Reference: AN002

Chemically Patterned DPN® Templates for Bottom-up Nanofabrication: Molecular Glue

Introduction

A significant challenge in current nanoscience and nanotechnology is the organization of nanostructures into functional materials, especially with precise control over relative positions of the individual building blocks. One way to achieve this level of control is to introduce directionality using chemically patterned surface templates. Appropriate chemistry can be used to program assembly of nanoscopic components into 2-D and 3-D structures or addressable devices. The building block interactions that drive templated assembly can be as simple as electrostatic attractions, and as selective as oligonucleotide hybridization. Regardless of the nature of the chemistry, such surface-templated orthogonal assembly methods can provide a powerful approach to investigating problems in fields ranging from colloidal crystallization to magnetic data storage, and from photonics to nanoscale electronic devices.

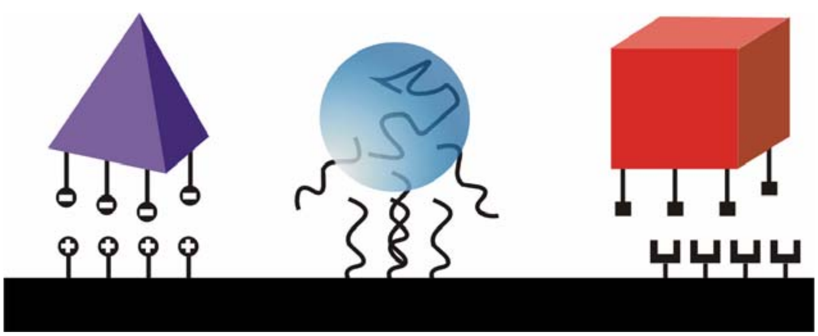

Figure 1. The template assembly strategy. Attachment strategies: (left to right)
1) charge-based recognition; 2) macromolecular encoding (i.e., DNA); 3) specific binding of ligands

The synthesis of a wide variety of nanoparticle materials with unique and potentially advantageous properties is now well known and the surface chemistry of these fundamental building blocks of nanofabrication can be tailored to enable a number of different possible assembly strategies, (Fig. 1)[1] One of the goals of such work is to study and take advantage of the novel collective properties of nanoscale building blocks. A fundamental challenge for implementing these assembly strategies is the ability to print a variety of "molecular glue" templates onto many different surfaces using small molecules and salts to delicate biomacromolecules.

Dip Pen Nanolithography® (DPN®), a direct write lithography process provides this capability. DPN combines molecular deposition of virtually any material on any substrate at nanometer scale resolutions with the capability to precisely align multiple patterns of chemically distinct inks at the nanoscale.[2] In this application note we describe the use of the DPN process for generating chemical and biomolecule templates for directing the assembly of complex structures based on choice of template-particle interaction.

Combinatorial Arrays

The benefits of using the DPN process for generating templates for bottom up nanofabrication are a result of the direct-write nature of the method. This technique literally writes molecules onto a surface without the need for harsh conditions such as ultra-high vacuum, temperature, or the use of resists, making the DPN process compatible with a great number of different ink and surface chemistries. This feature enables relatively high throughput and flexibility to rapidly design and generate a large number of test templates on a single substrate which can be screened under identical conditions, e.g. (Fig. 2). Thus, for experiments such as particle assembly, DPN can be used to quickly optimize templates (e.g. dot size, shape, spacing, and chemistry) for immobilizing single particles in an ordered array.

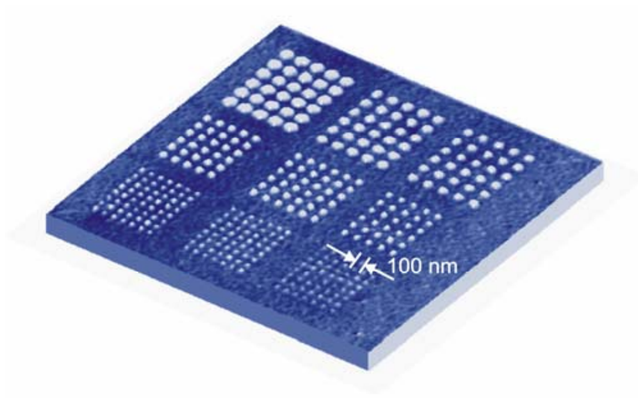

Figure 2. Combinatorial pattern (16-mercaptohexadecanoic acid on Au) used for screening template properties for particle assembly process.

