Mat. Res. Soc. Symp. Vol. 635 © 2001 Materials Research Society

DNA-Directed Assembly of Anisotropic Nanoparticles on Lithographically Defined Surfaces and in Solution

Brian D. Reiss, Jeremiah N. K. Mbindyo, Benjamin R. Martin, Sheila R. Nicewarner, Thomas E. Mallouk, Michael J. Natan, and Christine D. Keating*
Department of Chemistry, The Pennsylvania State University
University Park, PA 16802, USA
*Author to whom correspondence should be addressed at keating@chem.psu.edu

Abstract

Anisotropic, noble metal nanoparticles have been synthesized using a template synthesis strategy. In short, metallic salts are reduced in the nanometer scale pores of either an alumina or polycarbonate membrane. The particles can then been released from the template to form suspensions of anisotropic nanoparticles. These nanoparticles have been modified with deoxyribonucleic acid (DNA) oligomers of varying length using several different attachment chemistries. The thermodynamics and kinetics of modifying these particles with DNA has been explored. DNA has also been used to assemble the particles on planar Au surfaces as well as lithographically defined Au pads on Si wafers. In addition to surface assembly, DNA has been used to assemble the nanowires into simple, yet deterministic structures in solution.

Introduction

Since the mid twentieth century there has been a great deal of interest in the miniaturization of electronic devices. Currently state of the art photoloithographic technology can fabricate devices in the 100 nm size range, but there is an economic motivation to reduce the dimensions of electronic circuitry even further. Due to scientific constraints, there are limitations in the extent to which devices can be fabricated using photolithography.[1] For this reason, there has been a great deal of interest in the development of novel technologies for fabricating smaller devices than can be prepared using photolithography. One such alternative is the "bottom up" approach where devices are self-assembled from very small building blocks as opposed to being etched out of larger pieces of material (a "top down" strategy).[2] Such an approach offers two key advantages. First of all, since devices can be fabricated from nanoparticles or even individual molecules, it is feasible to fabricate much smaller devices than can be prepared using photolithography. The second key advantage is cost. Modern fabrication facilities for photolithography cost over a billion dollars to build, but one can start self assembling devices for a fraction of that cost.

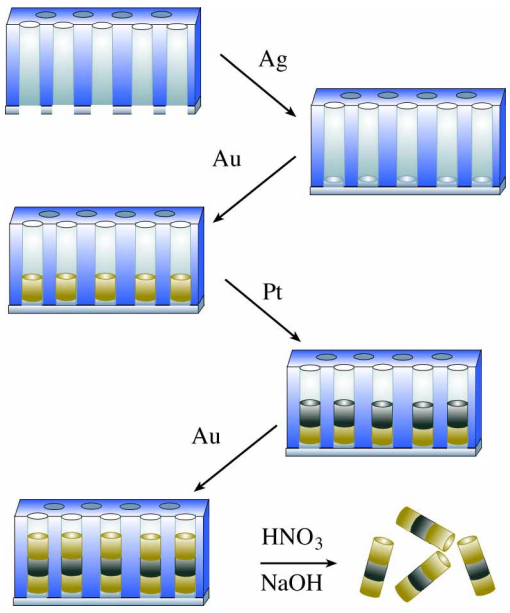
The goal of this research is to assemble anisotropic nanoparticles into functional electronic devices, including memory devices, logic gates, etc. To accomplish this task, two things are necessary: the anisotropic nanoparticles and a "smart glue" to make the particles self assemble into desirable geometries. DNA was chosen as a glue because it offers several unique advantages. [3-5] The primary advantage is selectivity, which results from the specificity an oligonucleotide has for its complementary oligonucleotide. Oligonucleotides have been shown to bind selectively in the presence of hundreds of thousands incorrect sequences.[6] This selectivity allows the user to design systems using different attachment chemistries that are all based on the same fundamental chemistry. For example, if oligonucleotides n bases long are used, 4^n different attachment chemistries could be designed that all work at similar pHs, ionic

strengths, and temperature. The second main advantage of DNA is reversibility. If two oligonucleotides hybridize to form an incorrect structure, they can be dehybridized by raising the temperature, changing the ionic strength, or adjusting the pH, which introduces the possibility of annealing the system to get the desired structure.

