Nanoparticle manipulation by mechanical pushing: underlying phenomena and real-time monitoring

To cite this article: C Baur *et al* 1998 *Nanotechnology* **9** 360

Nanotechnology **9** (1998) 360–364. Printed in the UK PII: S0957-4484(98)94946-7

Nanoparticle manipulation by mechanical pushing: underlying phenomena and real-time monitoring

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Received 9 June 1998, in final form 7 August 1998

Abstract. Experimental results that provide new insights into nanomanipulation phenomena are presented. Reliable and accurate positioning of colloidal nanoparticles on a surface is achieved by pushing them with the tip of an atomic force microscope under control of software that compensates for instrument errors. Mechanical pushing operations can be monitored in real time by acquiring simultaneously the cantilever deflection and the feedback signal (cantilever non-contact vibration amplitude). Understanding of the underlying phenomena and real-time monitoring of the operations are important for the design of strategies and control software to manipulate nanoparticles automatically. Manipulation by pushing can be accomplished in a variety of environments and materials. The resulting patterns of nanoparticles have many potential applications, from high-density data storage to single-electron electronics, and prototyping and fabrication of nanoelectromechanical systems.

1. Introduction

The pioneering work of Eigler [1], Lyo [2], Beton [3] Jung [4], and others has shown that it is possible to precisely position atoms and molecules on a surface by using a scanning probe microscope (SPM). These are remarkable achievements. However, manipulation of particles with dimensions of a few to a few tens of nanometres is likely to have a greater impact in nanometre-scale science and technology in the near future. Patterns of colloidal nanoparticles can be constructed by SPM manipulation, and have several potential applications that are worth investigating. They can be used to efficiently store digital information, as explained below; to build single-electron transistors, as suggested in [5]; or as templates for building nanostructures that can function as components of nanoelectromechanical systems (NEMS). For example, Au nanoparticles can be linked by dithiols [6], and the resulting structures can (potentially) be used to construct more complex objects in a bottom-up fashion.

Storage applications are illustrated in figure 1, which shows a pattern of 15 nm Au colloidal particles built in our laboratory by the methods described below. Each row of Au balls in figure 1(*a*) can be interpreted as one byte (i.e. 8 bits) of information, with the presence of a ball at a grid point signifying a binary '1', and its absence a '0'. The three rows spell 'LMR', the initials of our laboratory, in ASCII code. Reading these 'nanobits' is illustrated in figure 1(*b*), which shows the trace produced by a single-line, non-contact atomic force microscope (AFM) scan over the second row. This scheme can be used to store information in an 'editable nano-CD', i.e. a medium analogous to a current compact disk but which is rewritable and has a storage density that is higher by several orders of magnitude.

Reliable and accurate manipulation of nanoparticles has been difficult to achieve in the past. This is due largely to a lack of understanding of the underlying phenomena, and to a lack of suitable control software. Detailed experimental studies of tip/particle/sample interactions during manipulation are very few [7]. Typical nanomanipulations are done blindly, i.e. without real-time information about the operation being performed. Being blind during the actual manipulation makes any attempt to understand the pushing process difficult, and no model for it has been published until now. While a few studies have obtained lateral-force signals during manipulation [8, 9], their focus was on elucidating sample properties rather than on gathering information about manipulation. The importance of real-time feedback has been recognized since the early times of STM manipulation in Eigler's group, which used acoustic feedback of the tunnelling current to help the operator move atoms and molecules. Recent work reviewed by Gimzewski [10] shows that the tunnelling current, which is the feedback signal in the STM, provides useful information about the progress and type

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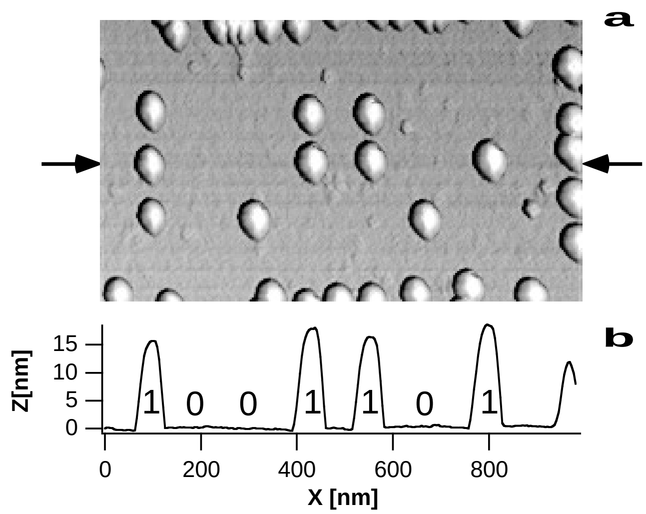

Figure 1. (*a*) The characters 'LMR' ASCII-encoded in rows of nanobits, and (*b*) the trace obtained by reading the second row with an AFM.

of STM manipulation operation (pushing versus pulling) being performed. The research described below shows that in AFM manipulation the simultaneous acquisition of the feedback signal (non-contact amplitude) and the cantilever deflection tells us much about the underlying physics and the temporal evolution of the operation.

