

Using Molecular Self-Assembly for Surface Charged Monolayers to Control Bio-Assembly

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Abstract/Introduction:

Self-assembled biological molecules are being utilized in many ways to include forming hydrogel networks and nanoscale tubes. The goal of this project is to develop a method to preferential assembly biomaterial on surfaces using ionic interactions. We employ photolithography and prepare a simple pattern—an array of gold (Au (111)) on mica. We form a monolayer of 4, 4'-dimercaptobiphenyl on the Au (111) surface. The monolayer is then treated with a photoresist, followed by selective exposure leaving part of the monolayer inaccessible. The monolayer is exposed to a solution of mercury (II) per chlorate hydrate. The mercury (II) per chlorate provides a positive charge to exposed area of the patterned surface. Finally the array is introduced to various biomaterials with the expectation that localized ionic interactions will result in preferential assembly of biomaterial. The array is examined by Kelvin force microscopy (KFM) before and after their introduction to the biomaterial.

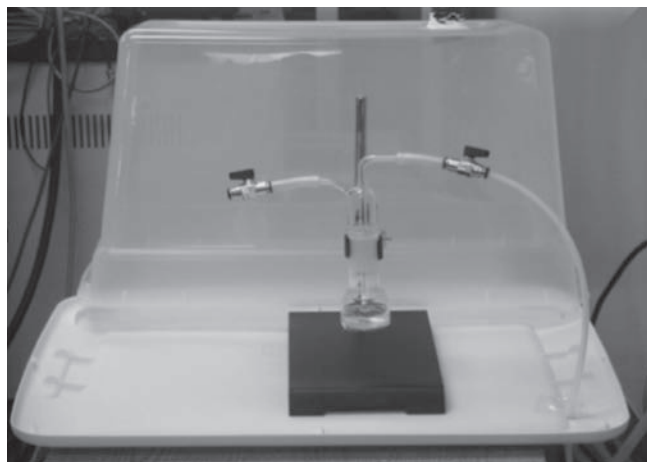


Figure 1: Homemade vented box. The bubbler flask is connected to a nitrogen gas tank allowing the self-assembly to occur in a nitrogen atmosphere.

Experimental Procedure:

The experiment was performed under a homemade vented box (Figure 1). The box contained a bubbler flask that was connected to a nitrogen tank. It was important for the solutions to be in a nitrogen atmosphere in order to prevent the formation of dual mechanism bifunctional polymer (DMBP) via disulfide bonds. Therefore, all the glassware were cleaned using a piranha solution. Cleanliness was important because impurities could interfere with the formation of a monolayer.

A 1 μM solution of DMBP was prepared and introduced to the bubbler flask. A gold sample was obtained and cleaned using an argon plasma. After cleaning the substrate, the optical constants were obtained using ellipsometry. These optical constants were later used to find the thickness of the monolayer. After measuring the optical constants, the substrate was put into the bubbler flask containing DMBP and left to self-assemble for four hours (Figure 2). After self-assembly, the gold substrate was rinsed with 200 proof ethanol and dried with a stream nitrogen gas. The monolayer thickness was obtained using ellipsometry.

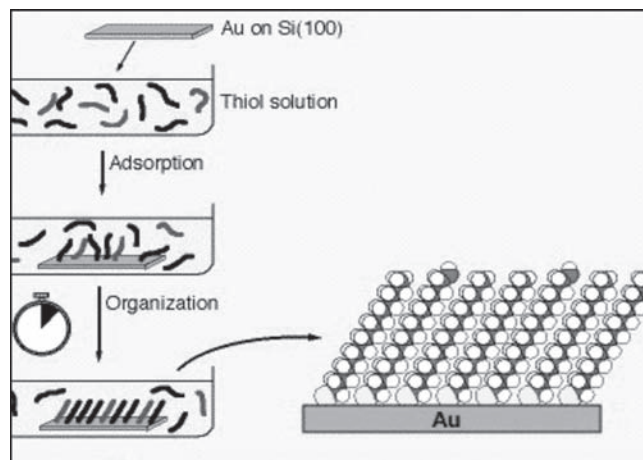


Figure 2: Gold substrate is put into a DMBT solution, DMBT self-assembles onto Au (111) substrate in a four hour period, to form a monolayer. Ref. <http://www.ifm.liu.se/applphys/jtir/sams.html>.

