

# Directly Monitoring the Growth of Gold Nanoparticle Seeds into Gold Nanorods

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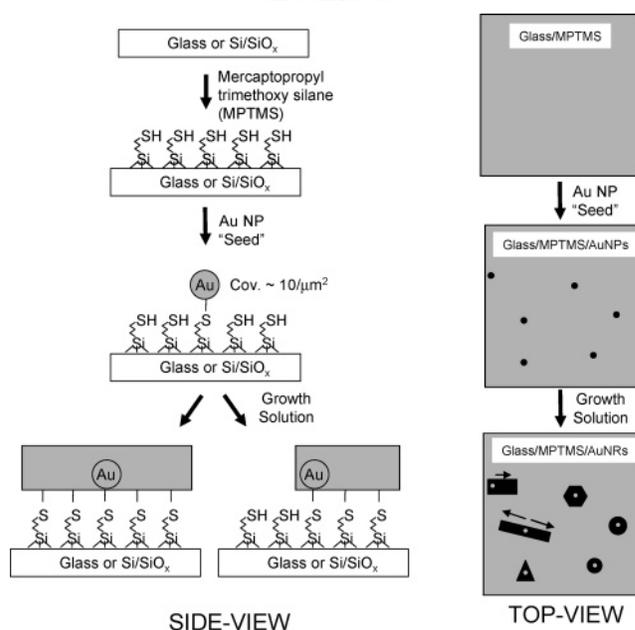
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This paper describes the use of atomic force microscopy to directly image surface-attached 3–5 nm diameter gold nanoparticle seeds before and after seed-mediated growth into gold nanorods (Au NRs) and other shapes (spheres, triangles, and hexagons). Results show that Au NRs form from seeds growing in either one or two directions. A direct correlation exists between seed diameter and NR diameter; small diameter seeds form small diameter NRs. However, correlation between seed diameter and nanostructure shape or NR length is less evident. We describe our results in terms of growth mechanisms proposed in the literature and discuss possible reasons for the large size dispersity observed for surface-grown Au NRs. A better understanding of Au NR and other metal and semiconductor one-dimensional (1D) growth processes is necessary to improve synthesis, tailor their properties, and utilize 1D nanostructures for useful technological applications.

One-dimensional (1D) metal and semiconductor nanostructures<sup>1</sup> have been gaining widespread interest because of their unique structure, size-dependent properties, and potential applications in nanoelectronics, chemical sensing, mechanical devices, and plasmonics. Obtaining high yields and low size dispersity are major challenges that need to be overcome in order to pursue fundamental and applied studies on these materials. Microscopic techniques are useful for directly monitoring and gaining a better understanding of 1D growth processes.<sup>2</sup>

In this paper, we describe the use of atomic force microscopy (AFM) to directly monitor surface-confined gold nanoparticle (Au NP) “seeds” growing into 1D gold nanorods (Au NRs). This research is motivated by the work of Murphy and co-workers who synthesized Au NRs with controlled aspect ratio (AR) in aqueous solutions using a simple seed-mediated growth method.<sup>3,4</sup> Their method was later extended to the growth of Au NRs directly on surfaces,<sup>5,6</sup> where the length and AR were controlled synthetically.<sup>6</sup> Generally, the NRs suffer from low yields and large size dispersity, although recent variations have led to higher yields for low AR Au NRs grown in solution.<sup>7,8</sup> The work described here is significant because by direct monitoring of seeds, we reveal important mechanistic details about the growth process that are unobtainable with transmission electron microscopy (TEM) and UV–vis spectroscopic data commonly obtained on NR samples grown in solution.<sup>9,10</sup> A better understanding of the growth mechanism is needed to improve yields, lower

## Scheme 1. Procedure for Growing Au NRs Directly on Surfaces



size dispersity, and synthesize a wider range of lengths and ARs. This would enable fundamental studies of structure–function relationships and the development of new, exciting applications, especially since Au NRs have been shown to exhibit size-dependent optical<sup>7</sup> and mechanical<sup>6</sup> properties, interesting thermal behavior,<sup>11</sup> surface Raman scattering<sup>12</sup> and fluorescence<sup>13</sup> enhancement of molecules, and wave guiding properties.<sup>14</sup>

**Procedure for Growing Au NRs on Surfaces.** Au NRs are grown directly on surfaces as previously described (Scheme 1).<sup>6</sup> First, a Si/SiO<sub>x</sub> substrate is functionalized with mercaptopropyltrimethoxysilane (MPTMS) by plac-

