

Ag Dendrite-Based Au/Ag Bimetallic Nanostructures with Strongly Enhanced Catalytic Activity

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Dendritic Ag/Au bimetallic nanostructures have been synthesized via a galvanic replacement reaction (GRR) of Ag dendrites in a chlorauric acid (HAuCl₄) solution. After short periods of time, one obtains structures with protruding flakes; these will mature into very porous structures with little Ag left over. The morphological, compositional, and crystal structural changes involved with reaction time *t* were analyzed by using scanning and transmission electron microscopy (SEM and TEM, respectively), energy-dispersive X-ray spectrometry (EDX), and X-ray diffraction. High-resolution TEM combined with EDX and selected area electron diffraction confirmed the replacement of Ag with Au. A proposed formation mechanism of the original Ag dendrites developing pores while growing Au flakes cover this underlying structure at longer reaction times is confirmed by exploiting surface-enhanced Raman scattering (SERS). Catalytic reduction of 4-nitrophenol (4-NP) by sodium borohydride (NaBH₄) is strongly enhanced, implying promising applications in catalysis.

1. Introduction

Recently, growing interest in bimetallic nanostructures comprised of noble metals such as gold (Au), silver (Ag), platinum (Pt), and palladium (Pd) has been justified by their fascinating optical,^{1,2} electronic,³ and catalytic^{4,5} properties, leading to a wide range of applications, including surface-enhanced Raman scattering (SERS),⁶ biosensors,⁷ and catalysis.⁸ A variety of approaches to preparing bimetallic nanomaterials have been investigated, including simultaneous chemical reduction of mixed metal ions,^{9,10} electrochemical reduction,¹¹ and successive reduction of metal ions on the surface of sacrificial nanoparticles, also known as galvanic replacement reaction (GRR).¹² Among them, as an effective and simple yet still versatile tool, GRR has been extensively employed to synthesize bimetallic nanostructures

in aqueous^{13–16} or organic^{17–19} media, among them hollow/porous^{14,17} and core/shell particles.^{14–16,18} However, their applicability is still limited because of the assembly of individual particles from solution being a major challenge.²⁰ Therefore, growing efforts have been aimed toward creation of already assembled larger bimetallic structures, like nanowires^{21–23} or thin films.^{20,24} However, there are few reports about the creation of bimetallic dendrite structures.^{25,26}

In recent years, metallic dendrites have aroused intensive interest because of their attractive shapes and large surface area, resulting in pronounced surface reaction activity.^{27,28} In particular, noble metal dendrites are widely utilized as catalysts.^{29,30} Bimetallic often exhibit better catalytic activities than the corresponding monometallic counterparts.³¹ We therefore immersed Ag dendrites in a HAuCl₄ solution to undergo GRR. This resulted in bimetallic Ag/Au nanostructures with a novel morphology. At short reaction times *t*, one obtains structures with

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protruding flakes; these will mature into very porous structures with little Ag left over. A series of characterizing techniques, including scanning and transmission electron microscopy (SEM and TEM, respectively), energy-dispersive X-ray (EDX) spectrometry, and X-ray diffraction (XRD), were applied to systematically explore the changes in the morphology, composition, and crystal structure. High-resolution TEM combined with EDX and selected area electron diffraction (SAED) confirmed the replacement of Ag by Au. On the basis of these experimental results, a possible process of how Au covers Ag as the GRR unfolds is presented. By employing rhodamine B (RhB) as the probe molecule, we were able to confirm the suggested formation mechanisms via the structures' SERS effects.

These structures are expected to supply significantly enhanced catalytic activity even compared with monometallic dendrites, because they moreover present the newly introduced metal on the surface of the original dendrite and also present metal/metal interfaces. We therefore explored the products' catalysis of the reduction of 4-nitrophenol (4-NP) by sodium borohydride (NaBH_4). The catalytic activity increased monotonically along with the degree of Ag-to-Au substitution in the investigated range. Even the almost completely substituted product still greatly enhanced catalysis over that available with pure Au porous structures. Catalytic activity increases monotonically over the whole investigated range of Au content, while SERS activity was optimized by a certain time of replacement reaction. This difference in the behaviors of the catalytic and SERS activity is consistent with a strong influence of the changing morphology of the structures.

