Fabrication of Anisotropic Metal Nanostructures Using Innovations in Template-Assisted Lithography

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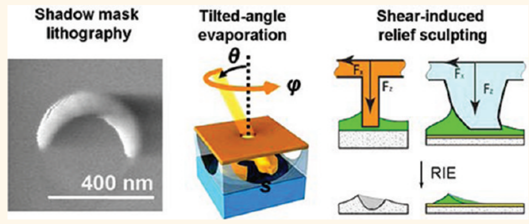
ABSTRACT Advances in the burgeoning field of plasmonics are increasingly dependent on the ability to fabricate metal nanostructures with precisely defined shapes and orientations, on a scale suitable for technological developments. Recent innovations in top-down lithography have created new windows of opportunity to produce anisotropic metal nanostructures *en masse*, with near-term applications in photonics, biosensing, and other nanotechnology-enabled pursuits. We focus specifically on C-shaped nanostructures (nanocrescents and split-ring resonators), which can be fabricated by using novel variants of shadow-mask lithography, substrate etching, or microcontact printing.



Nanoplasmonics—the science and engineering of metal–dielectric interfaces for the nanoscale control of electromagnetic fields—has experienced a tremendous growth spurt in the past decade. Much of this has been driven by recent advances in the prediction and characterization of novel optical properties, far below the optical diffraction limit. Plasmonics has now evolved to the stage of having a transformational impact on the field of optics, in large part through the introduction of so-called "metamaterials" with refractive indices below that of vacuum ($n < 1.0$).[1] The electromagnetic properties of metamaterials border on the surreal: a planar slab with a negative refractive index makes it possible for light to "bend backwards" with direct application toward subwavelength optics; alternatively, a metamaterial with a refractive index between 0 and 1 can be fashioned into an "invisibility cloak" for a given frequency band. Metamaterials operating at optical frequencies are still emerging, but many of the designs are based on three-dimensional (3D) architectures composed of anisotropic metal nanostructures, often closely spaced or with specific orientations.

In order to reach its full potential, the nascent field of metamaterials must be complemented by advances in synthesis and fabrication that enable the scalable production of metal nanostructures. Electron-beam (EB) and focused ion-beam (FIB) lithography are excellent tools for producing nanostructures in small quantities for proof of concept, but many challenges lie ahead for nanoscale manufacturing. Reproducibility, throughput rate, reasonable cost, and flexible design are several of the criteria to be addressed in the practical fabrication of nanoplasmonic devices.

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Developments along these lines have resulted in innovative methods of substrate patterning that combine top-down lithography with bottom-up approaches based on solution chemistry or surface patterning. In an early demonstration of nanoscale control using this hybrid approach, Hatzor and Weiss introduced a method of sequential layering of heterobifunctional resists on lithographically defined wires followed by electroless plating and lift-off, to produce Au-plated wires with 2 nm resolution in gap width between metal structures (Figure 1).[2]

Examples in which other substrates have been patterned or modified for the templated synthesis of metal nanostructures

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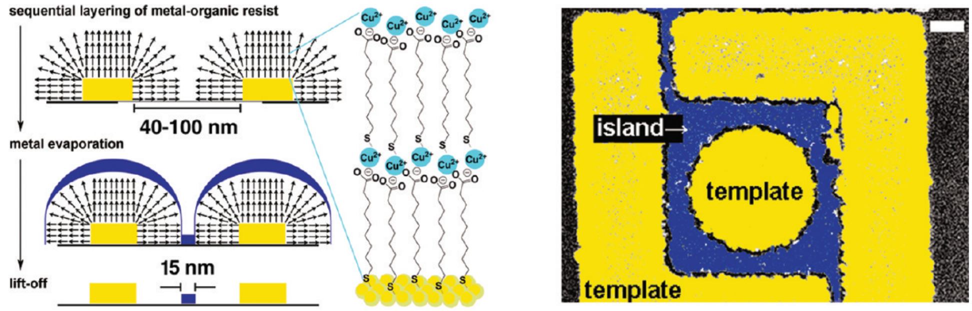

Figure 1. Templated fabrication of metal nanostructures with nanoscale control by combining top-down and bottom-up technologies.[2] (Left) Sequential layering of supramolecular metal–organic resists on adjacent metal structures (yellow), followed by metal evaporation and lift-off to produce an island nanostructure (blue); (right) SEM image of square metal ring connected by two 15 nm leads (shaded blue), prepared by templated-assisted evaporation using the method above (scale bar = 100 nm). Reproduced with permission from ref 2. Copyright 2001 American Association for the Advancement of Science.

include nanosphere-mask lithography (rings, prisms, inverse-opal structures),[3–5] nanopatterned etch or imprint lithography (pyramids, grills),[6,7] nanoporous membranes (wires, tubes),[8,9] and surfaces coated with block copolymer films (various structures).[10] Many of these have been used to fabricate plasmonic nanomaterials with tunable optical responses on the centimeter scale or higher (Figure 2).

