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Promotion of SERS and Catalytic Activities with Bimetallic and Ternary Concave Nanolayers

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A seed growth process accompanied by a galvanic replacement reaction (etching and alloying) using CTAB/HAuCl₄/AgNO₃/ascorbic acid was developed to fabricate silver nanocubes with concave AuAg nanolayers. The solid nanostructure consisted of a concave face of the inner Ag solid counterpart with a hole surrounded by a AuAg nanowall. We found that the CTA⁺ ions played a vital role in the adsorption of Au(I)/CTA⁺ micelles selectively at the {100} facets to trigger galvanic replacement etching. Meanwhile, the reaction involving AgNO₃ helped to switch the co-reduction of metal atoms from the [110] sites to the [100] vector and favored AuAg co-reduction of atoms along the {100} vector for concave AuAg nanolayer formation. Such AuAg atoms at the concave layer induced strong charge transfer-based surface-enhanced Raman scattering (SERS) when thiol molecules were bound to the active atoms and enabled the detection of the toxin malachite green at the fM level via physisorption. These highly active atoms at the concave facets aided superior electron-transfer catalysis. After etching with H_2O_2 to produce pure-Ag-removed and concave AuAg nanowalls, the efficiencies of the SERS and catalytic performances were degraded due to the decrease in the active atom density. This reaction strategy of simultaneous etching and co-reduction could be further extended to the trimetallic AuAg:Pd concave nanocomposite synthesis to improve the hydrogenation reaction thus obtaining a very high kinetic constant.

Introduction

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Recent advancements in the field of concave nanoparticles have provided promising opportunities to improve the catalytic activity and surface-enhanced Raman scattering (SERS)-based sensing performance through the exposure of highly active atoms on concave facets.¹⁻³ The fabrication of diverse concave nanocomposites using a seed-mediated growth process to individually direct the creation of an outer coating of atoms, in general, has successfully generated binary AuAg,⁴ AuPt,⁵ CuPt,⁶ AuPd,⁷ and PtNi⁸ nanoparticles and has been widely employed in the exploration of electrocatalytic activity. A straightforward strategy for the preparation of a complete and thin concave nanolayer with bimetallic and ternary composites is important but synthetically challenging to achieve. Several groups have adopted the site-selective dissolution of a host metal and partial co-deposition of host and guest metals to generate cave-like concave side faces.9-10 After removal of the interior core, a nanoframe is produced rather than a concave nanolayer structure.9 To achieve complete protection of whole faces and

investigate the growth of local sites, adjustment of the pH played an essential role in controlling the reduction potential of the ascorbic acid (AA) molecule to affect the reduction kinetics of HAuCl₄ in the final Au-based bimetallic nanostructures.¹¹⁻¹³

Commonly, core-free nanoparticles demonstrate higher catalytic reactivities and sensing abilities than their starting solid nanomaterials because of their large specific surface-to-volume (S-to-V) ratio.¹⁴⁻¹⁸ Despite the fact that different heterogeneous-structured concave nanoparticles produced by a secondary growth process have been successfully developed, the fabrication of a complete concave nanolayer has rarely been reported in the current studies but is important. In addition, separate studies on merely heterogeneously structured concave nanoparticles have been independent reported and have not been thoroughly compared.¹⁹⁻²⁰ The possibility that a secondary wet-chemistry reaction, such as an oxidation reaction to dissolve the inner core, may destroy the highly active atoms and thus lead to an underestimation of the actual catalyst activity is a concern.

Therefore, a re-review of 'concave layer' nanoparticles with and without solid counterparts before and after chemical manipulation needs to be conducted via a specific analysis method. To provide better analysis, we performed SERS measurements to determine the level of signal improvement as a cautious assessment of the relative atom reactivity at the concave sites before and after etching the solid support of the pure Ag atoms. For the preparation of concave layer nanoparticles, we developed a single-step growth process in

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which Au and Ag ions were co-reduced around pure Ag nanocubes with Au(I)Br2⁻/AgNO₃/CTA⁺ micelles. Meanwhile, selective etching of the {100} facets of the Ag nanocubes, blocking of AuAg atom growth at the {110} facets, and codeposition of AuAg at the etched sites occurred. In addition to Au/Ag atom co-deposition, the interior of the particle was transformed into a AuAg nanowall via a galvanic replacement reaction-assisted alloying process, as shown in Scheme 1. After reaction with H_2O_2 to oxidize the pure Ag atoms in the inner area, a single particle with a double AuAg nanolayer structure was fabricated. Improvements in the SERS intensity by 19.5- and 14.1-fold were observed for the solid-supported concave AuAg nanolayers relative to the Ag nanocubes and pure-Ag-removed concave AuAg nanolayers (removal of pure Ag atoms), respectively. Efficient chemisorption would occur at the unetched concave AuAg atom nanolayer due to retention of highly crystalline and active atoms. These atoms readily exhibited high hydrogenation reactivity in the catalytic conversion of 4nitrothiophenol (4-NTP) to 4-aminothiophenol (4-ATP) with a shorter initialization time of the reaction. Finally, this synthetic strategy of co-reduction at the particle surface accompanied by alloying at the internal interface could be extended to fabricate complicated concave AuAgPd nanocomposites by reacting the solid-supported concave AuAg nanolayer with a Pd(II)/CTA⁺/AA growth solution, not only retaining a high SERS activity but also further accelerating the release of electrons from NaBH₄ to reduce 4-NTP.

