

ESI (Electronic supporting information)

A New Route for the Synthesis of Polyhedral Gold Mesocages and Shape Effect in Single-particle Surface-enhanced Raman Spectroscopy^s

Jixiang Fang,^{a, b} Sergei Lebedkin^b, Horst Hahn^b

^a School of Science, Xi'an Jiaotong University, Shann Xi, 710049, People's Republic of China

^b Karlsruhe Institut für Technologie (KIT), Institut für Nanotechnologie, Karlsruhe 76021, Germany

To whom correspondence should be addressed. E-mail: jxfang@mailst.xjtu.edu.cn

Fig. S1 Schematic illustration summarizing the structural changes involved in the replacement reaction between sacrificial template, e.g., Cu₂O nanocube and HAuCl₄ in aqueous solution.

The replacement reaction of our synthetic protocol is schematically shown in Figure S1. With Cu₂O/Au system as an example, the formation sequences are as follows. Stage 1: the initiation of replacement reaction at some specific sites on the surface of Cu₂O (typically include steps, point defects, and stacking faults).^[18] Stage 2: once the reaction has started on the active sites, the Cu₂O will be continually dissolved and oxidized to provide electrons for gold ions. At the same time, the opening sites or the formed porous wall allows all the reaction species (e.g., AuCl₄⁻, Cu⁺, Cl⁻, and Au) to continuously diffuse in and out of the interior of the incompletely architected hollow nanocages. Stage 3: the final formation of hollow polyhedron, nanospheres, nanowires, nanotubes, or even more complex structures – defined by the shape of sacrificial template. Compared with a conventional template synthetic process, the subsequent template removal treatment can be omitted since the formed Cu²⁺ ions can dissolve into the final solution.

Fig. S2 Ag cubic nanocages obtained by the reduction of Cu₂O cubes using 0.5 mM AgNO₃.

Fig. S3 Pt octahedral nanocages obtained by the reduction of Cu₂O octahedrons using 0.5 mM H₂PtCl₆ (aq.).

Fig. S4 AuPt octahedral nanocages obtained by the reduction of Cu₂O octahedrons using 0.5 mM HAuCl₄ (aq.) 50 vol. % and 0.5 mM H₂PtCl₆ (aq.) 50 vol. %.

Fig. S5 SEM images of gold mesostructures synthesized at 10mM HAuCl₄ (aq.) 20 mL reaction with 1mL Fe suspension.

Fig. S6 UV-vis-NIR extinction spectra of gold nanocages with (A) spherical, (B) cubic and (C) octahedral shapes.

Synthesis of polyhedral Cu₂O nanoparticles: Various polyhedral Cu₂O nanoparticles (cubic, octahedral or spherical shape) were synthesized using a procedure described elsewhere [1] by controlling the poly (vinyl pyrrolidone) (PVP) concentration in the solution. The obtained Cu₂O nanoparticles were collected following centrifugation and subsequently dispersed into deionized water for a further characterization and a preparation of gold nanocages.

Synthesis of polyhedral gold mesocages: In a typical synthesis of Au nanocages, a certain amount of a stock Cu₂O suspension was injected into 100 mL deionized water. Under vigorous magnetic stirring, various amount of 0.5 mM HAuCl₄ (aq.) was slowly added drop by drop into 100 mL Cu₂O suspension hosted in a flask. The initially brick-red solution gradually changed the color to light-yellow, indicating the formation of gold nanocages. The reaction mixture was stirred for another ~5-10 minutes after completing the feeding. The precipitates were separated by centrifugation, washed with deionized water, and finally redispersed into deionized water for further experiments.

Syntheses of polyhedral silver and alloy mesocages: to synthesize noble metal alloys, such as PtAu, PtPd or PdAu, the corresponding H₂PtCl₆ or H₂PdCl₄ (aq.) and HAuCl₄ (aq.) were used to co-droplet into above Cu₂O suspension with desired ratio so as to control the alloy composition. The synthesis of silver mesocages was particularly designed with HNO₃ to adjust the pH value of the Cu₂O suspension to around 2. Then, immediately, the 0.5 mM AgNO₃ (aq.) was droplet into above Cu₂O suspension. The products were separated as above procedure.

Characterizations: The obtained gold polyhedral mesostructures were characterized by scanning electron microscopy (Zeiss LEO 1530), transmission electron microscopy (HRTEM) and selected area electron diffraction (SAED) (FEI Titan 80-300 operated at 300 kV), UV-vis-NIR extinction spectroscopy (Varian Cary 500 spectrophotometer) and Raman microscopy (Witec CRM200, laser excitation wavelength of 633 nm). For SERS measurements on individual particles, the diluted water suspensions were used so that predominantly well-isolated particles could be deposited by drop coating onto a ~10 x 10 mm² silicon wafer substrate. Crystal violet (SERS analyte) was deposited on a substrate with gold particles by drop coating of 0.1 mL of its solution in water. The substrates were then rinsed with deionized water and dried in air at ambient temperature. Single-particle SERS imaging was performed using a high-resolution objective (100×, NA = 0.9) and an X-Y piezo table to scan a sample under the objective. Typically, an area of 3×3 μm² (with a gold particle in the middle) was scanned. This area was “partitioned” into 225 square pixels (each of a 0.2×0.2 μm² size) and a full Raman spectrum was acquired at each pixel with a 2 sec acquisition time.