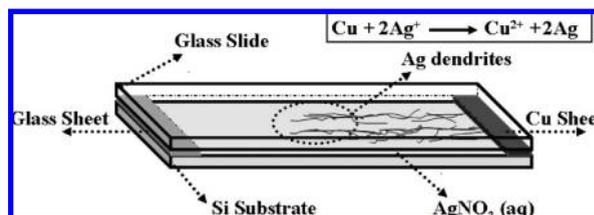
2. Experimental Section

2.1. Chemicals and Materials. Silver nitrate (AgNO_3), chlorauric acid (HAuCl_4), sodium chloride (NaCl), 4-nitrophenol (4-NP), rhodamine B (RhB), and sodium borohydride (NaBH_4) were obtained from Nanjing chemical Reagent No. 1 Factory. Ethanol (99%), acetone (99%), and 100 μm thick copper sheets (> 99.8% pure) were supplied by the Chemical Reagent Co., Ltd., of the National Pharmaceutical Group of China. All chemical reagents were analytical grade and used without further purification. Silicon (Si) wafers were purchased from the No. 55 Research Institute of Electronics Technology of China. A JL-RO100Millipore-Q Plus water purifier supplied deionized water with a resistivity of > 18.0 $\text{M}\Omega\text{ cm}$. The Cu sheet was cut into 3 mm \times 15 mm slices. Cu slices and Si wafers were used after ultrasound cleaning in acetone, ethanol, and deionized water.

2.2. Synthesis of Ag Dendrites. Ag dendrites were synthesized with an apparatus similarly used for electrodeposition³² with some modifications: the electrode was replaced with a thin copper sheet, and the lower surface was changed from glass to a silicon wafer to facilitate later SEM observations. The replacement reaction needs no counter electrode and uses instead a glass slide for a spacer as illustrated in Scheme 1. In a typical procedure, 0.2 mL of 0.05 M aqueous AgNO_3 was placed into the space between an additional glass slide on top and the silicon support. Ag dendrites start to grow immediately from the thin edge of the copper sheet exposed to the solution. The growth process was maintained at room temperature (rt). After 4 min, the solution was drained and the Ag dendrites were allowed to settle on the Si substrate, which was subsequently immersed in water for several minutes to remove residual ions. The products were finally air-dried and stored in air for further usage.

2.3. Preparation of Ag/Au Bimetallic Nanostructures. Pre-prepared Ag dendrites on the Si substrate were immersed in 5 mM HAuCl_4 for a reaction time t of up to 12 min at rt. The AgCl

Scheme 1. Schematic Diagram of the Experimental Apparatus Used To Synthesize Ag Dendrites



byproduct that may possibly have settled on the synthesized structures was removed with a saturated NaCl solution. The products were then transferred from the salt solution into deionized water for further cleaning, which was repeated several times. The products were finally air-dried before analysis.

2.4. Characterization and Study of Catalytic and SERS Activities. SEM analysis was performed on a FESEM microscope (Sirion XL, FEI, Hillsboro, OR) operated at 5 kV. TEM analysis was conducted with a JEOL microscope (JEM-200CX) operated at 200 kV. Both electron microscopes were equipped with an EDX spectrometer. XRD measurements were conducted on a SHIMADZU XRD-6000 instrument with $\text{Cu K}\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$). To study the catalytic activity, 0.6 mg of the Ag/Au bimetallic product was removed from the Si substrate and suspended in 2.8 mL of 4-NP ($7.1 \times 10^{-5} \text{ M}$) while being constantly stirred at rt. A freshly prepared aqueous solution of NaBH_4 (0.20 mL, $1.5 \times 10^{-1} \text{ M}$) was then added. The mixture was immediately transferred into a quartz cuvette with an optical path length of 1 cm, and UV–visible absorption spectra were recorded to monitor changes in the reaction mixture (Shimadzu UV-3600 UV-vis-NIR spectrophotometer).

For SERS investigation, a 10^{-6} M aqueous RhB solution was dropped on the as-prepared samples. The samples were then dried in N_2 and subjected to Raman scattering measurements using the 514.5 nm line of an argon laser (Jobin-Yvon T64000 triple Raman system). The whole SERS measurement was taken at rt.

3. Results and Discussion

Since the standard electrode potential of the $\text{AuCl}_4^-/\text{Au}$ pair [0.99 V vs standard hydrogen electrode (SHE)] is higher than that of the AgCl/Ag pair (0.22 V vs SHE), silver undergoes a GRR with AuCl_4^- ions according to the following equation:



The oxidation of Ag^0 into Ag^+ leads to the gradual consumption of Ag and, at the same time, the production of Au^0 , which is deposited on the Ag dendrites.

Figure 1a gives a typical FESEM image of Ag dendrites before they reacted with HAuCl_4 . The image reveals the self-similar hierarchical structure expected for a fractal dendrite formed by diffusion-limited growth. The branching angles are all 60° . As more clearly visible in the inset, the trunks and branches mostly consist of almost hexagonal “beads”, the average size of which is ca. 100 nm. The morphological changes during the reaction can be seen in Figure 1b–d. As is shown in Figure 1b, while the overall shape is still that of the initial dendrite, the previously edgy beads quickly evolve into more spherical shapes and the protruding flakes can already be identified even when the reaction lasts only 4 min. If the reaction proceeds for 8 min (Figure 1c), the dendrite is covered with flakes that stand on their edges on top of it. The flakes have a smooth surface and uniform thickness. The inset is a magnified image, from which one finds that the flakes also often mutually intersect and overlap. Moreover, from this inset, one can already discern how the flakes form the walls of

