Gold-Based Cubic Nanoboxes with Well-Defined Openings at the Corners and Ultrathin Walls Less Than Two Nanometers Thick

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Supporting Information

ABSTRACT: We report a facile synthesis of Au-based cubic nanoboxes as small as 20 nm for the outer edge length, together with well-defined openings at the corners and walls fewer than 10 atomic layers (or <2 nm) in thickness. The success relies on the selective formation of Ag2O at the corners of Ag nanocubes, followed by the conformal deposition of Au on the side faces in a layer-by-layer fashion. When six atomic layers of Au are formed on the side faces to generate Ag@Au6L core−shell nanocubes, we can selectively remove the Ag2O patches at the corner sites using a weak acid, making it possible to further remove the Ag core by H2O2 etching without breaking the ultrathin Au shell. This synthetic approach works well for Ag nanocubes of 38 and 18 nm in edge length, and the wall thickness of the nanoboxes can be controlled down to 2 nm. The resultant Au nanoboxes exhibit strong plasmonic absorption in the near-infrared region, consistent with computational simulations.

KEYWORDS: gold, hollow nanostructures, site-selected deposition, surface plasmon resonance, near-infrared

Gold nanostructures embrace fascinating optical properties, commonly known as localized surface plasmon resonance (LSPR), for a broad range of applications.1–8 For Au nanoparticles with a solid structure and spherical shape, it is feasible to tune their LSPR peaks from 520 to 580 nm by increasing the diameter from 20 to 80 nm.9 The location of LSPR peaks in the visible region is instrumental to the development of colorimetric sensing devices.10 For most biomedical applications, however, it is essential to tailor the LSPR peaks to the near-infrared (NIR) between 800 and 1200 nm, in which soft tissues are highly transparent to enable deep penetration. By elongating spherical Au nanoparticles into nanorods, El-Sayed,11–13 Murphy,14–16 Liz-Marzán,17,18 and many others19–22 were able to shift the longitudinal LSPR peaks up to 2000 nm by increasing the aspect ratio of the nanorods. On the other hand, Halas and co-workers demonstrated the fabrication of Au nanoshells by depositing Au onto silica beads. They established the capability to manipulate the LSPR of Au nanoshells from 700 to 1050 nm by reducing the Au thickness from 20 to 5 nm.23,24

Parallel to those developments, Xia and co-workers introduced Au nanocages with hollow interiors and porous walls, which could be prepared with precisely tuned LSPR peaks up to 1200 nm by leveraging the galvanic replacement reaction between Ag nanocubes and HAuCl4.25–27 In a typical process, Au atoms are derived from a Au3+ precursor at the expense of three Ag atoms, followed by their deposition onto the surface of a Ag nanocube. Ultimately, the Ag nanocube is transformed into a nanobox and then a nanocage through the interplay of alloying and dealloying between Au and Ag. Although the galvanic replacement approach is simple and versatile, it does have a number of limitations. For example, it is impossible to reduce the wall thickness down to a scale below 5 nm without breaking the hollow structure. It is difficult to separately tune the size and wall thickness of the hollow structures because the wall thickness is stoichiometrically related to the size of the Ag nanocubes.28 It is also nontrivial to precisely control the location and size of the pores generated in the walls of nanocages. By employing Ag nanocubes with an