Instrument errors such as creep, hysteresis, and thermal drift, lead to a manipulation environment with high spatial uncertainty, especially in ambient air and at room temperature. These errors must be physically eliminated (e.g. by operating at low temperatures), which leads to elaborate and costly procedures and equipment, or the control software must compensate for them, which is the approach taken in our work.

This report presents experimental results that provide new insights into nanomanipulation phenomena. It also shows that nanoparticle manipulation operations can be executed reliably with an AFM in ambient conditions, and can be monitored in real time, by using the strategies and special-purpose control software we have developed.

2. Experimental procedures

Our samples are prepared by exposing a mica substrate functionalized with poly-L-lysine to a colloidal solution containing gold particles with diameters of 15 or 28 nm. Details of the sample preparation are described elsewhere [11]. The AFM used for the experiments is a commercial AutoProbe CP from Park Scientific Instruments. The manipulation software is home written, and built upon the application programming interface provided by the instrument vendor. We use single-crystal silicon cantilevers with spring constants between 21 and 36 N m^{-1}, and supplied by Park, Digital Instruments and NT-MDT. Tip radii are approximately 25 nm.

The sample is imaged in non-contact mode, and a tilt correction is performed to ensure that the tip moves parallel to the substrate surface even with the feedback disabled. The user chooses the desired pushing path by drawing an arrow with the mouse over the previously acquired image. The control software automatically executes single line scans along the specified line segment and displays the corresponding topography. The operator translates the arrow until the displayed topography indicates that the path is centred over the particle to be pushed. (The latest version of our software automates this procedure by tracking the centroid of the selected particle.) This ensures that the pushing operation is successful, and corrects for creep of the piezo and thermal drift. The last step before actual pushing is to select on the line scan the points where the manipulation starts and ends. For the data reported here, the pushing protocol consists of disabling the feedback between the start and the endpoints, and is similar to a procedure published by Junno *et al* [12]. During the pushing scan, the signals of interest are acquired simultaneously by our probe control software.

3. Results

Figure 2 shows the data gathered in a typical pushing event. Curves (*a*) and (*b*) show the topography signal before and during manipulation. The feedback is turned off during pushing (curve (*b*)) and thus no topography information is available. We observe that after the feedback is turned on again, a portion of the particle is imaged (curve (*b*)). During the pushing process, we acquire the non-contact vibration amplitude (NC amplitude)† (curve (*c*)), and the DC tip deflection signal (curve (*d*)), by using our own probe control software. An additional line scan after the operation proves that the particle has indeed moved (curve (*e*)).

Analysis of figure 2, and of additional data obtained in similar experiments reveals the following.

• The particle does not move entirely beyond the selected point for enabling the feedback, which determines

† The AFM uses a phase sensitive (lock-in) amplifier to determine the NC amplitude. Measuring lateral forces, as in [7], would also be useful, but cannot be done in our instrument in the set-up needed for non-contact operation.

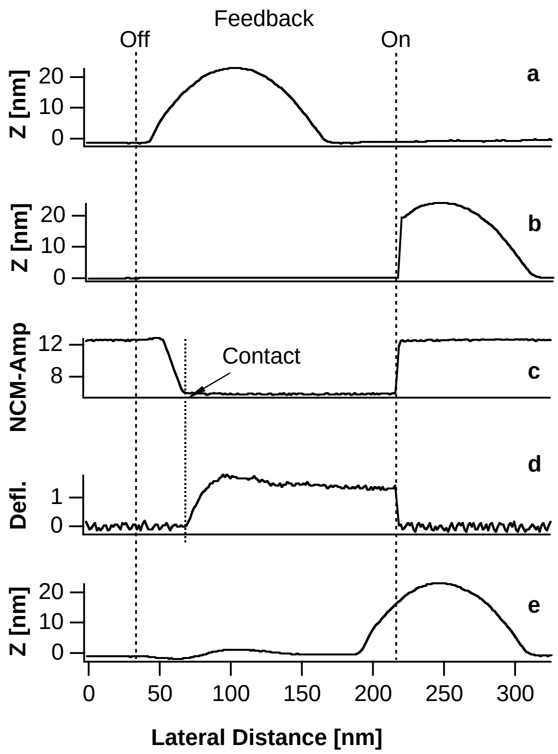

Figure 2. Data associated with a pushing event, as explained in the text. The vertical broken lines denote the points where the feedback is turned off and on.

