all cases, Casa XPS software (version 2.3.5) was used for data processing and peak fitting. In Chapter 6, mapping mode was performed with a spot step size of 200 μm and X-ray spot size of 100 μm . Snapshot spectra were collected and images were processed with Advantage software (version 5.952) and interpolated to 512 points.

In Chapter 4, a PHI 5600 instrument with a monochromatic Al $K\alpha$ source at a 45° take-off angle and base pressure of 1.3×10^{-7} Pa was used to collect spectra. Survey spectra were collected over a binding energy range of 0-1000 eV and high-resolution spectra were collected with a 20 eV pass energy and step size of 0.1 eV; 15 scans were collected per region. All spectra were calibrated to the Au $4f_{7/2}$ peak at 83.8 eV and Casa XPS software (version 2.3.5) was used for data processing and peak fitting.

2.3.6 Time-of-Flight Secondary Ion Mass Spectrometry

Another technique that can be used to identify the chemical species present within the top layers of a material is time-of-flight secondary ion mass spectrometry (ToF-SIMS). SIMS is a surface-sensitive mass spectrometry method that is performed by directing a focused primary ion beam onto the sample surface, causing ejection of atomic and molecular fragments from the top few nanometers of the material. ToF-SIMS can be operated in positive or negative ion mode, in which only positively- or negatively-charged fragments, respectively, are collected. As the emitted secondary ions travel with the same kinetic energy, the time required for individual ions to reach

the detector is a function of their respective masses (i.e. light fragments will travel faster to the detector than heavier ones). The output from ToF-SIMS is a plot of counts as a function of mass-to-charge ratio (m/z). Like XPS, ToF-SIMS is carried out under UHV conditions to prevent collisions between ions and gas molecules in the chamber before detection and to prevent contaminants adsorbing onto the sample surface. SIMS can be performed in static or dynamic mode. The former allows for monolayer-scale surface analysis while the latter permits bulk analysis. Dynamic SIMS can be used in tandem with a sputtering beam to analyze, then remove, multiple layers so that three-dimensional compositional analysis can be performed (“depth profiling”). ToF-SIMS is generally considered a qualitative method; however it can be quantitative if known standards are used for calibration.

In Chapter 3, ToF-SIMS was performed with a TOF-SIMS V (ION-TOF, Münster, Germany) to confirm the presence or absence of fragments that indicate covalent binding between CNTs and chemically-modified substrates. A Bi_3^+ primary ion beam (25 kV) was run in high-current bunched mode to the static SIMS limit of 1×10^{12} ions/cm². The spectra had a mass resolution of $m/\Delta m = 9000$ recorded at $m/z = 29$ and were each collected over an area of $200 \times 200 \mu\text{m}^2$ with a 128×128 pixel density. Both positive- and negative-ion mode spectra were collected but only the negative-ion mode results were analyzed. The extraction cone of the TOF analyzer was held at +2 kV for negative ion extraction, with a post-acceleration of 10 kV and a detector voltage of 9 kV. Peak calibration was performed with ION-TOF measurement explorer software (version 6.3) and all negative-ion mode spectra were calibrated to the following fragments: H^- , H_2^- , C^- , CH^- , CH_2^- , CH_3^- , C_2^- , C_2H^- , C_3^- , C_4^- , C_5^- , C_6^- ,

and C_7^- . Further calibration was performed to the fragment of a single gold atom (Au^-) for all spectra, except those for carbon nanotube powders.

2.3.7 Attenuated Total Reflectance Infrared Spectroscopy

Infrared (IR) spectroscopy is an important vibrational spectroscopic technique that is ubiquitous in all fields of chemistry because it provides information on the types of bonds and functional groups present in a material. The operating principle is that electromagnetic radiation in the infrared region is directed at a material (which can be a solid, liquid, or gas, depending on the instrumental capabilities) and interacts with the molecules of the material. Bonds within a molecule that have a non-zero dipole moment vibrate with characteristic resonant frequencies that can be detected with IR spectroscopy. When infrared radiation of matching frequency interacts with the bond, that energy is absorbed. After interacting with the material molecules, the light is detected. The signal detected at absorbed frequencies is decreased relative to those that are transmitted and the resulting output is a plot of absorbance (or transmittance) as a function of frequency (typically in units of cm^{-1} or wavenumbers).

To decrease collection time, the light can be guided through an interferometer that splits the light so that part of the light interacts with the sample, and part does not. A configuration of moving mirrors within the instrument results in an interferogram from which, by a mathematical process called a Fourier transform, a spectrum of absorbance at different frequencies can be produced. This technique is called Fourier-transform infrared (FTIR) spectroscopy.

Sometimes the signal produced from conventional IR spectroscopy methods is too small to garner useful information for analysis. One approach to overcoming this is by utilizing attenuated total reflectance. Using this method, the sample is pressed

against the face of a single crystal and the light is passed through the crystal where it interacts with the sample at the crystal interface. As the light passes through the crystal and is reflected at the crystal edges, the signal-to-noise is increased. This is especially valuable for systems in which chemical changes of interest at the surface of a material might otherwise be overwhelmed by the bulk. This approach in conjunction with FTIR is referred to as attenuated total reflectance Fourier-transform infrared (ATR FTIR) spectroscopy.

In Chapters 4 and 5, ATR FTIR was used to compare the azide-modified gold surfaces before and after the addition of the nanoparticle layers. An unmodified gold wafer sonically cleaned in ethanol was used as the background signal. Measurements were collected with a Bruker Optics (Billerica, MA) Vertex 70 FTIR spectrometer with a liquid nitrogen-cooled MCT detector. The instrument was equipped with a Bruker Hyperion 2000 microscope attachment and a dedicated single-point ATR attachment with a germanium crystal tip. Spectra were collected over a range of 4000-600 cm^{-1} from 64 (Chapter 5) or 256 (Chapter 4) scans at a 4 cm^{-1} resolution.

2.3.8 Computational Methods

In addition to the numerous experimental techniques outlined above, computational methods are a valuable resource for understanding the chemical reactions taking place on surfaces. A great number of computational methods are used for this purpose, but only one will be discussed here. Briefly, density functional theory (DFT) is a computational modeling method based on the electron density of a system, taking into account the molecular structure, composition, and electron kinetic energies and interactions. It is less computationally expensive than other types of quantum mechanical calculations and it allows for a fundamental understanding of the chemical

processes by predicting energetic profiles and mechanisms as well as providing a baseline for comparison to experimentally-collected binding and vibrational energies. Optimized structures can be predicted by finding the geometries that result in the lowest energy state within a set number of iterations until the desired convergence is reached. The energies of possible reaction products can be compared to their reactants to identify the most likely product and full mechanisms can be predicted by calculating transition states. From the optimized structures, core level binding energies can be calculated to compare to XPS spectra and vibrational frequencies can be predicted to result in expected spectra for comparison to experimental techniques such as IR and Raman spectroscopies.

In Chapters 3-6, DFT computational methods were employed using the Gaussian 09 Suite [60] of programs to compare the relative energies of reaction products or intermediates and/or to predict core level binding energies for XPS comparison. In Chapter 3, semiconducting single-walled carbon nanotube models with (10, 0) chirality and zigzag structure (commonly used in the literature to represent semiconducting carbon nanotubes for computational studies) were built using TubeGen3.4 [61] and imported into Gaussian 09. The amine-modified gold substrate was modeled by cysteamine on a single gold atom and the amine-modified silicon substrate was modeled by 11-amino-1-undecene on a Si_4H_9 cluster. Attachment of the nanotubes onto the substrates was investigated in two different configurations, termed “parallel” ($\parallel$), in which the primary amine of the modified substrate dissociates across a C-C bond that is parallel to the direction of the length of the nanotube, and “non-parallel” ($\perp$), in which the amine dissociates across a bond that is not parallel to the length of the nanotube. Optimization was carried out using the B3LYP functional and

LANL2DZ basis set. The predicted N 1s binding energies were calibrated with a correction factor of 8.50 eV for the LANL2DZ basis set using a previously-published procedure [62]. The predicted N 1s binding energy for the primary amine nitrogen atom was shifted to match the fitted experimental N 1s binding energy for the -NH_2 nitrogen peak. This process has been used in the literature to compare the binding energy differences between nitrogen species [50,63–65].

In Chapters 4 and 5, geometry optimization calculations were performed using the B3LYP functional and 6-311+ G(d,p) basis set to obtain N 1s binding energy predictions for the azide and triazole ring species. The predicted binding energies were shifted by a correction factor of 8.76 eV for the 6-311+ G(d,p) basis set [62]. The azide-modified substrate was modeled with 1-azidoundecan-11-thiol and the attachment of the first layer of nanoparticles was modeled by 1-azidoundecan-11-thiol and 4-pentyn-1-ol bound together by triazole ring formation between the azide and alkyne groups. In Chapter 4, the second layer was modeled by a triazole linkage between 4-pentyn-1-ol and 2-azidoethanol. In Chapter 5, the energies of the one- and two-copper center intermediates were compared using the B3LYP functional and 6-311+ G(d,p) basis set. The terminal alkyne-containing molecule was modeled with 1-hexyne and the copper atoms were stabilized with acetonitrile ligands. The +1 charge on copper was maintained by placing chlorine atoms within close proximity to the copper atoms.

In Chapter 6, geometry optimization was performed to predict core level N 1s and C 1s binding energies using the B3LYP functional and 6-311+ G(d,p) basis set. The predicted binding energies were shifted by a calibration factor of 10.03 eV for N 1s and 11.97 eV for C 1s for the basis set using a previously-published procedure

[62,66]. The azide-modified substrate was modeled using 1-azidoundecan-11-thiol and the attachment following the “click” reaction was modeled by the triazole linkage between 1-azidoundecan-11-thiol and 3,4,5-trifluorophenylacetylene.

Chapter 3

COVALENT ATTACHMENT OF CARBON NANOTUBES TO AMINE-MODIFIED SUBSTRATES DIRECTLY THROUGH THE CARBON CAGE

3.1 Abstract

In this chapter, the chemical processes taking place during the attachment of carbon nanotubes to modified substrates were probed. A fundamental understanding of the covalent interactions between carbon nanotubes and their support materials is vital to maintaining the physical and chemical stability of the interface. Commonly-utilized procedures to result in covalent attachment typically involve interactions between the support materials and the functional groups present on carbon nanotubes; however, this study focused on direct bonding between the modified substrate and the cage of the carbon nanotube. Following process development, microscopic and spectroscopic methods were used to confirm that bonding occurs through the cage of the nanotubes and that, in fact, extra functional groups on the carbon nanotubes are not required for forming a covalently-bound interface. The results of this method offer a greater level of insight into the foundations of carbon nanotube integration into devices and present alternative methods for fabricating robust materials while preserving control over electronic properties. Figures in this chapter are reprinted with permission from [47]. Copyright 2017 American Chemical Society.

3.2 Introduction

The integration of carbon nanotubes into devices spans multiple disciplines for applications including sensors [1,67,68], hydrogen storage [69,70], nanoelectronic devices [71], and field emission devices [72,73]. To preserve the targeted characteristics of the CNTs, such as their unique mechanical or electronic properties, it is very important to maintain a high degree of control over the chemistry of their attachment to various material substrates. To this end, a number of methods have been reported in the literature for the controlled covalent attachment of CNTs to modified substrates. One of the most commonly-practiced methods is the attachment of carbon nanotubes containing functional groups (typically carboxylic acid) to amine-terminated alkylthiol self-assembled monolayers (SAMs) on gold [74–76]. This works well for many cases, however, the stability of the system may become compromised due to the tendency of the SAMs to undergo photooxidation or thermal degradation [13]. To avoid this, attachment of the nanotubes can be performed on organic monolayers (commonly terminated with functionalities such as amines or hydroxyl groups) on silicon [77–79]. This can be completed with or without additional steps to remove the oxidized silicon layer [80].

In both of these cases, coupling usually takes place through functional groups that are located on the ends of the carbon nanotubes, which results in vertical alignment of the carbon nanotubes. Additionally, the presence of these additional functional group linkers can affect the charge transfer through the materials [81–83]. This may be the desired outcome for some applications, but for others, it may be more important to preserve the intrinsic electronic properties of the carbon nanotubes or to have multiple points of attachment along the length of the carbon nanotubes. In this

case, it would be ideal to facilitate bonding directly to the cage of the carbon nanotube itself.

This has been found to be possible with similar caged structures, such as C_{60} buckminster fullerenes [50,84–86]. Moreover, it was concluded that, in the case of phenyl- C_{61} -butyric acid methyl ester, a C_{60} derivative containing an ester functional group, attachment occurs preferentially through the cage rather than the ester [63]. Therefore, the goal of this work was to determine if similar attachment schemes are possible with non-functionalized carbon nanotubes.

Two systems were investigated—silicon and gold substrates functionalized with terminal amine groups. It was hypothesized that non-functionalized carbon nanotubes could be covalently-bound to the substrate by dissociation of the monolayer amine groups across the carbon bonds of the nanotubes. This general scheme can be observed in Figure 3.1. As a point of comparison, carboxylic acid-functionalized carbon nanotubes were also attached to these surfaces. In this case, it was expected that binding by amide formation with the carboxylic acid would occur, but additional attachment events through the carbon cage were also expected. A combination of microscopy and spectroscopic techniques, along with computational methods, was used to examine the chemistry of attachment taking place.

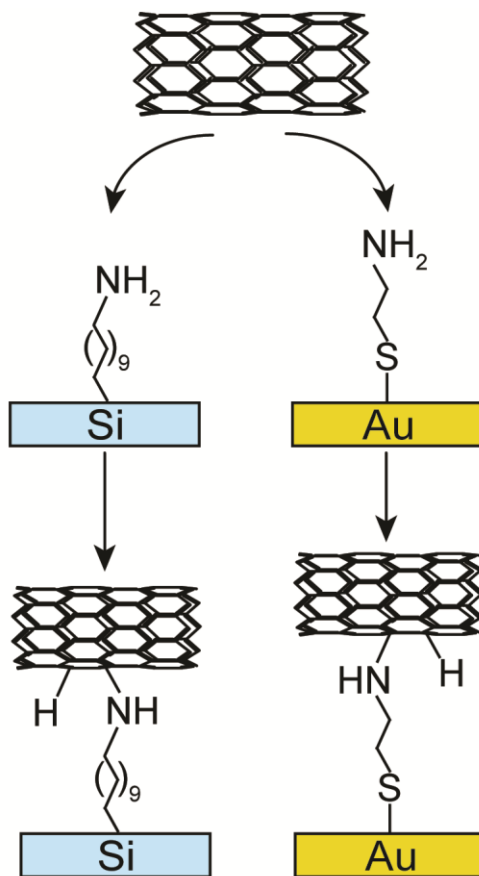


Figure 3.1: General reaction scheme illustrating the attachment of non-functionalized carbon nanotubes to amine-modified gold and silicon surfaces

3.3 Results and Discussion

3.3.1 Confirmation of Carbon Nanotube Presence Following Reaction

Following the sonication-assisted interaction between the modified substrates and carbon nanotube solutions described in Section 2.2.1, SEM was used to confirm the presence of CNTs remaining on the surface after rinsing to remove physisorbed species. Figure 3.2 summarizes the SEM results, comparing the amine-modified silicon before (a) and after the reaction with the NF-CNT (c) and COOH-CNT (e)

solutions. Images (b), (d), and (f) show magnified views of (a), (c), and (e), respectively. Similar images on the amine-modified gold substrate are shown in Figure 3.3.

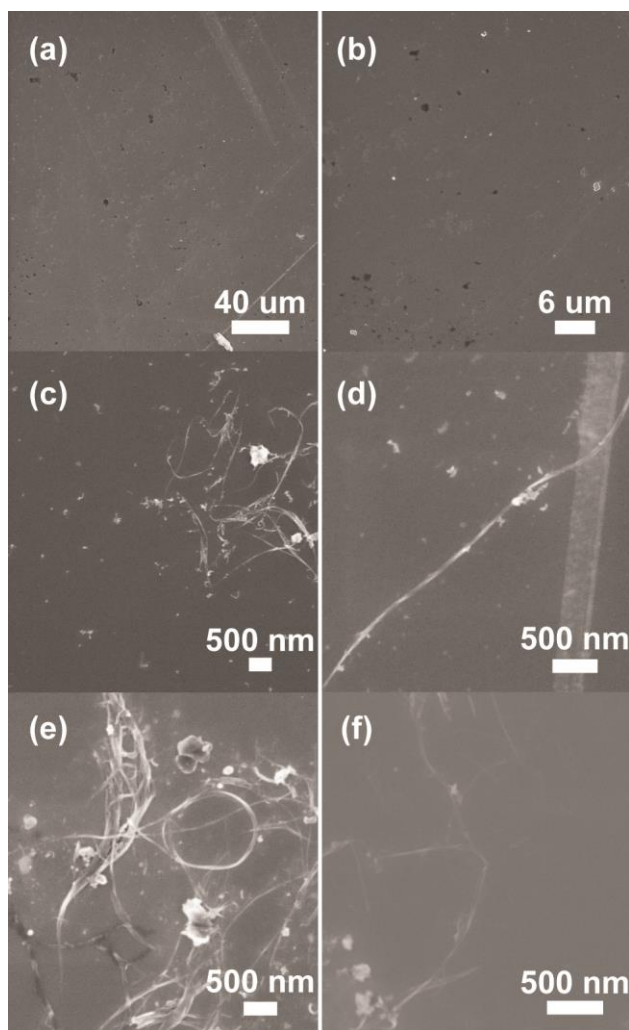


Figure 3.2: SEM images collected from AUD-modified silicon before (a) and after reaction with the non-functionalized (c) and carboxylic acid-functionalized (e) carbon nanotube solutions. Images (b), (d), and (f) show magnified views of (a), (c), and (e), respectively

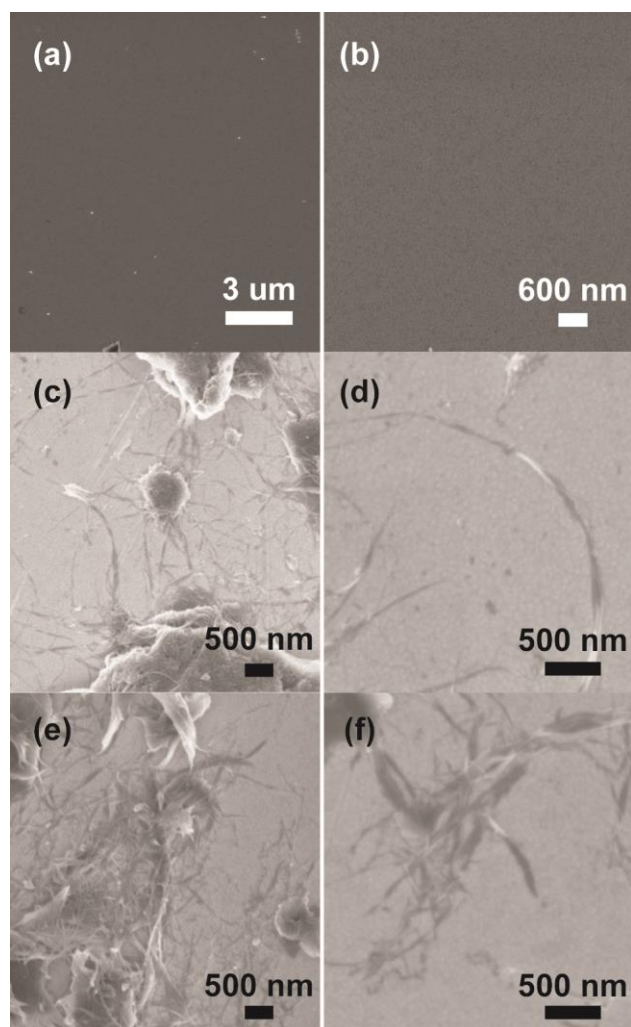


Figure 3.3: SEM images collected from cysteamine-modified gold before (a) and after reaction with the non-functionalized (c) and carboxylic acid-functionalized (e) carbon nanotubes. Images (b), (d), and (f) show magnified views of (a), (c), and (e), respectively

It is clear from SEM studies that both functionalized and non-functionalized carbon nanotubes are observed on the chemically-modified surfaces following the rinsing steps, but that the amine-modified substrates are bare. To confirm that the primary amine functionality on the substrate is necessary for attachment, control

experiments were also performed in which a bare (unmodified) gold substrate and a chemically-inert (t-BOC-protected) silicon wafer were allowed to react under sonication with the CNT solutions. SEM showed that these experiments result in bare surfaces, indicating that the sonication step itself does not induce attachment by damaging the carbon nanotubes. A representative SEM image showing the t-BOC protected silicon following the reaction with NF-CNTs (a) and the amine-terminated silicon following reaction with the NF-CNTs (b) can be observed in Figure 3.4].