Experimental Section

Methods. Hexadecyltrimethylammonium Materials and bromide (CTAB), polyvinylpyrrolidone (PVP) with an average molecular weight of 55 000 (PVP-55k), nitric acid (HNO₃), and hydrogen peroxide solution (H₂O₂, 34.5~36.5%) were all acquired from Sigma-Aldrich. Silver trifluoroacetate (CF₃COOAg, 98%) and methylene blue trihydrate (MB) were acquired from Alfa Aesar. Hydrogen tetrachloroaurate(III) trihvdrate (HAuCl₄·3H₂O, 99.9%) and palladium chloride (PdCl₂) were acquired from Bio-Tech. Ethylene glycol (EG), silver nitrate (AgNO₃) were acquired from Fisher chemical. Sodium hydrosulfide hydrate (NaHS·xH₂O) and 4-Nitrophenol (4NP) were acquired from Acros Organics. L-(+)-Ascorbic acid (AA, 99%) was purchased from J. T. Baker. Hydrochloric acid (37% HCl) was purchased from Fluka. Sodium borohydride (NaBH₄) was purchased from Riedel-de Haen. 4-Nitrothiolphenol (4-NTP) was purchased from Matrix Scientific. All chemicals were used as received without purification. All the aqueous solutions were prepared using deionized (DI) water with a resistivity of 18.2 $M\Omega$ cm at room temperature.

Synthesis of Ag nanocubes. First, 10 mL of EG was added into a 100 mL round bottom flask and heated under magnetic stirring in an oil bath at 160 °C, followed by the fast injection of 0.24 mL of NaHS (3 mM). After 2 min, 0.5 mL of HCl (3 mM in EG) and 2.5 mL of PVP-55 (20 mg/mL in EG) were sequentially added. After another 2 min, 0.8 mL of CF₃COOAg (282 mM in EG) was introduced into the mixture. After stirring for 1 hour, the reaction was quenched in an ice water bath. After repeated centrifugation and redispersion in acetone/DI water more than

Synthesis of bimetallic AuAg and trimetallic AuAg:Pd concave nanoparticles. To prepare the Au(I) precursor, 4.95 mL of DI water containing 9 mg of CTAB was reacted with 50 μ L of HAuCl₄ (5 mM), 6 μ L of AgNO₃ (10 mM), and 30 μ L of ascorbic acid (10 mM), all of which were aqueous solutions. The pH of the HAuCl₄/CTAB solution was 6.61. Next, 0.314 mL of the Au(I) precursor was removed from the stock solution and reacted with 0.5 mL of the purified Ag nanocubes (56 ppm) under magnetic stirring. After stirring for 45 min, the mixture was centrifuge at 6000 rpm for 10 min, the supernatant of the sample was discarded, and the solid was redispersed in DI water. This process was repeated more than three times, and the final precipitate was stored in DI water.

To prepare the Pd precursor, 4.95 mL of DI water containing 9 mg of CTAB was reacted with 50 μ L of PdCl₂ (5 mM) in a 120 mM HNO₃ aqueous solution and 30 μL of aqueous ascorbic acid (10 mM). Next, 0.3125 mL of the Au(I) precursor was removed from the stock solution and reacted with 0.5 mL of the purified Ag nanocubes (56 ppm) under magnetic stirring. After stirring for 5 min, 0.157 mL of the Pd precursor solution was added into the Au/Ag mixture, which was reacted for another 45 min. The metal precursor molar ratio of the Pd precursor (0.314 mL) over Ag nanocubers plus CTAB/HAuCl₄/AgNO₃/AA solution is \sim 4.8 mol%. To prepare 9.6 mol% Pd dopant, 0.628 mL of Pd precursor was employed. The supernatant of the sample solution was discarded after centrifuging at 6000 rpm for 10 min, and then the solid was redispersed in DI water. This process was repeated more than three times, and the final precipitate was stored in DI water.

Raman scattering measurements. The Raman microscope was equipped with a 785 nm excitation laser. For SERS detection, 5 μ L of the AuAg bimetallic NCs or the AuAgPd trimetallic NCs (25 ppm _[Ag]) was mixed with an equal volume of methylene blue (0.05 mM MB) on a silicon substrate to enhance the Raman signal of the dye. All the SERS properties were characterized by a Raman spectrometer with a 5 s acquisition time.

Catalytic reduction of 4-nitrophenol. A 10 mL stock solution of NaBH₄ (50 mM) was prepared fresh in ice-cold water. Afterward, 1 mL of 4-nitrophenol (4-NP) (0.35 mM) and 1 mL of NaBH₄ (50 mM) were mixed, resulting in a yellow solution. A UV-vis spectrometer was used to record the absorption peak of 4-NP at 405 nm once 125 ppm_[Ag] nanoparticles was rapidly added into the 4-NP/NaBH₄ solution. Data were collected at 1 min intervals. The kinetic constant of the conversion of 4-NP to 4-AP was calculated based on the slope of the ln (Ct/C₀) versus time plot according to the pseudo-first-order reaction model.