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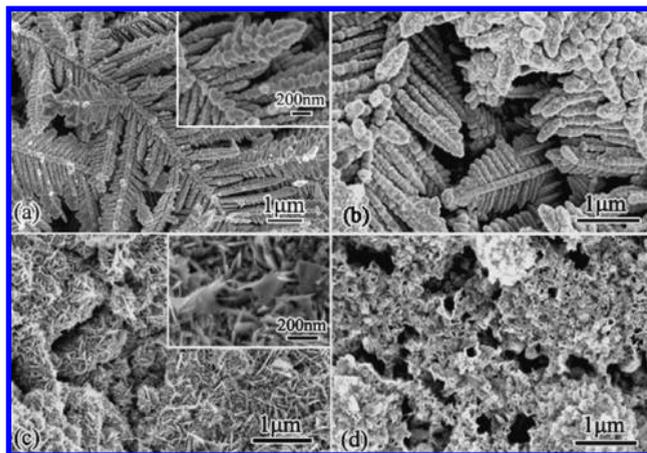


Figure 1. FESEM images showing (a) the initial Ag dendrites (reaction time zero) and Ag/Au structures after GRR for (b) 4, (c) 8, and (d) 12 min. The insets are corresponding magnified views.

the cavities that are the most recognizable feature of the structures determined at even longer reaction times (we will henceforth always call Au-wall-build pores “cavities” to clearly distinguish them from the pores due to removal of Ag from the original Ag dendrite). If the reaction proceeds for 12 min, almost all the flakes seem to disappear and numerous cavities are visible instead (Figure 1d).

To examine the composition of the structures, EDX measurements were also performed. In the case of the initial Ag dendrite, the spectrum shows only the for Ag characteristic peaks (Figure 2a). The gradual depression of Ag peaks and the development of Au ones (Figure 2b–d) are direct evidence for the ongoing replacement of Ag with Au during the whole reaction time. Semiquantitative EDX analysis estimates the Au content of the four samples to be 0, 33, 60, and 90% for 0, 4, 8, and 12 min, respectively.

XRD patterns (Figure 3) imply that the samples are crystalline with face-centered cubic (FCC) structure, as five diffraction peaks can be indexed to characteristic diffractions from (111), (200), (220), (311), and (222) of Ag and Au crystals (JCPDF No. 4-0783 and 4-0784). After reaction with AuCl_4^- ions for 8 min, the XRD pattern is almost identical (curve b) with that from the original Ag dendrite (curve a). This is expected since the unit cell size of Ag/Au alloys changes by less than 1% over the entire range from pure Ag to pure Au, and no superlattice reflexes are observed in the bimetal.¹⁰ It is noteworthy that the intensity ratios of the (200) to (111) diffraction peaks (0.26 for panel a and 0.21 for panel b) is much lower than that of the bulk metals (e.g., ~ 0.53 for silver³³). This indicates that the (111) planes of the investigated structures are preferentially oriented parallel to the surface of the supporting substrate, although the initial silver dendrites do not know the location of the substrate when they begin to grow. This orientation is thus given by the two-dimensional structure of the initial dendrites that fall flat onto the Si wafer when the solution is drained after their synthesis. The GRR apparently largely conserves this orientation inside the silver dendrites throughout all the radical morphological changes.

Figure 4a shows a TEM image of two typical Ag dendrites whose shape was discussed above with the help of FESEM observations (Figure 1a). From the SAED pattern of a region in a tip (see the inset), we identify the (111), (200), and (311) planes of FCC Ag. The dendrite is highly crystalline, yet the two sets of

diffraction spots also indicate the existence of a twinned structure. From the HRTEM data (Figure 4b), we can also detect a lattice spacing of 0.235 nm which is the interplanar spacing of Ag (111). After reacting with AuCl_4^- ions for 8 min, the Ag dendrites have become porous (Figure 4c) because of the consumption of Ag. The circled region's SAED pattern (top inset of Figure 4c) displays discontinuous concentric rings, which implies a polycrystalline bimetallic Ag/Au structure due to the deposition of Au on Ag dendrites. The generation of Au is reanalyzed by the EDX recorded from the same area (bottom inset of Figure 4c). The Ag/Au bimetal has an Au atomic percentage of 58.4%, which confirms the result reported with Figure 2c. The polycrystalline nature of the bimetallic nanostructures is also seen in the HRTEM image (Figure 4d); various domains with different crystallographic orientations positioned around a pore can be identified. Analyzing the lattice spacings of the various domains reveals ones that can be assigned to (111) and (200) planes. Since the lattice structures of Au and Ag are too similar, it cannot be established whether these domains are Au, Ag, or mixed regions. The mutual solubility of Ag and Au and high diffusion rates at high reaction temperatures (e.g., boiling) result in the formation of single crystalline Au/Ag alloys.³⁴ The polycrystalline nature of the obtained nanostructures is therefore to be expected from our rt experiments. One can conclude that the GRR turned almost single crystalline Ag dendrites (up to twinning) into polycrystalline bimetallic Ag/Au nanostructures.