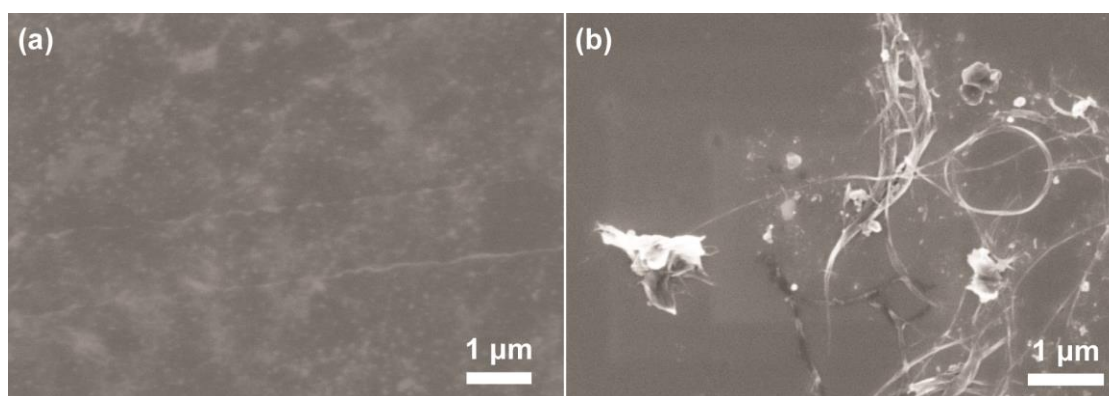


Figure 3.4: SEM images comparing the (a) t-BOC-protected silicon and (b) AUD-modified silicon after reaction with the NF-CNT solution

The features observed with SEM are on the order of tens of nanometers. Manufacturer specifications for the carbon nanotube powders claim that the nanotubes are 1-2 nm in diameter. In this case, the limitations of SEM do not permit the resolution of individual CNTs—instead, the features observed in Figures 3.2 and 3.3 show CNT bundles. This is a good starting point to support the hypothesis of CNT attachment, but alternative methods must be used to provide stronger evidence of individual nanotubes attaching to the substrates. Transmission electron microscopy,

which provides higher resolution than SEM, was used to take a closer look at a single bundle of NF-CNTs. Figure 3.5(a) shows a TEM micrograph of one of these bundles, with the average diameter of the CNTs in the bundle being 1.7 nm, consistent with the manufacturer specifications.

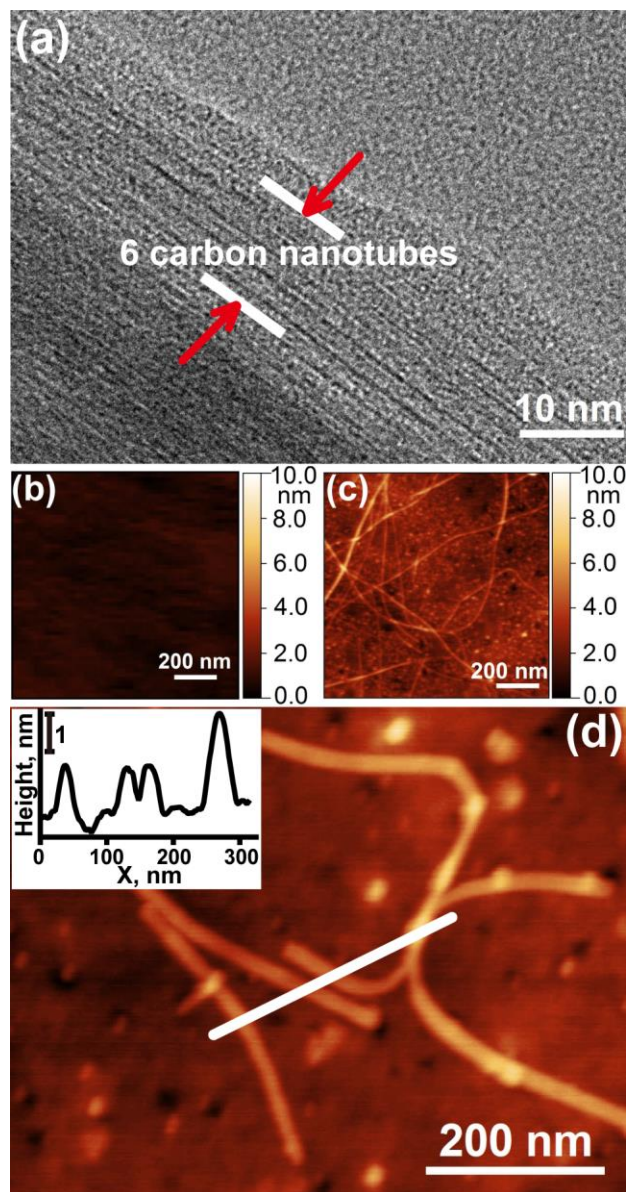


Figure 3.5: (a) TEM micrograph of a bundle of non-functionalized carbon nanotubes. AFM images of the AUD-modified silicon before (a) and after (b) reaction with the NF-CNT solution. Image (d) displays a magnified view of (c); the line profile in the inset reveals the height of the CNT features

The system on the silicon substrate was studied using AFM, as summarized in Figure 3.5, comparing the amine-functionalized surface before (b) and after (c)

reaction with the NF-CNTs. It is, once again, clear that carbon nanotubes are present on the surface following the reaction that are not present before the reaction. Figure 3.5(d) provides a closer view of (c). The line profile in the inset shows the height of the features, and they are consistent with the manufacturer-reported and independently-confirmed diameter of individual carbon nanotubes. This proves that in addition to having carbon nanotube bundles present on the surface, there also exist individual carbon nanotubes in intimate contact with the substrate. This provides ample opportunities for amine-attachment to the CNT cage to occur. While this prospect is made possible by the presence of CNTs in close physical contact with the modified substrate, AFM cannot confirm that any chemical reaction is occurring, nor can it differentiate between the kinds of reactions that may be taking place to anchor the nanotubes to the substrate. For this, spectroscopic methods must be applied.

3.3.2 Energetic Feasibility of CNT Attachment Through the Carbon Cage

It is a well-known fact that carbon nanotubes can and will bind to primary amine-modified materials through functional groups such as (and most notably) carboxylic acids. While non-functionalized carbon nanotubes are specifically targeted in this study, defect sites are likely to exist on the carbon nanotubes, which can introduce unintended functional groups along the length of the tube. It is possible that attachment between the nanotubes and primary amine groups of the substrate may occur through these defects rather than through the cage structure. It is important therefore to investigate chemical attachment directly through the cage.

Density functional theory computational methods were applied to compare the energies of carbon nanotubes attached to amine-modified gold and silicon substrates. Because the exact configuration of attachment was unknown, two different geometries

were investigated. These geometries, which are described in detail in Section 2.3.8, are termed “parallel” and “non-parallel” and designate the direction of the C-C bond of the cage across which the primary amine dissociates. Three different diameters of carbon nanotubes were also studied to determine how diameter affects the energy. The attachment product geometries were optimized and compared to the optimized structures of their individual components. Figure 3.6 summarizes the results on the gold system.

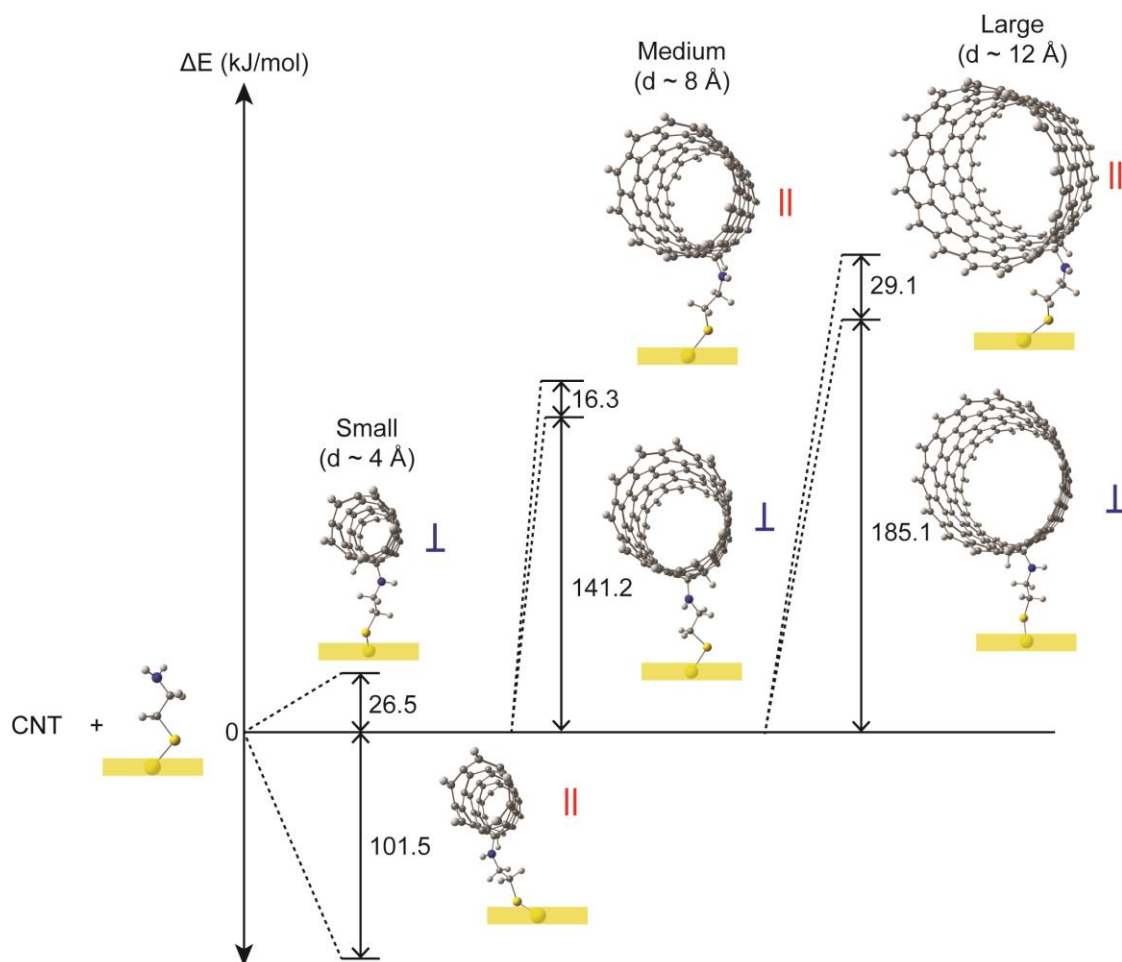


Figure 3.6: DFT-computed energy comparison between reactants and final attachment products for small, medium, and large diameter carbon nanotubes. The red and blue symbols next to the models identify the attachment configuration as “parallel” or “non-parallel”

The parallel attachment of a small-diameter (~ 4 Å) carbon nanotube is exothermic relative to its starting components, compared to the non-parallel attachment, which is slightly endothermic. As the nanotube diameter increases to medium (~ 8 Å) and large (~ 12 Å) sizes, the reaction becomes more endothermic. This is likely due to the fact that a small diameter introduces strain in the bonds

between the carbon atoms of the cage; however, as the radius of curvature increases, the structure becomes more graphene-like and is less susceptible to interactions with other species. Furthermore, in both cases of the medium and large-diameter CNTs, the change in energy is slightly lower for the non-parallel configuration. This makes sense because in this configuration, the amine dissociates across a more strained C-C bond compared to the parallel configuration. Similar computational results were obtained for the system on silicon; a summary of the relative energies on both systems is presented in Table 3.1.

Table 3.1: Relative Energies for NF-CNT Attachment to Gold and Silicon

CNT Size	 Attachment ΔE (kJ/mol)		⊥ Attachment ΔE (kJ/mol)	
	Silicon	Gold	Silicon	Gold
Small ($d \sim 4 \text{ \AA}$)	-105.0	-101.5	-31.5	26.5
Medium ($d \sim 8 \text{ \AA}$)	151.0	157.5	134.1	141.2
Large ($d \sim 12 \text{ \AA}$)	210.1	214.2	180.0	185.1

The nanotubes that were used experimentally in this study are most similar in diameter to the large diameter CNTs investigated computationally and as such, require energy to promote attachment. Because the attachment procedure is a sonication-assisted method, it is reasonable to believe that this added energy is sufficient to induce attachment. While this interaction may be energetically feasible, these computational results do not prove that attachment is due to chemical interactions at the interface taking place through the cage, so spectroscopic methods were used to study the system more closely.

3.3.3 Spectroscopic Confirmation of Interfacial Interactions

In order to compare the amine-modified substrates before and after reaction with the carbon nanotube solutions, *ex situ* XPS was used to study both the gold and silicon systems. Figure 3.7 displays XPS spectra in the N 1s region of the AUD-modified silicon substrate after (a) and before (b) reaction with the non-functionalized carbon nanotubes. The spectra in Figure 3.7 (c) and (d) were collected on the cysteamine-modified gold wafer after and before reaction with the NF-CNTs, respectively. On the amine-modified substrates, there are two primary features. The larger feature at 399.5 eV represents the nitrogen of a primary amine. The smaller component at 402 eV is consistent with oxidized nitrogen species which is reasonable to expect due to the ambient conditions under which the wafers were transported to the XPS. These assignments are based on the literature [50,63–65]. N 1s core level binding energies were predicted using DFT computational methods and these predicted values are denoted by the green bars underneath the experimental spectra.

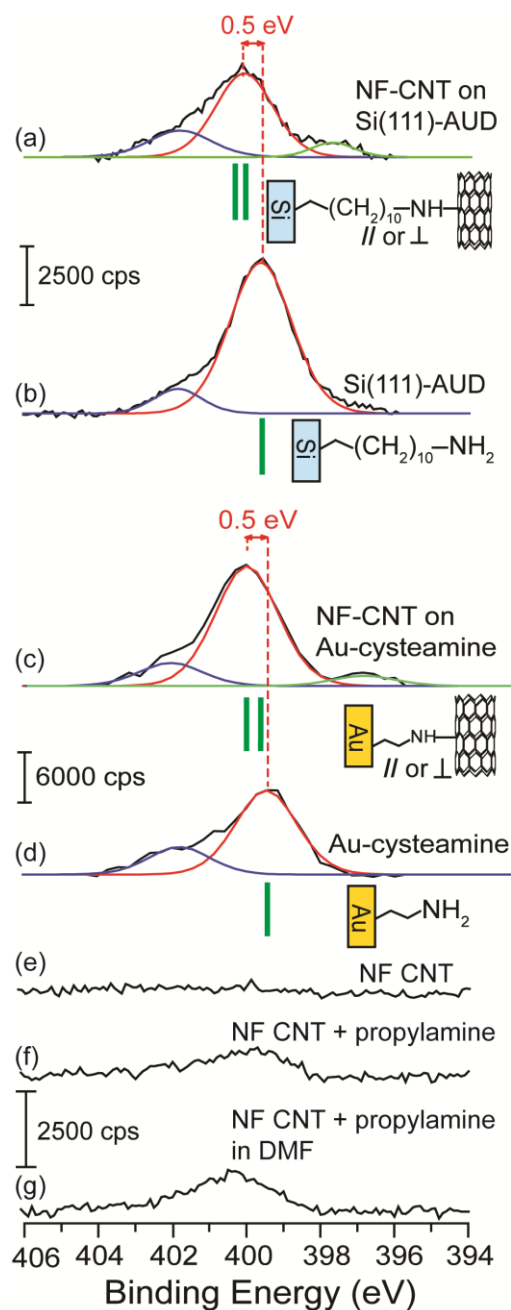


Figure 3.7: XPS spectra in the N 1s region of the amine-modified silicon (b) and gold (d) substrates before reaction with the NF-CNT solutions. These surfaces following reaction with the NF-CNTs are displayed in spectra (a) and (c), respectively. Spectrum (e) shows the XPS results for the NF-CNT powder. The spectra for the powder after reacting with neat propylamine and propylamine in DMF can be observed in (f) and (g), respectively

Following the reaction with the non-functionalized carbon nanotubes (a, c), the position of the largest feature shifts 0.5 eV to a higher binding energy, which represents a combination of primary and secondary amine nitrogen species that would be present in the case of the -NH_2 species interacting with the CNTs. This shift is fully consistent with the predicted shift in binding energies from DFT calculations; in this case, there are two bars underneath each spectrum to indicate predicted energies for the parallel and non-parallel configurations. The smaller feature at 402 eV may indicate a combination of oxidized nitrogen species and amide formation in the case of attachment through defect sites, although the two cannot be differentiated in these experiments. Additionally, a very small peak appears on both gold and silicon systems at 397.5 eV. The appearance of this feature is believed to be largely due to the insertion of a nitrogen atom into the aromatic system of the CNT cage at defects. This process has been suggested in the literature [87] and is supported by our own DFT-calculated predictions. In addition to revealing the binding energy shift (substantiated by DFT) following reaction with the CNTs, the XPS results disclose another important piece of information: the chemistries occurring on both the silicon and gold systems are very similar to one another. This becomes important later for drawing conclusions based on ToF-SIMS analysis.

The N 1s XPS spectrum of the NF-CNT powder in Figure 3.7 (e), shows no observable features, which reveals that the nitrogen signal in spectra (a-d) originate from the functionalized substrates rather than from nitrogen-containing defects or species adsorbed on the carbon nanotubes. Control experiments were performed, in which non-functionalized carbon nanotubes were allowed to react under ultrasonic agitation with neat propylamine and with propylamine in DMF. In this case, the

propylamine could interact with the cage as hypothesized, as well as with any carboxylic acid defects on the carbon nanotubes. The solutions were drop cast onto wafers and dried and the resulting XPS spectra are presented in Figures 3.7 (f) and (g). The small features present are consistent with one another and with the large peak positions in (a-d). This confirms that the solvent is not responsible for producing the large nitrogen signal observed in the test cases.

The C 1s region was also analyzed via XPS although due to a number of overlapping species and likely contamination due to adventitious carbon, the peaks were not assigned to specific species. The spectra in the C 1s region are shown in Figure 3.8. It is clear that there are some changes taking place upon addition of the carbon nanotubes to the amine-modified substrates. Additionally, after reaction with the CNT solutions, a subtle π^* shake-up peak can be observed (highlighted in the inset), indicating the presence of the aromatic system of the carbon nanotube structure.

