

Large-Area Nanoscale Patterning: Chemistry Meets Fabrication

JOEL HENZIE, JEREMY E. BARTON,
CHRISTOPHER L. STENDER, AND
TERI W. ODOM*

Department of Chemistry, Northwestern University,
2145 Sheridan Road, Evanston, Illinois 60208

Received October 10, 2005

ABSTRACT

This Account describes a new paradigm for large-area nanoscale patterning that combines bottom-up and top-down approaches, merging chemistry with fabrication. This hybrid strategy uses simple nanofabrication techniques to control the alignment, size, shape, and periodicity of nanopatterns and chemical methods to control their materials properties and crystallinity. These tools are highly flexible and can create surface-patterned nanostructures with unusual properties and free-standing nanostructures that are multifunctional and monodisperse. The unprecedented scientific and technological opportunities enabled by nanoscale patterning over wafer-sized areas are discussed.

Introduction

The rational engineering of surface architectures has enabled many exciting observations, such as the enhanced properties of molecules adsorbed on metallic particles, the extraordinary optical transmission of light through metallic films perforated with subwavelength holes, and the incorporation of weakly interacting molecules into higher affinity multivalent surfaces.^{1–4} Although the physical origins of these phenomena are different, one striking similarity is that the surfaces have well-defined structures with feature sizes on the order of 100 nm or less. What is even more intriguing is that the arrangement of the nanofeatures on surfaces—the nanoscale patterns—is responsible for much of this interesting behavior.

Research in nanoscale patterning is motivated by two objectives: (i) tool development and (ii) scientific opportunities at small length scales. The first goal focuses

on designing techniques that can generate features as small as possible. Because initial efforts in nanopatterning were in part driven by the microelectronics industry, it was critical that the techniques were compatible with semiconductor processing.⁵ This constraint allowed the *principles* of microfabrication (parallel processing over wafer-sized areas) to be applied to nanofabrication so that the costs would not increase prohibitively as the feature sizes were reduced. Generating sub-100 nm structures using optical lithography techniques, however, has been challenging and will require short-wavelength light sources and optics and other extensive equipment upgrades.⁶ Other efforts in nanopatterning rely on serial lithographic techniques, such as electron-beam writing, focused ion beam (FIB) milling, and scanning probe methods.⁷ Compared to parallel nanofabrication approaches, these direct-write methods are low throughput and are capable of writing only small areas (hundreds of square micrometers).⁷ The second research objective focuses on how sub-100 nm structures can enable studies of physical and biological processes in unprecedented detail and, also, how nanopatterns can facilitate the assembly and growth of functional nanostructures. The ability to manipulate individual (or small numbers of) electrons, molecules, or nanoparticles opens groundbreaking possibilities for fundamental research and revolutionary technological advances.^{8,9}

Why would chemists be interested in nanoscale patterning? Or, phrased another way, are there interesting scientific questions or advances if chemistry is combined with fabrication? At the microscale, we need to look no further than the impact that microarray technology has had on DNA analysis or combinatorial organic synthesis to answer *yes*—both the small spot sizes and the patterns have enabled new ways to approach complex problems.^{10,11} Nanoscale patterning does not simply offer prospects for shrinking the sizes of micrometer-sized spots and increasing their density on surfaces but provides a platform for discoveries, especially for interfacing molecules with metals or semiconductors. For example, an understanding of molecule–materials interfaces is important for controlling metal–molecule contacts in molecule-based electronics and assessing semiconductor–biomolecule compatibility in nanomedicine.^{8,12} Moreover, strategies to control the assembly and organization of molecules and nanostructures on surfaces are critical for the direct integration of the patterns into practical devices and architectures.

Nanopatterning tools not only enable new scientific discoveries; they are the primary driving factor—science and tools are interwoven. There are, however, challenges in nanofabrication that can stymie progress, such as (i) expensive equipment, (ii) limited access to facilities, (iii) time required to generate patterns, (iv) inability to pattern large areas easily, and (v) difficulty in making functional nanostructures. To overcome these problems, we and

Joel Henzie received his B.S. from the University of Nebraska-Lincoln in 2000 and is a Ph.D. candidate in Chemistry at Northwestern University. His research focuses on the design and characterization of nanoscale photonic structures.

Jeremy E. Barton received a B.A. in Biology from Grinnell College in 2002 and is a Ph.D. candidate in Chemistry at Northwestern University. His research focuses on nanotechnology tool development.

Christopher L. Stender received a B.S. in Chemistry from Linfield College in 2002 and is a Ph.D. candidate in Chemistry at Northwestern University. His research interests include synthesis, patterning, and applications of nanostructured materials.

Teri W. Odom received her B.S. in Chemistry from Stanford University and her Ph.D. in Chemical Physics from Harvard University. After postdoctoral training at Harvard University, she joined the Department of Chemistry at Northwestern University in 2002. Her current research focuses on the optical properties of nanostructures fabricated by unconventional nanopatterning techniques and nanocrystals synthesized by chemical methods.

* Corresponding author. E-mail: todom@northwestern.edu.

others are developing a new paradigm for nanopatterning that combines both bottom-up and top-down approaches,^{13–20} merging chemistry with fabrication. This hybrid strategy uses simple *fabrication techniques* to control the alignment, size, shape, and periodicity of the nanopatterns over large areas and *chemical methods* to control their local structure, crystallinity, and materials properties.

Below we describe research from our laboratory directed toward large-area nanopatterning tools that can create *surface-patterned* nanostructures with unusual optical or physical properties and *free-standing* nanostructures that are monodisperse and multifunctional. First, laser-assisted embossing using nanosphere molds to generate nanowells for nanocrystal growth is presented. Second, strategies to extend soft lithographic techniques to sub-100 nm patterning are described. Third, methods for the directed growth and assembly of nanostructures on surfaces are discussed. Last, procedures to construct anisotropic, multifunctional nanoparticles and free-standing films of nanoholes are outlined. We conclude by highlighting the exciting scientific and technological prospects that are enabled by large-area nanopatterning.

Chemistry in Zeptoliter Beakers

The intersection of nanopatterning with synthetic methods enables chemical reactions to be performed in extremely small volumes. One bottom-up strategy for producing nanopatterns is the assembly of sub-microspheres. Polystyrene or silica spheres can be packed into two-dimensional (2D) or three-dimensional (3D) hexagonal arrays by a variety of methods, including drop coating, spin-casting, and convective self-assembly.^{17,21,22} Assembled sphere arrays are most often used as a “mask” through which materials (typically metals) are deposited within the interstitials of the spheres. After the mask is removed, truncated prisms or interconnected honeycomb patterns are formed with reasonably good local order. These patterns have been used in localized surface plasmon resonance (LSPR) studies, as surface-enhanced Raman spectroscopy (SERS) substrates, and as catalysts for the growth of zinc oxide (ZnO) nanorods and carbon nanotubes.^{21,23–25}

Besides their function as a mask, self-assembled spheres can also be used as a nanosphere mold.¹⁷ We have used 100-nm silica spheres to generate hemispherical wells in silicon by laser-assisted embossing (Figure 1A,B). The sizes of the nanowells can be controlled by changing (i) the size of the spheres in the mold, (ii) the energy density of the incident laser pulse, and (iii) the applied mechanical pressure between the mold and the surface. Thermal oxidation of the patterned silicon substrates can reduce the size of the wells by 10–20 nm. Since the nanowells are patterned in silicon or silicon oxide, they can be functionalized with hydrophobic or hydrophilic silane molecules.

