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Site-Specific Metallization of Multiple Metals on a Single
DNA Origami Template

Bibek Uprety

A thesis submitted to the faculty of
Brigham Young University
in partial fulfillment of the requirements for the degree of

Master in Science

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Department of Chemical Engineering
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October 2012

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ABSTRACT

Site-specific Metallization of Multiple Metals on a Single DNA Origami Template

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Department of Chemical Engineering
Master of Science

This work examines the selective deposition of two different metals on the same DNA origami template for nanofabrication. DNA, with adjustable size and shape serves as a suitable template for fabricating metal junctions in the nanometer domain via bottom-up assembly. Bottom-up assembly utilizes the recognition capability of molecules like DNA to self-assemble and form structures. In this regard, DNA origami provides a useful means for forming nanostructures by folding single-stranded DNA into different two and three dimensional shapes. Selective deposition of metal on specific locations of a DNA template is essential for making DNA-templated electronic circuits.

Site-specific metallization of DNA origami templates was recently demonstrated, for a single metal at molecularly designated sites. This study addresses the next important step of depositing multiple metals on the same template. Specifically, it is an experimental study to demonstrate the gold-copper metal junction on a DNA origami template, and to understand the challenges associated with junction fabrication. DNA-templated circuit fabrication depends on the ability to deposit multiple components on a DNA template. To achieve this, a section of the DNA template was seeded with Au nanoparticles and electrolessly plated with Au. This Au plated section of the template was then masked with an organic layer to protect it from additional deposition. The remaining section of the same template was subsequently seeded with Pd and plated with copper to form the desired metal junction.

This work is the first of its kind to demonstrate metal junctions on a DNA origami template. Metallized origami templates were characterized with the help of SEM imaging and EDX composition data to confirm the presence of the two different metals on the same template. In addition, a chemical “mask” was also used successfully at nanometer resolution to protect previously metallized sites (gold plated) to prevent further metal deposition. The results obtained represent important progress toward the realization of DNA-templated components for nano-circuit fabrication. The work also provides the basis for the next step to make metal-semiconductor junctions on a DNA template.

Keywords: Bibek Uprety, DNA origami, site-specific metallization, selective deposition, gold, palladium, copper

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1 INTRODUCTION

Integrated circuits have come a long way since their inception in the 1950's, consistently decreasing in size and increasing in capacity. Over the years, increased functionality and lower production costs of integrated circuits have singlehandedly revolutionized the world of electronics. While current fabrication methods seem to be doing well for the near term, the same technology appears inadequate to meet the global demands of increased capacity per unit area and lower costs for next generation devices. In this regard, bottom- up nanotechnology, which enables construction of complex architectures from molecular building blocks, is seen as a promising alternative to develop future generation integrated circuits^{1, 2, 5}. Bottom- up technology utilizes the recognition capability of molecules to self-assemble and form structures with nanometer resolution⁵.

DNA is a molecule of interest for use as a self- assembled template for nano electronic circuit fabrication via bottom-up assembly^{4, 10}. Watson-Crick base pairing in DNA, where only portions of strands which are complementary will bind to each other, is one particular characteristic of DNA that can be exploited to design sets of DNA strands that self-assemble to a desired geometry. Likewise, the presence of functional groups that interact with various metal ions is another DNA characteristic of interest. Metallization of DNA templates with Ag^{7, 8, 14-16}, Au^{1 - 3, 8, 11, 16, 27}, Pd^{17, 18}, Pt¹⁹, Cu⁹ or Ni¹¹⁻¹³ to form nanowires is one way to form complex nano structures¹. Numerous studies have been conducted on the metallization of DNA templates of

various shapes and sizes. Although the metallization process has been demonstrated with considerable success, the ability to metalize specific locations of the same DNA template with different metals has not yet been demonstrated. The present work focuses on the development of heterogeneous metallization to form a metal-metal junction on a DNA origami template as shown in Figure 1-1.

Figure 1-1: Process used for making a heterogeneous metal junction on a DNA origami template. (A) Seed particles for the first metal group on a select segment of the template. (B) Electroless plating of the seeded section. (C) Seed particles for the second metal group on the adjacent section of the template. (D) Electroless plating on the second seed layer to make the desired metal junction.

The ability to selectively metallize a particular area of a DNA origami template will be of utmost importance when making the desired metal junction. Site-specific metallization of DNA origami templates has been demonstrated only recently, but challenges remain for selectively localizing different metal components on the same template. This work on metallization of DNA origami will provide an enabling step in realization of DNA-templated electronic circuits. For

future work, one metal group can be displaced with semiconductor materials such as Te and Bi_2Te_3 to produce a metal - semiconductor junction that is important for nano-electronic circuits.

Scope of the Project

Development of a heterogeneous metal junction on a DNA origami template has not been demonstrated. The primary objective of this research is to experimentally demonstrate a metal-metal junction on DNA origami, and to understand the challenges associated with its fabrication.

2 BACKGROUND

2.1 Bottom-up Nanotechnology

Bottom-up technology utilizes the recognition capability of single molecules to self-assemble those molecules into useful conformations⁵. Bottom-up approaches essentially seek to arrange smaller components into complex assemblies. Self-assembly shows promise as a potential way of reducing cost, decreasing size and enabling fabrication of complex nano-assemblies. DNA, with nanoscale size, self-recognizable base pairs and arbitrary length is an ideal template for nanostructure assembly. As DNA itself is not conductive, metals and semiconductors will need to be deposited onto the DNA templates for use in nano-circuits.

2.2 DNA

2.2.1 Basic Properties

DNA is a double helix structure consisting of two long polymers made up of small units called nucleotides; it has a backbone made up of sugar and phosphate groups¹⁰. A nucleotide is an organic compound made up of nitrogenous base, a sugar (deoxyribose for DNA) and a phosphate group. Adenine (A), guanine (G), thymine (T) and cytosine (C) are the four kinds of bases present in a DNA strand. The interaction between the base pairs in the form of hydrogen bonds holds the two strands of DNA together. However, hydrogen bonding of base pairs is non-covalent; hence, they can be broken and rejoined relatively easily. The two strands in the double

helix can be pulled apart at higher temperatures to yield single- stranded DNA. The base pairing is very specific, i.e. each type of base on one strand bonds with just one type of base on the other strand¹⁰. The only base pairs possible are A with T and G with C. Within the double helix structure of DNA, A forms 2 hydrogen bonds with T on the opposite strand, and G forms 3 hydrogen bonds with C on the opposite strand. A-T and G-C base pairs are roughly the same length of about 2.84-2.92 Angstroms¹⁰. In the B form of DNA (Figure 2-1), which is the normal double helix structure, the helix makes a turn every 3.4 nm, and the distance between two adjacent base pairs is 0.34 nm¹⁰. The total diameter of DNA is also only about 20 Angstroms making it suitable for use as a template for fabrication of components for nano-circuits.

Figure 2-1: DNA Structure (modified from [34])

2.2.2 Metal Ion Interaction with DNA

The interaction between DNA bases and a variety of metal groups represents a key aspect of DNA metallization. DNA, with a negatively charged phosphate backbone, shows considerable attraction to charged species, which to a large extent is electrostatic²⁶. Alkali metal ions like Li^+ , Na^+ , K^+ , Cs^+ have been shown to electrostatically bind to the DNA backbone²⁶. In addition to the electrostatic interactions, Duguid et. al used laser Raman spectroscopy to show that divalent metal cations like Mg^{2+} , Ni^{2+} , Cu^{2+} , Pd^{2+} have specific metal interactions with acceptor sites (bases) on the purine (N7) and pyrimidine (N3) rings²². Experiments also showed that metals interact more strongly with bases than with phosphates, except for Cu^{2+} which binds strongly to both of these groups. With the exception of Hg^{2+} , metal ions prefer to bind to guanine and cytosine regions over adenine and thymine regions²². Hg^{2+} , Cu^{2+} and Pb^{2+} are metals with strong base affinity; however, these metals also disturb hydrogen bonding between base pairs, destabilizing the B form of DNA²². The interaction of different metal ions with either the phosphate backbone or the nucleotide bases is of critical importance for several methods of DNA metallization.

2.3 DNA Origami

DNA origami is the folding of single stranded DNA to create different two and three dimensional shapes. The specific interaction of base pairs, that is A with T and G with C, is what makes DNA a useful material and DNA origami a useful tool to make a wide variety of nano-structures^{20, 21}. Developed by Paul Rothemund in 2006, the general approach in designing an origami template involves use of single-stranded staple strands to fold a long scaffold strand (also single stranded DNA) into the desired size and shape. Each staple strands, due to Watson Crick base pairing, give direction and act as links to connect portions of the scaffold strands. The

designs are first made in a computer program that determines the placement of individual staple strands. Scaffold and staple strands are then mixed, heated and cooled. As the mixture cools, the staples pull the long scaffold into the desired shape. Figure 2-2 shows the computer generated model for a bar shaped DNA.

Figure 2-2: DNA origami technique (A) Scaffold and staple strands (B) Arrangement of scaffold and staple strands to give a bar shaped DNA (C) AFM image of bar shaped structure. Height scale for (C) is 10 nm. Scale bar for (C) is 500 nm.

In addition, DNA origami designs can also be made with attachment points at specific places for attaching different functional groups. The staple strands in the template can be extended with additional nucleotides where the desired functional group with complementary sequences can be placed. As shown in Figure 2-3, the staple strands in the DNA origami

template with additional 8A's (blue strands) hybridize with 8T's in the DNA functionalized (red strands) nanoparticles and thus, deposit particles on the template. The nanoparticles interact with the DNA strands (red strands) via metal-thiol (SH) interaction. Thus DNA origami provides a useful means to make DNA templates of varying complexity.

Figure 2-3: DNA origami template with attachment strands for nano particle deposition

2.4 Electroless Deposition

Electroless plating is a method of plating conductive substrates with metals such as gold, copper or nickel without the use of an external power supply or expensive chemicals. The general procedure involves immersing the substrate in aqueous solution, whereupon metal deposition on the substrate begins immediately. The first deposited metal layer catalyzes subsequent plating and allows metal deposition to continue. Since the deposited layers catalyze the subsequent reaction, the plating process is often called autocatalytic²⁵. Electroless plating of copper, gold, nickel, palladium and cobalt have been successfully demonstrated in the literature²³⁻²⁵.

An electroless plating bath typically consists of a source of metal ions, a reducing agent, suitable complexing agents and stabilizers. The reducing agent supplies the electrons required for the reduction of the metal ions. Complexing agents are usually organic acids or their salts, which exert a buffering action to maintain pH of the plating solution²⁵. In addition, complexing agents form stable complexes with metal ions, thus enhancing the stability of metal ions and the selectivity of the plating reaction²⁵. Stabilizers help to prevent the homogeneous reaction that triggers the random decomposition²⁵.

The overall reaction can be divided into a cathodic reaction where the metal ions are reduced and the anodic reaction where the reducing agent is oxidized.

where, Red and Ox are the reducing agent and the oxidation product respectively. The above reactions do not represent the actual stoichiometry. Both the oxidation and reduction reactions occur on the same surface, forming a mixed potential at steady state^{23, 25}. In other words, the rates of the separate partial reactions depend only on the electrode potential, the mixed potential²⁵. The partial reactions are very dependent on each other because the electrons released during oxidation are consumed in the reduction of metal ions²⁵. For metal deposition to occur, the reduction potential must be high and the reduced metal should provide a catalytic surface suitable for additional plating. Understanding the concept of mixed potential can be useful for manipulating the reaction kinetics in order to achieve the desired metal deposition. For example, changing the concentration of either the reducing agent or the metal ions will change the mixed potential, which will thus change the rate of electroless deposition.

Previous research at BYU has successfully demonstrated electroless deposition of different metals on DNA templates. Geng et. al showed electroless deposition of palladium on lambda DNA and gold on DNA origami templates². Similarly, Liu et. al and Pearson et. al have successfully demonstrated electroless gold plating on various DNA origami templates^{1, 3}. Building on this previous work, this project will use site-specific electroless deposition to produce continuous metal segments on DNA origami templates.

2.5 The Seeding Process

Seeding is the first process in DNA metallization, and is used to create the platform for electroless plating of DNA. As mentioned in the section above, sites are needed to catalyze electroless deposition reaction. DNA itself does not possess metal particles (catalytic sites), so a seeding process is used to deposit transition metals like Ag, Pd, Pt or Au onto DNA to enable subsequent electroless deposition. Seeding selectivity is defined as the ratio of number of metal seeds deposited on the DNA template to the total number of seeds deposited on the entire surface. For good selectivity, the seeds should only attach to the DNA with little or no seeding on the rest of the surface.

