Direct Writing of Metal Nanostructures: Lithographic Tools for Nanoplasmonics Research

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ABSTRACT Continued progress in the fast-growing field of nanoplasmonics will require the development of new methods for the fabrication of metal nanostructures. Optical lithography provides a continually expanding tool box. Two-photon processes, as demonstrated by Shukla *et al.* (doi: 10.1021/nn103015g), enable the fabrication of gold nanostructures encapsulated in dielectric material in a simple, direct process and offer the prospect of three-dimensional fabrication. At higher resolution, scanning probe techniques enable nanoparticle particle placement by localized oxidation, and near-field sintering of nanoparticulate films enables direct writing of nanowires. Direct laser "printing" of single gold nanoparticles offers a remarkable capability for the controlled fabrication of model structures for fundamental studies, particle-by-particle. Optical methods continue to provide a powerful support for research into metamaterials.

The remarkable optical properties of nanostructured metals are attracting intense interest, as a glance through recent issues of *ACS Nano* will quickly confirm. Gold and silver nanocrystals yield large enhancements in the signals of common optical reporters (*e.g.*, fluorescent labels, Raman dyes), ushering in a new era of ultrasensitive biomolecular analysis.[1] Carefully tailored morphologies (hemispheres, rods, crosses, holes, bow-ties, crescents, and others) enable the design of structures to yield bespoke optical phenomena. Metamaterials interact in new and unprecedented ways with electromagnetic radiation, promising to render science fiction into reality in the form of cloaking devices,[2] plasmonic waveguides, and other new technologies.

In many of these fast-developing areas, the development of fabrication tools remains a primary focus of attention, and often, the lack of suitable tools is an obstacle to the development of new technologies. Without doubt, electron-beam lithography continues to set the bar for ultimate performance. An illustration of its capability for fundamental studies was provided by Banaee and Crozier in the January 2011 issue of *ACS Nano*.[3] They described the fabrication of gold nanoparticle pairs, in which the particles were shaped (90−110 nm rods or 100 nm diameter rings) and placed in different arrangements on surfaces to yield varying extinction spectra. However, e-beam methods rely upon serial processing and utilize expensive instrumentation that is not readily accessible to many workers. In the semiconductor device industry, e-beam techniques remain a means of fabricating photolithography masks but not a manufacturing tool; in the study of metamaterials, likewise, e-beam methods are a precise tool for fabrication of model materials but undoubtedly suffer limitations.

The simplest, most inexpensive approach to the fabrication of metal nanostructures, and one that has been used by many workers in the field of plasmonics, is colloidal lithography.[4] A film of colloidal particles is formed on a substrate and used as a shadow mask: metal is evaporated onto the particle film, which typically exhibits hexagonal close packing under optimal conditions. The particles mask the substrate effectively during metal deposition, but the metal atoms can penetrate through the particle film at the interstices, where pyramidal structures form in a regular, periodic array (Figure 1). The colloidal particle mask can then be removed in a simple lift-off step. Some control of the periodicity is possible by controlling the particle diameter. An alternate but analogous approach is to deposit colloidal particles more sparsely on the substrate; metal deposition then yields a continuous metal film punctuated by holes where nanoparticles masked the substrate.[5]

Despite the attractive simplicity of such approaches, they offer access to a limited range of architectures, and there has thus

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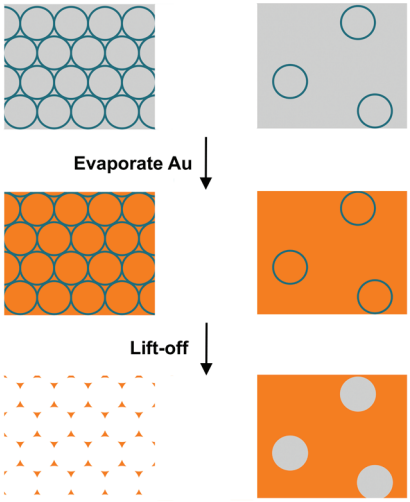

Figure 1. Schematic illustration showing the fabrication of gold nanoprisms (left) and nanohole arrays (right) using colloidal lithography.

