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Fabrication of Polystyrene Latex Nanostructures by Nanomanipulation and Thermal Processing

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ABSTRACT

The capability to fabricate nanoscale structures is a fundamental step toward realizing the promise and potential of nanotechnology. We report on precise manipulation and thermal processing using 100-nm polystyrene latex nanoparticles. This approach is illustrated by fabricating a three-dimensional nanostructure by using an AFM tip to position nanoparticles and then thermally processing to "sinter" the particles to form a contiguous, stable structure. We suggest that this is a general approach, but the use of polystyrene latex particles offers an advantage of low-temperature processing. Use of polystyrene latex also extends the range of materials for which we have demonstrated manipulation and suggests applications including fluorescent doping and electrically conducting polymers.

Introduction. In the past few years we have seen dramatic advances in the tenacious pursuit of creating nanoscale materials and structures with the hope of eliminating our dependence on limiting, "top down" technologies such as high-resolution lithography.[1] With the advent of the scanning tunneling microscope (STM)[2] and in particular the atomic force microscope (AFM)[3] as tools for both imaging and manipulation, controlled positioning of single, submicron particles is possible. While most of the focus has been on synthesizing metallic nanowires,[4,5] structures from polymers hold substantial promise. Small polymer particles have interesting properties that give them an advantage over their larger counterparts. For instance, nanoscale polymer particles respond faster to environmental changes because of their small size and higher surface-to-volume ratios.[6] Polymer particles with functionalized surfaces could aid in the fabrication of nanoscale devices and add interesting sensing,[7] electrical,[8] and fluorescent[9] properties.

Polystyrene (PS) is of particular interest because it has been extensively studied and is readily available. Several groups have demonstrated the ability to manipulate polystyrene particles with sizes on the scale of 0.5 microns or larger. For example, Kim and Lieber[10] reported on manipulation of 500-nm polystyrene clusters with the use of carbon nanotube nanotweezers. Sitti and Hashimoto[11] demonstrated positioning of polystyrene latex particles with diameters between 0.5 and 1 μm with an accuracy of ± 30 nm using the tip of an AFM while imaging with a scanning electron microscope (SEM).

The ability to manipulate single PS particles has led researchers to consider it as a promising candidate for nanostructure building blocks. Recently, linking of adjacent polystyrene latex beads by thermal processing has been demonstrated. Yi et al.[12] have fabricated submicron sized wires by means of sintering densely arrayed colloidal nanoparticles on patterned substrates using 500-nm diameter polystyrene latex beads that were organized and "sat" along groves, held there by lateral capillary forces. As with previous groups, SEM was used for imaging, which limited height information of structures during and after the sintering process.

Here, we report on the precise manipulation of polystyrene latex particles smaller than 100 ± 20 nm in diameter adsorbed on a Si substrate. When sintering above the glass transition temperature (T_g) of PS, the particles exhibited a significant (50 ± 10%) reduction in height and became strongly attached to the substrate. By using AFM manipulation, we studied and characterized the formation of several sintered, two-dimensionally shaped nanostructures. Finally, we constructed a rudimentary three-dimensional nanostructure by pushing a particle on top of a prefabricated sintered island structure. By eliminating the need for a template, we allow for greater control of the desired nanostructures and fabrication of arbitrary shapes.

Experimental Methods. All samples were prepared on a Si (100) substrate with uniquely patterned gold features that