Of special interest are fabrication methods that can produce highly anisotropic, plasmon-resonant nanostructures that taper to just a few nanometers. The high aspect ratios of such metal nanostructures extend the range of accessible frequencies from the visible to the infrared or beyond,[11,12] and the ultrafine tips can serve as point sources for electromagnetic field gradients. These localized fields are well-known to support plasmon-enhanced spectroscopies such as surface-enhanced Raman scattering (SERS) and nonlinear optical emissions in general, particularly when the tips are juxtaposed to form a nanosized gap.[13,14] A particularly promising geometry in this regard is a C-shaped nanostructure, popularly referred to as a nanocrescent or a split-ring resonator.[1,14,15] C-shaped nanostructures have become popular elements in the design of metamaterial architectures and plasmonic biosensors, and have been fabricated by EB lithography with gaps of just a few nanometers (Figure 3).

Nanocrescents are good candidates for template-assisted lithography, as they can be traced from two nonconcentric circles with an internal tangent (Figure 4a). This design is appealing in its simplicity: highly tapered structures can be obtained from a single cylindrical or spherical template by using etching or deposition conditions that produce inner and outer circles of slightly different sizes. Templates may also be devised with two internal tangents by using an elliptical outer ring to produce a double crescent separated by two narrow gaps (Figure 4b). Numerous variations to these themes can be conceived simply by changing the geometries or relative positions of the inner and outer rings.

The challenge is to match these templates with appropriate methods of patterning or metal deposition. Discounting direct-write approaches such as EB and FIB lithography, the most common tactic has been to use shadow-masking techniques, in which metal sputtering or evaporation is directed at a large angle of incidence onto substrates covered with colloidal spheres or cylinders (Figure 5).[11,12,16–18] Nanocrescents prepared by unidirectional shadow-mask lithography tend to have large opening angles (60 to 180°), with a distance between tips of tens or hundreds of nanometers. However, if the shadow masking is repeated after rotating the sample with respect to the evaporation

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source, crescent-like geometries with opening angles of just a few degrees are possible (Figure 5d).[19] This can be used to make smaller, nanosized gaps, although doing so uniformly requires considerable practice.

A different approach to shadow-mask lithography, described by Cataldo *et al.* in the previous issue of *ACS Nano*, involves angled metal deposition through nanosized pinholes (Figure 6).[15] The hole-mask template is generated using colloidal nanosphere templates embedded on a polymer film, followed by metal evaporation and oxygen plasma treatment to generate a nanohole mask with micrometer-sized etch pits in the substrate. A tilted evaporation beam is then pivoted about the axis normal to

