

# Fabrication and Wetting Properties of Metallic Half-Shells with Submicron Diameters

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*Received June 4, 2002*

## ABSTRACT

The deposition of a thin, metal film onto an array of spherical silica colloids, followed by dissolution of the colloidal template, produces metallic half-shells with nanometer-scale dimensions. Half-shells of gold, platinum, and palladium were fabricated, with diameters of the particles ranging from 100 to 500 nm, and shell thicknesses of 8–15 nm. The half-shells have three useful properties because of their geometries: (i) a high ratio of surface area to volume, (ii) a large length of edge relative to size, and (iii) an entropic resistance to assembling into close-packed structures. The surface properties of these half-shells can be modified with self-assembled monolayers (SAMs), formed by adsorption of alkanethiols. The surfaces composed of aggregated gold half-shells are superhydrophobic; the measured contact angle of water on a surface of unmodified gold half-shells was  $\sim 151^\circ$  and on a surface of gold half-shells functionalized with a hexadecanethiolate SAM was  $\sim 163^\circ$ . Aggregates of half-shells were patterned using template-assisted self-assembly.

This paper describes a versatile and experimentally simple technique for fabricating hollow metallic hemispheres (which we call “half-shells”) with diameters of 100–500 nm and thicknesses of 8–15 nm. The method uses monolayers or multilayers of spherical silica colloids on glass substrates as templates on which the half-shells are formed. The silica exposed at the surface of the array is coated with a thin film of metal by physical vapor deposition. Subsequent dissolution of the colloidal template releases the half-shells into a suspension. This work provides a route to another class of nanostructures useful for bottom-up assembly.<sup>1</sup>

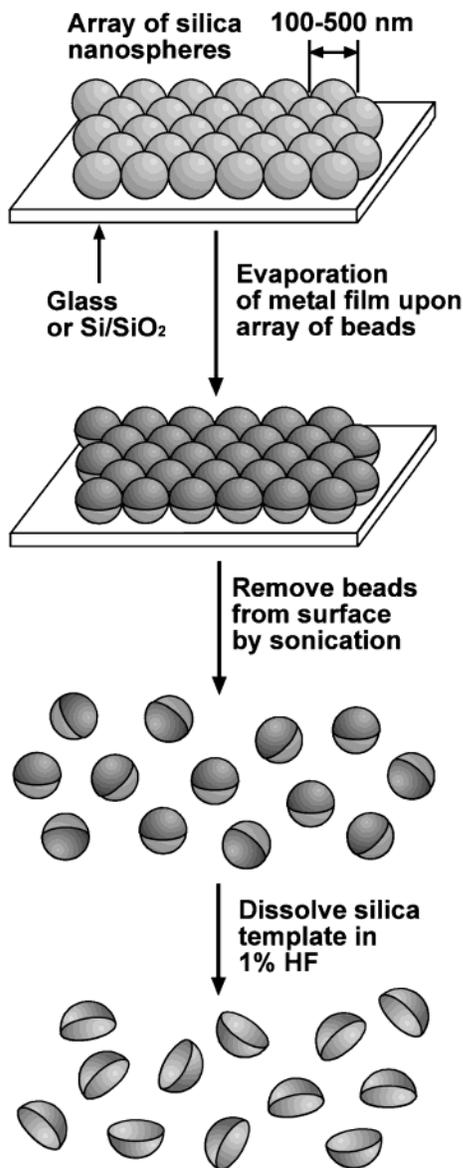
The semiconductor industry has developed a number of techniques, including molecular beam epitaxy (MBE), physical vapor deposition (PVD), and chemical vapor deposition (CVD), for depositing thin solid films.<sup>2</sup> These techniques provide control over the composition and thickness of a deposited film with precision on the order of Å. Natelson et al. used MBE and selective chemical etching to fabricate narrow trenches with critical dimensions of 3 nm on the cleaved edge of an alternating stack of AlGaAs/GaAs thin films.<sup>3</sup> Electron-beam and thermal evaporation sources can deposit a wide array of materials, including metals, semiconductors, alloys, and refractory compounds.<sup>2</sup> The combination of these methods for the deposition of thin films with the use of sacrificial structures as templates to guide the

formation of particles provides a method of synthesizing nanoparticles of materials that are difficult to synthesize using other procedures.

