

Growth of Gold Nanorods on Surfaces

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The surfactant-assisted seeded growth method was adapted for growth of gold nanorods directly on mica surfaces. Spherical gold seed particles were first linked to the surface and then dipped in a cationic surfactant growth solution. Part of the grown particles were nanorods with a typical length of several hundred nanometers and diameter of 10–20 nm. The probability to grow elongated particles out of a seed on the surface was found to be larger than the comparable solution growth process. Successive dipping in the growth solution was found to increase the length and thickness of the gold nanorods without a significant increase in aspect ratio.

Rodlike nanoscale colloidal particles have recently become a major subject of interest among scientists studying colloidal nanocrystals, including semiconductor,¹ magnetic,^{2,3} and insulating^{4,5} nanorods. More specifically, in the past few years, several methods for the production of colloidal silver and gold nanorods were published.^{6–11} It is generally understood that in many of the nanorod synthesis processes the anisotropic growth of a crystal nucleus is induced or enhanced by a difference in the adsorption strength of a capping surfactant on different crystalline faces.¹² The same has been proposed for aqueous gold and silver nanorod growth,¹³ which employs alkylammonium bromide surfactants.

One of the obvious interests that motivate metallic and semiconductor nanorod work is the development of a chemical technology to produce dense nanowire arrays for use in future nanoelectronics. However, as in the case of carbon nanotubes and semiconductor nanowires, long solid objects are typically unstable in a solvated state and readily aggregate. Even with the aid of surfactants, the dispersibility of long nanorods (or nanowires) is very limited, and we are not aware of any report of well-controlled solution self-assembly of long nanowires into ordered structures on surfaces. Only small nanorods were observed to self-assemble^{14,15} into locally ordered structures.

Considering the difficulties experienced with solution-phase self-assembly of nanowires on surfaces, we decided to take a different strategy toward forming nanowire arrays on surfaces, similar to the directed growth of carbon nanotubes or semiconductor nanowires from catalytic seed particles. Because some solution-phase gold and silver nanorod preparations make use of small metal nanocrystals as seeds for the growth of the nanorods,⁸ such techniques would be a good starting point for developing surface-supported growth of long metal nanorods. Thus, in this letter, we report on the development of a technique to grow gold nanorods directly on surfaces starting from small gold crystallites that are chemically attached to the surface.

The technique, illustrated in Figure 1, is based on the solution seeded nanorod synthesis scheme published by Murphy and co-workers⁸ and was performed in several stages. First, aqueous gold seed nanoparticle solution was produced using the proce-

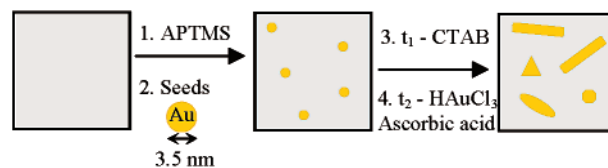


Figure 1. Schematic diagram of the surface growth process. In step 1, APTMS was adsorbed to the mica surface, followed by step 2 in which the gold seeds were attached to the APTMS linkers. In step 3, the substrate with seed particles was dipped in CTAB solution for a period t_1 , and then in step 4, the growth precursors, HAuCl_4 and ascorbic acid, were added, and the growth was allowed to proceed for a period t_2 . Steps 3 and 4 could be repeated for several times to increase the size of the grown particles.

cedure described in ref 8; chloroauric acid solution was reduced by sodium borohydride in the presence of sodium citrate to produce 3 nm diameter gold particles. Second, a clean mica or Si substrate ($10 \times 10 \text{ mm}^2$) was treated with a 0.01% toluene solution of aminopropyltrimethoxysilane (APTMS) for about 10–30 min, and then the substrate was thoroughly washed and sonicated in ethanol and distilled water. Afterward, the substrate was immersed in the seed solution for a period of 15–30 min (to control the density of adsorbed particles), washed again by sonication in distilled water, and finally dried with a N_2 stream. At this point, atomic force microscope (AFM) imaging was performed to check for seed density on the surface.

For the growth of nanorods, the substrates with the seed particles were immersed in a 0.06 M cetyltrimethylammonium bromide (CTAB) solution for a variable amount of time ($t_1 = 0\text{--}30 \text{ min}$). Next, 0.5 mL of $2.5 \times 10^{-4} \text{ M}$ HAuCl_4 solution was added, followed by an addition of 25 μL of 0.1 M ascorbic acid solution. The growth was allowed to continue for a variable duration ($t_2 = 5\text{--}60 \text{ min}$), and then the substrates were thoroughly cleaned in an ultrasonic bath and dried under a stream of nitrogen. We have also conducted sequential growth experiments in which the growth process was repeated several times with AFM monitoring between the growth steps.

