Ag@Au Concave Cuboctahedra: A Unique Probe for Monitoring Au-Catalyzed Reduction and Oxidation Reactions by Surface-Enhanced Raman Spectroscopy

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ABSTRACT

We report a facile synthesis of Ag@Au concave cuboctahedra by titrating aqueous HAuCl_4 into a suspension of Ag cuboctahedra in the presence of ascorbic acid (AA), NaOH, and poly(vinyl pyrrolidone) (PVP) at room temperature. Initially, the Au atoms derived from the reduction of Au^{3+} by AA are conformally deposited on the entire surface of a Ag cuboctahedron. Upon the formation of a complete Au shell, however, the subsequently formed Au atoms are preferentially deposited onto the Au{100} facets, resulting in the formation of a Ag@Au cuboctahedron with concave structures at the sites of {111} facets. The concave cuboctahedra embrace excellent SERS activity that is more than 70-fold stronger than that of the original Ag cuboctahedra at an excitation wavelength of 785 nm. The concave cuboctahedra also exhibit remarkable stability in the presence of an oxidant such as H_2O_2 because of the protection by a complete Au shell. These two unique attributes enable *in-situ* SERS monitoring of the reduction of 4-nitrothiophenol (4-NTP) to 4-aminothiophenol (4-ATP) by NaBH_4 through a 4,4'-dimercaptoazobenzene (*trans*-DMAB) intermediate and the subsequent oxidation of 4-ATP back to *trans*-DMAB upon the introduction of H_2O_2 .

Noble-metal nanocrystals with concave surfaces embrace unique properties for applications in catalysis,¹⁻³ plasmonics,⁴⁻⁵ and surface-enhanced Raman spectroscopy (SERS)^{6,7} due to the involvement of high-index facets and sharp corners/edges. For concave nanocrystals made of Au, Pd, and Pt, for example, they have been demonstrated with significantly enhanced catalytic activity on their high-index facets toward a number of reactions owing to the presence of atomic steps and kinks with low coordination numbers in high densities.⁸⁻¹¹ For Ag or Au concave nanocrystals, they have been reported with considerably improved SERS activity because of the hot spots at their sharpened corners/edges.^{12,13} Although it is straightforward to synthesize Au@Ag concave nanocrystals *via* seed-mediated growth,¹⁴⁻¹⁶ it is far more challenging to generate Ag@Au concave nanocrystals because of the inherent galvanic replacement reaction between elemental Ag and a salt precursor to Au.¹⁷

In recent years, a number of groups have successfully demonstrated the deposition of Au on Ag nanocrystals by defeating the galvanic replacement reaction. One strategy involves the retardation of the galvanic replacement reaction. Specifically, Yin *et al.* used Γ^- ions or sulfite to substantially reduce the reduction potential of Au^{3+} and thus inhibit the galvanic replacement for the generation of Au-coated Ag nanoplates.^{18,19} Kitaev *et al.* noted that the galvanic replacement reaction between Ag decahedra or pentagonal nanorods and HAuCl_4 could be retarded when they titrated the HAuCl_4 solution at an extremely slow rate to minimize the local concentration of Au^{3+} precursor.²⁰ Most recently, we demonstrated that the co-introduction of Ag^+ ions with Au^{3+} ions could effectively push the galvanic replacement reaction between Ag nanocubes and Au^{3+} backward and thus impede it, achieving the co-deposition of Ag and Au atoms on Ag nanocubes in a fashion essentially identical to seed-mediated growth.²¹

An alternative strategy relies on the introduction of a reducing agent such as ascorbic acid (AA) or NaBH_4 to compete with and thus defeat the galvanic replacement reaction. To this end, Mirkin and Xue reported the use of AA to assist the formation of Ag-Au alloy shells on the surfaces of Ag nanoplates.^{22, 23} Recently, we successfully extended this concept to the deposition of Au on Ag nanocubes for the generation of Ag@Au core-shell nanocubes.²⁴ We demonstrated that the galvanic replacement could be completely blocked when the reduction of Au^{3+} was dominated by AA. As a result, the Au atoms derived from the reduction of Au^{3+} by AA were deposited on the entire surface of Ag nanocubes, leading to the formation of a conformal, complete Au shell that could protect the Ag core from oxidation by H_2O_2 . We could adjust the

thickness of the Au shell by controlling the amount of HAuCl_4 relative to the number of Ag nanocubes involved in the reaction. Because each Ag nanocube was mostly covered by the $\{100\}$ facets, we observed the formation of conventional core-shell nanocrystals without any unusual shape or morphology.

