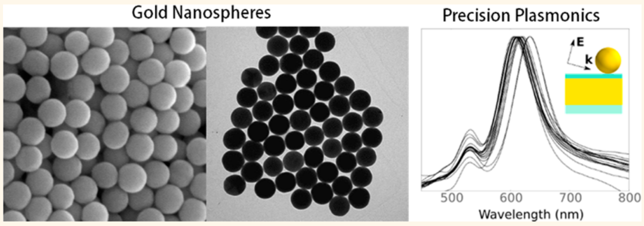
Ultrasmooth, Highly Spherical Monocrystalline Gold Particles for Precision Plasmonics

You-Jin Lee,[†,‡,▽] Nicholas B. Schade,[§,▽] Li Sun,[⊥,▽] Jonathan A. Fan,[#] Doo Ri Bae,[‡] Marcelo M. Mariscal,[‖] Gaehang Lee,[‡,*] Federico Capasso,[⊥] Stefano Sacanna,[△] Vinothan N. Manoharan,[⊥,§] and Gi-Ra Yi[†,*]

[†]Department of Polymer Science and Engineering and School of Chemical Engineering, Sungkyunkwan University, Suwon 440-746, Republic of Korea, [‡]Division of Materials Science, Korea Basic Science Institute, Daejeon 305-806, Republic of Korea, [§]Department of Physics, Harvard University, Cambridge, Massachusetts 02138, United States, [⊥]School of Engineering and Applied Sciences, Harvard University, Cambridge, Massachusetts 02138, United States, [#]Beckman Institute, University of Illinois, 405 North Mathews Avenue, Urbana, Illinois 61801, United States, [‖]INFIQC/CONICET, Departamento de Matemática y Física, Facultad de Ciencias Químicas, Universidad Nacional de Córdoba, XUA5000 Córdoba, Argentina, and [△]Molecular Design Institute, Department of Chemistry, New York University, New York, New York 10003, United States. [▽]Y.-J. Lee, N. B. Schade, and L. Sun contributed equally to this work.

ABSTRACT Ultrasmooth, highly spherical monocrystalline gold particles were prepared by a cyclic process of slow growth followed by slow chemical etching, which selectively removes edges and vertices. The etching process effectively makes the surface tension isotropic, so that spheres are favored under quasi-static conditions. It is scalable up to particle sizes of 200 nm or more. The resulting spherical crystals display uniform scattering spectra and consistent optical coupling at small separations, even showing Fano-like resonances in small clusters. The high monodispersity of the particles we demonstrate should facilitate the self-assembly of nanoparticle clusters with uniform optical resonances, which could in turn be used to fabricate optical metafluids. Narrow size distributions are required to control not only the spectral features but also the morphology and yield of clusters in certain assembly schemes.



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In equilibrium, a nanoscale crystal adopts a polyhedral morphology to minimize its surface free energy. As a result, metallic nanoparticles grown near equilibrium form facets.[1−3] Although the plasmon resonances and ease of functionalization[4] make such particles promising[1] for bottom-up assembly of optical resonators[5,6] and isotropic metamaterials,[7] it is difficult to make structures whose optical properties are reproducible from one particle or one multiple-particle cluster to the next since the resonances are often sensitive to features such as sharp corners,[8] number of facets,[9] roughness,[10] and overall size and shape.[11] Moreover, the interparticle optical coupling varies significantly with nanometer-scale changes in gap distance[12] and orientation.[13] The ideal particle for self-assembly of plasmonic structures is therefore not a polyhedron, but a spherical crystal without facets or grain boundaries. However, producing such particles is a materials challenge, since spherical crystals are not stable under any growth conditions. Here we show that a cyclic process of slow growth followed by slow chemical etching, which selectively removes edges and vertices, results in ultrasmooth, highly spherical monocrystalline gold particles. The etching process, which is functionally similar to (but chemically different from) that used to make monocrystalline silver nanospheres for surface-enhanced Raman spectroscopy,[14,15] effectively makes the surface tension isotropic, so that spheres are favored under quasi-static conditions. The resulting spherical crystals display uniform scattering spectra and consistent optical coupling at small separations, even showing Fano-like resonances[16] in small assemblies. The cyclic process we demonstrate could be extended to other metals and, because it is scalable up to particle sizes of 200 nm or more, might be used to create strongly scattering particles for sensors,[17,18]

* Address correspondence to
yigira@skku.edu,
ghlee@kbsi.re.kr.

