Gold Nanorod-Seeded Growth of Silver Nanostructures: From Homogeneous Coating to Anisotropic Coating

Yanjun Xiang, Xiaochun Wu, Dongfang Liu, Zhizhen Li, Weiguo Chu, Lili Feng, Ke Zhang, Weiya Zhou, and Sishen Xie

Beijing National Laboratory for Condensed Matter Physics, Institute of Physics, Graduate School of the Chinese Academy of Sciences, Beijing 100080, People’s Republic of China, and National Center for Nanoscience and Technology, Beijing 100080, People’s Republic of China

Received October 7, 2007. In Final Form: December 7, 2007

Single crystalline gold nanorods (Au NRs) dominated by {110} side facets were employed as seeds to tailor the deposition of Ag. Apart from homogeneous coating, anisotropic coating of Ag was observed and resulted in an orange slice-like shape for the Au@Ag nanocrystal. Different growth rates for the {110} side facets were responsible for this shape: among the four {110} facets, two of the neighboring {110} facets grew more quickly and another two grew more slowly, thus inducing the anisotropic deposition of Ag around the Au NR. This growth behavior is believed to be a consequence of competition between the strong stabilization of cetyltrimethylammonium bromide (CTAB) molecules to the {110} facets of Ag and minimization of the overall surface energy. Although the reason for the anisotropic coating remains to be clarified, our results lead to one important conclusion: The interaction of CTAB and metal can be utilized to tune the shapes of bimetallic structures.

Introduction

Au and Ag nanocrystals have attracted much attention particularly due to their potential applications in chemical and biochemical sensing, medical diagnostics and therapeutics, and biological imaging. These potential applications are closely related to their unique optical properties, especially surface plasmon resonance (SPR). Because of the strong dependence of SPR on the shape of metal nanocrystals, great effort has been made concerning their shape-controlled synthesis. As one example, seed-mediated techniques have been developed to control the shape of noble metal nanostructures, where the seeds are often spherical shapes without well-defined facets. A subsequent random symmetry breaking event occurs to initiate the anisotropic growth of metal. Growth rate ratios of different facets determine the final shape. Up to now, how to intentionally control the breaking of the initial symmetry is an interesting yet unsolved issue. As the growth rate ratios determine the final shape, we decided to use metal nanocrystals with well-defined facets as seeds to mediate the shape-controlled synthesis of metal nanocrystals. On one hand, this method avoids the problem of symmetry breaking; on the other hand, the growth of different facets can be well-followed, thus providing valuable information on the controlled growth of different lattice planes. The latter will help us guide the symmetry breaking in the case of small spherical seeds as well. Single crystalline gold nanorods (Au NRs) were synthesized with a high quality and yield. Au NRs have a cylindrical shape with well-defined facets: The side facets consist of the {110} and {100} surfaces, whereas the endcaps are enclosed by the {111} and {110} planes. Such a well-defined and rich surface structure undoubtedly provides us with an ideal seed to study the growth behaviors of different facets. In addition to the well-defined facets, amazingly, unstable {110} facets dominate in Au NRs. This is rare for gold nanocrystals considering their high surface energy. The appearance of the {110} facets is suggested to bring some novel properties to the Au NRs. Recently, we have demonstrated one example. By using the Au NRs as seeds, competing growth of the Pd shell on the {110} and {100} side facets of the Au NR was observed. This led to the disappearance of the unstable {110} side surfaces and the formation of a square-shaped Pd shell/Au core bimetallic nanorod.