In this work, we demonstrate the synthesis of Ag@Au concave cuboctahedra by depositing Au on Ag cuboctahedra that are covered by a mix of $\{111\}$ and $\{100\}$ facets at a ratio of 1:1.7 in terms of surface area. In a typical synthesis, we titrate aqueous HAuCl_4 into an aqueous suspension containing Ag cuboctahedra, AA, NaOH, and poly(vinyl pyrrolidone) (PVP). As illustrated in Figure 1, the deposition of Au follows a growth pattern completely different from what we have observed in the case of Ag nanocubes due to the presence of $\{111\}$ facets on the surface of a cuboctahedron. In the very early stage, the reduction of Au^{3+} by AA generates Au atoms, followed by their deposition onto the entire surface of a Ag cuboctahedron because PVP lacks the selectivity in capping different types of Ag surfaces in an aqueous medium.²⁵ As a result, the Ag cuboctahedron is transformed into a Ag@Au cuboctahedron. As soon as a complete Au shell is created on the Ag cuboctahedron, however, the subsequently formed Au atoms will be preferentially deposited onto the Au $\{100\}$ facets due to the selective passivation of Au $\{111\}$ facets by PVP in an aqueous solution,²⁶ slowing down deposition at the sites of $\{111\}$ facets and eventually leading to the formation of a Ag@Au concave cuboctahedron.

We also demonstrate the concave cuboctahedra as an excellent SERS probe, with an activity more than 70-fold stronger than that of the original Ag cuboctahedra at an excitation wavelength of 785 nm. The concave cuboctahedra also exhibit remarkable stability against oxidative etching by H_2O_2 due to the presence of complete Au shells for protection. By combining their SERS activity and chemical stability, we further establish the use of the concave cuboctahedra for *in-situ* SERS monitoring of two Au-catalyzed reactions, *i.e.*, the reduction of 4-nitrothiophenol (4-NTP) to 4-aminothiophenol (4-ATP) by NaBH_4 through a 4,4'-dimercaptoazobenzene (*trans*-DMAB) intermediate and the oxidation of the resultant 4-ATP back to *trans*-DMAB upon the addition of H_2O_2 , respectively. Our SERS results confirm that the Au-catalyzed reduction of 4-NTP to 4-TP proceeds *via* a condensation route that involves the formation of *trans*-DMAB molecules. During adsorption, the 4-NTP molecules are likely oriented parallel to the surface of the nanocrystal, facilitating the formation of *trans*-DMAB through *intra*-particle N=N bonds on a single concave cuboctahedron. As for the Au-catalyzed oxidation of 4-ATP derived from the

reduction of 4-NTP, our results indicate that 4-ATP can be oxidized to produce *trans*-DMAB but not 4-NTP. Interestingly, we also observe some major differences in the SERS spectra of the *trans*-DMAB derived from the oxidation of 4-ATP and the reduction of 4-NTP, respectively. Our data suggest that the oxidation reaction may involve two concave cuboctahedra, leading to the formation of *trans*-DMAB molecules *via inter*-particle N=N bonds.

RESULTS AND DISCUSSION

In the first step, we used Ag cubes of 40.5 ± 4.4 nm in edge length (Figure S1A) to generate Ag cuboctahedra with an average size of 48.2 ± 3.2 nm (Figure S1B, together with the definition of size) by following a protocol reported in literature.²⁷ Different from a nanocube whose surface is mainly covered by {100} facets, the surface of a cuboctahedron is enclosed by a mix of {111} and {100} facets with a ratio of 1:1.7 between their areas. We then dispersed the as-prepared Ag cuboctahedra in an aqueous solution (pH = 11) containing AA, NaOH, and PVP, followed by the titration of aqueous HAuCl₄ using a syringe pump at a relatively slow injection rate of 0.02 mL/min under the ambient condition. Samples were collected from the system after different volumes of the HAuCl₄ solution had been introduced. To elucidate the deposition pattern of Au atoms on the Ag cuboctahedra, we etched the samples with aqueous H₂O₂ to selectively remove the Ag, but not Au, from the nanostructures.

Figure 2 shows SEM and TEM images of the products before and after etching with aqueous H₂O₂. After the addition of 0.2 mL HAuCl₄ solution, we observed very little change to the Ag cuboctahedra (Figure 2A). The absence of pits on the surfaces of the cuboctahedra indicates that no galvanic replacement was involved during the introduction of HAuCl₄ under the experimental conditions. After H₂O₂ etching, we found that the structure and shape of some cuboctahedra were preserved while the others were transformed into nanocages with hollow interiors and porous walls (Figure 2B). In this case, the number of Au atoms derived from the reduction of Au³⁺ by AA was insufficient to form a complete shell on every Ag cuboctahedron. Those nanoparticles without complete Au shells evolved into nanocages when the Ag was etched away by H₂O₂. By comparing the UV-vis spectra recorded from the samples before and after H₂O₂ etching (Figure S2A), we noticed that there was very little change to the localized surface plasmon resonance (LSPR) peak in terms of position while the intensity dropped by almost 60%. This observation is consistent with the TEM image shown in Figure 2B because the LSPR peak of the nanocages

should be located in the near-infrared region beyond 800 nm due to their extremely thin walls, out of the detection range of the spectrometer.²⁸

When the volume of added HAuCl_4 solution was increased to 0.4 mL, the shape of the Ag cuboctahedra was largely retained, with no noticeable pits on the surface of each cuboctahedron (Figure 2C). After H_2O_2 etching, the concaveness at the sites of $\{111\}$ facets was somewhat increased (Figure 2D). In this case, UV-vis spectra recorded from the sample before and after H_2O_2 etching remained essentially the same, with a slight red shift from 454 to 465 nm for the LSPR peak (Figure S2B). This observation indicates the formation of a complete shell of Au on the surface of each Ag cuboctahedron for the creation of a Ag@Au core-shell cuboctahedron. Since the concaveness at the sites of $\{111\}$ facets just started to appear, we call such a sample “Ag@Au cuboctahedra” in our discussion.