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electromagnetic resonators,[7] and other optical devices.[19]

The challenge of synthesizing metallic nanoparticles with controlled morphology is intimately connected to how crystals grow. Unlike silica or polymer nanoparticles, metallic nanoparticles are crystalline and tend to adopt distinct facets when grown in a bulk suspension. As first described by Gibbs[20] and Wulff,[21] facets form because they minimize the surface free energy, which is a function of the exposed crystal planes. The number of facets can be controlled by chemically inhibiting the growth of certain crystal surfaces. This method has been used to produce nanoparticles with a variety of different shapes, including tetrahedra,[1] octahedra,[2,8] cubes,[8] and higher-order polyhedra.[3] However, even pseudospherical particles[22] produced this way have small facets.

We are not aware of any growth method that results in smooth, spherical nanocrystals. Quasi-spherical gold nanoparticles grown near equilibrium tend to increase in polydispersity and ellipsoidal eccentricity with increasing average particle diameter.[23,24] Nevertheless, fundamental studies of plasmonic phenomena[6,25] have proceeded under the assumption that such particles are adequate substitutes for spheres. An alternative is heterogeneous growth on a spherical dielectric shell, which produces nanoshells[26] that are spherical but polycrystalline, and as a result have rough surfaces and grain boundaries that can lead to additional losses in plasmonic applications. Nanoshells are also subject to dewetting[27] and thermal instabilities.[28]

Our solution to this quandary is to use both growth and etching, rather than simply adjusting the growth conditions, to make solid gold nanospheres (Figure 1a). The growth step produces single-crystalline polyhedral particles, while the chemical etching step selectively removes edges and vertices while leaving the crystal structure intact. It is important that both steps are quasi-static, to avoid instabilities. The effect of the reduction–oxidation etching process is analogous to introducing an isotropic surface tension, which leads to spherical particles as the particle size decreases. By alternating between anisotropic growth and isotropic etching, we create smooth, spherical, single-crystalline particles of any desired size, up to 200 nm and conceivably larger. These spherical gold crystals are smoother than state-of-the-art polycrystalline or commercial particles and, as a result, show much more uniform optical properties, making them ideal building blocks for self-assembly of plasmonic nanostructures.

RESULTS AND DISCUSSION

Synthesis of Uniform, Monocrystalline Gold Nanospheres. We start by synthesizing single-crystalline gold octahedra, following a procedure similar to that of Li *et al.*[2] (See Materials and Methods and Supporting Information for details.) The particles grow by the slow reduction of chloroauric acid ($HAuCl_4$) in ethylene glycol, which acts as a reducing agent at elevated temperature, with poly(diallyl dimethyl ammonium chloride) (polyDADMAC) and phosphoric acid (H_3PO_4). PolyDADMAC, a cationic polyelectrolyte, stabilizes the nanoparticles, and phosphoric acid controls the reduction rate of chloroauric acid.[2] The resulting uniform gold octahedra are 135.4 ± 12.5 nm in edge length (Figure 1a). A small number of particles with different shapes, such as decahedra and truncated triangular bipyramids, are also formed in this reaction but constitute less than 5% of the total.