The surfaces with the grown particles were imaged using an AFM (P47, NTMDT) operated in tapping mode. Several samples were also imaged using a high-resolution scanning electron microscope (HRSEM, JSM-6700F) to confirm that the particles appearing in the AFM images were metallic.

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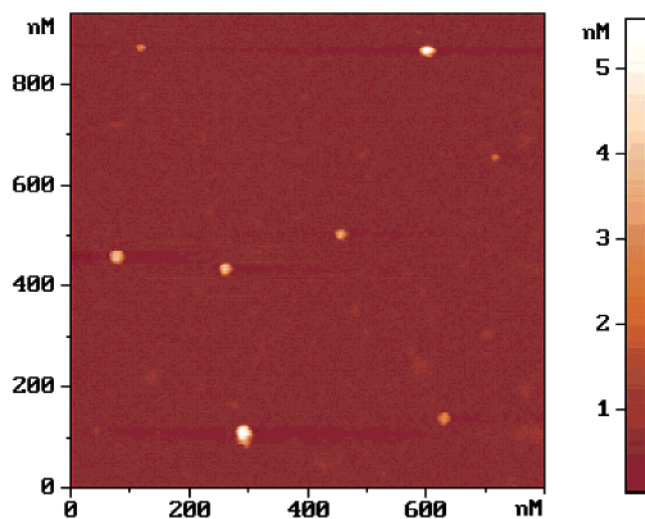


Figure 2. AFM image of gold seed particles adsorbed on APTMS-functionalized mica surface.

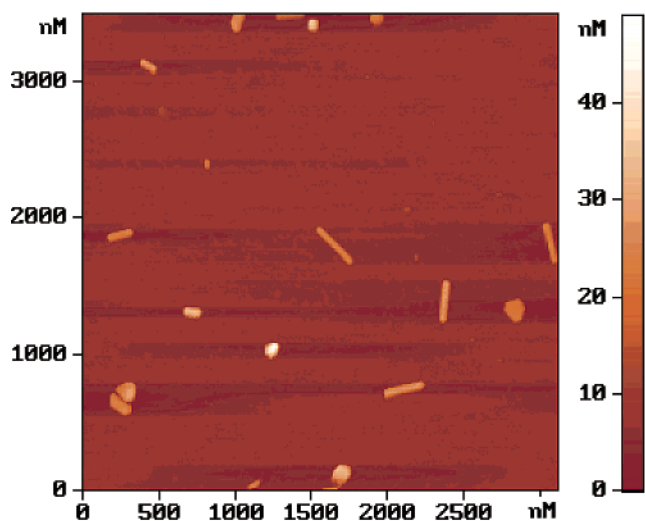


Figure 3. AFM image of the grown gold particles on mica. The height ("diameter") of the nanorods is 15–20 nm.

To observe the growth of well-separated particles, the surface coverage of the seed particles was tuned to about 1–10 particles per $1\ \mu\text{m}^2$ by adjusting the dipping time of the mica in the APTMS, the subsequent dipping time in the seed solution, and the APTMS concentration. Figure 2 presents a typical AFM image of low seed density linked to a mica surface. Although there was no direct evidence that the negatively charged seed particles were directly bound to positively charged amine groups, it should be noted that without the APTMS treatment of the substrates no seeds were observed in the AFM images.

By changing delay time t_1 and growth time t_2 , we optimized the yield of the nanorods. It was found that the CTAB should be allowed to adsorb on the surface longer than 1 min prior to the addition of the gold ions and the ascorbic acid to obtain a relatively high nanorod yield but not longer than 10 min, after which the particles were not able to grow at all. In accordance with this, it was found that most of the growth occurred within 10 min after the addition of the HAuCl_4 and ascorbic acid to the CTAB solution. Yield and aspect ratio of the nanorods continued to increase by a few percent up to $t_2 = 1\ \text{h}$.