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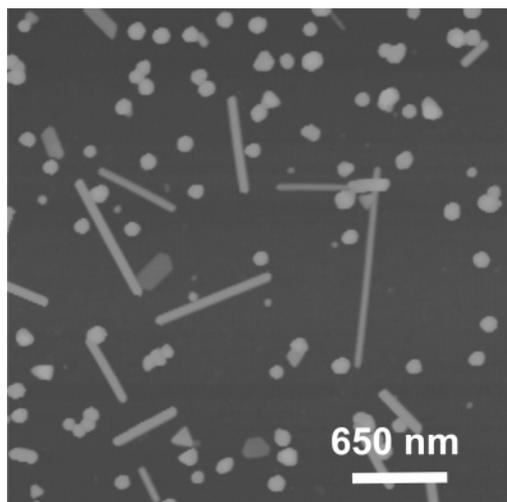
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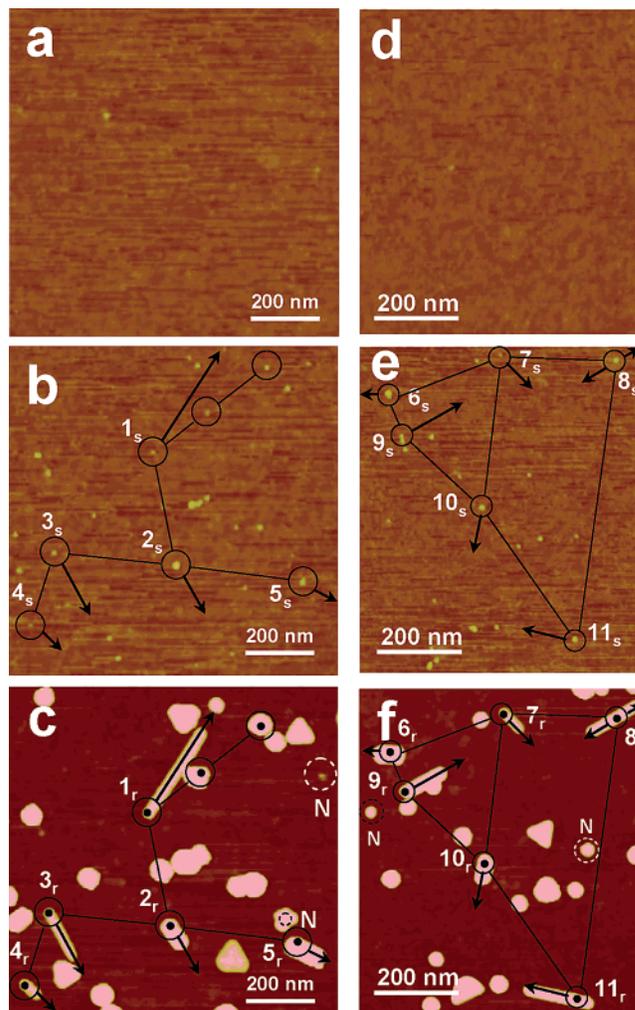
**Figure 1.** Au NRs grown directly on a Si/SiO<sub>x</sub> substrate for 60 min using the procedure in Scheme 1. The Z-range is 200 nm.

ing the sample into a solution containing 10 mL of 2-propanol, 100  $\mu$ L of MPTMS, and a few drops of water and heating just below boiling for 30 min. The substrate is rinsed with 2-propanol, dried with N<sub>2</sub>, and functionalized with 3–5 nm diameter Au NP seeds by placing the substrate into an aqueous seed solution<sup>6</sup> for 20 min. After rinsing with water, the Au-seeded surface is then placed into a “growth solution” containing 9 mL of 0.1 M cetyltrimethylammonium bromide (CTAB), 450  $\mu$ L of 0.01 M AuCl<sub>4</sub><sup>-</sup>, and 0.05 mL of 0.1 M ascorbic acid (AA) for various times.<sup>6</sup> An AFM image of a typical sample prepared this way is shown in Figure 1 (growth time = 60 min). The Au NPs grow by seed-mediated growth into larger structures, such as rods, spheres, triangles, and hexagons. The yield of NRs is 5–15%, and the size dispersity is 25–30%.<sup>6</sup> We previously showed that the NR length and AR increase with increasing HAuCl<sub>4</sub> concentration in the growth solution, allowing us to vary the average length between 200 and 1200 nm and the AR between 6 and 22 synthetically.<sup>6</sup>

There are several unanswered questions regarding the seed-mediated growth of Au NRs. Why do certain seeds grow into NRs, hexagons, and triangles, while most grow into spheres? What causes the large size dispersity for the seeds that grow into NRs? Why do they grow at such different rates and with different lengths and diameters? Current growth models do not provide explanations for these questions, and the mechanism is still not fully understood. We feel that the initial seed structure plays an important role in the growth process. In an attempt to better understand the role of the seed in the growth mechanism, we monitored the growth of individual seeds for two different times (20 and 60 min) with AFM, keeping the concentration of HAuCl<sub>4</sub> in the growth solution constant at  $4.5 \times 10^{-4}$  M (450  $\mu$ L).