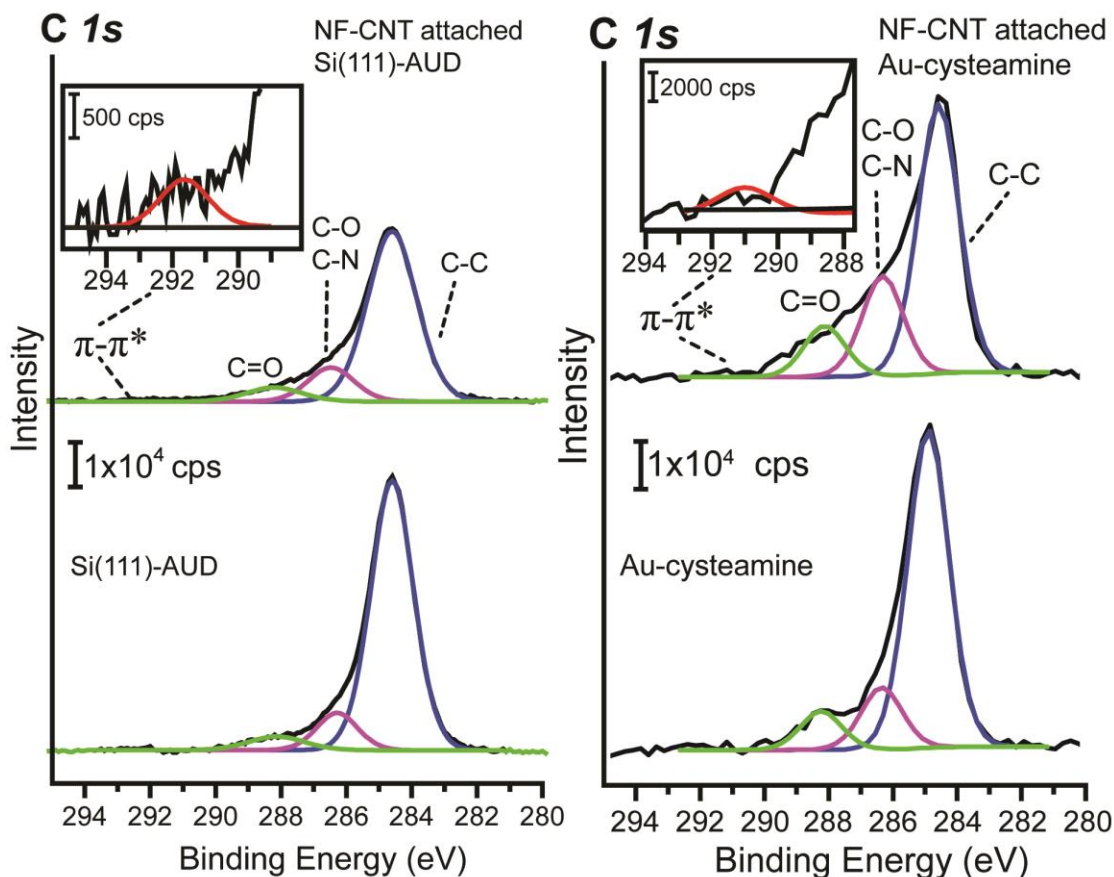


Figure 3.8: XPS spectra in the C 1s region for the silicon (left panel) and gold (right panel) systems. The bottom spectra represent the amine-modified substrates and the top spectra show those surfaces following reaction with the NF-CNT solutions. Insets show magnified views of the aromatic π^* shake-up peaks

The conclusions that can be drawn from the XPS studies are numerous and can be summarized as follows: (1) the sonication-assisted reaction of amine-terminated substrates with non-functionalized carbon nanotubes results in a distinct 0.5 eV shift of the major nitrogen species to a higher binding energy that is consistent with computational predictions, (2) the nitrogen species observed in XPS originate from the amine-modified substrates and not from the nanotubes or solvent, and (3) the surface

chemistries taking place are very similar between the gold and silicon systems. XPS confirms that the state of the nitrogen species on the surface is changing upon this interaction but, while it is consistent with covalent binding between the amine groups and the cage structure of the carbon nanotubes, it does not confirm that this is the process taking place. To study this particular interaction in detail, ToF-SIMS investigations were performed.

3.3.4 Confirmation of Attachment Through the Carbon Nanotube Cage

Time-of-flight secondary ion mass spectrometry was used to compare the surfaces and materials involved in the reaction with the aim of identifying the bonding involved during attachment. ToF-SIMS studies were focused exclusively on the system on gold, rather than silicon. This was done because gold has only one stable isotope (^{197}Au). In contrast, silicon has three stable isotopes (^{28}Si , ^{29}Si , and ^{30}Si). The system is already very complicated by the many isotopes of other species involved in the CNTs and alkyl linkers and the numerous potential cracking patterns within the complex structures. The deconvolution of these fragments on the multiple isotopes of silicon would be nearly impossible but because XPS analysis suggests that the chemistry is similar on the gold and silicon systems, it was assumed that conclusions drawn from ToF-SIMS analysis on gold could be extended to the silicon system as well.

Figure 3.9 shows several ToF-SIMS spectra over a m/z range of 200 to 400 amu. The spectra for the COOH-CNT and NF-CNT attached to cysteamine-modified substrates show some differences, but they are primarily related to the different kinds of nanotubes used. However, a few m/z regions were identified that could be explicitly assigned to specific fragments.

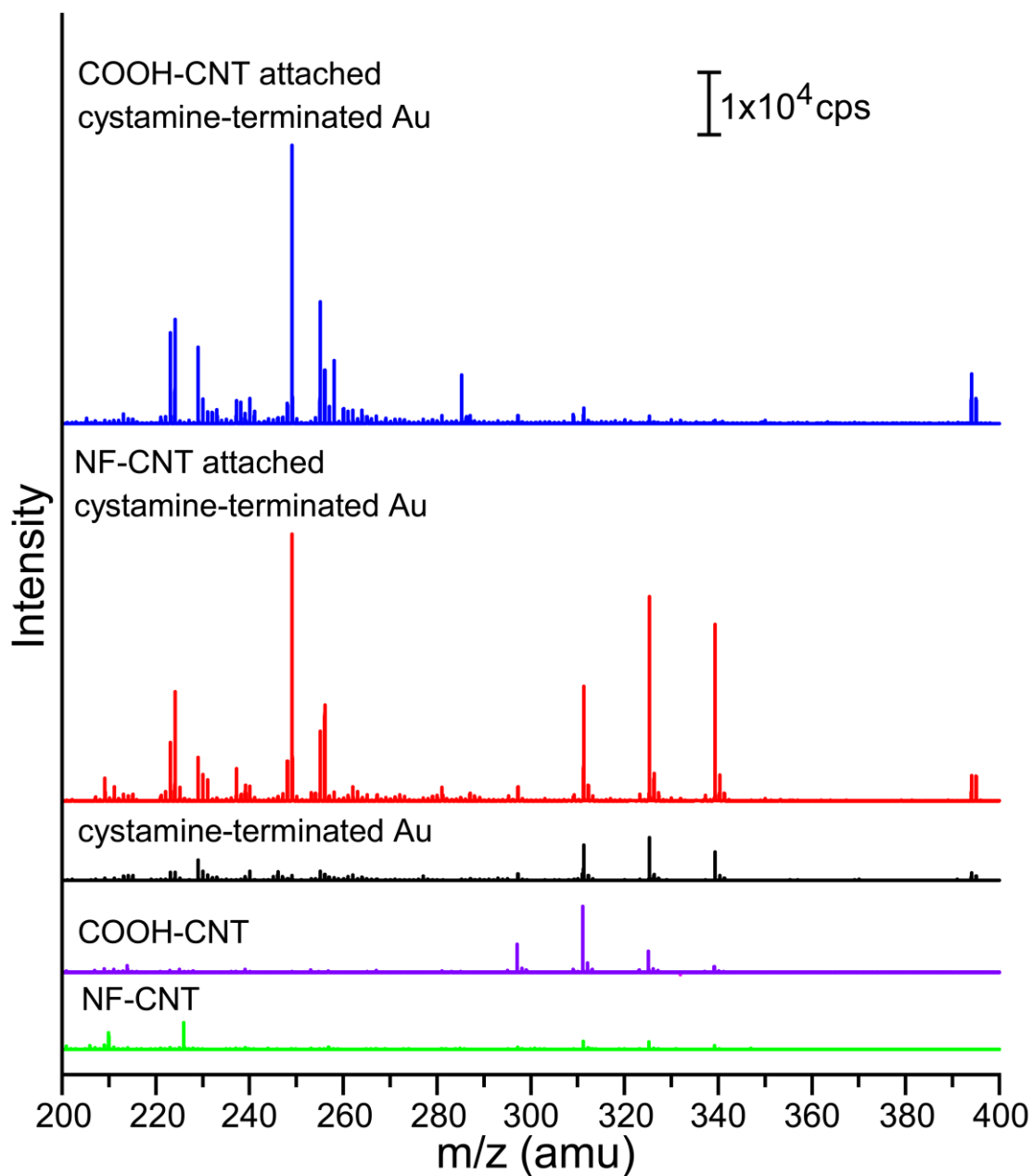


Figure 3.9: ToF-SIMS spectra of the attachment components and products on the gold system over a broad m/z range

Figure 3.10 shows a number of spectra for different types of systems. Spectra (a) and (b) represent the cysteamine-modified gold surface following reaction with the

COOH-CNT and NF-CNT solutions, respectively. Spectrum (d) was collected on the cysteamine-modified gold, and (e) and (f) were collected from carboxylic acid-functionalized and non-functionalized carbon nanotube powders, respectively. A control experiment was carried out in which the gold wafer was functionalized with dimethylamino ethanethiol. This functionalized substrate was sonicated in the NF-CNT solution under the same reaction conditions as the test samples, followed by washing to remove any physisorbed species. In this case, the organic monolayer is terminated with a tertiary amine, rather than the primary amine of cysteamine and the additional methyl groups should prohibit attachment of the amine nitrogen to the carbon nanotubes. The ToF-SIMS spectrum from this sample is shown in Figure 3.10 (c).

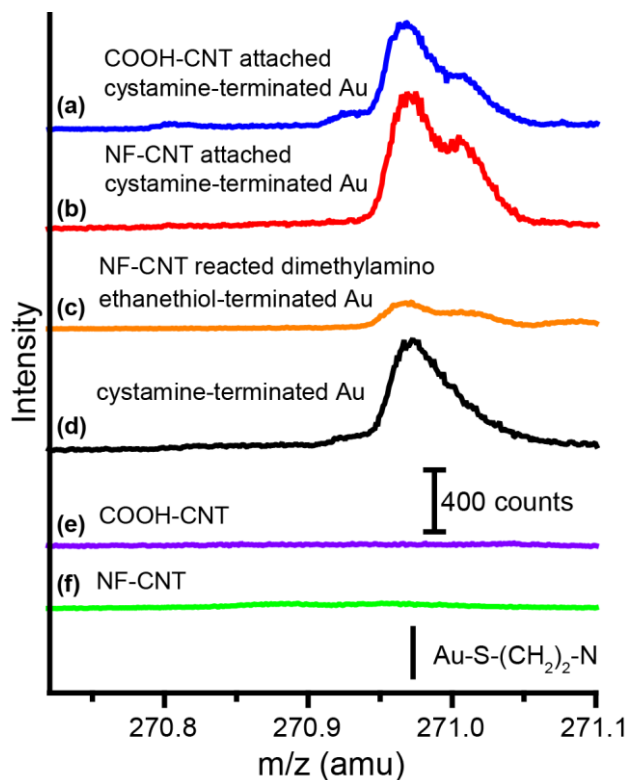


Figure 3.10: ToF-SIMS spectra for the region in which the $\text{Au-S-(CH}_2)_2\text{N}^-$ fragment appears

The fragment $\text{Au-S-(CH}_2)_2\text{N}^-$ has an expected mass of 270.973 amu; this position is illustrated by the black line underneath all the spectra in Figure 3.10. This fragment would be expected to originate from any gold surface modified with cysteamine or dimethylamino ethanethiol. Indeed, a peak can be observed in this position for all samples on gold but is absent from the spectra for the carbon nanotube powders.

A second important fragment, $\text{Au-S-(CH}_2)_2\text{NH-C}_5^-$, with a mass of 331.981 amu, would be expected for a gold atom modified with a cysteamine molecule bound through the nitrogen (to form a secondary amine) to a five-carbon

fragment broken off of a CNT. The region containing this fragment mass can be observed in Figure 3.11 all spectra represent the same surfaces as those with the same labels in Figure 3.10. Again, no features are observed at the m/z of interest for the carbon nanotube powders. There is also no peak at this mass for the cysteamine-modified gold (spectrum (d)), which is expected because this surface did not interact with the nanotubes. Most importantly, a large feature can be observed at this mass for the cysteamine-modified substrates that were allowed to react with the CNTs (spectra (a) and (b)) and this feature is absent from the dimethylamino ethanethiol-modified substrate that was allowed to react with the CNTs (spectrum (c)). This indicates that attachment of the five-carbon fragment of the nanotube cage takes place through the primary amine of the organic monolayer.

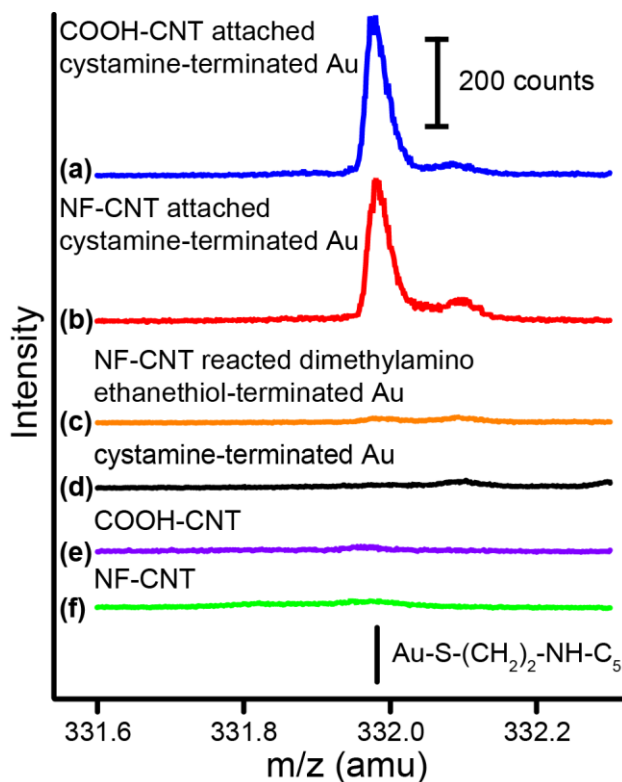


Figure 3.11: ToF-SIMS spectra for the region in which the $\text{Au} - \text{S} - (\text{CH}_2)_2\text{NH} - \text{C}_5^-$ fragment appears

The final region of interest is that in which the $\text{Au} - \text{S} - (\text{CH}_2)_2\text{N} - \text{CO} - \text{C}_5^-$ fragment is expected to appear at 358.968 amu. This fragment is expected to result from a five-carbon fragment that is broken off of a carbon nanotube, bound to the primary amine of the monolayer through formation of an amide bond from a carboxylic acid functional group. This ToF-SIMS region is displayed in Figure 3.12, in which the spectra are labeled the same way as in Figures 3.10 and 3.11. Here, a large peak is observed in spectrum (a), representing the cysteamine-modified gold following reaction with the COOH-CNT solution. This is not surprising, as the amide formation between carboxylic acid-functionalized carbon nanotubes and primary

amine-modified surfaces is a well-established reaction. There is even a very small feature here for the cysteamine-modified gold after reaction with the NF-CNTs (spectrum (b), which is not unexpected due to the presence of carboxylic acid-containing defect sites through which attachment can occur. The other spectra contain no features at this position.

ToF-SIMS is typically considered a qualitative measurement so the number of binding events taking place through direct attachment through the cage or through amide formation cannot be determined from Figures 3.11 and 3.12. However, a rough estimate of the relative amounts of the two types of binding can be computed by integrating the peaks. If the ionization cross-sections are assumed equal for the $\text{Au} - \text{S} - (\text{CH}_2)_2\text{NH} - \text{C}_5^-$ and $\text{Au} - \text{S} - (\text{CH}_2)_2\text{N} - \text{CO} - \text{C}_5^-$ fragments, approximately 75% of the attachment events take place through the carbon cage for the carboxylic acid-functionalized carbon nanotubes. An overwhelming 90% of the attachment events take place through the cage in the case of the non-functionalized carbon nanotubes, indicating that direct attachment through the cage structure is not only possible, but also that it is a considerably important process.

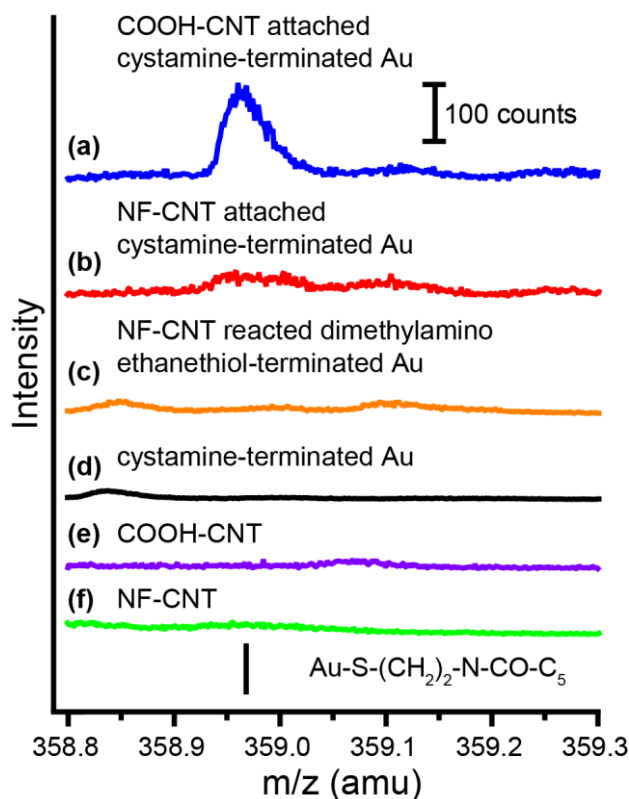


Figure 3.12: ToF-SIMS spectra for the region in which the $\text{Au-S-(CH}_2)_2\text{N-CO-C}_5^-$ fragment appears

3.4 Conclusions

This chapter outlines an investigation into the covalent attachment of carbon nanotubes to amine-modified surfaces. In the literature, methods for such attachment have been focused on binding through functional groups present on the nanotubes. It was hypothesized in this study that attachment is also possible directly through the carbon cage of the nanotubes. A sonication-assisted procedure was used to bind carboxylic acid-functionalized and non-functionalized carbon nanotubes to organic monolayers and a number of techniques were used to probe the chemistry of attachment. SEM, TEM, and AFM were used to confirm the presence of carbon

nanotube bundles and individual CNTs on the surface and show that damage induced ultrasonic agitation is not the process that drives the reaction. XPS (coupled with DFT calculations) and ToF-SIMS confirm that covalent binding occurs between the modified substrate and the carbon cage of the carbon nanotubes and that this process is very efficient. The work outlined here studies and verifies competing reaction processes that occur during the anchoring of CNTs to solid supports and concludes that the addition of functional groups is not necessary for strong covalent binding to modified substrates. The next two chapters will focus on extending the fundamental understanding of attachment chemistry to larger structures for the formation of nanoscale layered structures and understanding the effects of various aspects of the fabrication process on surface coverage and film thickness.

Chapter 4

NANOPARTICLE LAYER DEPOSITION FOR HIGHLY-CONTROLLED MONO- AND MULTILAYERS BY “CLICK CHEMISTRY”

4.1 Abstract

Chapter 4 focuses on the development of a layer-by-layer approach to producing nanoparticle monolayers and multilayers on a solid flat substrate in which each layer is covalently-bound by “click chemistry”. This general idea has been reported previously in the literature, although the structures formed often result in submonolayer coverage and the number of nanoparticle layers formed in multilayer structures does not reflect the number of deposition cycles performed. While these are not necessarily drawbacks depending on the intended application, this work aims to identify the factors in the fabrication method that affect surface coverage and precision over the desired film thickness. Following method development, microscopy studies show that the layers exhibit very high surface coverage and precision in film thickness. Spectroscopic techniques, coupled with computational methods, confirm covalent binding as the mechanism of attachment. It was concluded that the sonication-assisted attachment procedure results in random attachment events between the substrate and nanoparticles to form a robust monolayer that acts as a starting platform for further addition of nanoparticle layers. Figures in this chapter are reprinted with permission from [52]. Copyright 2016 Elsevier.