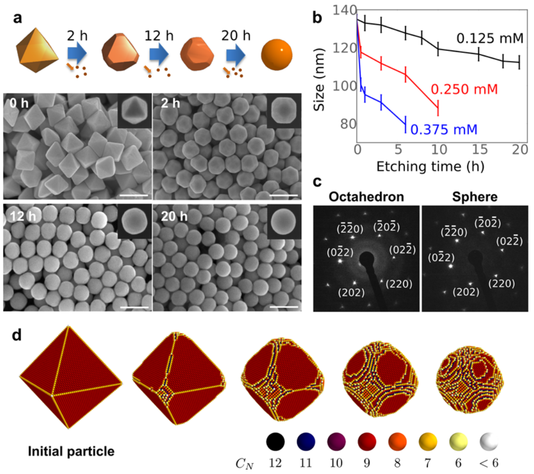

Figure 1. Growth followed by etching produces uniform, monocrystalline nanospheres. (a) Schematic diagram of shape evolution of gold particles during the etching process. SEM images of gold nanoparticles after chemical etching for various durations show the gradual transformation from octahedra to spheres. Scale bars are 200 nm. (b) Particle size as a function of etching time after the addition of $HAuCl_4$ in different concentrations. (c) Electron diffraction pattern of an octahedral particle and a spherical particle, showing that both are single crystals. (d) Sequential states in the simulated etching of a gold octahedron with an edge length of 40 atoms. The color of each atom corresponds to its coordination number C_N and energy.

To smooth the vertices and edges, we add an oxidizing agent, chloroauric acid, to the unwashed gold octahedron suspension after it cools. Chloroauric acid favors oxidation of the gold atoms specifically at vertices and edges, where the atoms have the lowest coordination.[29] Although chemical etching processes have been used to change the shape of polyhedral metal nanoparticles into exotic shapes, in general these processes do not produce uniform spheres.[30] Our etching process differs in that it is designed to be slow, so as to avoid instabilities leading to anisotropy, polydispersity, or significant reductions in particle size. Over the course of 20 h, the particles progress from octahedra to truncated octahedra, quasi-spheres, and finally smooth gold nanospheres of diameter 112.3 ± 8.2 nm (Figure 1a). As shown in Figure 1b, the particle size decreases abruptly at first and then decreases more slowly as the oxidation–reduction reaction

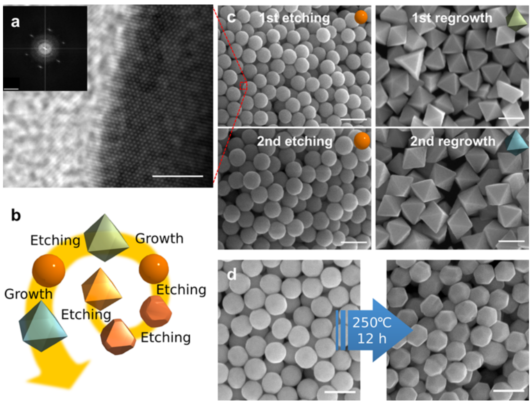

Figure 2. Nanospheres produced by growth and etching are single crystals that can be used as seeds for further growth. (a) High-resolution transmission electron micrograph of a gold nanosphere shows that the crystalline order extends to the edge of the particle. Scale bar is 2 nm. Inset shows the electron diffraction pattern. (b) Schematic diagram of iterated etching and regrowth of gold nanoparticles to produce large particles. (c) Scanning electron micrographs show particles after repeated etching and growth steps. Scale bars are 200 nm. (d) Scanning electron micrographs taken before and after annealing a sample of gold microspheres at 250 °C in pentanediol for 12 h. Scale bars are 200 nm.

approaches equilibrium, and the chemical potential difference vanishes. Electron diffraction patterns of individual octahedra and spheres (Figure 1c) indicate that each nanoparticle is a single, face-centered cubic crystal, both before and after the etching reaction.

Monte Carlo simulations of the etching process, using atom energies calculated as a function of coordination number using the embedded atom method,[31] show that the oxidation conditions alone can explain the transformation to a sphere. The embedded atom method calculations predict that gold vertex atoms have a free energy of 26 k_BT and edge atoms of 10 k_BT relative to the [111] faces. These conditions favor the removal of vertices and edges before faces, as shown in Figure 1d and in Supplementary Movie 1. Although these simulations do not model diffusive dynamics, they do show that energetics favor the transition to a spherical morphology before the surface layers on the faces of the original octahedron are completely removed. Because the difference in free energy between faces is only 3.9 k_BT, the anisotropy in the surface tension is small compared to the difference in free energy between edges and faces or between vertices and faces. Thus the surface tension is effectively isotropic, and it favors the removal of regions of high curvature.

