Redox-Controlled Orthogonal Assembly of Charged Nanostructures

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Two of the greatest challenges facing researchers working in the areas of nanoscience and nanotechnology are the following: the development of straightforward methods for organizing structures with sub-100 nm dimensions on surfaces into functional architectures and then interfacing such structures with macroscopically addressable components in predefined ways. Although "self-assembly" is often cited as a potential route to addressing these issues, nonliving self-assembled systems lack the hardwired interconnects between their nanoscale components and the macroscopic world. Therefore, it is likely that directed-assembly methods, where a predefined pattern guides a desired nanostructure assembly process, rather than self-assembly, will be the first route to device organization on this length scale.

One of the emerging strategies for directed-assembly is to use lithographically generated surface templates to guide the assembly of building blocks that recognize such templates through predesigned chemical or physical interactions.[1,2] Dip-Pen Nanolithography (DPN),[3] electron-beam lithography,[4] and a variety of resist-based scanning probe lithographies[5−7] have emerged as tools that provide the necessary resolution to create templates that can be used in a directed-assembly processes that involve nanomolar-scale structures. The direct-write nature and soft-matter compatibility of DPN make it particularly attractive for fabricating such templates, especially when they are made from organic molecules. Thus far, it has been demonstrated that DPN-generated templates, comprised of either charged molecules or oligonucleotides, can be used to guide the assembly of particles with complementary charge[8] or oligonucleotide recognition elements,[9] respectively. Herein, we show how one can use redox-active ferrocenylalkylthiol "inks" ($Fc(CH_2)_{11}SH$ (**1**) and $Fc(C{=}O)(CH_{11})SH$ (**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 (Scheme 1).

The ferrocenyl-based inks were designed to exhibit nonoverlapping redox processes ($\Delta E_{1/2}$ of 255 mV) by virtue of the alkylthiol and acylthiol functional groups directly attached to the cyclopentadienyl rings in **1** and **2**, respectively[10−12] (Figure 1A).

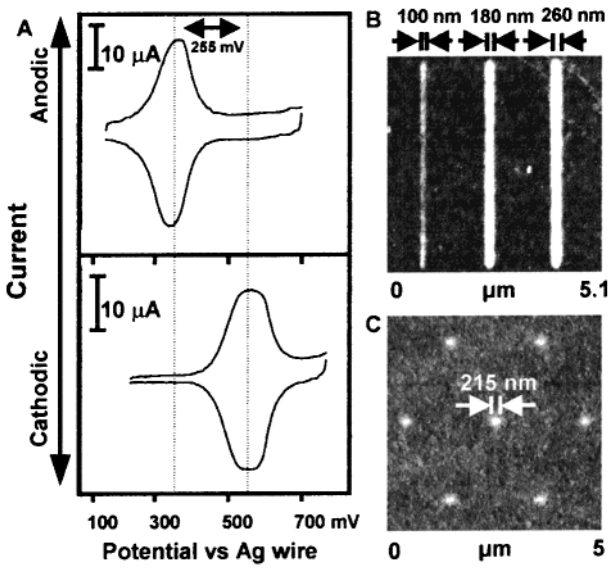
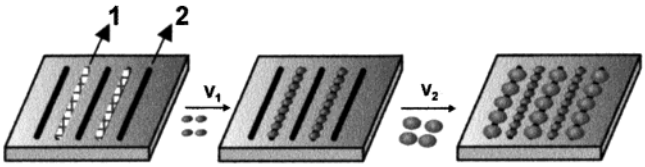


Figure 1. (A) Cyclic votammograms in 0.2 M $HClO_4$ of monolayers of **1** (top) and **2** (bottom) vs Ag/AgCl. Scan rate = 200 mV/s. (B) LFM image of DPN-generated lines of **1**. The writing speed for each line from left to right was 0.8, 0.6, and 0.4 μm/s, respectively. (C) LFM image of an array of dots drawn with a **2**-coated tip that was held at specific locations for 1 s. All AFM experiments were carried out at room temperature and 38% relative humidity, and the LFM images were collected with an ODT coated tip at a scan rate of 2 Hz.

