**Controlled manipulation of thiol-functionalised gold nanoparticles on Si (100) by Dynamic Force Microscopy.**

G Paolicelli 1*, K Mougin 2, A Vanossi 2 and S Valeri 2

1 CNR-INFM National Research Center S3, Via Campi 213/A, 41100 Modena, Italy
2 CNR-INFM National Research Center S3 and Department of Physics, University of Modena and Reggio Emilia, Via Campi 213/A, 41100 Modena, Italy
3 I.C.S.I. - C.N.R.S. - UPR 9069 15, Rue Jean Starcky B.P. 2488 - 68057 Mulhouse Cedex, France

* Corresponding e-mail: paolicelli.guido@unimore.it

**Abstract.** Mechanical control of nanometer size objects and the dynamic behaviour at this length scale are subjects of growing interest. One promising approach to operate and perform quantitative measurements in this regime is to use dissipation processes in atomic force microscopy. We obtained a controlled manipulation of thiol-functionalised gold nanoparticles on silicon dioxide and a measurement of the energy depinning threshold as a function of nanoparticles characteristics by using the AFM microscope in a particular dynamic regime. Detailed procedure and preliminary results will be described in this contribution.

1. **Introduction**

Understanding different regimes of friction for nanosized sliding objects is going to be very important from both fundamental and technological view points. The sliding behavior of these nano-objects is often distinctive (mostly due to their large surface-to-volume ratio), being qualitatively different from those of their constituent parts and from those of bulk material.

It has been recently shown that cluster motion at the nanoscale can be stimulated by using the AFM microscope in a particular dynamic regime [1,2]. The movement is induced by operating the AFM in tapping mode with amplitude feedback (AM-AFM) and by using a tip amplitude oscillation intentionally larger than that optimized for imaging purpose. The extra energy transferred to the cluster physisorbed on the surface may cause its detachment and displacement.

In this contribution we will present a successful application of the method to obtain controlled manipulation of thiol-functionalised gold nanoparticles on silicon dioxide and to estimate the energy depinning threshold as a function of cluster characteristics. These preliminary results will serve as a basis to the systematic application of the method to the investigation of size dependent effect on adhesion and friction at the nanoscale.

2. **Preparation and Experimental set-up**

Gold nanoparticles with sizes ranging between 1 and 100 nm were dispersed in a colloidal suspension, consisting in an aqueous solution of tetrachloroauric (III) acid hydrate ([HAuCl4]-H2O), stabilized with citric acid trisodium. The size of the particles was controlled by temperature, addition of reducing...
agent (NaBH4) and modification of the concentration of tetrachloroauric (III) acid hydrate. Two different sizes were selected with nominal diameter 12 ± 2 nm (NP12) and 24 ± 3 nm (NP24). Dimension and size distribution was checked by TEM. Specific molecules, such as thiols according to self-assembling procedures in aqueous environment, were used to coat the particles with functional overlayers. Functionalized nanoparticles were deposited on clean silicon substrates (Si (100) + native oxide) by dipping the substrate into the solution (about 1 hour) and then drying it with a nitrogen flux.

Experiments were performed in air, at room temperature using a commercial AFM microscope (Enviroscope+Nanoscope IV, by VEECO). The humidity during the experiments was about 40% and it was regularly monitored. Two different sets of standard silicon cantilevers have been used (Veeco RTESP5, RFESP), characterized by nominal frequencies f₀ = 75 kHz and 350 kHz and spring constants K of 3 N/m and 40 N/m respectively. The spring constant of each cantilever has been individually checked following the criterion on Ref. [3]. The corrected K values were used during the energy calibration procedure to better compare measurements performed with different tips and to minimize non systematic errors. Anyhow, small but systematic errors on the evaluation of K parameter may affect the absolute energy scale and they cannot be completely ruled out.

3. Experiment

A single manipulation measurement consists in a sequence of images on a fixed area and a dedicated calibration procedure. The AFM is used in tapping mode with amplitude feedback (AM-AFM) with scan rate of 1 Hz and 512 sample/lines. During the sequence, we alternate a standard imaging scan and a manipulation scan where the amplitude oscillation of the cantilever driving piezo is progressively increased with respect to the previous manipulation scan. All the other parameters that control the AFM response bring kept unchanged. The sequence usually ends when the number of detachment events between subsequent manipulation scans is close to zero.

Fig. 1. represents a standard topographic image of NP12 sample (nanoparticles with nominal diameter of 12 nm). Single nanoparticles are easily identified while the measurement of their apparent diameter (~25 nm in this case) reveals a large influence of tip dimensions.

Fig. 2. displays a phase contrast image during a typical manipulation scan over that same area of fig. 1., showing the details that characterize the cluster movement induced by the tip.

