Capturing Electrochemically Evolved Nanobubbles by Electroless Deposition. A Facile Route to the Synthesis of Hollow Nanoparticles

Chienwen Huang,† Jiechao Jiang,† Mingyu Lu,‡ Li Sun,§ Efstathios I. Meletis,† and Yaowu Hao*,†

The Department of Materials Science and Engineering, The Department of Electrical Engineering, University of Texas at Arlington, Arlington, Texas 76019, and The Department of Mechanical Engineering, University of Houston, Houston, Texas 77004

Received August 4, 2009; Revised Manuscript Received October 21, 2009

ABSTRACT

Gas evolution during electrochemical deposition has long been regarded as undesired and deliberately suppressed. Here, we show a new role of electrochemically evolved hydrogen bubbles, serving as both templates and reducing agent to form hollow Au nanoparticles via electroless deposition. Hollow gold nanoparticles with a complete nanocrystalline shell and a 50 nm hollow core were fabricated. By controlling the shell thickness, particle size can be varied from 100 to 150 nm. The process is very simple, scalable, and with a high throughput. Using this method, more complicated hollow nanostructures such as double nanoshells (“nanomatryoshka”) can also be synthesized. These hollow nanoparticles possess desirable plasmonic properties and can potentially be used as nanocontainers to store and deliver gaseous materials. In addition, the process can be used for fundamental studies of nanobubble formation mechanism.

Noble metal nanoparticles, especially Ag and Au, have been a subject of intensive research in the past decade. These nanoparticles show a strong enhancement of absorption and scattering of visible or infrared light in resonance with their surface plasmon resonance (SPR) frequency, which leads to many promising applications. Some of these include surface-enhanced Raman scattering,1 bioimaging contrast enhancement,2 and photothermal therapy.3 Spherical gold nanoparticles can be prepared in a broad range of diameters (2 to 250 nm) with a high degree of precision.4 Also, a number of methods have been developed to synthesize noble metal nanoparticles with other shapes such as nanorods and nanoprisms.5–7 Au nanoshells, composite nanospheres consisting of Au shell and a dielectric silica core, have also been synthesized, giving rise to SPR tunability over a broad range of the spectrum.8 Xia and colleagues9 have developed a process to produce gold nanocages which have a hollow interior. In their two-step synthesis process, single crystal silver nanoparticles were first synthesized using a polyl process followed by a galvanic reaction replacing Ag with Au. The product of the reaction is “open” (perforated walls), hollow Au nanoparticles. The wall thickness is controlled by the size of the silver particles.

Here, we report a one-pot route to synthesize Au hollow nanospheres that have a completely closed shell with tunable thickness. The synthesis process was conducted in a typical three-electrode cell (as illustrated in Figure 1a). Similar to the commonly used electrochemical template synthesis of nanorods and nanotubes, anodic aluminum oxide (AAO) membranes were used. However, instead of one membrane, two to five membranes were stacked on top of each other. A commercial electroplating sodium gold sulfite (Na3Au(SO3)2) solution (pH ≈ 7.5) was used as the electrolyte. The pH was adjusted to about 6.0 by adding sulfuric acid or NiSO4 solution.

Electrodeposition experiments were carried out in potentials below −0.6 V (vs Ag/AgCl reference electrode). In addition to electrodeposition on the surface of the working electrode (at the bottom of the first membrane), the inner pore wall surfaces in all membranes were filled with distinct and well-defined Au nanoparticles. The number of these nanoparticles gradually decreases with the distance from the bottom electrode. Figure 1b,c shows the scanning electron micrographs of these nanoparticles as formed within the pores of the second membrane. Figure 1d shows accumula-
tion of Au nanoparticles on top of the electrodeposited metal on the working electrode after dissolving the first membrane by using NaOH solution.

The morphology of these nanoparticles can be controlled by the electrolyte chemistry, specifically by means of adjusting the pH of the solution. When sulfuric acid is used to adjust the solution pH, hemispherical Au nanoparticles form initially on the pore walls (Figure 2a). If the reaction is allowed to progress for longer time (Figure 2b), Au nanorods form as a result of subsequent growth of metal Au from a small Au nanoparticle (originated from a nanobubble) to fill the pores via the autocatalytic disproportionation reaction of Au electrolyte. At the same time, nanobubbles and nanoparticles continue to be generated, resulting in a mixture of Au nanorods and nanoparticles. It is important to note that a round void is always present in every particle regardless of its size or shape.

If NiSO₄ solution is used to adjust the electrolyte pH, hollow Au nanospheres with a complete shell are formed. Figure 3 shows scanning and transmission electron micrographs of these spherical nanoparticles. The transmission electron micrographs show a hollow interior enclosed by a polycrystalline Au shell with an average grain size of about 5 nm. Nanospheres were spread from dilute aqueous suspension on the surface of a silicon wafer, and then ion milled to remove their top part. Figure 3c,d shows scanning electron micrographs of nanospheres before and after ion milling, confirming the hollow nature of these nanoparticles.