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were fabricated by electron-beam lithography, in order to examine identical surface areas before and after sintering. Fluorescent polystyrene (PS) beads (Molecular Probes, 100 ± 20 nm in diameter) with pendent carboxylic acid functionalized groups at the surface were deposited on a thin (1−2 nm), Poly-L-lysine (PL)-coated substrate of Si (100) with its native SiO_2 surface layer. After sonicating the samples for 10 min in acetone, isopropyl alcohol, and methanol consecutively, we placed the sample in an UV/ozone chamber for 10 min to oxidize any organic residue. PL deposition (5 min of deposition followed by annealing at 120 ± 2 °C for 30 min) was followed by PS (1:1000 dilution) deposition for 5 min on the sample to achieve low particle coverage. Imaging and manipulation of the deposited nanoparticles was achieved with the use of an Autoprobe CP scanning probe microscope (SPM) from TM Microscopes operated in noncontact mode in air with a triangularly shaped silicon cantilever (TM Microscopes, 13.0 Nm^{-1} spring constant, and 340 kHz resonance frequency). The particles were manipulated by using USC's Probe Control Software (PCS) to form a desired structure. Then, the samples were heated in an oven for 10 min at 160 ± 2 °C.

Results. We chose polystyrene (PS) as a "building block" because of its relatively low glass transition temperature (T_g), availability, and ease of modification. In addition, submicron PS particles exhibit physical properties not inherent in the bulk because of a higher surface area that subsequently lowers their T_g and melting point. SPM is an ideal analysis tool for such small systems because of its precision and its ability to work in ambient conditions without the need for elaborate vacuum and cooling systems.

Figure 1a shows an AFM image of randomly deposited polystyrene latex nanoparticles. As an imaging tool, the AFM provides more than just topographic information; it can provide insight into the chemical nature of the surface. For example, the AFM can measure lateral forces as the tip is dragged across the surface and, thus, study friction on an atomic and molecular level.[13] In addition, it can provide information on adhesion and binding phenomena by measuring the force needed to break contact between the tip and sample.[14] If there is insufficient force binding particles to the substrate, then the particles will move when imaged by the tip of the AFM. In our case, the carboxylate-modified surface of the PS nanoparticles provides an electrostatic attraction to the amine functional groups of the PL layer, and the PS particles are stable, i.e., are not displaced laterally, when imaged.

As a manipulation tool, the AFM can provide useful information about physical characteristics such as hardness or softness of individual particles or whether two particles are physically bonded or just adjacently located and "in contact". For instance, when pushing two particles close together with the feedback off (the manipulation procedure is described in ref 15) for too long, we observed that the particles would become "entangled" and act like a dimer unit or that the particle being pushed would deform the other, behaviors indicating that the polystyrene latex nanoparticles were soft and malleable. This can be explained by a relatively low degree of cross-linking between the PS polymer chains.

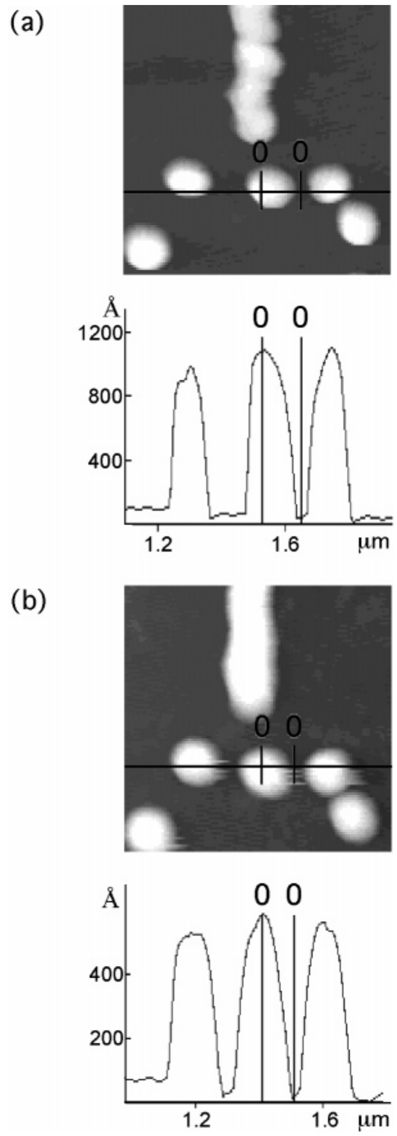

Figure 1. AFM images of PS single particles (a) before and (b) after sintering at 160 ± 2 °C for 10 min. The height scale is 120 and 60 nm from black to white (above the height threshold) for images (a) and (b), respectively.

