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Self-Organized Materials: From Organic molecules to Genetically Engineered Gold-Binding Proteins

Hadi Zareie^{*†}, Mehmet Sarikaya[‡], Andrew M. McDonagh[†], Jeffery Barber[†], Michael Cortie[†] and Matthew Phillips[†]

[†]Institute for Nanoscale Technology, University of Technology Sydney, PO Box 123, Broadway NSW 2007, Australia. Telephone: (61) +2 9514 8330, Fax: (61) 2 95141703

[‡]Materials Science & Engineering, University of Washington, Seattle, WA 98195-2120 (USA)

Abstract: We present examples of ordered assemblies of organic and biological molecules on gold(111) surfaces. The first example shows how control over mono- or multilayer assemblies of 1,4-phenylenedimethanethiol can be achieved and monitored. The second example shows how monolayers on gold can be prepared using amine groups to anchor aromatic molecules to the surface. A third example shows how ordered assemblies of genetically-engineered inorganic-binding polypeptides can be formed on gold surfaces using a 3-repeat, 14 amino acid gold-binding protein (GBP1).

Keywords: 1,4-phenylenedimethanethiol, GBP1, SPM, SPR

I. INTRODUCTION

Structural and functional patterning of organic and biological molecules on solid surfaces is important in the development of molecular electronics, biosensors and bioreactors [1-2]. Control and understanding of the factors affecting structure formation, and the ability to observe the resultant structures, is therefore an important aspect in this area of research. The self-assembly of organic molecules and biomolecules on surfaces is based on covalent/non-covalent interactions such as hydrogen-bonding, π -stacking, and van der Waals forces or metal ion-ligand coordination [3].

We present here examples of ordered assemblies of organic and biological molecules on gold(111) surfaces. The first example shows how control over mono- or multilayer assemblies of 1,4-phenylenedimethanethiol can be achieved and monitored. The second example shows how new types of monolayers on gold can be prepared using amine groups to anchor aromatic molecules to the surface. A third example shows how ordered assemblies of genetically-engineered inorganic-binding polypeptides can be formed on gold surfaces using a 3-repeat, 14 amino acid gold-binding protein (GBP1).

II. EXPERIMENTAL SECTION

Monolayer preparation. 1,4-phenylenedimethanethiol, 2-aminoanthracene and 2-aminoanthraquinone were purchased from Aldrich and used as received. A clean Au(111) substrate was immersed in a 1 mM solution of the relevant molecule for 24 hours before thorough rinsing with solvent and drying under N_2 gas. Tetracyanoethylene treatment involved immersing a 1,4-phenylenedimethanethiol SAM in a 0.5 M

solution of TCNE in absolute ethanol for 48 h. The substrate was then rinsed liberally with ethano and dried under N_2 gas.

Scanning tunneling microscopy. STM images were acquired using a Nanosurf EasyScan system under ambient conditions. The STM tip was prepared from Pt/Ir wire cut under ambient conditions. All images were acquired in a constant-current mode. Typical imaging conditions are bias voltages of ± 0.2 to ± 1 V and a tunneling current of 3 pA to 1 nA.

Surface plasmon resonance. Surface Plasmon Resonance Spectroscopy: The SPR instrument used is based on a planar prism (Kretschmann) configuration, described and characterized elsewhere. It can detect changes in bulk solution refractive index down to $\sim 2 \times 10^{-6}$ (corresponding to $\sim 1 \times 10^{-3}$ protein monolayers for a system). White-light is directed at the gold-coated substrate through the prism at a fixed angle (78° from normal), and adsorption-induced changes in the refractive index (RI) near the gold sensor surface are observed by automated monitoring of the changes in wavelength where the SPR reflectance minimum occurs. These shifts are converted into coverage's of the proteins using a formalism for quantitative SPR which involves a sensitivity calibration based on the sensor response to the changes in the bulk RI, an exponential probe-depth estimated from Frensel equations, and the known RI for these class of proteins.

