

Linking and Manipulation of Gold Multinanoparticle Structures Using Dithiols and Scanning Force Microscopy

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Rigid nanoscale 2D structures of up to four individual gold nanoparticles were formed by using bifunctional organic molecules (dithiols) in combination with scanning force microscopy manipulation. These structures can be either precisely translated by mechanical pushing across the surface or rotated about a specific axis. Experimental results are presented that show how simple geometric shapes can be manipulated and assembled to form more complicated structures. The nanoparticles were linked either by (i) forming a multiparticle structure and subsequent treatment with dithiols or by (ii) pushing together individual particles, which were treated with dithiols prior to manipulation.

Introduction

Assembly from molecular-sized components is one promising approach for the construction of nanostructures. Although regular, symmetric patterns of nanoparticles can be constructed by self-assembly,^{1–3} many of the possible applications require asymmetric shapes. Several methods have been proposed to construct such structures.^{4–7} Among these is a promising strategy using the SFM (scanning force microscope) as a manipulation tool to move nanoparticles and nanostructures without restrictions imposed by the physics of self-assembly.^{8–16} However, manipulation of nanoparticles with the SFM has been mostly limited until now to clearing areas on a surface or to moving single particles sequentially to create 2D patterns.^{10–16}

By connection of individual nanoparticles, it may be possible to construct relatively rigid structures, “primitives”, of arbitrary (planar) shapes. These, in turn, may serve as components for building complex nanoelectromechanical systems (NEMS). We have recently reported the successful linking and manipulation of a unit of two gold particles by using aminopropyltrimethoxysilane (APTS) polymers as the linking material.¹⁷ However, this technique requires an islandlike film of APTS and may not be applicable to particles with diameters of ~ 5 nm. Another method of linking adjacent gold nanoparticles involves using organic molecules with reactive functional groups at the end of the molecule. Linking of such particles that were arranged on a self-assembled, regular, 2D grid has been achieved experimentally by using dithiols.^{1,18,19} This suggests that gold nanoparticles in asymmetric patterns can also be connected provided that the distances between the nanoparticles are approximately equal to the length of the connecting elements. Furthermore,

by adjustment of the electronic properties of these molecules, it should be possible to tune the electrical properties of the structure itself.

In this study we demonstrate the successful construction of linked multiparticle structures by (i) pushing individual nanoparticles together and subsequently treating these structures with a mixture of dithiols and by (ii) pushing individual nanoparticles together that were pretreated with a mixture of dithiols. In both cases the resulting structures can be translated and rotated across the surface, proving that connection indeed occurred.

Experimental Methods

The experiments were conducted in air and at room temperature with an Autoprobe CP AFM (Park Scientific Instruments) operated in dynamic mode (with oscillating cantilever) using triangularly shaped silicon cantilevers (Park Scientific Instruments) with a spring constant of approximately 13.0 N m^{-1} and resonance frequencies around 180 and 340 kHz.

A previously described setup^{14–16} for nanomanipulation with an SFM was utilized to build 2D patterns by pushing individual nanoparticles together and to rotate and translate the linked multiparticle structure. In this setup, manipulation of the nanoparticles is performed by utilizing the probe control software (PCS), which has been developed in our group and built upon the application programming interface (API) provided by PSI. This software allows the user to take single line scans by setting an “arrow” in a previously recorded dynamic mode image. The arrow determines the direction and length of the scan line and can be moved by the operator in the *x*- and *y*-direction until the displayed topography indicates that its path is centered over the particle. To compensate for relative position drifts, a tracking tool based on the differential height between the particle and the surface can be activated to keep the arrow aligned at the center of the particle. Two bars are positioned along the scan line within which alternative operating conditions

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of the SFM, and therefore the “start” and “end” points of the manipulation, can be selected. In the experiments described in this work the feedback was turned off just before the tip was scanned across the particle and switched back on after reaching the desired lateral position. Once the tip hits the particle (with the feedback turned off), the oscillation of the cantilever breaks down and the tip climbs up on the particle until a particular deflection (loading force) of the cantilever occurs. At this point, the force at the tip generated by the cantilever overcomes the adhesive force of the particle at the substrate and the particle is pushed. The cantilever was driven at the low frequency because studies of the tip–sample distance in dynamic force microscopy revealed that the tip is much closer to the surface when operating at the lower frequency.²⁰ Therefore, the cantilever deflection needed to successfully push a particle can be achieved under the best imaging conditions just by switching the feedback off.^{15,16}

The sample was prepared by depositing gold colloidal particles (EM.GC15; Ted Pella Inc.) with a diameter of 27 nm from aqueous solutions on a silicon/gold grid that had been previously treated with poly-L-lysine. Prior to deposition of the nanoparticles, the grid was successively rinsed with deionized water, acetone, and methanol. The use of the grid was necessary to return to the desired, assembled nanostructures, which were built prior to dipping the sample into dithiol solution.

