High-Yield Synthesis of Hollow Octahedral Silver Nanocages with Controllable Pack Density and Their High-Performance Sers Application

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Nanoparticle-assembled octahedral Ag nanocages with sharp edges have been successfully synthesized through a Cu$_2$O-based template-assisted strategy. In the reaction system, Ag nanoparticles can be self-assembled on the surface of Cu$_2$O octahedrons, which is accomplished by the reduction of Ag$^+$ by NaBH$_4$ in the presence of sodium citrate as a capping agent. The hollow octahedral Ag nanocages are obtained after removing the inner Cu$_2$O cores with acetic acid. According to the scanning electron microscopy (SEM) and transmission electron microscopy characterization, the Ag nanocages are weaved by small nanoparticles, the rough surfaces are bestrewed with pores and sharp edges. It is found that the pack density of Ag nanoparticles strongly affects the surface enhanced Raman scattering (SERS) activities. The as-prepared 1.05-Ag cages with optimal pack density have suitable interparticle distance and suitable size of pores, which significantly enhance SERS signals. The SERS signals of rhodamine 6G (R6G) molecules can be detected at an ultralow concentration of $10^{-14}$ M when 1.05-Ag cages are used as substrates. In addition to sensitivity, 1.05-Ag cages also exhibit good reproducibility. It is expected that the ultrahigh sensitivity will endow the Ag nanocages to become a promising candidate as high-performance SERS-based chemical sensor.

1. Introduction

In the past decades, the design and synthesis of noble metal nanostructures have aroused widespread interest in many fields, as their intrinsic optical/electrical properties can be tailored by controlling their size, shape, composition, crystallinity, and structure (solid or hollow). Different from their bulk counterparts, noble metal nanomaterials with hollow interiors possess some special properties, such as low density, large surface area, permeability, and porous structure,[1] which make them more advantageous in some practical applications, e.g., drug delivery,[2] catalysis,[3–5] therapeutics,[6,7] and surface enhanced Raman scattering (SERS).[8–11] The template-assisted approach provides a convenient and versatile route for the synthesis of hollow nanostructures. Typically, the desired material can be easily deposited on the template to create a core–shell composite; after removing the template core, the hollow structures can be obtained. The hollow structure possesses huge surface area due to its nanoscale roughness and porous surface. For example, Zhang et al. have demonstrated that the surface area of as-prepared Ag cage is almost 20 times larger than original Cu$_2$O templates.[12] The large surface area can facilitate the adsorption of larger amount of probe molecules, leading to the higher SERS sensitivity. Also, Yang’s group has demonstrated that...
Ag microsphere with hollow and porous structures showed better SERS performance than its solid counterpart.\cite{13} Moreover, it is well known that the local electromagnetic field (LEMF) can be strongly enhanced at the sharp edges or tips of nanostructures due to the surface plasmon resonance (SPR) effect.\cite{14} The LEMF can effectively enhance the Raman scattering of the probe molecules and resulting in strong SERS effect.\cite{15} Thus, hollow noble metal nanostructures with porous surface and sharp morphology should be a promising candidate for obtaining an excellent SERS activity. Fang’s group found that the octahedral silver mesocage with shell thickness about 100 nm exhibited superior SERS activity to cubic and spherical Ag mesocages.\cite{16} In addition, the LEMF is also determined by the internanoparticle distance and arrangement pattern. Wang’s group used Cu$_2$O cubes as templates to prepare Ag hollow microcuboctahedron assembled by nanosheets, and investigated the effect of pack density of nanosheets on SERS signals.\cite{17} They found that the products with thinner nanosheets and higher pore density showed highest enhancement efficiency. Since the SERS performances of noble metal hollow structures are determined by these several factors, including the shape of structure, the density of self-assembled nanoparticles and the size of pores, thereby it is urgently needed to develop a facile strategy for synergistically manipulating all these factors in one smart platform to obtain an optimal SERS effect.

