Towards Hierarchical Nanoassembly

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Abstract

Assembly of nanometer-scale objects by using a Scanning Probe Microscope (SPM) as a robot is a promising aproach for the fabrication of nanoelectromechanical systems (NEMS). This paper describes several techniques for positioning nanoparticles, linking them to form subassemblies, and moving entire subassemblies. These are first steps towards the hierarchical construction of complex nanoassemblies. Results of experiments conducted in ambient air and in liquid environments are presented. Nanomanipulation in liquids opens new research directions involving interactions with single biomolecules, and fine control of forces between tips, particles and surface substrates.

Introduction

Nanoelectromechanical systems (NEMS) are the new frontier in miniaturization, and promise revolutionary advances in science and engineering. Very small sensors, computers and actuators will bring about a new era of micro and nanorobots, and will play an important role in the emerging paradigm of *ubiquitous interaction*, which is likely to be central to information technology in the 21st century. Highly mobile humans and robots will be able to interact with enormous amounts of information, *and* also with the physical world through large numbers of distributed sensors and actuators, most of which will have extremely small sizes.

Manipulation of molecularly-sized components with Atomic Force Microscopes (AFMs) and other Scanning Probe Microscopes (SPMs) has been demonstrated recently–see [Requicha *et al.* 1998] and references therein. Until now, nanomanipulation has been used primarily to construct patterns of disconnected, individual particles. Although nanoparticle patterns have many potential applications [Requicha 1999], to build NEMS the particles must be linked so

as to form more complex components, and eventually entire systems. The fundamental operations required by these applications are precise *positioning* of nanoscale objects, and *linking* them. The remainder of this paper discusses techniques for performing these fundamental operations at the nanoscale, and presents experimental results.

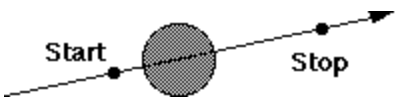
Positioning Operations

AFMs exploit the interatomic forces between tip and sample for imaging and manipulation. The force is sensed through the deflection of the cantilever that holds the tip. Imaging is normally accomplished by maintaining a constant force between tip and sample while the tip is scanned across the surface of the sample. In contact mode operation (C-AFM) the tip/sample interaction is repulsive, and the force is measured by the deflection of the cantilever. In dynamic mode operation (D-AFM) the cantilever vibrates at a frequency near its resonant frequency, and the tip/sample force is measured by its effect (damping) on the cantilever vibration amplitude. (For more information on AFM operation, see [Requicha *et al*. 1998] and references therein.)

Our experiments were conducted using an AutoProbe CP microscope from Park Scientific Instruments, and a PicoSPM from Molecular Imaging (for experiments in liquids) coupled to the AutoProbe controller. The manipulation software, called Probe Control Software, was developed by our group, and uses the Application Programming Interface (API) supplied by Park.

We discuss below several manipulation methods. They are based on the generic operation illustrated in Figure 1. The AFM tip moves in a straight line across the object to be positioned. Initially, the AFM parameters such as force or amplitude setpoints are kept at values suitable for imaging. Then, the conditions are changed temporarily, between the starting point t_1 and the stopping point t_2, while the object is moved. Finally, they are restored to imaging conditions. We have experimented with the following protocols.

Figure 1 — Generic manipulation operation.



Protocol 1

Image in D-AFM mode at a suitable amplitude setpoint
At t_1 lower the amplitude setpoint to get closer to the surface
Turn off the feedback
At t_2 restore the initial conditions

Protocol 2

Image in D-AFM mode at a suitable amplitude setpoint
At t1 turn off the feedback
Move the tip by D z to get closer to the surface
At t2 restore the initial conditions

Protocol 3

Image in C-AFM mode at a suitable force setpoint
At t_1 increase the force setpoint to get closer to the surface
At t_2 restore the initial conditions

Protocol 4

Image in C-AFM mode at a suitable force setpoint
At t_1 increase the force setpoint to get closer to the surface
Turn off the feedback
At t_2 restore the initial conditions

When the forces between particles and substrate are relatively low, imaging must be done in D-AFM mode, otherwise the particles will move uncontrollably. Protocols 1 and 2 are suitable for such particle/substrate combinations. We have used them successfully for moving gold colloidal nanoparticles with diameters of 15 and 30 nm on mica and silicon substrates, in air, at room temperature. Mica was coated with poly-L-lysine and silicon with a self-assembled monolayer (SAM) of silane.