We used the AFM in our experiments to analyze such physical characteristics before and after thermal processing. Effects of heating randomly deposited particles at 160 ± 2 °C are shown in Figure 1b. Measurement of the height of the center particle, as shown in the line scans in Figure 1 showed a 54 ± 1% reduction in height, while the width showed only a ± 10% change. Although convolution of the AFM tip in the image diminishes precise quantitative analysis in the *x-y* plane,[16] particle height measurements are accurate. The height reduction indicates that the polymer structure reorganized into a more densely packed configuration. One expects that polymer chain reorganization would become facile at temperatures above the T_g, where kinetic barriers for chain migration and rearrangement can be overcome to lower the total free energy of the system and reduce the nanoparticle surface area. For larger polystyrene clusters, a value of the T_g of 98 °C has been observed, but solvent hydration and reduced particle size would be expected to lower the T_g for our PS nanoparticles to below this value. Similar height reductions of single particles were also observed at baking temperatures at or above 100 °C (at or above the T_g) for heating times longer than 10 min.

In addition to the volume change observed because of heating, the polymer particles were more strongly adhered to the PL layer. It was no longer possible to push the particles with the tip of the AFM without deforming the spherical shape or disrupting the nanoparticles (smearing the polymer chains across the substrate). We think that this anchoring stems from condensation reactions between the carboxylic acid groups on the PS surface and amine groups of the PL to form strong amide linkages. This physical stability imparted by thermal treatment proved important for construction of a layered, three-dimensional structure, as described below.

We also examined the effects of heating constructed structures from PS nanoparticles, seeing if they behaved as did single particles. Polystyrene latex nanoparticles were manipulated using the AFM operating in noncontact mode in air as previously reported for manipulation of Au nanoparticles using our PCS.[15] Figure 2b shows the results of manipulation of eight randomly deposited polystyrene latex nanoparticles (Figure 2a) to form a line. This "nanowire", nearly 1 μm in length, had an average peak height of 100 ± 20 nm. The wire structure showed increased stability, i.e., the constituent nanoparticles could not be removed easily (without deformation) from the structure using the AFM tip. Entanglement of polymer chains across the bead−bead interface, as mentioned earlier, could explain this observation. Measurements of the distance between the highest points of adjacent particles were 90 ± 5% of the sum of the radii of the nanoparticles, which indicates that adjacent particles were in contact with one another. Figure 2c shows the same structure after sintering at 160 ± 2 °C for 10 min. It is no longer possible to discern individual particles. The height showed a reduction to a more uniform value of 62 ± 5 nm, although the length remained within 95 ± 5% of the initial value. This methodology for creating wires attains uniform, thermally stable nanowires of a desired length and width in multiples of the diameter of the constituent building blocks.

Structures with more arbitrary, curved forms were also investigated. Figure 3a shows such a structure, constructed from nine polystyrene latex particles with diameters of 100 ± 20 nm. By comparing the sum of the radii of two adjacent particles with the distance between peak maxima determined by peak height measurements, we concluded that particles were "in contact" with neighboring particles, although the dimers at the ends of the structure apparently have less surface area contact with the five-member backbone than between the members of the dimers or backbone themselves. Figure 3b shows the affects of heating this structure at 160 ± 2 °C for 10 min. The structure split into three parts, corresponding to the two dimer units and the main five-member unit.