Despite the success of the seed-mediated growth in obtaining a variety of shapes for gold nanocrystals, its extension to silver has been quite limited. Hence, using the gold nanocrystals as templates is a nice alternative. On the basis of this idea, Au core/Ag shell (Au@Ag) nanorods were formed using Au NRs as templates. Often, instead of cylindrical shapes, dumbbell shapes are often observed as the dominate shapes for Au@Ag

1 Graduate School of the Chinese Academy of Sciences.
2 National Center for Nanoscience and Technology.
3 To whom correspondence should be addressed. E-mail: (X.W.) wuxc@nanoctr.cn or (S.X.) ssxie@aphy.iphy.ac.cn.
4 Department of Nanochemistry, National Center for NanoScience and Technology.
5 Department of Nanochemistry, National Center for NanoScience and Technology.
6 Department of Nanochemistry, National Center for NanoScience and Technology.
7 Department of Nanochemistry, National Center for NanoScience and Technology.
8 Department of Nanochemistry, National Center for NanoScience and Technology.
9 Department of Nanochemistry, National Center for NanoScience and Technology.
10 Department of Nanochemistry, National Center for NanoScience and Technology.
11 Department of Nanochemistry, National Center for NanoScience and Technology.
12 Department of Nanochemistry, National Center for NanoScience and Technology.
13 Department of Nanochemistry, National Center for NanoScience and Technology.
14 Department of Nanochemistry, National Center for NanoScience and Technology.
15 Department of Nanochemistry, National Center for NanoScience and Technology.
16 Department of Nanochemistry, National Center for NanoScience and Technology.
17 Department of Nanochemistry, National Center for NanoScience and Technology.
18 Department of Nanochemistry, National Center for NanoScience and Technology.
19 Department of Nanochemistry, National Center for NanoScience and Technology.
20 Department of Nanochemistry, National Center for NanoScience and Technology.
The difference in the packing density of cetyltrimethylammonium bromide (CTAB) bilayers on different facets is believed to be responsible for the formation of the dumbbell shape: CTAB molecules are expected to bind much more strongly to the less closely packed {110} surface than to the {111} facets.\(^{11}\) Hence, more metal deposition occurs at the endcaps. Overall, the two ends of the nanorod become thicker than the middle of the rod, thus forming the so-called dumbbell shape. The same mechanism also is believed to be responsible for the dumbbell shapes observed in the overgrowth of Au on Au NRs.\(^{12}\) Here, rather than using Au NRs as templates, we employed them as seeds to tune the growth rates of different surfaces for the shape control of the Ag shell. Instead of the dumbbell shape, we observed either a cylindrical shape or an orange slice-like shape according to the amounts of added Ag ions. At lower Ag\(^+\) concentrations, Ag homogeneously grows on the Au NRs. The resulting Au@Ag nanorod maintains its original cylindrical shape. At higher Ag\(^+\) concentrations, anisotropic Ag coating occurs, which results in an orange slice-like shape for the Au@Ag nanocrystal. As compared to the octagonal cross-section of the Au NR, the Au@Ag nanocrystal has a cross-section of small truncated squares/rectangles. It is the Ag {110} side facets that become enlarged despite their higher surface energies. Surprisingly, the four {110} side facets show different growth rates: Two of the neighboring {110} facets grow more quickly, and the remaining two grow more slowly. The consequence is that the position of the Au core is closer to the two {110} Ag side facets that grow more slowly. Although the mechanism behind this growth mode needs further investigation, our results demonstrate that seeding anisotropic Au NRs is an effective way to fabricate different shapes for Au@Ag nanostructures.

**Experimental Procedures**

**Chemicals.** Sodium borohydride (NaBH\(_4\)), hydrogen tetrachloroaurate(III) trihydrate (HAuCl\(_3\)·3H\(_2\)O), CTAB, silver nitrate (AgNO\(_3\)), sodium hydroxide (NaOH), and L-ascorbic acid (AA) were purchased from Sigma and used as received. Milli-Q water (18 M\(_2\) cm resistivity) was used for all solution preparations. All glassware used in the synthesis procedures was cleaned in a piranha solution (70 %H\(_2\)SO\(_4\)/30% H\(_2\)O\(_2\)) and was boiled for 30 min.

