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Gold Nanorods Grown Directly on Surfaces from Microscale Patterns of Gold Seeds

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We report a strategy for patterning surfaces with high aspect ratio gold nanorods (Au NRs) by using a poly(dimethylsiloxane) (PDMS) stamp to microcontact print 3−5 nm diameter gold nanoparticle (Au NP) "seeds" onto mercaptan-functionalized Si/SiO$_x$ surfaces and subsequently grow the seeds into Au NRs via seed-mediated reduction of HAuCl$_4$ with ascorbic acid in the presence of cetyltrimethylammonium bromide (CTAB). The patterns also contain a large number of spherical particles, which are largely removed and separated from NRs using adhesive tape. The same PDMS stamp was used more than 30 times to produce well-defined patterns without reinking with Au NP seeds. Controlled patterning of Au NRs on surfaces is important for electronics, sensing, optical, and plasmonic applications.

Introduction

The synthesis of one-dimensional (1D) metal, semiconducting, and carbon nanostructures, including rods, wires, tubes, and belts, has gained enormous attention in recent years.[1] Several examples in the literature reveal the fascinating electronic,[2−15] optical,[16−18] optoelectronic,[19−21] and mechanical properties[22,23] of individual 1D nanostructures, such as semiconductor nanowires,[3−8,19−21] carbon nanotubes (CNTs),[2,9,12,13,22] and metal nanowires/nanorods.[10,14−18,23] These important studies demonstrate the potential for incorporation of these structures into functional electronic, optoelectronic, or sensing devices, which could lead to extreme miniaturization and enhanced performance because of their nanoscale dimensions. These future applications will require integration of numerous addressable 1D nanostructures through assembly, patterning, and alignment on solid supports over large areas.

There are currently three main strategies for the assembly, patterning, and alignment of 1D nanostructures on surfaces (Scheme 1). The first is by standard lithographic methods, where a material is etched or deposited into 1D structures on a surface through a patterned resist. Electron beam or scanning probe lithography is the method of choice for features below 100 nm. This method allows for excellent alignment with control of the pitch and the generation of complex patterns. A negative is that extremely small diameter (<10 nm) nanostructures are difficult to fabricate, the structures are often not crystalline, and they are limited to structures that are derived from films. A second approach involves solution- or vapor-phase synthesis of 1D nanostructures followed by dispersion in solutions and subsequent assembly/patterning on surfaces. An excellent example of this approach is the work of Lieber and co-workers on Si NWs grown by chemical vapor deposition, which were dispersed in organic solvents, assembled and aligned by the Langmuir−Blodgett technique, and patterned onto surfaces using photolithography.[24] Crossed patterns could also be made and the NWs were electronically addressable. Others have used the Langmuir−Blodgett method,[24−26] liquid crys-

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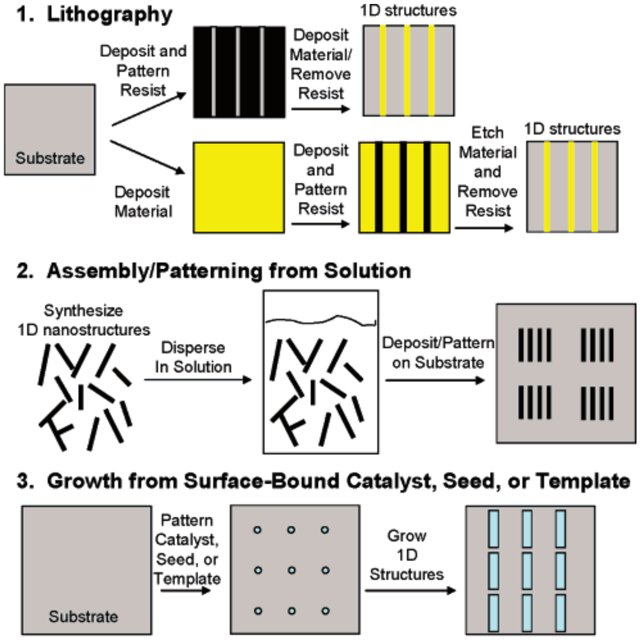
Scheme 1. Methods for Assembling, Aligning, and Patterning 1D Nanostructures on Surfaces