Cyclic Growth and Etching Process. The etching process leaves the crystal structure of each particle unperturbed, resulting in true spherical crystals, as evidenced by high-resolution transmission electron micrographs (Figure 2a). To further confirm that the crystalline order extends to the boundary of the nanospheres, we used 112.3 ± 8.2 nm gold spheres produced by our growth and etching process as seeds for a second growth reaction (Figure 2b) (Materials and Methods). This resulted in larger octahedra with edge length 156.5 ± 13.8 nm (Figure 2c). If the original spheres were not monocrystalline, we would not expect that the regrowth reaction would result in such uniform and smooth octahedra.

The seeded growth experiments also illustrate a route to larger gold nanospheres through cyclic etching and growth. We initiated another etching reaction using the regrown octahedral particles and found that these too transformed into spheres. The new batch of nanospheres was larger (131.2 ± 9.5 nm) than the original seed spheres we had obtained after 20 h. We produced larger octahedral gold particles in a third growth step (173.3 ± 15.1 nm), and as we continued this procedure, we obtained smooth gold spheres of diameter 200 nm after seven iterations (Supporting Information). We know of no other route to such large and uniform gold particles.

Annealing experiments (Supporting Information) show that these spherical crystals, though metastable with respect to the polyhedral morphology, are in fact more stable than quasi-spherical gold nanostructures. We find that in the absence of etching reagents the nanospheres maintain their shape at temperatures up to 200 °C. At 250 °C, the particles start developing facets, as shown in Figure 2d. In contrast, gold nanoshells melt at temperatures as low as 175 °C due to grain boundaries and fissures.[28] The enhanced stability suggests that the spherical crystals not only are monocrystalline but also have a low level of defects that might compromise thermal stability.

Circularity and Size Distribution. The other state-of-the-art particles for studies of plasmonic phenomena are quasi-spherical gold particles produced from citrate reduction of $HAuCl_4$ in water.[32,33] These have been used in several recent experiments to study phenomena such as surface-enhanced Raman scattering,[18] Fano resonances,[6] nanoparticle-microcavity-based sensing,[34] and quantum limits of plasmonic coupling.[25] However, we find that these particles are much less smooth and spherical than the nanospheres produced through growth and etching. We quantify these differences using image analyses of transmission electron micrographs (Figure 3).

Starting with a TEM image of a single nanoparticle, we use the software program ImageJ to threshold and filter the image. We then sample over all angles in the plane of the image to compute the maximum Feret's diameter (d_F) of the region representing the nanoparticle. This represents the longest line segment that can be drawn from one side of the particle to another. We define the "circularity" (c) of the particle as the ratio of its area (A) in the filtered image to the area of a circle whose diameter is equal to d_F, expressed in the