The D-AFM protocols are unable to move particles that are strongly attracted to the substrate. Protocols 3 and 4 are suitable for such cases. For example, we have used Protocol 3 to move 5 nm Au particles on mica coated with poly-L-lysine, and Protocol 4 to manipulate gold particles coated with thiols on a silicon substrate. (Of course, if the adhesion is very strong, none of the protocols succeeds.)

Protocols 1-4 are normally used to move a single particle at a time, by pushing it along a trajectory that passes (approximately) through the particle's center. If a particle is hit off center, it tends to move sideways. This can be used to construct lines of particles, by using the following protocol.

Protocol 5

Image in D-AFM mode at a suitable amplitude setpoint
Scan over a rectangular region with the feedback on

Figure 2 shows a line constructed by pushing sideways zinc sulfide islands with dimensions of 2-6 nm. The tip scans in the horizontal x direction, then moves one step up by a delta y and continues the scan. The particles accumulate at the top of the scanned region. The islands

were deposited on mica by using thin film techniques. Similar results were obtained with lead sulfide nanocrystals with dimensions of 3-10 nm.

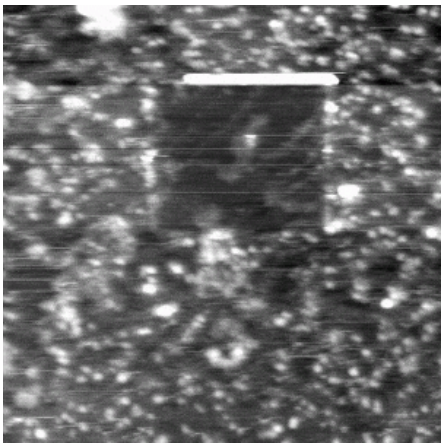


Figure 2 — A line of ZnS nanoparticles constructed by pushing all the particles in a rectangular region towards the top of the figure.

We have studied Protocol 1 carefully [Baur *et al.* 1998, Resch *et al.* 1998a], and concluded that the particle is mechanically pushed by the force generated by the average, or d.c., deflection of the cantilever. Figure 3 is a screenshot of an unsuccessful attempt at pushing a particle in the sample imaged at the top right. The vertical bars indicate the region where the feedback is turned off. During pushing, the feedback is off and the topography signal is flat (top left). The D-AFM amplitude shown on the bottom left starts to decrease as the tip approaches the particle. It becomes zero (the flat region between the two bars in the figure) while there is contact. At the same time the d.c. cantilever deflection begins to increase (bottom right), indicating that the cantilever is bending as the tip goes over the particle. In this example, the cantilever deflection was insufficient to move the particle. In a successful attempt, the cantilever deflection reaches a pushing threshold and remains approximately constant while the particle is moving. We have measured pushing thresholds and other data that provide a very good description of the phenomena involved.