As mentioned above (Section 2.4), transition metals can be attached to DNA by electrostatic interaction or complex formation with the negatively charged phosphate backbone. Braun et. al were the first to seed DNA with Ag^+ ions, using an ion exchange process and forming a complex with the DNA bases⁷. Silver ions attached to the DNA structure were then reduced to form the seed layer. Likewise, divalent metal ions like Pd (II)^{17, 18} and Pt (II)¹⁹ have been shown to seed DNA by forming complexes with the Lewis bases on DNA. Richter et. al and Geng et. al have shown the use of Pd(II) to make palladium wires^{3, 17}. The general approach is activation of DNA with Pd (II) ions to form coordination complexes, reduction of the ions to

form the seed layer, and subsequent electroless plating with palladium to make nanowires. Similarly, Gu et. al have demonstrated the use of Pd (II)¹² and Pt (II)¹¹ ions for seeding DNA to make nickel wires. While ionic interaction or complex formation have been used frequently in the literature to form a seed layer on DNA, the selectivity of the seeding is often low, leading to higher background deposition.

To make DNA-templated electronic components, both good seed selectivity and the ability to attach seeds to specific sections of the template are very important. Attachment of metal binding ligands (Figure 2-3) has been shown to improve seed selectivity and localization on DNA origami templates^{3, 8, 15, 16, 27}. Metal particles are attached via metal binding groups such as thiols to the ends of short DNA strands that are designed to bind at specific complementary locations on DNA origami templates. Conversely, metal binding ligands can be first attached to the DNA template and then metal nanoparticles can be attached to the ligand. Since longer reaction time is required for metal-thiol interactions^{3, 8}, it is most convenient to first attach ligands to the metal and then attach metal to the DNA by complementary base pairing. Use of metal binding ligands to seed DNA origami templates can increase seed selectivity by limiting background deposition of seeds on the surface. Since, the metal seeds do not covalently bind to the surface like metal ions, introducing additional rinsing steps can reduce the background deposition.

Studies in this area have shown the attachment of Au or Ag nanoparticles using metal-thiol interaction in designated sites of DNA template. Hung et. al localized Au nanoparticles on triangular shaped DNA origami using this method. Similarly, Yan et al. localized Ag particles on self-assembled triangular shaped DNA origami using nanoparticles conjugated with phosphorothiolated DNA as supporting blocks⁸. The group also showed the possibility of

attaching both the Au and Ag nano particles on the same template. However, the group attached only one Ag NP and one Au NP in the origami template and did not demonstrate higher particle density required to make continuous metallized origami structures as proposed for this study.

While studies have successfully shown the attachment of nanoparticles to DNA, only recently the possibility of using particles as seeds to metallize DNA origami has been shown. Pais-Pilo et. al demonstrated seeding origami tiles with Au nano particles and subsequent plating with Ag²⁷. In parallel study, a recent paper from Pearson et. al. from BYU demonstrated the localization of Au nanoparticles on select locations in DNA origami with the use of modified staple strands containing thiol³ as shown in Figure 2-4. Specific locations of DNA origami were functionalized with staple strands modified at the end by adding A₁₀ (10 base long poly adenine strands)³. These dangling ends provide the attachment sites for Au NPs functionalized with thiolated T₈ (8 bases long poly thymine strands) to the DNA template (Figure 2-3). The particles attach to the origami by base pairing of the complementary segments, adenine and thymine.

Figure 2-4: T shaped DNA seeded with 5 nm Au NP. (A) T shaped DNA (B) T structure seeded along half of the top section. (C) T structure seeded along the entire top section. Height scale is 6 nm. Scale bar is 500 nm.

The paper demonstrated the use of metal-thiol interaction to localize particles at select locations of an origami template. Similarly, the use of attachment strands showed good selectivity with majority of the seeds attached to the DNA template. The current study will build up from the above study to metallize DNA origami templates with two different metal groups. The findings from the study regarding site specific metallization of DNA origami templates will be helpful in moving forward with the present study.

2.6 Summary

DNA, with its small size, functional groups and complementary base pairs, is emerging as a desirable template for fabricating components of nanodevices. The advent of DNA origami enables fabrication of wide variety of 2D and 3D structures, and the placement of base pair specific attachment points at desired locations on those structures. Metallization of DNA to make continuous structures is important for fabrication of nano devices. The bulk of the work in this field has focused on metallization of lambda DNA due to its longer size and stability compared to DNA origami structures. Continuous metallization of DNA origami templates has only recently been shown³. However, metallization of a DNA template to make continuous structures of two or more metal metals has not been demonstrated. The ability to deposit heterogeneous metal structures on the same template would provide an important step forward towards the development of nanodevices. The metal-metal junction targeted in the current study will also enable future fabrication of metal-semiconductor junctions, representing a spectrum of new possibilities for DNA-templated nanodevices.

3 MATERIALS AND METHODS

This chapter describes the basic materials and procedures used for this study. Since the objective of the study was to develop and demonstrate a process of creating a metal-metal junction on a DNA origami template, important procedural developments are included in the results chapter (Chapter 7) of this document.

3.1 Materials

M13mp18 were purchased from New England Biolabs (Ipswich, MA). Staple strands (100 μ M in TE buffer) for DNA origami folding were obtained from Operon Biotechnologies (Huntsville, AL). Single-stranded DNA functionalized with thiol to enable attachment to metal nanoparticles was also purchased from Operon Biotechnologies with PAGE purification and diluted to 1 mM in water. PCR primers to make scaffolds for DNA origami were also ordered from Operon. PCR purification kits were acquired from Qiagen (Valencia, CA). DNA polymerase and PCR buffers were purchased from either Invitrogen (Grand Island, NY) or New England Biolabs. BSPP (bisp-sulfonatophenyl phenylphosphine dihydrate dipotassium salt) for concentrating gold nanoparticle solution was obtained from Strem Chemicals (Newburyport, MA). Gold nanoparticles (5 nm) were obtained from Ted Pella (Redding, CA). Silver nanoparticles (10 nm) were purchased from nanoComposix (San Diego, CA). 30 kDa Amicon ultra-0.5 mL centrifugal filters were obtained from Millipore (Billerica, MA). NH_4Cl was obtained from EM Science (Gibbstown, NJ). MgCl_2 and MgAc_2 were obtained from EMD

Chemicals (Gibbstown, NJ). HEPES, $\text{KNaC}_4\text{H}_4\text{O}_6 \cdot 4\text{H}_2\text{O}$ (99.0%), $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (99.1%), HCHO (37.4%) were purchased from Mallinckrodt Baker (Phillipsburg, NJ). NaOH (97%) was obtained from Spectrum Chemical Mfg. Corp (New Brunswick, NJ). Ethyl alcohol (200 proof) was purchased from Decon. Labs, Inc (King of Prussia, PA). PdCl_2 , DMAB (dimethylamine borane), 1-Octadecanethiol, C_{18}DMS (95%), hydroquinone and methanol (99.9%) were purchased from Sigma-Aldrich (St. Louis, MO). Gold plating solution (GoldEnhance EM, Catalog #2113) was obtained from Nanoprobe (Yaphank, NY). Water (18.3 $\text{M}\Omega \text{ cm}$) treated by an EASYPure UV/UF purification system was used for all rinsing and aqueous solution preparations.

3.2 T Origami Design

T shaped origami was designed from a 2958-base scaffold, amplified from M13mp18 as reported in the literature³. For gold (Au NP) and silver nanoparticles (Ag NP) attachment, staple strands in the origami were modified to contain a sequence of 10 adenine nucleotides on the 3' end. The entire top section of the "T" (67 strands in total) or half of the top section (33 strands in total) was modified. Staple strand sequences for T origami are included in the Appendix.

3.3 Bar Origami Design

As a part of this work, a longer bar shaped origami was designed using the entire 7249 base M13mp18 scaffold. For Au NP attachment, staple strands in the origami were modified to contain a sequence of 10 adenine nucleotides on the 3' end. Half of the "bar" origami strands (110 strands in total) were modified for Au NP attachment. Staple strand sequences for the bar origami are included in the Appendix.

3.4 DNA Origami Folding

T and Bar structures were made by heating a mixture of the scaffold and staple strands (2 nM scaffold and 20 nM of each staple strand in 1 X TAE-Mg²⁺ buffer) to 95°C for 3 min and then slowly cooling to 4°C over 90 minutes in TECHNE TC-3000 thermocycler.

3.5 Au NP Preparation

The procedure was similar to that previously reported by Pearson et. al³. Au NPs were first phosphinated and concentrated with BSPP. To do this, 1.5 mg of BSPP was added to 5 mL of Au NP solution as received and shaken overnight. The nanoparticles were precipitated by adding 100 mg of NaCl to the reaction mixture until the color changed from red to dark red/purple. The solution was centrifuged to separate the nanoparticles and the supernatant was removed. Au NPs were then re-suspended in 100 µL of 2.5 mM aqueous BSPP solution. 100 µL of methanol was added to the solution until the color changed to dark purple/brown, at which point the mixture was centrifuged to separate Au. Au NPs were again suspended in 100 µL of 2.5 mM aqueous BSPP solution. The concentration of Au NPs was then estimated with a Nanodrop 1000 spectrometer using the absorption at 520 nm.

3.6 Nanoparticle (Au NP and Ag NP) – DNA Conjugates

Au NPs treated with BSPP and thiolated DNA in water was combined in a 1:200 concentration ratio and left to react at room temperature for at least 19 hours³. The Au NP DNA conjugates were filtered using 30 kDa Amicon filters to remove unbound thiolated DNA. Samples were rinsed twice using 450 – 500 µL 0.5 X TBE (44.5 mM Tris base, 44.5 mM boric acid, 1 mM EDTA) buffer during filtration. About 40 µL of Au NP-DNA conjugates in 0.5 X TBE buffer were recovered with concentration around 1- 3.5 µM. The procedure used for

making Ag NP-DNA conjugates was similar to that for gold with a few exceptions. First, Ag NPs were used as received without the treatment with BSPP. Second, Ag NP-DNA conjugates were dispersed in 1 X TBE buffer. Third, the Ag NP-DNA conjugate solution was left to react at room temperature for three days⁸ with addition of NaCl in 1 mL aliquots to raise the NaCl concentration to 350 mM. After filtration, about 40 μ L of Au NP DNA conjugates were recovered with concentration around 24-26 nM.

3.7 Depositing DNA Origami on SiO₂ Surfaces

The procedure used in this study is similar to that previously reported in the literature³. Silicon dioxide surfaces were plasma cleaned (Harrick Plasma Asher, PDC-32G) for 30 seconds at 18 W to remove impurities from the surface. 3 μ L of DNA origami (0.22 nM for both T and Bar-shaped origami) in 10 X TAE – Mg²⁺ buffer was allowed to absorb onto the cleaned surface (roughly 1 cm X 1 cm) for 15 minutes in a humid chamber at room temperature. Since the plasma cleaned substrates are hydrophilic, 3 μ L of origami solution spreads over the entire surface area of the wafer. The sample was then rinsed with 4 mM MgAc₂ solution for 3-4 sec and deionized water for 1-2 seconds. Finally, the surface was dried with a stream of filtered air and imaged in AFM.

3.8 Seeding with Au and Ag Nanoparticles

12 μ L of seeding solution (Au NP-DNA or Ag NP-DNA conjugates diluted in 10 X TAE-Mg²⁺ buffer, 2 nM for both) was pipetted onto the silicon surface with DNA origami and allowed to seed DNA by complementary base pairing (Adenine with Thymine) for 40 minutes at room temperature in a humid chamber. The seeding solution covered the entire surface area of the substrate. The sample was then rinsed with 4 mM MgAc₂ solution for 3-4 sec, followed by

rinsing with deionized water for 1-2 seconds. After rinsing, the sample was dried with a stream of filtered air.

3.9 Surface Masking with Octadecanethiol Solution

Octadecanethiol was used to make an organic layer on the surface of the metals present to inhibit further plating. To do this, 2 mM octadecanethiol solution in 100% ethanol was prepared. Plasma cleaned silicon substrates (roughly 1cm X 1cm) with metallized DNA origami were placed inside a glass vial and sufficient octadecanethiol solution was added to cover the surface of the wafer. The glass vials were kept at room temperature for about 24 hours. During this time, the thiolated end of octadecanethiol binds to form an organic layer on the surface of the metals present. The samples were then rinsed with ethanol and air dried. A background test was also performed with use of the same procedures on a surface containing DNA origami that had not been metallized. The substrate surface after overnight placement in octadecanethiol solution became less hydrophilic, so further seeding or plating solution would not spread over the entire surface of the substrate. The solution covered all but the edges of the substrate ensuring further metallization of the DNA templates.