A dithiol coating of the nanoparticles was prepared by dipping the sample into a dilute solution of the dithiols in ethanol (containing 1.0 mM 1,6-hexanedithiol, 1.0 mM 1,8-octanedithiol, and 1.0 mM 1,9-nonanedithiol, all commercially available from Aldrich) for 18 h, followed by rinsing with ethanol and drying with nitrogen gas. The coated nanoparticles and nanostructures were then manipulated by using SFM.

Results and Discussion

Two procedures were used to achieve and prove linkage between nanoparticles in the nanostructures assembled by SFM manipulation. The first procedure involved pushing of arbitrarily deposited nanoparticles in order to form the desired structure and subsequent treatment with dithiol solution. Manipulation of the (now) linked structures completed this procedure. The second procedure involved dithiol treatment of arbitrarily deposited nanoparticles, before any manipulation, and then subsequent pushing of the dithiolated nanoparticles to form linked nanostructures upon contact of the nanoparticles. Again, manipulation of the linked structures completed this procedure.

The sequence of top-view images in Figure 1 reveals the construction of a three-particle structure and its successful manipulation as a unit utilizing procedure 1. The scan area in all images is 800 nm × 800 nm. Figure 1A shows the topography of a region of the sample before manipulation. Three particles with a diameter of approximately 27 nm and marked with the numbers 1, 2, and 3 can be observed. Figure 1B records the pushing of particle 2 against particle 3. To show that no connection occurs by simple contact between the two particles, particle 2 was pushed away from particle 3 afterward as displayed in Figure 1C. Following the subsequent pushing of particle 1 and particle 2, Figure 1D shows the resulting three-particle unit. The two-particle unit consisting of particles 4 and 5 was assembled previously from individual particles.

After construction of the multiparticle structures, the sample was treated with the dithiol solution. The use of a silicon/gold grid as substrate enabled us to image the same sample position as that used for the assembly processes in order to study the effect of the dithiol treatment on the multiparticle structure. Parts