When the titration volume of HAuCl_4 solution was further increased to 0.8 mL, the deposition of Au on the $\{111\}$ facets became less pronounced relative to the $\{100\}$ facets, leading to the formation of Ag@Au cuboctahedra with obvious concaveness at the sites of $\{111\}$ facets (Figure 2E, in particular, the magnified images in the insets). Remarkably, these concave cuboctahedra could survive in an aqueous H_2O_2 solution for a period up to 1 h, without showing any changes to their shape or morphology (Figure 2F). This result also indicates the complete protection of the Ag cores by Au shells. The UV-vis spectra shown in Figure S2C further support the excellent stability of these nanostructures against H_2O_2 etching. In the following discussion, we refer to such a sample as “Ag@Au concave cuboctahedra”.

We then used aberration-corrected high-angle annular dark-field scanning TEM (HAADF-STEM) to characterize the Ag@Au concave cuboctahedra. Figure 3A shows a HAADF-STEM image taken from an individual concave cuboctahedron that was oriented along the $\langle 110 \rangle$ zone axis. Because the contrast is proportional to the atomic number, we were able to resolve the distributions of Au and Ag atoms on both the $\{111\}$ and $\{100\}$ facets, as shown in Figure 3, B–D, respectively. Specifically, the projected thicknesses of Au overlayers on the $\{100\}$ and $\{111\}$ facets were 9–10 atomic layers (or ~ 2 nm) and 4–5 atomic layers (or ~ 1 nm), respectively. These results indicate that more Au atoms could be deposited on the $\{100\}$ facets than the $\{111\}$ facets. Figure 3E shows a HAADF-STEM image of another concave cuboctahedron that was oriented align with the $\langle 100 \rangle$ zone axis, clearly showing the Au shell around the Ag core. To resolve the distributions of Ag and Au elements, we conducted STEM-electron energy-loss spectroscopy

(EELS) mapping with the $M_{4,5}$ edges of Ag and Au, respectively. Figure 3F shows the distributions of Ag and Au for the concave cuboctahedron shown in Figure 3E, confirming the uniform deposition of Au on the $\{100\}$ facets. Figure S4 shows the individual EELS mapping with the $M_{4,5}$ edges of Ag and Au, respectively. Collectively, the HAADF-STEM and STEM-EELS results strongly support our claim that more Au atoms were deposited on the $\{100\}$ facets for the formation of Ag@Au cuboctahedra with a concaved structure on the site of $\{111\}$ facet. It should be pointed out that the resistance of our Ag@Au cuboctahedra (without or with concaved surfaces) against H_2O_2 etching can be attributed to the formation of a complete Au shell around each cuboctahedron. During the deposition of Au, some Ag atoms could be mixed into the Au shell through inter-diffusion and/or other mechanisms.^{24,29} However, the atomic ratio of Ag to Au should be an extremely small number although it is still impossible to determine the exact value by EDX mapping or HAADF-STEM.

We also used inductively-coupled plasma mass spectrometry (ICP-MS) to quantify the Au content in the as-obtained samples after the Ag cuboctahedra had been titrated with different volumes of $HAuCl_4$ solution. Specifically, we collected the solid products *via* centrifugation, followed by their dissolution in aqua regia for ICP-MS analysis to determine the Au content. The masses of Au in the solid products increased linearly with the volume of $HAuCl_4$ solution titrated into the suspension of Ag cuboctahedra (Figure S3, solid line). By assuming that the added Au^{3+} precursor was completely reduced to Au atoms for their deposition onto the Ag cuboctahedra, we calculated the mass of Au at different titration volumes (Figure S3, dotted line). These results indeed support our argument that the added $HAuCl_4$ was completely reduced by AA to generate Au atoms, followed by their deposition onto the Ag cuboctahedra.

By combining the data from SEM, TEM, HAADF-STEM, and ICP-MS, now we can obtain a good understanding of the pathway that led to the formation of Ag@Au concave cuboctahedra. From the ICP-MS data, the Au atoms derived from the complete reduction of Au^{3+} ions should be able to form shells of 3 and 6 atomic layers thick when the titration volumes of $HAuCl_4$ were 0.4 and 0.8 mL, respectively, if the Au atoms were assumed to be evenly deposited across the entire surface of a Ag cuboctahedron. However, for the sample obtained at a titration volume of 0.8 mL, the projected thickness (from HAADF-STEM) of Au shell on the $\{111\}$ facets were 9–10 atomic layers, much thicker than the number of 6 derived from the ICP-MS data under the assumption of even deposition, suggesting the formation of a concave structure on the surface.