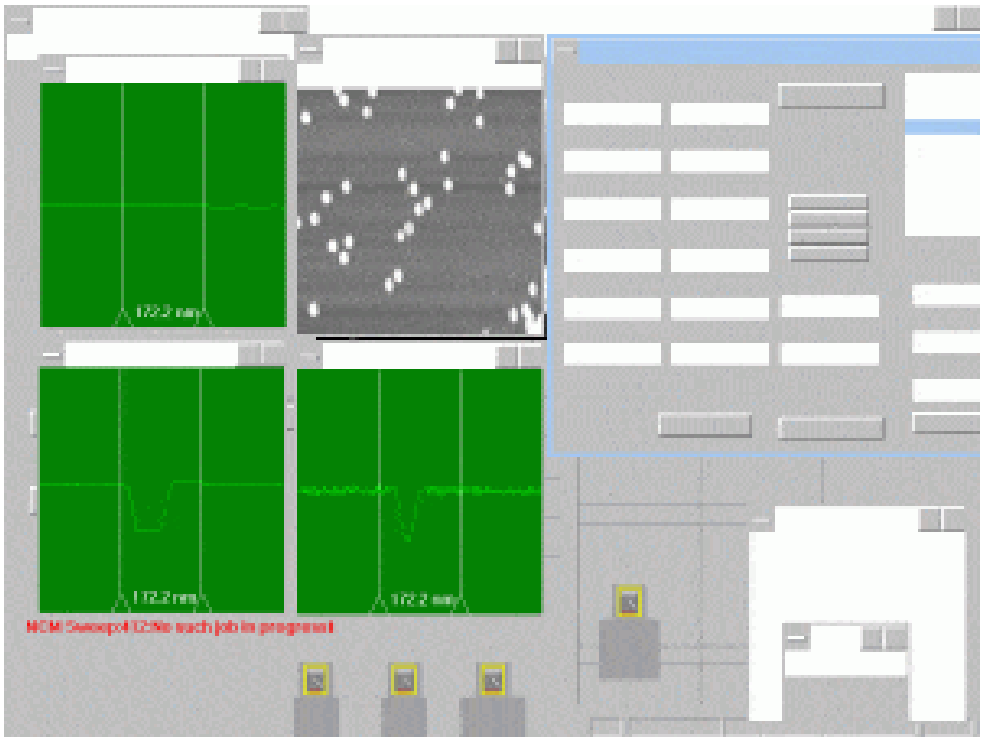


Figure 3 — Feedback off without pushing

A major problem in AFM manipulation at room temperature is the thermal drift between the tip and the sample. The drift is due to material inhomogeneities in the instrument, and small fluctuations in temperature. The sequence of images in Figure 4 illustrates the problem and its solution. The left, top picture shows the initial conditions, with randomly dispersed particles. An arrow is added near the center of the top right picture, specifying the particle to be moved and the desired trajectory. Each of these images takes several minutes to acquire. The bottom left image shows the result of a new scan after the arrow was drawn. The specified particle has moved significantly towards the bottom right. If the AFM tip were to move along the specified trajectory, it would miss the particle altogether. We solve this problem by tracking the particle. A tracking system predicts the position of the particle and then updates it by searching with single line scans. The bottom left image shows that the tracker successfully and automatically followed the particle, which was moved vertically by the pushing operation.

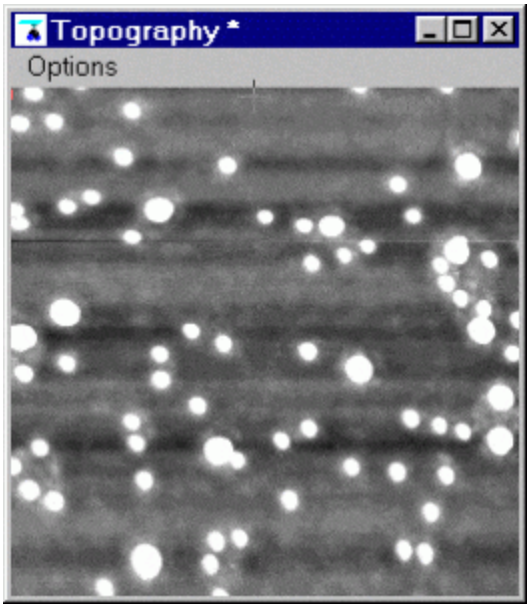


Figure 4 — Tracking and pushing a particle

Very recently we have demonstrated pushing operations in a liquid environment. Figure 5 shows a simple example, in which a gold nanoparticle with 15 nm diameter is pushed in water by using Protocol 1. We believe this is the first time that such capabilities are reported in the literature. Operation in a liquid opens new and interesting avenues for research. For

example, the forces between tip, particle, and substrate can be modulated by changing the pH or other properties of the liquid. In addition, liquid environments are the most suitable for studying and manipulating biological objects.