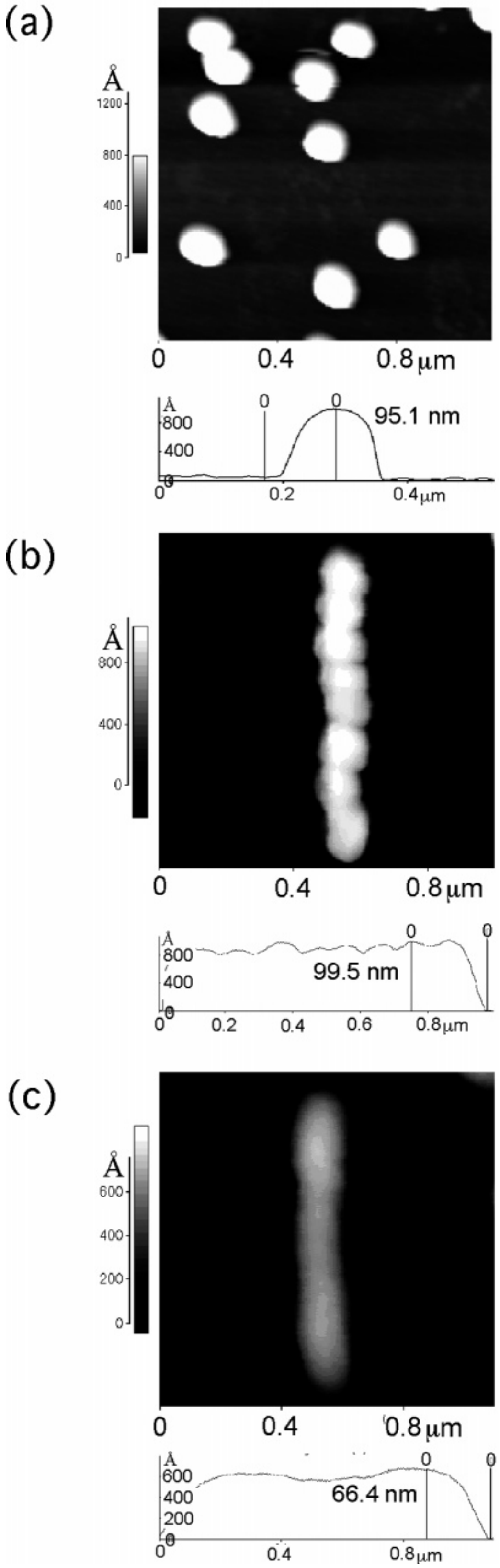

Figure 2. (a) Randomly deposited latex nanoparticles, 100 ± 20 nm in diameter, (b) eight-member, 1-μm long wire after manipulation with an AFM, (c) after sintering for 10 min at 160 ± 2 °C. Height measurements of the wire are 62 ± 5 nm from peak to baseline.

As a practical matter in creating curved structures, a large (or reasonable) radius of curvature may be necessary to avoid