On the basis of the analysis mentioned above, a possible process of how Au covers Ag as the GRR unfolds is briefly presented as follows (Scheme 2). Initially, the GRR between Ag and AuCl_4^- deposits gold nuclei on Ag dendrites (Scheme 2a). Subsequently (Scheme 2b), the nuclei grow into flakes while nucleation continues, resulting in different sized flakes later in the process. Also, Ag is depleted, leading to pores in the Ag dendrite. The Ag surface is progressively covered with gold, and the concentration of AuCl_4^- gradually decreases, both slowing the GRR so that nucleation is terminated (Scheme 2c). Finally, a porous bimetallic structure results from cavities between Au flakes and pores inside the more and more depleted original Ag dendrite (Scheme 2d), where the Ag pores are basically hidden from view by the Au flakes.

To further confirm the suggested process, one can employ SERS measurements of the various nanostructures. We used RhB as the probe molecules and the 514.5 nm line of an argon laser as excitation, to ensure that the SERS effects are sensitive only to the Ag yet still strong with little Ag present. Au is completely unresponsive to this excitation because its nanostructures' plasmon resonances are well-known to be further in the red wavelengths. In this way, one can monitor the covering of the Ag by the Au. We chose RhB as the probe molecule because of its large Raman cross section, leading to strong SERS signals even if the Au has already replaced much of the Ag substrate. Figure 5 shows Raman spectra of substrates prepared with one drop of a 10^{-6} M RhB solution. Figure 5a shows the result when using a bare Si substrate, for the sake of comparison. It is a featureless spectrum at the resolution chosen. Panels b–f of Figure 5 are the spectra of RhB adsorbed on Ag dendrites before GRR (0 min) and after GRR with AuCl_4^- ions for 2, 4, 8, and 12 min, respectively. Most characteristic Raman shifts agree with the literature³⁵ (left inset), and only a few Raman shifts (underlined values) have no previous

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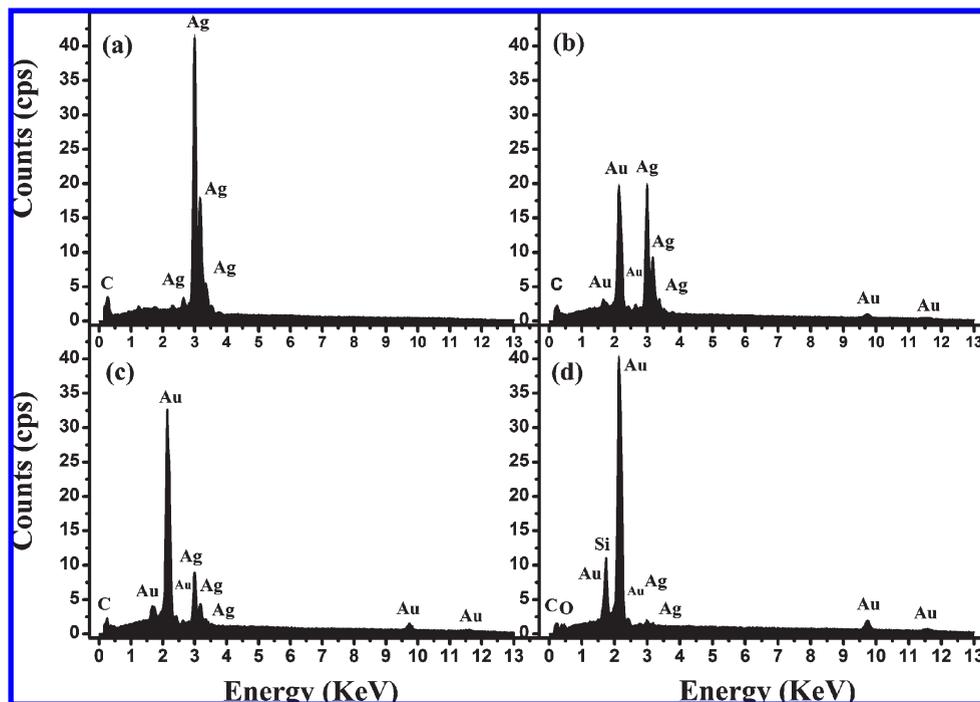


Figure 2. EDX profiles showing compositional information about (a) the initial Ag dendrites and Ag/Au structures after GRR for (b) 4, (c) 8, and (d) 12 min.

