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Direct assembly of three-dimensional mesh plasmonic rolls

Fu Min Huang,[1,a)] Jatin K. Sinha,[2] Nicholas Gibbons,[1] Philip N. Bartlett,[2]
and Jeremy J. Baumberg[1]
[1]*Nanophotonics Centre, Cavendish Laboratory, University of Cambridge, Cambridge CB3 0HE, United Kingdom*
[2]*School of Chemistry, University of Southampton, Southampton SO17 1BJ, United Kingdom*

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A direct-assembly method to construct three-dimensional (3D) plasmonic nanostructures yields porous plasmonic rolls through the strain-induced self-rolling up of two-dimensional metallic nanopore films. This route is scalable to different hole sizes and film thicknesses, and applicable to a variety of materials, providing general routes towards a diverse family of 3D metamaterials with nano-engineerable optical properties. These plasmonic rolls can be dynamically driven by light irradiation, rolling or unrolling with increasing or decreasing light intensity. Such dynamically controllable 3D plasmonic nanostructures offer opportunities both for sensing and feedback in active nano-actuators. © *2012 American Institute of Physics*. [http://dx.doi.org/10.1063/1.4711923]

Three-dimensional (3D) metallic nanostructures are important architectures in nano-optics and metamaterials for exploiting plasmonics. Complex architectures not reachable by one-dimensional and two-dimensional (2D) planar structures expand the opportunities for creating a broad range of photonic materials underpinned by non-conventional fundamental principles but with practical applications. In addition, their large surface areas are favourable for applications such as molecular sensing and catalysis. Three-dimensional plasmonic nanostructures have thus been of increasing research focus in recent years, with a variety of nano-engineered structures exhibiting intriguing optical effects such as superlensing,[1,2] negative refraction,[3,4] optical cloaking,[5] as well as mimicking intricate structures from nature such as butterfly wings.[6] However, fabrication of 3D metallic nanostructures is non-trivial and is a challenge for modern nanotechnology. Previous approaches involve state-of-the-art lithography, such as layer-by-layer electron beam lithography,[7] focussed ion beam milling,[3] and atomic layer deposition,[6] which are time-consuming, costly, and not suitable for scaling to large-area samples (mostly limited to $<100\ \mu\text{m}^2$). Other methods, including direct laser writing[5] and nanotransfer printing,[4] also place severe limits on possible nano-architectures and size scales.

Here, we report an alternative method for the construction of a class of 3D plasmonic nanostructures, *porous plasmonic rolls*, which are the photonic analogues of graphene rolled up into nanotubes (Fig. 1). Such plasmonic rolls cannot be fabricated through the traditional lithographic techniques above. Just as for carbon nanotubes in which a basic planar lattice is rolled up, here we construct plasmonic tubes by strain-induced self-rolling of 2D metallic nanopore films of "plasmene," which can be mass-fabricated through directed self-assembly. Plasmonic tubes with lengths up to several millimeters and core diameters of a few microns are fabricated with optical properties tuneable across a broad spectral range by simply varying the hole size and thickness of the base nanopore films. More importantly such plasmonic tubes can be dynamically manipulated by light irradiation, rolling or unrolling with increasing or decreasing light intensity, providing active and reversible tuning which is of considerable utility.

Large-area two-dimensional metallic nanopore films are fabricated through a self-assembly and multiple electrodeposition processes (Fig. 2(a)). A monolayer of polystyrene spheres (PSs) is self-assembled onto Au-coated (200 nm) glass substrates,[8,9] which are then used as templates for electrodeposition of a thin layer of silver, followed by a second layer of gold. The polystyrene spheres are removed by dissolving in dimethylformamide (DMF) solvent, resulting in a regular array of nanovoids as discussed previously.[8,9] To create free-standing Au nanopore films, the silver layer is dissolved through a slow etching process by soaking in diluted NH_4OH (17.5%)/H_2O_2 (5%) solution for more than 24 h,[10] leaving plasmene films that can be transferred to any desired substrate through a stamp and lift-off process. Large areas ($>1\ \text{cm}^2$) of uniform Au nanopore films can be fabricated with this method.