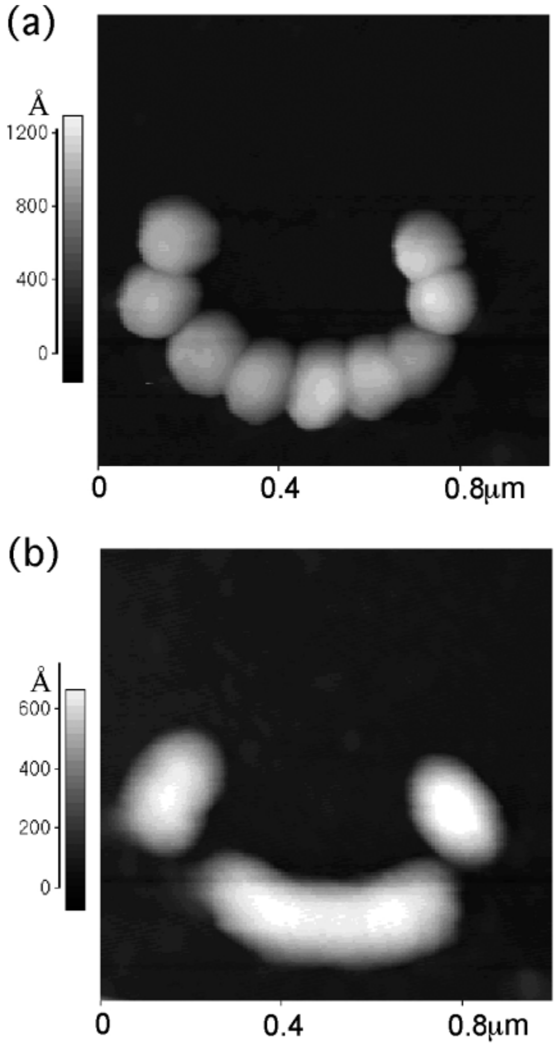

Figure 3. (a) AFM image of nine, 100 ± 20 nm, latex particles manipulated into a curved 'C' structure prior to sintering. Image (b) shows the effect of sintering at 160 ± 2 °C for 10 min. Cross-section measurements show a 40 ± 10% reduction in height.

subsequent separation. If manipulation does not cause sufficient surface-area contact, not enough minor chains will cross the bead−bead boundary to provide enough force to hold the particles together. Because tee-structures have added stability at the tee-junction due to neighboring particles, we would predict that they would be more likely than, e.g., 45° bends, to stay intact after sintering. As with the line structure in Figure 2, this structure showed an approximately 50% reduction in height.

Understanding the mechanism involved in forming these thermally stable wires would provide insight into the optimal conditions for creating them with improved control. Previous work has reported on the sintering mechanism at the bead-bead interface for large, 500-nm diameter beads.[12] At temperatures above the T_g, the polymer chains have sufficient mobility that, as time increases, the minor chain lengths of the polymer increase and eventually cross the bead−bead interface until the boundary disappears. Then, the chain migration region expands from the surface to the center of the bead and the neck expands due to viscous flow. One can imagine that a similar mechanism exists for smaller beads, such as the ones studied here, but that even a lower thermal processing temperature suffices to provide the energy for chain migration.

We discovered that larger structures comprised of particles with varying numbers of neighbors exhibited different characteristics upon sintering than wires, which differ in that each particle has a nearly identical environment with two neighbors on either side. When larger, close-packed 2-D structures were sintered, these structures did not show any noticeable reduction in peak height when given the same heat treatment as their single-particle or wire counterparts, as shown in the upper left panel of Figure 4. This is because particles in the center of structure have a larger number of nearest neighbors than particles on the edge, with six or seven surrounding particles instead of two or three. Neighboring particles help to stabilize the center particles, reducing the driving force for reorganization. As the temperature rises above the T_g, the agglomerate takes on a dome-like shape with a steep rise at the edges and maximum height at the center, as shown in the three-dimensional rendering in the lower right panel of Figure 4. This shape arises from the dual constraints of minimizing the particle surface area and maximizing the interactions with the PL substrate.

Taking advantage of the physical stability of islands formed by 2-D manipulation and sintering, a rudimentary three-dimensional structure was built by depositing a second layer of polystyrene latex particles on a preannealed sample, which contained a 2-D island, and then pushing a new particle on top of the island. Figure 5 illustrates this process. Once on top of an island, lone particles were stabile when imaged, but could still be manipulated subsequently with the tip of the AFM. Short heating times permanently fixed the top particle to the underlying island surface, and long heating times caused the particle to merge into the island structure as shown in Figure 5e.

In another experiment, we attempted to use this approach to fabricate fluorescent nanostructures by manipulating and sintering particles that had been doped with a fluorescent dye. Sintering at 160 °C for 10 min greatly reduced the fluorescence, limiting this procedure. Presumably, the fluorescent dye molecules agglomerate during heating and fluorescence is lost due to self-quenching.