From the zoom-in SEM images shown in Figure 2E, it is clear that the {100} facets had a flat surface while the {111} facets were clearly concaved, with majority of the Au atoms being deposited on the edges. Taken together, we can conclude that the majority of the Au atoms were preferentially and evenly deposited on the {100} facets once a complete Au shell had been formed. In comparison, the deposition of Au atoms on the {111} facets were retarded upon the formation of a complete Au shell. This observation suggests that PVP could selectively bind to and thus passivate the Au{111} facets in an aqueous medium,²⁶ slowing down the deposition of Au on these facets and eventually leading to the formation of stellated structures as a result of the continuous deposition and extension at the edges and {100} facets, but not the {111} facets.

We characterized the LSPR properties of the Ag cuboctahedra, Ag@Au cuboctahedra, and Ag@Au concave cuboctahedra using UV-vis spectroscopy. Figure 4A shows UV-vis spectra of the Ag cuboctahedra before and after they had been titrated with 0.4 and 0.8 mL of the HAuCl₄ solution, respectively, followed by their removal from the reaction solution and re-dispersion in DI water for UV-vis characterization. It is worth mentioning that, after correction for the dilution factor resulting from the different titration volumes of the HAuCl₄ solution, the change in peak intensity is directly proportional to the variation in extinction coefficient associated with the nanoparticles. At 0.4 mL, the LSPR peak of the products showed a shift from 434 to 454 nm, together with drop in intensity and broadening in width. This observation is consistent with prior reports on Ag-Au bimetallic nanoparticles.³⁰ It has been established that the LSPR peaks of Ag-Au bimetallic nanoparticles are always considerably broader than those of the Ag or Au counterparts because of the scattering at the Ag-Au interface and the difference in frequency dependence for their dielectric constants. At 0.8 mL, the LSPR peak of the products showed a further shift to 458 nm, together with further decrease in intensity and broadening in width. Such changes to the LSPR features are consistent with the findings reported by other groups during the formation of concave surfaces.¹²

We evaluated the SERS properties of the Ag@Au cuboctahedra and concave cuboctahedra by benchmarking against the Ag cuboctahedra. With excitation at 532 nm, Figure S5 shows the SERS spectra collected from 1,4-benzenedithiol (1,4-BDT) adsorbed on the Ag cuboctahedra before and after they had reacted with 0.4 and 0.8 mL HAuCl₄, respectively. The SERS activity of the Ag cuboctahedra did not change much at all upon the deposition of Au on their surfaces. For example, the intensity of the SERS peak at 1564 cm⁻¹ (the benzene ring mode) was increased

by 10% and then decreased by 20% when the Ag cuboctahedra were switched to Ag@Au cuboctahedra and concave cuboctahedra respectively. This observation is in agreement with prior findings.^{21,31} Typically, the inclusion of Au atoms into Ag nanostructures would result in stronger plasmon damping at visible wavelengths and thus attenuation in SERS intensity because the interband transition edge of Au is located around 500 nm (or 2.5 eV).³² However, by switching the excitation wavelength from 532 to 785 nm and thereby eliminating plasma damping, the intensity of the SERS peak at 1564 cm^{-1} was increased by 15- and 74-fold for the Ag@Au cuboctahedra and concave cuboctahedra related to that of the Ag cuboctahedra (Figure 4B). The corresponding enhancement factors (EFs) associated with the Ag cuboctahedra and Ag@Au concave cuboctahedra were 6.5×10^4 and 4.8×10^6 , respectively. In comparison, at excitation of 532 nm, the EFs were only 5.0×10^4 and 4.4×10^4 for the Ag cuboctahedra and Ag@Au concave cuboctahedra, respectively. We believe that the sharpened corners and edges on a concave cuboctahedron could concentrate the electromagnetic field at these sites, leading to enormous SERS signals.^{12,33} A stronger Au-thiolate bond over that of Ag-thiolate could make an additional contribution to the increased SERS signals through a chemical mechanism.³⁴⁻³⁷

By combining the excellent SERS activity of the concave cuboctahedra with the catalytic activity of Au atoms on their surfaces, we further demonstrated a unique SERS probe for *in-situ* monitoring of the reduction of 4-NTP to 4-ATP by NaBH_4 in a colloidal suspension. After the functionalization of the concave cuboctahedra with 4-NTP, we collected a UV-vis spectrum to confirm the preservation of particle morphology and dispersion state (Figure S6). Upon the introduction of NaBH_4 to initiate the catalytic reaction, we collected SERS spectra from the same reaction solution at different time points at excitation of 785 nm and 10% of the laser output power (Figure 5A). At $t=0$, the SERS spectrum of 4-NTP shows three characteristic vibrational bands (marked by dashed orange lines) at 1108 cm^{-1} (C-N stretching, ν_{CN}), 1336 cm^{-1} (O-N-O stretching, ν_{NO_2}), and 1572 cm^{-1} (C-C stretching phenyl-ring, ν_{CC}),^{37,38} respectively. At $t = 6$ min, the ν_{NO_2} of 4-NTP was blue-shifted from 1336 to 1330 cm^{-1} , together with slight decrease in intensity. The intensities of ν_{CN} and ν_{CC} decreased while their peak positions were essentially retained. On the other hand, four new bands emerged in the SERS spectrum. Specifically, the band at 1595 cm^{-1} can be assigned to ν_{CC} of 4-ATP (marked by a dashed black line) and the other three bands at 1142 cm^{-1} , 1388 cm^{-1} , and 1429 cm^{-1} can be assigned to $\beta_{\text{CH}+\nu_{\text{CN}}}$, $\nu_{\text{NN}+\nu_{\text{CN}}}$, and