The AFM images of samples grown under $t_1 = 5\ \text{min}$ and $t_2 = 30\ \text{min}$ (as seen in Figure 3) revealed that practically all particles have grown substantially and that part of the particles were in the shape of nanorods. About 15% of the particles have

grown to become nanorods of aspect ratio > 2 with a length in the range of 100–500 nm and diameter (height in AFM image) of 10–20 nm. This yield is larger than the 4% obtained for the equivalent solution growth technique in a single growth step.¹³

This surface growth experiment has been repeated about 20 times resulting in grown particles similar to those observed in Figure 3 for about 90% of the times.

It was possible to further increase the size of the nanorods, as well as the other shapes, by dipping the substrate with the grown particles in a CTAB solution and adding the gold ions and ascorbic acid after t_1 , similar to the sequential process reported by Murphy and co-workers.⁸ However, in the present case, the relative gain in nanorod length in subsequent growth steps was modest, while their relative thickness increase was substantial. In addition, possibly because of the thorough ultrasonic cleaning of the substrates after each growth step, the surface density of particles decreased and the fraction of nanorods out of the total number of particles increased.

Figure 4 contains AFM images of a sample grown in three subsequent stages after the first stage (a) and after the third stage (b). In this particular sample, the first growth step yielded relatively small nanorods (100–200 nm long). The length of the nanorods after the third stage appears to be limited to about 500 nm, as in the sample of Figure 3, while the height (representing diameter) of the nanorods increased to about 30–50 nm. Figure 5 shows the shifts in height and length distributions with the three successive growth steps. From these data, it appears that after the first growth step the relative increase in average diameter of the nanorods is somewhat larger in comparison to the relative increase in average length. Thus, the average aspect ratio hardly increased in the second (5.7) and third (5.5) growth steps compared to the average aspect ratio after the first step (5.1).

Analysis of the surface growth process in comparison with the solution growth process brings up several differences: (1) The amount of seed particles on the surface is negligible compared with the concentration of seeds added in the solution growth process. (2) Diffusion of seed particles within the growth solution is absent in the surface growth process. (3) The CTAB surfactant probably forms different micellar structures on the mica surface.

Thus, in the surface growth process a large excess of chloroauric acid is present throughout the dipping of the substrate into the growth solution. This could be verified through the observation of the solution changing color into pink after more than 12 h, indicating that gold(I) ions remained in the solution long after the growth process ended. On the other hand, the solution growth process was found to be sensitive to the concentration of seed particles and probably terminates with the consumption of all gold precursor from the solution. Another manifestation of the large excess of gold ions in the surface growth process is the length of the nanorods produced by a single growth step in this technique, which is significantly larger than that obtained in a single step of the solution growth process.

We therefore believe that the surface growth is terminated because of accumulation of multilayers (or large aggregates of other forms) of CTAB at the surface around the growing particles and blocking of the access of gold precursor ions to the particle's metallic cores. It is well-known that CTAB has a high affinity toward mica surfaces, and it is clear that with the large concentration of CTAB in solution, a large quantity of it would be accumulated at the surface, either as lamellar or micellar structures.¹⁶ The high concentration of CTAB in solution is critical for protection of the gold(I) ions against