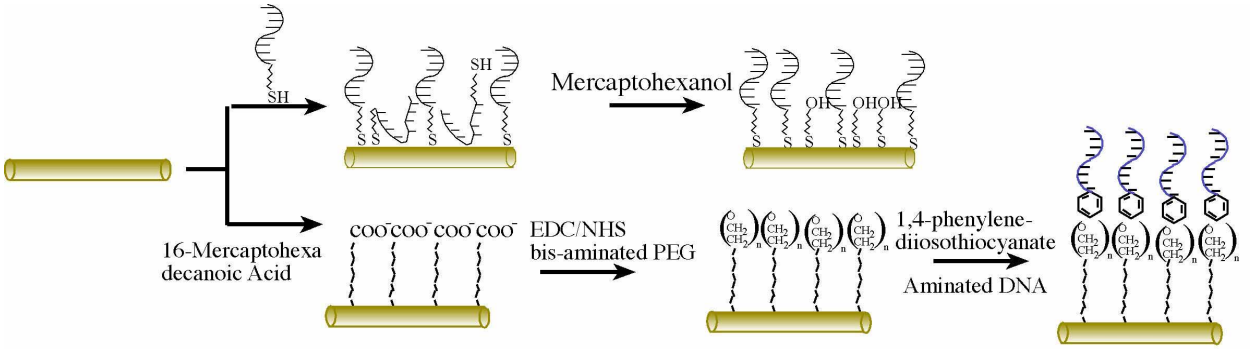
Experimental Details

To prepare the anisotropic nanoparticles a template synthesis technique was chosen in which metallic salts are electrochemically reduced into the pores of either an alumina or polycarbonate membrane (scheme 1).[7, 8] To accomplish this, Ag is thermally evaporated onto the backside of the membrane where it acts as a macroscopic electrode. Metallic salts are then reduced into the pores of the membrane using a three electrode electrodeposition technique. Once the particles are grown, the Ag is dissolved in HNO_3, and the membrane can then be dissolved in NaOH, yielding a colloidal sol of anisotropic particles that are nanometers in diameter and several microns long.[9] These particles can be made of different metals, including Au, Ag, Pt, Ni, Pd, and Cu, or they can be composed of semiconducting or polymeric materials. By controlling the amount of material reduced into the pores of the template, particles can be grown of any desired length up to approximately ten microns. Furthermore, by varying the pore size, particles can be grown at any desired diameter, ranging from 12 nm to 300 nm, so there is complete control over the dimensions of the resulting particles as well as their composition. This synthetic strategy was modified so that stripes of different materials could even be included along the length of the nanoparticles. Since the ultimate goal of this work is to fabricate devices from these structures, the particles are often described as nanowires.