In Situ SERS Monitoring of the Reduction of 4-Nitrothiophenol. First, 100 μ L of the AuAg bimetallic NCs or the AuAgPd trimetallic NCs at 25 ppm [Ag] was mixed with 900 μ L of 4-NTP (1 μ M) for 1 h at room temperature to form a monolayer of immobilized 4-NTP on the surface of the concave nanoparticles. After purification by centrifugation and redispersion, 100 μ L of water was added to suspend the 4-NTP-immobilizing concave nanoparticles, and the mixture was transferred to a silicon wafer. Raman spectroscopy was used to record the signal

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response of the hydrogenation reaction upon the addition of 100 μL of the freshly prepared NaBH_4 solution (25 mM). Data were collected with a 5 s acquisition time and recorded every 1 min.

Characterization. Electron micrographs were obtained using a transmission electron microscope (TEM) at 80 kV (JEM-2000EXII), a high-resolution TEM at 300 kV (JEOL 3010), and a field emission scanning electron microscope (SEM) at 10 kV (XL-40 FEG; Philips). The absorption spectra of the metal nanoclusters were measured using a UV-vis spectrophotometer (V-730 UV-Vis, Jasco). The concentrations of Au, Ag, and Pd ions in all samples were quantified using an inductively coupled plasma atomic emission spectrometer (ICP-AES, JY138 Spectroanalyzer; Horiba Jobin Yvon, Inc., Edison, NJ). X-ray photoelectron spectra (XPS) (VG Scientific 210) of the metal nanoparticles were recorded using a Mg K α source (12 kV and 10 mA). The binding energy scale was calibrated to 284.6 eV for the main C ls peak.

In the Raman analysis, the SERS substrates were placed on a glass template and subjected to micro-Raman spectroscopy using a 785-nm laser (DPSSL Driver II, 10 mW) on an MRS-iHR320 modular Raman system equipped with an Olympus BX53 microscope. A Jobin-Yvon LabRAM high-resolution Raman spectrometer (Horiba iHR 320) was applied to record the Raman shift. Furthermore, 20X objective lens and a 1-s or 5-s accumulation time were applied for the Raman measurements. All spectral controls, manipulations, and data analyses were performed using LabRAM systems.

Results and discussion

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Fig. 1 Morphological and structural characterization of the solidsupported concave AuAg nanolayers: a) TEM, b) high-magnification TEM, c) HAADF, d) HAADF integrated with line-scan EDS, and e) HR-TEM images. f) Elemental analyses of the solid-supported concave AuAg nanolayers by the STEM-EDS, AAS, and XPS methods. The green lake and red lines on the curve profile in the EDS line model analysis d) represent Ag and Au atoms, respectively.

Fresh Au(I)Br₂⁻/CTA⁺ micelles²¹⁻²² with a trace of Ag ions were formed by mixing the chemicals CTAB, HAuCl₄, AgNO₃, and AA at pH = 6.26 (Figure S1). Figure 1a shows transmission electron microscopy (TEM) images of the nanoparticles obtained by reacting Ag nanocubes (45.5 nm edge length and 59.8 nm average body-centered diagonal length) with 0-314 mL of the AuBr2-/CTA+ micelle reagent. The nanoparticles exhibited light contrast at the six side planes (white arrows) of the Ag nanocubes, which is attributed to the loss of metal atoms. Thus, side-selective etching of the Ag atoms along the <100> directions was proposed. The average body-centered diagonal length of the particles was 73.6 nm. In addition, a core-free structure can be seen in certain nanocubes, as indicated by red arrows. Figure 1b shows a magnified TEM image that clearly shows a single hole inside the Ag nanocube. This specific structure was possibly ascribed to the oxidation of Ag in the interior by a galvanic replacement reaction.²³ The corresponding high angle annular dark field (HAADF) image (Figure 1c) revealed a sharp interface with a curved wall structure (~ 14.4 nm) and a dark section in the interior of the particle. Note that the solid framework still possessed the concave structure of the internal solid counterpart, as marked by black arrows. The light contrast corresponds to the dissolution of heavy Au atoms in the concave nanowall structure (labeled with yellow arrows). Intriguingly, the inner interface labeled with a blue arrow showed a slight increase in contrast, which is perhaps due to the incorporation of a certain level of Au atoms. The line scan measurements demonstrated that a large amount of Au resided in both the outer and inner interfaces (Figure 1d), forming a Ag-rich portion in the inner framework that supported both nanolayers. The structures were composed of highly crystalline features consisting of continuously repeating 0.20 nm and 0.14 nm lattice distances corresponding to the (200) and (220) planes (Figure 1e). High crystallinity was also observed at various hollow structures in other concave nanoparticles (Figure S2).