talline assemblies,[27−29] microfluidics,[30,31] chemical[32,33] and biochemical[34−37] assembly, and electric-field alignment[14,38] to assemble/align/pattern 1D nanostructures dispersed in solutions. Aggregation of 1D nanostructures often makes it challenging to assemble well-separated, individually addressable nanostructures on surfaces in this way. The third method involves direct growth of 1D nanostructures from catalysts, "seed" particles, or templates that are attached directly to surfaces. Patterning the catalyst or template on the surface leads to patterned 1D structures. Recently, GaN NWs have been grown using the vapor−liquid−solvent (V−L−S) method from surface-bound catalysts that were patterned by electron-beam lithography[39] and dip pen lithography.[40] CNTs,[41−44] ZnO nanorods,[45,46] and InP nanowires,[47] among other materials, have also been grown on surfaces from patterned or ordered arrays of catalysts. Depending on the situation, the 1D structures may align parallel to the surface, as illustrated in Scheme 1, or extend perpendicular to the surface. In some cases, extremely long CNTs were grown and aligned on surfaces in the direction of gas flow of precursor molecules.[48] Surface-attached templates can also serve as sites for growing 1D metal nanostructures. Molecular combing has been used to align DNA strands onto a surface from solution, which then acted as a template to grow metal 1D nanostructures.[49] DNA-directed assembly also has led to well-organized and conductive metallic Ag nanowires.[50] Other methods not included in Scheme 1, such as those involving molecular beam epitaxy[51] and electrochemistry,[52] also have been used to assemble/align arrays of 1D nanostructures.

In this paper, we describe a method, using strategy 3 in Scheme 1, for patterning high aspect ratio (AR) gold nanorods (Au NRs) on surfaces. This is achieved by microcontact printing gold nanoparticle (Au NP) seeds on a surface[53] and then growing the seed particles into Au NRs using the seed-mediated growth method described by Murphy and co-workers.[54−57] The seed-mediated growth method is attractive because it is a simple benchtop, wet chemical method allowing control of the AR.[58] It involves reduction of $HAuCl_4$ with ascorbic acid (AA) directly onto preformed Au NP seeds in the presence of cetyltrimethylammonium bromide (CTAB) in aqueous solutions. The assembly of seed-mediated grown Au NRs onto surfaces is hampered by the large amount of CTAB in solution. Recently, though, our group[23,59] and others[60−62] have shown that direct growth from

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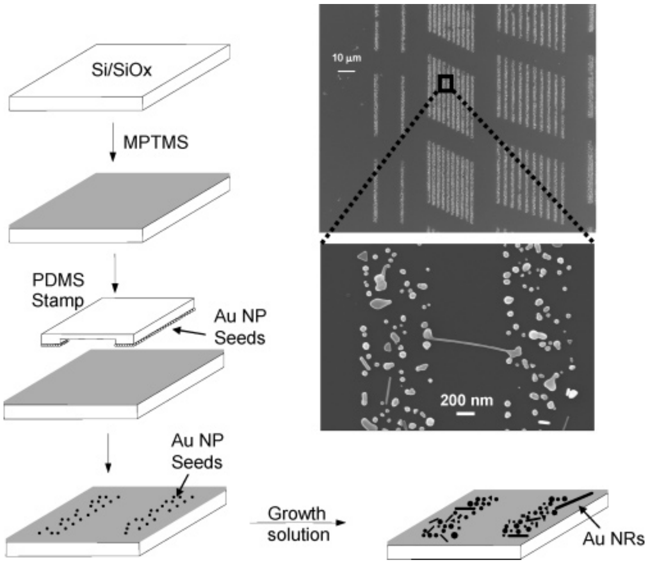
surface-attached seeds have led to well-separated surface-attached Au NRs. Electrostratic attachments of solution-grown Au NRs onto surfaces has also recently been demonstrated.[32,63] Au NRs have been assembled in solution using DNA,[35] Langmuir−Blodgett techniques,[25] liquid crystalline assembly,[27] bifunctional linkers,[64] and biotin-streptavidin connections.[34] Electric field[14] and chemical/biochemical[33,37] assembly has been used to address Au NWs/NRs electronically. There have not been any examples to our knowledge of patterned Au NRs on surfaces using these approaches.

