Fabrication of Nanostructures by Selective Covalent Attachment of Nanoparticles on Nanopatterned Monolayers

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Self assembled monolayers are of great interest in the semiconductor industry as ultra-thin resists for patterning high resolution features on various substrates.[1,2] Moreover nanostructured surfaces fabricated by electron-beam lithography or X-ray irradiation can be used as templates for the assembly of three dimensional architectures by selective immobilise materials on patterned templates.

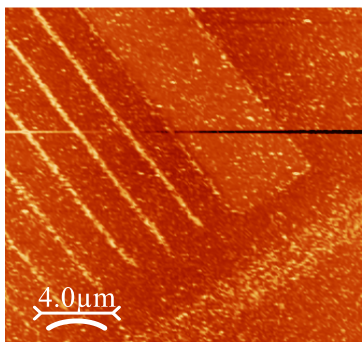


Figure 1. AFM image of citrate gold nanoparticles on an e-beam patterned monolayer of NPPTMS.

In our group some work has already addressed the fabrication of nanopatterned arrays of gold nanoparticles on Si/SiO_2.[3] The method involves first the assembly of a 3-(4-nitrophenoxy)-propyltrimethoxysilane (NPPTMS) monolayer on a Si/SiO_2 substrate followed by electron-beam induced conversion of the NO_2 terminal group to the NH_2 functionality that allows gold-nanoparticles to be adsorbed in a selective manner only on the modified area of the SAM. (Figure 1)

The limitation for this process was that the differentiation between adsorption of the nanoparticles to the NO_2 and NH_2 surfaces was not very efficient, because of the nature of the relative weak electrostatic interaction between citrate nanoparticles and the protonated amino surface.

Thus, present work is concerned with incorporating a reactive ester on the passivant of the nanoparticles that will react with the NH_2 surface to form a strong amide covalent bond. It will allow vigorous rinses of the surface after nanoparticles assembly in order to obtain better differentiation of particles attachment.