**Synthesis of Au@Ag Core/Shell Nanocrystals.** Initial Au NRs were synthesized using the seed-mediated growth procedure.\(^{12}\) The aspect ratio (AR) of the Au NRs used here was 3.6. After preparation, the Au NRs were purified by centrifugation (12 000 rpm for 10 min) twice. The reduction power of AA is pH dependent.\(^{12}\) AA is incapable of reducing silver ions, whereas monoanionic ascorbate species do (Figure S1 in Supporting Information). Therefore, we changed the pH value of the growth solution to 10 by adding NaOH. The formation of the Ag shell was as follows: Five sets of the purified Au NR solution (4 mL, 1 × 10\(^{-3}\) M) were mixed separately with 2 mL of a 0.1 M CTAB aqueous solution containing 22 μL of 0.1 M AA. For each set, a certain amount (25, 45, 65, 85, or 110 μL) of the 0.01 M AgNO\(_3\) aqueous solution was added. Finally, the NaOH solution was added to initiate the deposition of the Ag shell at pH 10. All five sets were then shaken vigorously and put in a 30 °C water bath. Within several minutes, the colors of the solutions changed from brown to green, blue, purple, rose, and orange according to the amount of added Ag\(^+\) ions. The formation of the Ag shell was verified by XRD measurements (Figure S2 in Supporting Information). Except for elemental Ag, neither Ag\(_2\)O nor AgBr was detected.

FTIR measurements indicated that similar to the Au NRs,\(^{8}\) the surface of the Au@Ag nanocrystals was also capped by CTAB molecules (Figure S3 in Supporting Information). In the case of fine-tuning the thickness of the Ag shell for isotropic coating, Au NRs having lengths of 61 ± 7 nm and widths of 14 ± 2 nm were used as seeds.

**Instruments.** UV–vis absorption spectra were obtained on a PerkinElmer UV–vis/NIR spectrophotometer (Lamda 950). For transmission electron microscopy (TEM, Tecnai F30) and scanning electron microscopy (SEM, Hitachi S-5200) measurements, solutions were centrifuged (8000 rpm 10 min) 3 times to remove excess amounts of CTAB.

**Results and Discussion**

**From Homogeneous Coating to Anisotropic Coating.** Figure 1 shows the shapes of the Au@Ag core/shell nanocrystals obtained with increasing Ag\(^+\) ion concentrations in the growth solution. The Au NR seeds have an average aspect ratio of 3.6. The control experiment indicated that the reduction of Ag\(^+\) ions can be neglected in the growth solution without adding Au NR seeds (Figure S4 in Supporting Information). At lower Ag\(^+\) concentrations (4.16 × 10\(^{-3}\) M), less Ag atoms are deposited on the Au NRs. The Ag shell seems to be more or less homogeneous over the entire nanorod. The resulting bimetallic nanorod shows no obvious shape change and remains in the original cylindrical rod shape of the Au NR (Figure 1b). When the Ag\(^+\) concentration reaches a certain value (7.5 × 10\(^{-3}\) M), however, anisotropic Ag coating occurs, which results in an orange slice-like shape for the Au@Ag nanocrystal (Figure 1c). An obvious transformation from homogeneous coating to anisotropic coating takes place at an Ag/Au molar ratio of 0.49 for this sample. Increasing the Ag\(^+\) concentration further (from 1.1 × 10\(^{-4}\) to 1.8 × 10\(^{-4}\) M), the width of the orange slice also increases (Figure 1d–f), indicating
the deposition of Ag at the long axis direction of the Au NR was an increased anisotropic degree. In the case of anisotropic coating, the Au@Ag core/shell nanocrystals with Ag/Au molar ratios as described in Figure 1. The inset in panel A shows the relationship between the longitudinal SPR position and the Ag/Au molar ratio. (B) Photographs of nanocrystal dispersions corresponding to the curves in panel A.