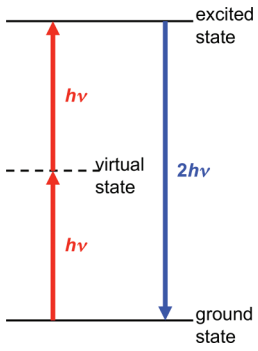

Figure 2. Schematic diagram showing a two-photon excitation *via* a virtual quantum state.

been a great deal of interest in the development of methods that would enable much greater control to be exercised over the morphologies of the metal nanostructures. A wish-list for fabrication tools for nanoplasmonics would include high-resolution, low-cost, high-throughput, simplicity in processing, and perhaps, also, the capacity for three-dimensional fabrication. In this issue of *ACS Nano*, Shukla *et al.*[6] report an elegant new approach that blends several of these desiderata in a single, simple process—simultaneous photopolymerization and photoreduction by two-photon exposure. Using a femtosecond-pulsed laser, they exposed a film of photoresist that was doped with both chloroauric acid and a two-photon dye. Energy was absorbed from the incident beam by the dye, causing reduction of the gold salt, simultaneously with cross-linking of the photoresist. The result was the formation of gold nanostructures that were encapsulated by the cross-linked photoresist. Shukla *et al.* found that the dimensions of features could be controlled by varying the exposure, yielding gold-particle-doped polymer structures ranging in size between 150 and 1000 nm. This work is intriguing for a variety of reasons.

Two-photon processes are attractive for materials processing. In the high transient intensities achieved in femtosecond pulses delivered by a Ti-sapphire laser, nonlinear optical responses are excited. In a two-photon transition, a system is excited from a ground state to an excited state *via* a virtual quantum state; for incident photons of frequency ν, the energy absorbed is equal to $2h\nu$, where h is Planck's constant (Figure 2). In photolithography, two-photon processes may be used to achieve enhanced resolution. The strength of two-photon absorption varies quadratically with the intensity of the incident illumination; hence there is an effective sharpening of the excitation beam. By careful selection of the excitation source, photons may be used that have energies that are too small to cause modification of the photoresist but, when combined in a two-photon absorption, deliver adequate energy. Because the cross section for two-photon absorption is small, high transient powers are required (high mean powers would degrade the resist through heating), hence the use of femtosecond-pulsed laser systems.

An important feature of two-photon processes is the capacity that they offer for three-dimensional fabrication. They offer exquisite precision, exemplified by the stunning reproduction of the *Venus de Milo* in photoresist by Chichkov and co-workers, the model boasting a waist measurement that is numerically realistic but measured in micrometers rather than inches.[7] Three-dimensional fabrication would be an obvious extension of the work described by Shukla *et al*. Already, a number of groups are exploring the possibility of

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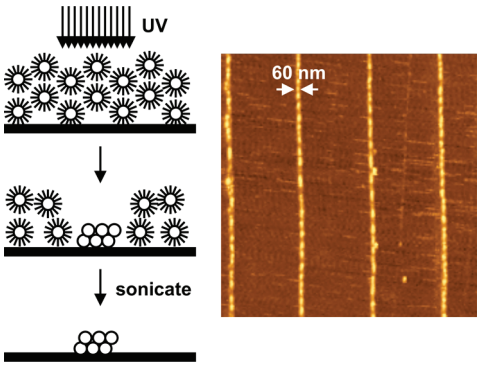

Figure 3. Direct writing of gold nanowires from nanoparticle bilayers, by UV-induced near-field sintering. Reproduced from ref 10. Copyright 2006 American Chemical Society.

fabricating three-dimensional structures from a photoresist onto which metal can be deposited to form a metamaterial; clearly, however, the availability of a process in which the development of the polymeric scaffold and the metal nanostructure occur in a single step is attractive. One can thus envisage adapting the methodology described by Shukla *et al.* to fabricate three-dimensional metamaterials consisting of metallic frameworks encased in dielectric material.

Shukla *et al.* report the fabrication of a variety of dense gold structures, including blocks and a variety of rings and meshes that appear to be promising candidate metamaterials. Four-point-probe measurements revealed a reasonable conductivity, given the small size of these structures. Whether the particles are simply formed at high density or whether they sinter to form continuous gold structures is not clear. Certainly, however, sintering of gold particles offers a promising route to the fabrication of conductive metal nanostructures. Gold nanoparticles are sintered by heat, pressure,[8] chemical reaction,[9] or the application of UV light. At the smallest length scales, exposure of films of gold nanoparticles to near fields can cause sintering to yield densified structures. Using a scanning near-field optical microscope (SNOM) coupled to a UV laser, thiol-stabilized gold nanoparticles were fused together to yield 60 nm wide nanowires (Figure 3).[10] Unmodified particles were simply removed by rinsing in toluene, making the method attractive because of the small number of steps involved in the fabrication process (nanoparticle film deposition/exposure/rinsing) and their simplicity. Although scanning-probe-based methods are thought to be slow and serial in nature, parallel approaches to near-field optical lithography have recently been developed,[11] in which arrays of separately controlled probes write in parallel over an area several millimeters wide. An alternative approach to the exploitation of near fields has been reported by Pan *et al.*,[12] who used solution deposition methods to form films of small (1−3 nm diameter) gold nanoparticles that could then be sintered. Instead of using a SNOM, they utilized fluidically assembled microsphere arrays with a predetermined pitch as arrays of lenses. The result was much the same—the fabrication of sintered gold structures—albeit with limited resolution because of the type of lens utilized.