#### Direct AFM Monitoring of Seeds Grown for 20 min.

Figure 2 shows AFM images obtained on the same area of a Si/SiO<sub>x</sub>/MPTMS substrate throughout the growth procedure described in Scheme 1. Figure 2a shows the initial Si/SiO<sub>x</sub>/MPTMS substrate, and Figure 2b shows the same area after functionalization with 3–5 nm diameter Au NP seeds. The bright dots represent the Au NP seeds as confirmed by height analysis. Figure 2c shows the same area after the seed surface was placed in growth solution for 20 min. Figure 2d–f shows the same sequence of images on another area of the same surface. The circles are used to indicate various seeds before growth, and cir-



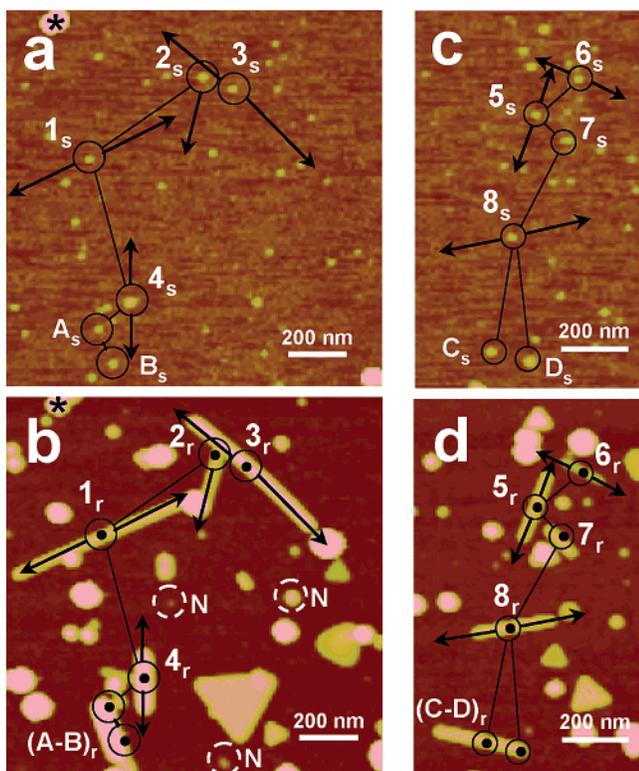
**Figure 2.** AFM images of Si/SiO<sub>x</sub>/MPTMS (a) before seed deposition, (b) after seed deposition, and (c) after NR growth for 20 min. Frames d–f show another region of the same sample. The Z-range is 20 nm in all images.

cles with dots show the original placement of the seeds after NR growth. These images directly confirm that the growth of NRs and other structures mainly originates from Au NP seeds, as expected for seed-mediated growth. Occasionally a new structure (labeled “N”) appears that cannot be correlated with a seed, but this accounts for less than 5% of all nanostructures. Seeds that grow into NRs are numbered in the images with subscript “s” and the resulting NRs are numbered with subscript “r”. The position of the seed with respect to the resulting NR shows that most of the seeds grow in one direction. This is true for every seed in these images, except for 8<sub>s</sub>, which grows in two opposite directions. This is a surprising result considering recent growth models, which are consistent with two-directional growth.<sup>9,10,15</sup> By growing NRs directly on surfaces, we are able to show the growth direction for seed-mediated-grown Au NRs for the first time. In this sample, ~60% of the NRs grew in one direction after 20 min.