III. RESULTS AND DISCUSSION

Structures of 1,4-phenylenedimethanethiol films. 1,4-phenylenedimethanethiol (Figure 1) has been used extensively to assemble molecules on gold surfaces via the thiol-gold interaction. Recently, 1,4-phenylenedimethanethiol has been shown to form multilayered structures on gold surfaces under certain conditions, with implications for any subsequent molecular conductivity experiments [4]. Here we present high-resolution, STM images showing monolayers of 1,4-phenylenedimethanethiol on gold substrates under solution deposition conditions.

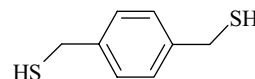


Figure 1. 1,4-phenylenedimethanethiol.

The structures of self-assembled films of 1,4-phenylenedimethanethiol were studied at atomic resolution using

scanning tunneling microscopy. Figure 2A shows an STM image of a 1,4-phenylenedimethanethiol film after 48 h immersion in a solution maintained at 55 °C. Large structured domains are apparent. Inter-row separation is 1 ± 0.6 nm, and

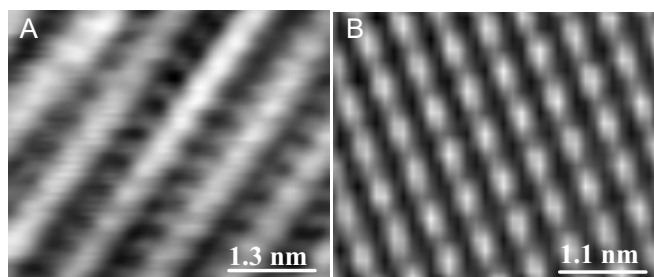


Figure 2. (A) after 48 h at 55 °C, and (B) after 8 h room temperature. Images are contrast enhanced and slightly low-pass filtered to accentuate molecular features.

is similar to structures assembled for 48 h at room temperature. The distance between the centres of two adjacent phenyl rings within a row is 0.49 ± 0.08 nm. The domains yield a nearly rectangular lattice with $\alpha = 9.8 \pm 0.5$ Å, $\beta = 5.1 \pm 0.1$ Å, $\gamma = 82 \pm 0.2^\circ$. Surprisingly, immersion of gold substrates in solutions of 1,4-phenylenedimethanethiol for shorter time intervals such as 8 to 10 h at room temperature resulted in the formation of structures of the type shown in Figure 2B. Analysis of the Fourier transform of the image reveals a rectangular surface net with lattice constants of $\alpha = 3.9 \pm 0.3$ Å, $\beta = 3.7 \pm 0.1$ Å, $\gamma = 88 \pm 0.2^\circ$. It is apparent from the high-resolution STM images that the 1,4-phenylenedimethanethiol structure formed on gold is highly dependent on the time and temperature of sample preparation.

Molecular etching experiments were performed to probe single and multilayer (image not shown here) structures. These experiments, in which a molecular layer is removed by the STM tip under high current, show that as well as monolayer structures, multilayers of 1,4-phenylenedimethanethiol are formed in regions of the surface structure.

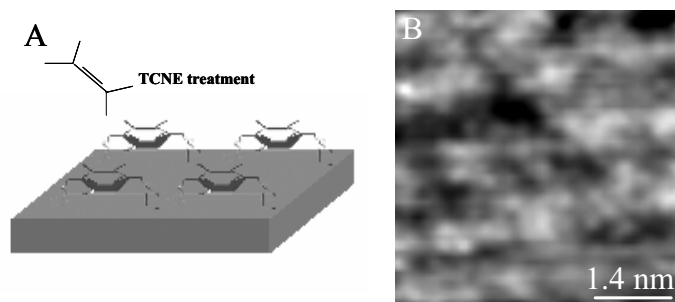


Figure 3. (A) Horizontal configuration of 1,4-phenylenedimethanethiol after treatment with TCNE (B) STM image of 1,4-phenylenedimethanethiol on Au(111) after treatment with TCNE.