Energy dispersive spectrometry (EDS), atomic absorption spectroscopy (AAS), and X-ray photoelectron spectroscopy (XPS) analyses were carried out to characterize the composition of the concave nanolayer formed from the AuBr₂-/CTA+-assisted growth at the surface of the Ag nanocubes. Figure 1f shows that 97.6% and 94% Ag atoms were present in the resulting AuAg colloidal sample, as determined by EDS and AAS, respectively. The Ag/Au ratio is consistent with the initial molar ratio of Au and Ag precursors in the reaction. It is reasonable to conclude that the oxidation of Ag was capable of facilitating the coreduction of the Au(I) species in the formation of a concave nanostructure around the Ag nanocubes. XPS analysis is very sensitive within 3-4 nm of the surface of materials. Indeed, an increased Au content of 20.3% appeared in the surface structure according to the XPS measurements. The incorporation of Ag atoms into the nanolayer structure with a composition of roughly Au_{0.2}Ag_{0.8} was attributed to the coreduction of the dissolved Ag and Au(I) species by AA.24 Meanwhile, high-resolution XPS spectra (Figure S3) were obtained to characterize the Au 4f orbitals and Ag 3d orbitals of the concave AuAg nanolayer. The binding energy of the Ag atoms upshifted by ~ 0.59 eV from the 367.2~367.4 eV binding energy in the bulk Ag material, while the binding energy of the Au atoms downshifted (~ 0.21 eV) relative to that in the bulk Au material (84.0 eV).²⁵ This phenomenon could be attributed to

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charge transfer from the smaller atoms to the larger metal atoms in the solid solution. $^{\rm 26}$



Scheme 1 Scheme illustrating the Au/Ag atom distribution and concave structure/interior hole in a 2-D cross-section and a 3-D structure of the solid-supported concave AuAg nanolayer. Green lake and red spheres represent Ag and Au atoms, respectively.

It has been reported that Au and Ag materials have similar unit cells.²¹ Thus, they may easily form a miscible AuAg alloy at the surface upon co-reduction of Au and Ag ions to achieve epitaxial decoration of the outermost surface of the solid Ag nanosupport. Scheme 1 shows the complicated structure of the concave-structured Ag nanosupport decorated with a concave AuAg nanolayer and containing a single hole, which has not been reported previously.5, 27-30 For example, this concave core/concave shell structure was not found in the Pd-coated Au nanocubes formed from a similar synthetic system,¹⁰ which might be due to the higher reduction potential of Au hindering the selective chemical oxidation by the Pd/CTA⁺ complex. In contrast, the formation of a complete concave nanolayer did not occur at the high reduction potential of the AA molecule, which was favorable for accelerating the deposition of Au atoms at the {110} and {111} facets of the Ag nanocube.9

We further investigated the roles of the CTAB, HAuCl₄, AgNO₃, and AA (pH=6.3) reagents in this etching and concave layer-forming reaction. In the absence of the CTAB reagent, selfnucleated Au nanoparticles and smooth Ag nanocubes coexisted (Figure S4a). This result indicated the poor adhesion of the Au atoms to the (100) facet of the Ag nanocubes without the assistance of CTA⁺ micelles. In contrast, a large portion of the Ag was removed from the Ag-rich inner area of the nanocubes (Figure S4b) when the AA reagent was not present. It is not surprising that extensive dissolution of the Ag atoms occurred with the addition of the trivalent Au species. Note that a concave layer was still generated at the surface of the cubic nanoparticles under these conditions. A large portion of the particle interior was removed from these particles, which had a 59.6 nm diagonal length, close to that of the initial Ag nanocubes, implying that the etching of the side facets, alloy formation in the concave wall, and hollowing of the interior dominated rather than the co-reduction of the Au(III) and Ag(I) ions. In another control experiment in which HAuCl₄ was excluded, the side facets were not etched out (Figure S4c). Notably, most particles in the AgNO₃-free condition generated a concave surface structure with a wide channel, embedded in the interior along the <100> direction (Figure S4d). Huang and co-workers' investigation suggest that AgNO₃ could assist the metal atom deposition along the [100] direction and block the

growth along the [110] direction.³¹ It was proposed that the AgNO₃-containing AuBr₂⁻/CTA⁺ micelle solution doubd switch the co-reduction of metal atoms from the [110] sites¹² to the [100] vector, providing the opportunity to form a complete nanolayer and prevent the continuous etching along the [100] direction. On the basis of these results, it was concluded that the reduction of the CTA⁺ micelles containing Au(I) or Au(III) ions predominately involved dissolution of the side planes of the Ag nanocubes rather than of the metal atoms grown at the cubic edge and tip sites due to the high reduction potential of the AA molecules¹² and AgNO₃-free condition.

On the other hand, it has been reported that CTA⁺ and Cl⁻ /Br preferentially adsorb to the {100} planes of Ag nanocubes.³²⁻³³ Thus, it is possible that the AuBr₂-/CTA⁺ micelles preferentially adsorb to the Ag {100} side planes, which is followed by local etching via a galvanic replacement process. Subsequently, concave Ag nanoparticles were obtained. Deposition on the concave surface by the co-reduction of Au(I) and dissolved Ag(I) ions led to the formation of a concave AuAg nanolayer at the same time. In contrast, the sole galvanic replacement reaction of the AuBr₄-/CTA⁺ species (Figure S1) and Ag nanocubes resulted in alloying of a AuAg nanowall around the surface of the concave Ag nanoparticle (Figure S4b). Excess Au(I) or Au(III) species did not cause dealloying of the concave AuAg nanolayer, but continuous elimination of the Ag atoms from the interior occurred via galvanic replacement through the microchannels.³⁴⁻³⁵ When the volume of the AuBr₂-/CTA⁺ micelle reagent increased to 0.63 mL, we did not observe additional filling of the inner hole by atom-by-atom deposition of Au (Figure S5), and the hole was maintained even though etching of the interior was not complete.