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edge length of 94 nm and truncation at the corners, Xia and co-workers demonstrated the fabrication of Au-based nanocages with pores (~10 nm) located at the corners (the sites with truncation) and 15 nm thick walls in high yields by confining the dissolution of Ag and the deposition of Au to the corners and side faces, respectively. However, it is challenging to extend this synthetic approach to Ag nanocubes with sharper corners or smaller sizes because of the complications inherent to galvanic replacement, alloying, and dealloying processes. We recently established that Au ions could be reduced to Au atoms by introducing a faster parallel reduction reaction to compete with and thus suppress the galvanic replacement reaction. More significantly, the Au atoms could be deposited on the surface of Ag nanocubes in a layer-by-layer fashion to generate Ag@Au core–shell nanocubes (where n is the number of Au atomic layers), with a tightly controlled thickness for the Au shells from three to six atomic layers. Herein, we demonstrate that AgO patches can be specifically generated at the corner sites of Ag nanocubes when the synthesis is conducted in the presence of NaOH at pH = 11.2. Remarkably, we can selectively dissolve the AgO patches using a weak acid, lifting off any Au overlayers deposited on the AgO patches and thus exposing the Ag core at the corner sites without affecting the ultrathin Au layers on the side faces. When subjected to Ag etching with an aqueous H2O2 solution, the Ag core can be completely removed to transform the Ag@Au nanocube into a Au-based nanobox. In the first step, we believe that a small number of Au atoms are formed and deposited on the side faces at the expense of Ag atoms dissolved from the corners. Because of the presence of NaOH in the reaction solution (pH = 11.2), the resultant Ag+ ions are supposed to react with OH− for the generation of AgO at the corners, preventing the underlying Ag from further reacting with Au3+ ions. In the second step, the reduction of Au ions by NaAsc would become a dominant pathway for the generation of Au atoms, followed by their conformal deposition on the side faces of nanocubes in a layer-by-layer fashion. Some of the deposited Au atoms can migrate to corners through surface diffusion. As such, the Ag nanocubes are transformed into Ag@Au core–shell nanocubes with multiple Au atomic layers on side faces, together with some Au atoms deposited on the AgO regions at the corners.

In the third step, we dissolve the AgO at the corners with a weak acid, lifting off the Au deposited on the AgO regions. Specifically, we collect the Ag@Au nanocubes by centrifugation and then redisperse them in an aqueous acidic solution containing HAsc and PVP (pH = 3.2). We confirm that HAsc could dissolve AgO without compromising the integrity of the Au layers on the side faces. Other weak acids such as citric acid also worked. Finally, we use aqueous 3% H2O2 to etch away the Ag cores, leading to the production of Au-based nanoboxes with hollow interiors, ultrathin walls, and well-defined openings at the corners. We speculate that Ag could be included in the Au walls due to the interdiffusion between the two elements for the formation of an alloy. We could use a stronger dealloying agent based on Fe(NO3)3 to remove additional Ag in order to generate nanoboxes with a higher Au content. By varying the edge length of the Ag nanocubes and the thickness of Au layers deposited on the Ag templates, we can independently control the physical dimension and wall thickness of the Au-based nanoboxes.

RESULTS AND DISCUSSION

Figure 1 illustrates the four major steps involved in the fabrication of Au-based nanoboxes. The synthesis relies on the use of Ag nanocubes with slight truncation at the corners as templates for the conformal deposition of ultrathin Au shells. In a typical process, the Ag nanocubes are dispersed in an aqueous solution containing NaOH, ascorbic acid (HAsc, which should react with NaOH to form NaAsc, a reducing agent), and poly(vinylpyrrolidone) (PVP, a stabilizer), immediately followed by the titration of aqueous HAuCl4 using a syringe pump under ambient condition. In the first step, we believe that a small number of Au atoms are formed and deposited on the side faces at the expense of Ag atoms dissolved from the corners. Because of the presence of NaOH in the reaction solution (pH = 11.2), the resultant Ag+ ions are supposed to react with OH− for the generation of AgO at the corners, preventing the underlying Ag from further reacting with Au3+ ions. In the second step, the reduction of Au ions by NaAsc would become a dominant pathway for the generation of Au atoms, followed by their conformal deposition on the side faces of nanocubes in a layer-by-layer fashion. Some of the deposited Au atoms can migrate to corners through surface diffusion. As such, the Ag nanocubes are transformed into Ag@Au core–shell nanocubes with multiple Au atomic layers on side faces, together with some Au atoms deposited on the AgO regions at the corners.

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In the first set of experiments, we used Ag nanocubes with an average edge length of 38.0 ± 1.1 nm with slight truncation at the corners (Figure S1) as templates to generate Ag@AuL nanocubes and then Au-based nanoboxes with an outer edge length of 39.7 ± 3.0 nm (see Experimental Section for details). Figure 2A shows a transmission electron microscopy (TEM) image of the Ag@AuL nanocubes with the introduction of 0.8 mL of aqueous HAuCl4 (0.1 mM) to generate six atomic layers of Au on the side faces. We also characterized the sample using scanning electron microscopy (SEM). As shown in Figure S2, some of the nanocubes show small holes at the corner sites, but not the side faces. To confirm the formation of a conformal shell of Au on the Ag core, we used aberration-corrected high-angle annular dark-field scanning TEM (HAADF-STEM) to characterize the core–shell nanocubes (Figure 2B). The contrast between the shell and the core clearly verifies the conformal deposition of Au on the entire surface of the Ag nanocube, with a somewhat thinner projection along the edges. The dark contrast at the corners suggests a higher degree of truncation at the corners than the edges due to the formation of AgO at the corner sites. Figure S3 shows the atomic resolution HAADF-STEM image when the nanocube was tilted to the [001] zone axis. We also conducted a control experiment by titrating the Ag nanocubes with HAuCl4 in the presence of PVP and NaOH (pH = 11.2) in the absence of HAsc. Figure S4