In addition to the control of 1,4-phenylenedimethanethiol structures on Au(111) imparted by the deposition conditions, we found that chemical doping also resulted in re-arrangement of the molecules. Using a procedure first reported by Labonte et al [5], addition of a strong electron acceptor (in this case,

tetracyanoethylene, TCNE) caused the previously upright molecules to adopt a horizontal configuration with respect to the gold surface, as shown in Figure 3A. Figure 3B shows an STM image of the 1,4-phenylenedimethanethiol molecules on Au(111) in this horizontal arrangement. Line profile measurements reveal that the height of upright 1,4-phenylenedimethanethiol molecules (before TCNE treatment) is larger than those measured after treatment with TCNE. The scanning tunneling spectroscopy (STS) of 1,4-phenylenedimethanethiol SAMs prepared by either of the two methods above show that the molecules lying flat have a smaller energy gap than those standing upright.

Amine-bound films on gold. During the course of our investigations into the effect of UV light on SAMs,[5] we required an organic monolayer bound to Au(111) by an anchoring group other than the thiolate unit. We found that the amine group was a suitable candidate and so experiments were performed to prepare surface-bound layers of 2-aminoanthracene and 2-aminoanthraquinone (Figure 4). Interestingly, amine-bound monolayers on gold have not been reported to date.

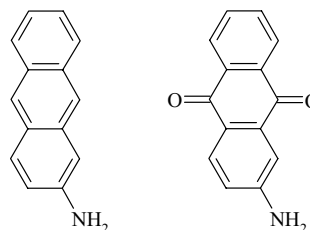


Figure 4. 2-Aminoanthracene (left) and 2-aminoanthraquinone (right).

Figure 5 shows STM images of the structure that results from immersing a Au(111) substrate into a dimethylformamide solution of 2-aminoanthracene for 24 h. Adsorption of

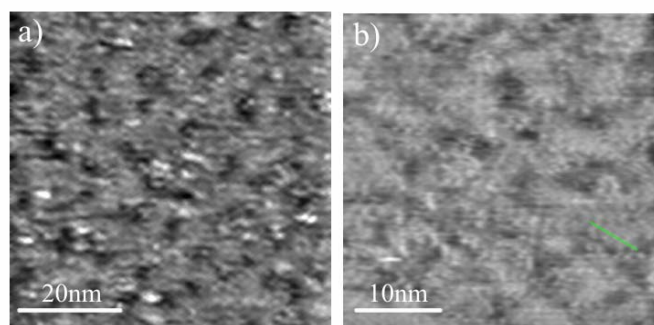


Figure 5. (a) STM image of 2-aminoanthracene on Au(111) (b) magnified region.

molecules to the gold surface occurs with features of 7×3 Å observed. These correspond to individual aminoanthracene molecules. Although some small regions of order can be seen, no long-range ordering is evident in the structure.

Similarly, 2-aminoanthraquinone formed monolayers with a low degree of ordering (Figure 6) with individual molecular units observed on the surface. Comparison of the 2-

aminoanthraquinone surface structure with that of 2-aminoanthracene (Fig.5) illustrates some significant differences. The 2-aminoanthraquinone structure has series of voids of 4-5nm in diameter. We propose that these differences are due to the oxygen atoms affecting π - π interactions.

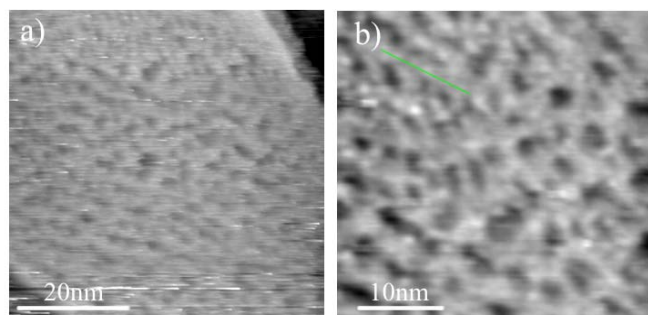


Figure 6. (a) STM image of 2-aminoanthraquinone on Au(111) (b) magnified region.