Fig. 2 Structural and composition characterization of the pure-Agremoved concave AuAg nanolayers: a) low-magnification TEM image, b) high-magnification TEM image, c) HAADF image, and d) corresponding EDS line scan of Au and Ag in two particles. The green lake and red lines on the curve profile in the EDS line model analysis d) represent Ag and Au atoms, respectively.

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To prove the hypothesis that a AuAg bimetallic nanolayer existed at the internal interface, the H₂O₂ etching process was performed to remove the pure Ag atoms from the solidsupported concave AuAg nanolayer. Figure 2a shows that ~ 58% of the nanoparticles produced an internal nanobox structure inside the concave AuAg nanolayer after this process. Over 90% of concave nanolayers comprised a nanobox structure when the CTAB/HAuCl₄/AgNO₃/AA solution volume increased to 4 times its original value. The concentration effect will be studied further for the next report. Moreover, the inner and outer nanowalls displayed similar contrast in the HAADF image (Figure 2b), suggesting that similar AuAg atomic composites were formed. EDS measurements showed that the etched concave particle contained ~18% Au in the AuAg composite, which is close to the surface composition of the solid-supported concave AuAg nanolayer determined by XPS spectroscopy (Figure 1f). A slight decline in the Au ratio to 13% occurred inside the nanobox, which contained ~87% Ag, as determined by EDS analysis. Line scan analysis provided direct evidence showing that the inner and outer walls consisted of Au and Ag composites (Figure 2d). Because of the low Au content in the inner wall, the presence of a textured structure (a black arrow) and/or fragments (red arrows) inside the concave AuAg nanolayer (Figure 2a) would be related to the incomplete formation of the AuAg nanobox and the collapse of the low content Au-based nanobox after etching with H₂O₂, respectively. A HR-TEM image (Figure 2c) showed relatively weak crystallinity for both nanolayers compared to the solid-supported product, as shown in Figure 1a. The change in the crystalline structure was due to the disordered lattice alignment according to the elongated diffraction spots observed in the corresponding Fast Fourier transform (FFT) pattern (Figure S6).



Fig. 3 a) UV-visible experiment in which the absorption at 405 nm was recorded to plot $ln(C_t/C_0)$ versus time in the conversion of 4-NT to 4-AP with Ag nanocubes, solid-supported concave AuAg nanolayers, and pure-Ag-removed concave AuAg nanolayers. SERS measurements of b) 4-NTP, c) MB, and d) MG with Ag nanocubes, solid-supported concave AuAg nanolayers, and pure-Ag-removed concave AuAg nanolayers, and pure-Ag-removed concave AuAg nanolayers.

Despite the similar concave structures obtained at the outmost layer for both the solid-supported and pure-Ag-

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removed materials, the difference in the catalytic, and SERS performances between both samples DShidult03be8taPePany examined. UV-visible spectra (Figure S7) were recorded at 405 nm during the reaction of 4-nitrophenol with NaBH₄ as a reductant in the presence of 1.15 $mM_{\left[Ag\right] }$ solid-supported concave nanocatalyst. The intensity of this peak decreased as a function of the reaction time, indicating the reduction of 4nitrophenol (4-NP) to the amine form, 4-aminophenol (4-AP). The plot of $In(C_t/C_0)$ versus time for 4-NP reduction is shown in Figure 3a. The resulting catalytic rate constant (k) of ~ 6.9×10^{-3} sec⁻¹ for the solid-supported concave AuAg nanolayer is consistent with pseudo-first-order reaction kinetics. It is worth noting that the reactivity of the Ag nanocube was weak with a very low k (1.73 x 10^{-4} sec⁻¹), showing the possible hindrance of the catalytic process by the solid Ag nanocubes. In addition, the solid-supported concave AuAg nanolayers showed a 1.5-fold higher activity than the pure-Ag-removed concave AuAg nanolayers ($k \approx 4.56 \times 10^{-3} \text{ sec}^{-1}$). Our results showed that this catalytic performance did not merely result from the high S-to-V ratio ¹⁴⁻¹⁸ and the large number of Au atoms.²⁰