3.10 Seeding with Palladium

The procedure used in this study was modified slightly from that reported previously in the literature². The seeding step consisted of activation with palladium solution and reduction to form seeds. For activation 20 μ L of Pd(II) solution (1 mM PdCl₂ and 1 M NH₄Cl in HEPES buffer, pH 6.5) was pipetted onto the surface upon which DNA origami templates had been previously deposited, and left to stand for 1 hour in a humid chamber at room temperature. Next, the liquid on the surface was removed using a spin coater by rotating at 1200 rpm for 12 sec.

Then, 20 μL of reducing agent (40 mM DMAB) was pipetted onto the activated DNA samples and allowed to react for 1 minute. The reaction was quenched by rinsing the samples with 4 mM MgAc_2 for 3-4 secs, followed by rinsing with water for 1-2 secs and drying with air. The seeding process was repeated three times to ensure larger seed sizes and a sufficient number of seeds on the DNA origami.

3.11 Ionic Seeding with Silver

40 μL of basic silver nitrate solution (0.1 M AgNO_3 , 0.33 M ammonia hydroxide) was pipetted on a silanized surface (SiO_2 surface modified with C_{18}DMS) and allowed to interact with the surface for 5 min. The silanized surface is hydrophobic, so the solution only covered a small portion in the midsection of the substrate. The solution on the surface was then air dried and 40 μL of 0.05 M hydroquinone solution was pipetted on the surface for 2 min to reduce silver ions to silver nanoparticles. The surface was then rinsed with water for 5 seconds and air dried.

3.12 Electroless Au Plating

Gold plating solution was prepared as per the manufacturer's instructions. To this mixture, an equal volume of 10 mM MgCl_2 was added to stabilize DNA origami under the plating solution. Plating was done by putting 40 μL of plating solution onto a SiO_2 sample surface at room temperature. The plating was allowed to proceed for one minute. The plating solution covered the entire area of the hydrophilic substrate. The sample was then rinsed with 4 mM MgAc_2 solution for 3-4 sec, then with deionized water for 1-2 seconds and finally dried with a stream of filtered air.

3.13 Electroless Ni Plating

The electroless nickel plating solution²⁵ consisted of 30 g/L $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, 2.1 g/L NaBH_4 , 60 g/L $\text{NH}_2(\text{CH}_2)_2\text{NH}_2$ and 40 g/L NaOH . Plating was done by transferring 50 μL of plating solution onto the sample surface. Electroless Ni plating was carried in a water bath at about 70°C. The samples were placed in a plastic petri dish (60 X 15 mm) and allowed to float on the surface of the water bath. The reaction was allowed to proceed for 1-4 min. The samples were then taken out of the bath, rinsed with water for 5 seconds and finally dried with a stream of filtered air.

3.14 Electroless Cu Plating

The electroless copper plating solution²⁵ consisted of 5 g/L CuSO_4 , 25 g/L $\text{KNaC}_4\text{H}_4\text{O}_6 \cdot 4\text{H}_2\text{O}$, 7 g/L NaOH and 10 g/L 37 weight % HCHO . Plating was done by putting 70 μL of plating solution onto a sample surface at room temperature for 2-4 min. The sample was then rinsed with 4 mM MgAc_2 solution for 3-4 sec and with, deionized water for 1-2 seconds. Following rinsing, the sample was dried with a stream of filtered air.

3.15 AFM Imaging

The samples were imaged using tapping mode on a Digital Instruments Nanoscope IIIa MultiMode AFM (Veeco) with Aluminum coated conical silicon tips (Vistaprobes, 3N/m, 45-75 kHz).

3.16 SEM Imaging

The DNA samples on silicon surfaces were imaged in high vacuum mode on a Philips XL30 ESEM FEG. EDX analysis was also performed with the same instrument.

4 SCREENING EXPERIMENTS FOR SELECTIVE NICKEL DEPOSITION

To make a dissimilar metal junction on a single DNA origami template (refer to Figure 1-1), a section of the origami template is initially seeded. The seeded section is then plated to make a continuous metal structure. Next, the adjacent section of the same template is seeded and subsequently plated to fabricate the required structure. However, the processes involve several challenges. It is important to localize the first seed material to a specific section of origami, which would then be metallized further. Similarly, the second electroless deposition should only occur on the unplated section following the second seeding step. To move forward, the initial strategy was to identify metals that would selectively deposit on specific seed materials. Essentially, different seed materials had to be investigated to determine if a particular metal would plate on one seed material and not on another, thus giving the selectivity needed to get the desired DNA structure.

Gold was initially chosen as one of the metals for the proposed dissimilar metal junction due to our successful experience with site-specific metallization of DNA with this metal. A section of the origami template would be seeded with Au nanoparticles and electrolessly plated with Au to make a continuous structure. Having made the decision to use gold for half of the junction, it was next necessary to find a second metal that would not plate on gold, but would plate on second seed material that would be placed on the DNA template. It was previously observed in our lab that nickel plated on silver seeds, but not on gold seeds [Jianfei personal

communication]. Consequently, we decided to look at silver seeding and designed some full-surface experiments to test the specificity of nickel deposition on Au and Ag seeds.

Another advantage of nickel is that it can be displaced with semiconductor materials like Te or Bi_2Te_3 using galvanic reaction. The galvanic displacement reaction works due to the difference in the reduction potential between the materials. Nickel has lower reduction potential compared to Te or Bi_2Te_3 , while that of gold is higher than that of these semiconductor materials. Thus, use of gold and nickel opens up the possibility of creating a metal (gold)-semiconductor (Te and others) junction on the DNA template.

4.1 Initial Full Surface Experiments

Based on procedures described previously²⁹ and the materials available for making nanowires, silanized silicon surfaces (SiO_2 surface modified with C_{18}DMS) without DNA templates were seeded with either Au NPs or Ag seeds (ionic seeding). Both Au- and Ag-seeded samples were then subjected to the electroless nickel plating solution used in this study. Figure 4-1 shows the results obtained from this experiment. SEM imaging and EDX analysis showed a change in height and composition on Ag-seeded surface indicating the presence of nickel. The plating could be visually seen in the surface. On the other hand, no such change was observed for the gold-seeded sample. AFM analysis did not show a change in height and EDX analysis did not indicate the presence of nickel on the gold-seeded sample.

Figure 4-1: (A) AFM image of Ag-seeded sample. (B) SEM image of Ag-seeded sample introduced to nickel plating bath. (C) EDX analysis on the sample in (B). (D) AFM image of Au-seeded sample. (E) AFM image of Au-seeded sample introduced into nickel plating bath. (F) EDX analysis of Au seeds introduced into nickel plating bath. Height scales are 6 nm. Scale bar is 500nm.

The above full surface experiments confirmed the selectivity of our electroless nickel plating solution as previously observed. Nickel selectively plated on silver seeds, while no such plating was observed on gold seeds. This result was important as it appeared to provide the required selectivity.

4.2 Seeding of DNA Origami with Ag NPs

Next, we decided to look at the possibility of using Ag nanoparticles as the second seed material based on the above observations and the expectation that the Ag nanoparticles would

behave similarly to the ionically seeded silver. After seeding and plating a section of the origami template with Au, Ag would be seeded in the adjacent section and plated with nickel to make a gold-nickel junction. The results above indicated that the nickel would not plate on the gold, but would plate on the Ag seeds, providing the required selectivity.

The DNA template used for these experiments is shown in Figure 4-2. The “T” shaped structure had been previously used with considerable success to make metallized origami templates^{1, 3}. We realized the structure could also work as a template for the present work with half of the top section metallized with gold and the other half metallized with nickel. The origami was prepared as previously reported in the literature by Pound et. al²⁰. The top branches were 120 nm long and 3 helices (~8 nm) wide, while the stem was 75 nm long and 4 helices (~11 nm) wide.

Figure 4-2: (A) Design of T shaped DNA. (B) AFM image of T shaped DNA. Height scale is 6nm. Scale bar is 500 nm.

For silver nanoparticle attachment, one of the top arms of the “T” template was functionalized with staple strands modified at the end by adding A₁₀ (10 base long poly adenine strands). These dangling ends provide sites for the attachment of Ag NPs to the DNA template. Likewise, Ag NPs were functionalized with thiolated T₈ (8 base long poly thymine strands),

complementary to the adenine strands in the DNA as shown in Figure 2-3. Using the procedures described in Chapter 3, DNA origami was deposited on an oxidized silicon substrate and the Ag NP solution was allowed to interact with the DNA on the surface. The samples were then imaged with AFM. Next, the samples were introduced into the nickel plating bath and characterized with SEM. Figure 4-3 shows the results obtained from the experiment.

Figure 4-3: AFM image of T shaped DNA seeded with Ag NP along one section of the top arm. (A) AFM image of T shaped DNA. (B) T shaped DNA seeded with Ag NPs. (C) Image zoomed from (B). (D) Nickel plating on Ag seeded T. (E) EDX analysis of the sample in (D) using spot scan. Height scales are 6 nm. Scale bar is 500 nm.

Although SEM images showed some structures whose length was consistent with that expected from the DNA origami, significant background deposition was also observed. The seeding step was selective with very little background; however, the samples after electroless plating showed higher particle density. To determine if the background deposition was due to the SiO_2 surface we were using, an unseeded SiO_2 surface was introduced into the nickel plating bath. It was observed that nickel readily plated on the surface without any seed material. Figure 4-4 shows the results of introducing an unseeded SiO_2 surface into the nickel plating bath. SEM image and EDX analysis shows the change in surface chemistry due to the presence of nickel on the surface.

Figure 4-4: (A) SEM image of a blank SiO_2 surface. (B) SiO_2 surface introduced to Nickel plating bath. (C) EDX analysis on the surface in (B). Scale bar is 2 μm .

The results we obtained were completely different from the previous full surface experiments we performed. The full surface experiments with Ag and Au NPs were done on a SiO_2 surfaces modified with C_{18}DMS , while the experiments with T origami samples were

placed on an unmodified SiO_2 surface. The C_{18}DMS treated surfaces apparently blocked the background deposition of nickel in the absence of seeding. In contrast, Ni readily plated without seeding on the unmodified SiO_2 surface. Unfortunately, the C_{18}DMS modified surface is not suitable for use with our branched DNA origami since the surface is very hydrophobic, and the DNA origami samples deposited on the surface do not retain their shape and size. Use of an unmodified, hydrophilic SiO_2 surface provides us with a smooth and even surface that is suitable for origami deposition without affecting its shape. Moreover, we had successfully used the SiO_2 surface previously to lay down “T” and “circular circuit” origami structure and subsequently metallize the origami with gold³. So, we decided to use the unmodified SiO_2 surface to put down our metallized origami structures.

Since the unmodified SiO_2 surface was not compatible with our electroless nickel plating solution, we concluded that our nickel plating bath could not be used to make the desired DNA-templated metal junction. Moving forward, we had to identify one or more metal plating solutions, in addition to the gold plating solution, that were compatible with the surface we were using. Once identified, we could then return to the issue of selectivity.

5 EVALUATION OF COPPER AS THE SECOND METAL FOR DEPOSITION ON THE DNA TEMPLATE

Since, our nickel plating bath wasn't suitable for use with a SiO_2 surface, we decided to look for a different metal that could substitute for nickel. Copper was examined as an alternative because it is an important material used for electronic circuits and like nickel, copper can be displaced with semiconductor materials to make metal-semiconductor junctions. However, we did not have any prior knowledge or any data suggesting the selectivity of copper with different seeds. The initial concern, however was to determine if copper was suitable for use with the SiO_2 surface we were using.

5.1 Full Surface Copper Experiments

To explore the possibility, we started with experiments on a SiO_2 surface to study the effect of exposing the surface to the copper plating bath. Unlike the nickel plating bath, the copper bath had no effect on the unseeded SiO_2 surface as shown in Figure 5-1. There was no evidence of copper deposition after the exposure of the unseeded surface to the plating bath. This was an important result for our work that depends highly on the selectivity of metal deposition.

Figure 5-1: (A) SEM image of blank SiO₂ surface. (B) Unseeded SiO₂ surface introduced into the copper plating bath. (C) EDX analysis of the surface in (B) showing no Cu. Scale bar is 2 μ m.

5.2 Copper Deposition on NPs

Next, we designed some experiments to test the specificity of copper deposition on silver and gold seeded samples. Ideally, copper would selectively plate only on one type of seed. Au NPs and Ag NPs functionalized with DNA strands were allowed to absorb on the surface according to procedure described in Chapter 3. The samples were then exposed to the copper plating bath. AFM images of samples taken before and after exposure to the plating bath showed no significant change of height. The seed density was also less after exposure to the plating bath. Figure 5-2 shows the images before and after exposure of Ag seeds to a copper bath. Similar results were obtained from a surface seeded with Au NPs, which also showed no evidence of plating when exposed to the electroless Cu plating bath.