These nanowells are ideal reaction vessels or “beakers” to grow isolated and monodisperse nanocrystals that are

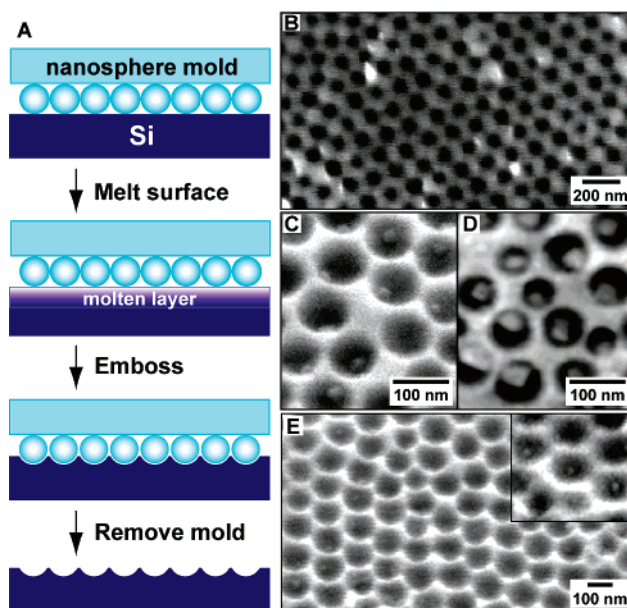


FIGURE 1. (A) Scheme for generating nanowells, (B) nanowells in Si, (C) NaCl crystals from 1 M salt solution, (D) NaCl crystals from 5 M salt solution, and (E) CdS nanocrystals in nanowells (inset—zoom of CdS nanocrystals). Adapted from ref 17.

well-ordered on a substrate. Because of their small volumes and chemical functionality, low concentrations of precursor materials can enable the growth of different types and sizes of nanoparticles. We have achieved size control of NaCl crystals down to 25 nm (Figure 1C,D) and have grown CdS nanocrystals as small as 2 nm (Figure 1E). What is most surprising about the CdS particles is that they are crystalline, even though these reactions were performed at room temperature. By limiting the amount of material available for reaction in each well, we can control nucleation so that only one crystal is formed within a nanowell.

This first example of nanopatterning combined with chemical syntheses shows significant promise for the growth and parallel assembly of individual nanocrystals. Because isolated particles can be formed in well-defined locations, detailed studies of the properties of individual nanoparticles are now possible. We anticipate that these reactors can also be used to synthesize new types of nanomaterials at high temperatures, that is, solid state reactions using molecular precursors. A drawback of using the bottom-up assembly of spheres to generate nanopatterns is that it is somewhat inflexible, since the patterns are limited in shape, pitch, and symmetry. In addition, patterned areas without defects are typically on the order of hundreds of square micrometers, although recent work has reported patterned areas several square inches.²⁶ One large-area, top-down nanopatterning method can meet many of these drawbacks: soft nanolithography.

Soft Nanopatterning Essentials

Soft lithography is a catch-all term for techniques that use a patterned, polymeric stamp or mask to transfer patterns (made of molecules, polymers, or metals) from one surface

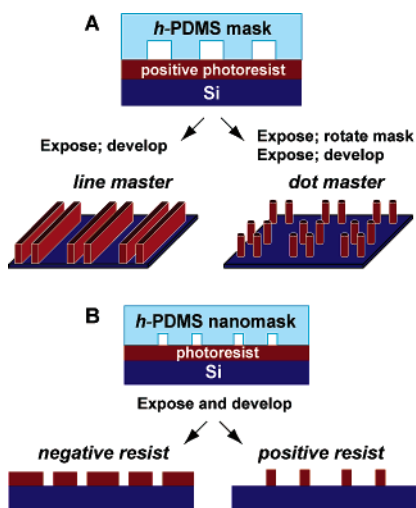


FIGURE 2. (A) Fabrication of nanoscale masters by PSP using *h*-PDMS masks patterned with microscale features and (B) sub-250 nm patterns in photoresist generated using *h*-PDMS nanomasks.

to another.²⁷ These methods, using the form of poly-(dimethylsiloxane) (PDMS) most commonly used for fabricating stamps (Sylgard 184), are best suited for patterning features and fabricating structures on the micrometer scale.²⁸ To expand the capabilities of soft lithography to the sub-100 nm regime, the mechanical properties of the PDMS stamp must be improved.²⁹ We have designed composite PDMS stamps composed of a thin, stiff layer of hard *h*-PDMS supported by a thick slab of 184 PDMS.³⁰ This *h*-PDMS material is a key enabler for our suite of soft lithographic nanopatterning tools, which can generate small (sub-30 nm) features over relatively large areas (>1 in²).^{15,18–20,30,31}

Our techniques have four important advantages over serial lithographic methods: (i) Use of masters. Masters are high-quality patterns from which many low-cost copies can be duplicated. We can fabricate inexpensive masters patterned with arrays of sub-250 nm features in photoresist generated by phase-shifting photolithography (PSP),^{15,30} although soft nanopatterning is readily applicable to masters prepared by other methods. (ii) Parallelism. PDMS is cast against a master to form an elastomeric mask, which is then used to fabricate arrays of structures simultaneously. (iii) Simplicity. We use widely available lithographic techniques including photolithography, wet chemical etching, and e-beam deposition. (iv) Flexibility. We can generate patterns with different symmetry and spacing, out of multiple materials, and with exquisite control over the thickness of each layer.

Fabrication of Masters with Sub-250 nm Features.

Nanoscale patterns in photoresist (the master) can be generated by PSP using composite PDMS masks. Feature sizes of 100–500 nm can be produced in positive-tone photoresist by exposing UV-light through a PDMS mask patterned with micrometer-sized lines. If only one exposure is made, lines as narrow as 50 nm are formed at the edges of the features in the mask (Figure 2A). After two exposures (the mask is rotated after the first exposure and

exposed again), 100–300 nm dots are formed and spaced at the pitch of the lines. If the second exposure is through the same mask but rotated by 90° (60°), square (hexagonal) patterns are formed (Figure 2A). If the second exposure is through a mask patterned with lines having a different spacing but rotated by 90°, rectangular or quasi-1D lattices can be generated.¹⁸ Hence, masters with 250-nm features can be produced easily with a broad range of pitch and symmetries. To transfer these patterns into functional materials, we usually replicate the nanomasters in *h*-PDMS to make “nanomasks,” so that the size, shape, and symmetry of the patterns can be readily reproduced on a variety of substrates.

Phase Shifting Photolithography at the Sub-250 nm Level. Standard PSP is an edge lithography that produces narrow features in photoresist at the edges of patterns in a PDMS mask. As the patterns in a *h*-PDMS mask are reduced to ca. 250 nm or less, the edges of the generated features overlap, and thus the photoresist patterns are *identical* in size and pitch to the mask (Figure 2B).¹⁵ We took advantage of this observation to generate, in parallel, patterns or templates in negative photoresist for depositing metal or assembling nanomaterials. The primary limitation for creating holes and trenches using optical lithography is the inherent resolution (sub-micrometer) of negative-tone resists.³² We have overcome this challenge by using a negative resist that does not require the postbaking step, which often broadens feature sizes.⁵ We can also use features in positive resist to fabricate interesting free-standing metallic nanostructures. Now that we have the tools to generate nanopatterns in well-defined locations, we need to do chemistry on them, or in other words, make them functional.