We questioned whether the Ag-containing and pure-Agremoved concave AuAg nanoshells had any additional structural effects on the chemical and physical interactions with adsorbed molecules. It is well-known that the SERS activity is very sensitive to the surface-related activity and specific surface area of plasmonic nanocrystals.³⁶ To prove the formation of reactive sites and a potentially relatively Au-rich structure at the surface, we utilized a micro-Raman instrument equipped with a 785 nm laser to examine the chemisorption of 4-NTP to the solidsupported (Figure 1a) and pure-Ag-removed (Figure 2a) concave AuAg nanolayers with the same Ag concentration. Figure 3b shows 19.5- and 14.1-fold signal amplifications (at 1311 cm⁻¹) in the SERS intensity for the chemisorption of 4-NTP onto the solid-supported concave AuAg nanolayer compared to that onto the pure Ag nanocubes (152.7 counts) and the pure-Ag-removed nanoparticles (211.3 counts), respectively. Compared with Ag nanocubes, only a 5.4-fold amplification of the SERS intensity was observed for smooth Au-coated Ag nanocubes.¹¹ It is expected that 4-NTP bonds to the Au atoms rather than the Ag atoms with a high selectivity.^{20, 37} Therefore, the promotion of the SERS intensity by both the solid-supported and pure-Ag-removed concave AuAg nanolayers originated from an increase in the number of Au-S binding sites to provoke a chemical (CHEM) enhancement.⁴ However, the CHEM effect does not effectively explain the strong SERS effect observed for the solid-supported concave AuAg nanolayers because a similar Au/Ag atom ratio is present in the concave surface structures of both particles. Furthermore, an additional SERS experiment for detecting methylene blue (MB) at 447 cm⁻¹ with solid-supported concave AuAg nanolayers showed a 4.8-fold improvement compared with the pure-Ag-removed AuAg concave nanolayers (Figure 3c). However, this smaller increment (4.8 times) in the MB-based SERS activity was distinct from the 14.1-fold increase induced by the CHEM effect. It is considered that the MB molecules in proximity to the plasmonic metal nanoparticles are sensitive to the electromagnetic (EM) field generated by the concave surface structures, especially in the region of a hot

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spot.³⁸ At the same MB concentration, the relative enhancement factor (EF) of the solid-supported concave AuAg nanolayers was measured to be as large as 6.75×10^6 , compared with the EF of 1.8×10^5 for pure Ag nanocubes.¹¹

It is worth mentioning that the solid Ag nanocubes retarded the catalytic process of one electron transfer during the catalytic reaction at the interface (Figure 3a). In contrast, the retention of a large amount of pure Ag atoms in the solidsupported concave AuAg nanolayer resulted in a very high catalytic efficiency. Considering the highly ordered lattice atoms observed in the HR-TEM images of the fresh concave AuAg nanolayer (Figures 1e and S2), the relatively high density of reactive sites was uniform within the interfacial region. Regarding this feature, chemical etching might deplete the number of active atoms. Significantly, both the physisorption and chemisorption SERS effects were strongly promoted by the solid-supported concave AuAg nanolayer. Ag nanocubes did not promote a strong SERS response. Therefore, the increase in the scattering cross-section by the Ag-rich composite³⁹ was not completely explained by the difference between the physisorption and chemisorption SERS effects of the solidsupported and pure-Ag-removed concave nanoparticles, ignoring the influence of the uniform active atoms on the surface effects. In particular, the active atoms in high-index structural planes were exposed on the particle surface.^{19, 33} Although both particles had similar Au/Ag ratios (Au₁₈Ag₈₂ ~ $Au_{20}Ag_{80})$ in the concave nanolayers, the active sites of Au and/or AuAg atoms were possibly co-etched and subsequently dissociated when the oxidant H₂O₂ was employed.

Figure 3d shows that the label-free SERS signal presented a potential sensing range from below 100 pM to 50 fM for malachite green (MG), a molecule whose use is prohibited in aquaculture. This result suggests a practical application of the solid-supported AuAg concave nanolayers in the SERS detection of toxic molecules in natural environments.



Fig. 4 a) Low-magnification, b) high-magnification, and c) high-resolution TEM images of the c-AuAg:4.8Pd nanolayers. SERS spectra of d) MB and e) 4-NTP with the c-AuAg:4.8Pd nanolayers and the solid-supported concave AuAg nanolayers.

In addition, the manipulation of the reaction of the Ag solidsupported AuAg concave nanolayers with a 4.8 mol%- Pd/CTAB/AA solution could be applied to prepare.complicated ternary Au-Ag-Pd nanolayers. Figure 4a and 4b shows are well images of several concave surface-structured nanoparticles that had square-like nanoboxes in the interior. The concave AuAg:Pd layer nanostructures consisted of a highly crystalline lattice structure (Figure 4c). A real Au:Ag:Pd ratio of 15.5:82.4:2.1 was recorded based on EDS measurements (Figure S8a). However, the distribution of Au, Ag, and Pd was not homogeneous in the whole structures, in accordance with the EDS analysis in the spot-capture mode (Figure S8b and S8c). Pd atoms mainly appeared in the inner and outer nanolayers, where a higher Pd concentration was observed in the inner wall due to the inward deposition driven by galvanic replacement oxidation of the interior Ag atoms. Figure S9a shows the possible structure and composition of ternary Au-Ag-Pd nanolayers.

