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13. ABSTRACT (Maximum 200 Words)
Nature utilizes molecular recognition between complex macromolecules to form sophisticated meso- and macroscopic architectures with tremendous control over the placement and orientation of nanoscopic building blocks within the extended architectures. The structures of proteins, duplex DNA, and phospholipid bilayers are maintained by cumulative weak and reversible interactions (hydrogen bonding and van der Waals interactions), and pairing principles for the constituent molecules. The biosyntheses are remarkably efficient, self-manufacturing, and high yielding; therefore, they are excellent models for how the synthetic chemist should consider designing complex nanostructured materials. The specific objective of the proposed research was to demonstrate orthogonal assembly of charged particles by electrochemically controlling particle deposition. In addition, the use of applied potentials to selectively miniaturize microscopic features to nanoscopic dimensions was explored.

14. SUBJECT TERMS
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"MURI: Electrochemically-Controlled Orthogonal Assembly of Monolayers on a Gold Surface via DPN,"

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Grant Number: F49620-00-1-0345

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1. OBJECTIVES

2. STATUS OF WORK

We have shown that we can initiate and direct the assembly of polyanionic oligonucleotide-modified particles in an orthogonal manner using predesigned templates comprised of redox-active components on gold substrates. We generate the multicomponent structures via Dip-Pen Nanolithography (DPN) by utilizing alkanethiols with electroactive end groups as inks, e. g. Fe(C=O)(CH₂)₁₀SH and Fe(CH₂)₁₁SH. The design and choice of inks allows us to successively oxidize the terminal ferrocenyl groups of the different inks in the pattern in order to bind negatively charged oligonucleotide-modified nanoparticles in an orthogonal manner. This novel approach not only provides a method for addressing individual nanostructures fabricated via DPN, but also offers a route to assembling complex, multicomponent structures on these redox-active templates.

We have also realized a simple and convenient strategy for reducing the dimensions of organic micro- and nanostructures on metal surfaces. By varying electrochemical desorption conditions, features consisting of linear alkanethiols or selenols patterned by Dip-Pen Nanolithography (DPN) or Micro-Contact Printing (μ-CP) can be gradually desorbed in a controlled fashion. The process is called electrochemical whittling because the adsorbate desorption is initiated at the exterior of the feature and moves inward as a function of time. The whittling process and adsorbate desorption were studied as a function of substrate morphology, adsorbate head and tail groups, and electrolyte solvent and salt. Importantly, one can independently address different nanostructures made of different adsorbates and effect their miniaturization based upon a judicious selection of adsorbate, applied potential, and supporting electrolyte. Some of the physical and chemical origins of these observations have been elucidated.

By taking advantage of the electrochemical whittling process, we have recently developed a methodology for fabricating metal nanostructures from DPN generated templates. This strategy takes advantage of the different desorption rates between alkylselenols and alkylthiols. Using DPN, we can generate a pattern consisting of alkylselenols and then passivate of the bare gold with alkylthiol. The alkylselenol can be selectively desorbed by applying the appropriate potential, thus leaving a bare gold template. This template can be used to electrochemically deposit metal salts to generate the desired metal nanostructures.

ACCOMPLISHMENTS/NEW FINDINGS

Redox-controlled orthogonal assembly of charged nanostructures. We have shown how one can use predesigned, redox-active ferrocenylalkylthiol “inks” (Fc(CH₂)₁₀SH (1) and Fe(C=O)(CH₁₁)SH (2)), patterned on a gold substrate, and appropriately applied changes in electrode potential that result in ink oxidation, to trigger and guide the assembly of polyanionic oligonucleotide-modified particles in an orthogonal manner (Figure 1).
The ferrocenyl based inks were designed to exhibit nonoverlapping redox processes by virtue of the alkythiol and acetylihol functional groups directly attached to the cyclopentadienyl rings in 1 and 2, respectively. Indeed, cyclic voltammetry of gold electrodes modified with monolayers of 1 and 2, respectively, exhibit a $\Delta E_{1/2}$ of 255 mV (Figure 2A). The rationale behind choosing these two molecules was that one could selectively address nanostructures made of 1 and then 2 by sweeping the potential of an electrode modified with them in linear fashion. The concomitant oxidation of the nanostructures would result in the selective deposition of oppositely charged species onto the nanostructure of interest (Figure 1). In the case of the system described, oligonucleotide modified nanoparticles were chosen as nanostructure building blocks for two reasons. First, they exhibit low nonspecific adsorption on uncharged monolayer modified surfaces, and second, they provide a proof-of-concept system for demonstrating the suitability of this strategy for arranging complex, chemically tailorablere, and functional nanostructured building blocks on a templated surface.

In a typical experiment, the redox-active inks are patterned by DPN on a gold surface to generate charge-neutral nanostructures (Figures 2B, 2C). The structures are generated in serial fashion from tips coated with the appropriate ink. Prior to imaging the nanostructures, a tip coated with 1-octadecanethiol (ODT) was raster scanned across the patterned area to passivate the exposed gold surface. Upon completion of all DPN writing steps each sample was rinsed with ethanol, further passivated by soaking the substrate in a 1 mM ethanol solution of ODT for 1 min, and rinsed one more time with ethanol.