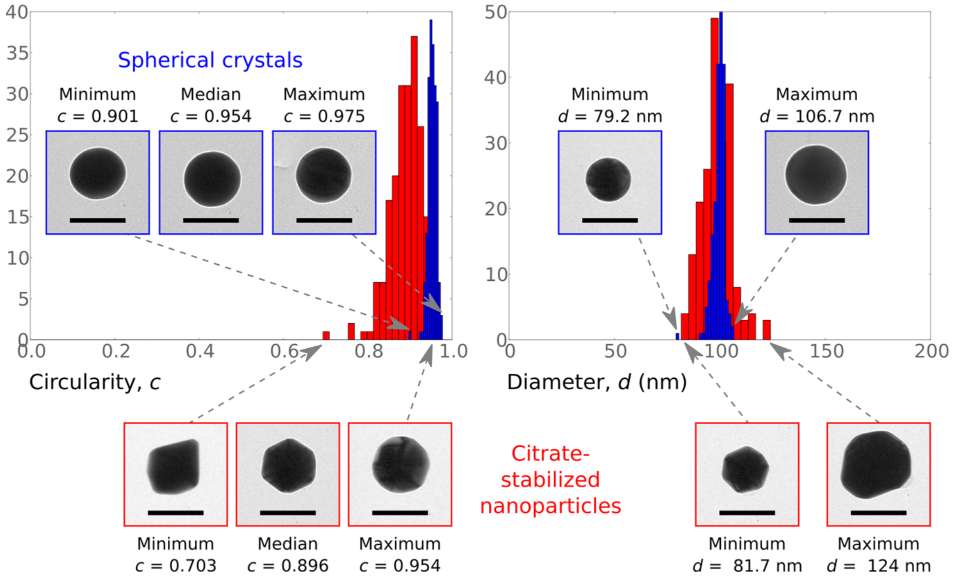

Figure 3. Distribution of circularity and diameter of spherical gold crystals (blue) and citrate-stabilized gold nanoparticles (red), as measured from TEM images of samples of 200 particles using image processing. A perfectly circular particle corresponds to $c = 1$; the circularity decreases toward zero as the particle's outline deviates from a circle. Insets show micrographs corresponding to key parts of each distribution. Scale bars are 100 nm.

equation $c = 4A/\pi d_F^2$. A perfectly circular particle corresponds to $c = 1$; the circularity decreases toward zero as the particle's outline deviates from a circle. From the area A that we measure in each image, we can also compute an average diameter of each particle, $d = (4A/\pi)^{1/2}$. From the distribution of d for each colloid, we can measure its polydispersity.

We measure c and d for equal numbers of gold nanospheres made through growth and etching and citrate-stabilized gold particles purchased from British Biocell International (BBI), which are prepared using a proprietary method based on the procedure developed by Turkevich *et al.*[32] As shown in Figure 3, the distributions of the circularity, c, and the diameter, d, for these particles are more than twice as broad as they are for particles of comparable size from the growth and etching technique. The spherical crystals have an average diameter of 99.5 nm with a standard deviation of 2.9 nm. They are more monodisperse than a comparable sample of citrate-stabilized particles, whose average diameter is 98.8 nm with a standard deviation of 7.2 nm. Moreover, the median citrate-stabilized particle deviates from perfect circularity (1.000) more than twice as much as the median spherical crystal; the median circularity of the spherical crystals is 0.954 and that of the citrate-stabilized particles is 0.896.

Reproducible Scattering Spectra of Gold Nanospheres. The qualitative advances in particle uniformity, sphericity, smoothness, stability, and monocrystallinity afforded by the growth and etching technique (Figure 4a) enable the assembly of plasmonic structures with uniform and reproducible optical properties. We demonstrate this through several experiments examining the spectra of individual particles and assemblies thereof.

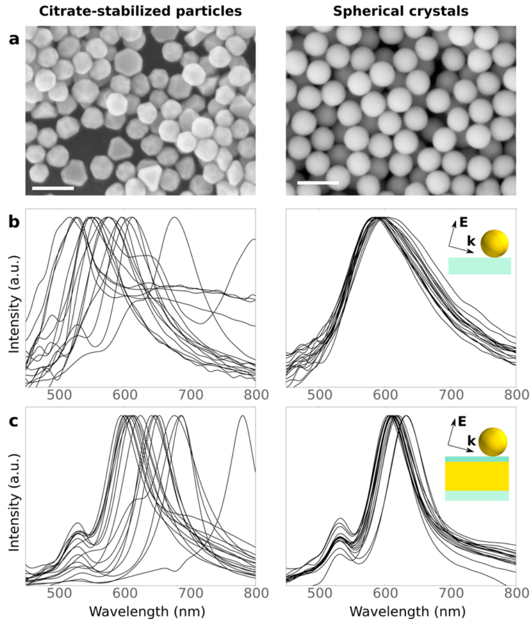

Figure 4. Reproducibility of gold nanoparticle scattering spectra. (a) Scanning electron micrographs of gold nanoparticles synthesized by citrate reduction or growth and etching. Scale bars are 200 nm. (b, c) Measured scattering spectra for citrate-stabilized nanoparticles and spherical crystals. Particles in (b) are on a glass slide and in (c) are on a gold film with a thin dielectric spacer. Insets show polarization direction.