The deposition of Pd atoms could be divided into three separate reactions. The first is the galvanic replacement triggered by the Pd ion species. The second reaction is the correduction of Ag ions with PdCl₂/CTA⁺ micelles by AA-generated alloying atoms that dissolved into the AuAg lattices of the asprepared concave nanolayers. The third reaction is the additional transfer of two electrons from the pure Ag counterpart to one PdCl₂/CTA⁺ species for subsequent alloy formation to produce a Au-Ag-Pd composite at the inner interface and generate an internal nanobox.

Again, the SERS effects of the concave AuAg:4.8 mol% Pd (c-AuAg:4.8Pd layer nanostructures nanolavers) was investigated for sensing MB by physisorption and 4-NTP by chemisorption. Retention of ~ 65% of the intensity was observed for MB (Figure 4d), while a significant drop in intensity to ~24% was observed for 4-NTP (Figure 4e) compared with the solid-supported AuAg concave nanolayer. Upon introducing the 1,4-benzenedithiol molecule to the c-AuAg:4.8Pd nanolayers, another example of a dramatic decrease in the Raman intensity to 33% in response to low CHEM was obtained (Figure S10). The co-deposition of Ag and Pd atoms might shield the Au atoms from binding to 4-NTP (see the proposed structure in Figure S9b), leading to depression of the CHEM effect.

The better remaining SERS activity for MB could be related to the EM field effects of the concave surface-structured nanolayer, which produce hot spots. Nevertheless, Figure S11 shows that the SERS sensing of MB via the application of c-AuAg:9.6Pd nanolayers was inferior. This approach exhibited a reduced Raman intensity of ~21% (at 447 cm⁻¹). This SERS signal decrease was due to an increase of the SERS inactive Pd in the nanowall structure, which thus further hindered the EM-based enhancement of SERS. ⁴⁰⁻⁴³

To take advantage of the superior hydrogenation activity of Pd atoms, Ag solid-supported AuAg concave nanolayers were reacted with 4.8 mol% and 9.6 mol% Pd ion species to exploit Pd concentration-dependent catalysis. After immobilizing 4-NTP on both of the nanocatalysts and then adding NaBH₄, the Raman peak at 1572 cm⁻¹ disappeared due to the depletion of the u_{CC} of 4-NTP (Figure 5a and 5b). An additional Raman peak at 1595 cm⁻¹ corresponding to the u_{CC} of 4-ATP appeared at 15

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Fig. 5 SERS spectra for monitoring the conversion of 4-NTP to 4-ATP as a function of the reaction time with a) the c-AuAg:4.8Pd nanolayers, b) the c-AuAg:9.6Pd nanolayers, and c) the solidsupported concave AuAg nanolayers. d) SERS experiment in which the peak change at 1332 cm⁻¹ (uNO₂) was recorded to plot $ln(C_t/C_0)$ versus time for the conversion of 4-NTP to 4-ATP under the same Ag_[ppm] concentration with the different structures and concave nanolayer composites from a) and b).

min and increased as a function of reaction time. Upon incorporation of 4.8 mol% Pd atoms (Figure 5a), the complete conversion time of 4-NTP to 4-ATP was ca. 15 min, and a higher k value of 5.5×10^{-3} sec⁻¹ was observed (Figure 5d). In addition, the sample in which 9.6 mol% Pd was used for the growth of concave AuAg:Pd layer nanostructures exhibited a slight increase in catalytic performance (Figure 5b), with a k value of 1.0×10^{-2} s ec⁻¹. It is noticeable that a very feeble generation of the intermediate trans-DMAB appeared for the c-AuAg:4.8Pd nanolayers. This side product was almost suppressed for c-AuAg:9.6Pd nanolayers, according to the Raman peak assignments. These results indicated that many Pd atoms were accessible on the facets of the concave surface. However, to the best of our knowledge, the concave AuAg:Pd layer nanostructures prepared with 4.8-9.6 mol% Pd not only presented a most efficient catalytic performance at the interface reaction among various noble metal nanomaterials (Table S1) but also exhibited a strong SERS signal, which was not obtained in a Pd-based alloy nanosystem. $^{40,41,\ 44\text{-}45}$ In fact, c-AuAg:4.8Pd nanolayers could be utilized to detect MG at 1 nM (Figure S12a), showing a 2.1-fold increase in the relative Raman intensity at 1173 cm⁻¹ compared with the detection of 1 nM MG when using c-AuAg:9.6Pd nanolayers (Figure S12b).

In the presence of 4-NTP immobilization, the SPR band of the solid-supported AuAg concave nanolayer and concave AuAg:Pd layer nanostructures exhibited a shift of 7-12 nm to a longer wavelength from the baseline (Figure S13). This phenomenon could be attributed to the local refractive index changes in the vicinity of the plasmonic metal surface.⁴⁶ By using the solid-supported AuAg concave nanolayer sample, the complete consumption of 4-NTP in the monolayer to generate 4-ATP was observed as the interface reaction progressed from 30 min to 210 min (Figure 5c). From 6-90 min, the intermediate

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species trans-DMAB was obtained. To rule out the plasmone driven reduction⁴⁷ of 4-NTP to trans-DMAB the to 42ATP the time-dependent SERS spectra of the 4-NTP-immobilized AuAg samples under laser illumination at λ = 785 nm and 632.8 nm were collected in the absence of NaBH₄ (Figure S14). Neither significant sample signal degradation due to laser damage nor the plasmon-induced reduction reaction⁴⁷ occurred in our colloidal analysis system.