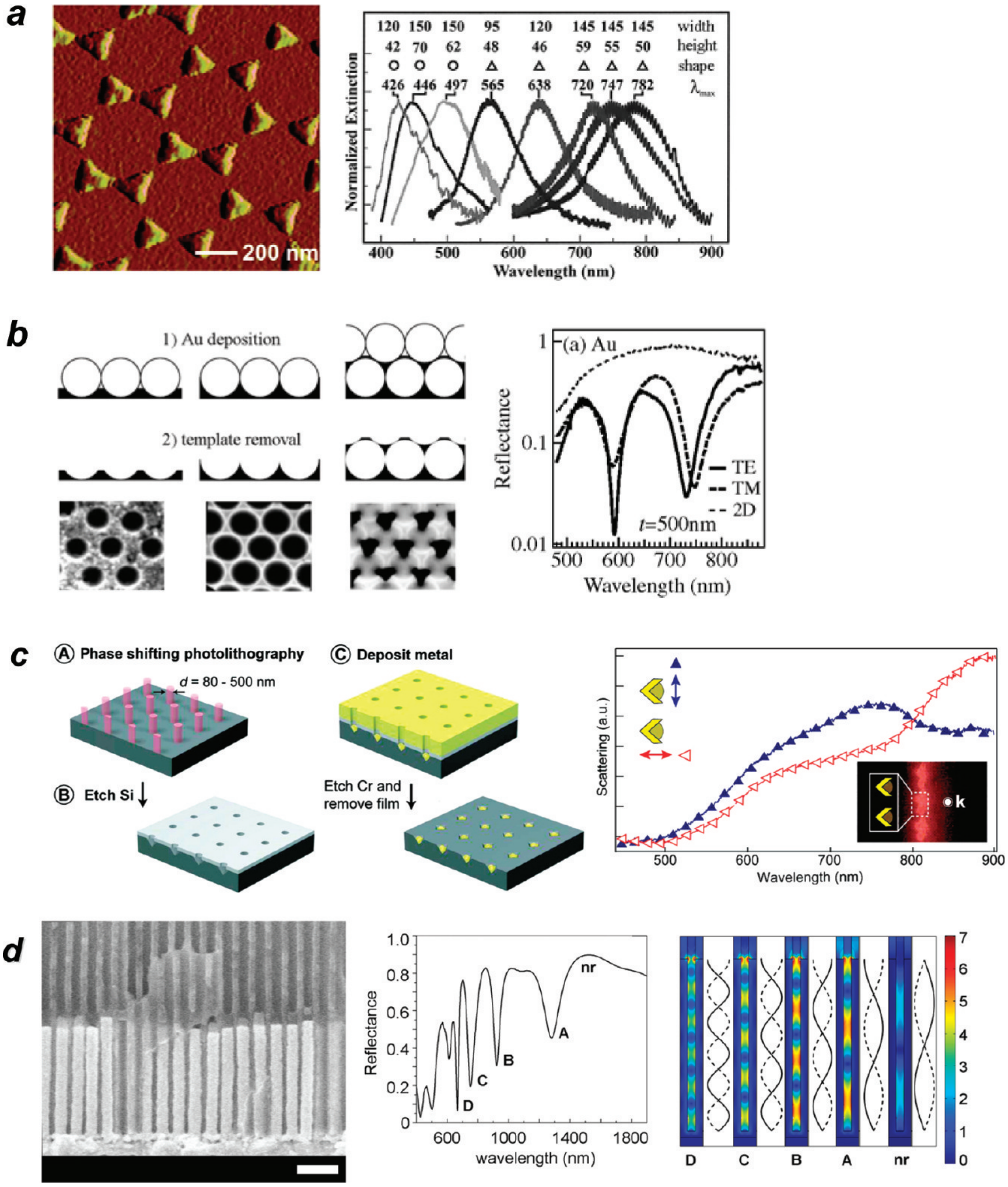

Figure 2. Anisotropic metal nanostructures fabricated by templated synthesis and their optical properties. (a) Ag nanoprisms of variable heights and cross sections, formed between the gaps of a 2D colloidal array (nanosphere lithography); (b) "inverse-opal" Au nanocavities, deposited within the excluded volume of a 3D colloidal array. Reproduced with permission from refs 3 and 5. Copyrights 2001 American Chemical Society and American Physical Society, respectively. (c) Au nanopyramids with orientation-dependent plasmon modes, templated by the etch pits of a polycrystalline Si wafer. Reproduced from ref 7. Copyright 2008 American Chemical Society. (d) Two-dimensional array of Au nanorods with multiple resonant cavity modes at near-IR wavelengths, deposited within a nanoporous Al_2O_3 membrane (scale bar = 250 nm). Reproduced from ref 9. Copyright 2008 American Chemical Society.

produce split Au nanorings with opening angles as low as 60°, presumably limited by the range of beam tilt and rotation. These C-shaped nanostructures have polarization-dependent plasmon resonances in the near- to mid-IR range and demonstrate some capacity for surface-enhanced IR spectroscopy (SEIRA), which amplifies vibrational modes by resonant coupling with IR-active plasmon modes.