To test the optical uniformity of the nanospheres, we record dark-field scattering spectra from individual particles deposited on a glass slide (Materials and Methods), shown in Figure 4b. We find that the standard deviation of the resonance peak wavelength for our spherical crystals is 5.7 nm, nearly 7 times smaller than that of commercial citrate-stabilized particles.

The nanospheres also show uniform spectra when their surface plasmons interact with those of a metal surface only 10 nm away. Unlike individual particles on a glass slide, this system enables us to probe higher-order plasmon modes in the context of coupling. We place the particles on a smooth gold film with an aluminum oxide spacer (Materials and Methods) and measure their scattering spectra with p-polarized light at a 65° angle of incidence. In this geometry, the interaction results in a low-energy bonding mode and a higher energy antibonding mode, both of which are broadened due to the finite film thickness.[35] We find that for the nanospheres produced through growth and etching, the standard deviation in peak wavelength is nearly 6 times smaller than it is for citrate-stabilized particles of similar size (Figure 4c). Furthermore, features like the smaller peak near 530 nm and the minimum near 550 nm are more reproducible for the spherical crystals than for the citrate-stabilized particles, some of which do not exhibit these features at all. For the spherical crystals, the wavelength of the small peak has a standard deviation of only 0.74 nm and may in fact be much smaller, as this value is comparable to the instrumental broadening of our spectrometer apparatus; for the citrate-stabilized particles the distribution is nearly 5 times as broad. The standard deviation of the ratio of the small peak intensity to the minimum intensity is 3.5 times larger for citrate-stabilized particles than for spherical crystals. Because the coupling that leads to these features depends sensitively on azimuthal symmetry and the distance between the particle and the gold film,[35] the results suggest that nanospheres produced by growth and etching are round and smooth down to the nanometer scale.

Scattering Spectra of Quadrumer Cluster. To demonstrate that these particles may be used for self-assembly of artificial plasmonic molecules and other nanostructures showing complex coupling between plasmon modes, we prepare symmetric four-particle clusters ("quadrumers") on TEM grids (Materials and Methods) and measure their scattering spectra using near-normal incidence dark-field spectroscopy.[36] A narrow minimum appears in the spectrum near 980 nm when the polarization of the incident light is parallel to the quadrumer's short axis (Figure 5a). The minimum disappears when the polarization is parallel to the quadrumer's long axis. These spectral features, characteristic of a Fano-like resonance,[16] are in good agreement with calculated scattering spectra (Materials and Methods, Supporting Information, and Figure 5b) for a quadrumer modeled by uniform, spherical gold nanoparticles. The resonance results from interference between quadrupolar and higher-order modes of the nanoparticles.[16] This shows that the spherical nanocrystals can be used to fabricate plasmonic structures with similar properties to those made using gold nanoshells.[5]