Figure 5-2: (A) AFM image of Ag seeding on a blank SiO₂ surface. (B) Sample in (A) after copper plating. Height scale is 6 nm.

These results were unexpected because we had successfully plated Au NP- and Ag NP-seeded origami samples with gold using a plating solution consisting of a modified commercial gold bath. We hypothesized that the presence of DNA strands around the nanoparticles (Figure 2-3) prevented the copper from depositing on the seed surfaces. On the other hand, the commercial gold bath might have some additives that could penetrate through the surface organics and permit plating on the nanoparticles. To test the hypothesis, we introduced our electrolessly gold-plated T origami samples to the copper plating bath. These gold-plated T samples were prepared according to methods described earlier (Chapter 3). We found that copper readily deposited on gold-plated origami samples. SEM images of the samples indicated a change in thickness and morphology of T structure, and EDX analysis confirmed the presence of copper as shown in Figure 5-3. After copper plating, the thickness of the structure changed from about 40 nm to about 70 nm. Likewise, the morphology changed from that of the gold-plated

structures, which looked like small beads attached together, to a structure after copper plating that looked more condensed with a smaller grain size.

Figure 5-3: (A) AFM image of Au seeded T shaped DNA. (B) SEM image of Au plated T shaped DNA. (C) SEM image of Cu plated T shaped DNA. (D) EDX analysis performed on the DNA in (C) using spot scan. Height scale in (A) is 6 nm. Scale bars are 200 nm.

Our copper plating solution had no effect on the nanoparticles (both Au NP and Ag NP) we used for seeding DNA templates. It seems likely that the presence of DNA strands inhibits

the copper plating reaction. In contrast, the gold plating solution readily plates on the nanoparticle-seeded origami samples. The composition of the gold plating solution appears to remove or circumvent the DNA layer covering the seed particles in order to facilitate the gold deposition. The plated gold does not have DNA on its surface and is readily plated by copper. The results obtained can also explain the selectivity we observed with nickel during earlier experiments. Nickel did not plate on the Au NPs due to the presence of a DNA layer around the seed, while nickel plated on Ag seeds (seeded ionically), which didn't have the DNA layer around them. It appears that the selectivity of nickel plating solution was due to the presence or absence of DNA and not to the type of metal as originally thought.

Given the above results, a couple of options existed for moving forward. One possibility was to determine the additive in the gold-plating bath that permits plating on the DNA-covered surfaces in order to facilitate copper plating on either Au or Ag nanoparticles. While this strategy would address the plating issue, it provides no mechanism for selective deposition. Another, perhaps more promising, alternative was to utilize the selectivity gained by coating the metal surface with organic molecules (does not plate with Cu, but plates with Au) by combining it with another seeding method for the Cu that does not have the inhibiting layer. This latter strategy is explored in the sections that follow.

5.3 Ionic Seeding with Palladium

Since copper plating did not work on nanoparticles functionalized with DNA strands, we decided to look for seed materials that directly catalyzed the copper deposition. Primarily, we wanted to examine the possibility of putting the seeds onto DNA templates without masking the seeds with DNA. In this regard, Geng et. al previously demonstrated palladium seeding on lambda DNA and T origami². The lambda-seeded samples were then electrolessly plated with

palladium to make nanowires, while origami samples were electrolessly plated with gold. Palladium ions complex with the phosphate backbone and the Lewis bases of the DNA template and can be then reduced with reducing agent (dimethyl borane) to form a Pd seed layer. Recently, Yanli Geng demonstrated the use of the palladium seeds to deposit copper on a modified (with strands for particle attachment) circuit-shaped origami³⁰. Leveraging off of her work, we decided to seed our T origami structures with palladium for subsequent plating with copper. We could have also used ionic Ag seeding to seed DNA templates as we did in previous experiments with nickel, but we wanted to proceed with the proven method demonstrated by Yanli to make copper structures on origami templates. Figure 5-4 shows the Pd seeding of T shaped origami and their subsequent copper plating.

SEM images of the T origami samples after exposing to a copper plating bath indicated the change in height and thickness of the origami. After seeding, the average height of the DNA origami measured with AFM was about 2.8 nm. After about 2 minutes of plating, the thickness of the plated wire increased to about 90 nm. EDX analysis confirmed the presence of copper. However, we also observed some background deposition of copper which could have been the seeds growing in size during electroless plating. To confirm the Cu features were DNA based, we exposed some samples without DNA origami to the processes used for palladium seeding and copper plating. Figure 5-5 compares copper plating on DNA origami and copper plating on a surface without DNA origami. As seen from the figure, without DNA origami, the copper was either present as an individual or agglomerated particles on the surface. On the other hand, with DNA templates, copper structures are arranged in a distinct pattern.

Figure 5-4: (A) Pd seeding of T shaped DNA. (B) Copper plating on Pd seeded T shaped DNA. (C) EDX analysis performed on the DNA in (B) using spot scan. Height scale is 4 nm. Scale bar is 500 nm.

Figure 5-5: (A) T shaped DNA seeded with Pd and exposed to a copper plating bath. (B) Surface without DNA origami exposed to a copper plating bath.

Use of Pd^{2+} ions for seeding made it possible to plate copper directly on the seeded sample. The only disadvantage of ionic seeding, however, is that it is not site specific like the nanoparticle seeding and therefore, cannot be restricted to a particular area of the DNA template. Since seeding occurs due to interaction of Pd ions with the DNA backbone and the bases, ions will interact with any and all exposed DNA sections.

From above experiments, we had some important observations. While copper directly plated on palladium-seeded samples, copper deposition was also observed on gold plated samples. So, a mechanism was needed to mask the gold-plated templates from further metal deposition. It is here where we hoped to take advantage of the inhibiting effect of an organic layer to protect the previously plated gold area. Also, palladium seeding does not utilize the sequence-specific recognition properties of DNA for seeding and hence cannot be restricted to a specific area of the template. This does not present a problem for the current study provided we can plate and protect gold, and then put Pd in the remaining areas of the template. Protection of the gold-plated section of the template is crucial to the selective placement of two different metals on a same template.

6 SELECTIVE DEPOSITION OF COPPER ON DNA ORIGAMI TEMPLATES

6.1 Masking Gold With an Organic Layer Of Octadecanethiol

Previous experiments showed copper plating on DNA origami samples previously plated with gold. In order to realize the gold-copper metal junction, we needed a mechanism to protect the gold-plated section of the origami template from copper deposition, thus giving us the required selectivity. Zamborini et. al demonstrated the use of self-assembled monolayers (SAMs) of *n*-alkanethiol to protect a Au substrate from corrosion in aqueous Br⁻ solutions²⁸. Experiments also revealed that corrosion resistance increased as the SAM thickness increased. Based on our observation of plating inhibition by DNA-coated samples, an attempt was made to mask gold-plated origami with octadecanethiol (C₁₈-SH). The hypothesis behind this was that the thiolated end of this molecule would attach to the gold-plated section of the origami and inhibit further metal deposition. To test the hypothesis, a few experiments were designed. Some gold-plated origami samples were masked with octadecanethiol and then introduced into a copper plating bath to test the effectiveness of the organic layer to prevent metal deposition. Likewise, origami samples that had not yet been seeded or metallized were also introduced into octadecanethiol solution to examine whether this additional processing step would affect subsequent metallization of the origami.

Figure 6-1 clearly shows the difference in morphology between gold plated DNA origami and gold-plated origami that was subsequently plated with copper. The gold plated origami structure looks like beads on a string, while the structure plated with copper looks bigger and more compact compared to the gold structure. On the other hand, the gold plated sample (Figure 6-1A) looks similar to the gold-plated sample protected with octadecanethiol and exposed to copper solution (Figure 6-1E). The structures both look morphologically the same, like beads on a string. Similarly, the EDX analysis performed on the sample protected with octadecanethiol using spot scan showed no significant copper. The above observations demonstrated that the octadecanethiol layer effectively protected the gold-plated origami samples against copper plating when immersed in a copper plating bath.

It was also observed that octadecanethiol solution had no effect on further seeding and copper deposition of the origami. The origami samples placed in octadecanethiol solution overnight were seeded with palladium and electrolessly plated with copper. The substrate surface, however, after the octadecanethiol step was less hydrophilic, but this did not affect the subsequent metallization of the DNA origami templates. The seeding and copper plating of the origami samples were similar to the results obtained before (Figure 5-4) as shown in the Figure 6-2.

Figure 6-1: (A) SEM image of Au plated T shaped DNA. (B) EDX analysis performed on the DNA in (A) using spot scan. (C) SEM image of Au plated T DNA plated with copper. (D) EDX analysis performed on the DNA in (C) using spot scan. (E) Au plated T shaped DNA masked with octadecanethiol after exposure to copper plating. (F) EDX analysis performed on the DNA in (E) using spot scan. Scale bars are 200 nm.

Figure 6-2: (A) Pd seeding of T shaped DNA after overnight placement in octadecanethiol solution. (B) Copper plating on Pd seeded T shaped DNA in (A). Height scale is 4 nm. Scale bar is 500 nm.

6.2 Fabricating Gold and Copper Structures on the Same Substrate Surface

With encouraging results from the above experiments, we next designed an experiment to produce separate copper-plated and gold-plated structures on the same surface. We designed two sets of T origami with different sequences on them as shown in Figure 6-3. One set of T origami was functionalized with staple strands modified by adding A_{10} (10 base long poly adenine strands) at the end of strands. These dangling ends provided attachment sites for Au NPs functionalized with thiolated T_8 (8 bases long poly thymine strands), complementary to the adenine strands in the DNA. This T origami set had staple strands on the whole body for attaching Au particles. Another set of T DNA was functionalized with staple strands modified at the end by adding a GTGCGTGT sequence. This design was originally intended for attaching Ag NPs. Previous experiments revealed no visible effect of palladium seeding on modified³¹ and unmodified² origami structures, so we decided to use this second type of DNA origami for Pd seeding. The two DNA sets were be mixed together and deposited onto the same sample surface.

The main objective of this experiment was to produce separate gold and copper plated DNA templates on the same surface. First, Au NPs would be selectively seeded on the T origami with A_{10} attachment strands on the DNA. Then the origami would be electrolessly plated with Au leaving the other DNA set intact. Au plated DNA would then be masked with a C_{18} layer. The next set of DNA would be seeded with Pd and plated with copper. The processes and results obtained in this experiment could then be applied to make copper-gold metal junctions on the same DNA template.

Figure 6-3: T origami design. (A) T origami with red attachment strands for Au. (B) T origami for Pd attachment. (C) Final expected result, separate Au and Cu origami structures.

Using the procedures described earlier, DNA origami (1:5 ratio of Design A to Design B, Figure 6-3) was first deposited on the SiO_2 surface. We used the above ratio to clearly characterize the two different origami samples after different metallization steps. After gold metallization, we noticed the gold plated origami samples seemed to cover the whole surface

area making it harder to differentiate further metallization steps on the second set of origami. So, we decided to use less of origami A compared to origami B. Subsequently, samples were seeded with Au NPs and electrolessly plated with gold. Next, the samples were immersed in an octadecanethiol solution for 24 hours. The samples were finally seeded with Pd ions and plated with copper at room temperature.

Figure 6-4 shows the results of this experiment. DNA origami was first allowed to interact with Au NP solution (2 nM) for 40 minutes in a humid chamber (Chapter 3). After seeding, the average height of the DNA origami was about 6.8 nm with a standard deviation of 0.35 nm ($n=20$). Likewise, after electroless gold plating for 1 minute, the average height of the plated origami was about 19 nm with standard deviation of 3.15 nm ($n=20$). The seeding and plating time used were based on the optimum time for the metallization of DNA with gold from a previous publication³. The origami samples were then immersed in 2 mM octadecanethiol solution for 24 hours. There was no visible change in the origami density on the surface after this process. The shape and structure of the metallized and unseeded DNA origami templates were still intact after a day in octadecanethiol solution as evident from Figure 6-4 (C) and (D). The substrate surface, however, became less hydrophilic after this step compared to the substrate surface after plasma cleaning (Chapter 3). There was a change in the contact angle between the solution and the surface. Previously, the SiO₂ surface was hydrophilic and the solution spread almost parallel all over the surface. In contrast, after the C18 step, the surface became less hydrophilic and the subsequent seeding and plating solution made a convex arc on the surface. The seeding and plating solution still covered the whole area since we were using more volume compared to DNA and seeding solution volume before the octadecanethiol step (Chapter 3). The samples were then seeded with palladium, which showed the average height change of the B

origami to 2.9 nm with standard deviation of 0.2nm (n=20). However, some significant background deposition was observed as a result of palladium seeding, which could further grow in size after copper plating.