4.2 Introduction

Layered nanostructures have been incorporated into devices for a variety of applications including catalysis [20,88], photovoltaics [89,90], and spintronics [91]. As the sizes of these devices shrink to approach the nanoscale, it becomes imperative to maintain a fine-tuned level of control over the surface processes taking place and the physical dimensions of the structures formed. Two approaches to achieving such a level of control of these structures, ALD and traditional LbL techniques are described in Chapter 1. The objective of the work outlined in chapter was to combine the precision of ALD with the scalability of LbL techniques.

Instead of utilizing atomic or molecular components as the building blocks to form layered structures, nanoparticles were used. Due to their high surface area-to-volume ratio, nanoparticles can exhibit interesting material properties (such as optical or magnetic) that differ from the bulk of the same material [92]. More importantly in this study, the (relatively) large size of the nanoparticles compared to their atomic or molecular counterparts in ALD result in the formation of layers that are orders of magnitude larger, in fewer deposition cycles, overcoming the scalability issue of ALD.

To achieve the selectivity and precision that may be difficult to master by employing traditional LbL methods, “click chemistry” is adopted. Described in detail in Chapter 1, the “click” reaction between azide and alkyne functional groups to result in a triazole ring linkage is a selective process that can be accelerated in the presence of a copper (I) catalyst. By modifying the nanoparticles and support material with azide and alkyne functional groups, the nanoparticles can be “clicked” onto the surface to result in a covalently-anchored thin film. Furthermore, subsequent deposition cycles of nanoparticles appropriately modified with complementary functional groups can be executed to result in multilayers in which each layer is covalently-linked to the layer

beneath it. A schematic of this process is illustrated in Figure 4.1. The rational selection of nanoparticle size affords control of the resultant film thickness in a process that is fundamentally similar to ALD.

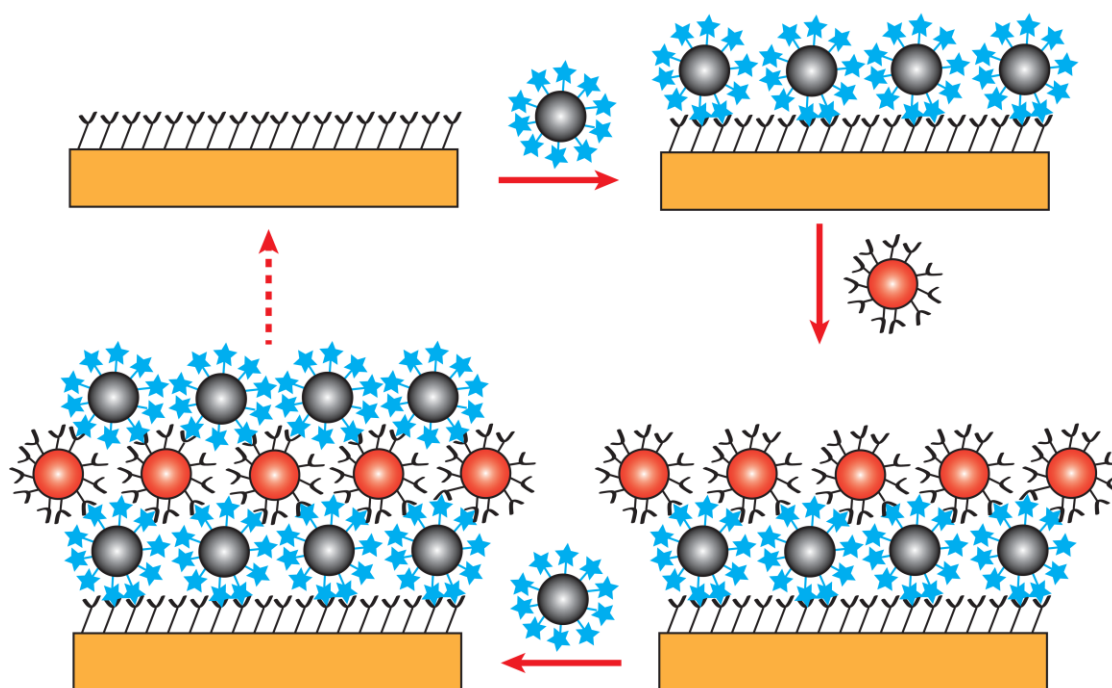


Figure 4.1: General scheme illustrating the nanoparticle layer deposition process

This general approach has been realized in a number of reports in the literature. The modification of nanoparticles and substrates of various materials to result in covalently-bound layers by “click chemistry” has been performed. Some of these reports have focused on the formation of nanoparticle monolayers, such as in the cases of magnetic nanoparticles anchored to functionalized substrates via drop-casting methods [57] or microcontact printing [93]. Other studies have focused on the

formation of multilayers through, for example, electrografting nanoparticles between organic films of polymer layers [94] or dip-coating with alternating solutions containing azide- or alkyne-functionalized nanoparticles and catalyst [95]. Although these reported methods and others have successfully confirmed the presence of nanoparticles on the substrate, some of these processes rely on self-assembly of the particles upon the substrate to form an incomplete monolayer of nanoparticles. In other cases, there is little precision maintained over the multilayers formed. In these cases, it is clear from microscopy results that the number of layers of nanoparticles does not always reflect the number of deposition cycles performed so that there are nanoparticles present in the structure that are not covalently bound to the layers beneath them. This may not be a problem for some applications of these processes, but it presents the challenge of developing a procedure of nanoparticle layer deposition with high surface coverage and with precisely one layer of nanoparticles added to the structure for each deposition cycle. Moreover, while spectroscopic results usually accompany these reports and are in general agreement with the physical results, it is rare that the spectroscopy categorically proves that attachment occurs through the “click reaction”.

The work described in Chapters 4 and 5 focuses on a method for achieving this goal and on identifying the experimental parameters that affect the surface coverage and layer height to offer a higher level of control over the resulting architecture. It uses a sonication-assisted procedure to form a monolayer of alkyne-modified 80 nm silica nanoparticles on an azide-terminated SAM on gold. This functionalization scheme is opposite those that are usually reported in the literature (azide-modified nanoparticles on alkyne-terminated substrate) and the implications of this difference

are discussed in Chapter 5. Silica nanoparticles were studied in this system as a proof-of-concept because they are inexpensive, available in a large variety of shapes and sizes, and the methods of surface functionalization are well known, but the use of any material nanoparticle is theoretically possible for this procedure and in fact, the use of iron oxide nanoparticles is demonstrated in Chapter 5.

Following the deposition of the first monolayer of nanoparticles by “click chemistry”, a second layer of azide-modified 50 nm silica nanoparticles was added to the structure. The difference in diameter allows for a simple means of differentiating between the types of particles using only microscopy. Finally, a third layer of alkyne-modified nanoparticles was added to the double-layer sample. Electron and atomic force microscopy methods were used to prove that the sonication-induced monolayer attachment process results in extraordinarily high surface coverage and precision over film thickness, in comparison to the literature. Spectroscopic techniques were used to analyze the surface chemistry at each step of the process to confirm evidence of covalent binding by “click chemistry”.

4.3 Results and Discussion

4.3.1 Microscopy Confirmation of High-Coverage Nanoparticle Monolayers

The procedure for fabricating the nanoparticle mono- and multilayers on the azide-terminated substrate is described in Section 2.2.2. The morphology of the sample containing the first layer of nanoparticles was studied following washing to remove physisorbed species. A representative image of the surface is shown in Figure 4.2 (c). A large part of the surface is covered by the nanoparticles. To determine whether “click chemistry” is responsible for the nanoparticles being adsorbed on the

surface, two other surfaces were investigated for comparison. First, an unmodified (no azide groups) gold substrate was allowed to sonicate for 24 hours in the solution containing alkyne-modified nanoparticles, copper sulfate, and sodium ascorbate. This was *not* followed by the standard solvent rinsing or sonication steps outlined in Section 2.2.2 used to remove physisorbed nanoparticles. The SEM micrograph of this surface, which can be seen in Figure 4.2 (a), shows a few physisorbed species but the surface is mostly bare. Second, this same control surface was washed using the solvent and sonication steps described in Section 2.2.2. This results in a completely bare surface, as shown in Figure 4.2 (b). The absence of nanoparticles in these cases, in comparison to the high surface coverage observed in Figure 4.2 (c) in which both nanoparticles and surface are functionalized appropriately, show that the presence of both the azide and alkyne functional groups are necessary for facilitating nanoparticle attachment and that the attachment is robust and capable of withstanding the multiple washing steps that are, seemingly, sufficient to remove physically-adsorbed particles.

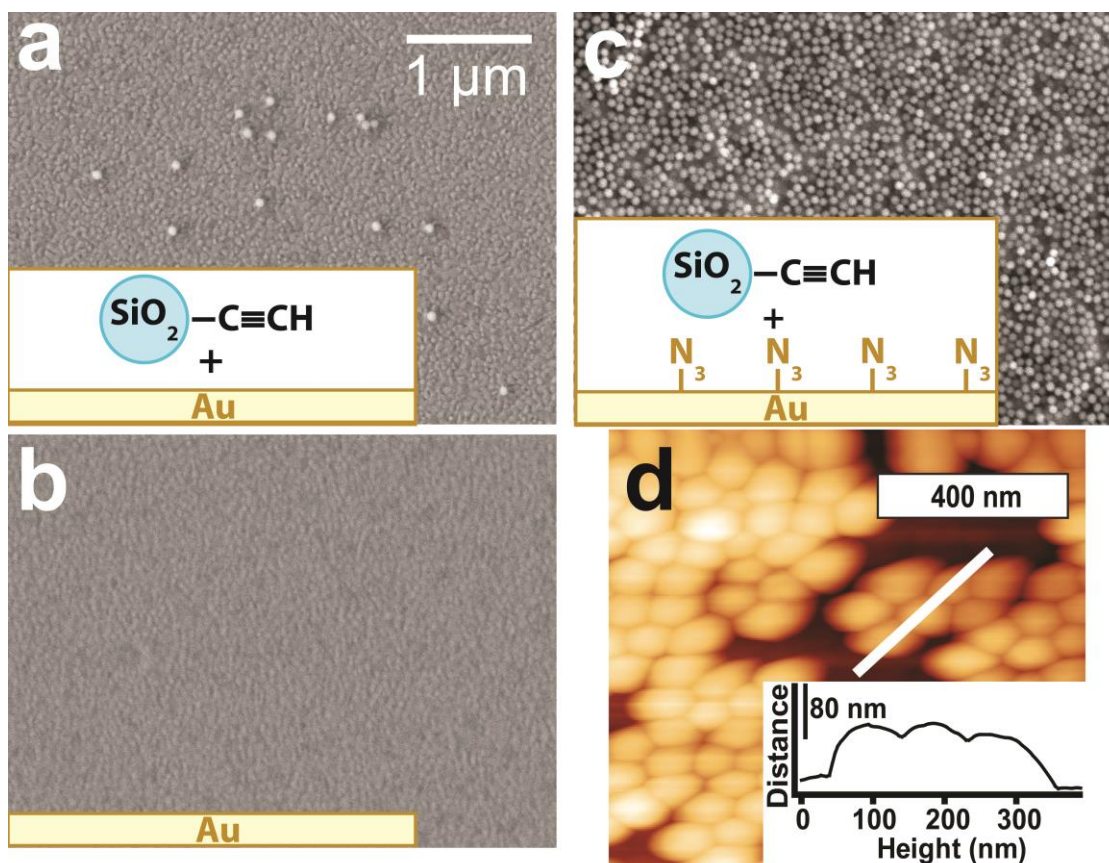


Figure 4.2: SEM images of the un-modified surface after reaction with alkyne-terminated nanoparticles without (a) and with (b) rinsing steps to remove physisorbed species. SEM image (c) shows the azide-modified surface after reaction with the alkyne-terminated nanoparticles. AFM image (d) shows the same surface as (c) with the line profile in the inset confirming a monolayer of nanoparticles on the surface

From the SEM images, the nanoparticles appear to form a monolayer on the surface; however to confirm this, AFM was performed on one of the edges of this monolayer. The AFM image, shown in Figure 4.2 (d), reveals individual nanoparticles on the surface. The line profile in the inset shows that the features are about 80 nm high which is consistent with a single monolayer of nanoparticles on the surface.

AFM is the ideal technique to investigate the height of the nanoparticle film for a monolayer; however, upon building multilayers, it becomes more complicated because the nanoparticles no longer lie on a flat surface. To determine the layer height for samples that undergo multiple deposition cycles, an alternative method was used. A focused ion beam was used to mill a trench in the surface. Figure 4.3 shows an SEM micrograph of the monolayer sample after the milling process. It can be noted in this image that the nanoparticle monolayer covers the entire surface, which shows that Figure 4.2(c) is representative of the entire sample surface. By adjusting the angle of the sample stage in the SEM following FIB treatment, it is possible to determine the height of the nanoparticle film via cross-sectional view.

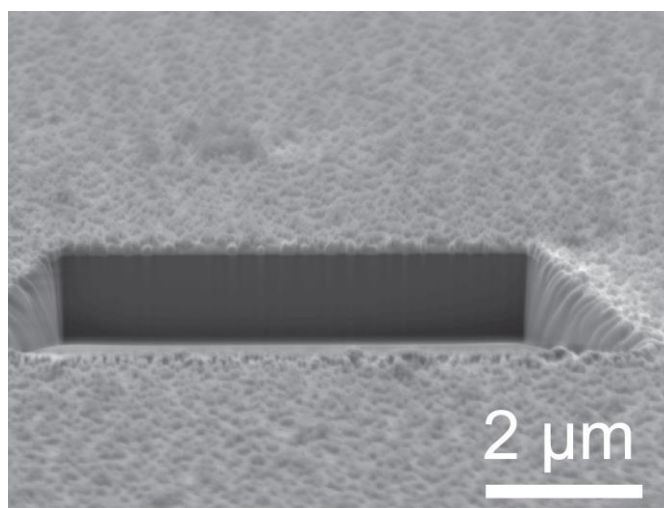


Figure 4.3: SEM image of the monolayer sample following FIB treatment of the surface

The nanoparticle monolayer can once again be observed in Figure 4.4 (a). The same sample following FIB treatment is observed in Figure 4.4 (b). It is clear from this

second image that the nanoparticle film thickness is 80 nm, completely consistent with the AFM results and with a single monolayer of nanoparticles on the surface. It was calculated from the number of nanoparticles present on the surface that the monolayer results in about $84 \pm 8\%$ surface coverage, with the assumption that 100% coverage refers to nanoparticles arranged in a close-packed hexagonal formation. This degree of coverage is exceptionally high considering that the attachment is driven by random interactions between the nanoparticles and the substrate induced by sonication, rather than by self-assembly. Figure 4.5 shows that the coverage is indeed random during this process, as these images were collected from samples that were removed early in the sonication process at low (top image) and higher (bottom) levels of coverage, but before a complete monolayer is formed.

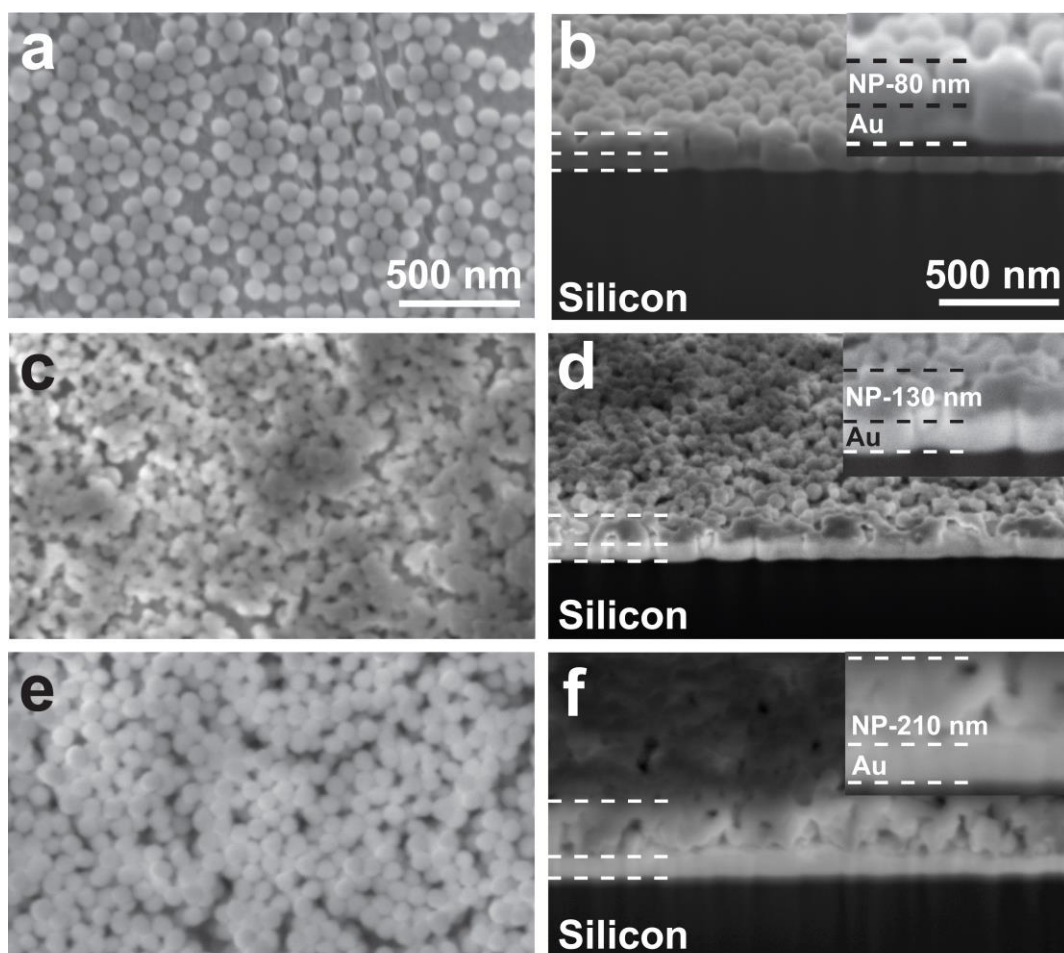


Figure 4.4: Plan view SEM images of the nanoparticle (a) monolayer, (c) bilayer, and (e) trilayer surfaces. Images (b), (d), and (f) show cross-sectional views of the layers seen in (a), (c), and (e), respectively

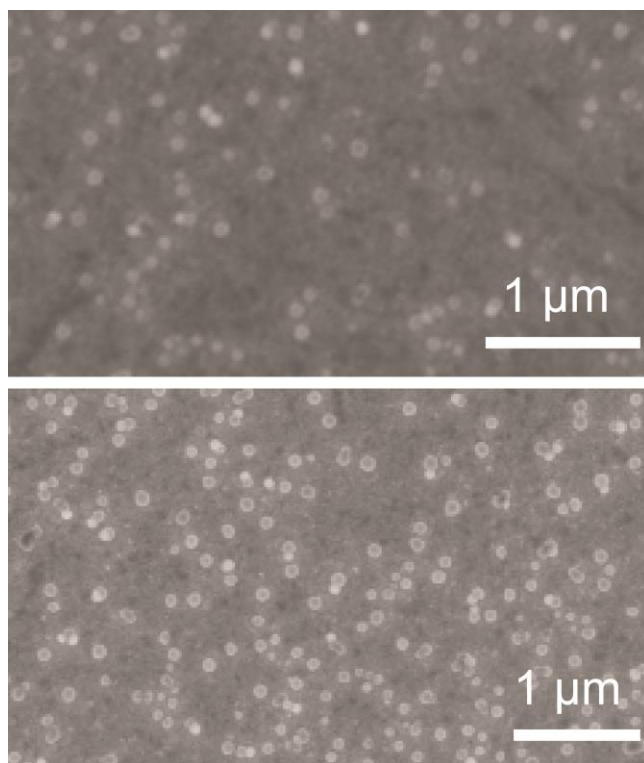


Figure 4.5: SEM images demonstrating that random nanoparticle assembly results in very low (top) and slightly higher (bottom) surface coverage

After the second deposition cycle of nanoparticles, a high coverage layer can be observed by SEM in the plan view and following FIB treatment (Figures 4.4 (c) and (d), respectively). Based on the number of nanoparticles identified in the plan view, the coverage was calculated to be 94%. Again, it should be emphasized that this surface coverage does not follow the same definition of coverage that is typically referred to in surface science, in which monolayer coverage is based on the number of bonding sites (or functional groups) present on the substrate. Instead, due to the size and geometry of the nanoparticles relative to the reactive binding sites, a full monolayer is defined here as the maximum number of nanoparticles that can fit on the

surface in a close-packed hexagonal formation. While this calculation assumes incorrectly that the second layer of nanoparticles lie on a flat substrate, the result is, nevertheless, reproducible.