First of all, in order to prepare polyhedron Ag hollow nanostructures, it is important to choose a suitable template. Though Ag$_2$O templates have been widely used to fabricate Ag hollow nanostructures with various shapes, it is not cost-effective for large-scale synthesis. Fortunately, Cu$_2$O crystals also possess various shapes, such as spherical, cubic, octahedral, cuboctahedral, and dodechedral shapes,\cite{18–20} which can be easily prepared and employed in the Cu$_2$O template-based strategy. Furthermore, comparing with Ag$_2$O, Cu$_2$O templates show more satisfactory advantages, such as low cost, good chemical stability, as well as facile large-scale production.\cite{21,22} Therefore, it is worthwhile to prepare roughened hollow Ag nanostructures with porous surface and sharp edges by Cu$_2$O-based templating strategy, which might effectively enhance the LEMF, resulting in ultrahigh SERS activity.

Herein, we report a simple and productive method to prepare well-shaped hollow octahedral silver nanocages with controllable pack density. Figure 1 shows the preparation procedure. First, citrate ions were absorbed on the Cu$_2$O surface, which could facilitate the deposition of Ag nanoparticles on Cu$_2$O templates. Second, NaBH$_4$ could reduce Ag$^+$/NaBH$_4$ to Ag rapidly, leading to a large amount of small Ag nanoparticles accumulated on the Cu$_2$O surface due to the affinity between Ag and citrate ions, and then Cu$_2$O@Ag core–shell structures were produced. Finally, the octahedral Ag nanocages were obtained through removing Cu$_2$O cores with acetic acid. In addition, the pack density of nanoparticles in the Ag nanocages can be easily modulated by adjusting the amount of NaBH$_4$ and AgNO$_3$. The obtained nanocages with suitable pack density and sharp edges showed stronger SERS effect than others, even can clearly detect the Raman signals of rhodamine 6G (R6G) at an ultralow concentration of $1 \times 10^{-14}$ M. These results demonstrated that our work provided a convenient and efficient strategy to synthesize hollow octahedral Ag nanocages, which can exhibit high sensitivity and reproducibility for practical SERS applications.

2. Results and Discussion

As seen in Figure 2a, the as-prepared Cu$_2$O templates exhibit octahedral structures with the edge length of about 600 nm. The transmission electron microscopy (TEM) image (Figure 2b) of Cu$_2$O templates reveals the smooth surface and solid internal structure. After depositing small Ag nanoparticles on the Cu$_2$O templates, the core–shell Cu$_2$O@Ag nanostructures were obtained. The core–shell structure could be identified by comparing the contrast difference along the edges in Figure 2b,d. The outer deposited Ag layers show rough surfaces, and duplicate the octahedral shape of the original Cu$_2$O templates. According to the scanning electron microscopy (SEM) image (Figure 2c) of the Cu$_2$O@Ag nanostructures, no free Ag nanoparticles are found in the products, indicating that Ag nanoparticles exclusively deposited on the surfaces of Cu$_2$O templates. After removing the Cu$_2$O templates by acetic acid, the final product named 1.05-Ag cages perfectly maintain well-defined octahedral shape (Figure 2e). The hollow interior structure can be confirmed by the strong color contrast between edges (dark) and the center (gray) in Figure 2f. Moreover, no fractured, deformed, or collapsed Ag nanocages are found, suggesting that the Cu$_2$O template-based strategy to prepare hollow Ag nanocages is productive and effective.

To further investigate the detailed structure of Ag nanocages, an individual Ag nanocage was characterized by TEM as shown in Figure 3a. It can be clearly seen that the octahedral Ag nanocage possesses twelve edges and sharp tips, and the shell is very thin with thickness about 15 nm. By magnifying one face of the octahedral Ag nanocage, it can
be found that the surface is weaved by numerous small Ag nanoparticles and bestrewed with many pores. The average size of these Ag nanoparticles was about 11 nm when randomly selecting 100 nanoparticles and measuring their sizes as shown in Figure S1. The high-resolution TEM (HRTEM, high-resolution transmission electron microscopy) image in Figure 3c clearly shows that the spacing for adjacent lattice fringe is 0.24 and 0.20 nm, which match well with the interplanar spacings of the (111) and (200) planes of the fcc silver.