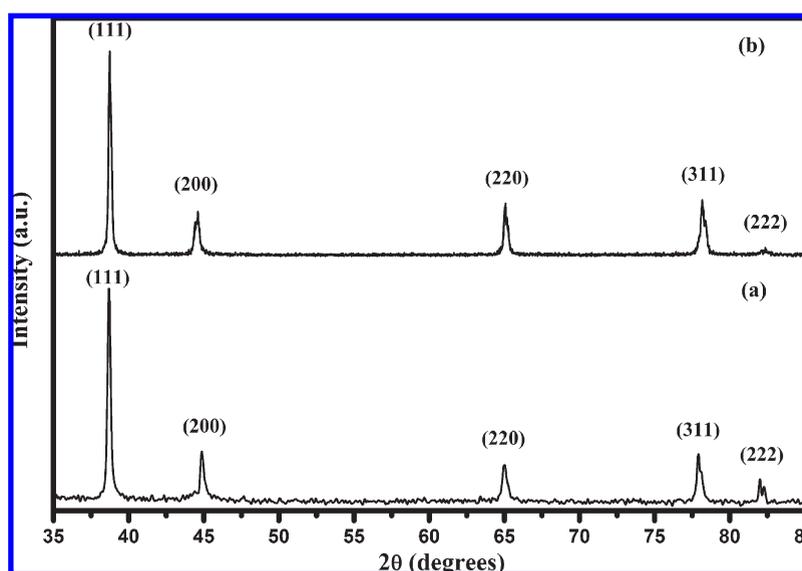


Figure 3. XRD patterns of Ag dendrites (a) and the Ag/Au ($t = 8$ min) sample (b).

assignments. It is also noteworthy that all these curves show a base slope due to the fluorescence extinction effect.³⁶

From the four right bars that compare the plateau with the intensity of the strongest peak (aromatic C–C stretching at ca. 1649 cm^{-1}) in curves b–e, we find that the Raman enhancements by the Ag/Au 2 and 4 min samples are both greater than that of pure Ag dendrites, although the SERS effectiveness of Ag is usually better than that of Au or as investigated alloys.³⁷ This SERS enhancement may be related to several factors. First, surfaces of bimetals provide more possibilities for molecules to

deposit on the boundaries between Ag and Au domains.⁶ Second, adequate amounts of Au in a homogeneous alloy (solid solution) may intrinsically enhance the SERS activity. However, since the intrinsic activity of Ag is much higher,³⁸ the most important reason may not be related to the added Au directly, but rather the corresponding morphological change of the underlying Ag dendrite. The GRR leaves pores where Ag is depleted. High-curvature features can cause very large enhancement (lightening rod effect) for molecules adsorbed on the tips of needles or on edges.³⁹ Two close metallic surfaces can enhance the electromagnetic

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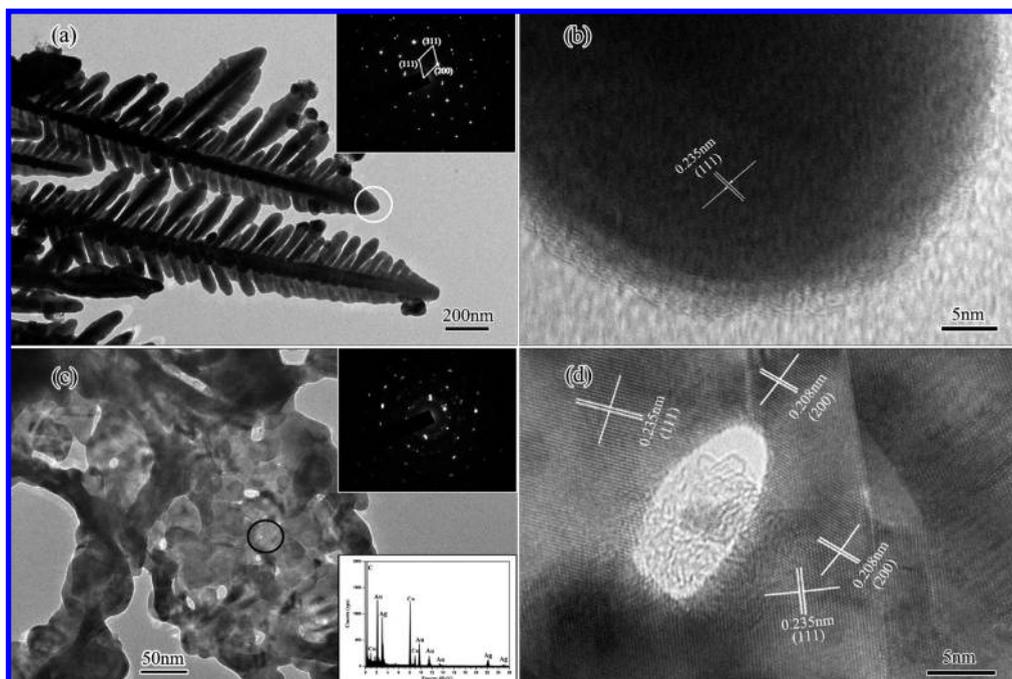
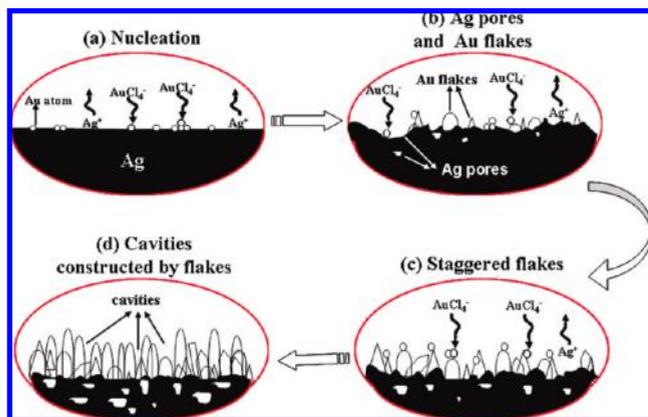