Figure 1. Schematic illustration (projected along the [100] direction) of the four steps involved in the transformation of a Ag nanocube into a Au-based nanobox.
After treating the as-prepared Ag@Au$_6$ nanocubes with an aqueous solution containing citric acid (CA, 100 mM) and PVP at pH = 11.2, together with a well-preserved highly ordered arrangement for the atoms and gives a wall thickness of about 2 nm, corresponding to 10 atomic layers along the [100] direction. As indicated by the white, dashed lines, the STEM image also clearly resolved an opening at the corner. Although six atomic layers of Au were originally deposited on the side faces, the wall thickness of the nanobox was increased to 10 atomic layers. This result suggests the involvement of interdiffusion and alloying of Au and Ag and thus the retention of Ag in the walls in the form of an alloy. Elemental mapping by energy-dispersive X-ray spectroscopy (EDS) confirms the presence of Ag in the nanoboxes, with an Au to Ag atomic ratio of 1.2:1 (Figure 2F). The inductively coupled plasma mass spectrometry (ICP-MS) analysis gives a Au to Ag atomic ratio of 1:1 for a bulk quantity of the sample. We suspect that the ICP-MS result tends to underestimate the relative Au content because any solid Ag@Au$_6$L nanocube remaining in the final sample would increase the Ag content.

We also fabricated Ag@Au$_3$L nanocubes from Ag nanocubes with an average edge length of 38.0 ± 1.1 nm, followed by the removal of Ag cores. Figure S6 shows a TEM image of the resultant nanoboxes. When the Au atomic layers on the side faces were reduced from six to three, the wall thickness of the nanoboxes would decrease, ultimately reducing their overall rigidity. On the other hand, we would anticipate that the amount of Au deposited on the corners would be reduced as the total amount of Au$_3^+$ precursor added into the reaction system was decreased, leading to the formation of Ag@Au$_3$L nanocubes with nonuniform Au coverage at the corners and thus the formation of openings with a less uniform distribution in pore size.

To confirm the critical role of HAsc in transforming the Ag@Au$_6$L nanocubes into nanoboxes, we recorded UV–vis spectra from the Ag@Au$_6$L nanocubes that were treated with DI water, an aqueous PVP solution, or an aqueous solution containing both HAsc and PVP and then etched with 3% aqueous H$_2$O$_2$. As shown in Figure 3A and B, the LSPR peak of Ag@Au$_6$L dropped only slightly in intensity after H$_2$O$_2$ etching when the nanocubes were treated with DI water or an aqueous PVP solution. In comparison, the original LSPR peak of the Ag@Au$_6$L treated with an aqueous solution containing both HAsc and PVP completely disappeared after H$_2$O$_2$ etching, with the emergence of a weak peak around 1000 nm (Figure 3C). These results suggest that it was HAsc that served as an acid to selectively dissolve the Ag$_2$O (a base) patches at the corners of these nanocubes, leading to the transformation of core–shell nanocubes into nanoboxes when the Ag cores are removed by H$_2$O$_2$.

To further support our argument that the Ag$_2$O was removed via an acid–base neutralization reaction without involving the reduction function of HAsc, we performed a control experiment to treat the Ag@Au$_6$L nanocubes with an aqueous solution containing citric acid (CA, 100 mM) and PVP at pH =...
2.2 before the removal of the Ag core by H$_2$O$_2$ etching. As shown in Figure 4A, we still obtained Au nanoboxes after the removal of Ag cores, confirming the formation of Ag$_2$O, a base that could be dissolved by an acid, at the corner sites of Ag nanocubes. Figure 4B shows UV−vis spectra of the Ag@Au$_{6L}$ nanocubes after the treatment with an aqueous solution containing CA and PVP, followed by etching with H$_2$O$_2$. We noticed that the original LSPR peak of the core−shell nanocubes completely disappeared after H$_2$O$_2$ etching, indicating the effectiveness of CA in dissolving the Ag$_2$O patches. Taken together, we believe that any acid should be able to dissolve the Ag$_2$O as long as it does not compromise the integrity of the Au layers on the side faces and compromise the etching of Ag by H$_2$O$_2$ or another oxidative etchant.