Directed Growth and Assembly of Semiconducting Nanostructures

Nanopatterns are well-suited to organize nanostructures on surfaces because they are of the same length scale. This assembly can occur by two general approaches: (i) the directed growth of the nanostructures at predefined locations and (ii) the synthesis of nanomaterials followed by assembly into architectures. The properties of these surface-patterned nanostructures can then be studied for interesting collective effects or tested for their use in macroscopic devices.

Directed Growth of ZnO Nanowires Arrays. ZnO nanostructures have received much attention because of their emission in the near-UV, strong absorption in the UV, and field-emission capabilities.³³ They can be organized on different substrates (e.g., sapphire, silicon) by patterning the appropriate catalyst or seed layer, and usually the ZnO nanorods are well-aligned with their *c*-axis perpendicular to the substrate.³⁴ Gold is typically the material used to catalyze the growth of ZnO nanowires in vapor–liquid–solid (VLS) methods, and silver has been shown to facilitate the assembly of ZnO nanorods from solution.³⁵ Early work on assembling ZnO nanowires focused on preparing Au areas patterned through masks

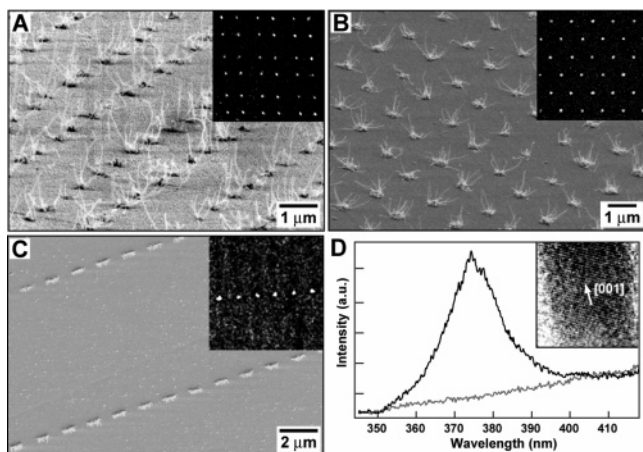


FIGURE 3. Arrays of ZnO nanowires grown from Au dots: (A) square lattice; (B) hexagonal lattice; (C) 1D arrays; (D) photoluminescence from ZnO nanowires patterned in a square lattice (inset—HRTEM image of a ZnO nanowire). Adapted from ref 18.

such as transmission electron microscopy (TEM) grids and monolayers of sub-microspheres.^{24,34} Using our simple nanofabrication tools, we have demonstrated the flexibility to pattern functional nanostructures at specific locations with periodic order, variable spacing, and symmetry over areas ~ 1 in².

Small diameter ZnO nanowires can be grown from patterned, thin gold dots using a VLS process. Arrays of nanowires have been grown in square, hexagonal, and 1D lattices (Figure 3); ZnO nanowires exhibited different lengths depending on the growth conditions, although their diameters were similar in size. These nanowires have very narrow diameters (10–15 nm) and relatively long lengths (2–10 μm). High-resolution TEM images (Figure 3D, inset) reveal that the wires are single-crystal with growth along the [001] direction. The photoluminescence of ordered ZnO nanowire arrays shows strong room-temperature emission at ~ 374 nm with a narrow (15 nm) full-width at half-maximum peak, which indicates the uniformity of diameters in the arrays of ZnO nanowires (Figure 3D).

Conversion of Metal Nanopatterns into Metal Disulfide Nanostructures. Besides using the patterned metallic areas to nucleate or catalyze the growth of nanomaterials, we have developed an important variant of the directed growth method: *chemically converting* the nanopatterns into crystalline nanostructures. We have demonstrated this strategy for MoS₂, a layered semiconducting material that has shown promise in chemical sensors,³⁶ in solar cells,³⁷ in catalysis,³⁸ and as low-friction surfaces.³⁹ Recent studies have suggested that reducing the size of the MoS₂ crystals can improve their lubrication properties in bearings, O-rings, or other heavy wear applications.³⁹ Although lines of MoS₂ ribbons can be grown on the step edges of graphite by electrochemical methods,⁴⁰ control of the height, spacing, and overall length of the ribbons remains a challenge.

Figure 4A outlines the procedure for patterning MoS₂ nanostructures.¹⁹ First, sub-300 nm lines of Mo were

patterned on silicon or quartz substrates by PSP followed by e-beam deposition of Mo and lift-off of the resist. We then placed the Mo patterns into a quartz tube furnace for sulfidation at 850 °C in the presence of Ar and H₂S gas. Surprisingly, the morphology of the patterned MoS₂ nanostructures depends on the location of the original Mo patterns in the furnace. Samples placed 9–10 in. downstream from the entrance formed MoS₂ plates parallel to the substrate (~ 200 nm in height; Figure 4C), while samples 3–4 in. downstream produced MoS₂ plates oriented nearly perpendicular to the substrate (50–150 nm thickness on the edge; Figure 4D). We propose that variations in the H₂S concentration along the tube furnace or the decomposition of H₂S gas along the length of the furnace contribute to the preferential orientation of MoS₂ nanocrystals.

What is most interesting about this system is that the lateral size of the metallic nanopatterns is responsible for the dramatic orientational growth of the MoS₂ nanocrystals. If the lateral size of the Mo patterns exceeds roughly 300 nm, the patterned MoS₂ nanocrystals do not exhibit any preferential growth; only a mixture of crystals oriented parallel and perpendicular to the substrate is observed. This unexpected result is another example of how nanopatterning can result in new physical properties of nanoscale materials. In addition, our nanopatterning-followed-by-chemical conversion method can generate nanostructures different from straight lines (Figure 4E,F). These patterned MoS₂ nanostructures are indeed functional, as demonstrated by their crystal structure and UV–vis absorption properties (Figure 4G).

These directed growth strategies to pattern semiconducting nanostructures are quite versatile for nanomaterials that can either form an alloy with catalytic metallic nanoparticles or be formed after reactions with H₂S gas. These materials have controllable orientation, height, width, and shape and can be integrated directly into device platforms. To organize other optical materials in well-defined locations, without pre patterning metallic nanostructures, we use soft templates to assemble preformed nanocrystals.