Figure 4. (a) TEM image of a typical Ag dendrite. The inset is the SAED pattern from the circled region. (b) HRTEM image of the circled area in panel a. (c) High-magnification TEM image of an Ag/Au ($t = 8$ min) sample together with the SAED pattern (top inset) and the EDX profile (bottom inset) from the circled region. (d) HRTEM image of the circled area in panel c.

Scheme 2. Formation of Bimetallic Ag/Au Nanostructures in GRR



(EM) field around molecules absorbed between them, which leads to SERS enhancement.^{40,41} However, as the GRR time t increases from 2 min to longer times, SERS enhancement again decreases. This confirms the increase in SERS-inactive Au covering active Ag. Especially the 8 and 12 min samples also possess rough surfaces and even more parallel flakes. However, as shown in curves e and f, their SERS enhancement is much below that of even the initial unmodified Ag dendrites. This is first because compared with that of the 4 min sample, the content of the SERS inert Au increases further. Again, this may be due to complex alloy surface chemistry or in the case of GRR (which is also used in ref 6) simply due to the fact that deposited Au increasingly starts to change and even more simply hide the rough SERS-active Ag structure beneath (see Scheme 2). In conclusion, the roughness of Ag increases strongly at the beginning (e.g., $t = 2$ min). However, as the time further increases (e.g., $t = 4$ min),

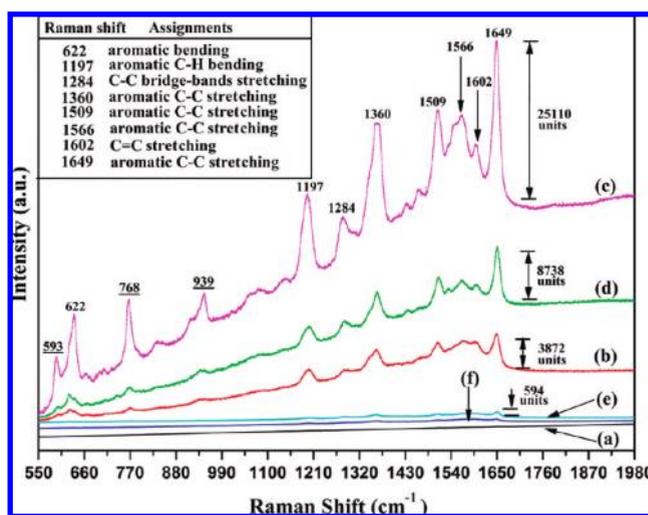


Figure 5. Raman spectra of 10^{-6} M RhB on (a) bare Si substrate and on substrates covered by (b) Ag dendrites or (c–f) Ag/Au nanostructures ($t = 2, 4, 8,$ and 12 min, respectively).

a larger amount of Au flakes covers the Ag, which, although it may still increase in roughness, is also hidden beneath the Au surfaces. When the reaction time increases to 8 and 12 min, most of the Ag surfaces are covered by Au. By investigating the SERS behavior, we can employ it to monitor how Au covers Ag as the GRR unfolds.

The morphology and compositional information obtained motivated us to explore the catalytic activity of the nanostructured Ag/Au bimetals. The reduction of 4-NP by NaBH_4 in aqueous solution is rapid and easily monitored and thus a model reaction.^{42,43} The UV–visible absorption spectrum of the aqueous

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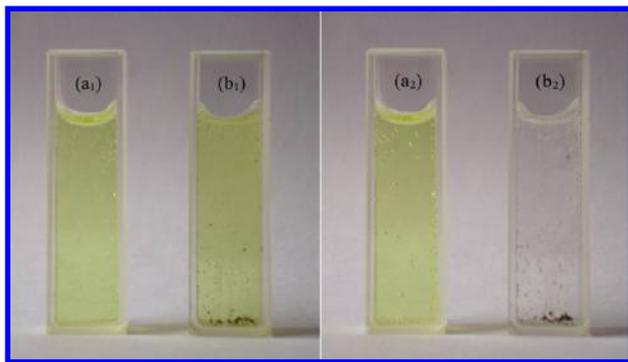