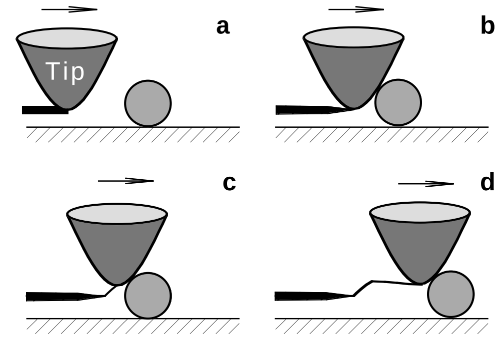

Figure 3. Schematic diagram of the relative motion of the tip and nanoparticle during manipulation. The full heavy line is the path of the tip apex, and the line thickness indicates the tip vibration amplitude.

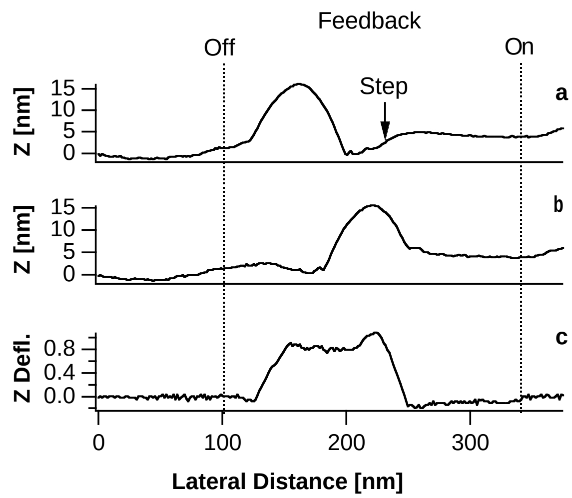

Figure 4. Pushing a particle against a step. Topography signal (*a*) before and (*b*) after pushing, and (*c*) cantilever deflection during pushing.

the end of the pushing operation—see curve (*b*). This effect must be taken into account by software that automates pushing operations.

- After the feedback is disabled, the NC amplitude stays constant until the tip is close to the particle.
- Within a few nm of this point, the amplitude decreases to a very small and constant value.
- When the NC amplitude reaches this low value, a change in tip deflection is observed, indicating that the tip is sliding up the particle (a few nanometres for the data shown).
- If the initial distance between tip and sample is too large, pushing does not occur, and the tip slides over the particle. A well defined cantilever deflection threshold for pushing can be determined.
- After the feedback is re-enabled, all the signals return to their values in imaging mode.

We suggest the following model to explain all these observations—see figure 3. (*a*) After the feedback is disabled, the tip moves parallel to the surface, and the NC amplitude as well as the cantilever deflection remain at their initial values. (*b*) As the tip approaches the particle, it starts to touch it intermittently, and the NC amplitude decreases until it reaches a very small value when the tip comes in continuous contact with the particle. The decrease is almost linear, as expected for a tapping tip [13]. Burnham *et al* also show that a small and constant-amplitude vibration is observed when the tip no longer lifts off the sample. Up to the point of uninterrupted contact, no change in cantilever deflection is detected, because of the small force and high spring constants of the cantilevers used. (*c*) After making contact, the tip starts to slide up the particle, and applies an increasing force, due to cantilever bending. The particle starts to move when the horizontal component of the force generated by the tip overcomes the sticking friction between particle and substrate. (*d*) Tip and particle then move together to a new location. After the particle moves a short distance, the cantilever deflection decreases, because sliding friction is lower than sticking friction. Re-enabling the feedback retracts the tip and stops the pushing process. This model also explains why we have never been able in our laboratory to move particles with soft cantilevers, and why we cannot image them in contact mode.