Assembly of Preformed Nanocrystals Using Soft Templates. Solution-synthesized nanocrystals are ideal building blocks for a range of devices because of their unique properties^{12,41} and because they can be produced in batch quantities.⁴² Assembly methods to manipulate them on surfaces include fluidic-based assembly,^{34,43} electric and magnetic field mediated assembly,^{44–46} and electrostatic assembly.^{47,48} Although these techniques can achieve good local order of nanoparticles, the throughput is low, and the sizes of the patterned areas are relatively small (hundreds of square micrometers). Template-based assembly is another promising approach for positioning nanoparticles from solution into well-defined locations.^{17,20,49–51} Nanopatterning techniques that can generate soft templates for assembly include PSP, e-beam lithography, and ion lithography, although only PSP can generate patterns over large areas (square inches) in parallel. Using PSP to define the nanopatterned templates

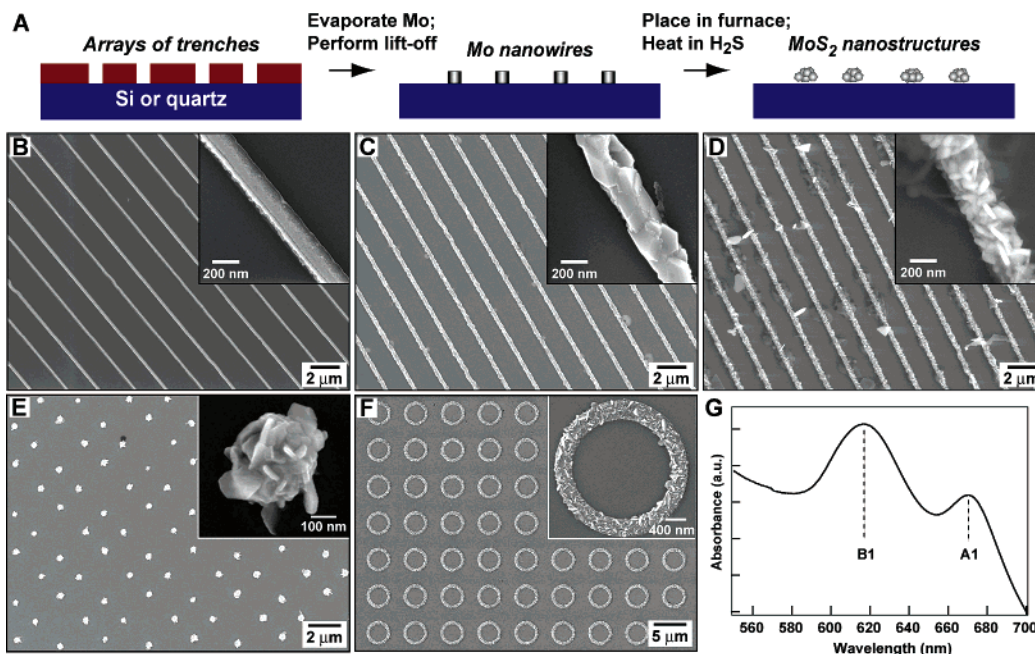


FIGURE 4. (A) Scheme for patterning MoS₂ nanostructures, (B) lines of Mo, (C) MoS₂ lines converted from panel B after reacting with H₂S gas, (D) MoS₂ lines converted from panel B with crystals oriented perpendicular to the surface, (E) MoS₂ dots, (F) rings of MoS₂ nanostructures, and (G) UV–visible absorption spectroscopy of a MoS₂ nanostructured film. Adapted from ref 19.

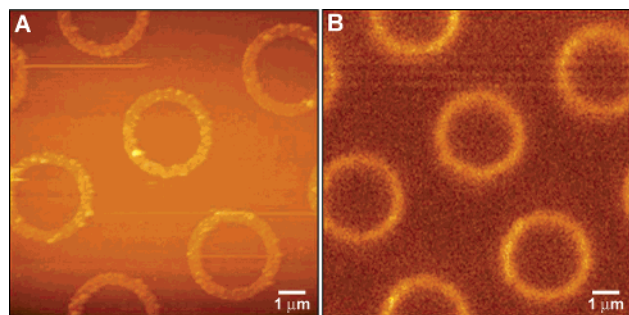


FIGURE 5. (A) CdSe/ZnS quantum dots patterned into rings using the photoresist ring template and (B) fluorescence NSOM image of dots assembled into rings. Adapted from ref 49.

and colloidal semiconducting quantum dots, we have developed a simple approach for hierarchical assembly on all length scales—organization over square nanometers (self-assembly of quantum dots), over square micrometers (template shape), and over square centimeters (arrays of template pattern).

We performed PSP using a mask patterned with 3- μ m circles on negative resist to generate ring templates for the assembly of CdSe/ZnS quantum dots. The template was immersed into a concentrated solution of water-soluble quantum dots for 12–36 h and was subsequently removed by dissolution in acetone. Patterned mesostructures of CdSe/ZnS quantum dots with curved and straight features were achieved over areas ~ 1 in². Figure 5A depicts quantum dots well-packed into rings. We tested the integrity of the assembled quantum dots by characterizing the localized photoluminescence from individual ring structures using near-field scanning optical microscopy (NSOM) (Figure 5B).

Multifunctional Metallic Nanostructures: View from the Top

So far we have described how our nanopatterning toolkit can generate *surface-patterned* nanostructures that are crystalline, functional, and assembled in a wide range of patterns. In this final section, we will demonstrate how top-down methods, using hard templates, can be used to mold the size and shape of *free-standing* metallic nano- and mesostructures. Although solution-phase synthesis is the typical route to control the size and shape of metallic nanoparticles, a common drawback is the formation of various other shapes in addition to the desired product.² Moreover, because metallic structures with sizes up to several hundred nanometers can exhibit interesting optical properties,^{52,53} large-area nanopatterning can easily achieve these sizes and with densities comparable to those of nanoparticles in solution.

Sacrificial templates are usually solid or supported structures, such as nanometer-sized pores in anodized alumina membranes or micrometer-sized etched pits in Si.^{54,55} Electro-deposition of conducting materials is used to reproduce the shape and structure of the template; the templates can then be removed by chemical etchants. Anisotropic structures such as metallic (and multilayered) rods, pyramidal tips for scanning probe applications, and metallic pyramidal shells can be produced from solid templates.^{20,52,55–57} Arrays of silica spheres can also be used to template metallic structures with unusual shapes.^{58,59} Top-down fabrication methods offer several advantages over bottom-up syntheses for the generation of nanoparticles: (i) monodispersity of particle size; (ii) uniformity of particle shape; (iii) increased flexibility to form particles

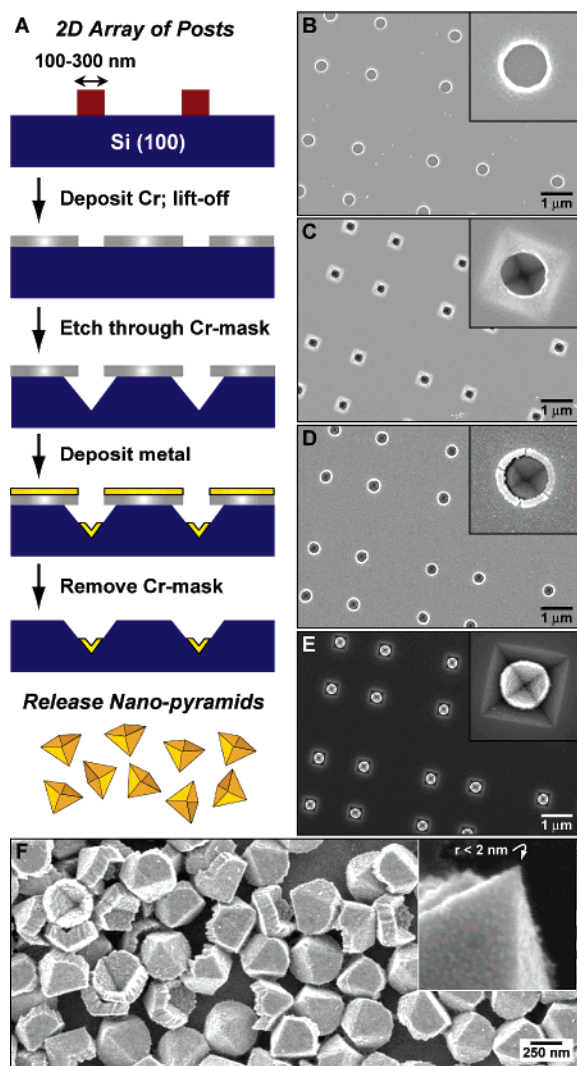


FIGURE 6. (A) Scheme depicting the fabrication of the free-standing metallic pyramids, (B) Cr mask of 250-nm holes, (C) etched Si(100) pyramidal pits undercutting the Cr mask in panel B, (D) 50-nm film of Ni deposited on the structures in panel C, (E) Ni pyramids situated in the centers of the etched Si pits (the insets are 500 nm \times 500 nm), and (F) released metallic pyramids (inset—tip of a Au/Ni/Au pyramid with $r < 2$ nm). Adapted from ref 20.

out of more than one material; (iv) precise control of the thicknesses of materials in multilayer particles.