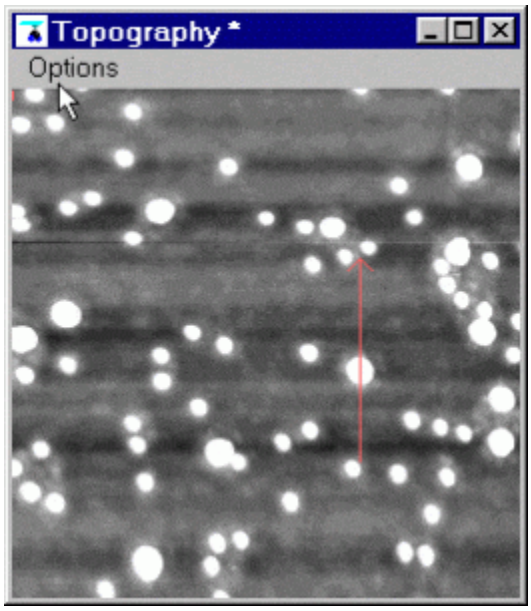


Figure 5 — Pushing in water

Assembly Operations

Structures formed by manipulation of nanoparticles can be stabilized by "glueing" the particles together. Insofar as we know, we are the first laboratory to demonstrate linking of arbitrarily-shaped patterns of nanoparticles. We do this by using di-thiols. These are organic substances with sulfur atoms at the ends of an atomic chain, and which are known to connect to gold at the sulfur ends. In our initial experiments we first moved several particles together through our usual protocols. Then we removed the sample from the AFM, dipped it in a di-thiol solution, and returned it to the AFM. (To be able to find the original position we used substrates patterned by electron-beam lithography with a grid of lines that are visible with an optical microscope.) We verified that the particles were linked by pushing each subassembly as a whole. Figure 6 shows on the left the initial situation with several groups of glued particles. On the right is the result of pushing the subassemblies together to form a wheel-like structure. We have also been able to link gold particles coated with a silane on a silicon surface [Resch *et al.* 1998b].

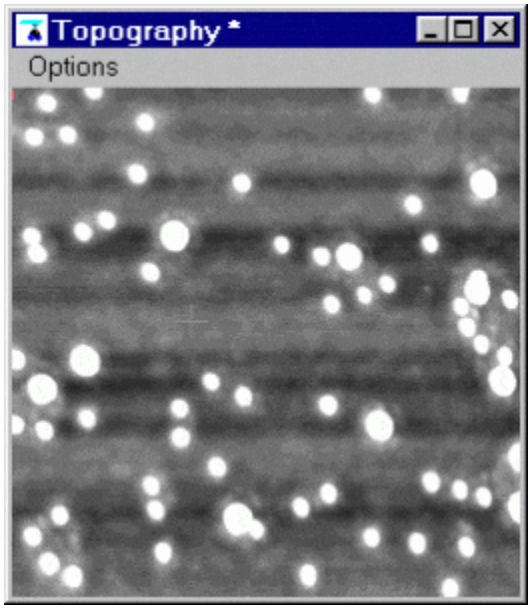
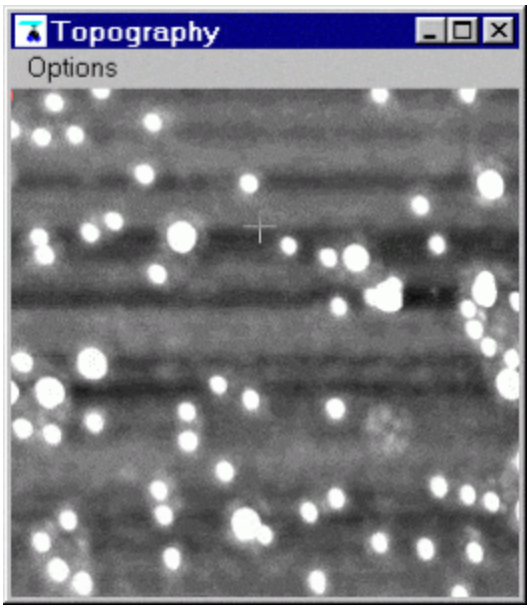