A benefit of directly imaging Au seeds and the resulting nanostructures is that we can determine if a correlation exists between them. An understanding of the role of the seed may lead to improved synthesis.<sup>16</sup> We did not observe an obvious correlation between seed diameter and nano-

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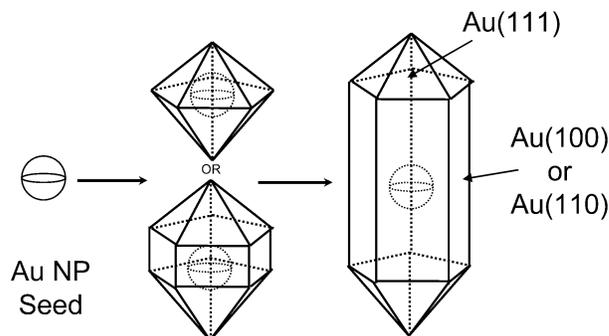
**Figure 3.** AFM images of Si/SiO<sub>2</sub>/MPTMS (a) after seed deposition and (b) after NR growth for 60 min. Frames c and d show another region of the same sample. The Z-range is 15 nm in frames a and c and 50 nm in frames b and d.

structure shape, since seeds ranging in size from 2.0 to 8.0 nm grew into NRs and other various shapes. This supports our belief that initial seed structure, rather than size, is a more dominant factor in NR growth. There is a correlation between seed diameter and NR diameter.<sup>2,16</sup> In general, smaller seeds tend to form thinner NRs (Table S1 and Figure S1, Supporting Information). For example, seeds 1<sub>s</sub>, 3<sub>s</sub>, and 7<sub>s</sub> are 2.6, 3.0, and 2.4 nm in diameter, respectively, and they grow into NRs 1<sub>r</sub>, 3<sub>r</sub>, and 7<sub>r</sub>, which are all 15 nm in width, respectively. Conversely, seeds 2<sub>s</sub>, 6<sub>s</sub>, and 10<sub>s</sub> are 8.9, 5.5, and 5.3 nm in diameter, respectively, and they grow into NRs 2<sub>r</sub>, 6<sub>r</sub>, and 10<sub>r</sub>, which are 29, 48, and 25 nm in width, respectively. Some of the larger seeds may actually be aggregates of a few seeds, contributing to the larger NR diameter. NR length does not correlate well with seed diameter (Figure S2, Supporting Information), although it is rare to see a large seed grow into a long NR. Clearly seed size is not the only factor affecting the vastly different growth rates and varied shape progression of Au seeds.

#### Direct AFM Monitoring of Seeds Grown for 60 min.

Figure 3 shows AFM images obtained on the same area of a Si/SiO<sub>2</sub>/MPTMS sample containing Au NP seeds before (Figure 3a) and after (Figure 3b) it was placed in growth solution for 60 min. Figure 3c,d shows another region of the same sample. The bright dots in the before image represents the Au NP seeds. The asterisk is a marker, circles are used to indicate various seeds before growth, and circles with dots show the original placement of the seeds after NR growth. Most of the grown nanostructures can again be correlated with a seed, and NRs are longer and wider on average compared to the 20 min data. Interestingly, in this experiment, most of the seeds (88%) form NRs by growing in two approximately equal and opposite directions. This is significantly different compared to the 20 min sample, where most seeds grew in one

#### Scheme 2. Mechanism for Au NR Formation



direction. We are not able to conclude that this is a true time-dependent phenomenon due to limited statistics, but the observation of NRs growing by two different mechanisms is important. NRs also form from two seeds merging. Seeds A<sub>s</sub> and B<sub>s</sub> merged to form NR (A–B)<sub>r</sub>, and seeds C<sub>s</sub> and D<sub>s</sub> merged to form NR (C–D)<sub>r</sub>. The merging of seeds to form rods is interesting and could potentially be used to controllably grow long, connected, or branched NRs. Figure 3 shows that nanostructure growth is also affected by other nearby structures, as evidenced by NR 3<sub>r</sub> preventing the growth of NR 2<sub>r</sub> in two directions.

The correlation between seed diameter and NR diameter is not as evident for these data, as most of the NRs are 20–25 nm in diameter (Table S2 and Figure S3, Supporting Information). The largest seed does grow into the widest NR (4<sub>s</sub>), however. NR length is again unpredictable, but it is rare to see long NRs growing from large seeds.