The use of templates in the formation of nanostructured structures is common: examples include mesoporous silica and zeolites,<sup>4</sup> nanotubes and rods,<sup>5</sup> colloidal crystals and inverse opals,<sup>6</sup> core/shell particles,<sup>7</sup> and others.<sup>8</sup> Evaporation of metal into the spaces *between* crystallized arrays of spheres has been used to form tetrahedral nanoparticles with useful optical properties.<sup>9</sup> Evaporation of thick films (>20 nm) of metal on nanospheres leads to asymmetric particles that are fused at the equators of the particles.<sup>10</sup>

Three potentially useful aspects of hollow, hemispherical particles are that: (i) the ratio of the surface area to volume is approximately twice that of spherical core/shell particles, (ii) they present a substantial linear, nm-scale edge ( $\sim 1.4 \mu\text{m}/\text{edge}$  for half-shells with  $d = 450 \text{ nm}$ ), and (iii) their shape makes it very difficult for them to assemble into arrays that obscure their edges. Figure 1 outlines the procedure for fabricating hollow, metallic half-shells. Monolayers or multilayers of silica colloid were prepared by drop-casting aqueous suspensions of particles onto glass slides. An adhesion layer of titanium or nickel (0.5–0.8 nm) was deposited on the templates by electron-beam evaporation, followed by a thin film of metal (gold, platinum, or palladium; 8.0–15.0 nm). After the deposition of the metal film, the spherical colloid particles were released from the

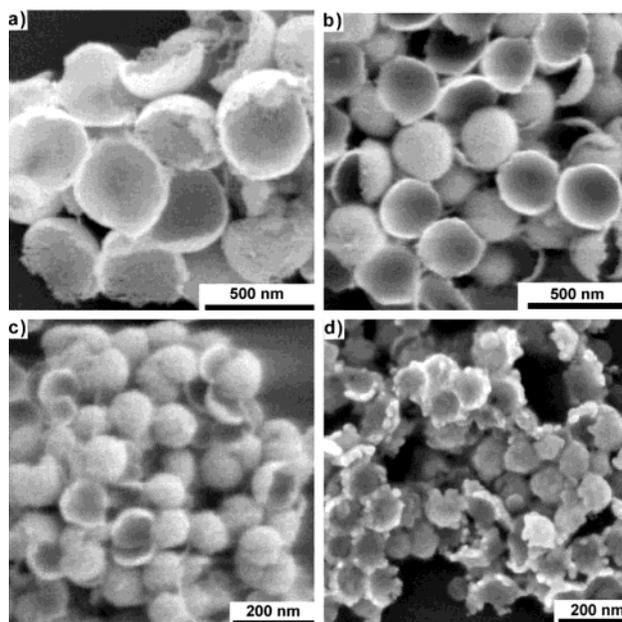
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**Figure 1.** Scheme for fabricating metallic half-shells.

surface by sonication. The silica core and adhesion layer were dissolved using an etch (aqueous HF) that left the metallic half-shells intact. (See Supporting Information for experimental details.)

Figure 2 shows examples of half-shells with different sizes and compositions. The morphology of the shells varied with the metal deposited. Gold half-shells were composed of grains of 40–50 nm in diameter and had small pores in the shell at the boundaries of the grains when the thickness of the shell was less than 15 nm (Figure 2a). Platinum and palladium half-shells with diameters of 100 nm or smaller had typical grain sizes of 15–20 nm (Figure 2b and 2c). Gold half-shells with diameters of 100 nm are much rougher at the edges and more textured than those composed of platinum (Figure 2d). The half-shells of platinum and palladium did not have visible (by scanning electron microscopy) pores for thicknesses greater than 8 nm. The differences in grain morphology of the metals developed, in part, as a result of the conditions of the deposition. In these