Figure 6 — Moving subassemblies of nanoparticles

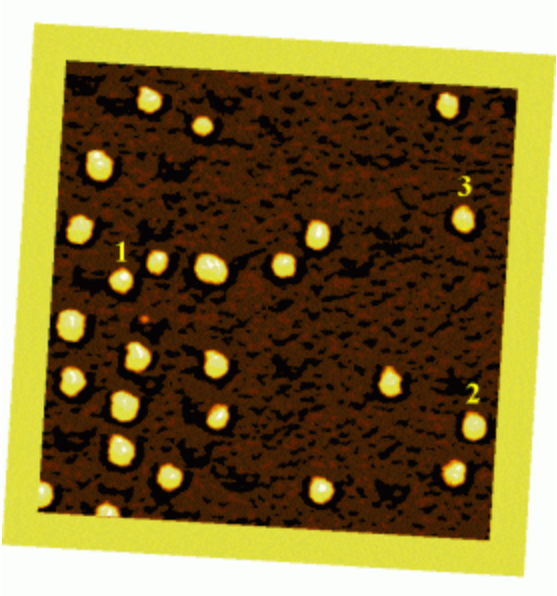
Interestingly, we also found that after the di-thiol treatment the particles can still be moved, and that they automatically attach to others when pushed together. Therefore we can construct the desired shapes before or after di-thiol treatment.

Conclusions

Particles with overall dimensions on the order of a few nm can be moved by mechanically pushing them with the tip of an Atomic Force Microscope (AFM) using the techniques discussed in this paper and implemented in our own Probe Control Software. (Commercial AFM software does not support the operations necessary for nanomanipulation.) We discussed pushing protocols suitable for different values of particle/substrate forces. Experimental results were presented that show that manipulation operations can be successfully performed in air, at room temperature, and also in liquid environments. These are especially interesting because they open new research directions in biological nanomanipulation and in the control of tip/object/substrate forces, which ultimately determine the success of manipulation operations.



The particles can be linked by using simple chemical means, so as to form subassemblies. Each subassembly can then be pushed by using our nanomanipulation protocols. Thus, we have demonstrated the first steps towards the hierarchical construction of arbitrarily-shaped (planar) assemblies at the nanoscale.



Acknowledgements

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References

[Baur *et al.* 1998] C. Baur, A. Bugacov, B. E. Koel, A. Madhukar, N. Montoya, T. R. Ramachandran, A. A. G. Requicha, R. Resch, and P. Will, "Nanoparticle manipulation by mechanical pushing: underlying phenomena and real-time monitoring", *Nanotechnology*, Vol. 9, No. 4, pp. 360-364, December 1998.

[Resch *et al.* 1998a] R. Resch, A. Bugacov, C. Baur, B. E. Koel, A. Madhukar, A. A. G. Requicha, and P. Will, "Manipulation of nanoparticles using dynamic force microscopy: simulation and experiments", *Applied Physics A* , Vol. 67, No. 3, pp. 265-271, September 1998.

[Resch *et al.* 1998b] R. Resch, C. Baur, A. Bugacov, B. E. Koel, A. Madhukar, A. A. G. Requicha and P. Will, "Building and manipulating 3-D and linked 2-D structures of nanoparticles using scanning force microscopy", *Langmuir*, Vol. 14, No. 23, November 10, 1998.

[Requicha *et al.* 1998] A. A. G. Requicha, C. Baur, A. Bugacov, B. C. Gazen, B. Koel, A. Madhukar, T. R. Ramachandran, R. Resch and P. Will, "Nanorobotic assembly of two-dimensional structures", *Proc. IEEE Int'l Conf. Robotics & Automation*, Leuven, Belgium, pp. 3368-3374, May 16-21, 1998.

[Requicha 1999] A. A. G. Requicha, "Nanoparticle Patterns", *J. Nanoparticle Research*, in press.