Our experimental observations strongly suggest that the formation of each Au nanoparticle occurs around electrochemically evolved hydrogen nanobubbles confined in the nanoscale channels in the alumina membrane. The evolved nanobubbles can serve as both templates and reducing agent for Au electroless deposition. Hydrogen evolution occurs electrochemically at a potential lower than the H⁺/H₂ equilibrium potential (−0.55 V vs Ag/AgCl) at pH 6.0. At potentials positive to the equilibrium, no Au nanoparticles were observed; only electrodeposited metal rods formed on the bottom electrode. Hydrogen bubble nucleation requires

Figure 1. Nanoparticles inside anodic alumina membranes. (a) Illustration of the three-electrode electrochemical cell. A stack of AAO membranes was used. A 500 nm Cu layer was sputter-deposited on the bottom side of the first membrane and served as the working electrode. (b,c) SEM micrographs of the bottom (first) and second membranes after the electrodeposition showing nanospheres formed on the wall of the channels and electrodeposited metal formed on the working electrode. (d) SEM micrograph taken after dissolving the first membrane showing a large number of particles on top of the electrodeposited metal on the working electrode. The electrodeposition was conducted potentiostatically at −0.75 V (vs Ag/AgCl) using a modified commercial gold sulfite electrolyte with pH of 6.0. The scale bars are 1 µm (200 nm for the inset).

Figure 2. Au nanoparticles with voids. SEM micrographs of nanoparticles synthesized from an electrolyte with the pH adjusted by H₂SO₄. (a) Short reaction time (10 min). (b) Long reaction time (60 min). The presence of a void in every particle is clearly shown, strongly suggesting that metal Au formation begins from a gas bubble. Shown in (b) is a mixture of Au nanorods and nanoparticles. The scale bars are 200 nm. The pH of the electrolyte was adjusted to 6.0, and the electrodeposition condition was the same as for Figure 1.
certain supersaturation level of hydrogen molecules which depends on the overpotential. When the potential is in the range from \(-0.7\) to \(-0.85\) V, nanoparticles with uniform void size can form. We believe that this narrow potential window promotes homogeneous hydrogen bubble nucleation. The void size is a clear measure of the critical nucleus size of the hydrogen bubble. At potentials more positive to \(-0.7\) V, a much smaller number of nanoparticles formed. At potentials more negative to \(-0.85\) V, copious hydrogen evolution occurs and the produced Au nanoparticles have a wide size distribution as a result of the wide size distribution of the produced hydrogen bubbles.

The inner walls of the AAO membrane also play a critical role in nanoparticle formation. Confinement of molecular hydrogen inside the pores results in a relatively high supersaturation. At the same time, the channel walls provide favorable nucleation sites for hydrogen nanobubbles. Thus, the nanobubbles form on the wall of the pores from the H₂ supersaturated solution. This hypothesis is also indirectly supported by the observation of larger number of Au nanoparticles formed in the bottom membranes and their gradual decrease with distance from the bottom electrode. Furthermore, the channels in one side of the alumina membranes used are branched with fine channels (\(\sim 20\) nm in diameter and can be seen in Figure 1b). When the branched side of the second membrane is facing down, Au nanospheres can still form demonstrating that the nanobubbles do not originate from the bottom working electrode. It would have been impossible for them to pass \(20\) nm narrow paths and travel upward into the second membrane. They form on the channel wall from a supersaturated solution.

Over the last five years, nanoscopic gas bubble formation at liquid—solid interfaces have attracted a lot of scientific interest due to their surprising stability and the great potential for applications in the field of surface science and nanofluidics. Convincing experimental evidence has shown the existence of nanobubbles with a radius in the order of \(100\) nm, which are stable for many hours. The results shown here could be evidence that a nanobubble with a radius as small as \(25\) nm can exist. Confirmation of the existence and understanding of the stability and formation mechanism of these nanobubbles certainly require a systematic investigation.

The next step following nanobubble formation is Au deposition on its surface. As a result of the electrolyte modification (changing pH from \(~7\) to \(~6\)), metallic Au can form from this solution through an autocatalytic disproportionation reaction

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3\text{Au}^{+1+} \text{(in sulfite complex)} \rightarrow \text{Au}^{3+} + 2\text{Au}
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The reaction of reducing \(\text{Au}^{1+}\) into metal Au takes place around the hydrogen bubble boundary. The narrow size distribution of the void in the Au nanoparticles suggests that the electroless deposition occurs immediately after a stable bubble has formed and prevents its growth. Furthermore, the encapsulation of the hydrogen bubble immediately after its formation is a critical step because this allows formation of additional bubbles further up in the nanopores producing a uniform Au nanoparticle size distribution.

The formation of metallic Au around the hydrogen bubble boundary is confirmed in an experiment where we used a Au-coated silicon wafer as the working electrode. When a high negative potential (from \(-0.9\) to \(-1.1\) V) was applied, hydrogen bubbles were generated at the working electrode surface and could be seen rising upward to the electrolyte surface. Pieces of metal debris that floated on the electrolyte surface were collected for analysis. Scanning electron micrographs and energy dispersive X-ray spectroscopy confirmed that the debris is comprised of bowl-shaped Au nanoparticles, indicating that metallic Au indeed form at the bubble boundary. There are two possible Au formation mechanisms. First, a high concentration of molecular hydrogen may be able to reduce the \(\text{Au}^{1+}\) into metal Au to form Au clusters, then the Au clusters act as catalyst to trigger the disproportionation reaction and more metal Au forms. Another possibility is that the hydrogen bubbles act as catalytic supports, just like metallic Au, for the disproportionation reaction to take place.