Figure 6-4 shows selective placement of Au on only a fraction of the DNA origami deposited on the surface. A fraction of DNA origami was left vacant throughout the process of gold seeding, electroless plating and immersion in the octadecanethiol solution (Figure 6-4 A-D). The DNA origami was designed such that Au seeds would selectively attach to one set of DNA with attachment points along the entire template. While the figure above shows Au deposition on only a fraction of DNA origami as expected, a control experiment was designed to prove Au NPs only attached to the DNA set A. In order to this, we decided to seed B origami (Figure 6-3 B) with GTGCGTGT sequence with Au NPs functionalized with T₈ sequence. Since Au NPs attach to the origami by complementary base pairing of DNA strands, the nanoparticles should not attach to the B set of origami. Figure 6-5 shows the result of this experiment. While the figure shows no attachment of Au NPs to the majority of DNA origami, some isolated Au particle attachment was observed. This could have been due to the landing of nanoparticles on top of the origami templates. Likewise, some background deposition was also observed. Since, Au NPs are seeded in TAE-Mg²⁺ buffer solution, the positive magnesium ions act as a bridge between the negatively charged SiO₂ surface and DNA (negative backbone) modified nanoparticles giving some background deposition. With this result, we can safely conclude that Au NPs only attached on the intended DNA set A.

Figure 6-4: (A) T origami. (B) Au seeding of one set of T origami. (C) Au plating on Au seeded T origami. (D) Sample after 24 hours in C₁₈ solution. (E) & (F) Pd seeding on the second set of T origami. Circles mark Pd seeded T origami. Height scale is 6 nm. Scale bar is 500 nm.

Figure 6-5: Seeding B origami with Au NPs. Height scale is 6 nm. Scale bar is 500 nm.

Figure 6-6 shows SEM images of samples after 2 minutes of electroless copper plating. One structure looks like a string of small beads while the other structure consists of big but fewer granules. EDX analysis on the structure that looks like beads on a string shows the presence of Au, consistent with the previous observations we made for gold-plated samples (Figure 6-1A). Likewise, EDX analysis on the structure with big granules showed the presence of copper. In addition, the composition data showed no copper on the Au plated structures, thus confirming the presence of gold and copper plated structures on the surface as we had originally planned.

Our samples also showed significant background deposition of copper particles. We observed some background deposition during ionic (palladium) seeding, which may have grown in size during copper plating. Some of our copper structures appear smaller than the designed template size (length of top arm of T origami = 240 nm), while some structures appear discontinuous (Figure 6-6 D). The issue could have been with palladium seeding of the origami templates. Some templates might have uneven seeding density, while some even when seeded

along the entire template might have bigger seed spacing that didn't fill out after plating. Electroless copper plating reaction was fast (usually ~ 1 min) as evident from the visual change in the surface (the SiO_2 surface turned brown indicating plating), but was still allowed to proceed for about 2-3 minutes to ensure continuous and uniform plating.

Our gold structures were very consistent throughout our experiments and the SEM imaging showed structures that appeared continuous with no gaps. However, the copper-plated structures showed considerable non uniformity. Within the same substrate surface, there were areas with no copper plating and areas with heavy copper deposition. We could distinctly see Au-plated structures only on the inner surface of the substrate and in the middle region of the substrate. The yield in those regions for our gold structures was close to 100 % based on the observation that all the gold structures were continuous and consistent with our design parameters. Likewise, there was virtually no copper structure present on the inner sections of the substrate. In the middle region, we could still see good gold structures because the change from inner sections with no copper to outer sections with heavy copper deposition was very gradual. It is in this region we managed to get some Au and Cu metal structures together consistent with our design size. The outside region had very high copper deposition, thus making it impossible to determine the yield of our either gold or copper structures.

Figure 6-6: (A) – (D) SEM image of Cu plated T and Au plated T origami. (E) EDX analysis using spot scan on Cu plated T in (B). (F) EDX analysis using spot scan on Au plated T in (B). Circles mark Au plated or Cu plated structures. Scale bars are 200 nm.

In conclusion, we have shown two different Cu- and Au-plated DNA origami templates on the same surface. First, we were able to localize Au seeds to the desired DNA template leaving other templates vacant. Second, the use of octadecanethiol layer protected Au-plated origami structures from further deposition. Finally, we were able to show palladium seeding on the remaining DNA origami templates to facilitate copper deposition. Some copper plated T structures look either small or discontinuous and further work is needed to improve the continuity and yield of templates. The problem with the copper-plated structures could be due to interaction between palladium ions and the organic layer or, perhaps, some problems with the plating and seeding solutions. These issues are examined in the next chapter where we introduce a new DNA template designed to facilitate copper and gold deposition adjacent to each other on the same origami template.

7 COPPER-GOLD METAL JUNCTION ON DNA ORIGAMI TEMPLATE

After demonstrating copper and gold metallized DNA templates on the same SiO_2 surface, we moved forward to developing a copper-gold metal junction on a single origami template. While the same processes and methods developed earlier would be useful, the ability to selectively metallize specific areas of a template with different metals will be of utmost importance in making the metal junction. Likewise, selective plating where metal is deposited only at previously seeded sites will be critical. Specifically, for a metal junction, localization of gold and copper to pre-designed locations of the template without affecting either structure will be the main challenge. It would be important that copper only deposits on its pre-designed location and not on the gold plated area. More generally, the utility of this approach for device fabrication in the future will depend on the precision with which multiple materials can be placed on the origami template.

To achieve the desired metal junction, we started with the design of a new DNA template as shown in Figure 7-1. The new DNA template was bar shaped with a length of 410 nm and a width of 6 helices (~17 nm). The longer design was useful for characterizing the Cu–Au junction as it facilitated compositional validation of the different metals via EDX on the SEM. In addition, the design helped to offset the influence of isolated particle attachment. When working with T origami, we observed some isolated cases of particle attachment to origami sections with different or no complementary strands, which enlarged after further plating and left very little

vacant space on the existing template (T origami). So, the longer template size helped to demonstrate proof-of-concept for metal junctions on DNA templates, which can then be used to guide work on smaller templates. The origami was designed with half the length functionalized with staple strands that included A_{10} linkers (10 base long poly adenine strands) on the ends of the strands. These dangling ends provided attachment sites for Au NPs functionalized with complementary T_8 (8 bases long poly thymine strands).

Figure 7-1: (A) Design of bar shaped DNA. (B) AFM image of bar shaped DNA. Height scale is 10 nm. Scale bar is 500 nm.

Using the procedures described earlier, DNA origami bar templates were first deposited on the SiO_2 surface. Subsequently, these samples were seeded with Au NPs and electrolessly plated with gold. Next, the samples were immersed in octadecanethiol solution for 24 hours. The samples were finally seeded with Pd ions as described above and plated with copper at room temperature.

The bar-shaped origami template was designed using the 7249 base M13mp18 scaffold to give a DNA origami structure with a length of 410 nm. Designs were made in a computer program (CADNANO) to determine the placement of individual staple strands. Scaffold and staple strands were then folded into the desired shape (see Chapter 3). Figure 7-2A shows the

bar-shaped DNA origami after assembly. As seen from the figure, most of the DNA origami that deposited on the surface had folded properly to yield the desired shape. The length of the folded origami was about 415 nm (from AFM images), which is consistent with the design size. Some of the origami structures had one or more kinks or bends in the folded structure and did not lay down completely straight on the surface. Two-dimensional DNA origami structures are flexible, so some twists or bends are expected, but the results were still a little surprising. Some structures appeared to bend at about the same location; however, there was no clear precise location where the kinks consistently occurred. Therefore, it did not seem that a defect in the DNA staple design was to blame. We examined the three-dimensional shape of the bar design using the program CanDo, and from that realized that the design most likely has an overall twist when it is in solution. Thus, if the origami lands on the surface as it falls, it could land in such a way that it would appear bent in different places. Overall, most of the DNA origami structures that landed on the surface were folded into visible bar shapes with some variation in the extent to which they laid straight on the surface.

Next, the origami was allowed to interact with the Au NP solution (2 nM) for 40 minutes in a humid chamber (see Chapter 3). After seeding, the average height of the DNA origami was about 7.04 nm with a standard deviation of 0.65 nm ($n=30$). The origami templates were then plated with gold for 1 minute. The average height of the plated origami was about 24 nm with standard deviation of 2.65 nm ($n=30$). The seeding and plating time used were based on previous experiments³ to obtain continuous gold plated structures. Figure 7-2 (B – C) shows selective placement of Au on only a fraction of the DNA origami template. The DNA origami was designed such that Au seeds would selectively attach to half of the DNA length; however, Au NPs were also observed to stick to the opposite end of the origami in some samples. During

origami design, some extra scaffold strands are usually present at the end of origami. These single-stranded DNA may have wrapped around nanoparticles to give instances of isolated particle attachment. SEM images of the samples (Figure 7-2D) after gold plating showed structures that looked like a string of small beads, which is consistent with previously observed structures for gold-plated samples. The length of the Au plated structure was around 200 nm which is close to the design value (~205 nm). EDX analysis of the structure showed the presence of Au only.

The origami samples were then immersed in 2 mM octadecanethiol solution for 24 hours. There was no visible change in the origami shape, size or density on the surface after this process (e.g., see Figure 7-3A & B). The substrate surface, however, became less hydrophilic after this step compared to the substrate surface after plasma cleaning (refer to Chapter 3). There was a change in the contact angle between the solution and the surface. Previously, the SiO₂ surface was hydrophilic and the solution spread almost parallel all over the surface. In contrast, after the C18 step, the surface became less hydrophilic and the subsequent seeding and plating solution made a convex arc on the surface. The seeding and plating solution still covered the whole area since we were using more volume compared to DNA and seeding solution volume before the octadecanethiol step (Chapter 3). The samples were then seeded with palladium.

Figure 7-2: (A) Bar origami. (B) Au seeding on half the length of the origami. (C) Au plating on Au seeded section of the bar origami. (D). SEM image of the Au plated structure height. Circles mark gold seeded and gold plated structures. Height scale is 10 nm. Scale bars are 500 nm.

Figure 7-3: (A) Au plated bar shaped origami. (B) Au plated origami after 24 hours in C₁₈ solution. Height scale is 10 nm. Scale bar is 500 nm.

Figure 7-4 shows a comparison of the height of the DNA origami before and after palladium seeding. Pd seeding changed the average height of the vacant DNA by 2.8 nm with standard deviation of 0.45nm (n=10), which is consistent with the values reported by Yanli Geng in her work³⁰. She used palladium to seed circular DNA origami templates. The image is saturated in order to highlight the change on the unplated section of the origami.

Figure 7-4: (A) Height analysis of unmetallized bar DNA. (B) Height analysis of palladium seeded section of bar DNA. Height scale is 6 nm. Scale bars are 500 nm.

Figure 7-5 shows the SEM images of samples after about 2 minutes of electroless copper plating, the last step in the formation of the Au-Cu junction. The pictures show origami structures with different morphology on the same template. A section of the structure consists of large granules arranged together like beads on a chain while the other section consists of smaller granules arranged closely. The first section is consistent with the gold morphology, and the presence of gold was confirmed by EDX analysis. EDX analysis on the larger section with smaller dense granules showed the presence of copper. As can be seen from the figure, the size and continuity of the copper section of the structure is not uniform. Unlike the uniform gold-plated structures, some copper structures are over-plated, while some structures appear discontinuous and shorter than the design length (~205 nm). Figure 7-5 D shows a discontinuous copper structure, while Figure 7-5 E shows an over-plated copper structure. The copper section of the origami in Figure 7-5 C is not the right length (much shorter than 200 nm) and looks like

one condensed structure. Some of the shorter structures could have been due to the presence of bends in the origami template and thus, when plated, they appear condensed and short. The electroless copper-plating reaction was fast (usually ~ 1 min) as evident from the visual change in the surface (the SiO_2 surface turned brown indicating plating), but was still allowed to proceed for about 2 - 3 minutes to facilitate continuous plating of the seeded templates.

Figure 7-5: (A) – (F) SEM images of Cu-Au junction on bar origami. Scale bar is 200 nm.

Figure 7-6 shows the EDX composition data on the fabricated metal junction. The first section with small granules like beads on a chain showed the presence of gold, while the adjacent section with smaller granules and compact structure showed the presence of copper. The images and the composition data establish the successful fabrication of Au-Cu metal junctions on the DNA template as intended.

Figure 7-6: (A) EDX analysis using spot scan on Cu plated section of the origami. (B) EDX analysis using spot scan on Au plated section of the origami.

In addition, we also observed that there were areas on the same substrate surface with little to no copper deposition and areas with heavy copper deposition as shown in Figure 7-7. The center of the substrate surface contained primarily gold-plated structures, while the copper

deposition was observed around the edges of the substrate. Almost, no copper particles were observed around the center of the substrate as shown in Figure 7-7 A. In contrast, the heavy deposition of copper around the edges is shown in Figure 7-7 C. The images shown (Figure 7-5) of metal junctions in the DNA template were found only in the region between the predominantly gold- and copper-deposited areas.