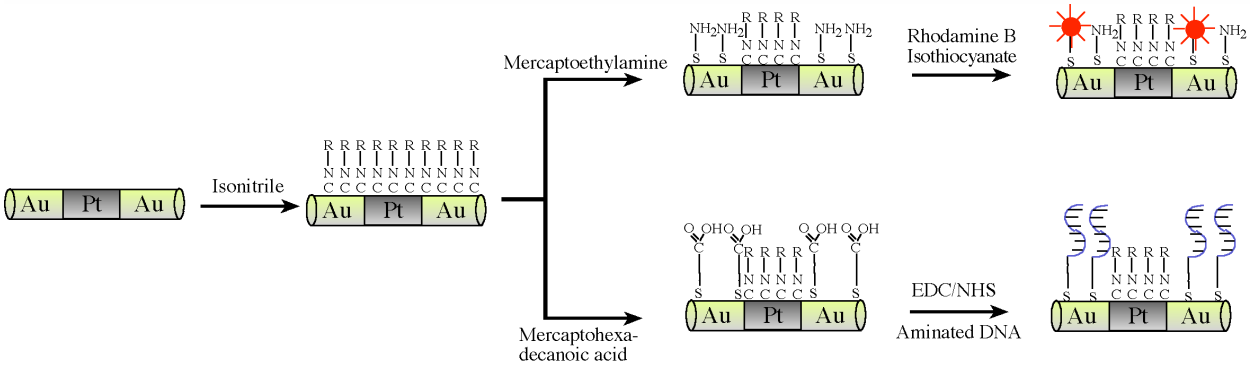
Once dispersed into solution, the nanowires were derivatized using a number of different strategies. The simplest involved mixing a solution of nanowires with a solution of 5 μm thiol-tagged DNA (scheme 2).[10] Once derivatized with DNA, the nanowires were then immersed in a solution of mercaptohexanol (MCH) to dislodge any nonspecifically attached oligonucleotides.[11] A more complex derivatization scheme consisted of modifing the nanowires with 16-mercaptohexadecanoic acid (MHDA). A *bis*-aminated PEG molecule was then attached to the carboxylate groups via carbodiimide coupling. Aminated DNA was then attached to the nanowire by first reacting it with 1,4-phenylene diisothiocyanate followed by immersion in a 5 μM solution of amine-tagged DNA. Nanowires containing stripes of different metals were derivatized by first immersing them in a solution of isonitrile (either butane isonitrile or 4-sulfophenylene isocyanide) followed by immersion in the thiol of interest,[12] mercaptoethylamine (MEA) or MHDA (scheme 3).



Scheme 1



Scheme 2



Scheme 3

The molecule of interest could then be attached to the Au stripes. Aminated DNA was attached to MHDA derivatized nanowires using carbodiimide couple, and rhodamine B was attached to MEA derivatived nanowires using isothiocyanate chemistry.

The surfaces used in these experiments consisted of Au films that could be derivatized with DNA using any of the attachment chemistries described above. For certain experiments, surfaces containing Au pads lithographically defined on Si wafers were used. In these experiments the surfaces were treated with 3-(triethoxysilyl)propyl succinic anhydride and then soaked in H_2O to hydrate the anhydride group, leaving the Si sections of the surface coated with carboxylate groups.

To assemble nanowires in solution, Au and Pt striped nanowires were derivatized as described above. The Au stripes were derivatized with DNA that was twelve bases in length, and different oligonucleotides were attached to different batches of nanowires. They would then be mixed together along with a twentyfour base oligonucleotide that contained two twelve base sections, one that was complementary to the oligonucleotide on each batch of nanowires. The solutions would then be allowed to stir overnight.

***Figure 1**: Optical micrograph of striped, Au, Pt, Au nanowires that are 200 nm in diameter and 5 microns long.*

Discussion

A batch of nanowires is shown in Figure 1. These nanowires are 200 nm in diameter and five microns long, and they consist of stripes of Au, Pt and Au. Figure 2 shows three optical microscope images of Au nanowires immobilized on Au films through selective DNA hybridization. Figure 2A illustrates nanowires that are 200 nm in diameter and 3 microns long that have been selectively immobilized on Au films using DNA chemistry. In figure 2A nanowires that were derivatized with DNA complementary to the oligonucleotides immobilized on the Au film. Figure 2B contains nanowires that were modified with DNA that was noncomplementary to the oligonucleotides the Au film. Typical surface coverages for these systems are on the order of 1.5×10^6 particles/cm^2 for the complementary experiment and 5×10^5particles/cm^2 for the noncomplementary experiment. This striking difference in surface coverage indicates that the DNA is preferentially attaching the nanowires to the complementary surface. Even though the complementary surfaces have much higher coverages than the noncomplementary surface, there is still a noticeable coverage of nanowires on the noncomplementary surface. A number of experimental parameters are being investigated to alleviate this trend including, varying the temperature of the reaction, adjusting the components of the buffer used in the reaction, reducing the dimensions of the nanowires, and altering the length and sequence of the DNA used.