Mesoscale Pyramids with Nanoscale Tips. We have developed a simple procedure that can generate free-standing, mesoscale metallic pyramids composed of one or more materials and having nanoscale tips. These anisotropic nanoparticles are interesting because their optical properties can be quite different from spherical particles of similar sizes.² Theoretical studies have shown that very sharp points—tips—in noble metals can concentrate electromagnetic fields, which can dominate the optical properties of nanoscale structures.^{60,61}

Figure 6 depicts the procedure for generating metallic pyramids within the etched pits of a Si(100) substrate using a Cr-film patterned with sub-250 nm holes as *both* the etch mask and deposition mask.²⁰ We took advantage of the Si undercutting the Cr mask to fabricate pyramids *smaller* than the size of the etched pyramidal pits and

defined by the size of the Cr hole. The crystalline Si(111) facets and the sharp tips of the pyramidal pits are ideal features of a template for preparing well-formed particles. Next, we evaporated different individual metals (Ni, Au) or combinations of metals (Au/Ni, Au/Ni/Au) through the Cr mask and then etched the Cr film to reveal metallic pyramids situated within the centers of the Si pyramidal pits. The metallic pyramids can be removed from the template by etching the Si. The four faces of the pyramids are remarkably smooth, and a majority (>99.9%) of the pyramidal tips had a radius of curvature $r < 10$ nm with many tips $r < 2$ nm.

One of the greatest advantages (besides creating nanoscale tips) of this top-down procedure for nanoparticles is our ability to control the materials and chemical functionality of these pyramids. We can use the layer-by-layer feature of e-beam deposition to create multilayered pyramids of Au and Ni with variable thicknesses. Such mesostructures can be manipulated with magnetic fields because of their magnetic interior and can easily be chemically functionalized on their outer shell. We anticipate that these multilayered pyramids generated out of different types of materials (including insulators) will be useful in investigations of certain biological systems.⁶² The production of free-standing and isolated noble metal particles with well-defined, ultrasharp tips also facilitates detailed studies of their optical properties (e.g., LSP resonances) and their use as SERS substrates.

Large-Area Arrays of Nanoholes. In the examples described above, we have focused on nanoparticles or nanostructures constructed by large-area nanopatterning methods. We want to close this Account by describing a system having a structure that is the inverse of particles: holes. In many aspects, the properties of nanoholes in metallic films are analogous to the properties of nanoparticles; for example, both can support LSP resonances that are tunable depending on their size and shape.² Interestingly, when nanoholes are patterned into periodic square arrays, they exhibit enhanced transmission with peaks characteristic of interacting holes.⁶³ These arrays are enabling new fundamental studies of surface plasmon interactions with periodic structures^{31,64–66} and novel technologies including spectroscopically based chemical and biological sensors and photonic devices.^{67–70} The most common method to fabricate hole arrays is FIB milling,⁶³ a serial and low throughput approach that can control the diameter and spacing of the holes with reasonable precision. We have developed a simple approach for generating free-standing, large-area films of nanoholes that will enable increased access to these films, which is critical not only for more detailed investigations but for their use in scalable device applications.

Large-area films of nanohole arrays were prepared in a procedure similar to that for creating metallic pyramids (Figure 7). After the Cr film is etched to expose the pyramids in the Si pits, a metallic film of nanohole arrays can be detached from the Si substrate and placed on a glass slide or any other substrate. Because the materials of these films are deposited by e-beam evaporation, these

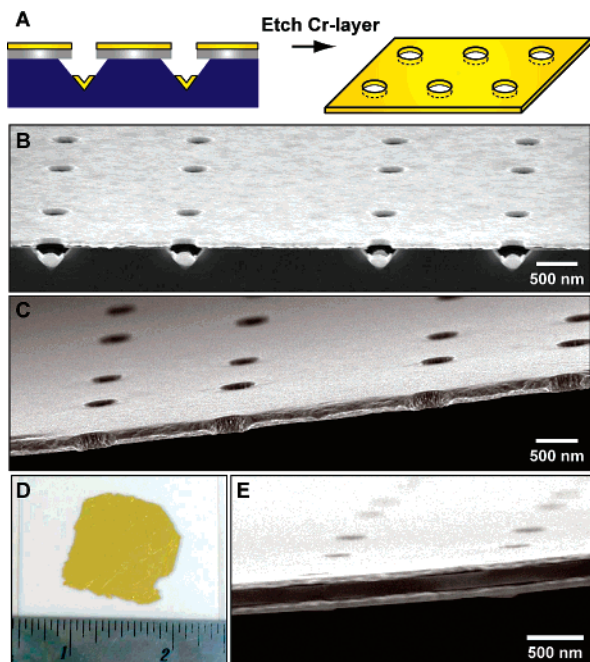


FIGURE 7. (A) Scheme to release free-standing film of large-area nanohole arrays, (B) nanohole film attached to Si with pyramids beneath the holes, (C) portion of a free-standing 100-nm Au film perforated with 250-nm holes, (D) optical micrograph of ~ 1 in.² film on a glass, and (E) portion of a free-standing Au/SiO₂/Au film. Adapted from ref 31.

hole arrays can be made of almost any material. We have constructed hole array films with a single materials layer, two layers, and three layers. Our materials general technique can even generate nanohole films from a combination of metal and dielectric materials (Figure 7E). Unlike hole arrays fabricated by FIB, the overall topography of these large-area films is flat and very uniform.

We tested the optical quality of the hole arrays using NSOM in transmission mode. Under local illumination (excitation wavelength, $\lambda_{\text{ex}} = 633$ nm) from the tip, a 100-nm thick Au film exhibited enhanced transmission at the holes as well as fringes reminiscent of standing wave patterns between adjacent holes (Figure 8A). These fringes can be attributed to the interference between surface plasmon polariton (SPP) waves generated by the NSOM tip and the SPPs reflected by the holes.³¹ We calculated that standing waves in the near-field intensity appeared on both the top and bottom metal surfaces and that these fringes in the near-field should lead to intensity maxima in the far-field with a period (λ_{sw}) approximately half of the SPP wavelength ($\lambda_{\text{SPP}} = 603$ nm⁶⁶) at the Au film/air interface (Figure 8B). Indeed, fringes with $\lambda_{\text{sw}} \approx 322$ nm, ca. $\lambda_{\text{SPP}}/2$, were measured in the experiment (Figure 8C).