Both 1 and 2 result in patterns, that exhibit higher lateral force (light) relative to the passivated gold substrates (dark) (Figures 2B, 2C). Thus far, we have generated features with linewidths as small as 55 nm and as large as 1 $\mu$m. The size of the pattern can be adjusted by changing the scan speed (line-based features) or tip-substrate contact time (dot-based arrays) during the writing procedure.

The orthogonal assembly of oligonucleotide functionalized nanoparticles was effected by using the patterned substrate as a working electrode in an electrochemical cell. To attach particles to substrates containing patterns drawn with only one ferrocenyl-based ink, the oxidation was done at room temperature using fixed pulse potentials at either 350 mV (for 1) or 620 mV (for 2) vs Ag/AgCl for 30 min in the presence of Au nanoparticle solutions in 0.15 M NaCl PBS buffer (10 mM phosphate buffer, pH 7). Gold nanoparticles, $\sim$5 nm and 13 nm in diameter, were functionalized with alkylthiol-terminated DNA strands based on published protocols. In the case of samples containing patterns drawn with both ferrocenyl alkanethiolates, linear sweep voltammetry was used to address each pattern where the potential of the working
electrode was ramped from 0 to 350 mV, held for 30 min in the presence of a solution of 5 nm Au particles, and then taken to 620 mV and held for 30 min in the presence of 13 nm particles. The cell and electrode were washed with 0.15 M NaCl PBS buffer between each step and at the end of the experiment. In addition, the substrates were rinsed with 0.05% Tween 20 solution and nanopure water and cleaned with Scotch tape, as described by Sagiv et. al., prior to imaging. Subsequent imaging of the multicomponent two-dimensional arrays of particles was performed using a Nanoscope IIIa and microscope from Digital Instruments in tapping mode under ambient conditions with silicon cantilevers (spring constant = ~40 N/m).

Single ink structures, comprised of either 1 or 2 can be used to guide the assembly of 13 nm particles (Figures 3A, 3B). Note that the electrode washing steps and scotch tape are very effective at removing particles that stick to the passivated areas of the gold electrode but not the oxidized and positively charged nanostructures. A substrate with two patterns, one comprised of 1 (the square) and the other comprised of 2 (the dots) can be used to sequentially assemble 13 nm particles on the preformed templates via the linear sweep voltammetry protocol (Figure 3C). To verify that we have indeed assembled a high density array of Au nanoparticles onto the desired patterns with a low degree of non-specific binding, we obtained a high resolution, field-emission scanning electron microscopy (FE-SEM) image of the patterned substrate after the electrostatic assembly process (Figure 3D). The data clearly show that the ~13 nm particles are closely packed and localized predominantly on the template features. Finally, we were able to attach different sized oligonucleotide modified nanoparticles onto two different nanopatterns (a line array of 1 and a dot array of 2) in an orthogonal manner using the linear sweep voltammetry protocol and 5 and 13 nm particles, respectively (Figure 3E). The height profile of the assembled structures confirms that 5 nm particles are present on the lines of 1 and the 13 nm particles are on the dot arrays drawn with 2.

Figure 3. Three-dimensional nano-structures assembled onto electro-chemically active patterns. (A) Tapping mode image of 13 nm particles assembled onto features drawn with 1. (B) Tapping mode image of 13 nm particles assembled onto features drawn with 2. (C) Tapping mode image of 13 nm particles assembled onto features drawn with 1 and 2. (D) High-resolution field-emission scanning microscopy image of a portion of a square pattern after particle assembly. (E) Tapping mode image of 5 nm particles assembled onto line features drawn with 1 and 13 nm particles assembled onto dot patterns made from 2.
Electrochemical whittling of organic nanostructures. We have recently realized a massively parallel strategy for reducing the size of DPN generated alkanethiol nanostructures on gold surfaces. This approach works by the electrochemical desorption of organic nanostructures (Figure 4). For example, by using a conventional three-electrode cell, we were able to reduce the size of MHA patterns from 90 nm to 55 nm by applying a potential of $-750$ mV for 1 minute, effectively reducing the diameter of these structures at rate of $\sim$1 molecule/sec (Figure 5). The periphery of nanostructures, which contains many defect sites are gradually whittled away at a rate dependant on the time and potential applied. Not only does this strategy provide a simple and convenient method to enhance the resolution of DPN, but also holds potential in improving the resolution of all soft lithography techniques. Also, by applying this procedure to structures patterned on atomically flat surfaces we should potentially be able to break the current 15 nm resolution limit of DPN.

Two Component Whittling. Due to the different reduction potentials of MHA and ODT on gold surfaces, it is possible to selectively desorb nanostructures of one ink on the surface while leaving the second ink. As shown in Figure 6, it is possible to completely desorb MHA (light in LFM) and leave the ODT nanostructures intact (dark in LFM) by applying a voltage of $-750$ mV for 6 minutes.