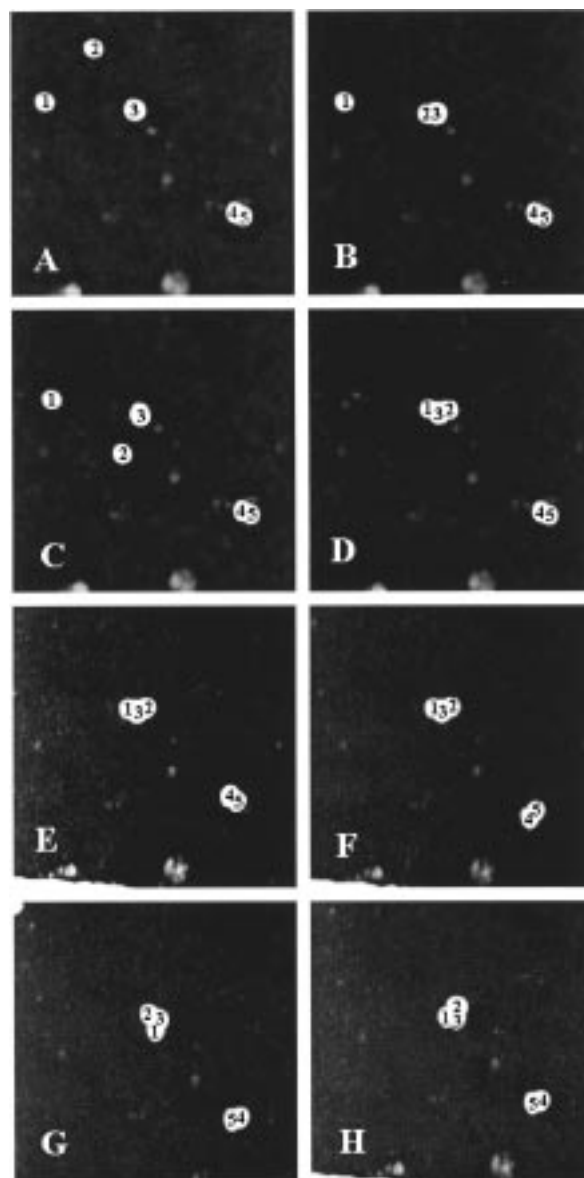


Figure 1. (A–H) Sequence of 800 nm × 800 nm SFM images showing the manipulation of a three-particle structure built of three individual gold particles marked as 1,3,2 and the two-particle unit 4,5 (A–D) before and after treatment (E–H) with dithiols. Part A shows an SFM image of the surface area before manipulation, and parts B–D show the SFM images recording the construction of the three-particle unit 1,3,2. Parts E and F display the successful manipulation of the two-particle unit 4,5, while parts G and H record the successful manipulation of the three-particle structure 1,3,2 after linking of the structures with dithiols.

E and F of Figure 1 record the successful rotation of the two-particle structure, while parts G and H of Figure 1 display successful rotation of the three-particle unit. Prior to the dithiol treatment the particles could easily be separated (Figure 1C), whereas after treatment the composite structure can be manipulated. This clearly shows that linkage due to the dithiol molecules occurred. This is further supported by experiments showing that the nanoparticles used in this study can be transferred from an aqueous phase to an organic phase (toluene or hexane). The Au colloids are nominally capped by a chlorine shell. While both phases with the organic phase containing 1-dodecanethiol (laurylmercaptan C₁₂H₂₅SH) or 1-dodecylamine (laurylamine C₁₂H₂₅NH₂) are stirred, this shell is displaced by the formation of an uncharged alkane shell around the particles that transfers them to the organic phase.

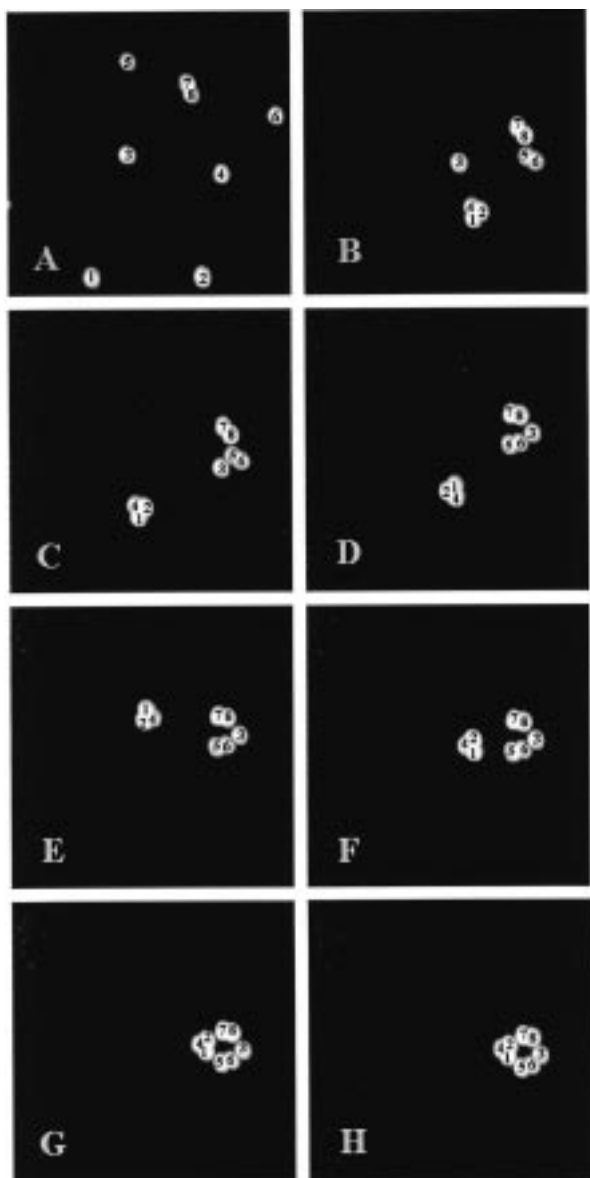


Figure 2. (A–H) Sequence of $800 \text{ nm} \times 800 \text{ nm}$ SFM images showing the construction of a ringlike structure by manipulating single particle 3, two two-particle units 5,6 and 7,8, and three-particle unit 1,2,4. The multiparticle units were formed and linked with single gold cluster covered with dithiols before manipulation.