Multilayered films (Au/Ni/Au) consisting of a Ni core sandwiched between two layers of Au with thicknesses of 40 nm/20 nm/40 nm (40/20/40) and 40/70/40 were also investigated. Under $\lambda_{\text{ex}} = 633$ nm light, both films exhibited standing wave patterns with a period of $\lambda_{\text{sw}} \approx 320$ nm, nearly identical to the pure Au film case. We also imaged the 40/70/40 film with $\lambda_{\text{ex}} = 800$ nm ($\lambda_{\text{SPP}} \approx 784$ nm⁶⁶) and observed fringes with an increased spacing, λ_{sw}

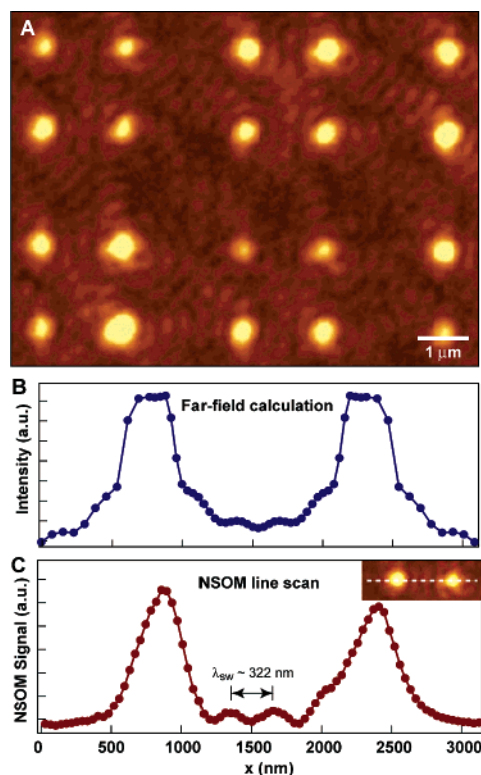


FIGURE 8. (A) NSOM optical image of holes in a 100-nm Au film on glass, (B) calculated far-field intensity of four holes, and (C) cross-section of two neighboring holes from panel A. Adapted from ref 31.

≈ 380 nm, which is ca. $\lambda_{\text{SPP}}/2$ at this excitation wavelength and consistent with our model. This technology provides a flexible strategy to create large-area films of high optical quality out of both metallic and dielectric materials and whose properties can be rapidly screened and tailored for sensing and photonics. Importantly, these tools enable new ways to think about combining SPPs for signal propagation with LSPs for coupling to and from the far-field and to imagine versatile metal and dielectric composites for negative index applications at optical frequencies.

Concluding Remarks

In this Account, we have introduced the concept of large-area nanoscale patterning—the new nanofabrication tools that emerge when chemistry meets fabrication. More than simply a necessary intermediate for practical devices or a “bridge” across the microscale–nanoscale divide, these tools allow hierarchical assembly, the patterning of materials on multiple length scales and with multiple functions, unusual shapes, and crystalline structure. Applying materials chemistry to nanopatterning not only produces a unique tool-kit that is general for many different materials but creates opportunities to observe unexpected behavior, such as the orientated growth of MoS₂ nanostructures or the room-temperature growth of CdS nanocrystals in nanobeakers. Another compelling outcome of patterning functional nanostructures is that a demand for more versatile characterization techniques is created—how

can the instrumentation for the in-situ analysis of surface-patterned nanostructures be developed or made more accessible? Most researchers must remove the structures (i.e., destroy the patterns) from the surface to carry out a detailed structural analysis.

To close, we want to emphasize the importance of patterning over large areas. The ability to pattern, in parallel, over several square inches allows nanofeatures to be used for rapid screening, high-throughput applications, and prototyping. Also, our development of large-area patterning tools using only simple materials (PDMS) and widely available lithographic techniques (e-beam deposition, photolithography, and etching) allows increased access to nanopatterned structures at a substantially reduced cost, both in time and in equipment resources. We believe, moreover, that these tools will enable exciting scientific opportunities and allow unprecedented flexibility for applications that were previously only a speck on the horizon.

We would like to thank our co-workers who have made significant contributions to the work described in this Account, including Yelizaveta Babayan, Eric Greyson, and Eun-Soo Kwak. We acknowledge Gilbert Chang and George Schatz for calculations. We thank the National Science Foundation (Grants CAREER CHE-0349302 and NSEC EEC-0118025), the ACS Petroleum Research Fund, and the URETI program of NASA (under Grant No. NCC 2-1363) subcontracted through Purdue University (under Agreement No. 521) at the MRI of Northwestern University for their generous financial support. T.W.O. is a DuPont Young Professor, an Alfred P. Sloan Fellow, a David and Lucile Packard Fellow, and a Cottrell Scholar of Research Corporation.