Another way of estimating the coverage is based on determining the number of nanoparticles that could reasonably fit into the region (i.e. determining the number of extra particles that could fit into the “holes” remaining in the layer and using that total number of nanoparticles to represent a 100% monolayer coverage. By this account, the image-based surface coverage shown in Figure 4.4 (c) was estimated to be 95%, which is, again, very high considering that the driving force of attachment is sonication-induced random interactions.

The cross-sectional view shown in Figure 4.4 (d) reveals a nanoparticle layer thickness of 130 nm. This is consistent of exactly two layers of nanoparticles, in which the first layer consists of 80 nm diameter particles and the second layer is made up of 50 nm diameter particles. Thus, the number of nanoparticle layers is consistent with exactly two deposition cycles and no more.

Following the third deposition cycle of nanoparticles, the SEM plan view and cross-sectional view were collected and shown in Figures 4.4 (e) and (f), respectively. The surface coverage compared to the ideal close-packed monolayer was calculated to be 94% and the image-based coverage was estimated to be 98%. The thickness of the film is 210 nm, consistent with one layer of 50 nm nanoparticles sandwiched between two layers of 80 nm nanoparticles. Once again, these results confirm that very high degrees of surface coverage and control of film thickness are achieved.

The results obtained from SEM and AFM confirm that robust attachment results from the sonication-assisted procedure and that the surface coverage of

nanoparticles is exceptionally high in comparison to previously-reported methods of covalent nanoparticle attachment. Moreover, the film thicknesses observed match the number of deposition cycles performed, which agrees with the hypothesis that each nanoparticle layer is covalently bound to the surface beneath it. These conclusions are in agreement with attachment facilitated by “click chemistry” but in order to confirm that this is the case, the surface interactions must be examined more thoroughly with spectroscopic techniques.

4.3.2 Spectroscopic Analysis of Interfacial Interactions

The nanoparticle mono- and multilayers appear to be bound to the surface via strong covalent interactions due to the facts that absence of the azide or alkyne functional groups result in no monolayer formation (see Figure 4.2) and that only one nanoparticle layer is added per deposition cycle (see Figure 4.4). However, microscopic techniques do not confirm that these interactions are driven by “click chemistry”. To compare the important functional groups present at the interface, ATR FTIR was utilized and a number of important findings are summarized in Figure 4.6. Figure 4.6 (a) shows the IR spectrum of the azide-modified gold substrate. A large peak present at 2096 cm^{-1} represents the azide stretch, indicating successful functionalization of the gold [53]. Two features, representing the symmetric and asymmetric CH_2 stretching can also be observed at 2854 and 2925 cm^{-1} , suggesting a partially-ordered alkyl monolayer [51,96,97]. Normally this system would be expected to demonstrate a high degree of order; however, as the ATR crystal tip is in physical contact with the surface, some disorder must be expected.

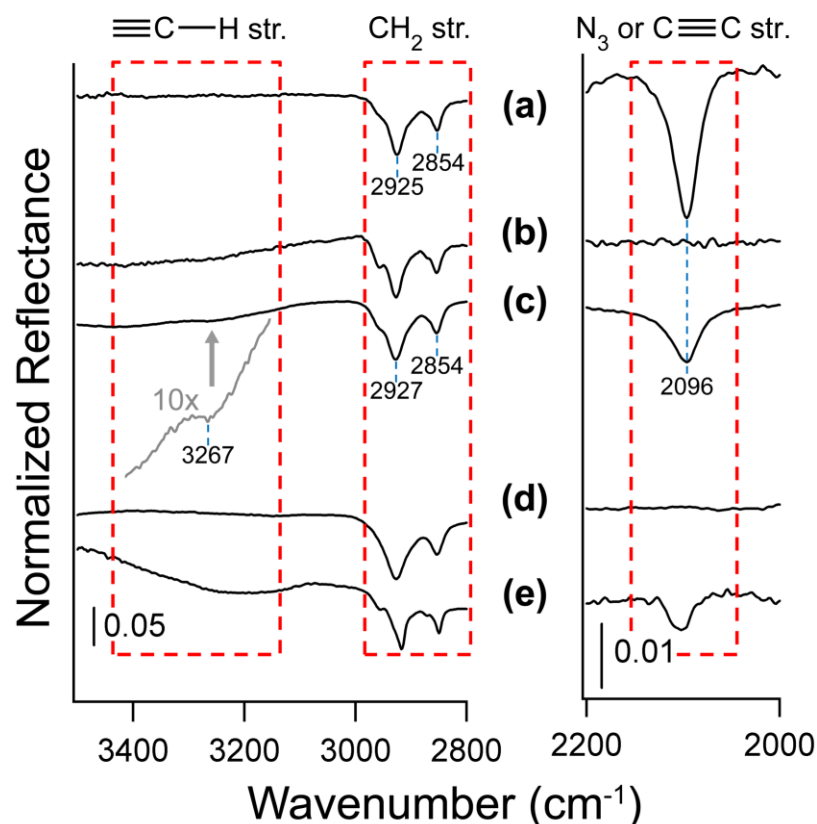


Figure 4.6: ATR FTIR spectra showing the azide-terminated substrate before (a) interaction with the alkyne-modified nanoparticles, after (c) deposition of the first layer of nanoparticles, and after (e) deposition of the second layer of nanoparticles. Spectra (b) and (d) were collected from surface (a) and (c), respectively, following titration with 5-hexynoic acid

The spectrum following the addition of the first layer of nanoparticles is displayed in Figure 4.6 (c). The feature observed at 2096 cm⁻¹ remains but has decreased in intensity. It cannot be said with certainty whether this feature represents the azide stretch or the alkyne C≡C stretch or a combination thereof, as they are both expected to occur at this frequency. It is reasonable to assume that not all of the azide groups on the substrate will react due to the geometry of the nanoparticles. At the

same time, the signal for both the alkyne $\text{C}\equiv\text{C}$ and C-H stretches should be small. This last stretching mode, which should be present near 3300 cm^{-1} is not easily observed in spectrum (c), however zooming in on the signal in this region (by a factor of ten) shows a small feature at 3267 cm^{-1} , indicating the presence of the alkyne groups [98]. As noted in spectrum (a), the CH_2 stretching is present following the alkyne-modified nanoparticles, but the frequency has shifted slightly to 2854 and 2927 cm^{-1} , as more disorder is introduced to the system [51,96,97,99].

To address the question of whether the feature observed at 2096 cm^{-1} represents unreacted azide groups or the presence of alkyne groups (or a combination of the two), an azide-modified gold wafer was titrated with 5-hexynoic acid to react all present azide functionalities. This is accompanied by the complete disappearance of the azide stretch, as shown in Figure 4.6 (b). When this titration is performed on a sample containing a monolayer of alkyne-modified nanoparticles (spectrum (d)), the peak at 2096 cm^{-1} is also absent, which means that this feature represents unreacted azide groups.

After the addition of the second layer of nanoparticles to the first, the ATR FTIR spectrum (Figure 4.6 (e)) again reveals the presence of azide functional groups and a weak peak suggests the presence of the alkyne C-H stretch. These results illustrated in Figure 4.6 are in agreement with the appearance and disappearance of the azide and alkyne functional groups that would accompany the formation of the triazole ring, but they do not confirm the ring formation itself. Indeed the presence of the triazole ring would be expected to result in absorption features around 1550 cm^{-1} [95], but as this frequency overlaps with other bands, it cannot be assigned unambiguously. While the results obtained from ATR FTIR analysis are in agreement with the

expected results of the “click” reaction, another spectroscopic method must be employed to gain better insight into the interactions facilitating attachment.

XPS studies were performed on the different surfaces formed during this process to observe the changes occurring on the surface. The results for the C 1s and N 1s regions are summarized in Figure 4.7. Spectra (a) and (e) result from the azide-modified gold substrate following functionalization with 1-azidoundecan-11-thiol. The C 1s region (spectrum (a)) shows a feature that has been fit with peaks corresponding to multiple species (C-C [84,100], C-O/C-N [101], and C=O [101,102]) that result from the alkyl chain overlayer and oxidized carbon species (due to the fact that the samples were transferred to XPS in ambient). The N 1s region (spectrum (e)) reveals two features that can be deconvoluted into three species. Density functional theory calculations were used to optimize and predict the core level energies of the azide nitrogen atoms (see Section 2.3.8 for full computational details). The predicted binding energies of 403.4 eV, 400.6 eV, and 400.0 eV were calculated for the $\text{--}\mathbf{N=N=N}$, $\text{--}\mathbf{N=N=N}$, and $\text{--}\mathbf{N=N=N}$ atoms (bolded and italicized for clarity), respectively. These predicted values are shown as the colored bars below spectrum (e) and represent the correspondingly-colored nitrogen atoms in the model. The experimentally-collected XPS spectrum is in agreement with these assignments, and with the literature [103], suggesting that azide is indeed present on the surface with minimum oxidation.

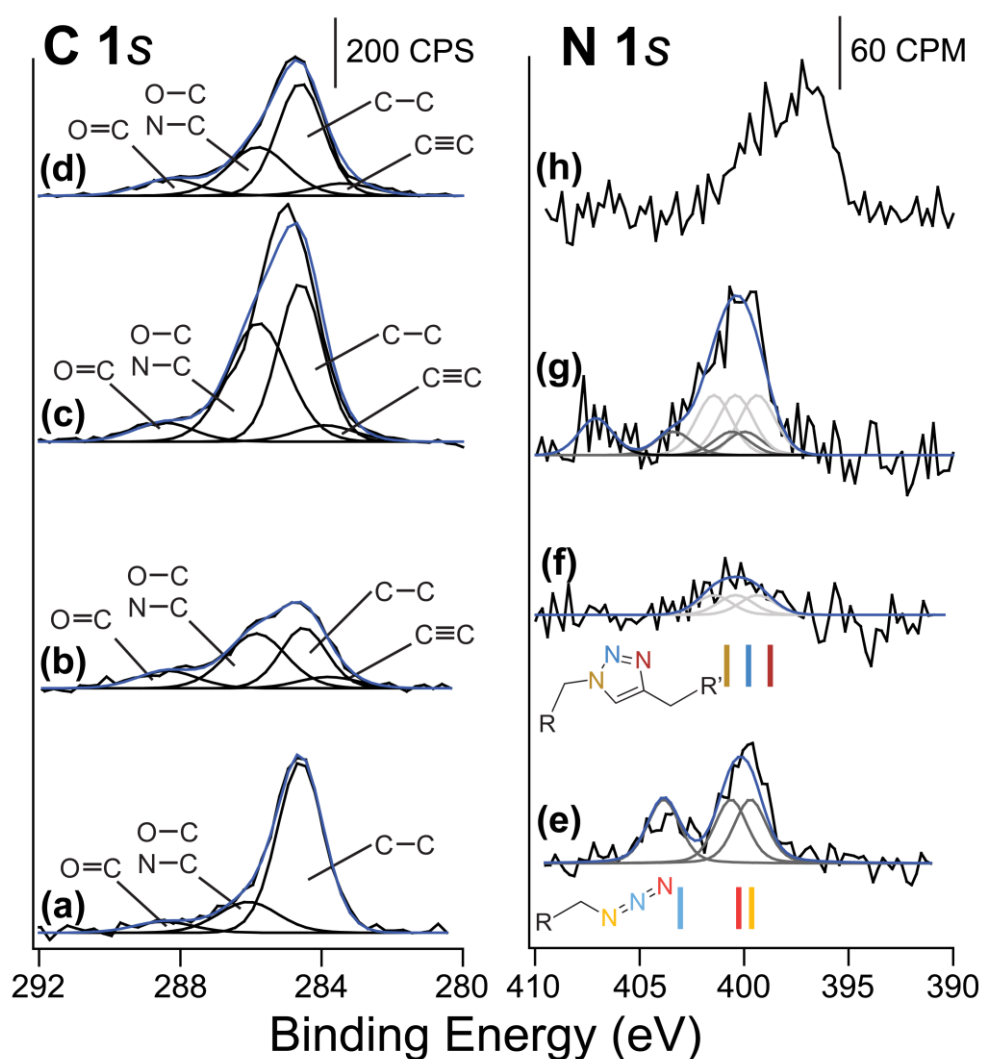


Figure 4.7: XPS spectra collected in the C 1s (left) and N 1s (right) binding energy regions. Spectra (a) and (e) represent the azide-terminated substrate. Spectra (b) and (f) show the surface with a monolayer of nanoparticles. Spectra (c) and (g) represent the bilayer and (d) and (h) represent the trilayer of nanoparticles deposited on the surface. The binding energies predicted by DFT computational methods are illustrated by the colored bars below spectra (e) and (f) and represent the correspondingly-colored nitrogen atoms in the adjacent models

After the first layer of nanoparticles is deposited onto the substrate, the C 1s spectrum (b) shows features that can be assigned similarly to spectrum (a) along with the addition of a small $C\equiv C$ feature at 284.0 eV. Spectrum (f) shows this system in the N 1s region and is characterized by a broad feature that can be fit with three species. These species are in agreement with the literature [103–105] and with the N 1s binding energies computed from DFT optimization of the triazole ring formed between the azide and alkyne functional groups. These are located at 401.5 eV, 400.4 eV, and 399.4 eV for the $-C-N-N-$, $-N-N=N-$, and $-N=N-C-$ (bolded and italicized for clarity) nitrogen atoms of the ring. This agreement between experimentally-determined and computationally-predicted energies indicates successful formation of the triazole ring.

Once the second layer of nanoparticles is added to the system, the XPS results become more complicated. The amount of carbon on the surface (spectrum (c)) increases, which likely results from a combination of an increased amount of carbon linkers on the nanoparticles (that can be assigned as those previously) and from adventitious carbon adsorbed onto the surface. The spectrum in the N 1s region (g) becomes equally complex with a mixture of both azide and triazole ring nitrogen atoms present on the surface. Additionally, a feature that appears at higher binding energy most likely originates from oxidized nitrogen species [106]. After the final layer of nanoparticles is deposited onto the surface, precise assignment of the components in the C 1s region (spectrum (d)) and N 1s region (spectrum (h)) becomes impossible due to the many species present in the system. At this point, the disorder of the layers, screening by the nanoparticles, and entrapment of nitrogen species between the nanoparticle layers prevent the isolation and identification of specific targeted

species; however, the overall intensities of the features are consistent and are in agreement with what is expected from the covalent binding between nanoparticle layers.

4.4 Conclusions

The spectroscopic results obtained from ATR FTIR and XPS studies provide supporting evidence for mono- and multilayer attachment facilitated by the azide-alkyne “click” reaction. This is especially apparent in the expected appearance and disappearance of the azide and alkyne functional groups identified in ATR FTIR and by the changes observed in the nitrogen species in XPS, coupled with core level N 1s binding energies predicted with DFT. Combined with the irrefutable evidence of selective attachment and high surface coverage of the nanoparticle layers presented in the SEM and AFM studies, this layer-by-layer process appears to offer an unprecedented level of control over surface coverage and precision in the layer height.

The sonication-assisted attachment of the first layer appears to be an important step in the process because it promotes attachment induced by random collisions between the substrate and nanoparticles. This means that physisorbed or weakly-bound nanoparticles are removed from the surface and the remaining monolayer that is strongly anchored to the substrate provides a robust scaffold for subsequently-deposited layers. The selective attachment means that only one layer of nanoparticles is deposited per deposition cycle, offering a fine-tuned level of control over the final thickness of the film. The next chapter will focus on nanoparticle layer deposition of a more complex system and identifying the reasons behind the exceptionally high surface coverage obtained using this approach.

Chapter 5

BUILDING HIGH-COVERAGE MONOLAYERS OF MAGNETIC NANOPARTICLES WITH “CLICK CHEMISTRY”

5.1 Abstract

In this chapter, the procedure for nanoparticle layer deposition and attachment by “click chemistry” was modified to achieve high-coverage layers comprised of magnetic nanoparticles. Spectroscopic methods were used to confirm the covalent binding through the formation of the triazole ring. SEM and AFM confirm the presence of a single layer of nanoparticles, indicating that the deposition and subsequent washing methods are sufficient for anchoring the particles while overcoming the natural tendency of the magnetic materials to agglomerate. The monolayers that were built demonstrate exceptionally high surface coverage. Computational studies comparing the possible reaction intermediates were used to conclude that the surface functionalization scheme (i.e. alkyne groups on the spherical nanoparticles and azide groups on the flat substrate) may be partially responsible for the remarkably high monolayer coverage. Figures in this chapter are reprinted with permission from [56]. Copyright 2016 Elsevier.

5.2 Introduction

The importance of understanding the bonding interactions and controlling the chemical and physical stability of layered nanostructures has been discussed previously in Section 4.2. The previous work on developing a method for mono-and

multilayer deposition of silica nanoparticles in a layer-by-layer process is fully described in Chapter 4. This method involves the selective attachment of functionalized nanoparticles to a modified flat substrate in a process that is fundamentally similar to ALD, but produces layers on the order of magnitude of those produced using traditional LbL techniques. This process offers the advantages of ALD, including selective, self-limiting attachment, true monolayer formation, and the potential for conformal filling, while achieving the desired result of thicker films in fewer deposition cycles. One of the most important findings of this project was the identification of experimental parameters that affect the stability of the resulting material. Specifically, it was determined that nanoparticle monolayers driven by random attachment to the substrate by ultrasonic agitation result in a stable interface that permits the formation of a robust scaffold for subsequently-added layers.

Another finding established in Chapter 4 was that the nanoparticle mono- and multilayers formed display exceptionally high surface coverage compared to similar methods reported in the literature. The project described in this chapter attempted to identify the reasoning behind this high coverage. Additionally, it aimed to expand the previously-established method focused on a silica nanoparticle system (as a proof-of-concept) to more complex and applicable materials. The integration of magnetic nanoparticles into devices has been realized for many purposes, such as biosensing [107] and the formation of magnetic tunnel junctions [108]. The properties of these materials are highly useful, but more complex than those for silica. They can be challenging to work with due to, for example, their intrinsic tendency toward agglomeration. This makes the application of our previously-reported nanoparticle layer deposition method to magnetic materials all the more interesting.

It has been reported that magnetic nanoparticles can be appropriately-functionalized and bound together using “click chemistry” [103]. Toulemon et al. have also demonstrated the use of the “click” reaction to anchor azide-modified magnetic iron oxide nanoparticles to an alkyne-terminated SAM using stirring [57], dip-coating [109], and microwave-assisted methods [110]. The successful deposition of nanoparticles in these cases cannot be denied. The surface coverage (as defined in Chapter 4) of these monolayers is above 50% after 1 hour of microwave irradiation [110]. Because the monolayer coverage obtained using the method in Chapter 4 was so high, this procedure was adapted to magnetic nanoparticles to determine whether this was still the case and if an explanation for the high coverage could be found.