Our results are significant because we show that Au NRs can be patterned with microscale precision using simple benchtop methods involving microcontact printing (μCP). At least 30 patterns can be fabricated with one stamp, demonstrating the potential for fabricating numerous samples quickly. One major problem of the seed-mediated growth method is the low 10−15% yield of NRs obtained versus spherical, triangular, and hexagonal shapes also present.[23,54,60] Here, we describe a simple procedure for increasing the percentage of Au NRs grown directly on surfaces by removing other shapes with adhesive tape. Au NRs have generated a great deal of interest because of their interesting optical,[65,66] thermal,[67] and mechanical properties[23] and their ability to enhance surface Raman scattering[68,69] and fluorescence[70] of molecules in their vicinity. They are also potentially useful for optical-based biosensing,[17,18] gene delivery,[71] and catalysis. Most recently, noble metal NRs, when well-aligned on surfaces, have been shown to behave as surface plasmon waveguides.[72,73] Au NRs could also serve as contacts in nanoscale electronic devices. All of these applications rely on the assembly, patterning, and alignment of Au or other metal NRs on surfaces.

Experimental Section

Chemicals. (3-Mercaptopropyl)trimethoxysilane $C_6H_{16}O_3SSi$ (Fluka, 97%), citric acid, trisodium salt (Bio-rad), sodium borohydride (Aldrich, 98%), cetyltrimethylammonium bromide (Aldrich), L-ascorbic acid (Aldrich, 99+%), 2-propanol (VWR, >99.9%), hexadecane (Aldrich, 99%), 184 silicone elastomer base (Sylgard), 184 silicone elastomer curing agent (Sylgard), hydrogen peroxide (VWR), and sulfuric acid (VWR) were used as received. $HAuCl_4{*}3H_2O$ was synthesized according to a literature procedure.[74] All aqueous solutions were prepared with Nanopure water (Barnstead, resistance ≈ 18 MΩ·cm).

Scheme 2. Method for Patterning Au NRs on Surfaces



Seed Synthesis. Three to five nanometer diameter gold nanoparticle (Au NP) seeds were synthesized by adding 0.6 mL of 0.1 M $NaBH_4$ to 19 mL of an aqueous solution of 2.5×10^{-4} M $HAuCl_4{*}3H_2O$ and 2.5×10^{-4} M trisodium citrate while stirring as described previously.[23,54] The Au NP seed solution was used for Au NR patterning between 2 and 4 h after preparation.

Substrate Preparation. Si/SiO_x substrates were cleaned with freshly prepared piranha solution (3:1 H_2SO_4/30%H_2O_2) for 15 min to remove organic impurities. (Caution: piranha solution is a powerful oxidizing agent and reacts violently with organic compounds.) Next, the slides were thoroughly rinsed with Nanopure water, dried under N_2, and immersed into a solution containing 10 mL of 2-propanol, 100 μL of (3-mercaptopropyl)trimethoxysilane (MPTMS), and a few drops of water. The solution was heated below boiling for 30 min, removed, rinsed with 2-propanol, and dried under N_2 before patterning with Au NRs.

Stamp Preparation. Poly(dimethylsiloxane) (PDMS) stamps were prepared by mixing 184 silicone elastomer base and 184 silicone elastomer curing agent in an 8:2 ratio and degassing until no visible bubbles were observed.[75] A Si/SiO_x substrate containing photolithographically defined patterns was cleaned in piranha, rinsed with water, rinsed with 2-propanol, dried under N_2, dipped in pure hexadecane, and dried under N_2 before placing the silicone elastomer mixture on the Si/SiO_x substrate in a defined form. The hexadecane prevents the PDMS stamp from adhering strongly to the Si/SiO_x substrate after curing. The silicone elastomer was heat cured at 80 °C in the oven for 12 h to ensure complete cross-linking and was peeled off from the patterned Si/SiO_x substrate to form a PDMS stamp with the negative pattern of the Si/SiO_x substrate. The PDMS stamp was rinsed with ethanol, acetone, 2-propanol, and Nanopure water in sequence and then dried under N_2 to remove impurities from its surface. A second PDMS stamp, prepared similarly, was a gift from Professor Mark Schoenfisch, UNC−Chapel Hill.