**Growth Mechanism.** Two mechanisms for the growth of Au NRs have been proposed previously.<sup>7,9,10,15</sup> The first involves the passivation of certain crystal faces of Au by CTAB to promote anisotropic growth. TEM experiments reveal the formation of decahedral particles with two pentagonal multiply twinned (MT) Au(111) faces, where growth is believed to occur preferentially to form elongated particles and eventually NRs (Scheme 2).<sup>9,10</sup> CTAB is thought to adsorb as a bilayer<sup>17</sup> and selectively stabilize and reduce growth along the long Au(100) or Au(110) faces of the NRs to promote NR growth at the ends. The TEM data are limited because they do not show the progression of the same seed growing into a NR. It is also unclear in these reports why only some of the MT particles form NRs. Two-directional growth in opposite directions would be expected if MT decahedral particles are precursors to NRs. Our results clearly show one-directional growth as well, suggesting that alternative seed structures and growth mechanisms may lead to NRs as well. Growth is inhibited along the faces of the long axis and along one of the ends of the NR with one-directional growth. The second proposed mechanism attributes anisotropic growth of NRs to the flux of Au<sup>+</sup>–CTAB being highest at the ends of the NRs (areas of high curvature) due to enhanced electric fields.<sup>15</sup> With this mechanism, it is difficult to explain the growth of NRs in one direction. Since both ends are similarly curved, enhanced electric fields on both ends would presumably lead to two-directional growth.

We believe that preferential adsorption of CTAB on certain crystal faces best describes the growth of Au NRs and that the initial seed structure plays an important role in determining whether a seed grows into a NR and whether it grows in one or two directions. Electric field effects may also play a role but cannot account for the growth of Au NRs alone. It is important to note that the

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growth of NRs directly on surfaces has several differences compared to solution growth. The largest difference is the influence of the substrate blocking diffusion of  $\text{AuCl}_2^-$ -CTAB complexes on one side of the seeds/NRs. Also, many processes that can occur in solution, such as seed particle aggregation and Ostwald ripening, are prevented when the seed is confined and immobilized on the surface. Coalescence of particles often leads to multiple twinning in solution; however, this process is likely forbidden with the seeds attached to the surface.<sup>9</sup> Despite these differences, NRs grown on surfaces are similar in appearance, length, width, and yield to those grown in solution.

**Size Dispersity.** TEM results showed that NRs grown in solution by multiple iterations of the seed-mediated growth process exhibit a bimodal or trimodal size distribution, depending on the number of iterations.<sup>9</sup> The yield increases with iterations, but size dispersity also increases because some seed particles form rods early on in the growth process and some form rods at later times. The diameter of the seed particle at the time it becomes a NR largely determines the width of the NR. This leads to populations of long, thin rods and short, wide rods. The formation of NRs at different times in the growth process may lead to size dispersity for surface-grown NRs as well. Our data show a correlation between seed size and NR diameter, suggesting that NR size dispersity may be reduced by reducing the initial seed size dispersity. Growth direction is another source of dispersity, since seeds growing in two directions grow differently compared to seeds growing in one direction. Finally, the spatial relationship of seeds affects the size dispersity of surface-grown Au NRs, which is probably not a factor in homogeneous, solution-grown NRs. Some seeds merge when growing into NRs and others block the growth of NRs. It has been shown that the electrochemical growth of metal particles is strongly affected by the spatial relationship between neighboring particles, due to interparticle diffusional coupling (IDC), which leads to increased particle size dispersity. We have observed two particles close together growing disproportionately in size, consistent with IDC (not shown). Taken together, reduced size dispersity may be achieved by increasing the distance between neighboring seed particles, narrowing the size

range of seed particles, and creating conditions where seeds grow in either one direction or two directions, but not both.

In summary, we directly monitored Au seeds growing into Au NRs by AFM, revealing three important findings. First, we directly confirm that Au NRs form by the seed-mediated growth of surface-confined Au seeds and that secondary nucleation events are minimal. Second, Au NP seeds can grow in either one or two directions when evolving into NRs. This information is not enough to provide a full understanding of the growth mechanism, but it shows that the NR growth process is very different on different seed particles, which must be considered in existing and future proposed mechanisms. Third, there is a correlation between seed size and NR diameter. Reduction in NR dispersity may be obtained by improving the seed size dispersity, increasing the seed particle spacing, and controlling the growth direction. Future high-resolution TEM experiments of Au seeds before and after seed-mediated growth will be conducted to determine the relationship between seed structure and resulting grown nanostructure (rod, sphere, triangle, hexagon, etc.) and further address issues of yield and size dispersity. There are still unresolved questions, but the results in this paper represent a significant step toward gaining a better understanding of the seed-mediated NR growth mechanism using a new strategy, which may lead to improved synthesis, control of NR properties, and future applications. This research is also relevant to other metal and semiconductor nanostructures having unusual shapes.

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**Supporting Information Available:** Tables and plots correlating seed diameter with NR diameter and length for Figures 2 and 3. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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