Of course, in many applications, one might wish to be able to position single particles. From a fundamental perspective, the ability to control interparticle spacing on genuinely nanometer length scales would enable the assembly of structures to test hypotheses concerning interparticle coupling, Raman hot-spot formation, and related phenomena. Sagiv and co-workers demonstrated a decade ago that constructive nanolithography (the use of an AFM probe with a bias voltage to cause oxidative degradation of bonds at the surface of a monolayer) could be used to define templates for the organization of metal nanoparticles.[13,14] Fresco and Frechet took this approach further by utilizing a biased AFM probe to decouple a protecting group from a thiol-terminated silane monolayer.[15] Following deprotection, the thiol is available for reaction and may be coupled to a gold nanoparticle. They formed both continuous lines and also, significantly, lines of uniformly spaced gold nanoparticles, indicating an impressive degree of control over the interfacial chemistry and the subsequent arrangement of the metal nanoparticles at the surface.

Two recent communications provide elegant examples of the use of optical methods for the direct manipulation and positioning of single gold nanoparticles.[16,17] Guffey and Scherer demonstrated the positioning of 40 nm gold nanoparticles with subwavelength accuracy using optical tweezers.[16] The particles were trapped in bulk solution using light from a Ti-sapphire laser emitting at 817 nm and then located to the desired position using the optical trap. A key problem in such work is the control of adhesion between the particles and the substrate: a net repulsive interaction is required to prevent rapid deposition of a film of particles on the surface, but it is also necessary to be able to adhere particles to the substrate as required. Guffey and Scherer adsorbed a cationic polymer onto a glass surface and stabilized the gold nanoparticles with a quaternary ammonium compound (cetyltrimethylammonium bromide, CTAB), ensuring that the net interparticle interaction was repulsive. Guffey and Scherer suggested that the CTAB was present in the nanoparticle suspension at a concentration that was less than the critical micelle concentration, ensuring that the CTAB coating on the particles was unstable. Hence, on approach to the surface under

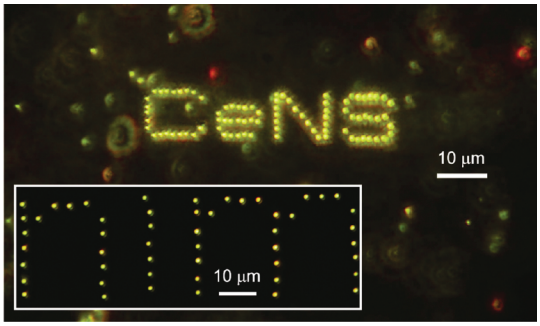

Figure 4. Dark-field optical image of two patterns made by optical printing of single gold nanoparticles. Reproduced from ref 17. Copyright 2010 American Chemical Society.

the guidance of the optical trap, adhesion could occur.

Control of adhesion was also important in the work of Urban *et al.*[17] A 532 nm laser beam was used in conjunction with a water immersion lens to manipulate 100 nm gold particles. In contrast to the work of Guffey and Scherer, Urban *et al.* did not trap the particles but used the laser beam to apply controlled amounts of momentum to the nanoparticles—gently kicking them into position in a nanoscopic football exercise (the authors drew an analogy with laser printing). Like Guffey and Scherer, Urban *et al.* also stabilized their nanoparticles using CTAB and adsorbed a cationic polymer onto the substrate to prevent particle adhesion. When the particle was located in position, an optical force was applied perpendicular to the surface, sufficient to overcome the repulsive force between the particle and the surface, and driving the particle into contact with the substrate, to which it adhered. Urban *et al.* achieved a positional accuracy of *ca.* 50 nm, that is, approximately half the diameter of the particles. In a stunning demonstration of the control that they were able to exert, they formed the letters shown in Figure 4.

To summarize, optical techniques continue to surprise us. Lithographic techniques based upon the use of light are varied, powerful, flexible, and usually require much less complex instrumentation than electron beam lithography. The work of Shukla *et al.* in this issue of *ACS Nano* demonstrates the use of two-photon processes for direct writing of gold nanostructures encased within dielectric materials and provides a potential template for fabrication in three dimensions;[5] other approaches offer exquisite spatial resolution, and optical trapping provides the means to manipulate nanoparticles one at a time. Optics will undoubtedly continue not only to be the basis of the exciting new science created by metamaterials but also to provide the means to meet many of the fabrication needs of the nanoplasmonics community.

The work of Shukla *et al.* in this issue of *ACS Nano* demonstrates the use of two-photon processes for direct writing of gold nanostructures encased within dielectric materials and provides a potential template for fabrication in three dimensions.

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