Selective Interactions for Template Assembly

Single particle organization using this template approach has been demonstrated by exploiting the electrostatic attraction that exists in aqueous solutions between 190 nm diameter amino-modified polystyrene particles and surface template patterns of 16-mercaptohexadecanoic acid (MHA) on gold.[3] In these experiments, we use automated software (DPNWrite™) to control the movement of the tip, depositing dot patterns of MHA glue onto polycrystalline gold in the form of a number of different lattices, each with a different dot size and spacing, ranging from 50 nm to 700 nm. After patterning, the surface is immersed in an ethanolic solution of octadecanethiol (ODT) to passivate the gold surface. Next, a droplet of water containing the polystyrene particles (~1% wt/vol) is placed on the patterned substrate for 1 h, and then rinsed off with distilled water. An AFM image of the dried pattern (Veeco AutoProbe™ M5, intermittent contact) reveals that single particles bound selectively to the 300 nm template dots, (Fig. 3A). As expected, multiple particles bound to larger template spots (not shown).

A similar process may be used to direct the assembly of citrate-stabilized gold nanoparticles. In these experiments, hydrophobic patterns (ODT) generated on gold using the DPN process provides a particle resistant layer. The surrounding area is covered with a monolayer of cysteamine hydrochloride which serves as a binding site for particles. In this case the assembly process is driven by a combination of electrostatic interactions between the particles and patterned surface as well as chemisorption of the particles to the alkylamine moieties, (Fig. 3B.) The electrostatic assembly strategy demonstrated in these experiments is limited to a maximum of 2 different components. However, Ivanisevic *et al* recently demonstrated that the electrostatically induced assembly can be 'turned-on' using electrochemistry of redox active (ferrocenylalkanethiols) as surface templates.[4] This multistep process enables assembly of 2 different sizes of (negatively charged) DNA modified nanoparticles on oxidized (positively charged) surface patterns.

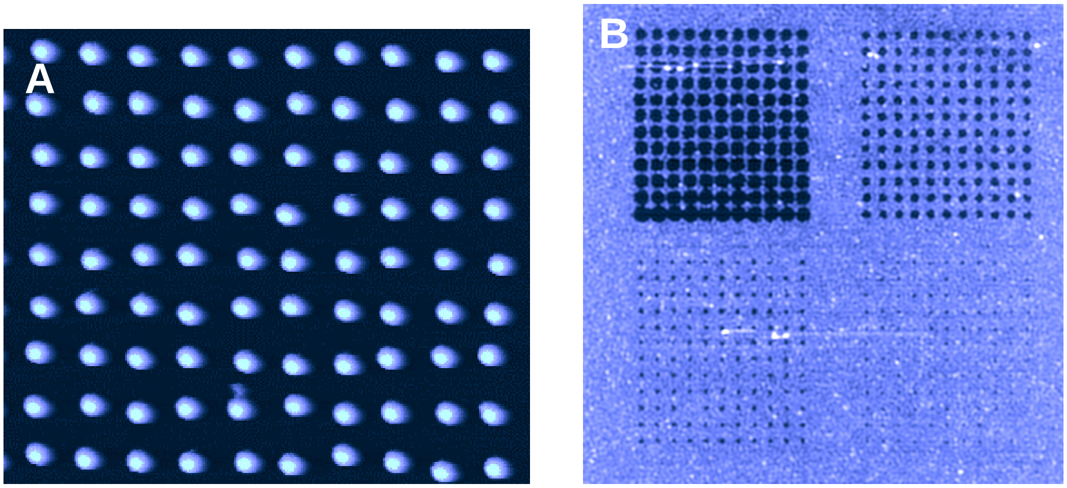

Figure 3. (A) Positive electrostatic assembly of amino-modified polystyrene particles (+) onto carboxylic acid alkanethiol (-) template. (B) Opposite electrostatic assembly of citrate-stabilized gold nanoparticles onto carboxylic acid alkanethiol (-) surrounding a hydrophobic, uncharged dot array (ODT).

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References:

1) Storhoff, JJ; Mucic, RC; Mirkin CA: J. Cluster Sci. 1997, 8, 179-216.
2) Piner, RD; Zhu, J; Xu, F; Hong, S; Mirkin, CA: Science 1999, 283, 661-663.
3) Demers, LM; Mirkin, CA: Angew. Chem. Int. Ed. Engl. 2001, 40, 3069-3071.
4) Ivanisevic, A; Im, JH; Lee, KB; Park, SJ; Demers, LM; Watson, KJ; Mirkin, CA: J. Am. Chem. Soc. 2001, 123, 12424-12435.