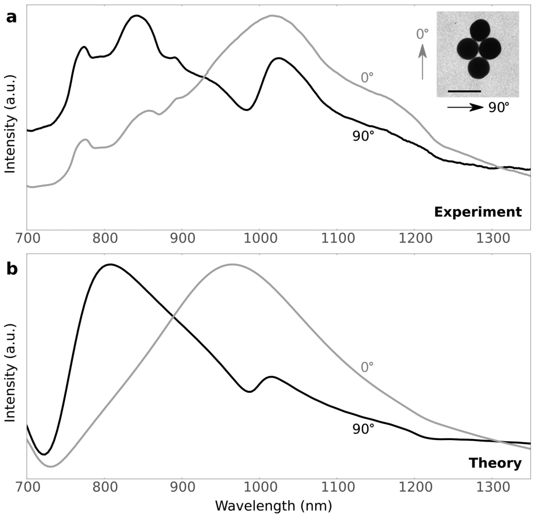

Figure 5. Scattering spectra of quadrumer cluster. (a) Experimental and (b) calculated near-normal incidence dark-field scattering spectra of a gold nanosphere quadrumer under long-axis (gray) and short-axis (black) polarization. Minima appear in both the experimental and calculated spectra near 980 nm when the polarization is parallel to the short axis of the quadrumer. We attribute this minimum to a Fano-like resonance because it occurs for only one polarization. Adsorption of organic molecules during the etching process results in a spacer on the order of 2 nm between the particles. Some discrepancies between the theoretical and experimental spectra at short wavelengths are likely due to scattering from other parts of the sample (Supporting Information) and have been observed in previous experiments.[5,16] Inset shows a transmission electron micrograph of a quadrumer. Scale bar is 200 nm.

CONCLUSION

The method we have demonstrated to produce highly uniform, single-crystalline gold nanospheres can be used to address long-standing problems in the field of plasmonics. Particles on the order of 100 nm and larger are important for many applications because the scattering cross section exceeds the absorbance cross section for gold particles larger than 80 nm.[17] The cyclic process we demonstrate can easily produce particles of 200 nm or larger, without the eccentricities and polydispersity typical of gold particles larger than 30 nm produced from established protocols. Indeed, conventional synthesis routes yield particles that are so heterogeneous that some groups have made use of the heterogeneity to fabricate asymmetric structures from a single batch of particles.[6] Furthermore, the high monodispersity of the particles we demonstrate should facilitate the self-assembly of nanoparticle clusters with uniform linear or nonlinear optical resonances, which could in turn be used to fabricate optical metafluids[7] or to investigate enhanced optical four-wave mixing.[37] Narrow size distributions are required to control not only the spectral features but also the morphology and yield of clusters in certain assembly schemes.[38] A similar cyclic process of anisotropic growth followed by isotropic etching could be used to design spherical crystals of other metals, which might find uses as building blocks for optical sensors and circuits,[18,19] probes for biomedical applications,[17,39] nucleation sites for nanobubble generation,[40,41] and components for other applications in which smoothness, thermal stability, and uniformity of the optical response are critical.

MATERIALS AND METHODS

Chemicals. Ethylene glycol (anhydrous, 99.8%), gold(III) chloride trihydrate (≥49.0% metals basis), poly(dimethyldiallylammonium chloride) (M_w 400 000−500 000, 20 wt % in H_2O), phosphoric acid (85 wt % in H_2O), chloroplatinic acid hydrate (99.995% metals basis), ethanol (99:5%), hexadecyltrimethylammonium bromide (≥99:0%), sodium dodecyl sulfate (92.5−100.5%), and polyvinylpyrrolidone (M_w ∼55 000) were purchased from Aldrich and used without further purification.

Synthesis of Octahedral Gold Particles. A 20 mL anhydrous ethylene glycol solution was stirred with a magnetic bar in a glass vial, and then 0.4 mL of polyDADMAC (20 wt % in H_2O, M_w 400 000−500 000) and 0.8 mL of 1 M H_3PO_4 solution were added. The mixture was stirred for 2 more minutes, and 0.02 mL of a 0.5 M $HAuCl_4$ aqueous solution was added under stirring. The mixture was maintained at room temperature for 15 min, and then the solution in the glass vial was loaded into an oil bath for 30 min, which was maintained at 195 °C throughout the reaction. During the reaction, the color of the solution changed from yellow to colorless and then, gradually, to purple and finally brown. We centrifuged the solution at 13 000 rpm and redispersed the precipitates in ethanol three times to remove the excess reactants and byproducts.

Chemical Etching Process of Octahedral Gold Particles. To convert the octahedral gold nanoparticles to gold nanospheres, 5 μL of a 0.5 M $HAuCl_4$ solution was added into the unwashed gold octahedra suspension (20 mL, 8.9×10^{-3} wt %) at room temperature. The color of the suspension changed from brown to pink. The size of the gold nanocrystals decreased from 135.4 ± 12.5 nm to 112.3 ± 8.2 nm over 20 h, and the gold nanocrystals evolved from octahedra to spheres.