Since the ultimate goal of this work is to assemble nanowires into functional devices, the nanowires need to be assembled on a patterned surface that can orient them as they adhere to it. Such an experiment is illustrated in Figure 2C. In this particular case, a Si wafer with Au pads lithographically defined on the surface was substituted for the Au film. The Si sections of the surface were modified with carboxylate groups as described above to reduce the number of nanowires attached to the Si. In this experiment, the Au nanowires (200 nm x 3 μm) can clearly be seen selectively assembling on the Au pads, but again, nonspecific adsorption of nanowires is a problem.

All the experiments discussed thus far consisted of solid Au nanowires. However, nanowires containing stripes of different materials are desirable because the stripes can be derivatized orthogonally allowing more complex assembly schemes. Nanowires derivatized in such a way are illustrated in Figure 3. These particular nanowires are 200 nm in diameter and 3 microns long, and they consist of stripes of Au, Pt, and Au. They were derivatized with butane isonitrile, followed by mercaptoethylamine, followed by rhodamine B isothiocyanate as described above. The left image is a simple bright field optical microscope image to show the psoitions of the nanowires. The right image is a fluorescence image. The nanowires are clearly fluorescing on the Au tips and not in the central portions of the nanowires. This trend results from the orthogonal derivatization that isolates the rhodamine selectively on the Au stripes.

A similar derivatization scheme was then used to assemble in solution. To create assemblies of nanowires, particles were grown that were composed of stripes of Pt, Au, and Pt.

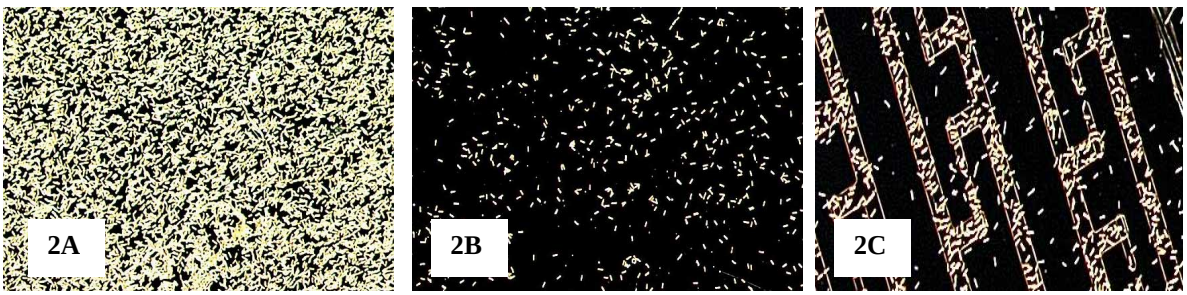


Figure 2: *DNA directed assembly of nanowires that are 200 nm in diameter and 3 mm long on Au films modified with complementary oligonucleotides (A), noncomplementary oligonucleotides (B), and on lithographically defined Au pads on a Si wafer(C).*

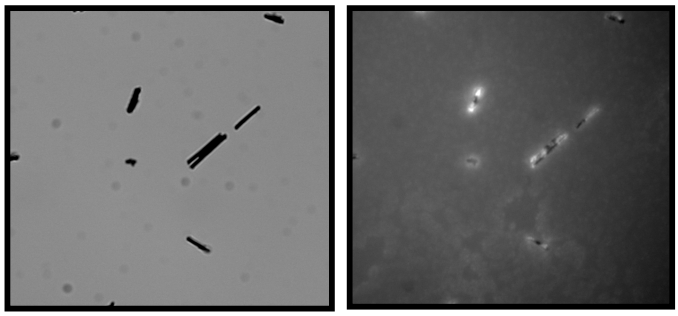


Figure 3*: Au, Pt, Au striped nanorods imaged using optical microscopy (left) and fluorescence microscopy (right).*

The Pt stripes were derivatized with a sulfonated isonitrile while the Au stripes were derivatized with DNA. The nanowires then self assemble into cross structures (Figure 4A) due to the hybridization of DNA and due to the coulombic repulsion of the sulfonate groups. Currently crosses can be fabricated in a 50 percent yield compared to 20 percent in controls. We are currently trying to optimize this process to get a higher yield of crosses. Cross structures are of interest due to their potential applications in the fabrication of memory devices and logic gates.