A pattern of 103 μm squares was created on a gold substrate using photolithography. A small area was covered with photoresist and left un-etched, leaving that part of the substrate available for measuring the thickness of the monolayer. The previous procedure was repeated to make the monolayer, then positive charges were partially introduced to the monolayer surface using mercury (II) per chlorate. In order to have a partially charged monolayer surface, half of the gold substrate was covered with photoresist. The photoresist was meant to keep the positive charges absent from certain areas. The charges were exposed in areas with no photoresist. The bubbler flask contained 50 μM of mercury (II) per chlorate in 50/50 200 proof ethanol in distilled H_2O . It seemed the photoresist adhered to the substrate well with 50/50 ethanol in distilled H_2O . After the two hour duration, the partially charged monolayer was taken out of the flask and analyzed using an atomic force microscopy — Kelvin force microscopy method, AFM/ KFM.

The maximum scan range for the AFM/KFM is 100 \times 100 μm while our Au substrate was 1 \times 1 cm. Therefore we double-masked the substrate so that each 103 μm square on the pattern had one half with a DMBP monolayer and the other half with a DMBP monolayer that had been exposed to mercury (II) perchlorate hydrate. This procedure rendered the sample a useful size for measuring by AFM. Biomaterial with inherent negative charges was then introduced to the partially charged monolayer surface.

Results:

After cleaning with the argon plasma, the optical constants obtained were $N_s = 0.186$ and $k_s = 3.400$. The average thickness of the monolayer was 14.90 \AA . After the two hour time duration of creating the partially charged monolayer, the substrate no longer had photoresist on certain areas. Using a different approach, 50/50 ethanol in distilled H_2O was used. It seemed the photoresist adhered to the substrate well with 50/50 ethanol in distilled H_2O . Photolithography was used to double mask the substrate. The size of the substrate was initially too big to measure by AFM/KFM. For this reason, a partially charged monolayer was made on each of the patterned squares as an alternative to using the entire substrate (Figure 3). The biomaterials exposed to the partially charged monolayer included red blood cells, cellulose, and sulfuric acid in cellulose. Unfortunately the biomaterials did not preferentially adhere to the positive charges on the



Figure 3: Patterned monolayer substrate (on left). Double patterned partially charged square (on right).

monolayer (Figure 4). The biomaterials covered the entire surface of the substrate.

Conclusion:

We successfully created a patterned surface of 102 μm gold squares using photolithography. We were also successfully in preparing a single monolayer of DMBP on Au (111). In addition, we developed a method to selectively place charges on a monolayer. However, we did not show preferential adhesion of biomaterials to the positively charged areas of the monolayer.

Future work will include using other biomaterials in proving preferential assembly to charged surfaces. Finally, the continued study of the surfaces by AFM/KFM will be pursued in an effort to improve the patterning of the surfaces.

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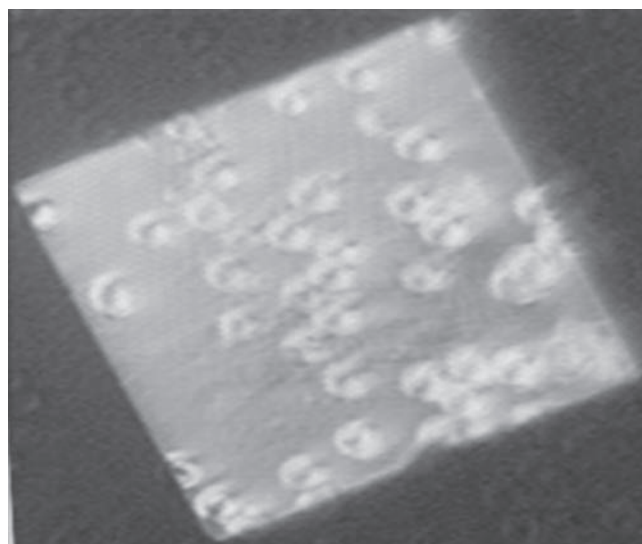


Figure 4: Blood cells did not seem to have a preference on the partially charged monolayer when exposed to the squares on the surface. In the picture above, the cells adhere to the whole square.