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Directing the Growth of Highly Aligned Gold Nanorods through a Surface Chemical Amidation Reaction

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Au nanorods (NRs) represent an interesting one-dimensional (1D) nanostructure that has recently been synthesized[1a−d] and patterned[1e] directly on surfaces through seed-mediated chemical growth[1f] of surface-attached Au nanoparticle (NP) "seeds". One drawback of this method is that the NRs were assembled with uncontrolled orientation and alignment. Here we describe a new procedure for growing highly aligned Au NRs directly on a Si(100) substrate. A simple chemical amidation reaction on NH_2-functionalized Si(100) promotes the growth of highly aligned NRs extremely well.

This work is important for two main reasons. First, controlled patterning and alignment of 1D nanostructures is critical for studying fundamental collective properties and for incorporating these promising materials into nanoelectronic,[2a] sensing,[2b] optoelectronic,[2c] and plasmonic[2d] devices. Second, the use of a surface chemical reaction to promote the growth of aligned nanostructures is very unique when compared to other approaches. Several methods have been employed to align 1D structures, perpendicular or parallel to the surface, either from solutions/suspensions of the materials postsynthesis or during their growth from a surface-bound catalyst. Langmuir−Blodgett (L−B) methods,[3a] microfluidics,[2a,3b] chemical templating,[3c] surface functionalization,[3d] electric field alignment,[3e] and growth along the direction of gas flow,[3f] surface crystal planes,[3g,h] and surface step edges[3i] are recent examples.

Au and Ag NRs/NWs, in particular, have been aligned by electron-beam lithography,[2d] L−B methods,[4a] stretched polymer matrices,[4b] self-assembly,[4c,d] attachment to carbon nanotubes,[4e] electric fields,[3e] and electrochemical deposition at surface step edges.[2b] They are interesting because they exhibit orientation-dependent absorption/scattering of polarized light[4b] and can act as waveguides.[2d] One-dimensional metals are also useful for nanoelectronics,[3e] chemical sensing,[2b] and surface-enhanced Raman spectroscopy (SERS)[4a] applications.

Our procedure is outlined in Scheme 1. First, a p-type Si(100) substrate with a native oxide layer was placed into a solution containing 100 μL of (aminopropyl)triethoxysilane (APTES), 10 mL of 2-propanol, and 2−3 drops of water while heating just below boiling for 30 min to create surface NH_2 groups.[1a,b] These groups were reacted with 10 mM acetic acid using 20 mM dicyclohexylcarbodiimide (DCC) and 20 mM dimethylamino pyridine (DMAP) as a catalyst, which results in the formation of an amide bond and renders the surface terminated mainly with CH_3 groups. Citrate-capped Au nanoparticles (NPs)[1] (3−5 nm average diameter) were attached to the surface, presumably to unreacted amine groups through electrostatic or Au−NH_2 interactions.[1a,b] The substrate was then placed into a growth solution containing 9 mL of 0.1 M cetyltrimethylammonium bromide (CTAB), 450 μL of 0.01 M $AuCl_4^-$, and 50 μL of 0.1 M ascorbic acid.[1] This step[1a−e] leads to the growth of surface-bound Au NP seeds into Au NRs via seed-mediated growth. The SEM image in Figure 1 shows the remarkable degree of alignment over a large area for Au NRs grown by this procedure.

Scheme 1. Method for Growing Aligned Au NRs

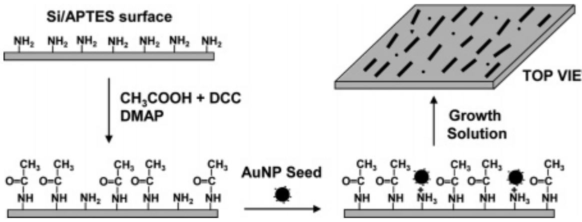

Figure 2A shows a scanning electron microscopy (SEM) image of Au nanostructures grown on a Si(100)/APTES surface that was not functionalized with acetic acid. The surface exhibits a high density of Au nanoparticles (175/μm^2) with just a very few unaligned short rods on the surface. Figure 2B is an SEM image of Au NRs grown on a Si(100) surface functionalized with mercaptopropyltrimethoxysilane (MPTMS) using our previous method.[1b,c] The surface contains a lower overall density of Au nanostructures (18/μm^2) compared to Si(100)/APTES and high aspect ratio Au NRs exhibiting no particular alignment. Figure 2C and 2D shows two images of Au NRs grown on Si(100)/APTES

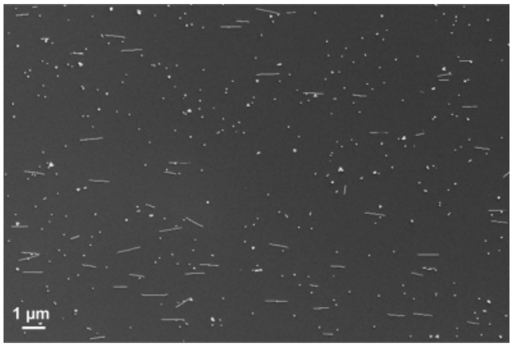

Figure 1. SEM image of Au NRs aligned over a large area on a Si(100) surface using the procedure described in Scheme 1.