Patterning NRs. Scheme 2 illustrates our procedure for assembling and patterning Au NRs on Si/SiO_x/MPTMS surfaces. First,

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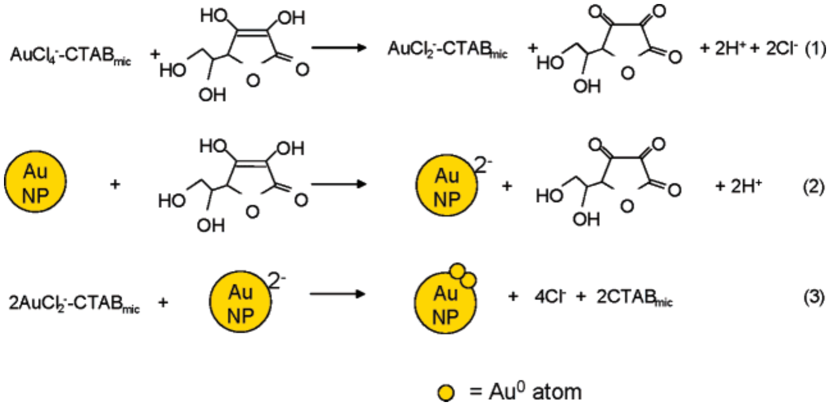
Scheme 3. Seed-Mediated Growth Process



the PDMS stamp was dipped into a 5−10 μL drop of Au NP seed solution and stamped[53] (while still wet) four times onto a clean glass slide before placing the stamp on the Si/SiO$_x$/MPTMS substrate. We found that the patterns were more defined and reproducible using this method as opposed to letting the Au NP solution dry on the stamp, which produced very ill-defined patterns and many structures outside of the stamped region. Pressure was applied to the stamp to ensure good contact with the substrate, and after 2 min, the stamp was removed. The substrate was then rinsed with Nanopure water, dried under N$_2$, and placed into an Au NR "growth solution" consisting of 9 mL of 0.1 M CTAB, 450 μL of 0.01 M HAuCl$_4$*3H$_2$O, and 50 μL of 0.1 M ascorbic acid (AA) for 1 h at 25 °C as described previously.[23,59] The substrate was removed from the growth solution, rinsed copiously with Nanopure water, and dried under N$_2$. An SEM image of a large area pattern and a zoomed-in region of a sample prepared this way are shown in Scheme 2.

SEM Characterization. Parameters. Images were obtained at different magnifications using a Carl Zeiss SMT AG SUPRA 35VP field emission scanning electron microscope (FESEM) operating at an accelerating voltage of 20.00 kV and using an in-lens ion annular secondary electron detector.

Results and Discussion

Scheme 2 shows the general strategy for patterning Au NRs and large-scale and zoomed-in SEM images of a patterned surface. Deposition of Au onto the surface-attached Au NP seeds proceeds via seed-mediated reduction, presumably involving the steps shown in Scheme 3. Step 1 is the reduction of AuCl$_4^-$ to AuCl$_2^-$ by AA in the growth solution prior to immersion of the Au NP patterned Si/SiO$_x$/MPTMS substrate. After the Au NP patterned substrate is introduced, additional AA can transfer two electrons to the surface-attached Au NP seed as shown in step 2. These two electrons are subsequently used to reduce 2AuCl$_2^-$ ions to metallic Au^0 directly on the patterned Au NP seed particle (Step 3). Steps 2 and 3 repeat over time and lead to the growth of larger nanostructures, including Au NRs. The AuCl$_4^-$ and AuCl$_2^-$ ions are associated with the CTAB micelle (mic).[76] The pattern on the substrate is a noticeable pinkish-red color while the growth solution remains colorless, indicating that no Au nanostructures formed in the solution and that the process was predominately confined to the Si/SiO$_x$ surface. Moreover, growth is confined to the areas where Au NP seeds were stamped, leaving the unstamped regions mostly free of nanostructures. This further indicates that the process involves a seed-mediated growth mechanism and that Si/SiO$_x$/MPTMS cannot nucleate the growth of Au itself.