References

- Kneipp, K.; Kneipp, H.; Itzkan, I.; Dasari, R. R.; Feld, M. S. Surface-enhanced Raman scattering and biophysics. *J. Phys.: Condens. Matter* **2002**, *14*, R597–R624.
- Xia, Y.; Halas, N. J. Synthesis and Plasmonic Properties of Nanostructures. *MRS Bull.* **2005**, *30*, 338–348, and references therein.
- Barnes, W. L.; Dereux, A.; Ebbesen, T. W., Surface plasmon subwavelength optics. *Nature* **2003**, *424*, 824–829.
- Auletta, T.; Dordi, B.; Mulder, A.; Sartori, A.; Onclin, S.; Bruinink Christiaan, M.; Peter, M.; Nijhuis Christian, A.; Beijleveld, H.; Schonherr, H.; Vancso, G. J.; Casnati, A.; Ungaro, R.; Ravoo Bart, J.; Huskens, J.; Reinhoudt, D. N. Writing patterns of molecules on molecular printboards. *Angew. Chem.* **2004**, *43*, 369–373.
- Madou, M. J. *Fundamentals of Microfabrication The Science of Miniaturization*, 2nd ed.; CRC Press: Boca Raton, FL, 2002.
- Peters, J. H. Status of EUVL mask development in Europe. *Proc. SPIE Int. Soc. Opt. Eng.* **2005**, *5853*, 297–307.
- Gates, B. D.; Xu, Q.; Stewart, M.; Ryan, D.; Willson, C. G.; Whitesides, G. M. New Approaches to Nanofabrication: Molding, Printing, and Other Techniques. *Chem. Rev.* **2005**, *105*, 1171–1196.
- Reed, M. A.; Zhou, C.; Muller, C. J.; Burgin, T. P.; Tour, J. M. Conductance of a Molecular Junction. *Science* **1997**, *278*, 252–254.
- Postma, H. W. C.; Teepen, T.; Yao, Z.; Grifoni, M.; Dekker, C. Carbon Nanotube Single-Electron Transistors at Room Temperature. *Science* **2001**, *293*, 76–79.
- Eisen, M. B.; Spellman, P. T.; Brown, P. O.; Botstein, D. Cluster analysis and display of genome-wide expression patterns. *Proc. Natl. Acad. Sci. U.S.A.* **1998**, *95*, 14863–14868.
- Korbel, G.; Lalic, G.; Shair, M. D. Reaction Microarrays: A Method for Determining the Enantiomeric Excess of Thousands of Samples. *J. Am. Chem. Soc.* **2001**, *123*, 361–362.
- Alivisatos, P. The use of nanocrystals in biological detection. *Nat. Biotechnol.* **2004**, *22*, 47–52.
- Yin, Y.; Gates, B.; Xia, Y. A soft lithography approach to the fabrication of nanostructures of single crystalline silicon with well-defined dimensions and shapes. *Adv. Mater.* **2000**, *12*, 1426–1430.
- Sun, Y.; Khang, D.-Y.; Hua, F.; Hurley, K.; Nuzzo, R. G.; Rogers, J. A. Photolithographic route to the fabrication of micro/nanowires of III–V semiconductors. *Adv. Funct. Mater.* **2005**, *15*, 30–40.
- Odom, T. W.; Thalladi, V. R.; Love, J. C.; Whitesides, G. M. Generation of 30–50 nm Structure Using Easily Fabricated, Composite PDMS Masks. *J. Am. Chem. Soc.* **2002**, *124*, 12112–12113.
- Wang, X. D.; Graugnard, E.; King, J. S.; Wang, Z. L.; Summers, C. J. Large-Scale Fabrication of Ordered Nanobowl Arrays. *Nano Lett.* **2004**, *4*, 2223–2226.
- Barton, J. E.; Odom, T. W. Mass-Limited Growth in Zeptoliter Beakers: A General Approach for the Synthesis of Nanocrystal. *Nano Lett.* **2004**, *4*, 1525–1528.
- Greyson, E. C.; Babayan, Y.; Odom, T. W. Directed growth of ordered arrays of small-diameter ZnO nanowires. *Adv. Mater.* **2004**, *16*, 1348–1352.
- Stender, C. L.; Greyson, E. C.; Odom, T. W. Patterned MoS₂–Nanostructures over cm²-Areas. *Adv. Mater.* **2005**, *17*, 2837–2841.
- Henzie, J.; Kwak, E.-S.; Odom, T. W. Mesoscale Metallic Pyramids with Nanoscale Tips. *Nano Lett.* **2005**, *5*, 1199–1202.
- Hulteen, J. C.; Van Duyne, R. P. Nanosphere lithography: A materials general fabrication process for periodic particle array surfaces. *J. Vac. Sci. Technol., B* **1995**, *13*, 1553–1558.
- Xia, Y.; Gates, B.; Yin, Y.; Sun, Y. *Handbook of Surface and Colloid Chemistry*; CRC Press LLC: Boca Raton, FL, 2003.
- Haynes, C. L.; McFarland, A. D.; Van Duyne, R. P. Surface-enhanced Raman spectroscopy. *Anal. Chem.* **2005**, *77*, 338A–346A.
- Wang, X.; Summers, C. J.; Wang, Z. L. Large-Scale Hexagonal-Patterned Growth of Aligned ZnO Nanorods for Nano-optoelectronics and Nanosensor Arrays. *Nano Lett.* **2004**, *4*, 423–426.
- Wang, Y.; Rybczynski, J.; Wang, D. Z.; Kempa, K.; Ren, Z. F.; Li, W. Z.; Kimball, B. Periodicity and alignment of large-scale carbon nanotubes arrays. *Appl. Phys. Lett.* **2004**, *85*, 4741–4743.
- Jiang, P.; McFarland, M. J. Large-Scale Fabrication of Wafer-Size Colloidal Crystals, Macroporous Polymers and Nanocomposites by Spin-Coating. *J. Am. Chem. Soc.* **2004**, *126*, 13778–13786.
- Xia, Y.; Whitesides, G. M. Soft lithography. *Annu. Rev. Mater. Sci.* **1998**, *28*, 153–184.
- Gates, B.; Xu, Q.; Love, J. C.; Wolfe, D. B.; Whitesides, G. M. Unconventional Nanofabrication. *Annu. Rev. Mater. Res.* **2004**, *34*, 339–372.
- Schimid, H.; Michel, B. Siloxane Polymers for High-Resolution, High-Accuracy Soft Lithography. *Macromolecules* **2000**, *33*, 3042–3049.
- Odom, T. W.; Love, J. C.; Paul, K. E.; Wolfe, D. B.; Whitesides, G. M. Improved Pattern Transfer in Soft Lithography Using Composite Stamps. *Langmuir* **2002**, *18*, 5314.
- Kwak, E.-S.; Henzie, J.; Chang, S.-H.; Gray, S. K.; Schatz, G. C.; Odom, T. W. Surface Plasmon Standing Waves in Large-Area Subwavelength Hole Arrays. *Nano Lett.* **2005**, *5*, 1963–1967.
- Shaw, J. M.; Gelorme, J. D.; LaBianca, N. C.; Conley, W. E.; Holmes, S. J. Negative Photoresists for Optical Lithography. *IBM J. Res. Dev.* **1997**, *41*, 81–94.
- Yang, P.; Haoquan, Y.; Mao, S.; Russo, R.; Johnson, J.; Saykally, R.; Morris, N.; Pham, J.; He, R.; Choi, H.-J. Controlled Growth of ZnO Nanowires and Their Optical Properties. *Adv. Funct. Mater.* **2002**, *12*, 323–331.
- Huang, M.; Mao, S.; Feick, H.; Yan, H.; Wu, Y.; Kind, H.; Weber, E.; Russo, R.; Yang, P. Room-Temperature Ultraviolet Nanowire Nanolasers. *Science* **2001**, *292*, 1897–1899.
- Hsu, J. W. P.; Tian, Z. R.; Simmons, N. C.; Matzke, C. M.; Voigt, J. A.; Liu, J. Directed spatial organization of zinc oxide nanorods. *Nano Lett.* **2005**, *5*, 83–86.
- Zhang, H.; Loh, K. P.; Sow, C. H.; Gu, H.; Su, X.; Huang, C.; Chen, Z. K. Surface Modification Studies of Edge-Oriented Molybdenum Sulfide Nanosheets. *Langmuir* **2004**, *20*, 6914–6920.
- Barreau, N.; Bernede, J. C. MoS₂ Textured Films Grown on Glass Substrates through Sodium Sulfide Based Compounds. *J. Phys. D: Appl. Phys.* **2002**, *35*, 1197–1204.
- Ho, W.; Yu, J. C.; Lin, J.; Yu, J.; Li, P. Preparation and Photocatalytic Behavior of MoS₂ and WS₂ Nanocluster Sensitized TiO₂. *Langmuir* **2004**, *20*, 5865–5869.
- Rapoport, L.; Bilik, Y.; Feldman, Y.; Homyonfer, M.; Cohen, S. R.; Tenne, R. Hollow Nanoparticles of WS₂ as Potential Solid-State Lubricants. *Nature* **1997**, *387*, 791–793.
- Li, Q.; Walter, E. C.; Veer, W. E. v. d.; Murrey, B. J.; Newberg, J. T.; Bohannon, E. W.; Switzer, J. A.; Hemminger, J. C.; Penner, R. M. Molybdenum Disulfide Nanowires and Nanoribbons by Electrochemical/Chemical Synthesis. *J. Phys. Chem. B* **2005**, *109*, 3169–3182.
- Klein, D. L.; Roth, R.; Lim, A. K. L.; Alivisatos, A. P.; McEuen, P. L. A single-electron transistor made from a cadmium selenide nanocrystal. *Nature (London)* **1997**, *389*, 699–701.