Outlook. The promise of this approach for nanofabrication has been demonstrated, but further studies optimizing conditions for thermal processing and sintering based on temperature control or solvent type would be helpful. By changing the surface functionality of the particles or substrate layer, different behaviors might be exhibited. Because polystyrene is readily available, such studies can be done inexpensively and without complicated synthesis techniques. This approach could also be extended to make conductive nanowires by the use of conducting polymer beads. Generally, polymer nanoparticles require much lower temperatures to sinter than do metallic nanoclusters, and this could offer an advantage for nanofabrication. Also, the fluorescent response of sintered polystyrene latex structures may be enhanced by a more careful selection of the polymer and dye components. Finally, more complex three-dimensional structures with a height of

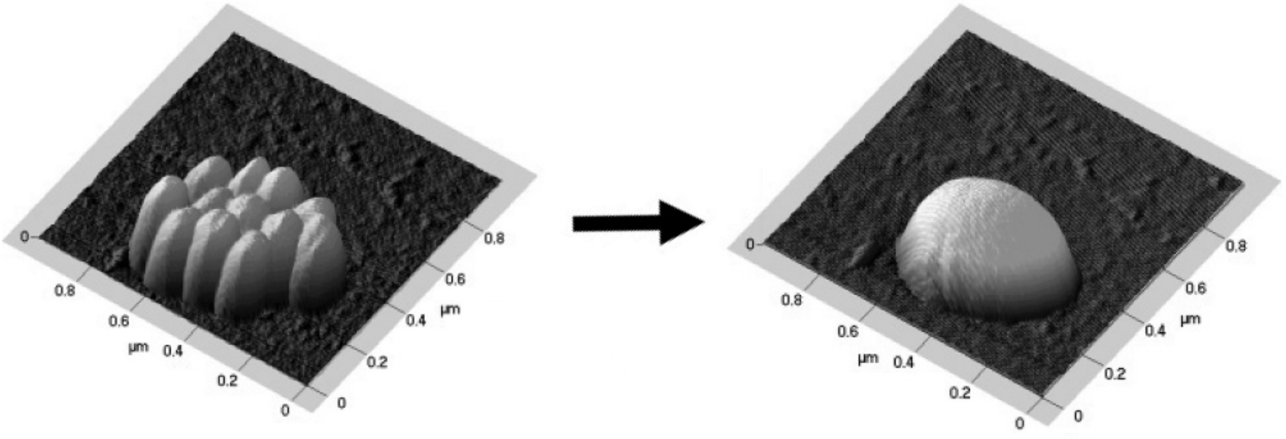

Figure 4. 3-D rendered image of the effects of sintering on a closely packed structure (upper left) to a stable island (lower right). AFM cross-sectional analysis show that the peak height of the structure prior to sintering was 100 ± 20 nm with a length of 600 ± 50 nm along its major axis and 400 ± 50 nm along its minor axis. After sintering the peak height was measured at 100 ± 5 nm with a length of 450 ± 50 nm along the major axis and 300 ± 50 nm along the minor axis.

