

## SELF-ASSEMBLY OF CITRATE- AND ACRYLATE-STABILISED GOLD NANOPARTICLES ONTO DERIVATISED SiO<sub>2</sub> SURFACES

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Self-assembled monolayers (SAMs) are of great interest in the semiconductor industry as ultra-thin resists for patterning high resolution features on various substrates.<sup>1,2</sup> 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 immobilisation of materials on patterned templates.

In our group some research has already addressed the fabrication of nanopatterned arrays of gold nanoparticles on derivatised Si/SiO<sub>2</sub>.<sup>3</sup> The method involved first the assembly of a 3-(4-nitrophenoxy)-propyltrimethoxysilane (NPPTMS) monolayer on a Si/SiO<sub>2</sub> substrate. This was followed by electron-beam induced conversion of the NO<sub>2</sub> terminal group to the NH<sub>2</sub> functionality that allows gold nanoparticles to be adsorbed in a selective manner only on the modified area of the SAM (Fig. 1). The limitation of this process is that the differentiation between adsorption of the nanoparticles to the NO<sub>2</sub> and NH<sub>2</sub> surfaces was not very efficient (Fig. 2).

Thus, in this work a systematic investigation of the immobilisation of citrate- and acrylate-stabilised gold nanoparticles onto hydroxyl-, amine- and nitro-terminated surfaces was carried out (Fig. 3). Smooth and homogeneous 3-aminopropyl-trimethoxysilane (APTMS) and 3-(4-nitrophenoxy)-propyltrimethoxysilane (NPPTMS) self-assembled monolayers on Si/SiO<sub>2</sub> substrates were formed and fully characterised by contact angle, ellipsometry, atomic force microscopy (AFM) and X-ray photoelectron spectroscopy (XPS). Citrate- and acrylate-stabilised gold nanoparticles were prepared as described previously<sup>4,5</sup> and characterised by TEM and UV-Visible absorption spectroscopy. The effect of pH on nanoparticles stability and immobilisation was investigated. The coverage of hydroxyl- (bare Si/SiO<sub>2</sub>), amino- (APTMS monolayers on Si/SiO<sub>2</sub>) and nitro- terminated (NPPTMS monolayers on Si/SiO<sub>2</sub>) surfaces by citrate- and acrylate-stabilised gold nanoparticles at different pHs was evaluated by AFM and XPS analysis.

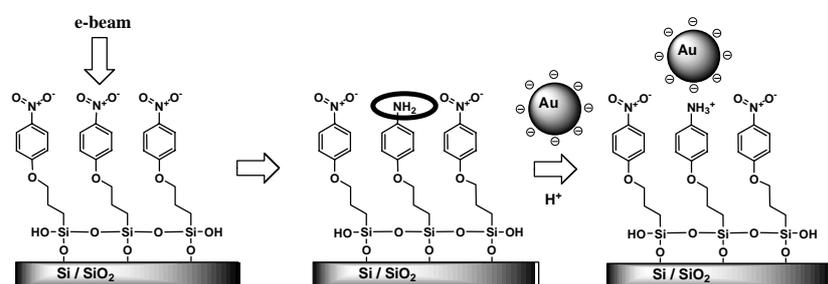
Our results showed that the surface coverage of hydroxyl-terminated surfaces (bare Si/SiO<sub>2</sub>) and nitro-terminated monolayers (NPPTMS on Si/SiO<sub>2</sub>) was negligible. On the other hand amino-terminated monolayers (APTMS on Si/SiO<sub>2</sub>) had higher coverages for citrate-compared with acrylate-stabilised gold nanoparticles (Fig. 4).

Moreover, it was observed that in the case of both citrate- and acrylate-stabilised gold nanoparticles the coverage was higher the lower the pH of the colloidal solution. These results are in agreement with previous studies on citrate-stabilised gold nanoparticles.<sup>6</sup> This behaviour could be do to the increased protonation of the amino-terminated surface at lower pH which enhances the electrostatic interactions with the negatively charged gold nanoparticles. This results in higher surface coverages<sup>7</sup> for both citrate- and acrylate stabilised gold nanoparticles.