Figure 7-7: (A) Section of the substrate with no copper deposition. (B) Section of the substrate with gold and copper structures. (C) Section of the substrate with heavy copper deposition. Scale bar is 500 nm.

To further understand the above observations, we designed a series of full surface experiments without DNA origami to test the variability of the copper deposition on the same substrate. To test for high background copper deposition, we prepared some SiO_2 substrates that were dipped in octadecanethiol solution overnight and then seeded with palladium and plated with copper. Likewise, some substrates were seeded with palladium and plated with copper without the octadecanethiol step. As seen in Figure 7-8, AFM and SEM images of sample treated with octadecanethiol solution shows significantly higher background compared to the sample

that was not treated with octadecanethiol. The sample with the additional treatment step has higher deposition of palladium seeds, which grow in size during electroless plating. So, the octadecanethiol step contributed to higher background deposition of copper.

Figure 7-8: (A) AFM image of a Pd seeded SiO₂ surface. (B) SEM image of sample in (A) after copper plating. (C) AFM image of a Pd seeded SiO₂ surface dipped in octadecanethiol solution prior to seeding. (D) SEM image of sample in (C) after copper plating. Height scale is 10 nm. Scale bar is 1 μ m.

Next, we seeded SiO₂ substrates (without DNA origami) with DNA modified Au NPs followed by gold plating for 1 minute. The substrates were then dipped in octadecanethiol solution overnight and then seeded with palladium and plated with copper. Figure 7-9 shows the result of this experiment. On the same substrate surface, we observed areas with little to no

copper deposition and areas with heavy copper deposition similar to our observation with DNA templates. Almost no copper particles were observed around the center of the substrate as shown in Figure 7-9 A, while there was heavy deposition of copper around the edges as shown in Figure 7-9 C.

Figure 7-9: (A) Section of the substrate with no copper deposition. (B) Section of the substrate with gold and copper deposition. (C) Section of the substrate with heavy copper deposition. Scale bar is 1 μm .

We also tried different copper plating times to see the effects on copper deposition on the origami templates. Usually, plating can be visually seen after approximately 1 minute, so we varied the plating time from 1 to 3 minutes. The different plating times had no effect on the apparent copper structure of the DNA template and the images were similar to the ones shown in Figure 7-7. We still observed non-uniform copper plating on the substrate surface. So, we think it's more of an issue with the seeding, which varied across the surface to yield non-uniform copper deposition.

A number of additional experiments were performed to try to determine the cause of non-uniform copper plating by changing different variables. Some of the variables we changed were Au seeds (functionalized with DNA or without), Au plating, C18 step and also the reaction time for octadecanethiol layer and the gold plated structures. Table 7-1 summarizes the experiments we performed to better understand our process.

For all the control experiments, the results we obtained were similar. For experiments involving gold and C18, there were areas with little copper deposition and areas with higher copper deposition. Gold structures were located more towards the center of the substrate, while copper deposition was observed towards the edges of the substrate. In the absence of the C18 step, copper deposited uniformly over the entire substrate surface. We observed higher background with experiments involving C18 step compared to the ones that did not have the C18 step. In case of experiment 10, where we introduced the unseeded origami structure into gold plating solution and then proceeded with the C18 step, palladium seeding and copper plating, the result we obtained was unexpected. Since the origami structures were unseeded; the gold plating solution shouldn't metallize the templates. In the absence of gold, the octadecanethiol has no attachment points in the substrate, so we expected uniform deposition of copper throughout the substrate surface. However, contrary to our expectation, there were areas with less background and areas with heavy deposition. It is possible that there was a small amount of gold deposition on the unseeded sample. On the other hand, for experiment 11, where the processes were similar to experiment 10 except for C18 coating, we observed uniform copper plating on the substrate surface as expected. Based on these observations, the observed non-uniformity appears to be associated with the presence of gold on the surface followed by exposure to the C18 solution.

Table 7-1: Summary of different control experiments

Variables	Exp 1	Exp 2	Exp 3	Exp 4	Exp 5	Exp 6	Exp 7	Exp 8	Exp 9	Exp 10	Exp 11	Exp 12	Exp 13
DNA Origami	X	X	X	X						X	X		
Gold seeding (DNA functionalized NP)	X	X					X	X	X				
Gold seeding (NP without DNA)												X	X
Au plating solution (no plating)										X	X		
Au plating on surface	X	X						X	X				X
C18 coating	X		X		X		X		X	X		X	X
Pd seeding	X	X	X	X	X	X	X	X	X	X	X	X	X
Cu plating	X	X	X	X	X	X	X	X	X	X	X	X	X
Different C18 coating time (15, 18, 24 hours)	X		X	X									
Number of Replicates	15-20	10-12	10-12	10-12	5-6	5-6	5-6	5-6	5-6	4-5	4-5	4-5	4-5
Result (uniform (U) or Non-uniform (N))	N	U	U	U	U	U	N	U	N	N	U	N	N
Background deposition (High, Medium or Low)	High	Low	Med	Low	Med	Low	High	Low	High	High	Low	High	High

Our gold structures were very consistent throughout our experiments and the SEM imaging showed structures that appeared continuous with no gaps. However, the copper section of the structure showed considerable non-uniformity. Within the same substrate surface, there were areas with little to no copper plating and areas with heavy copper deposition. We could distinctly see Au-plated structures only on the inner surface of the substrate (Figure 7-7A) and in the middle region (Figure 7-7B) of the substrate. The gold structures in the inner region of template were very consistent throughout the different experiments we performed. The yield in those regions for our gold structures was close to 100 %. The yield is based on the observation that all the gold structures were continuous and consistent with our design parameters. Likewise, there was virtually no copper structure present on the inner sections of the substrate. Most of the Au-Cu structures we obtained were from the middle region on the surface. The gold structures in the middle section again looked very consistent as evident from images above (Figure 7-7 B). At this point, we could still see good gold structures because the change from inner sections with no copper to outer sections with heavy copper deposition was very gradual. It is in this region we managed to get some working Au-Cu metal structures consistent with our design size. The outside region had very high copper deposition, thus making it impossible to determine the yield of our either gold or copper structures.

While the heterogeneous structures that we fabricated were not perfect, this is the first time that junctions of dissimilar metals have been demonstrated on a DNA origami template. The EDX composition data and the morphological variation verified the presence of two different metals (copper and gold) on the DNA template. A chemical “mask” was used to successfully protect the gold during copper deposition. Overall, these results represent important progress towards the realization of DNA-templated components for nano-circuit fabrication.

8 CONCLUSIONS AND FUTURE WORK

8.1 Conclusions

The fabrication of a Cu – Au metal junction on a single DNA origami template was successfully demonstrated as a result of this work. Specifically, we were able to direct copper and gold to pre-designed locations on a DNA origami template that was designed for this study. Site-specific deposition of a single metal on DNA origami templates has been demonstrated only recently^{3, 27}; however, selective deposition of multiple metal components on the same DNA template brings some additional challenges. These challenges include: (1) the ability to selectively plate only at previously seeded sites and (2) the ability to localize different metals to pre-designed locations of the template without affecting the structure of the other metal(s). These challenges were addressed in this study to develop Au-Cu metal junctions on a bar-shaped DNA template. To our knowledge, this is the first demonstration of a dissimilar metal junction on a DNA origami template.

To accomplish this, a series of process steps was required. First, complementary base pairing was used to attach Au NPs to designated areas of the template. This was followed by electroless plating with Au. Following metallization, the Au plated section of the template was masked with an organic layer to prevent further metal deposition. Subsequently, the remaining section of the DNA template was seeded with Pd and plated with Cu to form the desired Au-Cu metal junction. The resulting metallized origami templates were characterized with use of SEM

and EDX composition data to confirm the presence of copper and gold on the same template. In addition to the successful fabrication of the structure itself, use of an organic layer to prevent unwanted deposition during the metallization of origami templates is another important aspect of this work.

In light of the recent works in this field, this study represents an important step forward in the fabrication of nanostructures based on DNA templates. The ability to control the location of metal components for use in electronic circuits was one of the main goals of this project. An electronic circuit consists of different electronic components like resistors, transistors, diodes or capacitors connected by conductive metal wires. Our ability to localize two different metal components to specific section of a DNA template opens up future possibilities for a spectrum of work like metal-semiconductor junctions. The ability to control metal and semiconductor components is very essential for making field effect transistors (FETs) in the future which form the integral part of any modern day integrated circuits. The work we demonstrated here forms the basis for creating similar DNA templated FET structures in the future. This bottom-up approach combined with the existing top-down approach could provide a pathway to fabricate integrated circuit elements with smaller feature sizes and increased capacity per unit area than the ones in production.

8.2 Future Work

There are several opportunities for future work related to this study. These opportunities include: (1) understanding the issues with copper deposition to increase the yield of metal junction structures, and (2) leveraging the metal-metal junction created in this study to enable fabrication of a metal-semiconductor junction on a DNA origami template.

We observed non-uniform copper deposition on the substrate surface, which resulted in low yield of the Au-Cu structures. In contrast, the yield of the gold-plated structures was excellent. Based on a series of experiments we performed, the non-uniformity is likely due to the presence of gold on the surface followed by octadecanethiol exposure. In order to resolve this issue, we could look at modifications to our masking procedure that would minimize the negative impact on copper deposition. One alternative is to use a different molecule, such as DNA, as the chemical mask instead of the organic layer used in this study. We had previously observed the plating inhibition caused by the DNA layer around the nanoparticles, so we think DNA strands can be used for masking without negatively affecting the copper deposition. Another possibility would be to use different attachment chemistry. For example, diselenides³²,³³ bind to gold surfaces via Au-Se bonds, which may not have the same negative effect on selective copper deposition as the alkanethiols used in this study. Another possibility would be to investigate the effect of n-alkanethiol chain length and end groups like -COOH or -OH compared to the -CH_3 group we used for their masking abilities and subsequent effect on electroless plating²⁸. Likewise, we could analyze the additives present in the commercial gold plating solution that permits plating on thiolated nanoparticles. Next, we can work to determine if certain metal nanoparticles show specificity to a particular metal plating (either gold or copper), which could then help to make metal junctions without the use of a masking layer. Once we get uniform copper plating across all the templates in the substrate, we should be able to significantly increase the yield of Au-Cu metal junctions and then alter plating times to make continuous and conductive structures.

After addressing the issue with non-uniformity of copper, we can then proceed to make a metal-semiconductor junction on the same DNA template. One method to make such junctions is

to galvanically displace the copper-plated section of the template with semiconductor materials like Te ³¹ and Bi_2Te_3 ³¹. Galvanic displacement works due to the difference in the standard potentials between the elements. Semiconductor materials like Te and Bi_2Te_3 have a higher standard potential than copper but less than gold. Thus, copper will react with a solution containing Te or Bi_2Te_3 , while gold will not. This will enable fabrication of the metal-semiconductor junctions, such as Au-Te or $\text{Au-Bi}_2\text{Te}_3$. In this context, recent work by Liu et. al. demonstrated the fabrication of DNA-templated semiconductor nanowires by galvanic displacement^{29, 31}. Nickel and copper nanowires formed on λ DNA were galvanically displaced by Te or Bi_2Te_3 to make semiconductor wires^{29, 31}. Even though that work was performed on λ DNA, which is much simpler and more robust, the knowledge gained can definitely be applied to our DNA origami structures. The work can be further extended to form chalcogenide materials like Ag_2Te and CdTe by template engaged topotactic and cation exchange reaction to make a metal (Au)-chalcogenide structure that has potential application in next generation nanodevices, sensors and memory devices. Selective deposition of multiple metal and semiconductor materials on specific locations of a DNA template is important for making complete next generation devices. Thus, DNA origami offers a useful means to make DNA templates of varying complexity for applications in nanoelectronics.

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APPENDIX

DNA staple strand sequences

“T” DNA origami structure.