In order to further validate the crystallographic structures, the as-prepared products were characterized by X-Ray diffraction (XRD) measurement. According to curve a in Figure 4, all diffraction peaks of the as-prepared Cu$_2$O octahedrons are in good agreement with those of cubic Cu$_2$O (JCPDS, NO. 05-0667). 2θ of six peaks labeled * are 29.3°, 36.2°, 42.1°, 61.2°, 73.5°, and 77.36° corresponding to (111), (110), (200), (220), (311), and (222) respectively, confirming the formation of phase-pure Cu$_2$O. After Ag nanoparticles selectively and uniformly self-assembled on Cu$_2$O templates, clear peaks of Ag besides Cu$_2$O appear in curve b in Figure 4 according to JCPDS (NO. 04-0783). No remarkable shifts in diffraction peaks of Cu$_2$O are observed, indicating that the silver atoms are not doped into the Cu$_2$O lattice. Through chemical dissolution of Cu$_2$O templates with acetic acid, the final product showed face-centered cubic Ag with diffraction peaks indexed to (111), (200), (220), (311), and (222), respectively. Almost no characteristic peaks of impurity phases can be observed from curve c in Figure 4, indicating the Cu$_2$O templates have been totally removed. In summary, based on the SEM, TEM, and XRD characterizations it has been clearly demonstrated that the nanoparticle-assembled hollow octahedral Ag nanocages have been successfully fabricated through the Cu$_2$O-based template-assisted strategy.

Sodium citrate can easily adsorb on the surface of Cu$_2$O templates and promotes the self-assembling of Ag nanoparticles on the Cu$_2$O surfaces due to the affinity between Ag and citrate ions. Different concentrations of sodium citrate in the range of 0 to 0.36 mM were employed to investigate the concentration-dependent formation of Ag nanocages. The experiments were conducted while keeping the other experimental conditions unchanged. Without adding any sodium citrate, Ag nanoparticles could not selectively accumulate on the surface of Cu$_2$O, only irregular Ag nanoparticles without any cage-like products were obtained as shown in
Figure S2a. As the concentration of sodium citrate increased, more and more Cu$_2$O surfaces were fully capped by citrate ions, leading to the yield of quasi Ag nanocages as shown in Figure S2b–d. When the concentration of sodium citrate increased to 0.3 mM, all the Cu$_2$O surfaces could be fully coated by citrate ions, well-shaped Ag nanocages were successfully obtained without any dispersed Ag nanoparticles, as seen in Figure S2e. Excessive citrate ions such as 0.36 mM also produced Ag nanocages with the yield close to 100% in Figure S2f. According to these results, if all the Cu$_2$O surfaces were fully capped by enough citrate ions, Ag cages composed of uniformly self-assembled Ag nanoparticles could be prepared in high yield.

The molar ratio of NaBH$_4$ and AgNO$_3$ was another vital factor affecting the integrity of Ag nanocages. When the molar ratio of NaBH$_4$ : AgNO$_3$ was 10 : 1, small silver nanoparticles were uniformly located on the twelve edges and eight faces to form an intact octahedral Ag nanocages, as shown in Figure S3a. By keeping the amount of AgNO$_3$ unchanged and reducing the amount of NaBH$_4$ as the molar ratio NaBH$_4$ : AgNO$_3$ decreased from 5 : 1 to 1 : 1, silver nanoparticles tended to deposit along the edges and corners, the size of pores on the faces became bigger, as seen in Figure S3b,c. It is assumed that free Ag$^+$ ions prefer to react with the active sites (such as edges and corners) of Cu$_2$O octahedrons to form the Ag octahedral nanoframes. The redox reaction driving force comes from the reduction potential gap between the Ag$^{+/0}$ (0.799 V) and Cu$^{2+/+}$ (0.153 V). By further reducing the amount of NaBH$_4$, excessive Ag$^+$ ions reacting with the Cu$_2$O edges would produce many octahedral nanoframes. Nanoframes were not mechanically robust enough to maintain the structure’s integrity under ultrasonic washing, so collapsed Ag nanoframes mixed with irregular nanoparticles are observed in Figure S3d. To sum up, NaBH$_4$ is able to inhibit free Ag$^+$ ions from reacting with Cu$_2$O templates, and adding excess NaBH$_4$ is favorable to obtain perfect octahedral Ag nanocages coated with uniform Ag shells.