In a very few cases particles disappear from the observed region. These particles stick to the tip, as reported by Junno *et al* [12]. Therefore, considerable attractive forces exist, and the particles might be dragged, rather than pushed. To prove that this is not the case we pushed a 15 nm particle against a 5 nm step with the feedback disabled well beyond the step. The experimental data in figure 4 show that, for the selected parameters of operation, the particle's motion stops at the step. Figure 3(*d*) implies that the deflection signal should show that the tip climbs over the top of the particle, once the particle is stuck at the

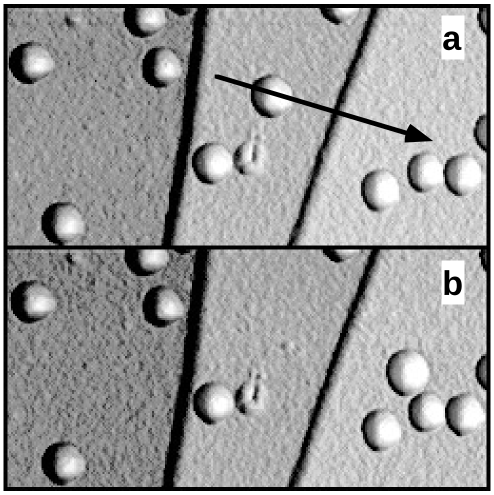

Figure 5. A 30 nm Au particle before (*a*) and after (*b*) being pushed over a 10 nm high step along the direction indicated by the arrow. Image sizes are both 1×0.5 μm.

step. This effect is observed in figure 4(*c*), and rules out dragging. It confirms earlier indirect evidence for pushing, which we obtained by varying the manipulation window without real-time feedback [7]. Experiments in which the driving piezo for the tip vibration is switched off while the feedback is disabled show no difference in pushing behaviour. Therefore, tip oscillation is needed only for non-contact imaging, and is not essential for the manipulation itself, as expected from the suggested model.

The pattern of figure 1 demonstrates the high accuracy and reliability that can be achieved routinely with our protocols. The Au balls are positioned with a precision of less than 10 nm. This is remarkably high, because particles do not snap into specific places on the substrate, unlike atoms or small molecules. Currently, our main source of error is the operator, and we expect to significantly increase the positioning precision by automating the pushing procedure.

All of the mechanical positioning and pushing work with an AFM or STM reported by other research groups until now has been limited to two dimensions, and steps of the substrate have been used mainly for alignment [14]. We used a stepped mica substrate to investigate pushing on uneven substrates, which might lead to applications in three-dimensional manipulation. Figure 5 shows a sample with a 10 nm high step, and colloidal Au particles with diameters of 28 nm. By choosing appropriate operation parameters, we were able to push a particle up the step without damaging the substrate. Step height and particle size are of the same order, and thus the experiment is a first step towards mechanical construction of three-dimensional structures.

We also have conducted other experiments using different substrates [16] or different pushing protocols [7, 15], pushing particles over protrusions [7, 15], and in liquid environments. Mechanical manipulation appears to be a technique of wide applicability.

4. Summary and conclusions

In summary, this paper shows that gold nanoparticles manipulated with an AFM on a mica surface are mechanically pushed by the repulsive forces between tip and particle. (Manipulation by pulling, which can be accomplished with an STM, has never been observed in AFM operations in our laboratory or elsewhere, as far as we know.) The pushing operations are performed by moving the AFM tip in non-contact mode against a nanoparticle with the feedback turned off. The cantilever vibration amplitude decreases as the particle is approached, and becomes essentially zero during pushing. The tip first moves upward, in contact with the particle, until the cantilever has flexed enough to exert the force necessary to move the particle. Then pushing begins, and continues until the feedback is turned back on. This breaks the tip/particle contact and restores the vibration amplitude. Monitoring simultaneously the non-contact amplitude and the cantilever deflection provides real-time feedback on the progress of the operation. We believe that this information, together with our new understanding of the phenomena and spatial reasoning techniques from the robotics field, will provide us with the tools we need in our current research on high-level programming of the AFM to automatically construct patterns with large numbers of particles, which are needed in many of the potential applications.

We demonstrate that patterns of colloidal Au nanoparticles can be accurately and reliably positioned by using our pushing protocols. Mechanical pushing is a versatile process, applicable to a wide range of environments and weakly coupled particle/substrate systems. Colloidal nanoparticles with a variety of characteristics (e.g. magnetic or semiconducting) are readily available. Automatic construction of patterns with these particles will open new avenues of research on nanostructures that exhibit interesting new behaviours, and have a wide range of applications, from nanoelectronics to biology.

Acknowledgment

The research reported in this paper was supported primarily by the Z A Kaprielian Technology Innovation Fund.

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