“T” DNA origami structure was formed as previously reported²⁰ and the scaffold came from M13mp18, bases 5734-1442, 2958 bp²⁰. For nanoparticle attachment, modified sequences containing an additional ten adenines on the 3' end of the strand were used in folding the DNA origami structure. For the attachment sites along the entire “T” structure, the entire staple sequences (95 staple strands in total) were modified and used in place of the original sequences. The sequences used are listed below.

```
GGTAGAAAGTCTATCAGAAAAAAAAAAAA
TACCACATACGTGGACTCCAACGTCAAAGGGCAAAAAAAAAAAAA
CAAAAGGATCCAGTTTGAACAAGAGTCCACTAAAAAAAAAAAA
ACTATCATAAAGAATAGCCCGAGATAGGGTTGAAAAAAAAAAAA
AAAAACCAGTTCGAAATCGGCAAAATCCCTTAAAAAAAAAAAA
GAAGTTTTGCCCCAGCAGGCGAAAATCCTGTTAAAAAAAAAAAA
TTTAGACTAGAGAGTTGCAGCAAGCGGTCCACAAAAAAAAAAAA
GGAACAACATTATTACAAAAAAAAAAAAA
AAGAAAAATCTACGTTAATAAACTTTAGGAAAAAAAAAAAAA
AACTGGCTCATTATACCAGTCAGGCATAACGCAAAAAAAAAAAAA
AATCATTGTGAATTACCTTATGCGAGAGCAACAAAAAAAAAAAA
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AATTGGGCTTGAGATGGTTTAATTACGACGATAAAAAAAAAAA
TGCCCTGACGAGAAACACCAGAACTTGCAAAAAAAAAAAAAAA
GTAACAAAGCTGCTCATTTCAGTGAGTAAAATGAAAAAAAAAAA
GAAAAACCGATTTCATCAGTTGAGAGAACTAACAAAAAAAAAAA
ATTAAAGATCAACTAATGCAGATAACGTTGGGAAAAAAAAAAA
AGTGTGTATTACGAGGCATAGTAATTTTAAGAAAAAAAAAAAA
ATAAATCAAACCCTCGTTTACCAGTCAACTTTAAAAAAAAAAAA
TGATGGTGAAATAGCGAGAGGCTTGAGTAGTAAAAAAAAAAAA
GCTGGTTTGCCAGAGGGGGTAATAATAAGGCTAAAAAAAAAAAA

CGTCATAAAACAGCTGATTGCCCTTACCGCCAAAAAAAAAAAA
GCTTTAAAGGGTGGTTTTTCTTTTCACCAGTGAAAAAAAAAAAA
TAAATCAAGCGGGGAGAGGCGGTTTGCGTATTAAAAAAAAAAAA
TATAGTCACGTGCCAGCTGCATTAATGAATCGAAAAAAAAAAAA
ACAAGAACCGGATATTCATTACCCTGCGGAATAAAAAAAAAAAAA
AGGCTGGCTGACCTTCATCAAGAGCCTCAAATAAAAAAAAAAAAA
GGACAGATGAACGGTGTACAGACCAATGACCAAAAAAAAAAAAA
ATAAGGGAACCGAACTGACCAACTCTGACTATAAAAAAAAAAAAA
TGGCCCTGGGATAGCGTCCAATACAAATCAACAAAAAAAAAAAA
AGACGGGCATATTCATTGAATCCCTAATCTTGAAAAAAAAAAAA
GGGCGCCACAGTTCAGAAAACGAGAGGCGCATAAAAAAAAAAAA
GCCAACGCAAATCAGGTCTTTACCTTGAAAGAAAAAAAAAAAA
AAACCTGTGAAGCAAAGCGGATTGGGTCAATCAAAAAAAAAAAAA

TCGCGTTTGCCGGAGAGGGTAGCTATTTTTGAAAAAAAAAAAA
GACCGGAATGATATTCAACCGTTCTAGCTGATAAAAAAAAAAAAA
GAGAGTACAAAGGCCGGAGACAGTCAAATCACAAAAAAAAAAAA

GGTCATTTGTAATGTGTAGGTAAAGATTCAAAAAAAAAAAAAA
GCTGAATAGAACCCCTCATATATTTTAAATGCAAAAAAAAAAAAA
ACTTAGCCGGAACGAGGCGCAGACCATCAAAAAAAAAAAAAA
ATTGTGTCGAAATCCGCGACCTGCTTCAAATAAAAAAAAAAAAA
GTACAACGGAGATTTGTATCATCGGCGAACCAAAAAAAAAAAA
ACCCCCAGCGATTATACCAAGCGCCAGGATTAAAAAAAAAAAA
GGCAAAGAATACACTAAAACACTTGATAAGAAAAAAAAAAAA
AAATTAATTAATTCGAGCTTCAAACCTGATAAAAAAAAAAAAA
CATCAATAGCAAACCTCCAACAGGTGAAACAAAAAAAAAAAA
AGGGTGAGCTTTAATTGCTCCTTTCATCTTTGAAAAAAAAAAAA
ATGCCTGATTGCGGATGGCTTAGAACGAAAGAAAAAAAAAAAA
AGATTAAGAGGAAGCCCGAAAGACTCCATGTTAAAAAAAAAAAA

GCATCAATTCTACTAATAAAAAAAAAAAAA
AAATATGCCCTTTATTTCAACGCAAGGATAAAAAAAAAAAAA
TTCATTCCATTATGACCCTGTAATACTTTTGCAAAAAAAAAAAAA
GCGAACGAGAGCATAAAGCTAAATCGGTTGTAAAAAAAAAAAA
ACATTTCTGAAGAATTAGCAAAATTAAGCAATAAAAAAAAAAAAA
TATATTTTATTAACATCCAATAAATCATACAGAAAAAAAAAAAA
CCACTACGAAGGCACCAACCTAAAGCTTAATTAAAAAAAAAAAAA
AAGTTTCCATTAAACGGGTAAAATCATGTTTTAAAAAAAAAAAA
AGGCTTTGAGGACTAAAGACTTTTCTGGAAGTAAAAAAAAAAAA
CAGCATCGGAACGAGGGTAGCAACCCAATTCTAAAAAAAAAAAA
TTTGCGGGATCGTCACCCTCAGCACATTAGATAAAAAAAAAAAAA
TCGCTGAGGCTTGCAGGGAGTTAATGTTTAGCAAAAAAAAAAAAA
CATAACCGATTGAAAAGGTGAAAAAAAAAAAA
AATTTTATAATGCTGTAGCTCAAACGTAATGAAAAAAAAAAAA

GGGAGAAGAACTAAAGTACGGTGTTCATGAGGAAAAAAAAAAAA
CCAAAAACATATAACAGTTGATTTCGGCTACAGAAAAAAAAAAAA
AAGCCTCAGTAGATTTAGTTTGACGCGAAAGAAAAAAAAAAAA
GCAAGGCACAAATGGTCAATAACCAGGCCGCTAAAAAAAAAAAA
GTAGTAGCCATTTGGGGCGCGAGCATATTCGGAAAAAAAAAAAA

AGATCGCACCAGTCGGGAAAAAAAAAAAA

TTCTGGTGACATTAATTGCGTTGCGCTCACTGAAAAAAAAAAAA
CGCCATTCAAGCCTGGGGTGCCTAATGAGTGAAAAAAAAAAAA
CGATCGGTACACAACATACGAGCCGGAAGCATAAAAAAAAAAAAA
GCTGGCGACCTGTGTGAAATTGTTATCCGCTCAAAAAAAAAAAAA
TAAGTTGGGCTCGAATTCGTAATCATGGTCATAAAAAAAAAAAAA
CGACGTTGCAGGTCGACTCTAGAGGATCCCCGAAAAAAAAAAAA
GAGATCTAGCCTCAGGAAAAAAAAAAAA

AGAGTCTGTCTGCCAGTTTGAGGGGGCACCGCAAAAAAAAAAAAA
GGTAATCGGTTGGTGTAGATGGGCGCGCCATTAAAAAAAAAAAA
TACCCCGGAACGGCGGATTGACCGGGGAAGGGAAAAAAAAAAAA
ACAGGAAGAGTAACAACCCGTCGGTTACGCCAAAAAAAAAAAA
GTAAACGTTAGCCAGCTTTCATCAAAGGCGATAAAAAAAAAAAAA
AAATTTTCCATCAAAAATAATTCCCAGTCAAAAAAAAAAAAA
CCAAGCTTGCATGCCTGTAAAACGACGGCCAGTGAAAAAAAAAAAA
CCCGCTTCTCCAGCCAGCTTTCGACGACGAAAAAAAAAAAA
GCTAACTCCCGGAAACCAGGCAAAGCATCGTAAAAAAAAAAAA
AAAGTGTAAGGCTGCGCAACTGTTTAATGGGAAAAAAAAAAAA
ACAATTCCGCGGGCCTCTTCGCTAATTCTCCGAAAAAAAAAAAA
AGCTGTTTAAGGGGGATGTGCTGCACATTAAAAAAAAAAAA
GGTACCGAGTAACGCCAGGGTTTTGCGTCTGGAAAAAAAAAAAA

TTTAACCAATAGGAACGGTTAAATCAGCTCATTTAAAAAAAAAAAA
 CAGTATCGCAAAGGCTATCAGGTCATTGCCTGAAAAAAAAAAAA
 ACCGTGCAGAGCAAACAAGAGAATCGATGAACAAAAAAAAAAAA
 TAGGTCATAAACTAGCATGTCAATCATATGAAAAAAAAAAAA
 TGGGAACATTGATAATCAGAAAAGCCCCAAAAAAAAAAAAAAAA
 TGTGAGCGATTGTATAAGCAAATATTTAAATTAAAAAAAAAAAA
 CCTTCCTGTAATATTTTGTAAAATTCGCATTAAAAAAAAAAAA

Bar shaped Origami sequence

For the ‘Bar’ structure, single-stranded M13mp18 was used for the scaffold. On one half of the structure, the staple strands (110 strands in total) were modified to contain an additional ten adenines on the 3’ end of the strands. The staple strands (116 strands in total) on the other half of the structure were modified to contain an additional GTGCGTGT sequence on the 3’ end of the strand. These modified staple strands were used in folding the DNA origami structure. Blue sequences are the staple strands modified with the additional ten adenines and the black sequences are the staple strands with the additional GTGCGTGT sequence on the end.

AGGCGAATTAGAACCTACCATATCAAATTA
 GCTTTGAATAAAACAGAAATAAAGAAATTGC
 AATCATAACAGCAGAAGATAAAACAGAGGTG
 AAATAAGGAGTATTAACACCGCCTGCAACAG
 ATTTAATGTGAGAGCCAGCAGCAAATGAAAA
 ATATTTTCATCACCTTGCTGAACCTCAAATA
 AAGACAAACTCAATCAATATCTGGTCAGTTGG
 TATATGTACAGTTGAAAGGAATTGAGGAAGG
 TTAACCTCAATATCTTTAGGAGCACTAACAA

ATCAAAATTTAGAGCCGTCAATAGATAATAC
TAAGACGATTTAGAAGTATTAGACTTTACAA
TCGGGAGATCAGGTTTAACGTCAGATGAATATAC
AGAATCCTGACAACCTCGTATTAAATCCTTTGC
GTAAATCGTATTAATTTTAAAAGTTTGAGTA
TCAATATAATTTTGC GGAACAAAGAAACCAC
ATTACCTTGCGGAATTATCATCATATTCCTG
AAAATTAATGATGGCAATTCATCAATATAAT
AGTAACAGTACAAACATGAAAG
AAAGAAGAGTTTGGATTATACTTCTGAATAAT
TTTGACGACGTACCAAGTTACAAAATGAGTAAC
CGAACCCTTACTAGAAAAAGCCTATTAGAGC
AGGCGGTCCGTAAATAAGAATATTACCATT
TGCCACGCGTTTGAAATACCGACTGAAACCA
ATCTAAAGAGTTAATTTTCATCTTCAGCGACAG
GTAGATTTAACAATAACGGATTCCCCCCTGC
TCAAACCGAACGCGAGAAAACCTTACTGTAG
CAAATCAAAATGCTGATGCAAATCCATAGCCC
TTATCTAACGGCTTAGGTTGGGTTCATAATC
CTAATAGACATAGGTCTGAGAGACACCGGAA
ATTTGAGGCTGAGAAGAGTCAATACTCAGAAC