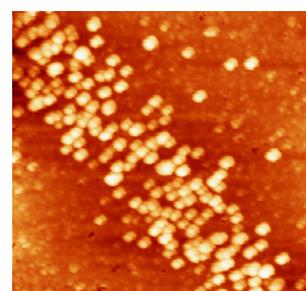
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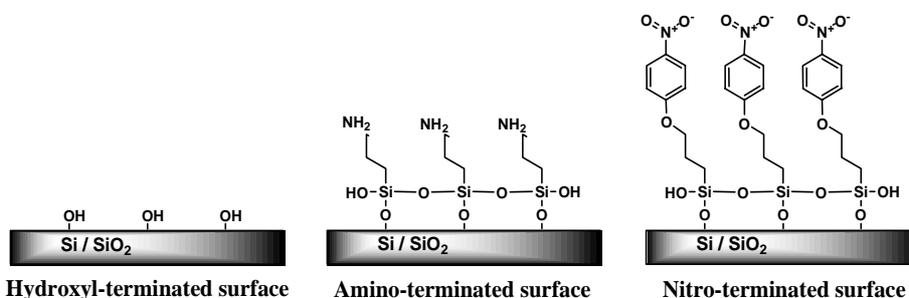
## Figures:



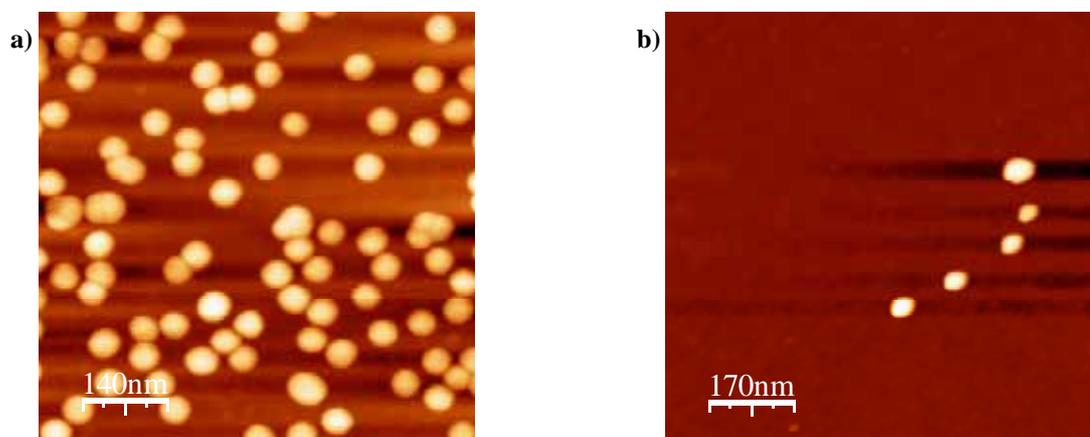
**Fig. 1** Chemical lithography was used to pattern the NPPTMS monolayer by conversion of the  $\text{NO}_2$  group to the  $\text{NH}_2$  group. Negatively charged citrate gold nanoparticles were selectively attached on the modified area of the monolayer by electrostatic interaction with the protonated amino functionality.



**Fig. 2** Tapping-mode AFM image  $1.5 \times 1.5 \mu\text{m}$  of citrate-stabilised gold nanoparticles attached preferentially to the exposed areas of the NPPTMS monolayer.



**Fig. 3** A scheme of the three different surfaces used for the investigation. From left to right: NPPTMS monolayer. APTMS monolayer and bare  $\text{SiO}_2$ .



**Fig. 4** Tapping mode AFM images illustrating the different behaviour of a) citrate- and b) acrylate-stabilised gold nanoparticles on amino terminated surfaces.