Parallel Size Reduction of Organic Microstructures. We have extended the electrochemical whittling method to organic structures fabricated by high-throughput parallel printing techniques. Indeed, this is where the utility of the technique could be realized for miniaturizing micro or relatively large nano-scale architectures in a massively parallel fashion. By printing 16-mercaptopentadecanoic acid (MHA) and 1-octadecanethiol (ODT), then applying a reducing
potential in 0.5 M KOH, we show that it is possible to electrochemically whittle these structures (Figure 7). We have figured out the conditions to optimize this process and have begun to take advantage of its utility.

![Image](example-image)

**Figure 7.** LFM images of (μCP-generated patterns before and after electrochemical whittling. (A) Original MHA dots array. (B) The MHA dot array in “A” after applying a potential of -920 mV vs Ag/AgCl for 30 sec. C) Original ODT dot array. D) The ODT dot array in “C” after applying a potential of -1100 mV vs Ag/AgCl for 5 min. The bar is 5 mm.

**Fabrication of Metal Nanostructures from DPN Generated Templates.** We have developed a novel method for fabricating solid-state metal nanostructures from DPN generated templates (Figure 8). This strategy relies on the careful choice of patterned and passivating molecules. For example, arrays of nanostructures comprised of dioctadecane diselenide (ODSe) are patterned on a gold substrate, and the bare gold surface is subsequently passivated using ODT. By applying a selectively desorbing potential the ODSe patterns are stripped, and a nanoscale bare gold template is generated. Subsequently, various metal salts can be electrochemically reduced and deposited on the exposed gold surface. We have demonstrated this approach by generating arrays of Ag nanostructures on a gold substrate (Figure 9). Interestingly, the resolution of nanostructures fabricated by using this approach is only limited by the size of DPN generated features.

![Image](example-image)

**Figure 8.** Alkylselenol patterns are selectively stripped, and the freshly exposed gold areas template the electrochemical growth of various metal salts.

![Image](example-image)

**Figure 9.** Darkfield optical micrograph of Ag nanostructures electrochemically grown on a thin film of Au. (Inset) TM-AFM image of the same nanostructures.
3. PERSONNEL SUPPORTED

Postdocs
None

Percentage of Salary Provided by Grant
0%

Graduate Students:
Martin Masar

Percentage of Salary Provided by Grant
100% (2000-2003)

Undergraduate Students:
None

Percentage of Salary Provided by Grant
0%

Unfunded Personnel:
Khalid Salaita (grad)
Yi Zhang (Post Doc)

Percentage of Salary Provided by Grant
100% (2003)

4. PUBLICATIONS

Peer-reviewed publications submitted and/or accepted during the 12-month period.

A. Journal Articles


6. INTERACTIONS

A. Presentations/Presentations at Meetings, Conferences, Seminars


7. MURI Review, Duck Key, FL: “Chemically Templated Colloidal Assembly via DPN” (2001)
15. 75th ACS Colloid and Surface Science Symposium, Pittsburgh, PA: “Dip-Pen Nanolithography: A Tool for Generating Organic and Biological Surface Architectures with 5 nm Resolution” (2001)
17. MURI review, Duck Key, FL: “Dip-Pen Nanolithography for Processing and Functionalizing Inorganic Semiconductor Substrates” (2001)
20. Gordon Research Conference, Polymers (East), New Hampshire: "2 and 3 D Nanoparticle Arrays" (2001)
23. DARPA workshop, Charleston, SC: “Massively Parallel Dip-Pen Nanolithography” (2001)
44. DARPA Advanced Lithography Program Review, Santa Fe, NM: “Parallel, Ultrafast Sub-100 Nanometer Dip-Pen Nanolithography” (2003)

B. Consultative/Advisory Functions

1. Mirkin consults for and serves on the Scientific Advisory Board and the Board of Directors of both Nanosphere and NanoInk, Inc.

C. Transitions

1. NanoInk, Inc. has licensed the “electrochemical whittling” invention.

9. NEW DISCOVERIES, INVENTIONS, OR PATENT DISCLOSURES

10. HONORS/AWARDS

1. 2004 Nobel Laureate Signature Award for Graduate Education in Chemistry (2003)
2. Dickinson College Metzger-Conway Fellowship Award (2003)
3. 2003 Raymond and Beverly Sackler Prize in the Physical Sciences (NU, 2003)
5. 2002 Feynman Prize in Nanotechnology (NU, 2002)
6. 2002 Ceramicographic Competition, American Ceramic Society 1st Place Entry (NU, 2002)
7. Esquire Magazine’s “Best & Brightest in the Nation” (NU, 2002)
8. 2001 Leo Hendrick Baekeland Award (NU, 2001)
9. Crain’s Chicago Business “40 under 40 Award” (NU, 2001)
10. Discover 2000 Award for Technological Innovation (NU, 2000)
11. Elected Fellow of the American Association for the Advancement of Science (NU, 2000)
12. I-Street Magazine’s Top 5 List for Leading Academics in Technology (NU, 2000)