Compared to bare particles, the junction of adjacent nanoparticles produced more hot spots. Moreover, it is well known that the LEMF at the hot spot is mainly determined by the gap distance between the nanoparticles. The smaller distance between particles, the stronger LEMF could be obtained. In order to achieve small gap distance and big amount of hot spots, we utilized the Ag nanoparticles with the size of only several nanometers as building blocks to assemble the Ag nanocages, as shown in Figure 3b. Since the size of Ag nanoparticles is relatively fixed, the pack density of Ag nanoparticles becomes the significant parameter in our system. When keeping the molar ratio of NaBH$_4$ : AgNO$_3$ as 10 : 1, the pack density of the self-assembled Ag nanoparticles could be controlled by simultaneously adjusting the amount of NaBH$_4$ and AgNO$_3$. The preparation conditions were listed in Table S1, the TEM images of the products labeled 0.9-Ag cage, 1.0-Ag cage, 1.05-Ag cage, 1.1-Ag cage, and 1.2-Ag cage were shown in Figure 5a–d. As the amount of NaBH$_4$ and AgNO$_3$ increased, their TEM images showed increasingly dark color contrast, indicating that the Ag nanoparticles assembled more and more compactly to weave the Ag nanocages. In addition, with increasing the amount of NaBH$_4$ and AgNO$_3$ the edges and corners of the Ag nanocage became sharper and more obvious due to the increasing deposition of Ag nanoparticles. At the same time, the size of nanoparticles tended to become bigger, the pores on the surfaces became smaller. In order to investigate the optimal pack density of Ag nanoparticles for SERS applications, the UV–vis–NIR absorption measurements of samples with different pack density have been performed as shown in Figure S4 (Supporting Information). It was found that the sample 1.05-Ag cage showed the strongest SPR response. This result indicated that 1.05-Ag cage would exhibit the strongest SERS activity in visible light range.

Since hollow Ag nanostructures are excellent SERS substrates, and the SERS activities strongly depend on the shape, porosity, or arrangements of nanoparticles,[24] the as-prepared Ag nanocages with sharp edges and corners were fully bestrewed with pores and small silver nanoparticles, which could significantly enhance the LEMF for applications of SERS substrates. The SERS activities of the as-prepared Ag nanocages with different pack densities of Ag nanoparticles were investigated by using R6G as probing molecules. For comparison, the SERS spectra of three samples labeled 0.6-Ag cage, 1.0-Ag cage, 1.4-Ag cage are shown in Figures S5–S7, respectively. Their corresponding SEM images are seen in Figure S8a–c, which all show octahedral shape while different pack densities. When 1.0-Ag cages are used as substrates, it is observed that the spectral intensity could be detected even when the concentration of R6G decreased to 10$^{-13}$ M. However, the detection limit of R6G is only 10$^{-10}$ M when 0.6-Ag cage and 1.4-Ag cage are used as substrates. In order to further investigate the best pack density, other samples around 1.0-Ag cage were detected by smaller interval. Figure 6 shows the SERS spectra of R6G absorbed on 0.9-Ag cage, 1.0-Ag cage, 1.05-Ag cage, 1.1-Ag cage, and 1.2-Ag cage which are shown in Figure 3a and Figure 5a–d. The peaks located at around 610, 770, 1180, 1360, and 1650 cm$^{-1}$ are associated with the R6G molecules. Vibrations at 1180, 1360, and 1650 cm$^{-1}$ are
and 1650 cm$^{-1}$ are assigned to C-H in-plane bending, C-O-C stretching, and C-C stretching of the aromatic ring. The peaks at 610 and 770 cm$^{-1}$ can be assigned to the C-H out-of-plane bending motion of the xanthene. According to curve (c) in Figure 6, it is obvious that the 1.05-Ag cages show the highest SERS activity. This can be attributed to the optimal amount of Ag nanoparticles and pack density, resulting in the sharpest edges and corners of Ag cages, which can provide numerous “hot spots” for SERS. These structural features contribute to the highest SERS activities among the other four samples.