Nano-construction of such metallic films allows significant control over their optical properties. By choosing different sizes of polystyrene spheres and adjusting the thickness of both sacrificial Ag and Au layers (Fig. 2(a)), a set of Au nanopore films with different hole sizes and thicknesses are created with a series of colours very different from that of bulk gold. Two sections of films with intense red and green

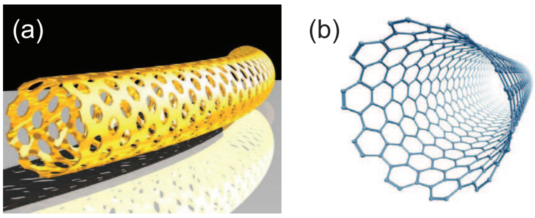

FIG. 1. Schematic of a 3D plasmonic tube (a) which is rolled from 2D metallic nanopore films of "plasmene," in a way analogue to graphene rolled up into a carbon nanotube (b).

[a)] Electronic mail: fh281@cam.ac.uk.

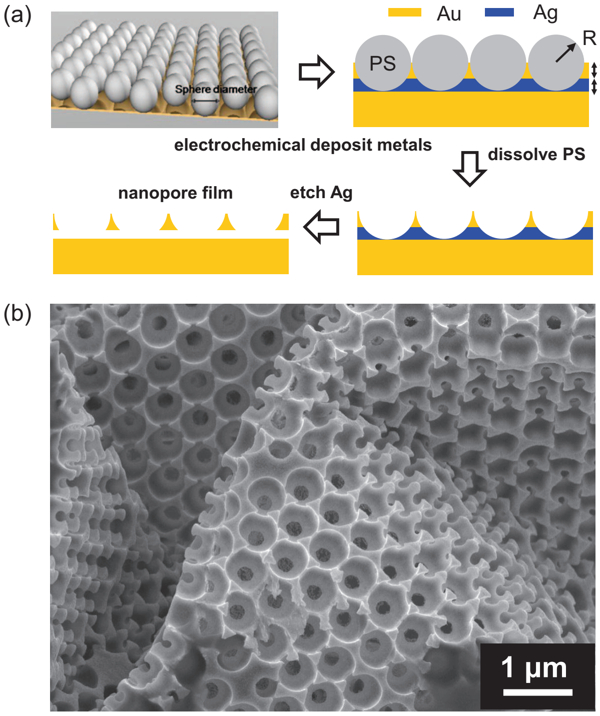

FIG. 2. Fabrication of Au nanopore films. (a) Schematic of fabrication process. (b) SEM image of folded free-standing Au nanopore film, showing bowl-shaped nanovoids. $R = 300$ nm, $t_1 = 30$ nm, and $t_2 = 400$ nm.

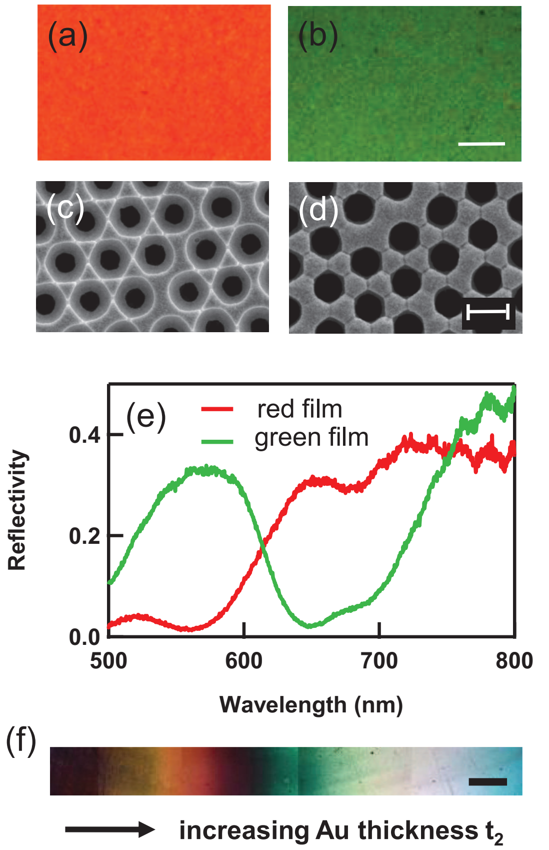

FIG. 3. Optical images of (a) red and (b) green Au nanopore plasmene films, with SEM images shown in (c, d) and optical reflection spectra shown in (e). Sphere radius $R = 300$ nm, with (red films) $t_1 = 30$ nm and $t_2 = 130$ nm, and (green films) $t_1 = 60$ nm and $t_2 = 440$ nm. Scale bars: 100 μm (optical) and 500 nm (SEM). (f) Single graded Au nanopore film showing smoothly varying colours with increasing Au thickness. $R = 300$ nm, Ag layer thickness $t_1 = 30$ nm, Au layer thickness increases by 30 nm/mm along the direction of arrow. Scale bar: 1 mm.