In contrast to the monolayer chemisorption of 4-NTP around the nanowall structure in response to the faster interfacial reduction reaction (k=1.0 x 10⁻² sec⁻¹), the resulting 4-AP products after reduction desorbed from the interface Au as a rate-limiting step and then were released into solution for the following re-adsorption of the 4-NP molecules, enabling continuous consumption of 4-NP molecules in the bulk solution (see Scheme 2a). These multiplex reaction steps caused a lower k value of 7.5 x 10⁻³ sec⁻¹ for the conversion of 4-NP to 4-AP in the solution with c-AuAg:9.6Pd nanolayers (Figure S15). This k value demonstrates the gradual improvement of the 4-NP to 4-AP reaction from ~6.9 x 10^{-3} sec⁻¹ and ~7.1 x 10^{-3} sec⁻¹ when using the solid-supported concave AuAg nanolayer and c-AuAg:4.8Pd nanolayers, respectively. Notably, the conversion of 4-NP to 4-AP occurs very fast (~ 1 min) for the c-AuAg:9.6Pd nanolayers. The atomic ratio of Pd in the ternary nanowall has



Scheme 2. Schematic illustration of a proposed adsorption/desorption and catalytic pathway for the 4-NTP to 4-ATP and 4-NP to 4-AP conversion reactions with c-AuAg:4.8Pd nanolayers. Green, red, and yellow spheres represent Ag, Au, and Pd atoms, respectively.

a pronounced influence on selective catalysis and rapid reduction of the nitro group to an amino group.

It is known that the Pd material is superior among most hydrogen adsorbents in forming metal-H bonds with lower active energy for a large variety of organic hydrogenation systems. ⁴⁸⁻⁴⁹ On the other hand, several Au atoms in the surface of the ternary nanowall are able to absorb the thiol group of 4-NTP. We assumed that the corresponding nitro group of 4-NTP has a polar structure of a positively charged nitrogen atom bonded with oxygen atoms, which would exhibit parallel adsorption to the neighboring electron-enriched gold,4, 41, 50 leading to the formation an inverted U-shaped adsorption configuration, as shown in Scheme 2b. Relying on the chemisorption and polar-polar adsorption, the released electrons supplied by the decomposition of NaBH₄ could intensify the electron transfer from the surface atom sites of the highly electronegative Au atoms to the 4-NTP molecule. Thus, a fast initiation ($\leq 1 \text{ min}$) of the hydrogenation process would be triggered by the neighboring Pd atom after the dissociation of Pd-H bonds. Such a synergistic effect in the interface would improve the reduction rate of 4-NTP through the Au-S linker to selectively generate 4-ATP. In contrast, the thiol-free catalytic reaction of 4-NP did not generate the inverted U binding configuration for the 4-NP at the Au atoms (Scheme 2a) but strongly relied on the adsorption energy to form a pentagonal M-O-N-O-M cyclic intermediate⁴⁹ Several studies reported that reforming the heterogeneous atoms into the alloy catalyst could generate a higher catalytic efficiency. ^{41, 49, 51} Possibly, the incorporation of Pd from 4.8 mol% to 9.6 mol% into the AuAg nanowalls could offer stronger adsorption energy between the Au and 4-NP. Through the assistance of hydrogenation with the Pd-H bonds in the neighboring sites, the catalytic conversion of 4-NP from the nitro group to the amino group could be initiated faster, which is a favorable occurrence in the Pd-enriched surface (see Figure S15).

Conclusions

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In summary, we demonstrated that the application of a CTA⁺/Au/AgNO₃/AA mixture as a growth/etching solution was capable of forming a concave AuAg nanolayer on the surface of a concave Ag nanocube. In addition to the co-reduction of AuAg on the particle surface, the slow reduction kinetics facilitated the galvanic replacement of Ag with AuBr₂-/CTA⁺ micelles, which produced additional AuAg alloy in the interior. This solid support structure maintained active sites in the concave layer that generated a superior SERS signal as well as an improvement of the catalytic performance. Upon reaction with H₂O₂ to oxidize the Ag inner counterpart, producing a hollow interior space, both the SERS and catalytic efficiencies were subsequently dampened due to the removal of active atoms. Therefore, we concluded that examination of the SERS and catalytic efficiencies should be carefully conducted if an etching process must be introduced in the fabrication of a concave particle system. Indeed, this co-reduction/galvanic replacement reaction for achieving the alloying process could be extended to the fabrication of concave AuAgPd nanocubes to promote the hydrogenation catalytic efficiency in combination with SERS detection.

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Conflicts of interest

There are no conflicts to declare.

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A new reaction strategy of the galvanic replacement reaction-assisted caving at six {100} side planes accompanying with interior alloying process was demonstrated to fabricated solid-supported concave AuAg and AuAg:Pd nanolayers. The activity atoms at the concave sites displayed fabulous SERS and improved the hydrogenation reaction with a very high kinetic constant. These enhanced phenomena disappear when the concave nanostructures are etched with H_2O_2 .