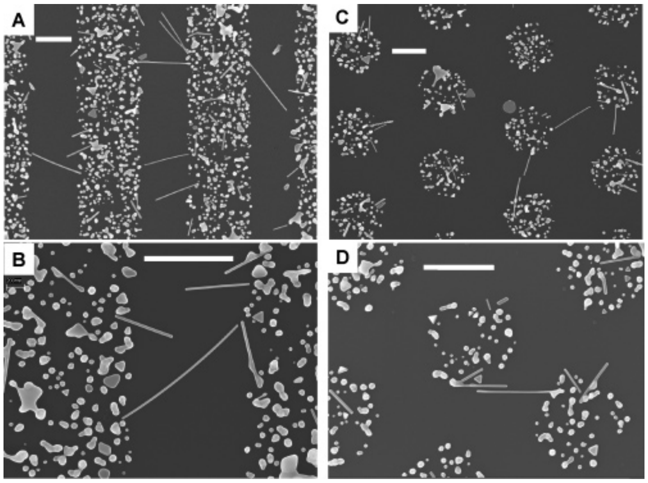


Figure 1. SEM images of Au NRs patterned on a Si/SiO$_x$/MPTMS substrate as described in Scheme 2. Scale bar is 1 μm in all images.

Scanning electron microscopy (SEM) images of different regions of a substrate patterned with Au NRs using the procedure in Scheme 2 are shown in Figure 1, frames A−D. These patterns were made with the 30th stamping of the PDMS stamp. The patterns are filled with NRs, but a large number of spheres, triangles, and hexagons also exist, causing the yield of NRs to be ∼8%. The low yield is consistent with previous solution and surface seed-mediated growth studies.[23,54,60] This is a drawback that will require further investigation and a better understanding of the growth mechanism to increase the overall yield. The average length of the Au NRs in the patterns is 605 ± 298 nm and the diameter of the nanoparticles is 30−40 nm (AR ∼ 20). By varying the synthetic procedure,[23] the average length could be varied from 200 to 1200 nm and the AR from 6 to 22. Some NRs are contained in the middle of the patterns, but a large number of NRs also protrude from the edges of the pattern. We believe this is due to the high density of particles within the pattern preventing the growth of Au NRs there. However, there is sufficient open space for the NRs to grow toward the unstamped regions. This result and previous

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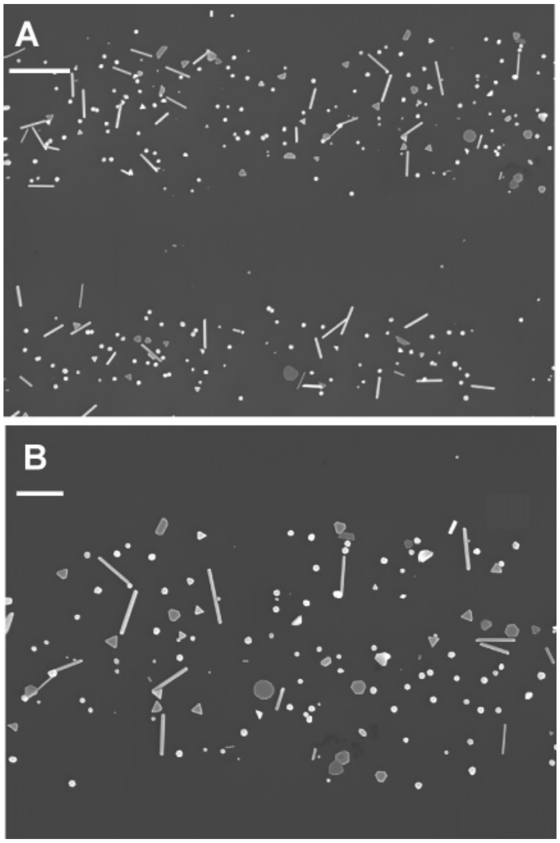

Figure 2. SEM images of Au NRs patterned on Si/SiO$_x$/MPTMS as described in Scheme 2. The seed density is lower compared to Figure 1. Scale bar is 1 μm in all images.

results[23] show that high AR rods are more likely to form in areas of low seed density. These images show that direct growth of Au NRs on surfaces may be useful for integrating and electronically connecting patterned structures on surfaces. Many of the rods growing from the edge of the pattern appear to have grown from seeds predominately in one direction. We previously showed that NRs can grow from seeds in either one or two directions.[59] This likely depends on the seed crystallinity and the spatial relationship with other seed particles.[77]

Figure 2 shows an example of Au NRs grown from a pattern containing a lower density of Au NP seeds. These patterns were prepared with the fifth stamping of a PDMS stamp. In contrast to Figure 1, these images show more NRs contained within the pattern, and it is rare to find NRs protruding from the edges of the pattern. We believe the lower density of seeds allows more room for NRs to grow within the pattern. The seed density is slightly variable from pattern to pattern and not controllable at this time. We are currently working on strategies to control seed density and NR density in the pattern. Figure 2 is similar to Figure 1 in terms of NR length, AR, and yield. Because of the lower density, there are fewer seed particles that have merged into larger structures in Figure 2 compared to Figure 1.