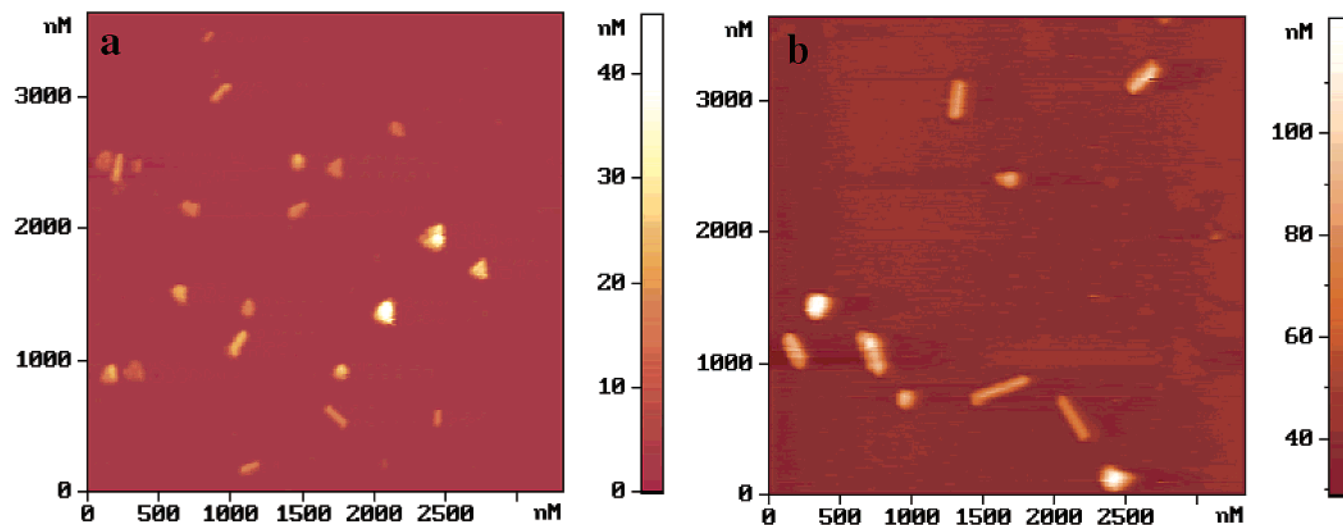


Figure 4. AFM image of (a) particles grown in a single growth stage with average nanorod length smaller than the sample in Figure 3, and height of 10–15 nm and (b) the same sample, at a different position, after three successive growth stages. Nanorod heights are in the range of 30–50 nm.

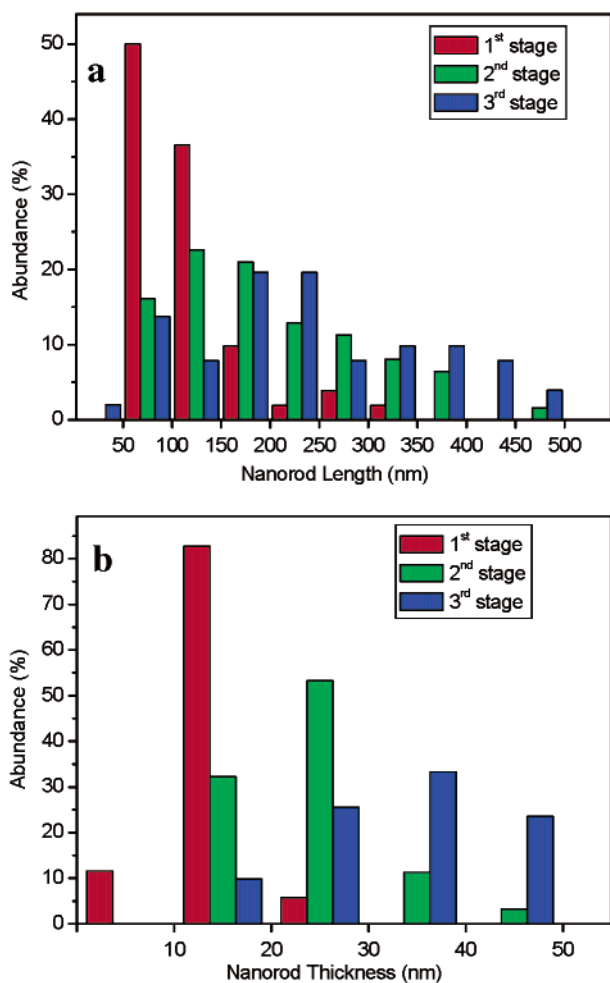


Figure 5. The change in nanorod length (a) and height (diameter) (b) distributions with the three successive growth steps of the sample shown in Figure 4.

spontaneous reduction into metallic gold and, thus, against consumption of all of the free gold ions in solution.

As reported earlier, gold and silver nanorod growth depends on the formation of twin defects in the growing seed particles.^{13,17} In the present work, it is expected that the binding of the seed particle to a surface should change the probability of the growing seed to develop twin defects. This fact could be

the reason for the enhanced yield of nanorods at the surface-bound seeds.

We believe that this surface growth procedure can be further improved to produce longer nanorods with better yields. Recently, significant improvements in the yield of nanorods were reported for modifications of the solution growth process.^{18,19} We did not find that these modifications, such as addition of Ag^+ ions to the solution, improve the yield of the process. Finding the optimal parameters for the surface growth process requires further search in parameters space.

The technique presented here is a first step along a path towards the fabrication of arrays of conducting nanowires in a pure wet-chemical lithography-less process. Further development of the process described above should first result in a technique to grow large aspect ratio gold and silver nanorods (i.e., nanowires) with high yields. Later on, control over the position of the seed particles on the surface, possibly by some self-assembly technique, and over growth orientation would lead to highly organized metal nanowire arrays on surfaces.

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Supporting Information Available: Figure 1S showing two high-resolution scanning electron micrographs of a sample similar to the one imaged in Figure 3 taken with low accelerating voltage. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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