The evident track that goes from the center to the upper right corner consists of a series of small jumps carried out by a nanoparticle after the first detachment. The particular direction of movement and the variability of jump amplitude clearly show that tip does not drag the particle but instead it forces the movement along the slow scan direction (from bottom to top in this case). It is also evident that the preferred direction is related to the movement and morphology of the tip because tracks within the same scan or sequence usually are parallel to each other while the substrate does not posses any particular symmetry. Other peculiar events have been marked on fig. 2.: 1) the indication of a track followed by a large displacement, moving the particle out of the field of view 2) a small jump to the right with the particle remaining pinned in the new position 3) a “collision” between a track and a pinned particle that traps the moving one 4) a detachment and a movement out of the field of view.

The comprehension of the intriguing effects described above requires certainly a detailed description of the mechanisms controlling the tip-cluster dynamics; for example, it is interesting to argue if some geometrical interlocking effects can play a relevant role in the observed tribological behaviour since the gold nanoparticles have been thiol-functionalized. Here, we are interested mainly in the energy dissipation taking place at the very first stage of the nanoparticle detachment, with the aim of relating depinning threshold and adhesion effect to cluster dimension (i.e. to the contact area at the nanoscale).

To measure the energy threshold associated with a particle detachment we use the phase contrast method described in details in recent publications [4][5][6][7]. The method relies on the description of the cantilever – tip system interacting with a surface as an externally driven anharmonic oscillator with damping. The external driver is the piezo oscillation at base of the beam, while the damping
contribution comes from two distinct channels: the intrinsic one (air damping and beam deflection) and the tip-substrate interaction.

Measurable quantities associated with damping effects are frequency, amplitude and phase shifts. Using the microscope with amplitude feedback at fixed frequency, we force the system to show all the dissipation effects in the phase shift. At the resonant frequency, the energy dissipation per cycle due to tip-surface interaction can be expressed as follows

$$E_{int} = \frac{\pi k A}{Q} \left( A_0 \sin \phi - A \right),$$

where $Q$ and $k$ are, respectively, the quality factor and the spring constant of the cantilever, $\phi$ is the phase shift between the external driving oscillation and the tip response, $A$ is the oscillation of the tip in contact with the surface (i.e. the amplitude setpoint which is kept constant by the feedback loop), and $A_0$ is the tip free amplitude oscillation.

Two important aspects have to be noted. First, $A_0$ is a function of the external driving oscillation amplitude $A_d$ which is the parameter we increase during a manipulation sequence and second, $A_0$ and $A$ have to be expressed in units of length. A calibration procedure is therefore associated to each manipulation sequence. It starts with the evaluation of the $Q$ factor and of the curve $V_0$ versus $V_d$ ($V_0$ is the photodiode measurement of $A_0$ and $V_d$ is the voltage applied on the driving piezo) and it ends with the estimation of the deflection sensitivity that turns photodiode measurement into units of length. Following this procedure, we are able to associate an energy value to each measured phase shift taking into account the particular cantilever and microscope set-up.

4. Result and Conclusion

During a manipulation sequence each increase of driving oscillation produces an increase of phase shift on the nanoparticles we are scanning on. Nevertheless we do not calculate the phase shift on each cluster, rather we consider an average over the whole set of nanoparticles including also the tracks of the moving ones. We have checked that the maximum error associated to this procedure is always smaller than the step induced by the driving oscillation increase and also, on different events where phase shift is clearly visible before detachment (n. 4 on fig. 2.), that no anomalous shift appears in these situations. Then, according to eq. 1., we calculate a unique energy value from a couple of $A$ and $A_0$. 

Figure 1. Deposition of nanoparticles with 12 nm nominal diameter (NP12) on clean SiO$_2$ (roughness 0.5 nm). Density: 65 particles over 1 $\mu$m$^2$. Topographic image, no filtering. 

Figure 2. Phase contrast image during a typical manipulation scan over that same area of fig. 1. Marked zone are described in the text.
measurements and we associate to that value the number of nanoparticles eventually been detached during the scan. The results of this analysis for both NP12 and NP24 samples are shown in Fig. 3.

**Figure 3.** Data represent the collection of a number of different manipulation sequences covering an equivalent area of 8 μm², containing about 400 (NP12) and 300 (NP24) nanoparticles. The left axis refers to the histogram of detachments events. The right axis refers to the curve representing the sum of the detachments events achieved up to the energy E. Both representations are normalized to the total particles number and give a clear evidence of the two separate energy detachment threshold. The abrupt change of the slope in the curves is a significant point to fix the energy threshold values: E₁ = 5*10⁻¹⁶ J (NP12), E₂ = 1.9*10⁻¹⁵ J (NP24). We estimate the error bar associated to these values equal to the width of the histogram column, ΔE = 2*10⁻¹⁶ J

The curves in Fig. 3 shows unambiguously that AM-AFM method and the calibration procedure we have described allow us to distinguish and measure the energy detachment threshold for cluster size down to the ten-nanometer scale. The results are in qualitative agreement with ref. 1 whit respect to the energy scale and at the same time, they represent a step forward to the direction of controlling nanometer mechanical object. Finally we foresee a systematic use of this method to the study of size dependent effect on adhesion and friction behavior at the nanoscale.

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