The extremely low yield of NRs limits the potential applications for assembling and patterning NRs with this method. We therefore sought ways to separate other particles from the NRs on the surfaces. Since the Au NRs have a greater footprint area, and likely more interactions with the surface, we hypothesized that spheres could be removed selectively with adhesive tape. Figure 3 shows SEM images obtained on different regions of an unpatterned substrate containing Au NRs before (frame A) and after (frame B) tape was applied to the surface and pulled off. The overall coverage of nanostructures decreased from 25 to 6/μm^2 but, more importantly, the percentage of NRs on the surface increased from 7 to 38% using this simple method. Other samples displayed regions covered with as high as 64% NRs. The tape removes most of the spheres and some of the rods, leaving an overall higher relative population of Au NRs without changing the synthetic conditions. The large triangular and hexagonal platelets also tend to adhere well to the surface because of their large contact area and are thus hard to separate from rods.

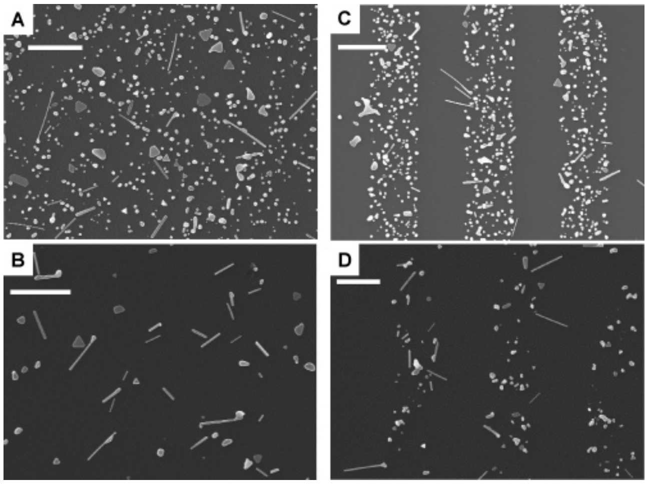

Figure 3. SEM images of unpatterned Au NRs grown directly on Si/SiO$_x$/MPTMS (A) before and (B) after tape was applied to the surface and removed. Patterned Au NRs (C) before and (D) after tape was applied to the surface and removed are also shown. Scale bar is 1 μm in all images.

To fabricate patterns containing mostly NRs, we first patterned and grew Au NRs as in Scheme 1 and then attempted removal of other shapes with tape. Frames C and D in Figure 3 show SEM images of different patterned regions before and after application of tape, respectively. The pattern is more difficult to discern following the tape procedure because the overall density of nanostructures in the pattern has decreased. The patterns are distinguishable and contain several NRs with fewer spherical particles, suggesting that this may be a reasonable approach for fabricating microscale patterns containing a high percentage of Au NRs. This procedure has not been optimized and more work needs to be done.

Conclusions

We have demonstrated a simple method for assembling Au NRs onto surfaces into well-defined microscale regions by combining μCP[53] and seed-mediated growth directly on surfaces.[23,59] High-density patterns contain a large number of rods protruding from the edge of the patterns, while lower density patterns contain more rods within the pattern. All patterns contain a low percentage of NRs among the large

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[77] Penner, R. M. *J. Phys. Chem. B* **2001**, *105*, 8672−8678.

number of spheres, triangles, and hexagons on the surface. Importantly, many of the spherical particles can be separated from the NRs with tape on the basis of differences in adhesion to the surface, which is likely due to different contact areas. The ideal situation would be to pattern and align surfaces with 100% yield of Au NRs in a highly controlled fashion. Future experiments aimed at gaining a better understanding of the seed-mediated growth process may allow us to synthesize NRs in higher yield. We are also exploring strategies for aligning NRs in a controlled direction on the sample. This work represents a step toward these future goals and provides a general method for patterning seed-mediated grown nanostructures on surfaces. Other methods for patterning Au NPs on surfaces could also be used to generate patterns of Au NRs with this general approach.

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