Anisotropic metal nanostructures can also be fabricated by generating templates with ridges or valleys through substrate deformation, followed by soft lithography and metal deposition or by etching and lift-off. Two recent works, one featured in this issue of *ACS Nano*,[20] illustrate how polymer-coated substrates can be sculpted into crescent-shaped relief patterns by applying a low shear force on embedded micropillars while the polymer film is above its glass-transition point. In the work presented by Gao *et al.* (tilted nanoimprint lithography, or tNIL),[21] an array of pillars is pressed onto Si substrates spin-coated with polymethylmethacrylate (PMMA) with a force directed a few degrees from normal, followed by reactive-ion etching (RIE) to produce a master

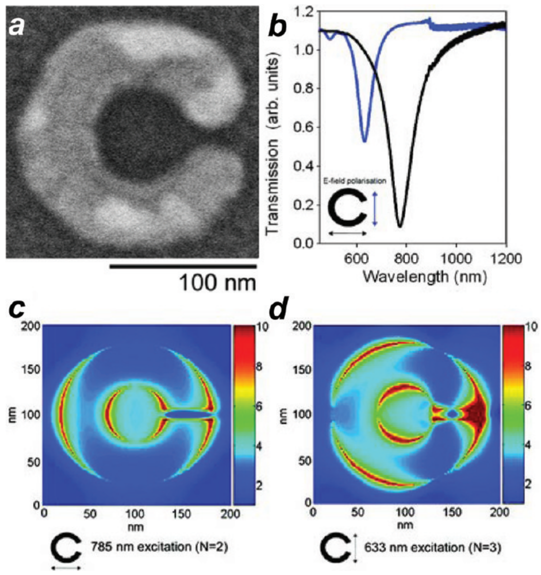

Figure 3. C-shaped Ag nanostructures (split-ring resonator), fabricated by EB lithography. (a) SEM image of single split-ring resonator; (b) plasmon-resonant extinction as a function of incident polarization; (c,d) simulations of electromagnetic field factors at resonant excitation. Reproduced from ref 15. Copyright 2009 American Chemical Society.

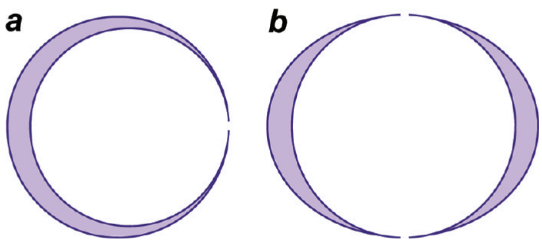

Figure 4. Template designs for C-shaped nanostructures (nanocrescents) with a narrow gap between tips. (a) Single crescent formed by two internally tangent (nonconcentric) circles; (b) double crescent formed by an ellipse and an internally tangent circle.

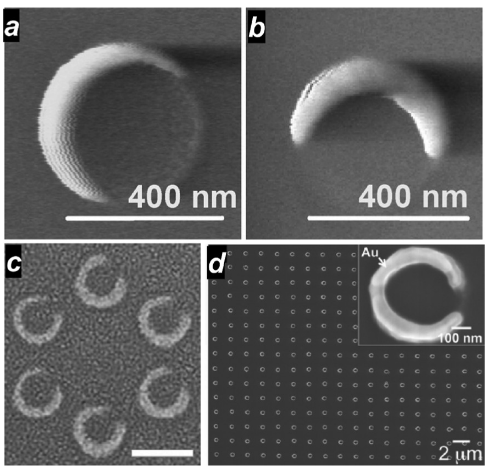

Figure 5. SEM images of C-shaped Au nanostructures fabricated by shadow-mask lithography. (a,b) Nanocrescents with plasmon resonances in the near- to mid-IR range. Reproduced form ref 8. Copyright 2007 American Chemical Society. (c) Split nanorings with opening angles of 60° (scale bar = 200 nm). Reproduced with permission from ref 13. Copyright 2009 Wiley-VCH. (d) C-shaped structures fabricated by reiterative shadow-mask lithography at different angles, followed by mechanical sectioning. Reproduced from ref 21. Copyright 2011 American Chemical Society.

with C-shaped ridges (Figure 7a). This relief pattern can be replicated by soft lithography methods into elastomeric stamps, which are then subjected to metal evaporation for the transfer of nanocrescents by microcontact printing. In the work presented by Cai *et al.* (deflected capillary force lithography, or dCFL),[22] an array of elastomeric pillars is pressed onto Au-coated glass substrates with a spin-coated layer of polystyrene (PS), with a shear force introduced by an iron block offset to one side. In this case, the C-shaped ridges are created by asymmetric capillary forces due to deformations in the surface curvature of the compressed pillars; Au crescents are produced following a sequence of reactive-ion etching, solution etching, and lift-off (Figure 7b). Most notably, increasing the shear force and decreasing the molecular weight of PS (resulting in a larger deflection angle and lower viscosity, respectively) can produce an opening angle as small as 10°, reducing the distance between tips to within 10% of the crescent's diameter. The aspect ratio of these nanostructures approaches that of split-ring resonators fabricated by EB lithography.[14]