Estimation of SERS enhancement factor (EF):

Following the procedure reported by Wang et al. [2] and employing the CV peak at 1174 cm⁻¹ as shown in Figure 3 (the strongest peak in the spectra), we estimated the EF of the silver polyhedral mesocages according to the expression $EF = (I_{\text{surface}}/I_{\text{solution}}) \times N_{\text{solution}}/N_{\text{surface}}$, where N_{solution} and N_{surface} are the numbers of molecules probed in a reference solution and on a nanocage and I_{solution} and I_{surface} correspond to the normal and SERS signal intensities, respectively. Several Raman spectra of a 10⁻⁴ molar aqueous CV solution were measured applying a laser intensity of 10 mW and then averaged. The height of the peak at 1172 cm⁻¹ which amounted to ~400 counts (20 s acquisition time) was divided by 100, the ratio of the laser intensities applied to acquire the normal Raman and SERS spectra, to give $I_{\text{solution}} \sim 4$. The effective excitation volume in solution was estimated to be ~ 400 μm³ [3], to give $N_{\text{solution}} \sim 2.5 \times 10^7$ and a normal Raman intensity of ~1.6 × 10⁻⁷ counts per CV molecule.

To compare, the SERS signal intensities, I_{surface} , obtained for individual octahedral and cubic nanocages were about 4000 and 1000 counts, respectively (Figure 3). The number of CV molecules on a nanocage, N_{surface} , is subjected to the most uncertainty. In our experiments, 0.1 mL of a 1 × 10⁻⁸ M aqueous CV solution

were dropped onto a 10×10 mm silicon wafer. Assuming a non-specific CV adsorption, about 600 CV molecules were deposited within $1 \mu\text{m}^2$ area. If we take an “effective” area of $2 \mu\text{m}^2$ and correspondingly $N_{\text{surface}} \sim 1200$ as a rough estimate for a nanocage with a size of ~ 600 nm, we obtain EF of about 2×10^7 and 5×10^6 for the octahedral and cubic gold nanocages, respectively.

Taking into account the roughened surface of the mesocages, the above mesocage area may be underestimated and the EFs, consequently, overestimated. On the other hand, rinsing the substrates after CV deposition with water can remove a significant fraction of CV molecules (assuming 1%~10% residual in Ref [2]) and thus the EFs, in this study, may be underestimated. It should be noted that our estimate of EFs seems reasonable, corresponding to that reported by Liang (EF $\sim 10^7$ - 10^8) for “flower-like” silver nanoparticles [4] which show a quite similar surface morphology and size as our spherical mesocages. Meanwhile, in this study, combining the anisotropic (shape) effect and hollow interior (see in Figure 2 and Figure 3), 1-2 orders of magnitude higher EFs have been achieved for individual silver octahedral and cubic mesocages, respectively, compared with spherical shell in this study (Figure 2) and the “flower-like” silver nanoparticles in Ref. [4].

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- [3] Cai, W. B.; Ren, B.; Li, X. Q.; She, C. X.; Liu, F. M.; Cai, X. W.; Tian, Z. Q., *Surf. Sci.* 406, 9(1998).
- [4] Liang, H. Y., Li, Z. P., Wang, W. Z., Wu, Y. S. & Xu. H. X. *Adv. Mater.*, 21, 4614-4618 (2009).