The strategy of creating a multiparticle structure first and subsequently treating it with dithiol solution resulted in linkage of the structures. The next set of experiments answers the question affirmatively, whether individual nanoparticles first treated with dithiol solution can be linked by subsequent nanomanipulation too (procedure 2). The series of images in Figure 2 shows the successful linkage and manipulation of two two-particle units and one three-particle unit into a larger structure. The scan area in all images is $800 \text{ nm} \times 800 \text{ nm}$. Figure 2A displays the surface area before manipulation. Six individual particles marked by numbers 1–6 and one previously assembled two-particle unit marked by numbers 7 and 8 can be observed. Following several manipulation steps Figure 2B records the construction of a triangular unit (1,4,2) and a second two-particle unit (5,6). Figure 2C displays the result of pushing the trimer horizontally to the left and the individual nanoparticle 3 to the right. Following several manipulation steps including translation and rotation of trimer 1,4,2 and dimer 5,6 recorded in parts D and E of Figure 2, parts F and G of Figure 2 illustrate

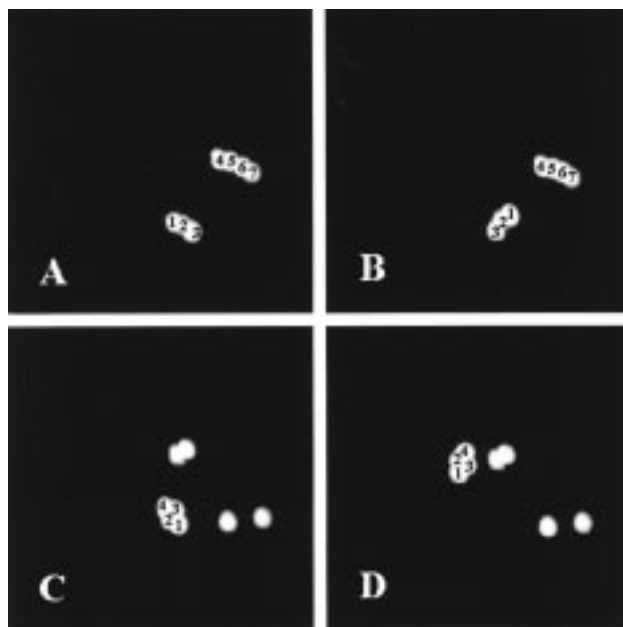


Figure 3. (A–D) Sequence of $800 \text{ nm} \times 800 \text{ nm}$ SFM images. Parts A and B show the manipulation of a three-particle line of particles attached to each other with dithiols, while parts C and D display the manipulation of a diamond-shaped four-particle structure.

the precision of the manipulation process. A close look in parts G and H of Figure 2 reveals that the trimer and the single nanoparticle displayed in Figure 2g are each translated only a couple of nanometers, resulting in the asymmetric, ringlike structure recorded in Figure 2h. A subsequent attempt to move the whole structure (not shown) failed and resulted in the separation of the trimer, the two dimers, and the single nanoparticle. Since the diameter of the particles is around 27 nm and the chain length of the dithiols used in this study varies between approximately 1.3 and 1.8 nm, it is not surprising that only structures with a small number of particles can be translated as a whole.

The ability to manipulate composite structures depends also on the geometry of the structures. Besides a two-particle unit, trimers shaped like a bow and a triangle could be translated. Figure 3 reveals that it is also possible to manipulate a trimer shaped as a line and a four-particle unit shaped as a diamond. Figure 3B records the rotation of the three-particle line 1,2,3 of Figure 3A. However, the four-particle line 4,5,6,7 could not be rotated as whole, resulting in fragments of two two-particle units (not shown). A single nanoparticle could also be separated from a line of three particles by choosing certain pushing angles. In contrast to the four-particle line in parts A and B of Figure 3, the four-particle unit 1,2,3,4 shaped like a diamond displayed in Figure 3C could be translated and rotated, as recorded in Figure 3D. The particle interactions in the triangle- and diamondlike units stabilized the units significantly, as one might expect from elementary, structural considerations.

Conclusions

The results presented here significantly extend the previously reported capabilities for the manipulation of nanoparticles using the tip of a scanning force microscope under ambient conditions. Multiparticle nanoscale 2-D patterns can be assembled from single gold nanoparticles and connected by using double-functional organic molecules (dithiols). The resulting structures can be precisely translated by mechanical pushing of these across the surface; they can be rotated about a specific axis, and they

can be assembled with other structures to build more complicated objects. This opens new avenues of research on the construction of complex nanoelectromechanical systems (NEMS). The results further imply that using nanoparticles with smaller diameter will increase the number of nanoparticles in stable, movable structures and will also reduce the length scale of possible artificial nanoassemblies.

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