Magnetic iron (II, III) oxide nanoparticles were functionalized with alkyne-terminated monolayers, and two methods (sonication and stirring) were carried out to induce attachment to the azide-modified substrate. SEM and AFM were used to confirm the formation of nanoparticle monolayers on the surface, and ATR FTIR and XPS were used to study the chemistry of attachment. DFT calculations were performed to compare predicted core level binding energies to the XPS results. Computational methods were also used to compare the intermediate structures of the copper-catalyzed reaction to help support the hypothesis that the surface functionalization plays a role in determining surface coverage.

5.3 Results and Discussion

5.3.1 Confirmation of Monolayer Formation by Microscopy

The procedure followed for deposition of magnetic nanoparticles is fully described in Section 2.2.3. Following multiple washing steps to remove physisorbed

nanoparticles, SEM was used to compare the morphology of the layers. Figure 5.1 (a) shows the surface resulting from the stirring method, while (b) displays the image of the surface after the sonication-assisted “click” reaction. Both surfaces reveal a nanoparticle layer that exhibits nearly 100% surface coverage (where, as in Chapter 4, 100% refers to a close-packed hexagonal nanoparticle layer), which is very high in comparison to similar systems [110]. This was determined by comparing the average center-to-center distance between adjacent nanoparticles (20.4 ± 2.6 nm) to the average diameter specified by the manufacturer (18-22 nm). While the coverage is clearly very high for both methods, the nanoparticle layer resulting from the stirring method exhibits slightly higher surface coverage and uniformity which may be due to the gentler treatment of the stirring.

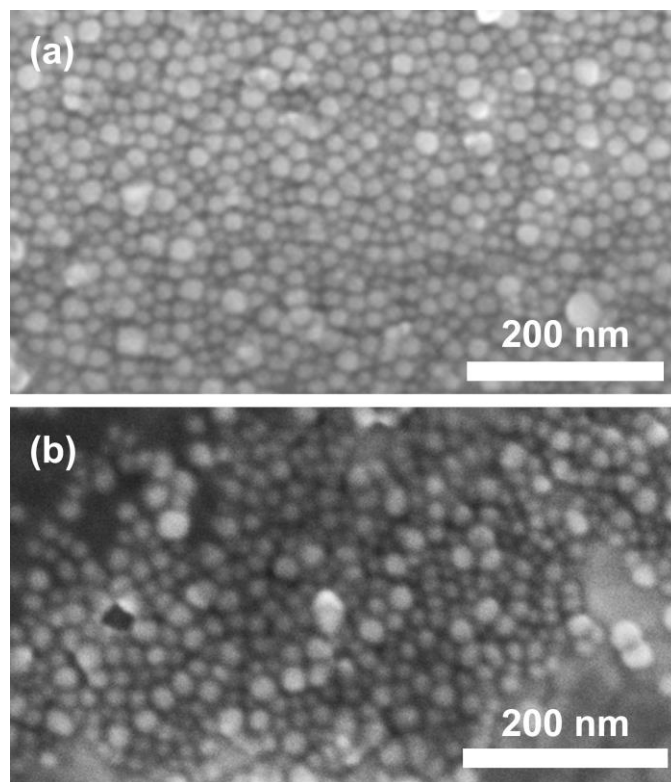


Figure 5.1: SEM images of the nanoparticle monolayer produced from the (a) stirring- and (b) sonication-induced methods

While it appears from SEM that a single monolayer of nanoparticles is produced, AFM was used to confirm this. Figure 5.2 shows two AFM micrographs comparing the azide-terminated gold surface (a) and the edge of the nanoparticle layer (b). The line profile in the inset shows that the nanoparticle layer is consistent with a single layer of nanoparticles that are 20 nm in diameter. This is significant, not only as a demonstration of the selectivity of this attachment mechanism, but also because unlike the silica nanoparticle system discussed in Chapter 4, magnetic materials tend to aggregate, and this method with appropriate washing steps appears to be sufficient to overcome the agglomeration of the magnetic nanoparticles while also promoting

attachment of a single layer to the substrate. These results are expected if the nanoparticles are bound to the surface by triazole ring linkages but the exact nature of the chemistry cannot be determined from microscopy. Instead, spectroscopic techniques were used to investigate the chemistry of the attachment processes taking place.

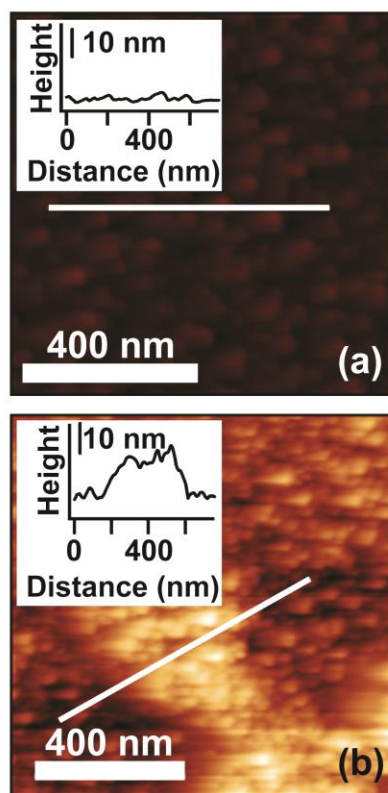


Figure 5.2: AFM images collected from (a) the azide-terminated substrate and (b) the edge of a nanoparticle monolayer. Insets display the line profile showing the height of the features across the white line

5.3.2 Spectroscopic Investigation of the Attachment Chemistry

ATR FTIR was used to compare the surface of the azide-terminated SAM on gold before and after attachment of the magnetic nanoparticles. A summary of the important vibrational modes is given in Figure 5.3. Spectrum (a) represents the azide-modified surface prior to any interaction with the iron oxide nanoparticles. The azide stretch at 2096 cm^{-1} is clearly observed and is consistent with results in Chapter 4 and with the literature [53]. The CH_2 stretching modes, indicating a slightly disordered alkyl overlayer, are also present at 2854 and 2927 cm^{-1} and are again consistent with the studies presented in Chapter 4 and literature values [51,96,97].

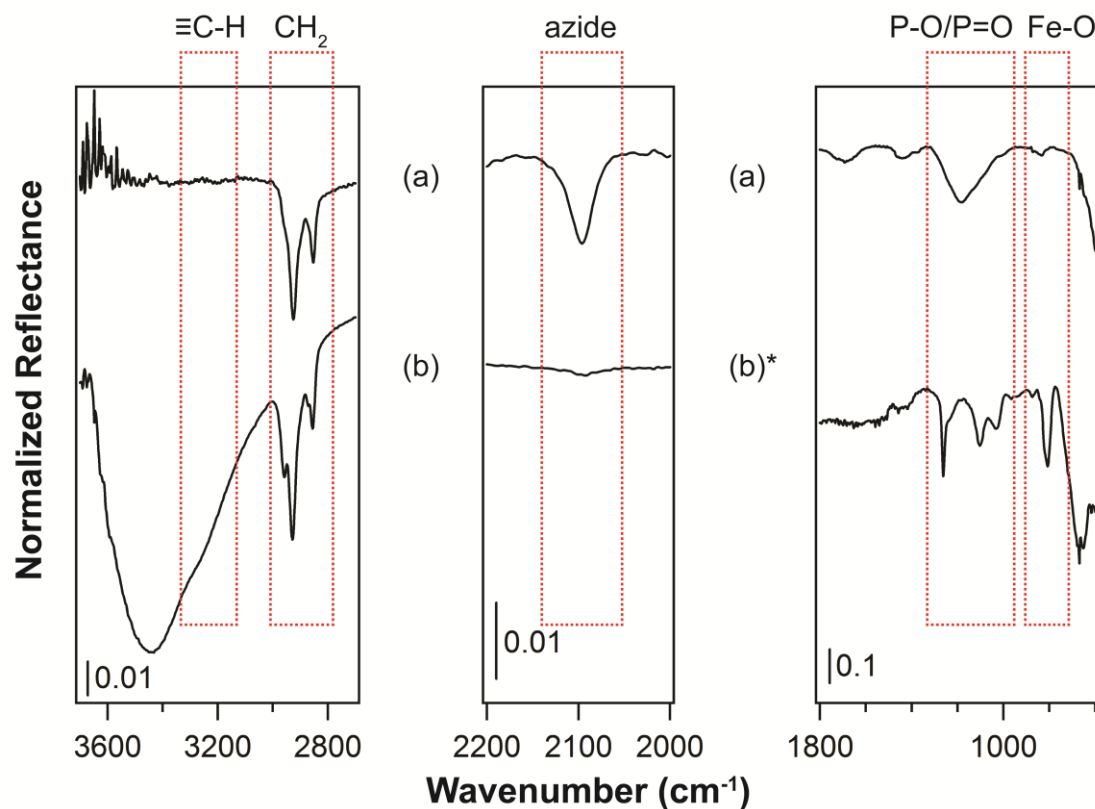


Figure 5.3: ATR FTIR spectra of the modified substrate before (a) and after (b) deposition of the magnetic nanoparticles. All spectra were collected from samples produced from the sonication-induced attachment method, except the one denoted with an asterisk (*) which was collected from a sample obtained using the stirring procedure

After deposition of the nanoparticle monolayer, the IR spectrum (displayed in Figure 5.3 (b)) changes. The azide stretch has decreased in intensity and is assumed to originate from unreacted azide groups present on the substrate, rather than from the alkyne $\text{C}\equiv\text{C}$ stretch that also is expected to appear within this spectral region [52,98]. This conclusion is based on the results from titration experiments discussed in Chapter 4. The reduction in intensity is likely due to most of the azide groups reacting with the nanoparticles or from nanoparticle screening of the interface. The symmetric and

asymmetric alkyl stretches remain and a large feature centered at 3300 cm^{-1} appears. This feature is assumed to be due to atmospheric water adsorbed on the surface or trapped between nanoparticles, but a small peak present at 3270 cm^{-1} that is not observed in spectrum (a) is consistent with the alkyne C-H stretch, indicating the presence of the modified nanoparticles on the surface [98].

As in Chapter 4, the feature near 1500 cm^{-1} indicating the presence of the triazole ring cannot be unambiguously assigned, however a number of other features occurring within the frequency ranges of $800\text{--}1300\text{ cm}^{-1}$ and $600\text{--}700\text{ cm}^{-1}$ may be tentatively assigned to bonds present in the phosphonic acid and iron oxide, respectively, supporting the successful deposition of nanoparticles on the surface [51,57,103,110–115]. Table 5.1 summarizes approximate assignments of these vibrational modes. The results from ATR FTIR are to be expected following the successful attachment by triazole ring formation, but since the presence of the ring cannot easily be detected by IR, alternative methods were used to further probe the attachment.

Table 5.1: Proposed IR Assignments for Figure 5.3

Assignment	Wavenumber (cm^{-1})
CH ₂ (asym.), CH ₂ (sym.)	2925, 2853
Azide	2094
Triazole ring	1560-1540
P=O	1261
P-O (asym.), P-O (sym.)	1104, 1030
P-C	808
Fe-O	700-630

XPS was used to compare the azide-modified surface before and after addition of the alkyne-modified nanoparticles. The XPS results in the N 1s and Fe 2p binding energy regions are presented in Figure 5.4. Spectrum (a) shows the azide-terminated gold substrate. Two components are present which can be deconvoluted into three components at 404.4 eV, 400.9 eV, and 399.4 eV. These are consistent with the nitrogen atoms of the azide group, specifically the ***N=N=N-***, ***N=N=N-***, and ***N=N=N-*** atoms (bolded and italicized for clarity) [52,103–105]. DFT computational methods were used to predict the core level binding energies for N 1s and the predicted values are indicated by the colored bars below the spectrum and represent the nitrogen atoms of corresponding color in the model. The experimental values are in agreement with the predicted binding energies. No features are observed for the azide-modified gold surface in the Fe 2p region (spectrum (a)) which is to be expected.

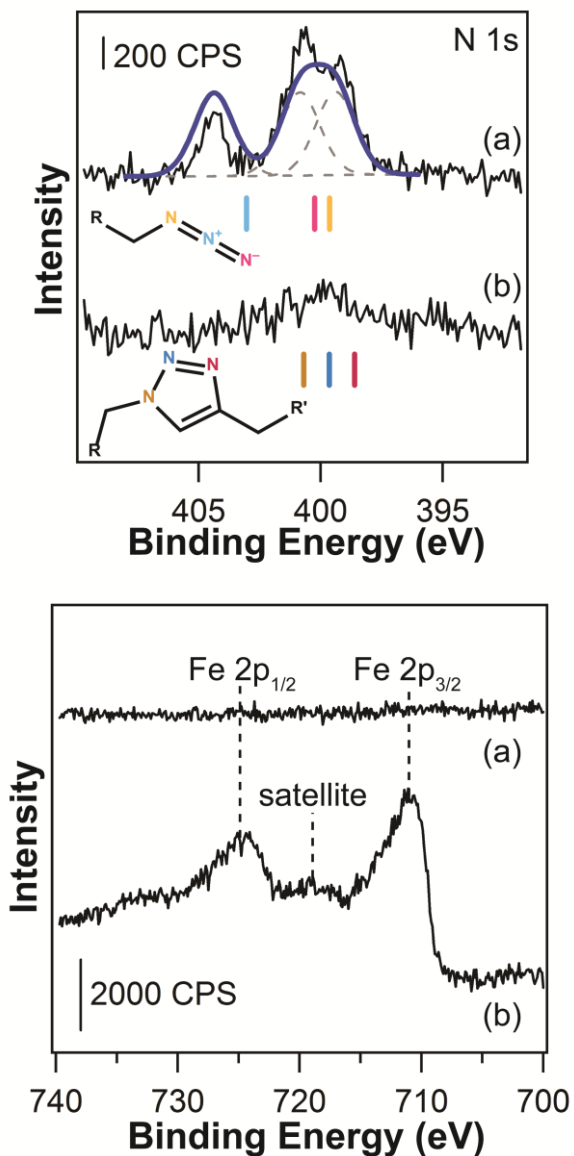


Figure 5.4: XPS spectra in the N 1s (top) and Fe 2p (bottom) binding energy regions. Spectrum (a) represents the azide-terminated gold substrate and spectrum (b) represents the same surface following nanoparticle deposition. The colored bars underneath the spectra in the N 1s region provide the positions of the computationally-predicted binding energies for the nitrogen atoms of corresponding color in the adjacent models

The XPS results following deposition of the nanoparticles are shown in spectrum (b). The Fe 2*p* region shows two distinct peaks at 725 eV and 711 eV, which correspond to Fe 2*p*_{1/2} and Fe 2*p*_{3/2}, respectively, providing further spectroscopic confirmation of successful nanoparticle deposition. There is also a small satellite shake-up peak that appears between the two main features that suggests that the surface of the Fe₃O₄ oxidizes to Fe₂O₃ [116]. In the N 1*s* region, one broad feature is observed in spectrum (b). This is consistent with the reaction of azide to form a triazole ring, as evidenced by the computationally-predicted binding energies of the triazole ring nitrogen atoms. Again, these are illustrated as the colored bars below the spectrum and represent the correspondingly-colored nitrogen atoms in the model. As in Chapter 4, the XPS results are in complete agreement with expected results, confirming that the nanoparticles are covalently stapled to the surface through the formation of the triazole ring and provide spectroscopic evidence of the “click” reaction.

5.3.3 Computational Study of Reaction Intermediates and the Resulting Effects on Surface Coverage

There is one question remaining that is not addressed by spectroscopic results: Why do the procedures that are outlined here and in Chapter 4 result in such unparalleled high surface coverage of the nanoparticle layers as compared to similar methods reported in the literature? It was suggested in Chapter 4 that the ultrasonic agitation is responsible for the formation of the stable, strongly-bound first layer of nanoparticles that provides the framework for subsequent nanoparticle layers. It was noted also that the surface coverage by the nanoparticles is exceptionally high compared to similar procedures in the literature considering that attachment is driven

by random interactions rather than self-assembly. This is also the case for the magnetic nanoparticle system to an even greater degree, as can be seen from Figure 5.1. In this work and in the method described in Chapter 4, attachment of the monolayer is facilitated by the “click” reaction between the azide-functionalized substrate and alkyne-modified nanoparticles. This functionalization scheme is reversed for the majority of procedures described in the literature, in which azide-modified nanoparticles are deposited onto flat alkyne-terminated substrates. While such a difference may seem inconsequential at first glance, it was hypothesized that the functionalization scheme plays a role in contributing to high surface coverage.

It was originally proposed [117] that the mechanism of catalysis that facilitates triazole ring formation involves the interaction of a single copper (I) center that interacts with the alkyne functional group. More recently however, it was suggested by the same group that two copper (I) centers are involved, in which one interacts with the terminal end of alkyne, and the other forms a π -complex with the alkyne group [118]. Only then will the azide group interact with the intermediate complex to form the triazole product.

In this work, density functional theory computational methods were used to optimize and compare the energies of the 1- and 2-copper center intermediate structures. The results, which are shown in Figure 5.5, conclude that the two-copper intermediate is lower in energy by 47.9 kJ/mol. While the overall mechanism is still a point of debate within the synthetic chemistry community, these DFT results provide support to the claim by Worrell et al. that two copper centers are involved [118]. Furthermore the optimized structure of the dinuclear complex is quite bulky, on the order of 10 Å. In a well-ordered alkyne-terminated monolayer, as is the case on a flat

substrate, the close packing of the alkyne tail groups may in fact hinder the formation of this intermediate complex. If one were to consider an alkylthiol SAM on a Au (111) surface, the intermolecular distance between adjacent alkylthiol groups is smaller than 5 Å for a full monolayer [119]. In this case, after the first copper center interacts with the alkyne it may be very difficult for the second copper center to maneuver around the closely-packed structures to form the π -complex. It becomes more complicated still for the azide groups to then navigate around this intermediate to insert into the monolayer and form the triazole ring.

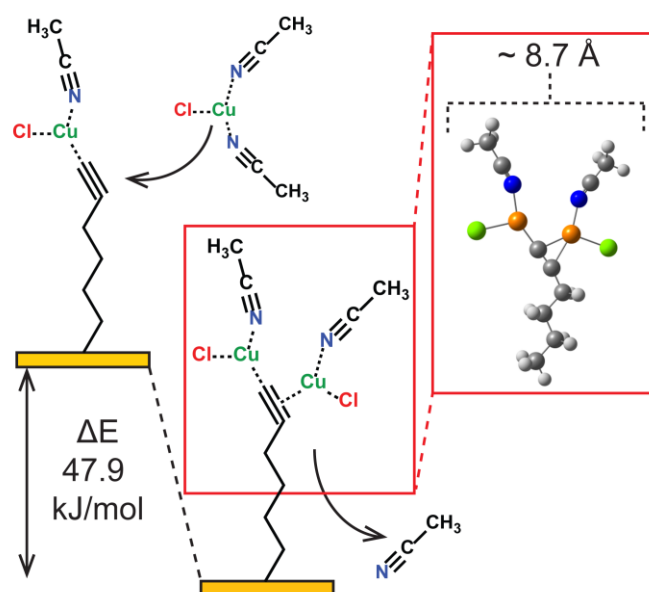


Figure 5.5: Energy difference between the mono- and dinuclear copper (I) intermediate structures determined from DFT calculations

By deliberately introducing disorder into the alkyne-terminated monolayer, it may be possible to promote better access to the alkyne groups for the copper catalyst

and azide groups. This is the case when the alkyne SAM is formed on the curved surface of the nanoparticles rather than the flat substrate. For this reason, the functionalization scheme of the nanoparticles and substrate, which is seemingly trivial, may actually be very important to achieving high surface coverage by aiding the “click” reaction.