$\nu_{\text{NN}} + \beta_{\text{CH}}$ of *trans*-4,4'-dimercaptoazobenzene (*trans*-DMAB, marked by dashed purple lines), respectively.^{39,40} As the reaction progressed to 14 min and then 17 min, we noticed that the ν_{NO_2} of 4-NTP (at 1330 cm^{-1}) started to decrease in intensity, together with a slight shift to the blue in peak position. Also, the ν_{CC} of 4-NTP (at 1572 cm^{-1}) gradually decreased in intensity as that of 4-ATP (at 1595 cm^{-1}) was continuously increased in intensity. The three bands of *trans*-DMAB eventually disappeared. At $t=19$ min, the bands associated with 4-NTP and *trans*-DMAB all disappeared. The remaining three peaks can be assigned to the ν_{CS} , $\beta_{\text{C-H}}$, and ν_{CC} of 4-ATP, respectively. These peaks essentially showed very little change up to $t=45$ min. It is also worth noting that the peaks at 1083 cm^{-1} and 1179 cm^{-1} can be assigned to 4-NTP, *trans*-DMAB, or 4-ATP, and they were relatively stable in all the SERS spectra during the course of the reaction.

Figure 5B outlines a plausible mechanism for the reduction of 4-NTP to 4-ATP by NaBH_4 on a Au surface. Because the SERS spectra indicate that the ν_{CS} (at 1083 cm^{-1}) of 4-NTP, *trans*-DMAB, and 4-ATP were essentially the same during the reduction, we assume that these molecules are preferentially adsorbed at a configuration parallel to the Au surface through the Au-S linkage.⁴¹ As the reduction by NaBH_4 proceeds, the blue-shift for the ν_{NO_2} band of 4-NTP indicates a change to the symmetric stretching band of NO_2 . The assignment of SERS peaks to *trans*-DMAB rather than *cis*-DMAB further supports our argument about a parallel configuration for the molecules on a Au surface rather than a vertical configuration. Likely, the first couple of reduction steps would involve the N-O bond for the generation of nitro- and hydroxylamine, followed by the condensation of these two intermediates to produce *trans*-DMAB.⁴² At the end, cleavage of the azo bond due to hydrogenation would lead to the formation of 4-ATP.

By leveraging the remarkable chemical stability of the Ag@Au concave cuboctahedra in 2.3% aqueous H_2O_2 , we further used *in-situ* SERS to investigate the Au-catalyzed oxidation reaction of 4-ATP that was produced by the reduction of 4-NTP on the surface of a concave cuboctahedron. Specifically, we used *in-situ* SERS to monitor the reduction of 4-NTP by NaBH_4 as described previously. Once we observed the SERS peaks of 4-ATP (see Figure 5A at $t=19$ min), we withdrew 300 μL of sample from the reaction solution and immediately mixed it with 100 μL of 2.3% aqueous H_2O_2 . Upon the introduction of H_2O_2 , we observed a significant decrease in SERS intensity for the reaction mixture. As such, we had to increase the laser power from 10% (used to collect the SERS spectra shown in Figure 5A) to 100% of the output in order

to collect SERS spectra at different time points of the oxidation reaction.

As shown in Figure 6, at $t=2$ min, the ν_{CC} and ν_{CS} of 4-ATP were blue-shifted from 1595 and 1083 to 1570 and 1075 cm^{-1} , respectively. Additionally, the intensities of these bands significantly dropped. For example, the intensity of the ν_{CS} band was only ~200 counts per second (CPS) at a power of 100% of the laser output. In comparison, during the reduction of 4-NTP to 4-ATP by NaBH_4 , the intensity of the ν_{CS} band could be maintained at a level of 2,000-4,000 CPS at a much lower power of 10% of the laser output (see Figure 5A). These results suggest that the monolayers of the Raman probe molecules formed on the surfaces of Ag@Au concave cuboctahedra were not stable in the presence of H_2O_2 . In fact, it has been reported that thiolate-based monolayers are susceptible to oxidation. In general, they tended to be desorbed from the surface upon treatment with 1% H_2O_2 .^{43,44} Concurrently, three characteristic bands of *trans*-DMAB appeared at 1143, 1393, and 1437 cm^{-1} , indicating the conversion of 4-ATP back to *trans*-DMAB. Afterwards, the SERS spectra remained essentially the same except some minor changes to their peak intensities up to $t=28$ min. From the SERS spectra, we did not observe the peaks associated with 4-NTP. These results suggest that the oxidation of 4-ATP by H_2O_2 proceeded rapidly to produce *trans*-DMAB, which could not be further oxidized to 4-NTP, the original reactant. This observation is consistent with the results of other groups.^{45,46}