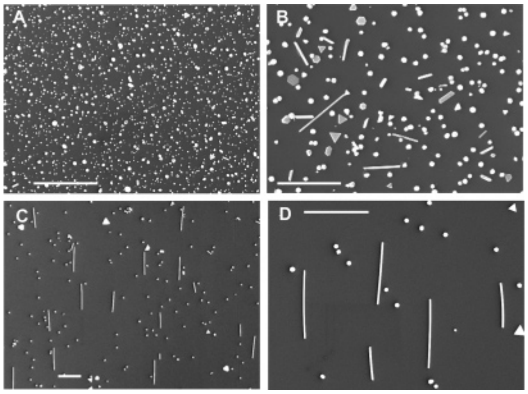

Figure 2. SEM images of (A) Si(100)/APTES, (B) Si(100)/ MPTMS, and (C−D) Si(100)/APTES/acetic acid after exposure to Au NP seed and NR growth solution. Scale bars are 1 μm in all images.

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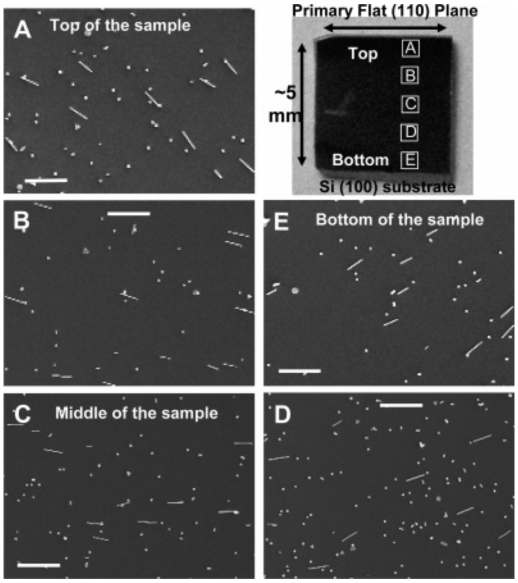

Figure 3. SEM images showing the change in alignment direction for Au NRs grown on a Si(100)/APTES/acetic acid substrate. The letters in the top right digital image of the substrate correspond to the approximate location of the SEM images. Scale bars are 1 μm.

functionalized with acetic acid as in Scheme 1. These surfaces show a more reduced nanostructure density on the surface ($3/\mu m^2$), and more importantly, the NRs show an incredible propensity for parallel alignment to one another. Statistics show that ~80% of the Au nanorods are oriented in the same direction within a ±30° range from the alignment direction. The yield of Au NRs is ~19%, the diameter is 25−30 nm, and the average length is 572 ± 203 nm (AR ~ 20).

We prepared similar samples as in Figure 2 on glass substrates to obtain visible spectra (Figure S1, Supporting Information). In short, these spectra confirm that the surface amidation reaction was successful and show that the absorbance values are consistent with the coverages observed in the SEM images in Figure 2.

The SEM images in Figure 3A−E were obtained from top to bottom of a ~5 mm Si(100) sample with the primary flat (110) plane parallel to the top of the images as shown in the digital picture. The letters on the digital picture correspond to the approximate location of the SEM images. The images show that the NR alignment direction changes from top to bottom of the sample, with no particular preference with respect to the (110) plane (or atomic arrangement) of the Si. The alignment direction gradually rotates counterclockwise ~90° with respect to the right end of the NRs from top to bottom of the sample. The middle of this sample showed parallel alignment to the (110) plane.

We examined the effect of surface functionality on alignment by growing Au NRs on Si(100)/APTES samples reacted with succinic acid, which terminates the surface with COOH instead of CH_3 groups. The SEM image in Figure 4A shows that this also leads to Au NR alignment. The SEM image in Figure 4B shows that Ag NRs grown on Si(100)/APTES/acetic acid surfaces using a similar seed-mediated growth procedure[5] are also aligned (~60%), but not to the extent of Au NRs.

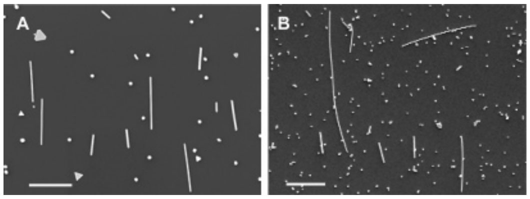

Figure 4. SEM images of (A) Au NRs grown on Si(100)/APTES/succinic acid and (B) Ag NRs grown on Si(100)/APTES/acetic acid. Scale bars are 1 μm.

We do not clearly understand the mechanism of NR alignment at this time. Since alignment is not observed on amorphous glass, we initially thought the Si crystallinity was important. However, the alignment direction changes throughout the sample, showing no direct correlation with the arrangement of Si atoms. The fact that alignment is not observed on MPTMS- and APTES-functionalized or bare Si(100) shows that surface chemistry plays a major role, but it is not clear how the amidation reaction leads to alignment. Preliminarily, surface hydrophobicity does not appear to play a major role since acetic and succinic acid surfaces both show alignment.

In summary, we have demonstrated a simple method for promoting the growth of highly aligned Au NRs directly on Si(100) surfaces through a surface amidation reaction. A remarkable degree of parallel alignment is observed over large areas. The alignment direction is localized since it rotates slightly from one area of the substrate to another. Research is currently underway to better understand the alignment mechanism and major factors involved.

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Supporting Information Available: More detailed description of synthesis and visible spectra of samples prepared on glass. This material is available free of charge via the Internet at http://pubs.acs.org.

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