Figure 6. Photographs of the reduction of 4-NP by NaBH_4 in the absence (a_1 and a_2) and presence (b_1 and b_2) of Au/Ag ($t = 8$ min) nanostructures. Tubes a_1 and b_1 show the initial mixtures ($t = 0$), and tubes a_2 and b_2 were taken at 5 min.

mixture of 4-NP and NaBH_4 has an absorption maximum at 400 nm due to the 4-NP ion under alkaline conditions. Without the addition of catalyst, the reduction will not proceed, the maximum absorption peak remains unaltered over time, and the mixture maintains a yellow color (Figure 6, a_1 and a_2).

However, when even only 0.6 mg of purified nanostructured Ag/Au bimetals ($t = 8$ min) is added (very little indeed compared with usual amounts of catalyst), reduction of 4-NP proceeds rapidly as can be seen from the bleaching of the yellow color (Figure 6, b_1 and b_2). Time-dependent UV–visible absorption spectra (Figure 7a) show the successive decrease in the absorption peak at 400 nm and concomitant development of a new peak at 300 nm corresponding to 4-aminophenol (4-AP), the reduction product of 4-NP. These results suggest that the bimetallic Ag/Au nanostructures are an effective catalyst for similar reactions by acting as an electron relay system.⁴²

Because the concentration of BH_4^- is very high compared with those of 4-NP and catalyst, it can be assumed to be essentially constant during the reaction. This high concentration protects the 4-AP from aerial oxidation.⁴³ Therefore, pseudo-first-order kinetics with respect to 4-NP was used to evaluate the catalytic rate. A good linear correlation with time in an $\ln A_{400}$ (A_{400} is the absorbance at 400 nm) versus reduction time τ plot was obtained (inset of Figure 7a). The pseudo-first-order rate constant determined from this plot is $6.07 \times 10^{-3} \text{ s}^{-1}$, which is larger than the previously reported constants of many catalysts.^{43,44} This is especially striking when the minute amount of catalyst used (0.6 mg) is taken into account. The ratio of rate constant to the amount of spongy gold⁴⁴ catalyst used for example is $0.35 \text{ s}^{-1}/\text{g}$, which is much lower than the value of $10.1 \text{ s}^{-1}/\text{g}$ for the Ag/Au ($t = 8$ min) dendrites.

We have repeated these catalytic experiments on Ag dendrites incubated in HAuCl_4 for 0, 4, and 12 min. The corresponding rate constants (Figure 7b) increase with reaction time t . In the case of the reduction of solvated 4-NP by BH_4^- , the kinetic barrier between the two negative ions is too high for the reaction to proceed unmediated. The presence of a catalyst (e.g., Ag dendrites) is important for this redox reaction. Donors like the BH_4^- ions supply electrons to the catalyst and thereby allow the 4-NP absorbed on the catalyst to take electrons at their leisure. With respect to the higher catalytic activity exhibited by Ag/Au bimetals, this may be first related to the number of Ag/Au interfaces. Ag has a lower work function than Au. Therefore, electrons leave the Ag from a thus depleted region near an Au/Ag interface

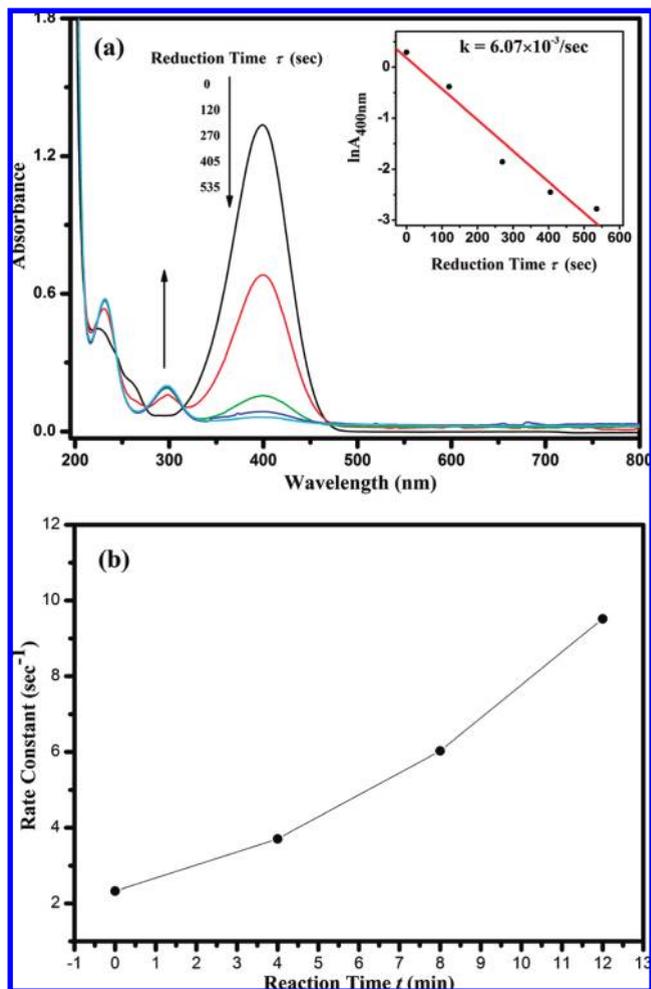
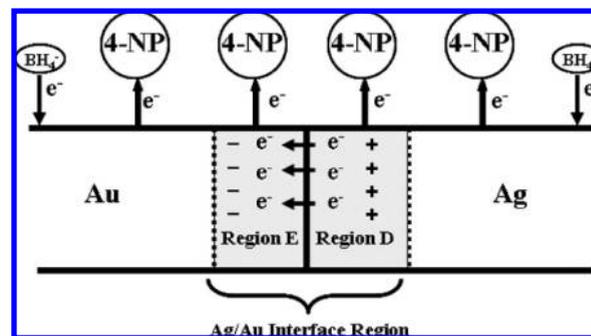