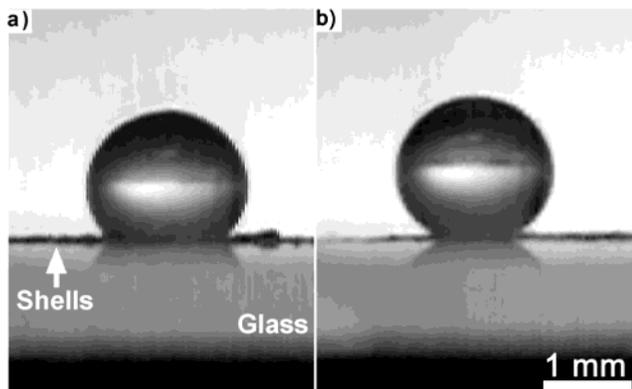
**Figure 2.** Scanning electron micrographs (SEMs) of (a) 10-nm thick gold half-shells (450-nm dia.), (b) 10-nm thick palladium half-shells (290-nm dia.), (c) 8-nm thick platinum half-shells (100-nm dia.) and (d) 8-nm thick gold half-shells (100-nm dia.).

experiments, the metals were deposited onto the silica colloid at or near 300 K at the same rate of evaporation (0.1–0.2 nm/s). We believe that the continuity (or porosity) of the thin film shells was determined by the ability of the metal to wet the silica surface coated with a submonolayer of titanium (0.5–0.8 nm). It seems that gold does not wet the templates well and that, consequently, it coalesces into large grains with interstitial pores rather than into smooth, continuous films. The high mobility of gold may also contribute to this behavior.

Uniformity of the half-shells depends on the uniform size of the silica templates and the degree of order in the crystallized templates. Hexagonally close-packed lattices of silica particles generated the most uniform particles for colloids with diameters greater than 200 nm. To produce collections of individual half-shells with diameters less than 200 nm, we used submonolayer coverages of the supporting substrate with the colloidal particles to reduce the number and size of the arrays of half-shells that were fused together at the equator of the colloid in a close-packed arrangement.

The half-shells are surprisingly robust structurally. Half-shells with diameters as large as 500 nm, and with shells as thin as 10 nm, did not collapse during the process of dissolving the template or drying on a surface for imaging. Dispersion of the particles by mild sonication in an ultrasonic cleaner also did not deform the hemispheres. A survey of both gold and palladium half-shells (450-nm diameter) by electron microscopy showed that fewer than 5% of the particles were distorted or broken after the fabrication procedure, including redispersion. The most common deformation was the elongation of one axis to form elliptical half-shells.

The properties of the individual half-shells—i.e., high surface area-to-volume, thin edges, structural rigidity, in-

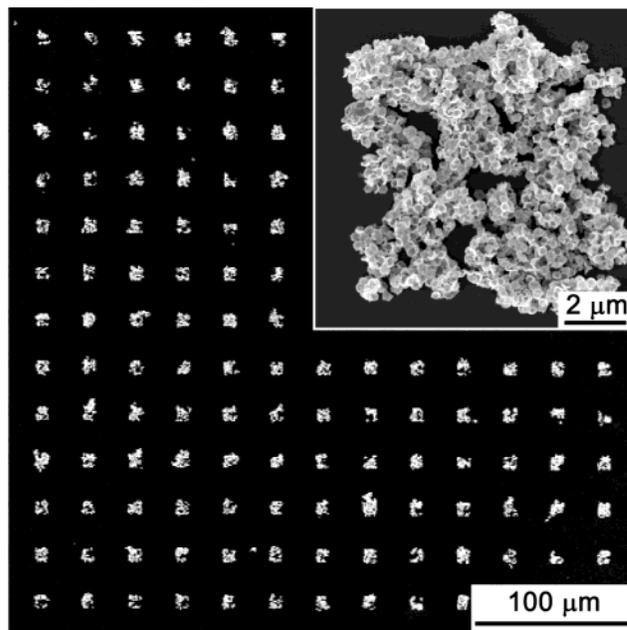


**Figure 3.** Optical micrographs of a static 5- $\mu\text{L}$  drop of water resting on the surface of a thin film of gold half-shells supported on a glass slide: (a) unmodified and (b)  $\text{C}_{16}\text{S}$ -coated. The film of aggregated half-shells was approximately 10 mm in diameter and 50  $\mu\text{m}$  thick.