Because the SERS spectra could provide “fingerprints” for identifying the chemical species attached to the surfaces of the concave cuboctahedra,⁴⁶⁻⁴⁸ we studied the Raman shifts for *trans*-DMAB molecules that were produced either by reduction of 4-NTP or oxidation of 4-ATP. Interestingly, we found that the two bands associated with the N-N stretching of DMAB, *i.e.*, ($\nu_{NN} + \nu_{CN}$) and ($\nu_{NN} + \beta_{CH}$), indicated subtle difference in their peak positions while the band of $\beta_{CH} + \nu_{CN}$ was located at essentially the same position. For example, the SERS peaks of DMAB molecules derived from the reduction of 4-NTP by NaBH_4 were located at 1388 ($\nu_{NN} + \nu_{CN}$), and 1429 cm^{-1} ($\nu_{NN} + \beta_{CH}$) (see Figure 5A). In comparison, when they were formed *via* the oxidation of 4-ATP by H_2O_2 , these peaks were red-shifted to 1393 and 1437 cm^{-1} , respectively. The difference in Raman shifts could infer the formation of *trans*-DMAB molecules via *inter*-particle N=N bonds that are formed between 4-ATP molecules located on two different concave cuboctahedra, which is consistent with a prior observation.⁴⁹ Likely, a *trans* configuration can be easily achieved for the *trans*-DMAB formed *via* inter-particle linkage, shifting the Raman peaks

to higher wavenumbers (frequencies). We also noticed that, during the reduction, the intensities of Raman bands for *trans*-DMAB were comparable to that of the signature band of 4-ATP at 1595 cm^{-1} (ν_{CC}) but much weaker than the C-S stretching band of 4-ATP at 1083 cm^{-1} (ν_{CS}) (see Figure 5A). Once the 4-ATP molecules had been oxidized, the bands of *trans*-DMAB became dominant in the SERS spectrum (see Figure 6). This data also supports our hypothesis that *inter*-particle linkage occurred during the oxidation of 4-ATP to *trans*-DMAB. We believe that individual *trans*-DMAB molecules could be sandwiched between two concave cuboctahedra to generate significantly enhanced SERS signals due to the involvement of a hot spot.^{50,51} In this case, although the molecules trapped in hot spots contributed most to the SERS signals, they were relatively small in terms of population, making it difficult to use SERS to monitor changes to those molecules outside the hot spots.

Conclusions

In summary, we have demonstrated the synthesis of Ag@Au concave cuboctahedra by simply titrating aqueous HAuCl_4 into a suspension of Ag cuboctahedra enclosed by both $\{100\}$ and $\{111\}$ facets in the presence of AA, NaOH, and PVP. As the titration volume of HAuCl_4 solution was increased, we discovered that the Au atoms were initially deposited on the entire surface of each Ag cuboctahedron, followed by switching to preferential deposition on the $\{100\}$ facets only. These results suggest that PVP did not have selectivity in binding to different types of Ag facets in an aqueous medium but it could selectively passivate the Au $\{111\}$ facets and thus slow down the deposition at these sites. The Ag@Au concave cuboctahedra exhibited excellent SERS activity that was more than 70-fold stronger than that of the original Ag cuboctahedra at an excitation wavelength of 785 nm. Together with remarkable chemical stability in aqueous H_2O_2 , we demonstrated that they could serve as an excellent SERS probe for *in-situ* monitoring of Au-catalyzed reactions, including both reduction and oxidation.

EXPERIMENTAL SECTION

Chemicals and Materials. Silver nitrate (AgNO_3 , 99+%), silver trifluoroacetate (CF_3COOAg , 98%), gold(III) chloride trihydrate ($\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$, 99.9+%), poly(vinyl pyrrolidone) with an average molecular weight of 29,000 (PVP-29) or 55,000 (PVP-55), ethylene glycol (EG, J.T. Baker), sodium hydrosulfide hydrate ($\text{NaHS} \cdot x\text{H}_2\text{O}$), aqueous

hydrochloric acid (HCl, 37%), sodium citrate tribasic dihydrate ($\text{HOC}(\text{COONa})(\text{CH}_2\text{COONa})_2 \cdot 2\text{H}_2\text{O}$, 99%), L-ascorbic acid (AA, 99%), sodium hydroxide (NaOH, 98+%), and hydrogen peroxide (H_2O_2 , 30 wt.% in H_2O) were all purchased from Sigma-Aldrich and used as received. All aqueous solutions were prepared using deionized (DI) water with a resistivity of $18.2 \text{ M}\Omega \cdot \text{cm}$.

Synthesis of Ag Nanocubes. The Ag nanocubes were prepared using a polyol method, with EG and CF_3COOAg serving as a solvent and a precursor to elemental silver, respectively. In a typical synthesis, 5 mL of EG was introduced into a round bottom flask (100 mL, ACE Glass) and heated under magnetic stirring in an oil bath held at 150°C , followed by the introduction of 0.06 mL of NaHS (3 mM in EG). After 2 min, 0.5 mL of HCl (3 mM in EG) was introduced, followed by the addition of 1.25 mL of PVP-55 (20 mg/mL in EG). After another 2 min, 0.4 mL of CF_3COOAg (282 mM in EG) was injected into the mixture. The flask was capped with a glass stopper, except for the introduction of reagents. We obtained Ag nanocubes of $40.5 \pm 4.4 \text{ nm}$ in edge length by quenching the reaction with an ice-water bath as soon as the major UV-vis absorption peak of the suspension was shifted to 434 nm. After centrifugation and washing with acetone and DI water three times, the Ag nanocubes were dispersed and stored in DI water.