The morphology of the resultant nanoparticles depends on the contact angle of bubbles on the nanopore walls, which is determined by the hydrophobicity of the wall surface. The half spheres resulted from bubbles with a contact angle of around \(90°\), and spheres from contact angles close to zero. The observation of the change of the nanoparticle morphology from half sphere to sphere by adding \(\text{Ni}^{2+}\) suggests that \(\text{Ni}^{2+}\) increases the hydrophobicity of the wall surface (the bubble contact angles). The interaction between \(\text{Ni}^{2+}\) ions and AAO wall surface has been proposed to explain the fact that tubular structures can easily form when Ni is electrodeposited inside the anodic alumina membranes.
are assumed to have higher affinity to AAO pore wall surfaces on which hydroxyl groups are usually present. The change of surface charge of the AAO wall surface due to the Ni$^{2+}$ ion may contribute to the change of hydrophobicity of the wall surface. More research on the alumina-electrolyte interface is certainly needed to test this hypothesis.

As the reaction time progresses, the Au shell thickness increases, and so does the total size of the particles. But the size of the interior hollow space remains around 50 nm. Aqueous suspensions of these hollow gold nanoparticles show typical surface plasmon resonance effects. Figure 4 shows the absorption spectra of particle suspensions together with the calculated results using Mie theory. Measured peaks shift to longer wavelengths as the particle size increases. The measured peak is red shifted compared to the calculation. This may be due to the displacement of voids from the center of the spheres.

We also found that some nanoparticles have a double-shell structure, as shown in Figure 5. These scanning electron micrographs were taken from Au nanoparticles as extracted from membranes prior to any treatment. It was often observed that a few particles were already open and revealed a second half sphere inside the original particle. This was also observed by TEM, as shown in Figure 5d. The possible route for the formation of these nanostructures can be considered as follows. After Au metal forms in the surrounding of a hydrogen nanobubble, a larger bubble grows on the same or a nearby site and engulfs the already-formed Au particle. Then again, Au metal forms on the surface of the larger bubble. As has been demonstrated both theoretically and experimentally by Halas group, much wider tunability of SPR can be achieved by double-shell structures (so-called “nanamatryoshka”). Even though only a very small number of double-shell nanospheres form under the present conditions, their formation shows that this process can potentially be a facile method to produce large amount of multiple-shell structures. Using pulse potentials to alternate the hydrogen evolution and electroless deposition may be one possible route in forming such complex nanostructures.

In summary, our results show that the electrochemically evolved hydrogen bubbles can serve as a template for the synthesis of metal hollow nanoparticles. Hydrogen bubbles with a radius of about 25 nm have been captured by electroless deposition of Au on the inner wall surfaces of channels inside AAO membranes, and hollow Au nanoparticles formed. Multilayer shell nanostructures can also be synthesized using this method. This process potentially opens up a new bubble template-based synthesis approach for nanostructures. From earlier publications, it suggests that nanobubbles can form spontaneously at the interface between a polar solvent saturated with gases and hydrophobic surfaces. For bubble template synthesis, the major requirement seems to be the selection of an electrolyte that is able to directly react with reactive gas molecules (such as reducing hydrogen or oxidizing oxygen) or to trigger a reaction at bubble boundaries. Hollow structures from many other materials may be synthesized using this method. The process may also be useful for controlled “placement” of nanoparticles. It has been demonstrated that the location of nanobubble formation can be manipulated using patterned surfaces with nanoscale domains of varying hydrophobicity. Using bubble template synthesis with this patterning, nanoparticles...
would only be generated on hydrophobic areas where nanobubbles exist, achieving highly localized selective deposit of nanoparticles.

The hollow Au nanospheres synthesized using this method can be used in a variety of plasmonic applications. More importantly, these hollow nanoparticles have a complete nanocrystalline shell, and gases can diffuse more easily in and out through grain boundaries. (It is a general finding that diffusion activation energy in a grain boundary is about half of that in lattice diffusion for FCC metals.) They can potentially be used as nanocontainers to store and deliver gaseous substances. For gas storage, gas molecules can diffuse into the hollow core at elevated temperatures or applied high pressure. At lower temperatures, the stored substance can be slowly released by diffusion or bursting out via photothermal heating. This opens up many new possibilities such as gaseous drug deliveries or nanoprobes by triggering localized chemical reactions. In addition, the process can be used for fundamental studies of nanobubble formation mechanism. Such nanobubble synthesis process can have many important implications on a wide range of bubble-related applications such as design of fluidic micro-channels and nanodevices.

Supporting Information Available: This material is available free of charge via the Internet at http://pubs.acs.org.

References