Figure 2. (A) UV–vis extinction spectra of (a) Au NRs and (b–f) the Au@Ag core/shell nanocrystals with Ag/Au molar ratios as described in Figure 1. The inset in panel A shows the relationship between the longitudinal SPR position and the Ag/Au molar ratio. (B) Photographs of nanocrystal dispersions corresponding to the curves in panel A.

an increased anisotropic degree. In the case of anisotropic coating, the deposition of Ag at the long axis direction of the Au NR was less. Corresponding UV–vis extinction spectra of the as-prepared Au NR seeds and Au@Ag core/shell nanocrystals are illustrated in Figure 2. The as-prepared Au NRs show a longitudinal SPR peaked at 765 nm and a transverse SPR band centered at 505 nm. With increasing the overall amount of the deposited Ag, the longitudinal SPR band blue-shifts obviously (Figure 2, inset), while the transverse SPR band blue-shifts slightly and is finally smeared out by the former. At a Ag/Au ratio of 0.49, two new peaks (340 and 380 nm) appeared at the short wavelength region. At this ratio, the orange slice-like shape has formed, indicating that the appearance of these two peaks might relate to the unsymmetrical structure of the Ag shell. With increasing the Ag\(^{+}\) ion amount, the peak at 340 nm was gradually smeared out by the 380 nm band. The latter blue-shifts slightly with increasing the Ag\(^{+}\) ion amount. At higher concentrations of Ag\(^{+}\) ions, the extinction spectra are dominated by two bands: a shorter wavelength SPR and a longer wavelength SPR. The intensity of the latter was finally overtaken by the former. The aqueous solutions of these nanocrystals show bright and distinctive colors when their long wavelength SPR bands are tuned across the visible spectrum (Figure 2B).

Shape Evolution of the Orange Slice-like Ag Nanoshell. To obtain more insight into the formation of the orange slice structure, its evolution process was monitored via UV–vis extinction spectroscopy and SEM measurements (Figure 3). For SEM measurements, a certain amount of the growth solution was taken out at a predetermined time and put into an acidic solution (pH 3) to stop the reaction. Figure 3a is the extinction spectrum of the original Au NRs, showing a strong longitudinal SPR band maximized at 815 nm and a weak transverse SPR band centered at 507 nm. After a reaction time of only 2 min, the longitudinal SPR band showed an enormous blue-shift (92 nm), accompanying a great enhancement in its extinction intensity. Additionally, at the shorter wavelength region, 340 and 380 nm peaks appeared, indicating an anisotropic growth mode. With the proceeding of the reaction, the longitudinal SPR band further blue-shifted, and the intensities of all peaks continued to increase due to the deposition of Ag. After 30 min, the reaction nearly finished and a 217 nm blue-shift was achieved. For SEM measurements, images of some typical intermediate shapes were taken. It was evident that the anisotropic growth took place immediately after the initiation of the reaction. With the proceeding of the growth, the fat side of the slice became large.

For two intermediate shapes with relatively smaller slice sizes, we were able to observe some standing nanorods with their endcaps pointing toward us (Figure 4a,b). Instead of the octagonal cross-section of the Au NR, the dominant cross-sections of the Au@Ag nanocrystals were squares/rectangles with small truncations at the corners. It is known that the side planes of the Au nanorod are enclosed alternatively by four \{110\} facets and four \{100\} facets. The appearance of the truncated square cross-section indicates that the growth rates of the \{110\} and \{100\} side facets are obviously different. This suggests two possible growth paths. One is that four \{110\} side facets grow quickly and become reduced, leaving the four \{100\} facets as the dominant side facets. The other is the opposite case where the four \{100\} side facets grow quickly and become the truncated parts of the square/rectangle. In addition, for most Au@Ag nanocrystals, the position of the Au core is closer to one corner of the square/rectangle. This indicates that among the four dominant side facets, two neighboring side facets grow more quickly than the other two. This is schematically drawn in Figure 4c for the \{100\} facet and in Figure 4d for the \{110\} facet as the dominant side facets, respectively.