5.4 Conclusions

This chapter extends the process developed for nanoparticle layer deposition and aims to develop an understanding of how experimental parameters affect the overall control of the resulting material. The nanoparticle deposition process facilitated by “click chemistry” in Chapter 4 was modified to result in nanoparticle layers of the more complex magnetic material. SEM and AFM investigations show that the nanoparticle layers exhibit extraordinarily high surface coverage but that only a single layer of nanoparticles is deposited, overcoming the intrinsic tendency of the magnetic materials to agglomerate. XPS and ATR FTIR studies provide supporting spectroscopic evidence of the attachment by “click chemistry” and confirm successful deposition of the iron oxide nanoparticles. DFT studies provided computationally-predicted core level binding energies that are in agreement with experimental results and were used to compare the energies of the mono- and dinuclear intermediate structures of proposed copper-catalyzed dipolar cycloaddition reaction. Results provide supporting evidence for a 2-copper center intermediate complex and show that the steric bulk of the intermediate may inhibit successful attachment on planar surfaces. On the other hand, this may be alleviated by rational design of the functionalization scheme so that the alkyne-terminated monolayer is formed on the spherical surface of the nanoparticles.

The last two chapters have focused on identifying the factors that affect control over surface coverage and film thickness during the application of “click chemistry” to modify surfaces. Additionally, the successful application of this deposition approach to different materials has been demonstrated. This introduces the possibility of building layered nanostructures of composite materials. The next chapter will describe the work performed to expand this fine-tuned level of control to include control over adsorbate placement.

Chapter 6

PHOTOLITHOGRAPHY OF SURFACES WITH “CLICK CHEMISTRY” BY INDIRECT REDUCTION OF COPPER

6.1 Abstract

This chapter describes work performed with the aim of expanding the customization of adsorbate attachment by “click chemistry” to include spatial control. Patterning of an azide-modified solid substrate was achieved by irradiating a solution containing a fluorine-tagged alkyne molecule, copper (II), and a photoinitiator through a photomask. Successful patterning was observed with XPS in mapping mode. High-resolution XPS results confirm covalent binding by “click chemistry” and are in agreement with the literature and with computationally-predicted values. A control series indicates that irradiation in the presence of both the copper (II) species and photoinitiator is necessary for efficient patterning to occur. The results of this study offer a fast, efficient, and reproducible method for selective attachment and patterning of a solid substrate. The indirect photo-reduction approach permits gentle treatment of the surface and wavelength tunability for various photosensitive systems and the resolution dependence on diffusion across the surface alludes to potential for non-line-of-sight surface modification. Figures in this chapter are reprinted with permission from [58]. Copyright 2018 Elsevier.

6.2 Introduction

The work outlined in Chapters 4 and 5 describes methods for improving control over the architectures formed on substrates based on utilization of the azide-alkyne “click reaction”. The rational design of substrate modification processes allows control over film thickness and surface coverage in these cases. The work described in this chapter extends this understanding to include spatial and temporal control for the selective attachment of adsorbates to result in patterned surfaces. Surface patterning is a highly important process for fabrication of small-scale devices [120–123]. Conventional methods for fabricating such surfaces include traditional photolithographic techniques. These processes typically require multiple steps (such as etching and photoresist application/removal), highly specialized equipment, cleanroom environments, and harsh photochemical treatments that may induce damage to certain sensitive organic or biological systems [124,125]. However, these are non-issues for the commercial manufacture of many devices, most notably in microprocessor fabrication, and the process is capable of producing highly-resolved spatial features with finely-tuned material properties. Photolithographic patterning can be combined with “click chemistry” to produce spatially-controlled modification with the high selectivity of attachment. In a report by Krause et al., spatial control of surface attachment by “click chemistry” was achieved by patterning the substrate with alkyne-terminated functional groups using resist-based photolithographic methods, followed by attachment of the azide-containing molecules in a solution-based procedure [126].

When the system to be modified is sensitive to damage induced by chemical treatment or high-energy photons, a gentler modification process is preferable. A variety of SAM-based approaches can be utilized to meet this goal [127]. Dip pen lithography uses a scanning probe microscopy tip coated with the adsorbate material

to draw the pattern onto the surface in an additive-based procedure (alternatively, subtractive methods, in which the tip removes adsorbates from the surface, can be employed instead). This produces highly-resolved features but it is a slow process because the features must be written individually [127]. Microcontact printing, as the name implies, requires coating a pre-fabricated stamp with the adsorbate, then stamping the pattern onto the substrate. This technique can pattern large areas of the substrate more quickly than dip pen lithography but requires template fabrication and a flat substrate. The resolution of the features can be affected by stamp swelling due to the solvent or from deformation of the stamp during the stamping process [127,128]. Another fast method for patterning over large areas is shadow masking, in which the sample is illuminated through a photomask to induce a photochemical reaction only on areas of the surface that are exposed to the light through the mask windows. Of course in this case, the resolution of the patterned features is limited by the mask features and the diffraction limit [127].

All of these SAM-based methods have been utilized in conjunction with the azide-alkyne cycloaddition “click reaction” to result in patterned surfaces modified with target functionalities [93,128–134]. Since the latter technique takes advantage of photo-induced chemical reactions, it affords the option of spatial control by light-mediated “click” reactions [135–137]. Both direct and indirect photo-induced reduction of copper (II) is possible. Direct photo-reduction has been successfully applied to catalyze the azide-alkyne “click” reaction through mechanisms such as ligand-metal charge transfer [137]. As an example, the direct reduction of copper (II) immobilized on a semiconductor substrate by exposure to ultraviolet A (UVA) irradiation to promote electron transfer from the substrate has been demonstrated and

shown to induce the cycloaddition [138]. This avoids the need for a reducing agent in solution but can require long irradiation times [135,137,139,140]. An alternative to this approach is the indirect reduction, in which the irradiation of a photoinitiator produces a radical system to reduce the copper (II) [137]. Numerous reports describing this method for polymer systems exist. Bowman et al. described, in 2011, spatial control of the Cu (I)-catalyzed azide-alkyne cycloaddition within a polymeric network via the photo-reduction of Cu (II) by irradiation of a commercially-available photoinitiator (Irgacure 2959 and Irgacure 819) under UV irradiation [128]. Later, they used sequential click reactions to form wrinkles in a polymer network. Using alkyne- and azide-containing polymers and Irgacure 819 and Cu (II) to form a network which was later irradiated, they took advantage of Cu (II) diffusion through the network prior to irradiation to form the wrinkles [141]. Similarly, Kloxin et al. have studied the kinetics of these commercial photoinitiators to form polymer networks via UV irradiation as well as the formation of a polymer network using a visible light photoinitiator system [134,142].

While pervasive in the field of polymer chemistry, lithographic patterning by direct or indirect photo-reduction of copper is less frequently reported on solid substrates in a non-polymer system. The ability to do so, however, would introduce the possibility of expanding this reaction to a host of applications, such as catalysis or MEMS, and offers a solution-based alternative for conformal filling over high aspect-ratio features. Alternative methods have been applied to achieve similar end results, such as in the work of Etschel et al., where traditional photolithographic steps were taken to pattern a solid substrate with hydrophilic azide- and hydrophobic fluorine-modified monolayers, followed by solution-based attachment of alkyne-modified

nanoparticles [143]. This produced a solid substrate patterned with nanoparticles using “click chemistry”. In a different approach, lithographic patterning by indirect copper (II) photo-reduction was performed to modify the surface of a polymer system [144]. This chapter describes a similar method to directly modify the surface of a solid non-polymer material with targeted functionalities bound by “click chemistry”. The premise is based on the indirect photo-reduction method of copper (II) in the presence of a photoinitiator to catalyze the attachment of an alkyne-containing molecule to a solid azide-terminated surface upon irradiation, as illustrated in Figure 6.1. By irradiating through a photomask, spatially-controlled attachment can be achieved to result in surface patterning in a simple wet chemistry approach. This fast and efficient process for creating a patterned substrate is summarized by the scheme in Figure 6.2. This proof-of-concept offers wavelength tunability to apply it to different systems and suggests a potential alternative to non-line-of-site deposition techniques.

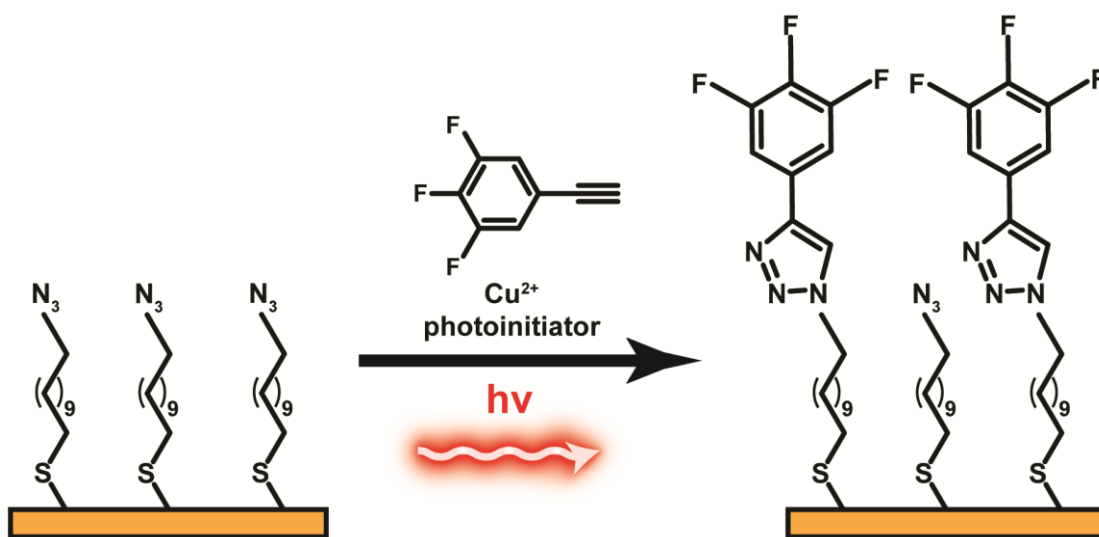


Figure 6.1: Reaction scheme for light-induced attachment of fluorinated-alkyne molecules to an azide-modified gold substrate

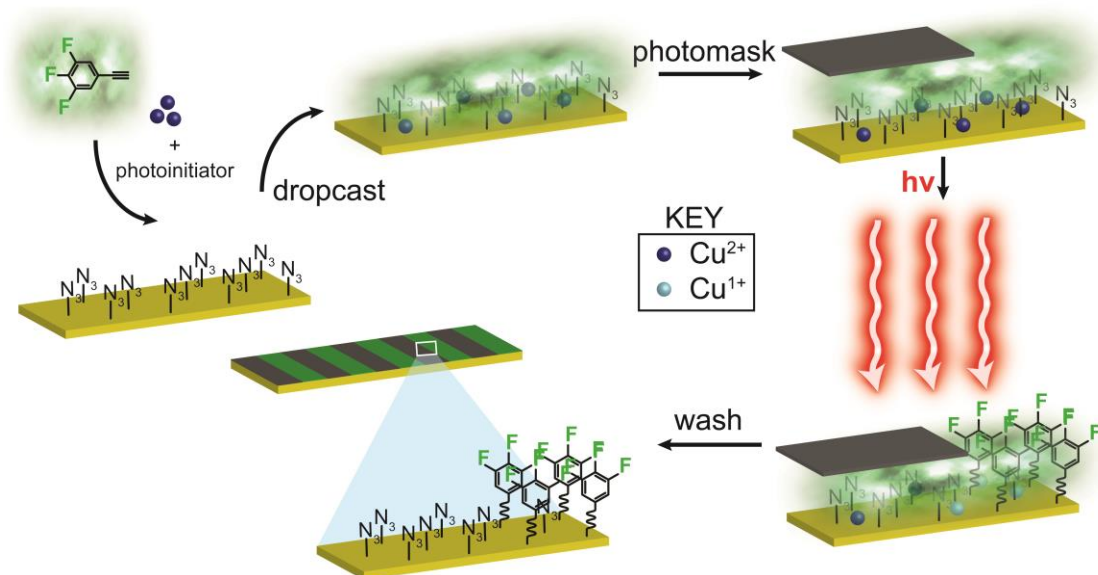


Figure 6.2: General scheme outlining the process for producing patterned surfaces by photo-initiated copper (II) reduction to catalyze the “click” reaction

6.3 Results and Discussion

6.3.1 Confirmation of Surface Patterning by “Click Chemistry”

The procedure carried out for patterned surface modification is described in detail in Section 2.2.4. XPS mapping was used to characterize the substrate following irradiation. The maps obtained for several important binding energy regions are shown in Figure 6.3 and reveal that patterning was successful. The N 1s and Au 4 $f_{7/2}$ regions, shown in Figure 6.3 (a) and (c), display bright areas in the masked regions of the surface and dark spots on the regions that were irradiated. This indicates a higher signal detected for nitrogen and gold on the regions of the substrate that were blocked from irradiation. This is reasonable because these areas should not have a large presence of the fluorinated alkyne molecule. This molecule would cover the azide-terminated monolayer, attenuating the signals originating from both the azide

functional groups and the gold substrate below. This is precisely the case on the dark spots that were not blocked by the mask and instead allowed the light to pass through unobstructed. While signals for gold and nitrogen are detected here, they are very low compared to the masked regions.

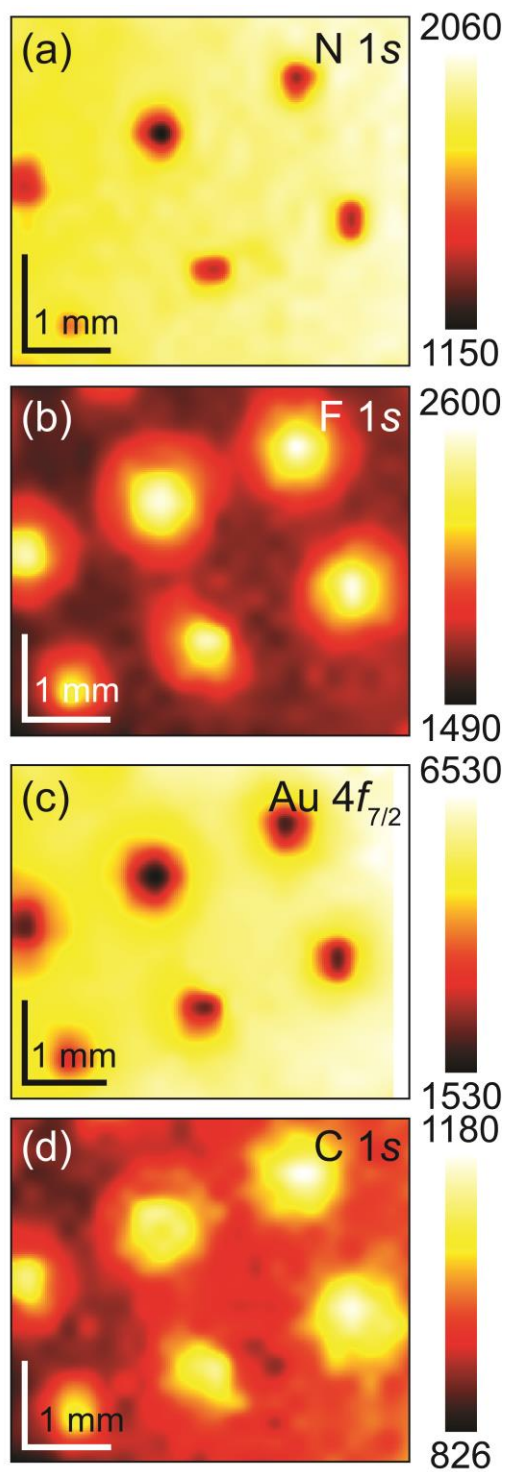


Figure 6.3: XPS maps of the surface following irradiation in the (a) N 1s, (b) F 1s, (c) Au 4f_{7/2}, and (d) C 1s binding energy regions

The opposite shading is observed in the F 1s and C 1s regions, shown in maps (b) and (d), respectively. The masked regions result in a lower (darker) signal while the irradiated spots exhibit high (bright) signal. This indicates a much higher presence of trifluorophenylacetylene in the spots exposed to the light, indicating that attachment has occurred in these regions to a much higher degree than in other areas. The larger amount of carbon detected in these areas also makes sense because the attachment of the trifluorophenylacetylene introduces eight more carbon atoms to the surface for each binding event to a 1-azidoundecan-11-thiol molecule that contains 11 carbon atoms. The carbon atoms in the alkyl linkers of the SAM are still present on the masked areas but they produce a lower signal than the carbon in the irradiated regions. The maps shown here confirm that patterning has occurred on the surface and the relative signals obtained in the masked and irradiated areas are consistent with covalent attachment of the adsorbates. By themselves, however, they do not confirm binding by “click chemistry”.

A closer inspection of the surface chemistry differences between the masked and irradiated regions is required by comparing high-resolution XPS spectra collected on the irradiated and masked spots of the sample. Figure 6.4 shows the high-resolution XPS spectra collected from (a) the center of an irradiated spot on the sample, and (b) a masked region on the sample. The leftmost panel compares the masked and irradiated regions in the F 1s binding energy region. The signal on the irradiated spot is much higher, which is consistent with the brightness observed on the spots in Figure 6.3 (b). There is a small amount of fluorine detected in the masked region. This may be a consequence of the fact that the azide-alkyne cycloaddition will proceed even in the absence of a copper (I) catalyst, although it is far less efficient [44,45].

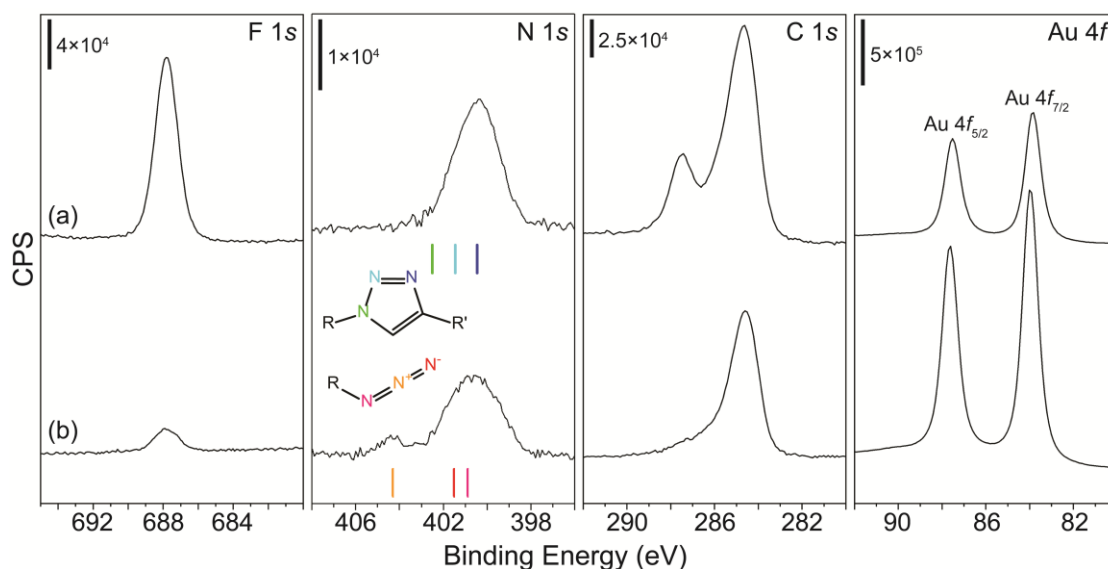


Figure 6.4: XPS high-resolution spectra collected from an irradiated (a) spot on the sample and from a masked (b) region on the sample. The colored bars below the spectra in the N 1s binding energy region represent the predicted binding energies from DFT calculations for the nitrogen atoms of corresponding color in the models

There is also an increase in the amount of carbon signal on the irradiated spot (a) as can be seen in the third panel. Again, this is consistent with the C 1s XPS map in Figure 6.3. In addition to the increased signal, a second peak is observed at 287.5 eV which is consistent with the introduction of a C-F species [96,145]. The irradiation of the surface also marks a decrease in signal in the Au 4f region, as can be seen in the rightmost panel of Figure 6.4. The peaks originating from gold that are observed on the masked region in spectrum (b) are much larger than those from the irradiated region (spectrum (a)) as the addition of the fluorinated alkyne monolayer attenuates the substrate. This was also confirmed visually in Figure 6.3 (c).