Figure 7. (a) Successive UV–vis absorption spectra of the reduction of 4-NP by NaBH_4 in the presence of Au/Ag ($t = 8$ min) nanostructures. The inset shows the logarithm of the absorbance at 400 nm vs reduction time. (b) Rate constant of 4-NP reduction vs reaction time t of Ag dendrites with a HAuCl_4 solution.

Scheme 3. Diagram of the Bimetallic Ag/Au Interface



(see Scheme 3, region D) into the Au, which ends up with an electron-enriched region (region E). The existence of these surplus electrons added inside the Au facilitates the uptake of electrons by 4-NP molecules that happen to be close to (on top of) these regions. The more interfaces there are, the more such regions with surplus electrons exist. This in turn increases the chances for randomly absorbed 4-NP to happen to be on top of such regions. According to SEM analysis (Figure 1), the number of accessible Ag/Au interfaces initially increases (see also Scheme 2) with

(44) Rashid, M. H.; Bhattacharjee, R. R.; Kotal, A.; Mandal, T. K. *Langmuir* 2006, 22, 7141–7143.

reaction time until ~ 8 min. At some point in time, the number of accessible interfaces is bound to decrease again, because Au flakes start to cover Ag/Au interfaces (make them inaccessible) and Ag is more and more depleted. That the rate constant still monotonically increases implies that another reason besides the existence of Ag/Au interfaces is responsible for the catalytic activity, either already initially or taking over at some later point. Pure gold is generally not catalytic unless its particle size is < 5 nm,⁴⁵ and the found rate constant of our 12 min sample (90% Au) is larger than that of conventional pure Au catalysts.⁴⁴ This strongly suggests that morphology is mostly responsible for the high catalytic activity of the dendrites with > 8 min (or even below). The Au structure that is achieved by the GRR seems to be rather unique, providing a shape that should be investigated in detail in future work. As of now, one can only speculate about how the way in which a certain size of Au feature (flake or cavity) is presented on the surface of the structure influences catalytic activity. However, regardless of these morphological details, the economical aspect of this bimetallic morphology is certain: Instead of having expensive material also making up parts of the structure that are actually inaccessible to reactive molecules (like inside stems of dense dendrites), these structures present a very expensive catalyst (here Au) precisely where it is needed, namely at the accessible surface, on top of a much less expensive substrate (Ag).

It should be noted that the discussion of the influence of morphology on SERS effects and the discussion afterward about

(45) Haruta, M.; Kobayashi, T.; Sano, H.; Yamada, N. *Chem. Lett.* **1987**, *16*, 405–408.

the catalytic reaction rate are consistent: the described interplay between pores in Ag and the Au flakes taking over and covering them is consistent with both the monotonous increase in the reaction rate and the observed maximum in the SERS signals.

4. Conclusions

In conclusion, bimetallic Ag/Au nanostructures were synthesized via galvanic replacement reaction. Different reaction times resulted in different morphologies, compositions, and crystal structures of the corresponding products, which were characterized by a series of techniques. On the basis of the results, the growth mechanism as the GRR unfolds is discussed. The original Ag dendrites develop pores, while the growing Au flakes slowly cover this underlying structure. The suggested process was further confirmed by SERS effects that respond strongly to the initial increase in roughness and then monitor how Au features replace and hide the Ag substrate. The exploitation of SERS effects in this work is a new application of SERS based on its more traditional use in the detection of molecules. Promising potential applications, the formed bimetallic Ag/Au nanostructures show excellent catalytic activity toward the reduction of 4-NP by NaBH_4 . A monotonic increase in rate with Au content should motivate further research involving structures produced with even longer reaction times.

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