We used UV−vis−NIR spectroscopy to characterize the optical properties of the as-prepared nanoboxes. When Ag@Au$_{6L}$ nanocubes were transformed into nanoboxes, the LSPR peak was red-shifted from 447 to 1080 nm (Figure 5A). When Fe(NO$_3$)$_3$ was used to remove more Ag from the walls of the nanoboxes (Figure S7), the LSPR peak was further red-shifted to 1135 nm. To better understand the optical properties of the nanoboxes, we used the discrete dipole approximation (DDA) to calculate their absorption and scattering cross sections. In the simulation, we assumed that a nanobox is surrounded by and completely filled with water. Also, we defined the geometry of a nanobox with an outer edge length of 40 nm, a wall thickness of 2 nm, and triangular pores (10 nm in edge length) at all corners, together with a Au−Ag alloy composition of 65% Au and 35% Ag because of its available dielectric constant. Figure 5B shows the calculated absorption, scattering, and extinction spectra. The peak was located at 1100 nm, in agreement with the experimental data (at 1080 nm). The calculated extinction, absorption, and scattering cross sections at resonance were 35.5 × 10$^{-15}$, 31.6 × 10$^{-15}$, and 3.9 × 10$^{-15}$ m$^2$, respectively. The absorption cross section is about 5 times greater than those reported for Au−Ag nanocages with an edge length of 36 nm but prepared by galvanic replacement reaction.

We have also extended the procedure to Ag nanocubes with an average edge length of 17.7 ± 0.9 nm (Figure S8) for their transformation into nanoboxes. Specifically, we adjusted the initial concentration of these nanocubes in the reaction solution with a goal to keep the total surface area the same as that of the nanocubes with an edge length of 38 nm. As a result, with the titration of 0.8 mL of aqueous HAuCl$_4$ (0.1 mM), Au atoms derived from the reduction by NaAsc could also be deposited on the nanocubes for the generation of Ag@Au$_{6L}$ nanocubes with an edge length of 19.8 ± 1.1 nm. Figure 6A shows a TEM image of the nanoboxes with an average outer edge length of 19.6 ± 1.4 nm upon removal of the Ag cores, indicating a well-preserved cubic shape and holes at the corners. Because some...
of the small Ag nanocubes had significant truncation at the corners, the 20 nm nanoboxes were not as uniform as the 40 nm nanoboxes. When the core−shell nanocubes were transformed into nanoboxes, the LSPR peak was red-shifted from 425 to 835 nm (Figure 6B). Again, we calculated the optical cross sections of a nanobox with an outer edge length of 20 nm and a wall thickness of 2 nm, a pore size of 10 nm, and an atomic composition of 65% Au and 35% Ag. The propagation direction (k-vector) and electric field (E-field) were perpendicular and parallel to the (100)-facet of the cubic box.

CONCLUSIONS

In summary, we have demonstrated a facile route to the fabrication of Au-based nanoboxes with a wall thickness less than 2 nm and well-defined openings at corners. When Au3+ is titrated into a suspension of Ag nanocubes with slight corner truncation in the presence of NaOH and NaAsc, a small amount of Ag will be dissolved from the corners because of its galvanic replacement with Au3+. Owing to the presence of OH− ions, Ag2O is immediately formed at the corners, impeding further dissolution of Ag from the nanocubes. Meanwhile, the resultant Au atoms are deposited onto the side faces, followed by the conformal, layer-by-layer deposition of more Au formed through the redox reaction with NaAsc. Some of the deposited Au atoms can also migrate from side faces to corners for the generation of Au overlayers thinner than those on the side faces. The Ag2O at the corners can be removed using a weak acid, such as ascorbic acid or citric acid, making it feasible to completely etch away the Ag core without breaking the Au shell as thin as 2 nm. Owing to the ultrathin wall thickness, Au nanoboxes as small as 20 nm in edge length can still be fabricated with strong absorption in the near-infrared region for immediate applications as contrast agents for optical imaging and as capsules for controlled release.
EXPERIMENTAL SECTION