Regrowth of Spherical Gold Particles. The unwashed gold sphere suspension in a glass vial was loaded into an oil bath at 195 °C for 1 h. We started with 112.3 ± 8.2 nm gold spheres in suspension with the 5 μL of chloroauric acid that had previously been added for etching. After the first regrowth, we obtained octahedral particles of edge length 156 ± 13.8 nm (Figure 2c). Then, we etched the octahedral particles again by adding 5 μL of chloroauric acid; the resulting spheres were larger (131.2 ± 9.5 nm) than the original seed spheres we had obtained after 20 h. During the reaction, the color of the suspension changed from orange-pink to brown as the particles evolved from spheres to octahedra.

Preparation of Nanoparticles on a Glass Slide. We prepared samples for spectroscopy measurements by drying a droplet of dilute gold nanosphere suspension on a glass slide. The slide was treated with oxygen plasma at 60 W for 10 s to make the surface more hydrophilic. Immediately afterward we placed onto the slide a droplet of gold nanosphere suspension that had been sonicated for at least 1 min in a bath sonicator. We measured spectra from individual particles after the droplet dried in air. Both the spherical crystals and the citrate-stabilized particles were deposited on the same glass slide for dark-field spectroscopy measurements. Scanning electron microscopy confirmed that the vast majority of particles on the sample were well-dispersed, sitting several micrometers apart rather than occurring in clusters.

Preparation of Particles on Gold Film Separated by a Dielectric Layer. We prepared samples by drying a droplet of dilute gold nanosphere suspension on a substrate consisting of a thin Al_2O_3 layer on top of a template-stripped gold film supported on a glass slide. To prepare the substrate, we first deposited 120 nm of gold onto a cleaned silicon wafer with electron beam evaporation. Then we placed a small drop of UV-curable epoxy (Norland Optical Adhesive 65 from Thorlabs, Inc.) on top of the gold film and put a glass slide on top before curing it under a UV lamp for 20 min. The wafer was stripped off of the film so that the film could be transferred entirely to the glass slide but retain a wafer-smooth surface. Next, 10 nm of Al_2O_3 was deposited onto the exposed surface of the gold film using atomic layer deposition. We treated the Al_2O_3 surface with oxygen plasma at 60 W for 10 s to make the surface more hydrophilic and then immediately placed a droplet of gold nanosphere suspension on it. We let the droplet air-dry and then measured the spectra.

Self-Assembly of Plasmonic Clusters and Dark-Field Spectroscopy. Gold nanoparticle quadrumers were prepared by drying a droplet of dilute gold nanosphere suspension on a London Finder Formvar TEM grid (LF200), purchased from Ted Pella. We placed 2 μL droplets of gold nanosphere colloid on the grids and let them air-dry. Some of the particles self-assembled into clusters on the Formvar surface due to capillary forces while drying.[5] Individual clusters were located on the grid using a Zeiss Libra 120 TEM operating at 60 keV, and micrographs were recorded at different magnifications so that the clusters could later be located (using the London Finder grid pattern) with dark-field spectroscopy.[5] We conducted near-normal incidence dark-field spectroscopy as described in an earlier report.[36]

Numerical Simulation of Scattering Spectra of Gold Nanosphere Quadrumer. To calculate the quadrumer's scattering spectra, we conducted finite-difference time-domain (FDTD) simulations at two different polarizations using the commercial software package Lumerical. The simulation assumed perfect spheres of diameter 130 nm with the optical properties of gold, following the Johnson and Christy standard.[42] The particle size in our model corresponded approximately to the size of the nanospheres in the quadrumer cluster whose scattering spectrum we measured. Additional FDTD simulation details are in the Supporting Information.

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

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Supporting Information Available: Supplemental figures, discussion, and movie. This material is available free of charge *via* the Internet at http://pubs.acs.org.

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