Scheme 1



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 (Scheme 1). In the case of the system described herein, 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 chemically tailorable and functional[13] 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 (Figure 1B,C). The structures are generated in serial fashion from tips coated with the appropriate ink (see Supporting Information). 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.[14] 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. Longer soaking times resulted in significant exchange of the ferrocenyl alkanethiolates with ODT, as determined by lateral force microscopy (LFM).[12]

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Both **1** and **2** result in patterns that exhibit higher lateral force (light) relative to the unmodified gold substrates (dark) (Figure 1B,C). Thus far, we have generated features with line widths as small as 55 nm and as large as 1 μm. 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.[10] 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, ∼5 and 13 nm in diameter,[15,16] were functionalized with alkylthiol-terminated DNA strands based on published protocols.[17] Particle and electrolyte concentrations reported herein were chosen in trial-and-error fashion to minimize nonspecific binding of nanoparticles onto unpatterned areas. 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.,[6,18] prior to imaging. Imaging of the multicomponent two-dimensional arrays of particles was performed with a Nanoscope IIIa microscope (Digital Instruments) in tapping mode under ambient conditions (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 (Figure 2A,B). 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 electrochemical protocol (Figure 2C). To verify that we have indeed assembled a high-density array of Au nanoparticles onto the desired patterns with a low degree of nonspecific binding, we obtained a high-resolution, field-emission scanning electron microscopy (FE-SEM) image of the patterned substrate after the electrostatic assembly process (Figure 2D). 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 2E).

This paper demonstrates how one can use appropriately designed redox-active inks and linear sweep voltammetry to control the assembly of charged nanostructures with sub-100 nm dimensions. The resolution limit of this process, once refined, is likely the limit of optimized DPN, which currently stands at ∼10 nm. The limitation is that one must use inks with well-separated $E_{1/2}$ values, and therefore, one is limited with respect to the number of redox-active inks that can be employed in a single experiment. The strategy, combined with the work of others,[1,2,8,9] points toward a way of generating multicomponent colloidal crystals that could be used for studying catalysis and preparing complex devices ranging from biosensors to photonic band gap structures.

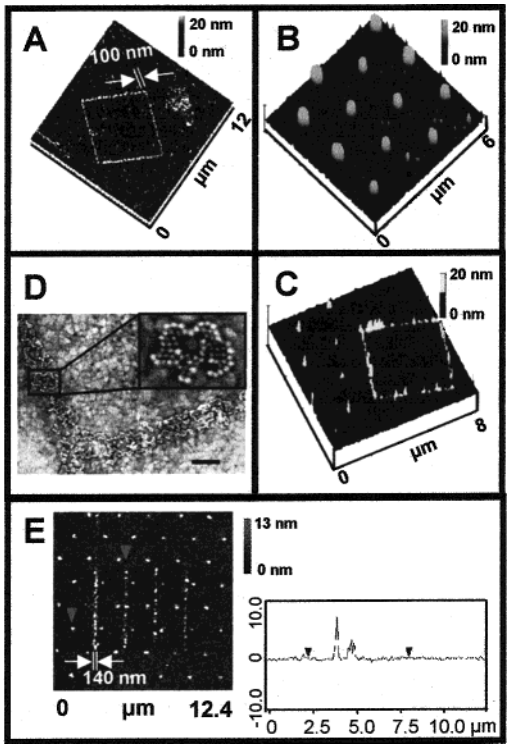

Figure 2. Three-dimensional nanostructures assembled onto electrochemically active patterns. (A) A tapping mode image of 13 nm particles assembled onto features drawn with **1**. To generate this pattern the coated tip was moved across the surface at a rate of 0.8 μm/s. (B) A tapping mode image of 13 nm particles assembled onto features drawn with **2**. The 2-coated tip was held at specific locations for 3 s to make each dot in the array. (C) A tapping mode image of 13 nm particles assembled onto features drawn with **1** and **2**. To generate the line patterns the **1**-coated tip was moved across the surface at a rate of 0.8 μm/s; each dot in the array was generated with a tip coated with **2** held in contact (0.5 nN) with surface for 1 s. (D) High-resolution field-emission scanning electron microscopy (FE-SEM) image of a portion of a square pattern after particle assembly (scale bar: 200 nm). (E) A 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**. To generate the line patterns, the **1**-coated tip was moved across the surface at a rate of 1 μm/s; the dots within the array were made with a tip coated with **2** held in contact with the surface for 1 s.

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Supporting Information Available: Experimental details regarding patterning of each ink, particle preparation, and electrochemistry conditions (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(15) Au particles (∼13 nm diameter) dispersed in 0.15 M PBS buffer solutions were used in the electrostatic assembly at a concentration of 3 nM. The DNA sequence used to modify them was 3′SH-$(CH_2)_3$-ATG CTC AAC TCT 5′. The 13 nm nanoparticles were synthesized as described by Storhoff et al.

(16) Au particles (∼5 nm diameter) dispersed in 0.15 M PBS buffer solutions were used in the electrostatic assembly at a concentration of 7 nM. The DNA sequence used to modify them was 3′SH-$(CH_2)_3$-ATG CTC AAC TCT 5′. The Au nanoparticles were purchased from Ted Pella.

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