A second interesting structure to attempt to assemble is a triangle. To fabricate these structures, nanowires that are 70 nm in diameter and containing stripes of Pt, Au, Pt, and Au were fabricated and derivatized as described above. Two batches of such nanowires were assembled into crosses. These crosses differ from the previous crosses because they have Au tips that are modified with DNA. A third DNA-derivatized nanowire can then be introduced into the system. It can hybridize to these two sticky Au ends to complete the triangle. Figure 4B is a SEM micrograph of such a structure. Currently the yield of such structures is very low (around 5%), but we are attempting to improve it by varying the temperature at which the assembly is performed, adjusting the buffer composition, altering the length and sequence of the oligonucleotides, and reducing the dimensions of the nanowires.

Conclusions

In conclusion, nanowires have been fabricated using a template synthesis technique. These nanowires can be monometallic, or they may contain stripes of different materials. Nanowires can be freed from their template and modified with DNA oligonucleotides. Once modified, they can be assembled on Au films or on Au pads that have been lithographically defined on Si wafers. The nanowires can also be assembled into simple structures in solution, including crosses and triangles. These simple structures may potentially form individual devices, or they may be assembled into more complicated devices. In the future we hope to optimize this assembly methodology and assemble functional devices.

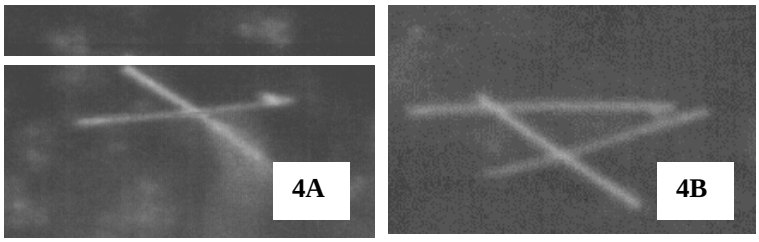


Figure 4*: SEM micrograph of two Pt, Au, Pt nanowires that are 70 nm in diameter and 3 microns long assembled into a cross structure via selective DNA chemistry (A). SEM micrograph three nanowires assembled into a triangular structure using similar chemistry*

References

1. T. Ito and S. Okazaki, *Nature,* **406**, 1027 (2000).
2. J. J. Storhoff, R. C. Mucic and C. A. Mirkin, *J. Clust. Sci.,* **8**, 179 (1997).
3. N. C. Seeman, *Acc. Chem. Res.,* **30**, 357 (1997).
4. C. A. Mirkin, R. L. Letsinger, R. C. Mucic and J. J. Storhoff, *Nature,* **382**, 607 (1996).
5. A. P. Alivisatos, K. P. Johnsson, X. Peng, T. E. Wilson, C. J. Loweth, M. P. Bruchez and P. G. Schultz, *Nature,* **382**, 609 (1996).
6. M. B. Eisen and P. O. Brown, *Methods. Enzym.,* **303**, 179 (1999).
7. D. AlMawlawi, C. Z. Liu and M. Moskovits, *J. Mater. Res.*, **9**, 1014 (1994).
8. C. R. Martin, *J. Mater. Res.,* **266**, 1961 (1994).
9. B. R. Martin, D. L. Dermoddy, B. D. Reiss, M. Fang, L. A. Lyon, M. J. Natan and T. E. Mallouk, *Adv. Mater.*, **11**, 1021 (1999).
10. J. K. N. Mbindyo, B. D. Reiss, B. R. Martin, D. J. Dermoddy, M. J. Natan and T. E. Mallouk, *Adv. Mater.*, **in press**, (2000).
11. T. M. Herne and M. J. Tarlov, *J. Am. Chem. Soc.,* **119**, 8916 (1997).
12. J. J. Hickman, P. E. Laibinis, D. I. Auerbach, C. Zou, T. J. Gardner, G. M. Whitesides and M. S. Wrighton, *Langmuir,* **8**, 357 (1992).