Genetically-engineered polypeptides on gold. Controlled binding and assembly of proteins onto inorganic substrates is at the core of biological materials science and engineering, with wide ranging applications such as diagnostics, tissue engineering and implants. Recently, a number of polypeptide sequences were identified using display technologies to specifically bind to inorganic substrates. A 3-repeat, 14 amino acid oligopeptide was found to bind specifically to gold. The binding motif does not contain cysteine, which is known to form a covalent thiol linkage with gold. With a new approach, we show self-assembly of this genetically engineered gold-binding protein as a monomolecular film forming self-patterned domains, immobilize a probe protein onto it, and show its utility in target recognition. Recently, a number of inorganic binding polypeptide sequences have been selected using display technologies. Selection of gold binders was designed to produce modular, independently folding metal recognition sequences. Gold-binding sequences had been isolated as extracellular loops of maltoporin.

Many proteins bind tightly to gold at low salt concentrations; however the engineered proteins were selected to bind at higher salt concentrations. The binding motif does not contain cysteine which is known to form a covalent thiol linkage with gold, the linkage to the gold surface in self-assembled monolayers (SAMs). We demonstrate the dramatic effect of assembly of GBP1 on Au(111) in Figure 7. Dynamics of the surface coverage and binding affinity of GBP1 onto gold surface were studied using surface plasmon resonance (SPR) spectroscopy. The shift in SPR wavelength is related to protein adsorption onto gold surface with respect to a base-line shift. In our experiments, a sharp increase in SPR shift represents a rapid assembly of GBP1 onto sensor surface. The decline of the SPR profile is due to the removal of unbound or physisorbed proteins upon rinsing. Indicative of stable coverage of the surface, the final buffer rinse drops the wavelength shift to a specific value (4.529 nm) corresponding to $1.49 \times 10^{12} \text{ molecules/cm}^2$. Time-sequence imaging of the adsorption process was also carried out using AFM to monitor

structural changes during the protein assembly process on the substrate surface (Figure 7 B - D). Although early on (within 5-10 minutes) proteins aggregate forming random and branched clustering (7B), after about 15 minutes of incubation, ordered assembly of protein domains form with straight boundaries and sharp corners (7C). A possible mechanism for the ordering could be that, following the adsorption onto the solid surface; the proteins could reorganize through a combination of forces involving Au-lattice recognition and intermolecular interactions among protein units. These studies reflect that nearly full ordered coverage of the GBP1 is obtained within about an hour (7D).

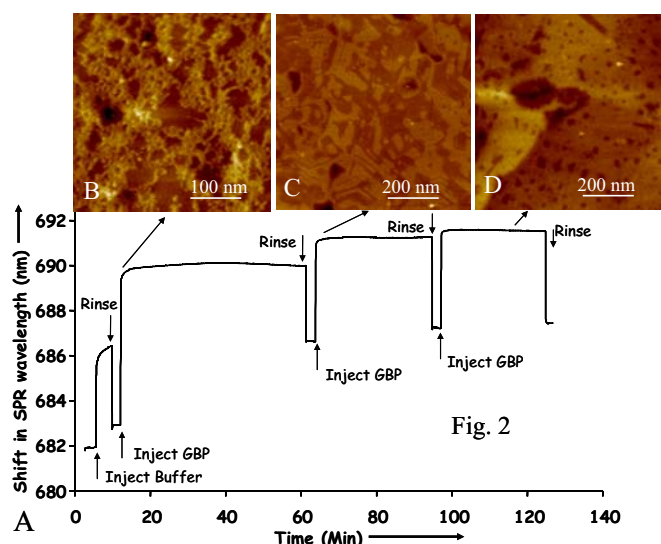


Figure 7. SPR and AFM study of GBP1 assembly on gold (H. Zareie and M. Sarikaya unpublished data)

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