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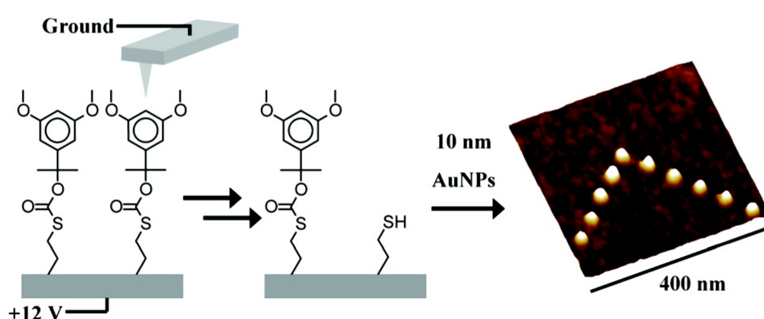

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Selective Surface Activation of a Functional Monolayer for the Fabrication of Nanometer Scale Thiol Patterns and Directed Self-Assembly of Gold Nanoparticles

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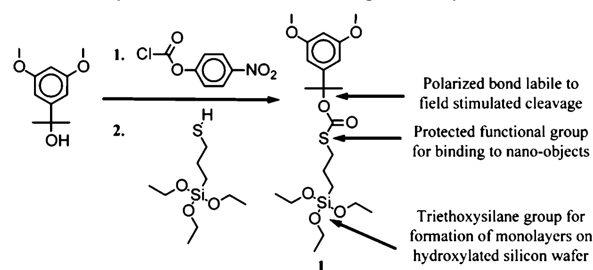
The directed self-assembly of gold nanoparticles (AuNPs) has been applied to prepare electrically conducting nanowires,[1] plasmonic waveguides for electro-optical devices,[2] or seeds for the growth of silicon nanorods.[3] Numerous approaches have been explored to access such structures.[4] For example, regularly spaced AuNP arrays have been made by self-assembly onto templates.[5] Arbitrary patterns of AuNPs have been made on the sub-100 nm scale using E-beam lithography[6] and dip-pen nanolithography,[7] while patterns as small as 30 nm have been obtained using other scanning probe techniques.[8]

This communication describes a straightforward method for the patternwise placement of AuNPs with nanometer resolution. The pattern is defined using an atomic force microscope (AFM) to apply a voltage bias between the tip and selected locations of a surface covered by a reactive monolayer. During this step, thiocarbonate moieties from the bound monolayer are selectively transformed into thiols. The thiol-patterned surface is then used to direct the subsequent self-assembly of 10 nm citrate-stabilized AuNPs. This patterning technique can be used to fabricate lines a single particle in width as well as to control the placement of individual gold nanoparticles.

Many methods for performing tip-induced surface chemistry have been described in the literature.[9] One method that is particularly relevant to this work relies on the application of a voltage bias between a surface and the tip of an AFM to locally oxidize the surface, producing nanometer relief features.[10] When ambient conditions are employed, this oxidation obscures observation of any more subtle effects that the applied voltage bias may have on an organic monolayer. However, in the absence of oxygen and water vapor, anodic oxidation of the underlying silicon no longer occurs, and it becomes possible to perform controlled chemistry on a monolayer.

Recent work in our laboratory has shown that under an inert atmosphere, the application of a voltage bias between the tip of an AFM and a silicon substrate causes local activation of a self-assembled monolayer (SAM).[11] We now outline the synthesis and characterization of a previously unreported organic monolayer containing a 3,5-dimethoxy-α,α-dimethylbenzyloxycarbonyl (DDZ)-protected thiol. The design and synthesis of this material is described in Scheme 1.

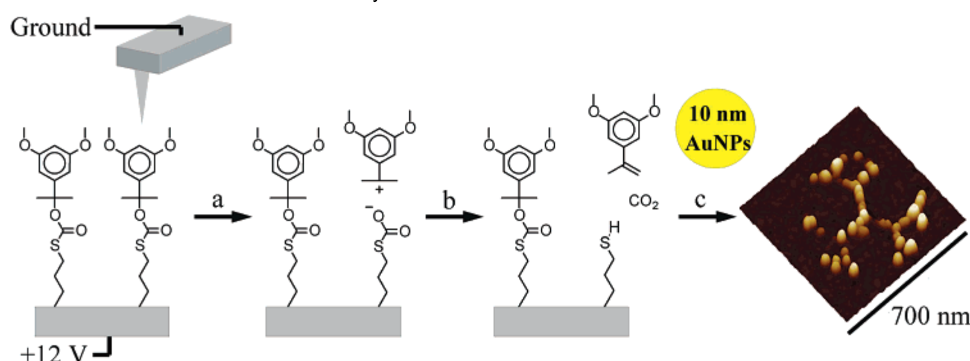
Scheme 1. Synthesis of Thiol-Producing Monolayer Precursor



The DDZ protecting group has previously been employed as a photocleavable group in organic synthesis[12] and lithography.[13] The accepted photochemical deprotection mechanism is homolytic bond cleavage followed by release of carbon dioxide and elimination of the tertiary carbocation to produce 3,5-dimethoxy-α-methylstyrene. The stability of the tertiary carbocation and the established ionic decomposition pathway were major factors in the choice of this protecting group. We hypothesized that the intense local electric field between the tip and the surface may induce decomposition via a pathway analogous to that of photochemical deprotection (Scheme 2). The triethoxysilane moiety was employed to form self-assembled monolayers on hydroxylated silicon surfaces.[14] The monolayers were formed by immersing a freshly cleaned and hydroxylated silicon wafer in a solution of **1** in dry toluene. All patterning was subsequently performed in an atmosphere of dry nitrogen.