The as-synthesized 1.05-Ag cages were further used as SERS substrates to evaluate the detection limit of R6G. The spectral intensity decreased as the concentration of R6G ranged from $10^{-9}$ to $10^{-14}$ M. As was shown in Figure 7, the typical peaks of R6G located at 1360 and 1650 cm$^{-1}$ were still detectable even at an ultralow concentration of $10^{-14}$ M. The SERS spectra of Cu$_2$O@Ag core–shell nanostructures were also performed as control experiments to demonstrate the advantage of hollow structures of Ag nanocages as shown in Figure S9. It was found that the detection limit of Cu$_2$O@Ag core–shell nanostructures could only achieve to $10^{-9}$ M. Several reasons could be responsible for the greatly enhanced Raman scattering signal. First, the roughened and porous surface (inner and outer surface) can facilitate the adsorption of more R6G molecules onto the substrate so that the number of effective excited molecules will increase greatly. In addition, the sharp morphology can provide strong LEMF for further enhancing the SERS signals. It is worth noting that the pack density of these Ag cages make a big difference in SERS sensitivity. The 1.05-Ag cages with suitable interparticle distance and suitable size of pores could afford abundant “hot spots” to amplify the LEMF, which significantly enhances SERS signals.

As we all know that a good SERS substrate should possess the stable reproducibility. Figure 8 displays the Raman spectra recorded from ten randomly selected positions on the 1.05-Ag cage substrate. The intensity of the typical peaks of R6G located at 610 and 1650 cm$^{-1}$ did not change much at different detecting positions. The peak at 1650 cm$^{-1}$ was chosen to calculate the relative standard deviation (RSD) of spot to spot Raman intensity. The value of RSD of the sample was about 11.6%. These results show that the 1.05-Ag cages possess high sensitivity and good reproducibility in SERS performance.

In summary, we have successfully developed a facile strategy for synergistically manipulating the shape of silver hollow structure, the pack density of self-assembled Ag nanoparticles, and the distance between particles in one smart platform to obtain the optimal SERS effect. Well-shaped hollow octahedral Ag nanocages assembled with Ag nanoparticles were efficiently synthesized at room temperature through a facile Cu$_2$O template-assisted method. Our results demonstrate that in the preparation process the sodium citrate is an indispensable agent which can effectively increase the affinity between Ag nanoparticles and Cu$_2$O templates. Appropriate
molar ratio of NaBH₄ and AgNO₃ is another vital factor for the formation of intact octahedral Ag nanocages. In addition, the pack density of the self-assembled Ag nanoparticles can be tuned by adjusting the amount of NaBH₄ and AgNO₃, and the SERS activities of Ag cages with different pack density were also investigated. The as-prepared 1.05-Ag cages show best Raman enhancement performance and good reproducibility for detecting R6G molecules. The high sensitivity of Ag nanocages for SERS detection is ensured by rough surface, which is facile for adsorption of probing molecules. In addition, the sharp corners and edges of octahedral Ag nanocages would generate strong LEMF, which could further enhance the SERS signals. The big difference in SERS sensitivity can be attributed to the difference of pack density of assembled nanoparticles. The 1.05-Ag cages with optimal pack density have suitable interparticle distance and suitable size of pores, which significantly enhance SERS signals. The typical R6G Raman peaks were even detectable at an ultralow concentration of 1 × 10⁻¹⁴ M when 1.05-Ag cages were used as SERS substrate. It is expected that the as-prepared 1.05-Ag cages could be used as excellent SERS substrate for ultrasensitive detection.