The high-resolution spectra in the N 1s binding energy region also mark a distinct difference between the irradiated and masked spots. Spectrum (b), which

represents the masked region of the sample, reveals two features that are consistent with the three types of nitrogen atoms present in the azide functional group [52,56,103–105]. The optimized geometry of 1-azidoundecan-11-thiol was computed with density functional theory calculations and provides predicted binding energies of 400.9 eV, 401.5 eV, and 404.3 eV for the $\text{N}=\text{N}=\text{N}-$, $\text{N}=\text{N}=\text{N}-$, and $\text{N}=\text{N}=\text{N}-$ azide nitrogen atoms, respectively. These predicted values are denoted by the colored lines below the spectrum and correspond to the like-colored atoms in the model. These are consistent with the experimental XPS spectrum. In the irradiated region of the sample, only one feature is observed. This is consistent with the reaction of the azide group to form a triazole ring [52,56,103]. DFT calculations predict N 1s binding energies of 400.5 eV, 401.5 eV, and 402.5 eV. Again, these predictions are illustrated by the colored bars below the spectrum and represent the correspondingly-colored nitrogen atoms in the model of the triazole ring. The predictions are in agreement with the XPS spectrum.

The high-resolution XPS results indicate successful binding of the alkyne molecule to the surface on the irradiated spots. Furthermore, the presence of the features corresponding to azide and triazole ring nitrogen atoms in the N 1s region suggest that the molecules are bound covalently by “click chemistry”. It is not well understood how efficient this process is though. To help determine this, the peaks in the F 1s and N 1s regions were integrated for comparison. It was assumed that the signal detected in the nitrogen region corresponds to a full monolayer of 1-azidoundecan-11-thiol adsorbed to the surface. The intermolecular distance between adjacent adsorbates in an alkylthiol SAM on Au (111) is 5 Å [119]. If this is assumed true in the case on the gold-coated silicon wafer, the density of azide-terminated

adsorbates on the surface is 1.26×10^6 functional groups per μm^2 . The ratio of F:N from the integrated peaks on the masked region of the sample (Figure 6.4(b)) is 0.365. Taking into account the atomic sensitivity factors (1.00 for F 1s and 0.38 for N 1s [146]), this ratio corresponds to one fluorine atom for every three nitrogen atoms. Despite the fact that these areas on the sample were not irradiated to enhance attachment by “click chemistry”, some degree of binding may still take place because the reaction is known to occur in the absence of the copper (I) catalyst as mentioned previously in Chapter 1, albeit at slower time scales. As this procedure takes place over mere minutes, it is possible that the presence of the fluorinated acetylene in these areas is a result of physisorbed species that were not removed during rinsing.

The F:N atom ratio in the irradiated region was calculated to be 2.08 from the integrated peaks in Figure 6.4(a). This corresponds to two fluorine atoms for every one nitrogen atom. While this is in excess of a full monolayer of 3,4,5-trifluorophenylacetylene, it confirms that the irradiation and rinsing results in the introduction of the fluorinated molecule without the formation of thick multilayers or polymers. The ratios were calculated at multiple spots on the sample surface from the maps in Figure 6.3 (a) and (b) and the average F:N atom ratios were found to be 0.32 ± 0.02 and 1.46 ± 0.29 for the masked and unmasked (irradiated) regions, respectively. These average values are consistent with about a third of a monolayer of the fluorinated alkyne molecule on the masked regions and slightly more than a monolayer on the irradiated spots.

The C 1s region of Figure 6.4 can also be analyzed more closely to help elucidate the efficiency of reaction. The two features observed in spectrum (a) for the irradiated region represent the C-F and non-C-F species. The ratio of these integrated

peaks is about 0.3 for C-F to other carbon species. The expected ratio is 0.19 as there should be three carbon atoms bound to fluorine and 16 carbons bound to other elements for each attachment of 3,4,5-trifluorophenylacetylene to a molecule of 1-azidoundecan-11-thiol. This small excess is consistent with the previous conclusion that the equivalent of just over one monolayer of the alkyne molecule is present on the irradiated surface. The XPS studies confirm qualitatively and quantitatively that the irradiation of the surface results in covalent attachment of the adsorbate to the SAM on the order of a single monolayer. The process is ostensibly driven by the reduction of the copper (II) species by the photoinitiator but this presumption remains unconfirmed at this point.

6.3.2 Verification of Indirect Copper Reduction

In this system, it was hypothesized that irradiation of the photoinitiator results in a radical system that reduces copper sulfate to the copper (I) oxidation state, which in turn, catalyzes the cycloaddition required for covalent attachment. In this case, patterning of the alkyne-containing molecule is possible by controlling where the photoinitiator is illuminated on the surface. Although mapping and high-resolution XPS results are consistent with spatially-resolved covalent attachment by triazole ring formation, they do not confirm that the indirect photo-reduction of copper (II) by the photoinitiator is the mechanism by which this occurs.

If this process is in fact the driving force of surface patterning, it is necessary for all components (i.e. azide and alkyne functional groups, copper (II), and photoinitiator) to be present to facilitate successful attachment. A series of control studies were carried out to identify which components are necessary for efficient patterning to occur. The XPS maps of this control set are shown in Figure 6.5. In the

first case, the alkyne solution (containing 3,4,5-trifluorophenylacetylene, copper sulfate pentahydrate, and Irgacure 819 photoinitiator) was drop-cast onto the azide-modified substrate. The coverslip and mask were placed onto the sample but it was kept in darkness for five minutes, instead of being irradiated, followed by the rinsing steps to remove physisorbed species. The map of this surface, present in Figure 6.5 (a), shows no evidence of patterning, suggesting that this length of time is not sufficient for the reaction to occur in any appreciable amount. To determine whether the photoinitiator is necessary, a solution consisting of the alkyne-containing molecule and copper sulfate (but no photoinitiator) was drop-cast onto the sample. Following five minutes of irradiation through the mask and subsequent rinsing, no patterning was apparent, as demonstrated in Figure 6.5 (b), indicating that the presence of the photoinitiator is required to induce the reaction.

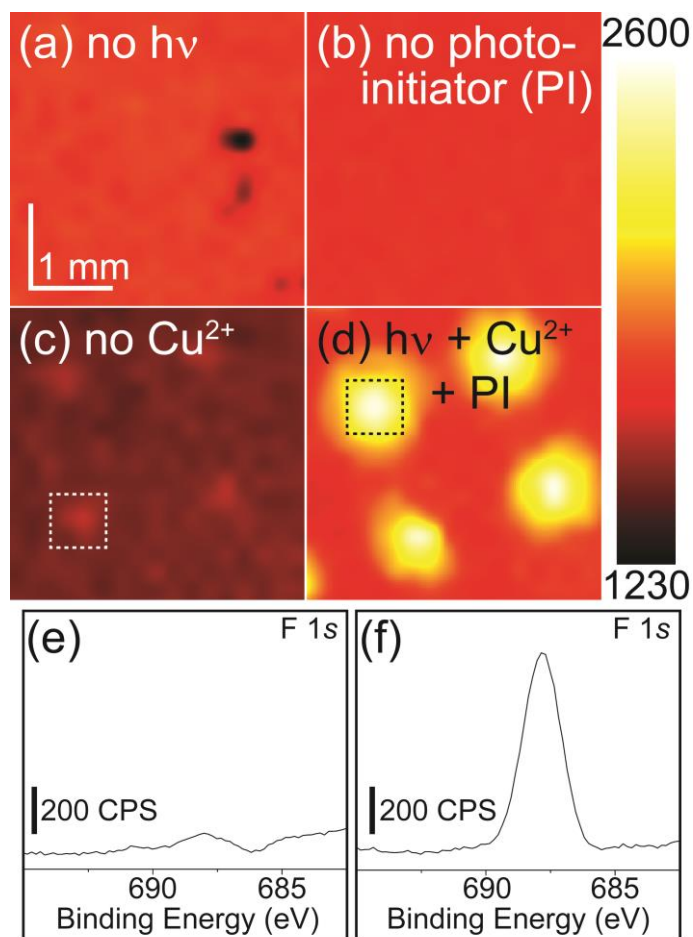


Figure 6.5: XPS maps of the azide-modified surfaces upon which (a) the solution was not irradiated, (b) the solution (sans photoinitiator) was irradiated, (c) the solution (sans copper sulfate) was irradiated, and (d) the solution (with all components) was irradiated. High resolution spectra (e) and (f) were collected in the F 1s region from the areas identified by the dashed boxes in maps (c) and (d), respectively

Likewise, a solution containing the fluorinated alkyne molecule and photoinitiator, but no copper sulfate, was drop-cast onto the surface, following by five minutes irradiation and rinsing. This surface, shown in Figure 6.5 (c) does exhibit a small degree of patterning. This suggests that the irradiation of the photoinitiator alone

may be sufficient to initiate the cycloaddition. However, in comparison to the test sample in which alkyne, copper (II), and photoinitiator were all irradiated through the mask (Figure 6.5 (d)), the amount of patterning in the absence of copper is negligible. High-resolution XPS spectra in the F 1s region were collected from the unmasked spots (denoted by the dashed-line boxes in images (c) and (d)). The spectra collected from the control sample containing no copper and the test sample containing all components can be compared in Figure 6.5 (e) and (f), respectively. The area of the F 1s signal in spectrum (f) is about 6 times that of spectrum (e) so it is clear that the reaction is much more efficient when all components are present on the sample and irradiated. This observation implies that the catalysis of the “click reaction” is induced by indirect photo-reduction of copper (II).

As a consequence of this conclusion, the resolution of the patterned features is limited by diffusion of the copper species. This is evidenced by the fact that the patterned features are similar, but not uniform, in size despite the fact that the windows of the photomask were uniform. The limitation in resolution due to diffusion was also found to occur in similar systems designed for the patterning of polymers by indirect copper reduction [128,134,141]. The implication of this is that very highly-resolved patterns are difficult to achieve using this process. On the other hand, the diffusion of copper can be an advantage in non-line-of-sight deposition. The surface modification of three-dimensional or high aspect-ratio features that would not otherwise be exposed to the light can be performed in the case where the copper (I) center can diffuse outside of the illuminated region. While conformal filling for such features can be achieved using ALD, the method presented here offers a fast and simple alternative. Furthermore, it presents the possibility of wavelength tunability, by

varying the photoinitiator used, to accommodate for various sensitive systems that would otherwise be damaged by more traditional photolithographic techniques.

6.4 Conclusions

The work described in this chapter extends the formation of surfaces modified using “click chemistry” to obtaining spatial control over adsorbate placement. Rather than relying on the *in situ* reduction of copper (II) using sodium ascorbate, this process takes advantage of a radical photoinitiator system for copper reduction when exposed to light. This permits spatial control by irradiating through a photomask and temporal control by inducing the cycloaddition on a timescale that is not sufficient to allow the reaction to proceed efficiently in the absence of irradiation. Successful surface patterning was confirmed by XPS mapping and the attachment by covalent triazole ring linkages was verified by XPS supplemented with computational predictions. It was determined that the reaction only proceeds efficiently upon irradiation of both functional groups, copper (II), and photoinitiator. This procedure is a gentler surface modification approach that can be tuned for various photosensitive systems. Diffusion of the copper species does limit the spatial resolution, but also presents potential for non-line-of-sight deposition.

Chapter 7

SUMMARY AND CONCLUSIONS

The common goal of all of the projects described in this dissertation has been to foster a fundamental understanding of the chemical reactions needed and processes taking place during the covalent adsorption of nanoscale materials to various surfaces. The procedures developed, and more importantly the mechanistic findings in these projects, offer a greater comprehension of the variety of factors that control the formation and the resulting physical properties of the material. Designing the attachment processes with the aim of maintaining control over these properties is imperative because the resulting characteristics (such as charge transfer, film thickness/coverage, and adsorbate placement) have profound effects on the final device or target applications.

Chapter 3 focused on discerning the binding processes involved in the solution-based adsorption of carbon nanotubes to modified surfaces. While it is unquestionably acknowledged that covalent binding takes place between the CNTs and amine-terminated SAMs through the functional groups present on the CNTs, this work confirms that an additional binding mechanism through the CNT cage directly to the SAM exists. A combination of microscopy, computational, and spectroscopic studies was used to support this conclusion. It was further established that the degree to which this direct binding between the SAM and CNT cage occurs, relative to the binding through additional functional groups, is nontrivial. This was shown to be the case on both gold and silicon substrates with similar chemistry. The results of this

study would be beneficial in the design of devices relying on electron transfer between the substrate and adsorbate. Further studies building upon this proof-of-concept to understand exactly how this direct attachment affects charge transfer and carrier lifetime would be important for integration into future devices.

The work described in Chapters 4 and 5 expands the understanding of large molecular structures to the nano- and microscale. The attachment chemistry relies on the highly-utilized copper (I)-catalyzed “click” reaction between azide and alkyne functional groups to form a triazole ring linker. A process was developed for nanoparticle layer deposition that is fundamentally similar to ALD, but produces films on the larger scale more commonly associated with traditional LbL techniques. The resulting nanoparticle mono- and multilayers were observed via microscopy and characterized with spectroscopy supplemented with density functional theory computational methods. The sonication-induced attachment described in Chapter 4 results in remarkable precision in layer thickness, in which each nanoparticle layer is covalently-bound to the layer below it. This is an improvement over many of the procedures cited in the literature that rely on self-assembly and result in films with thicknesses that are, in some regions, not well-defined.

This nanoparticle layer deposition procedure also results in unprecedented surface coverage of the nanoparticle layers. This observation was studied more closely in Chapter 5, which focused on the more challenging attachment of a single layer of magnetic nanoparticles. A computational comparison between the possible intermediate structures of the catalysis mechanism provided evidence supporting the hypothesis that the functionalization scheme affects surface coverage. The work identifies some of the most important parameters of the nanoparticle film fabrication

process that affect the physical dimensions of the resulting surface. These results should be considered during the design of layered microstructures in which the dimensions play a vital role in the targeted application of the device.

Chapter 6 extends the understanding of the principles responsible for rational tailoring of layers bound to solid substrates by “click chemistry” to encompass spatial and temporal control. Selective regional attachment of an alkyne-containing molecule to the azide-modified surface was accomplished using the “click” reaction. Unlike previously discussed methods that required the presence of sodium ascorbate in solution for *in situ* reduction of copper (II), this procedure is a light-mediated reaction. The presence of copper (II) and a photoinitiator ensures that the cycloaddition reaction does not occur until the system is irradiated, and only the regions of the sample that were exposed to the light undergo attachment of the fluorinated alkyne. XPS mapping was used to support successful patterning. High-resolution spectra, coupled with DFT-predicted binding energies, confirm attachment by triazole ring formation. Control studies affirm that the reaction is facilitated by indirect photo-reduction of the copper species, which allows for wavelength tunability that may be required to avoid photo-degradation of fragile organic species. The procedure is a gentler modification approach in comparison to the more conventional photolithographic methods. Moreover, diffusion of the copper species, as a consequence of the indirect reduction, offers the ability to modify high aspect-ratio features of the substrate that would otherwise not be fully exposed to the light.

This indirect photo-reduction approach that introduces spatial and temporal control of attachment could be utilized in conjunction with the procedure outlined above for the formation of highly-controlled nanoparticle architectures. The improved

understanding of how procedural parameters affect properties such as film thickness and surface coverage would be beneficial in aiding the design of three-dimensional structures comprised of appropriately-functionalized nanoparticles. Preliminary experiments have been performed to build spatially-controlled covalently-bound nanoparticle layers upon a modified substrate by combining the procedures and insight gained from the conclusions above. An illustration of this method is shown in Figure 7.1. The formation of the patterned nanoparticle layer and optimization of the process is a challenge because the nanoparticle system behaves quite differently compared to the solution used to form organic monolayers in Chapter 6. Factors such as the nanoparticle dimensions, relative concentrations of the functional group linkers, and irradiation wavelength and time must be carefully considered.

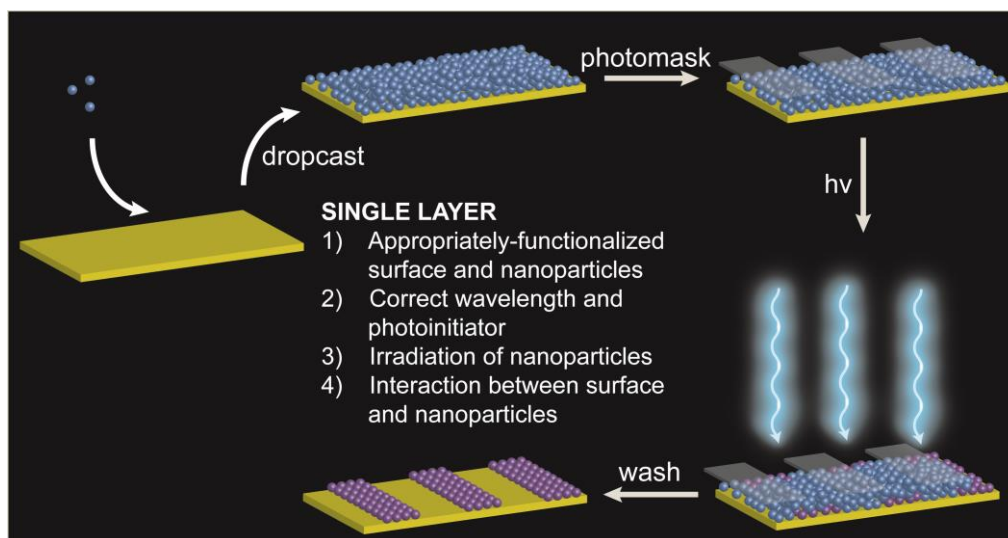


Figure 7.1: General scheme illustrating the procedure and requirements to form a spatially-controlled nanoparticle monolayer

Upon the successful optimization of this procedure, a two-photon stereolithographic version of this approach would allow fabrication of highly-resolved, three-dimensional microstructures composed of covalently-linked nanoparticles in solution. Akin to 3D printing on the microscale, this process would afford several potential advantages over existing stereolithographic 3D-printing methods, including nanoscale placement control and resolution, and the ability to form structures comprised of more accessible and less costly non-photopolymer materials. Moreover, the demonstration of binding nanoparticles composed of different materials together via “click chemistry” could be applied to construct spatially highly-resolved composite material architectures.

From the understanding of the bonding chemistry of molecular structures to the formation of two- and three-dimensional nanoarchitectures, the work reported and the conclusions drawn in this dissertation lay the groundwork for the design of future devices. These conclusions offer a fundamental insight into the processes, affording a large degree of control over the final structures. As the structures approach smaller scales, the surface interactions taking place become dominant factors in the resulting material properties. The architectures produced in this work offer both stable, well-defined attachment between the components, and nanometer resolution within the structure. As such, they present the ability to develop improved materials for applications such as medical devices, integrated circuits, MEMS/NEMS, and lab-on-a-chip devices. Moreover, the continued improvement of these materials will help foster a better understanding of the relationship between surface science and material design.

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Publication: Langmuir
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Date: Feb 1, 2017
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Title: Nanoparticle layer deposition for highly controlled multilayer formation based on high-coverage monolayers of nanoparticles

Author: Yue Liu, Mackenzie G. Williams, Timothy J. Miller, Andrew V. Teplyakov

Publication: Thin Solid Films

Publisher: Elsevier

Date: 1 January 2016

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Title: Building high-coverage monolayers of covalently bound magnetic nanoparticles

Author: Mackenzie G. Williams, Andrew V. Teplyakov

Publication: Applied Surface Science

Publisher: Elsevier

Date: 1 December 2016

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Title: Indirect Photopatterning of Functionalized Organic Monolayers via Copper-Catalyzed "Click Chemistry"

Author: Mackenzie G. Williams, Andrew V. Teplyakov

Publication: Applied Surface Science

Publisher: Elsevier

Date: Available online 3 April 2018

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