It was found that if the nanoparticle solution was applied to the surface immediately after patterning, gold features were not observed. It is likely that many of the newly exposed thiols are

Scheme 2. Surface Activation and Directed Self-Assembly of AuNPs[a]



[a] (a) Electrically stimulated bond cleavage. (b) Elimination of carbocation and release of carbon dioxide to produce surface-bound thiol. (c) Directed self-assembly of gold nanoparticles into a dendrimer pattern.

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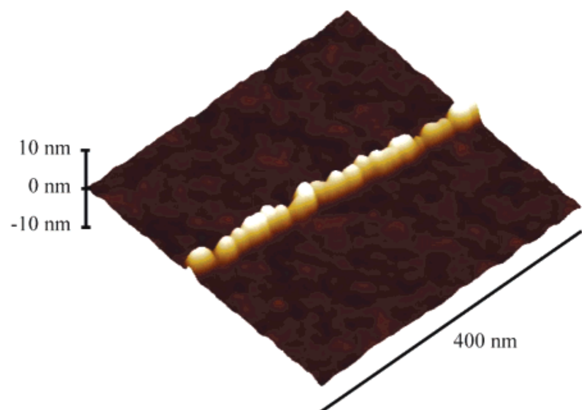

Figure 1. Line of AuNPs a single nanoparticle in width.

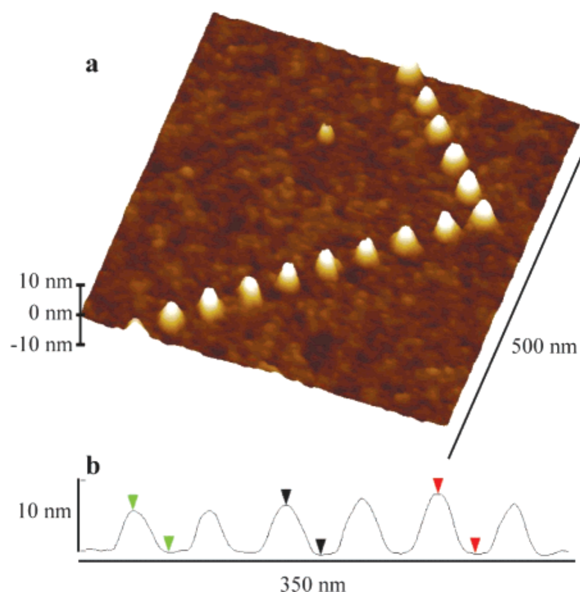

Figure 2. (a) AuNPs patterned with a 50 nm spacing between individual particles. (b) Cross-sectional analysis.

converted rapidly into disulfides either through exposure to atmospheric oxygen or during the patterning step itself. On the basis of this hypothesis, the surface was treated with an aqueous solution of a mild reducing agent, DL-dithiothreitol (DTT), to transform any disulfides back into thiols.[15] Applying this surface treatment prior to exposure to the AuNP solution for self-assembly of the gold pattern vastly improved the adhesion of the AuNPs to the patterned regions. While disulfides are known to bind to gold, the binding interaction is significantly weaker than that obtained with thiols.[16] The importance of the DTT treatment is demonstrated by the fact that surfaces showing no AuNP affinity immediately after AFM-based patterning become active after being treated with DTT.

An image of a line of close-packed gold nanoparticles is shown in Figure 1. It should be noted that this line has a width that corresponds to a single nanoparticle, demonstrating that this method is capable of producing lines of 10 nm or less depending also on the geometry of the tip. AuNP deposition follows the design defined by the field arising from the tip, and therefore, a great variety of patterns can be obtained. It is possible to control the placement of individual AuNPs on the surface by the programmed application of electrical pulses to the surface. For example, individual gold nanoparticles intentionally placed at 50 nm intervals are shown in Figure 2. The observed size variation in gold nanoparticles reflects the real (ca. 10%) variation in the commercial sample.

In conclusion, we have developed a novel method for the facile patternwise deposition of AuNPs onto a surface with nanometer scale precision. This method relies on a functional organic monolayer containing a thiocarbonate that is cleaved under electrical stimulation to produce a thiol. Applying a positive 12 V potential to the substrate while translating a grounded AFM tip across the surface results in cleavage of the thiocarbonate to the free thiol. After mild reduction with aqueous DTT, the activated areas of the surface were effectively used to direct the self-assembly of AuNPs. This method allows fabrication of lines of 10 nm AuNPs a single nanoparticle in width, as well as the placement of individual nanoparticles on the surface.

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Supporting Information Available: Experimental procedures and compound characterization data (PDF). This material is available free of charge via the Internet at http//pubs.acs.org.

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