Synthesis of Ag Cuboctahedra. We used the Ag nanocubes with edge length of $40.5 \pm 4.4 \text{ nm}$ as seeds to obtain Ag cuboctahedra. In a typical synthesis, 50 μL of the aqueous suspension of Ag nanocubes (6.6×10^{12} particles per mL) was introduced into an aqueous solution containing 5 mL PVP-55 (2 mg/mL), 50 μL sodium citrate (20 mM), and 100 μL aqueous AA (100 mM) hosted in a 20 mL glass vial. Next, 1.5 mL of aqueous AgNO_3 (1 mM) was titrated into the mixture using a syringe pump at a rate of 5 mL/h under magnetic stirring at room temperature. During the reaction, the major LSPR peak of the cubic seeds showed a slight red-shift from 434 to 436 nm whereas the peak at 380 nm for the cubic seeds disappeared during the formation to cuboctahedra. Finally, we collected the supernatant by centrifugation at 1,000 rpm to remove the impurity of large particles, followed by the collection of cuboctahedra by centrifugation of the aforementioned supernatant at 8,000 rpm. We washed the particles with DI water three times and then have them re-dispersed in 100 μL DI water for future use.

Synthesis of Ag@Au Cuboctahedra and Concave Cuboctahedra. In a standard synthesis, 2 mL of an aqueous solution of PVP-29 (1 mM, in terms of the polymer) was introduced into a

20 mL glass vial, followed by the addition of 0.5 mL of aqueous AA (100 mM), 0.5 mL of aqueous NaOH (200 mM), and 30 μ L of a suspension of the as-prepared Ag cuboctahedra (3.35 mg per mL) under magnetic stirring. Next, 0.4 mL or 0.8 mL of aqueous HAuCl₄ (0.08 mM) was titrated into the mixture using a syringe pump at a rate of 0.02 mL/min for the generation of Ag@Au cuboctahedra and concave cuboctahedra, respectively. After completion of titration, the reaction was allowed to proceed for another 10 min and the final product was collected by centrifugation at 8,000 rpm and washed with DI water twice prior to SEM characterization.

Etching of the Ag@Au Cuboctahedra and Concave Cuboctahedra. We took out 1 mL of the as-prepared sample, collected the solid product by centrifugation at 8,000 rpm, washed with DI water once, and then added 1 mL of aqueous H₂O₂ (2.3 wt.%, diluted from the original 30 wt.% solution) under magnetic stirring. After 1 h, the solid product was collected by centrifugation at 8,000 rpm and washed with DI three times prior to SEM or TEM characterization.

Instrumentation and Characterization. The UV-vis spectra were collected using a Cary 50 spectrometer (Agilent Technologies, Santa Clara, CA). The quantitative measurement of Ag content was performed using an inductively coupled plasma mass spectrometer (ICP-MS, NexION 300Q, PerkinElmer, Waltham, MA). An Eppendorf 5430 centrifuge was used for collecting and washing solid samples, as well as for the preparation of ICP-MS samples. Scanning electron microscopy (SEM) images were captured using a Hitachi-SU 8230 cold field emission microscope (Hitachi, Tokyo, Japan) operated at 20 kV. Transmission electron microscopy (TEM) images were taken using a Hitachi HT7700 microscope (Hitachi, Tokyo, Japan) operated at 120 kV. The high-resolution HAADF-STEM imaging and STEM-EELS mapping were conducted on a Hitachi HD2700C STEM operated at 200 kV and equipped with a probe aberration corrector. For HAADF-STEM imaging, collection angles from 64–341 mrad were used. Ag M_{4,5} edges at 367 eV and Au M_{4,5} edges at 2206 eV were collected using a Gatan Enfina ER spectrometer. For STEM-EELS mapping, we scanned an area of 100x100 pixels with a total collection time of 12 min.

Surface-Enhanced Raman Scattering (SERS) Measurements. The Ag and Ag@Au cuboctahedra were functionalized with a 0.6 mM ethanol solution of 1,4-BDT for 1 h. After washing with DI water twice, the 1,4-BDT-functionalized nanoparticles were re-dispersed in water to attain a concentration of approximately 3.3×10^{10} particles/mL. The Raman spectra were

recorded using a Renishaw inVia Raman spectrometer coupled with a Leica microscope using a 100x objective. The excitation wavelength was 532 or 785 nm, in conjunction with a grating of 2,400 or 1,200 lines/mm, at a power of 10% of the laser output (50 or 100 mW). Data was collected from the solution phase with a collection time of 30 s for all samples. A sample cell was fabricated from a polydimethylsiloxane (PDMS) block by punching a small hole to hold 20 μL of liquid sample. After the PDMS was attached to a glass slide, we loaded the sample solution and then placed a glass coverslip of 170 μm in thickness on top of the PDMS to prevent solvent evaporation. The cover slip also served as a reference point that allowed us to ensure the focal plane was positioned 200 μm into the sample.