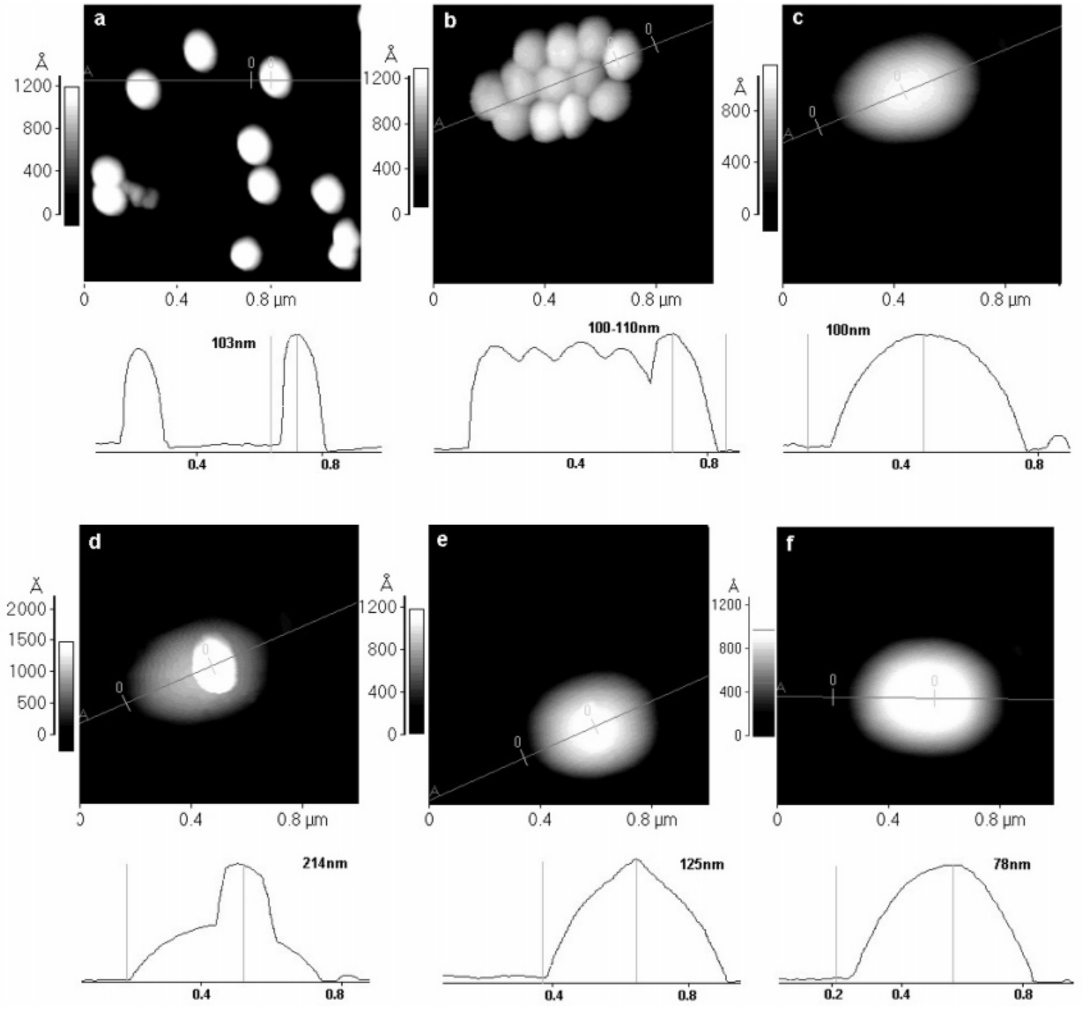

Figure 5. Sequence of AFM images showing the construction of a 3-D nanostructure: (a) randomly deposited particles, (b) after manipulation, (c) after sintering at 160 ± 2 °C for 10 min, (d) after a single particle is “pushed” on top of the island, (e) resintering (10 min), (f) resintering (24) h.

300−500 nm comprised of many (3−5) layers seems quite feasible using this approach for layered nanofabrication.

Conclusion. We report on the use of an AFM as a tool for manipulating and analyzing the physical properties of polystyrene latex nanoparticles smaller than 100 nm. We investigated the changes in morphology of individual particles and two-dimensional structures formed by manipulation of several particles due to sintering, caused by heating above the glass transition temperature of PS. AFM manipulation is precise enough to construct small structures with arbitrary size and shapes with straight and curved features. Heating above the T_g causes a reorganization of the polymer chains into a more densely packed form, decreasing the height of individual particles and structures formed by particles in contact. Thus, PS nanolines of uniform height and width were constructed. These were physically quite stable after sintering. More complex structures can be constructed, but a high degree of interparticle contact is needed for the structure to be retained during heating. By taking advantage of the additional physical stability imparted to a compact island of particles by thermal processing, a simple three-dimensional layered nanoassembly was demonstrated by manipulation, i.e., “pushing” a single particle from the surface layer to the top of a sintered island.

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