- (42) Park, J.; An, K.; Hwang, Y.; Park, J.-G.; Noh, H.-J.; Kim, J.-Y.; Park, J.-H.; Hwang, N.-M.; Hyeon, T. Ultra-large-scale syntheses of monodisperse nanocrystals. *Nat. Mater.* **2004**, *3*, 891–895.
- (43) Kim, F.; Kwan, S.; Akana, J.; Yang, P. Langmuir–Blodgett Nanorod Assembly. *J. Am. Chem. Soc.* **2001**, *123*, 4360–4361.
- (44) Zhang, H.; Boussaad, S.; Ly, N.; Tao, N. J. Magnetic-field-assisted assembly of metal/polymer/metal junction sensors. *Appl. Phys. Lett.* **2004**, *84*, 133–135.
- (45) Smith, A. S.; Nordquist, C. D.; Jackson, T. N.; Mayer, T. S.; Martin, B. R.; Mbindyo, J. K. N.; Mallouk, T. E. Electric-field assisted assembly and alignment of metallic nanowires. *Appl. Phys. Lett.* **2000**, *77*, 1399–1401.
- (46) Duan, X.; Huang, Y.; Cui, Y.; Wang, J.; Leiber, C. M. Indium phosphide nanowires as building blocks for nanoscale electronic and optoelectronic devices. *Nature* **2001**, *409*, 66–69.
- (47) Tang, Z.; Kotov, N. A.; Giersig, M. Spontaneous Organization of Single CdTe Nanoparticles into Luminescent Nanowires. *Science* **2002**, *297*, 237–240.
- (48) Kuiry, S. C.; Patil, S. D.; Deshpande, S.; Seal, S. Spontaneous Self-Assembly of Cerium Oxide Nanoparticles to Nanorods through Supraaggregate Formation. *J. Phys. Chem. B* **2005**, *109*, 6936–6939.
- (49) Babayan, Y.; Barton, J. E.; Greyson, E. C.; Odom, T. W. Templated and hierarchical assembly of CdSe/ZnS quantum dots. *Adv. Mater.* **2004**, *16*, 1341–1345.
- (50) Lu, N.; Chen, X.; Molenda, D.; Naber, A.; Fuchs, H.; Talapin, D. V.; Weller, H.; Mueller, J.; Lupton, J. M.; Feldmann, J.; Rogach, A. L.; Chi, L. Lateral Patterning of Luminescent CdSe Nanocrystals by Selective Dewetting from Self-Assembled Organic Templates. *Nano Lett.* **2004**, *4*, 885–888.
- (51) Cui, Y.; Bjork, M. T.; Liddle, J. A.; Sonnichsen, C.; Boussert, B.; Alivisatos, A. P. Integration of Colloidal Nanocrystals into Lithographically Patterned Devices. *Nano Lett.* **2004**, *4*, 1093–1098.
- (52) Hulteen, J. C.; Martin, C. R. A general template-based method for the preparation of nanomaterials. *J. Mater. Chem.* **1997**, *7*, 1075–1087.
- (53) Sioss, J. A.; Keating, C. D. Batch Preparation of Linear Au and Ag Nanoparticle Chains via Wet Chemistry. *Nano Lett.* **2005**, *5*, 1779–1783.
- (54) Martin, C. R. Nanomaterials- A Membrane-Based Synthetic Approach. *Science* **1994**, *266*, 1961–1966.
- (55) Xu, Q.; Tonks, I.; Fuerstman, M. J.; Love, J. C.; Whitesides, G. M. Fabrication of Free-Standing Metallic Pyramidal Shells. *Nano Lett.* **2004**, *4*, 2509–2511.
- (56) Nicewarner-Pena, S. R.; Freeman, R. G.; Reiss, B. D.; He, L.; Pena, D. J.; Walton, I. D.; Cromer, R.; Keating, C. D.; Natan, M. J. Submicrometer Metallic Barcodes. *Science* **2001**, *294*, 137–141.
- (57) Genolet, G.; Despont, M.; Vettiger, P.; Anselmetti, D.; Rooij, N. F. D. All-photoplastic, soft cantilever cassette probe for scanning force microscopy. *J. Vac. Sci. Technol., B* **2000**, *18*, 617–620.
- (58) Love, J. C.; Gates, B. D.; Wolfe, D. B.; Paul, K. E.; Whitesides, G. M. Fabrication and Wetting Properties of Metallic Half-Shells with Submicron Diameters. *Nano Lett.* **2002**, *2*, 891–894.
- (59) Lu, Y.; Liu, G. L.; Kim, J.; Mejia, Y. X.; Lee, L. P. Nanophotonic Crescent Moon Structures with Sharp Edge for Ultrasensitive Biomolecular Detection by Local Electromagnetic Field Enhancement Effect. *Nano Lett.* **2005**, *5*, 119–124.
- (60) Fischer, U. C.; Dereux, A.; Weeber, J.-C. *Near-Field Optics and Surface Plasmon Polaritons*; Springer: Berlin, 2001; Vol. 81.
- (61) Kelly, K. L.; Coronado, E.; Zhao, L. L.; Schatz, G. C. The Optical Properties of Metal Nanoparticles: The Influence of Size, Shape, and Dielectric Environment. *J. Phys. Chem. B* **2003**, *107*, 668–677.
- (62) Jackson, J. B.; Halas, N. J., Surface-enhanced Raman scattering on tunable plasmonic nanoparticle substrates. *Proc. Natl. Acad. Sci. U.S.A.* **2004**, *101*, 17930–17935.
- (63) Ebbesen, T. W.; Lezec, H. J.; Ghaemi, H. F.; Thio, T.; Wolff, P. A. Extraordinary optical transmission through sub-wavelength hole arrays. *Nature* **1998**, *391*, 667–669.
- (64) Lezec, H. J.; Degiron, A.; Devaux, E.; Linke, R. A.; Martin-Moreno, L.; Garcia-Vidal, F. J.; Ebbesen, T. W. Beaming Light from a Subwavelength Aperture. *Science* **2002**, *297*, 820–822.
- (65) Devaux, E.; Ebbesen, T. W.; Weeber, J.-C.; Dereux, A. Launching and decoupling surface plasmons via micro-gratings. *Appl. Phys. Lett.* **2003**, *83*, 4936–4938.
- (66) Chang, S.-H.; Gray, S. K.; Schatz, G. C. Surface plasmon generation and light transmission by isolated nanoholes and arrays of nanoholes in thin metal films. *Opt. Commun.* **2005**, *13*, 3150–3165.
- (67) Williams, S. M.; Rodriguez, K. R.; Teeters-Kennedy, S.; Stafford, A. D.; Bishop, S. R.; Lincoln, U. K.; Coe, J. V., Use of the Extraordinary Infrared Transmission of Metallic Subwavelength Arrays To Study the Catalyzed Reaction of Methanol to Formaldehyde on Copper Oxide, *J. Phys. Chem. B* **2004**, *108*, 11833–11837.
- (68) Brolo, A. G.; Gordon, R.; Leathem, B.; Kavanah, K. L. Surface Plasmon Sensor Based on the Enhanced Light Transmission through Arrays of Nanoholes in Gold Films. *Langmuir* **2004**, *20*, 4813–4815.
- (69) Brolo, A. G.; Arctander, E.; Gordon, R.; Leathem, V.; Kavanaugh, K. Nanohole-enhanced Raman Scattering. *Nano Lett.* **2004**, *4*, 2015–2018.
- (70) Levene, M. J.; Korfach, J.; Turner, S. W.; Foquet, M.; Craighead, H. G.; Webb, W. W. Zero-Mode Waveguides for Single-Molecule Analysis at High Concentrations. *Science* **2003**, *299*, 682–686.

AR050013N