Figure 5a shows a HRTEM image of an Au@Ag NR with a thin and homogeneous Ag shell. It clearly reveals the formation of a core/shell structure: The bright and dark regions correspond to the distribution of silver and gold atoms, respectively. The Ag shell grows epitaxially around the Au NR and is thus a single crystal structure. Considering the perfect match of the lattice constants of the two metals, epitaxial growth is expected. The Au@Ag NR shown in Figure 5a is aligned in the [110] direction. Therefore, the atoms at the (220) lattice plane are imaged.
As to the HRTEM images of the orange slice-like Au@Ag nanocrystals, most of them show unsymmetrical Ag coating on the Au NR. Figure 6a,b shows two typical HRTEM images of these nanocrystals. The anisotropic coating is apparent as the thickness of the Ag shell at the two sides of the gold rod is obviously different. Similar to Figure 5a, Figure 6a also shows atoms on the (220) lattice plane, indicating that the Au@Ag nanocrystal is oriented along the [110] direction. In comparison with Figure 5a, we can see that the {111} facets on the fatter side of Figure 6a are obviously enlarged in the sacrificing {110} facet. When the Au@Ag nanocrystal is aligned along the [100] incident direction, atoms on the (100) lattice plane are imaged as shown in Figure 6b. Most of the nanocrystals we have checked show {110} orientations. If the nanocrystals favor contacting the substrate with a larger and flat facet, the {110} facets should have a high probability to be imaged. From this and considering their square/rectangle cross-sections, we suggest that the {110} side facets grow more quickly than the other two, thus resulting in the anisotropic deposition of the Ag shell. Meanwhile, at the thicker part of the Ag shell, the faster growth of the {110} side facets accompanies the enlargement of the {111} endcaps connected to them. The complete disappearance of the {110} facet at the fat side leads to the formation of an orange slice-like nanocrystal with a triangular side surface. If the particle touches the substrate with one {100} side facet that is sandwiched by two fast growing {110} facets, the orange slice-like shape is observed in SEM images (see Figure 1c–f).

### Identification of the SPR Bands for Au@Ag Core/Shell Nanocrystals

To understand the SPR feature of the Au@Ag nanocrystal better, samples with thinner Ag thicknesses were prepared. Because of the thin thickness, the Ag shell looks more or less homogeneously coated over the Au NRs. Their extinction spectra were measured and compared with the theoretical extinction spectra obtained by discrete dipole approximation (DDA). A customer-made DDA code was used in the numerical simulation of the optical spectra. The complex-conjugate gradient iteration algorithm in combination with the fast-Fourier transform simulation of the optical spectra. The complex-conjugate gradient iteration algorithm in combination with the fast-Fourier transform technique were used to solve the simultaneous linear equations satisfied by the discrete dipoles used to model light scattering by the core-shell nanoparticle. The dielectric functions of Au and Ag were extracted from ref 16 and used to construct the local polarizability of each dipole in the DDA simulation. As small as a 1 nm grid size of the dipole has been used to model the core-shell particle.

It can be seen that with an increasing Ag shell thickness, the longitudinal SPR band gradually blue-shifted and its intensity also increased, except as shown in Figure 7A, spectrum b. Similar

---

**Figure 4.** SEM images of standing Au@Ag nanocrystals at reaction times of 2 min (a) and 4 min (b), respectively. The brighter part at the endcap of the nanocrystal reflects the detailed position of the Au NR at the core/shell structure. Schematic diagrams of the endcaps with {100} (c) and {110} (d) as the dominant side facets, respectively.

**Figure 5.** High-resolution TEM image of an Au@Ag NR with a thin Ag shell (a). The nanorod is aligned in the [110] direction. The inset is the corresponding FFT. The corresponding schematic diagrams for the cross-section (b) and the side profile (c) of the nanorod in panel a are shown.

**Figure 6.** HRTEM images of the orange slice-like Au@Ag nanocrystals with a thick and anisotropic Ag shell (a and b). The nanocrystal in panel a is oriented along the [110] direction, whereas the nanocrystal in panel b is aligned in the [100] direction. The insets are FFTs. Schematic diagrams of the side profiles for panels a and b are shown in panels c and d, respectively.