**Experimental Section**

**Synthesis of Cu₂O Octahedral Templates:** Cu₂O octahedrons were fabricated based on our previous report.[20] 4.5 g polyvinylpyrrolidone (PVP-K30, LAN YI REAGENT) was dissolved into 100 mL 0.01 M of CuCl₂•2H₂O aqueous solution (LAN YI REAGENT). Then, 10.0 mL 2.0 M NaOH aqueous solution (LAN YI REAGENT) was added dropwise into the above solution. After stirring for 0.5 h, 10.0 mL 0.6 M ascorbic acid aqueous solution (LAN YI REAGENT) was further added dropwise into the mixed solution. The mixture was aged for 3 h. All of the procedure was carried out under constant stirring and heated in a water bath at 55 °C. The resulting precipitates were collected by centrifugation, and washed with deionized water and ethanol repeatedly to remove the residual inorganic ions and polymer, and finally dried in vacuum at 60 °C for 5 h for further characterization and use.

**Synthesis of Octahedral Silver Nanocages:** 4.29 mg Cu₂O templates were dispersed in 100 mL deionized water by ultrasonic vibration for 10 min, then 1.0 mL 30 mM sodium citrate aqueous solution (Beijing Chemical Works) and 1.05 mL 100 mM NaBH₄ aqueous solution (LAN YI REAGENT) were dropped sequentially into the solution containing Cu₂O templates. After being stirred for 5 min, 1.05 mL 10 mM AgNO₃ aqueous solution (Beijing Chemical Works) was added dropwise into the vigorously stirred mixture. The solution color turned from orange to light yellow, indicating the formation of small Ag nanoparticles. As the reaction proceeded for 1 h, the solution gradually became dark yellow, indicating the formation of Cu₂O@Ag nanostructures. Subsequently, 1.7 mL vt 1% CH₃COOH aqueous solution (Beijing Chemical Works) was injected into the above-mentioned mixture, the reaction lasted for another 2 h in order to completely dissolve the Cu₂O templates. The resulting precipitates were collected by centrifugation and decanting, washed with distilled water and absolute ethanol several times, and then dispersed in absolute ethanol for further characterization, the product was named 1.05-Ag cage.

With regard to the pack density of self-assembled Ag nanoparticles in Ag cages, they could be easily modulated by simultaneously adjusting the amount of NaBH₄ and AgNO₃ while keeping other conditions unchanged. Various experimental conditions for preparing different pack densities of self-assembled Ag nanoparticles in Ag cages were listed in Table S1.

**The Preparation of SERS Substrate:** The as-prepared silver nanocages were centrifuged and carefully dropped on specially cleaned silicon wafer. After the samples were dried, the silicon wafer was immersed in R6G ethanol solution (100 µL) with different concentration for 12 h to ensure efficient binding of probe molecules on the surface of Ag nanocages. The silicon wafer was washed with ethanol three times to remove the excessive R6G molecules. After the samples were completely dried in air, the substrates were analyzed using the Raman instrument. Here, a Raman spectrometer (LabRAM HR800) with 514 nm laser as light source. The acquisition time was 10 s for each spectrum. For each sample, we took three SERS spectra in different positions of the substrate and then averaged them.

**Characterization:** The morphology and size of the samples were characterized by field emission scanning electron microscopy (FE-SEM) and transmission electron microscopy (TEM). For the FE-SEM measurements, a Quanta 250 FEG instrument was used, operating at an accelerating voltage of 10 KV. For TEM measurements, a JEOL 2100F instrument was used, operating at an accelerating voltage of 200 KV. XRD analysis was utilized to characterize the structure by a XRD-6000 X-ray diffractometer with Cu Kα radiation (λ = 1.5418 Å). Surface-enhanced Raman spectra were collected using a LabRAM HR800 instrument with 514 nm laser as light source. The laser power on the surface of the sample was typically 1.5 mW. The accumulation time was 10 s.

**Supporting Information**

Supporting Information is available from the Wiley Online Library or from the author.

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