OUTLOOK

The article by Cai *et al.* in this issue of *ACS Nano* is a worthy reminder that capillary and wetting forces are ubiquitous to liquid–solid interfaces, and can be applied creatively toward the scalable printing of 2D and 3D patterns with mesoscale features for template-assisted lithography.[22–24] Contact printing with nanoscale resolution is well within reach, as established some time ago by dip-pen nanolithography.[25,26] Capillary force lithography is already capable of reshaping polymer films into architectures of moderate complexity; increased control over aspect ratio and interparticle spacing can be achieved by introducing additional parameters such as unidirectional

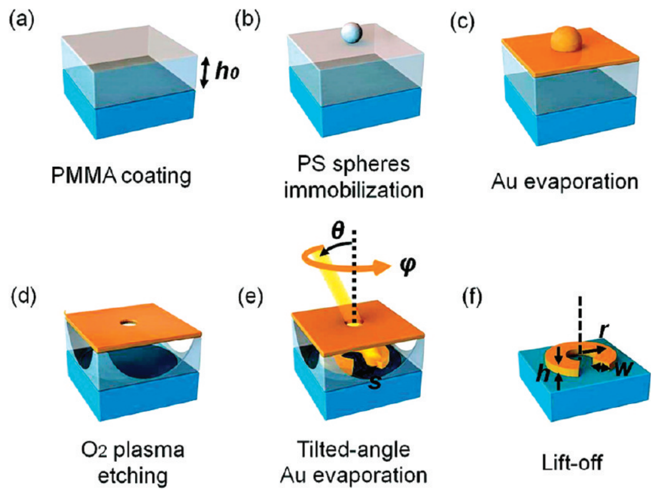

Figure 6. Scheme for generating C-shaped metal nanostructures by hole-mask lithography. Reproduced from ref 16. Copyright 2012 American Chemical Society.

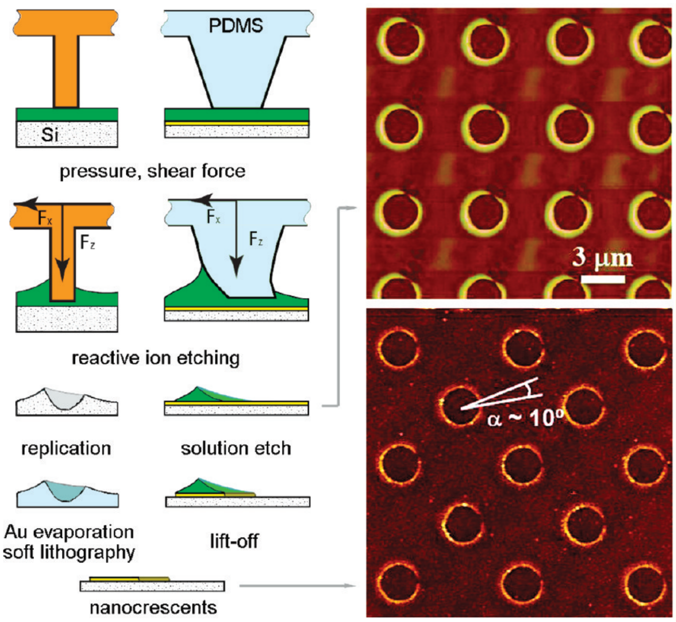

Figure 7. Preparation of crescent-shaped molds by applying a shear force on pliable polymer films. In tilted nanoimprint lithography (tNIL), the polymer mold serves as a mask during RIE to create anisotropic cavities in Si, which is then replicated into elastomeric stamps to mediate the transfer of C-shaped nanostructures by soft lithography. Reproduced with permission from ref 24. Copyright 2011 Elsevier. In deflected capillary force lithography (dCFL), the sculpted film acts as a negative resist during the etching steps, followed by lift-off to reveal the Au nanocrescent patterns. AFM images of the C-shaped templates and final Au nanocrescents shown at right. Reproduced from ref 22. Copyright 2012 American Chemical Society.

shear or strain on the mold or substrate.[27,28] Finally, it should be noted that the templated synthesis of anisotropic metal nanostructures is useful in other areas besides plasmonics: magnetic materials such as cobalt or Permalloy can be fashioned into split nanorings and other annular structures that can support magnetic flux closure states, which have been investigated in recent years as elements for nonvolatile data storage[29] or nanomagnet-based logic devices.[30]

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Conflict of Interest: The authors declare no competing financial interest.

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