We used the SERS peak at 1565 cm^{-1} (the benzene ring mode, 8a) for the 1,4-BDT molecule to calculate the SERS enhancement factor (EF) using the following equation:

$$EF = \frac{(I_{\text{SERS}} \times N_{\text{bulk}})}{(I_{\text{bulk}} \times N_{\text{SERS}})}$$

where I_{SERS} and I_{bulk} are the intensities of the 8a band of 1,4-BDT for the SERS and the ordinary spectra from a bulk sample, respectively. N_{SERS} and N_{bulk} are the numbers of probe molecules for a SERS sample and a bulk sample, respectively. I_{SERS} and I_{bulk} were determined by the areas of the 8a bands. N_{bulk} was determined from the ordinary Raman spectrum of a 0.1 M 1,4-BDT solution in 12 M aqueous NaOH and the focal volume of the Raman system. For these measurements, we used the same set of parameters to collect the ordinary Raman spectra and the solution-phase SERS spectra. As a result, the focal volume remained the same for all measurements.

***In-situ* SERS Monitoring of the Reduction of 4-Nitrothiophenol by Ag@Au Concave Cuboctahedra.** The Ag@Au concave cuboctahedra were dispersed in 5 mL of DI water containing 4-nitrothiophenol (4-NTP, 10^{-6} M) and incubated at room temperature for 1 h. The NTP-functionalized Ag@Au concave cuboctahedra were then washed with DI water twice and re-suspended in DI water to achieve a concentration of approximately 1.3×10^{11} particles/mL. Upon mixing 200 μL of the suspension with 200 μL of aqueous NaBH_4 (1 mg/mL) in a 1.5 mL centrifuge tube, the concave cuboctahedra were allowed to catalyze the NTP reduction reaction at room temperature. We withdrew 15 μL of sample from the reaction solution every several minutes and placed this sample in a PDMS-based cell for monitoring the progress of the reaction

by SERS. Successive SERS spectra were collected until complete reduction of 4-NTP to 4-ATP. All SERS spectra were recorded from the solution phase using a 5x objective. The data was collected with a collection time of 10 s at a power of 10% of the output of 785 nm laser (100 mW).

***In-situ* SERS Monitoring of the Oxidation of 4-Aminothiophenol Catalyzed by Ag@Au Concave Cuboctahedra.** When the reduction of 4-NTP to 4-ATP was completed, 300 μ L of the reaction solution was taken out and mixed with 100 μ L of 2.3% aqueous H_2O_2 . Again, we withdrew 15 μ L of sample from the reaction solution every several minutes and SERS spectrum was collected from the sample to monitor the oxidation 4-ATP using a 50x objective with a long working distance. All SERS spectra were recorded from the solution phase with laser excitation at 785 nm. The data was collected with a collection time of 90 s at a power of 100% of the output of 785 nm laser (100 mW).

ASSOCIATED CONTENT

Supporting Information Available: SEM images; UV-vis spectra; ICP-MS results; and EELS data. This material is available free of charge *via* the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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Figure 1. Schematic illustration of a proposed mechanism responsible for the transformation of Ag cuboctahedra into Ag@Au cuboctahedra, and ultimately Ag@Au concave cuboctahedra.

Figure 2. Electron microscopy images of products before (left panel) and after (right panel) etching with 2.3% aqueous H_2O_2 . The samples were prepared by reacting Ag cuboctahedra with different volumes of HAuCl_4 : (A, B) 0.2 mL, (C, D) 0.4 mL, and (E, F) 0.8 mL, respectively. A TEM image is shown in (B) while the rest is SEM image. Inset scale bar: 20 nm.

Figure 3. (A-D) HAADF-STEM images taken from one of the Ag@Au concave cuboctahedra shown in Figure 2E when it was oriented along the $\langle 110 \rangle$ zone axis. (E) HAADF-STEM image taken from another concave cuboctahedron that was oriented along the $\langle 100 \rangle$ zone axis. (F) STEM-EELS mapping of Au (red) and Ag (green) for the cuboctahedron shown in (E). The insets show models of the concave cuboctahedra in the appropriate orientations.

Figure 4. (A) UV-vis spectra of the Ag cuboctahedra, Ag@Au cuboctahedra, and Ag@Au concave cuboctahedra in aqueous suspensions. (B) SERS spectra collected from 1,4-BDT adsorbed on the Ag cuboctahedra, Ag@Au cuboctahedra, and concave cuboctahedra at the excitation of 785 nm. The Ag@Au cuboctahedra and concave cuboctahedra were prepared with the titration of 0.4 mL and 0.8 mL aqueous HAuCl₄, respectively

Figure 5. (A) SERS spectra recorded during the reduction of 4-NTP to 4-ATP by NaBH₄ at an excitation wavelength of 785 nm. The reaction was catalyzed by the Ag@Au concave cuboctahedra shown in Figure 2E. (B) Schematic illustration (atomic model) of the pathway responsible for the reduction of 4-NTP to 4-ATP on a Au surface.

Figure 6. SERS spectra recorded during the oxidation of 4-ATP by H_2O_2 at an excitation wavelength of 785 nm. The reaction was catalyzed by the Ag@Au concave cuboctahedra shown in Figure 2E.

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