colour (Figs. 3(a) and 3(b) with optical reflection spectra in Fig. 3(e)) show how different underlying geometries account for the distinct strong colours (corresponding SEM images in Figs. 3(c) and 3(d)). It is also possible to fabricate single films with gradually varying colours by electrodepositing different thicknesses of Au layers in a gradient (Fig. 3(f)). These phenomena arise from the collective response of electrons to incident light, as surface plasmon resonances,[11] which are significantly dependent on nanostructure geometries. These resonance phenomena are closely linked to the "extraordinary optical transmission" in which specific colours of light are resonantly transmitted through subwavelength hole arrays drilled through thin metallic films due to surface plasmon resonance effects.[12]

To form 3D plasmonic tubes, we employ methods based on a strain-induced self-rolling mechanism (Fig. 4(a)) similar to that reported by Schmidt and Eber[13] for MBE-grown semiconductors. First, the Au nanopore film is transferred and attached to a substrate (here a thick polydimethylsiloxane (PDMS) stamp), which is then placed on top of a multilayer substrate consisting of a Si substrate, a 500 nm polystyrene sulfonic acid (PSS) layer, and a second layer of 200 nm PDMS (Fig. 4(a), step 1). The Au/PDMS film is lifted off (Fig. 4(a), step 2) by dissolving the PSS sacrificial layer in water, upon which the thin PDMS film contracts due to the initial strain induced during the curing process (as PDMS shrinks when cured[14]). This consequently rolls up the complete film including the attached Au nanopore film to form 3D plasmonic tubes composed of rolls of double layers of porous metallic nanopore film and transparent elastic dielectric film (Fig. 4(a), step 3). Using this method, plasmonic tubes of various structures showing different colours are fabricated (Figs. 4(b)–4(d)), with tube lengths exceeding millimeters (Fig. 4(f)). The SEM images (Figs. 4(g)–4(i), for the tube shown in Fig. 4(c)), clearly show the hexagonally patterned regular array of nanopore holes and the PDMS layer (Fig. 4(i)). These rolls show colours strongly dependent on the exact nanostructure morphology.

The plasmonic tubes are loosely rolled multilayers (Fig. 4(h)), though single layer tubes can be fabricated by careful control of parameters.[13] Such non-bonded multilayers however allow dynamical tuning of the rolls. The plasmonic tubes are found to be very sensitive to light irradiation. Upon broadband illumination, they quickly roll inward (Fig. 5(a)). This is because optical irradiation heats up the tubes and as a consequence of the elevated temperature, the gold films expand and PDMS films shrink. These two effects drive the tubes to roll inward (as the gold film is outside and the PDMS is inside the double-layer film, see Fig. 5(a)). When the light is switched off, the tubes cool down and the process is reversed (Fig. 5(b)). Stills from real-time videos [Figs. 5(c) and 5(d) and full video] record the movement of a plasmonic tube under illumination. The dashed white line indicates the starting position of the tube and the red line indicates the position of the tube 1.5 s later (speed 22 μm/s), when the intensity of light is increased to 1 W cm^{-2}. The whole process is completely reversible (see video at Fig. 5).