ACAATTCTGAAAACATAGCGATACAGAGCC
CCGAACGTTGCTATTAATTAATTGCCGCCAG
ACATTATCTGTGAGTGAATAACCTCAGACGA
CAGAAGGATTTTAATGGAAACAGATAAATCC
ATTATCAGATTACATTTAACAATTGCAGTCTC
CCTGATTTGATGAAACAAACATCCATACAT

GGAAGGGTTATTCAATTTCAATTACCTGGTAAT
GAGGGTTGAACGGGGTCAGTGCCTTCGCGCAG
TGCTCAGTTATAAACAGTTAATGGCCTGATT
ATAGTTGCATCACCAGTAGCACCAAACACCGG
CGAGGTGACGGAAACGTCACCAACGTGTGAT
CTTTAATAGCACCGTAATCAGTTGACCTAA
AAAATCTCTTGCCTTTAGCGTCAGTTTCAAAT
AGGAATTGCATCGGCATTTTCGGTCAATCGC
CAGCGGAGAGCGTTTGCCATCTTTTATATAAC
TGGGATTTTCGGAACCAGAGCCACCTACCTTT
TTTCCAGCTCAGAGCCGCCACCGTGAATTT
TAGTTAGCTCAGAGCCACCACCCTGCTTAGAT
AACGCCTGAACCACCACCAGAGCCTTCCCTT
AACACTGAAGGAGGTTGAGGCAGGTTGCTTCT
ATAGCAAGGATATTCACAAACAATACATAAA
ACCCTCAGCCAGAATGGAAAGCTCATTGA
CCACCCTCCCGTTCCAGTAAGCGTAAGAAAAC
TATTAAGAGGCCTATCAGGTCA
TGTATCACATGATACAGGAGTGTACTGAGCA
AGTGCCCGACCAGGCGGATAAGTAACCGTT
CAGCAAAGCCGACAATGACAACGGCTTAGA
AGCAAGGCATTTCTTAAACAGCTTAGCTCA
TCGATAGCTGTATCGGTTTATCAGGTACGGTG
AATCAAGTCAAAAAAAGGCTCCACAGTTGAT
CTATTTCGGAAGGATTAGGATTAGAGGGTAGC
CGCGTTTTCGAATAATAATTTTTTTTAGTTT
CCTTATTTGAGAATAGAAAGGATGGTCAAT

AAAATCACTGCTAAACAACTTTCTGGGGCG
CCGCCTCCACGTTAGTAAATGAATCTACTAAT
CGCCACCCGTAACGATCTAAAGTTAATCATAC
GCCACCAGTAGCATTCCACAGACAATTAAGCA
CATTGACGTTTCGTCACCAGTAAAATCGGT
TTGGCCTTCCCAATAGGAACCCATAATACT
TCATTAAAGAGCCACCACCCTCATACGCAAGG
TGAATTTAAGAACCGCCACCCTCAATATTTTA
GGCTTTTGCGTACTCAGGAGGTTTAGGTAAAG
AAGTTTTATATAAGTATAGCCCGAGACAGT
GATAATCACATCAATATGATATTCGCCGTCGA
AAACTAGCTAAATTAATGCCGGAGCGGGGTTT
GGGGATGGCTGAATATAATGCTGTGATACCG
GGCCTCTTTAAATATGCAACTAAACTTGCTTT
TGCGCAACGTTTCATTCCATATAAAAAGGAGC
AACCAGGCCTGCGAACGAGTAGACACGTTG
CCAGCTTTGATACATTTTCGCAAAACAATAA
CAGTATCGTAGCTATATTTTCATTAACAGTTT
ACCGTGCAAAAGGTGGCATCAATTTTCTGTA
AGGTCACGGCATTAAACATCCAATATTGTCGTC
GGAACAAACAAAGAATTAGCAAAGCCCTCA
GAGCGAGTTCAGAGCATAAAGCTCAAACACTAC
CCTGTAGAAACATTATGACCCTGTGTACCGT
AACGCCATAGAAGCCTTTATTTTCATTCAGGG
TGTTAAATTTTTTAGAACCCCTCATGAACCGCC
TAATATTTGCCTGAGTAATGTGTAGTACCG
TTGCCTGAGAGTCTGGAGCAAACAAGGAGAGATC

TTGTATAAGGGTGAGAAAGGCCGGGAATAGG
CTAGCTGAATGTCAATCATATGTACCCCGGTT
GCTTAATTTGCTGCAAGGCGATTAAGTTGGGT
ACATGTTTCGCTATTACGCCAGCTGGCGAAAG
TCTGGAATGTTGGGAAGGGCGATCGGTGCG
TCCCAATTAAAGCGCCATTCGCCATTCAGGC
TATTTTTAGAATCGATGAACGGTAATCGTA
GACCATTACCGGCACCGCTTCTGGTGCCGGA
AACCTGTTGCCTCAGGAAGATCGCACTCCAG
CGAGCTGATCTGCCAGTTTGAGGGGACGACGA
AGTAGTATTGGTGTAGATGGGCGCATCGTA
AGGCAAGGCGGCGGATTGACCGTAATGGGAT
TACAAAGGTGAGACTCCTCAAGAGAACCTATTATTCTGCTTTTACA
ATAAAGCCAACAACCCGTCGGATTCTCCGTG
TGTACCAACCAGCTTTCATCAACATTAAATGT
TTTGCGGGCAAAAATAATTCGCGTCTGGCCTT
ATAAAAACAGCTCATTTTTTAACCAATAGG
AATGCAATTGTTAAAATTCGCATTAAATTTT
ATTCAAAAGCAAATATTTAAATTGTAAACGT
CAAATCACGAAAAGCCCCAAAACAGGAAGA

ATTTTCATGTGAGGCCACCGAGTAAAAGAGT
CGCACTCCACGCAAATTAACCGTTGTAGCAA
ATCATTCTTGATTAGTAATAACATCACTTGC
GAAACCAAAAGAACTCAAAC TATCGGCCTTG
ATAATATCATCCAGAACAAATATTACCGCCAG
ATCAACAAACAGGAAAAACGCTCATGGAAAT

CATGTTCTTTGACGCTCAATCGTCTGAAATG
AGTAATTCTACATTGGCAGATTACACAGTCAC
TAAGAGAATAATAAAAGGGACATTCTGGCCA
AATTTAGGAGAACCCTTCTGACCTGAAAGCG
AGAATCGCCGTGGCACAGACAATATTTTTGA
AAAGCCATAGTCTTTAATGCGCGAACTGATA
ATCATATGAACATCGCCATTAAAAATACCGAA
CTAACGAGCTGCGCGTAACCACCACACCCGC
AGCTACAAATGCGCCGCTACAGGGCGCGTAC
TTAAATCCTTTGACGAGCACGTATAACGTGC
GAACCTCCGTTAGAATCAGAGCGGGAGCTAAA
CCGGTATTCGATTAAAGGGATTTTAGACAGG
ATAGCAAGGCCAGAATCCTGAGAAGTGTTTT
CTGTCCATATCGAGAAC AAGCAAGAAATAGCA
TACTTCTAAGAACGGGTATTAAATTAAGAA
CTGAGTAGTCAATAATCGGCTGTCTTACCAGA
CTGGTAATCCATCCTAATTTACGTAACGGAA
CCATTGCATAGATAAGTCCTGAAAAGACTCC
ACCTACATAGCTAATGCAGAACGCCGTAGAAA
GATTATTTGTCCAGACGACGACAATAAAAG
ACGACCAGTATAAAGTACCGACAAGTTTATTT
ACAGAGATCAGAGGCATTTTCGATATGGTTT
TAAGAATACATATTTAACAACGCGACATTCA
ATGGCTATACGCTCAACAGTAGGGATATTGAC
GCCCTAACGTTATACAAATTC TTTATCACC
GCGCTAGGGCGCTGGCAAGTG TAG
CGGTCACGCGTCTTTCCAGAGCCTATTTATC

CGCGCTTATTTTATCCTGAATCTTTTGTTTA
TATGGTTGAAGATTAGTTGCTATTCTTTACAG
TTTCCTCCGACTTGCGGGAGGTTAGCGCAT
CAGGAGGCCTAAGAACGCGAGGCGCCTGAACA
AACGGTACCAAATCAGATATAGAAATATCAG
TATAATCACGTAGGAATCATTACTTAAGCCC
CATAAGGGAGCAAGAAACAATGCCGTTTTT
TACTTAGCCTTACCGAAGCCCTTTCCAAGTAC
ATTGTGTCAGATAGCCGAACAAAGTTTCCTT
TACAACGGCGAGGAAACGCAATAAAGCATGTA
CCCCAGCGAGAACTGGCATGATTCAAGAAAA
AAAAGAACAGTATGTTAGCAAAGCCTGTTT
CTACGAAGATAAAGGTGGCAACATATAAACAA
TTCCATTAAGACACCACGGAATAAAAGGTAA
TTGAGGACATCAATAGAAAATTCAGCCAGTAA
CGGAACGACAAAGACAAAAGGGCCAACATGT
GATCGTCAGGGAGGGAAGGTAACCTTAATTG
GGCTTGCATTCAATTAAGGTGAATACCAGTAT
CCCACGCACTTGAGCCATTTGGGAGTTTAGT
GTAGTAAAAAATAAGAAACGATTTTACCAACG
AGGCTTGAATGAAAATAGCAGCTTGCACCC
TCAACGTAACATAAAAACAGGGATTGAAGCC
CTTGACAAAGAATTAACCTGAACACTTTTAGC
CATAGGCTAGGGTAATTGAGCGCTAGGCTTAT
GAGGACAGCCCACAAGAATTGAGCGCGCCCA
ATAGCTATCGGAACGAGGCGCAGAGACGATAA
AAGTAAGCGAAATCCGCGACCTGCTGCAAAAG

AGGAAACAGATTTGTATCATCGGTAAAATG
TACCCAAAATTATACCAAGCGCGTGCGGAA
TTATTACGTACACTAAAACACTCACCTCAA
ATACATACGCACCAACCTAAAACGAGAATGAC
AAACGCAAAACGGGTAAAATACGTACCCTGAC
TGTCACATAAAGACTTTTTTCATATTGCATC
ACCAGCGCGGGTAGCAACGGCTAAGACTTC
ACCGATTGACCCTCAGCAGCGAAATCAAAGCG
GGAAATTAGGGAGTTAAAGGCCGCACAGGTCA
GTCACCGATAACCGATATATTCGGCTCCTTTT
AAATAAACAGCCATATTAATTTGCCAGTTACA
CCAATCCTTGGGCTTGAGATGGTTATGCG
ACGTCAAACCCTGACGAGAAACACCAGTCAGG
AGAGAATAACAAAGCTGCTCATTCTAATAAAA
TAGACGGGGAACCGGATATTCATTACAGGTAG
AAGTCAGGGCTGACCTTCATCAGGAATACC
AGAGATAAATGAACGGTGTACAGACGCCAA
AATAATAAGAACCGAACTGACCAAGCAAACT
CTGATTGCCCCCTCGTTTACCAGACCGGTCAAT
GAGGCGGTCCAGAGGGGGTAATACCTGATAA
CTGCATTGGATAGCGTCCAATACAAACAAAG
CCGCTTTCAATATTCATTGAATCCTCTTTGAC
TAACTCACAACAGTTCAGAAAACGAAAGAGGC
GTGTAAAGAAAAATCAGGTCTTTAATGCCA
TTCCACACTCAGAAGCAAAGCGGGAGGAAGT
TTTCCTGTTAAGAGGAAGCCCGAACAGAGGCT
CGAGCTCGCGTTTTAATTCGAGCTGACAGCAT

TGCAGGTCCCGGAAGCAAACCTCCATTTTGCGG
AAAACGACGAGTACCTTTAATTGTCGCTGA
AACGCCAGGTCATTTTGGCGGATAACCATCG
ACGTGGACAACCTGGCTCATTATACCAGAACGA
CCAGTTTGGAAGAAAAATCTACGTAGTGAATA
AGAATAGCCGGAACAACATTATTACCCAAA
CCGAAATCATCAGTTGAGATTTAAGAGTAAT
CAGCAGGCCTAATGCAGATACATAACCAGGCG
AGTTGCAGACGAGGCATAGTAAGACTTTGAAA
AAACCAAATTCACCAGTGAGACGGGC AACAG
AAGTTTTGTTGCGTATTGGGCGCCAGGGTGG
TTAGACTAATGAATCGGCCAACGCGCGGGGA
TCGTCATACAGTCGGGAAACCTGTCGTGCCAG
TGCTTTAATTAATTGCGTTGCGCTCACTGC
CATAAATCCCTGGGGTGCCTAATGAGTGAGC
TATTATAGAACATACGAGCCGGAAGCATAAA
AAAAAGATGTGAAATTGTTATCCGCTCACAA
AAATATCGAATTCGTAATCATGGTCATAGCTG
AACCAGAGACTCTAGAGGATCCCCGGGTAC
GGATTAGAGGCCAGTGCCAAGCTTGCATGCC
GATAAGAGGGTTTTCCCAGTCACGACGTTGT
ATCATTGTGAATTACCTTTAATTTCAACTTTA
ATTTTAAGTCCAACGTCAAAGGGCGAAAAACCGTCTATCA
ACGTTGGGAACAAGAGTCCACTATTAAAGA
CGAACTAACCGAGATAGGGTTGAGTGTTGTT
AAAGATTCGGCAAAATCCCTTATAAATCAAA
ACATTCAAGAAAATCCTGTTTGATGGTGGTT

AAGGAATTCAAGCGGTCCACGCTGGTTTGCCC
ATCATAACCTTCACCGCCTGGCCCTGAGAG
TTTTTCTTATAGCGAGAGGCTTTTCCATGT