ability to form regular, densely packed arrays (with a large reduction in surface area and edge length)—implied that foam-like superstructures or films formed from aggregates of the half-shells would have (i) large ratios of surface area or edge perimeter length to volume, (ii) a high density of randomly packed half-shells, and (iii) a high degree of surface roughness. These properties, combined with the ability to tune the surface properties of the individual half-shells using self-assembled monolayers (SAMs),<sup>11</sup> suggested that we could render such films “superhydrophobic”. The wettability of a surface is primarily determined by its chemical composition and roughness.<sup>12</sup> A surface with an advancing contact angle of water greater than  $150^\circ$  is generally considered superhydrophobic.<sup>13,14</sup> A typical contact angle value on a smooth, unmodified, thin film of gold deposited by PVD was  $\sim 73^\circ$  for films prepared in the same deposition as the half-shells and exposed to air for at least 1 day; this value varies somewhat depending on preparation conditions and handling, and reflects the adsorption of adventitious organic materials on the surface.

The static advancing contact angle ( $\theta_a^{\text{H}_2\text{O}}$ ) measured using a hanging, 5- $\mu\text{L}$  drop of water on a bulk surface of aggregated, unmodified gold half-shells ( $d = 290$  nm, thickness = 10 nm) was  $\sim 151^\circ$ . The drop remained pinned, however, at the points of contact as the drop was withdrawn from the surface, and a small drop of water remained on the surface. A free, static 5- $\mu\text{L}$  drop placed on the surface remained attached to the surface and did not slide off when the substrate was tilted up to  $90^\circ$ .<sup>13</sup> Modification of the gold half-shells by formation of a SAM of hexadecanethiolate increased  $\theta_a^{\text{H}_2\text{O}}$  measured with the hanging drop to  $\sim 163^\circ$ ;<sup>15</sup> the value for a free, static, 5- $\mu\text{L}$  drop was  $\theta_a^{\text{H}_2\text{O}} \sim 155^\circ$  (Figure 3). In addition, the drop did not adhere to the surface; it immediately released from the surface upon withdrawal. A free drop placed on the surface slid off the surface if the substrate was tilted  $\sim 1^\circ$  or if disturbed by ambient air currents near the drop.

To explore the feasibility of preparing surfaces micropatterned with aggregates of half-shells, we used a template-assisted self-assembly process<sup>16</sup> to aggregate gold half-shells



**Figure 4.** SEM of an array of porous, metallic structures assembled from gold half-shells (290-nm diameter). The inset shows an individual square of aggregated, gold half-shells.

into microfoams with discrete size and shape (Figure 4). The shells were deposited into arrays of microwells defined in a film of photoresist. The photoresist was selectively removed after the assembly process by gently rinsing the substrate with acetone. The dimensions of the microwells determined the shape, thickness, and periodicity of the micropatterned aggregates. We believe that these materials may be interesting in studies of wetting and magnetic filtration.

In conclusion, this procedure provides a route to hollow, metallic hemispheres with well-defined thicknesses, diameters, and compositions. We anticipate that the technique can be expanded to other materials and different techniques for thin film deposition (e.g., molecular beam epitaxy), and that it will enable the preparation of half-shells having multiple layers of different materials. One limitation of the current procedure is that the composition of the half-shells is limited to materials that are inert to HF (used to dissolve the silica colloid). The synthesis of composite half-shells in which materials dissolved by HF (e.g., nickel, titanium, silver) are encapsulated in inert inner and outer shells may overcome this limitation. Layers of different materials would also make it possible to develop different surface chemistries for both the inner and outer faces of the shells. We believe that the thin, metal edges of the half-shells will produce strong enhancements in optical and magnetic fields that will be useful in studies involving surface plasmons or magnetic filtration. Potential applications for porous microstructures formed from half-shells include metallic foams, heterogeneous catalysts, magnetic filters, and superhydrophobic surfaces.

**Acknowledgment.** This research was supported by DARPA and used the MRSEC Shared Facilities supported by the NSF under Award No. DMR-9400396. J.C.L. thanks

the DoD for a graduate fellowship. D.B.W. thanks the NSF for a graduate fellowship. The authors thank Stephen Shepard and Yuanzhang Lu for their technical assistance.

**Supporting Information Available:** Experimental protocols for the fabrication of half-shells and the template-assisted self-assembly process. This material is free of charge via the Internet at <http://pubs.acs.org>.

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NL025633L