Chemicals and Materials. Ethylene glycol (EG) was purchased from J. T. Baker. All other chemicals, including silver trifluoroacetate (CF3COOAg, 98%), gold(III) chloride trihydrate (HAuCl3·3H2O, 99.9+%), sodium hydrosulfide hydrate (NaHS·xH2O), poly-(vinylpyrrolidone) (PVP) with an average molecular weight of 29 000 (PVP-29) or 55 000 (PVP-55), aqueous hydrochloric acid (HCl, 37%), l-ascorbic acid (HAsc, 99%), sodium hydroxide (NaOH, 98%), citric acid (99.5+%) iron(III) nitrate nonahydrate (Fe(NO3)3·9H2O, 98.995%), and hydrogen peroxide (H2O2, 30 wt % in H2O) were obtained from Sigma-Aldrich. All chemicals were used as received, while deionized (DI) water had a resistivity of 18.2 MΩ·cm at 25 °C was used for the preparation of all aqueous solutions.

Synthesis of Ag Nanocubes. We followed the protocols reported by Xia and co-workers for the synthesis of Ag nanocubes with an edge length of 38 nm and 18 nm, respectively. For each synthesis, the reaction was carried out by centrifugation, washed with acetone and DI water three times, and then dispersed in DI water for future use. The final product was collected by centrifugation, washed with acetone and DI water three times, and then dispersed in DI water for future use.

Synthesis of Ag@AuL and Ag@AuH Core–Shell Nanocubes. A typical synthesis, we placed 2 mL of an aqueous solution of PVP-29 (29 mg/mL) in a 23 mL glass vial and then introduced 0.5 mL of aqueous HAuCl3 (100 mM) and 0.5 mL of aqueous NaOH (200 mM) under magnetic stirring and continuously after the introduction of 20 μL of the suspension of 38 nm Ag nanocubes (with a final concentration of 4.2 × 1010 particles per mL), 0.4 or 0.8 mL of aqueous HAuCl3 (0.1 mM) was injected into the reaction solution using a syringe pump at a rate of 0.02 μL/min. The reaction solution was maintained under magnetic stirring at room temperature for another 20 min once theapsulation had been completed. The solid sample was collected by magnetic stirring at room temperature for another 20 min once the encapsulation had been completed. The solid sample was collected by centrifugation at 6000 rpm for 20 min, followed by washing twice with DI water and redispersed in 0.5 mL of DI water.

Synthesis of Au-Based Nanoboxes with Further Dealloying. To 0.5 mL of an aqueous dispersion of the Au nanoboxes prepared by H2O2 etching (see above), 4 μL of aqueous Fe(NO3)3 (50 mM) was added and vortexed for a few seconds before the mixture was allowed to sit for another hour. The solid product was collected by centrifugation at 12 000 rpm for 20 min, washed twice with DI water, and then dispersed in 0.5 mL of DI water.

Instrumentation and Characterization. We used a conventional centrifuge (Eppendorf 5430) for the preparation of all samples. We collected all the UV–vis–NIR spectra with a LAMDA 750 (PerkinElmer, Waltham, MA, USA). An ICP-MS (NexION 300Q, PerkinElmer, Waltham, MA, USA) and an ICP-AES (NexION 300Q, PerkinElmer, Waltham, MA, USA) were used for the determination of gold in the samples. We used a conventional ICP-MS (NexION 300Q, PerkinElmer, Waltham, MA, USA) and an ICP-AES (NexION 300Q, PerkinElmer, Waltham, MA, USA) were used for the determination of gold in the samples.

DISCUSSION

We acknowledge the support from the National Science Foundation (CHE-1412006), start-up funds from the Georgia Institute of Technology, and a 3M nonfunded faculty award. We thank J. Yang for providing Ag nanocubes with an edge length of 18 nm. We thank E. J. Ahn for performing the ICP-MS analyses. J.L. acknowledges the support from start-up funds from the Arizona State University (ASU). We acknowledge the use of facilities in the John M. Cowley Center for High Resolution Electron Microscopy at ASU. T.A.F.K. is supported by the Cluster of Excellence Centre for Advancing Electronics Dresden.

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ASSOCIATED CONTENT

Supporting Information

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Notes

The authors declare no competing financial interest.

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