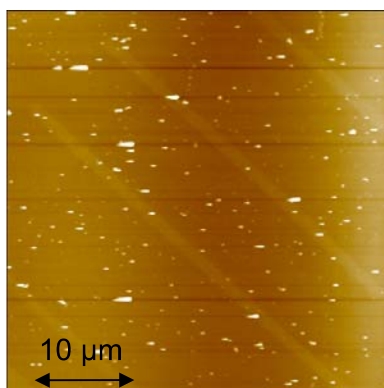
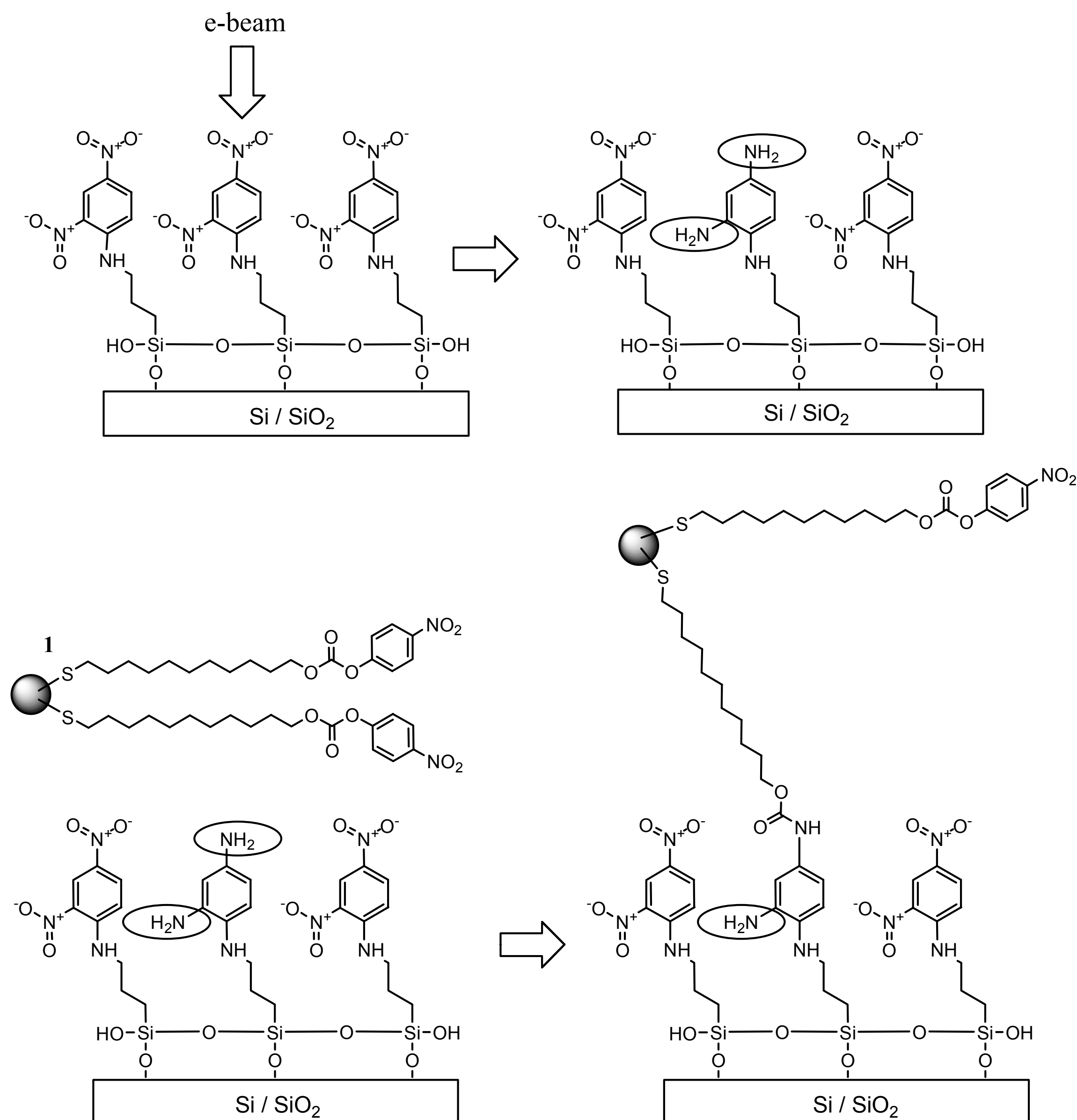


Figure 2. AFM image of citrate gold nanoparticles on a e-beam patterned monolayer of DNPTES.

In the present work SAMs of 3-(2,4-dinitro-phenylamino)-propyltriethoxysilane (DNPTES) on Si/SiO_2 substrate have been formed. Important aspects concerning the experimental conditions of SAM formation, including effects of solvent, time and the environmental conditions were analysed. The samples were fully characterised by contact angle, atomic force microscopy (AFM), ellipsometry and X-ray photoelectron spectroscopy (XPS). The samples were then patterned by e-beam writing to convert the NO_2 into the NH_2 moiety and the selectivity of the attachment of citrate nanoparticles on the amino terminated area of the monolayers was studied. (Figure 2)

Carbonic acid 11-mercapto-undecyl ester 4-nitro-phenyl ester passivated gold nanoparticles **1** (see scheme 1) were synthesised in a two step process. In the first step 11-mercapto-undecanol passivated gold nanoparticles were synthesised following the Brust procedure, characterised by ^1H

NMR and UV-Vis spectroscopy. In the second step the nanoparticles were modified by reaction with the 4-nitrophenyl chloroformate and characterised again by ^{1}H NMR and UV-Vis spectroscopy. The study of the selectivity of the particles on NH_2 and NO_2 terminated monolayers is in progress.



Scheme 1. Lithographic pattering of the DNPTES monolayer. The NO_2 group is converted in the NH_2 group by e-beam writing and gold nanoparticles are selectively attached by carbamate covalent bond only on the modified area of the monolayer.

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[2] A. Ulman, *An Introduction to Ultrathin Organic Films*, Academic Press Limited, UK **1991**.

[3] P.M. Mendes, S. Jacke, K. Critchley, J. Plaza, Y. Chen, K. Nikitin, R. E. Palmer, J. A. Preece, S. D. Evans, and D. Fitzmaurice, *Langmuir* **2004**, *20*, 3766-3768.