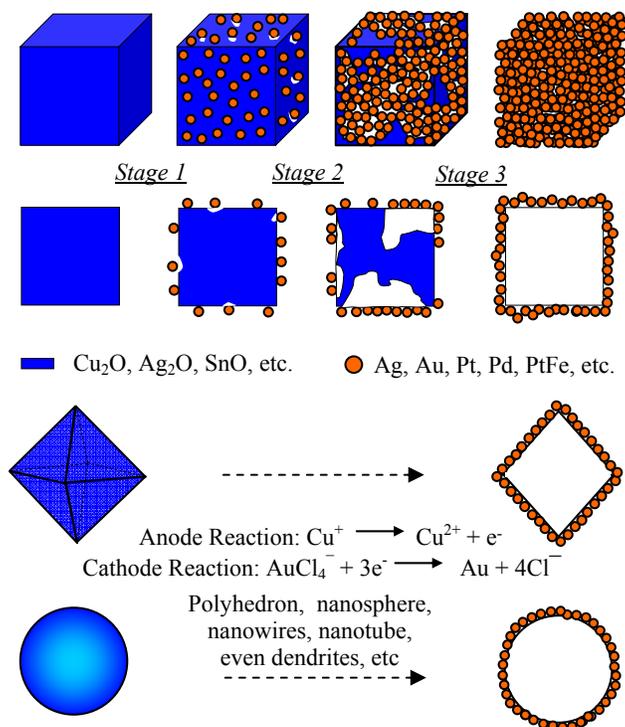


Figure S1. Schematic illustration summarizing the structural changes involved in the replacement reaction between sacrificial template, e.g., Cu_2O nanocube and HAuCl_4 in aqueous solution. **Stage 1:** initiation of the replacement reaction at some specific sites; **stage 2:** continuation of the replacement reaction between Cu_2O and HAuCl_4 and the formation of a partially hollow nanostructure; and **stage 3:** the formation of “mesoboxes”, or mesooctahedron shell or mesospheres depending on the shape of template.

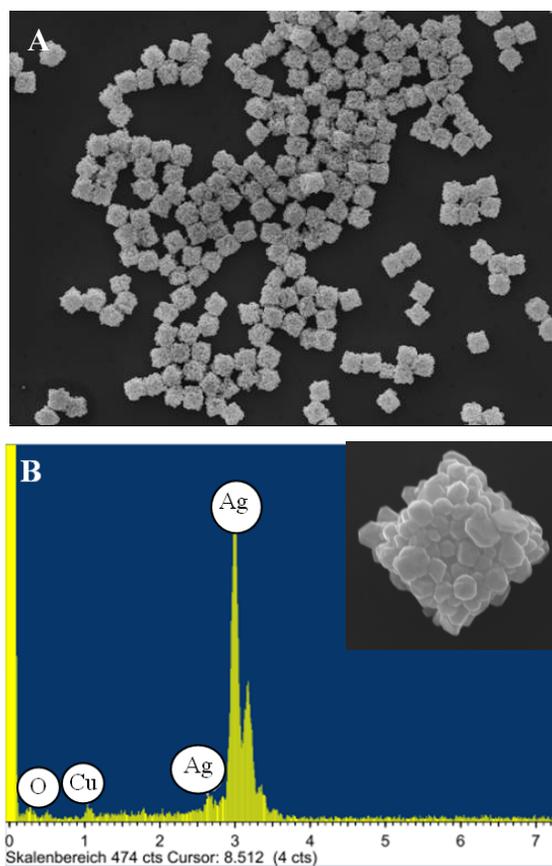


Figure S2. Ag cubic nanocages obtained by the reduction of Cu_2O cubes using 0.5 mM AgNO_3 .

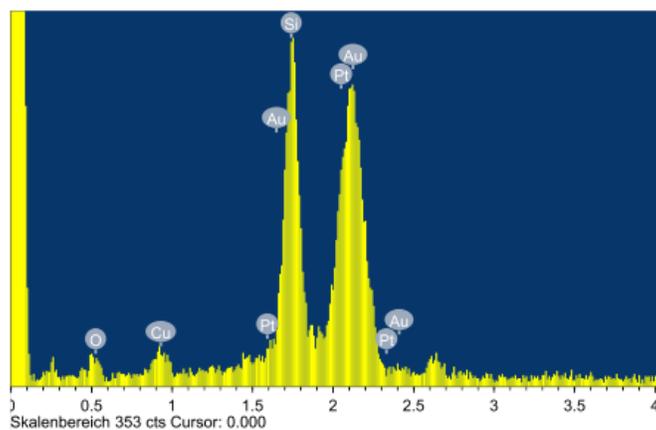
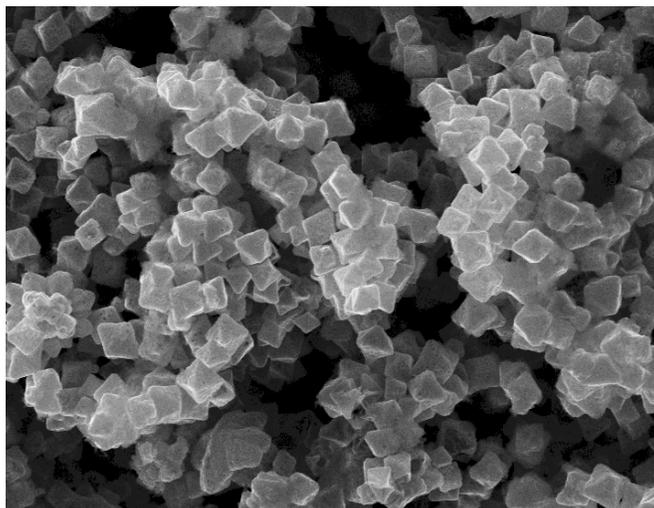


Figure S3. AuPt octahedral nanocages obtained by the reduction of Cu_2O octahedrons using 0.5 mM HAuCl_4 (aq.) 50 vol. % and 0.5 mM H_2PtCl_6 (aq.) 50 vol. %.