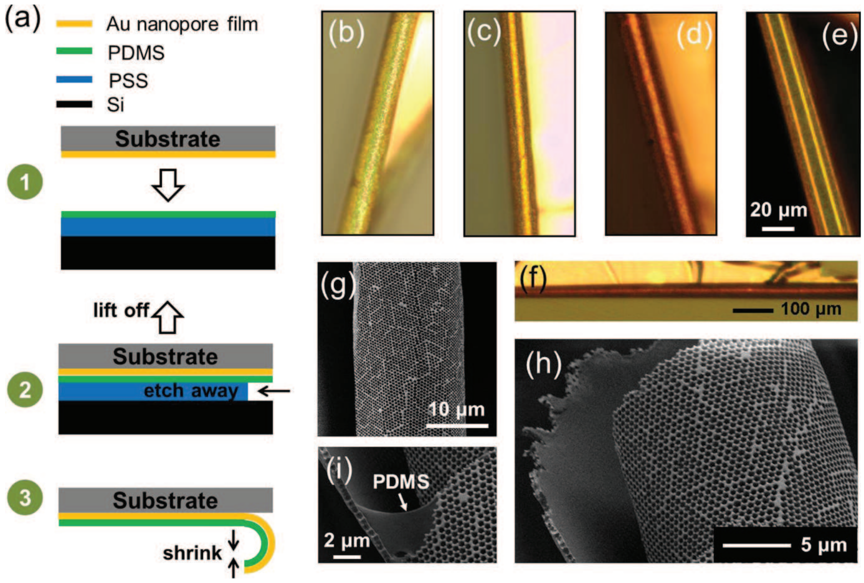

FIG. 4. Schematic of strain-induced self-rolling of plasmonic tubes. (a) Step 1: Au nanopore film is transferred to the top surface of multilayer substrate of PDMS on PSS on Si. Step 2: sacrificial PSS layer etched away by water, releasing the bilayer. Step 3: PDMS film shrinks due to initial strain between PDMS and PSS layers, hence rolling up together with attached Au nanopore film. (b–d) Optical images of plasmonic tubes showing various colours due to nano-geometry. (e) Dark-field optical image of tube (d) and (f) millimeter-long plasmonic tube. (g–i) SEM images of tube (c) showing (g) body, (h) end with hexagonally patterned holes and multilayer rolls, and (i) tube edge showing attached PDMS film.

Since the photonic properties of the tubes depend on their morphology, this allows direct control on the sub-μm scale.

Such light-sensitive dynamic control of 3D metamaterials not only allows active tuning of the optical properties of the metamaterials but also opens up opportunities for many interesting applications for dynamic rolling/unrolling such as in nano-actuators. The modification of the optical resonances allows mechano-optical feedback so that by irradiating with a specific colour of light which matches a resonant plasmonic absorption (which then selectively heats the Au nanopore film), a particular mechanical state is achieved. In addition, the strength of such thermo-mechanical effects can be modified by the nanostructure geometry which accommodates strain in tuneable ways.

Plasmonic rolls are known to possess intriguing optical properties including a strong anisotropy for subwavelength imaging[1,15] (optical hyperlens), and extreme chirality that can rotate polarizations by 90° in less than a wavelength of propagation.[16] Previous studies have been limited to spirals built by stacking flat continuous films.[1,15,16] Introducing periodicity into the sheets here further manipulates their optical properties through the hexagonal-symmetry bandstructure (similar to that of graphene) of the delocalised surface plasmons. In addition, it defines a rich set of localised plasmon modes.[17,18] The modified plasmonic dispersion of our 2D meshes and the redefined in-coupling conditions provide a wide spectrum of optical properties.

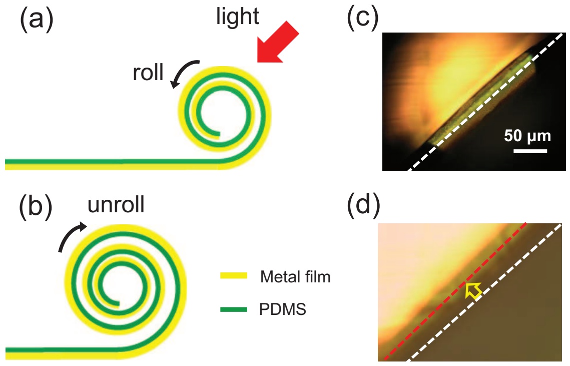

FIG. 5. Light-driven dynamic plasmonic roll-up. (a, b) Dynamic control of plasmonic roll through broadband light irradiation. (a) Incident light rolls up film, and (b) after switching off light, it unrolls. (c, d) Video stills showing starting position of a plasmonic roll (c, white dashed line) and displaced position after 1.5 s of light irradiation (d, red dashed line) (enhanced online) [URL: http://dx.doi.org/10.1063/1.4711923.1].

In summary, we report 3D plasmonic nanostructures constructed by direct assembly through strain-induced self-rolling of metallic nanopore sheets. The resulting plasmonic mesh rolls have widely tailorable optical properties across a broad range, and are dynamically tuneable through light irradiation, reversibly rolling and unrolling on demand. Although the results here focus on gold plasmonic rolls, the methods can be applied to a wide variety of materials providing that suitable selective etches are identified. A whole class of 3D plasmonic tubes which are inaccessible using lithographic techniques can thus be fabricated. Light-controllable active 3D plasmonic nanostructures have implications in superlensing, extreme chirality, sensors, and nano-actuators.

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