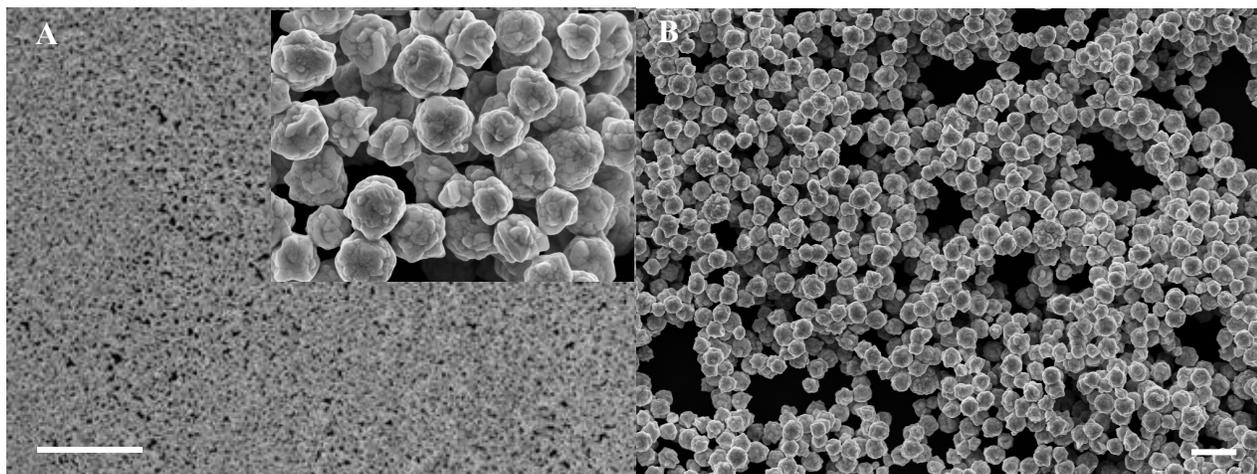


Figure S4. SEM images of gold mesostructures synthesized at 10mM HAuCl_4 (aq.) 20 mL reaction with 1mL Fe suspension. The scale bars shown in Figure S4A and S4B represent 20 μm and 1 μm , respectively.

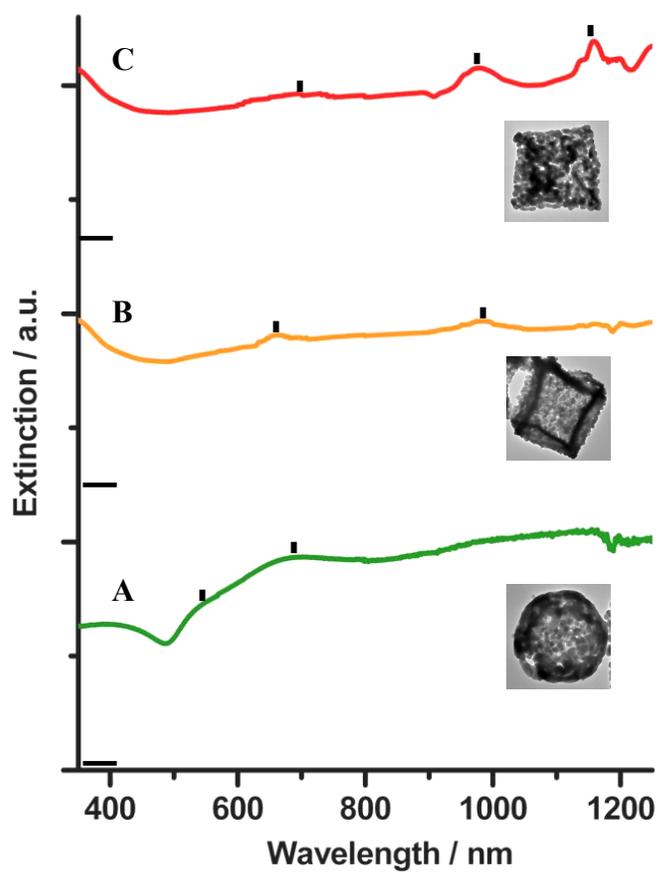


Figure S5. UV-vis-NIR extinction spectra of gold nanocages with (A) spherical, (B) cubic and (C) octahedral shapes. The nanocages were suspended in water and permanently stirred during the measurement. The inserts show typical SEM images of the corresponding particles. The short horizontal lines denote zero extinction level for each spectrum.