---

to pure Au NRs, for Au@Ag nanorods, the maximum of the longitudinal SPR band also showed a good linear relationship with AR (Figure 7A, inset). This indicates that the blue-shift is mainly due to the decrease of the AR. The slope of the straight line (123) is larger than that (94) of the pure gold nanorods. At shorter wavelength regions, apart from the transverse SPR band of pure gold nanorods at 510 nm, two new peaks at 340 and 380 nm appear. In the calculated DDA spectra (Figure 7B), longitudinal dipole resonance blue-shifts and enhances with the increasing Ag shell thickness. We believe that a small decrease in the longitudinal SPR intensity in Figure 7A, spectrum b is probably due to a low coating quality at very thin shell thicknesses. The calculated longitudinal SPR band showed a good linear relationship with the AR (Figure 7B, inset). The slope of the straight line (113) was close to the experimental value. The simulation results exhibit some discrepancies with the experimental data with regard to the SPR peak position for the longitudinal mode. This might be induced by the inaccurate determination of the geometric parameters of the core–shell particle through SEM images. A larger AR of the rod-like particle in the simulation than the actual value will induce a red-shift of the SPR peaks, as is the case shown in Figure 7.

At shorter wavelength regions, in addition to the transverse SPR of the gold nanorod, a new peak at 340 nm appeared and became dominate at thick shell thicknesses. Therefore, the 340 nm peak belongs to a transverse dipole resonance of the Ag shell. Except for the 380 nm band, the DDA simulation reproduces the main features of the experimental spectra well. Considering the difference between Figure 6A and 6B, we believe that the peak at 380 nm comes from the transverse dipole resonance of electrons at the fat side of the Ag shell. This was verified by checking the corresponding SEM images (Figure S5 in the Supporting Information). Although we only count those homogeneously coated samples, anisotropic coating already appeared in the samples shown in Figure 7A, spectra e and f. The anisotropic samples contribute to the 380 nm band in the experimental spectra.

Plausible Formation Mechanism of Anisotropic Coating.

After clarifying the formation process, the two questions remaining to be answered are the driving force of this growth mode and the reason for the anisotropic coating. For the first question, we believe that it is the consequence of competition between surface energy minimization and strong stabilization role of CTAB molecules to the Ag (110) facets. The fast growth of four {100} side facets not only reduces its own sizes but also limits the edge lengths of the connected {110} endcaps at the (100) lattice plane. This actually limits the enlargement of the {110} endcaps (see Figure 4c,d). This is energetically beneficial. Because of the stronger interaction with CTAB molecules, the growth rate of the {110} side facets is slower than that of the {100} facets. To decrease the surface energy, the growth of the {110} side facets accompanies the obvious enlargement of the connecting {111} endcaps. This is also energetically beneficial. Hence, from the viewpoints of energy, this growth mode will induce a decrease in the overall surface energy for the nanocrystal. This peculiar growth mode is therefore the balance between the surface energy minimization and the strong stabilization role of CTAB molecules to the Ag (110) facets. For the second question, the reason is unclear at present. One possibility might be that the sizes of the four {110} side facets are different, thus inducing their different growth rates. This assumption is supported by the fact that different growth rates for the {110} side facets are actually observed. But, the reason that two neighboring {110} side facets grow more quickly than the other two {110} facets needs to be explored further. Finally, our results have two important indications: (1) The stabilization of CTAB molecules to the {110} facet is limited and can be overtaken by tuning the reduction kinetics as we observed here for Ag and previously for Pd\(^{\text{A}}\) and (2) the interaction strength of CTAB molecules with metal is material dependent. For Ag, a stronger interaction of {110} facets with CTAB reduces the {110} facets but has not led to their complete disappearance. This also interprets the addition of Ag\(^{+}\) ions in controlling the shape of gold nanorods. In the case of Pd, a weaker interaction induces the complete disappearance of the {110} facets. This material dependence provides us with another path to control the shape of the metal nanocrystals.

Conclusion

Using the Au NRs with well-defined facets as seeds, we have succeeded in controlling the shape of the obtained Ag shell/Au core nanocrystals. The cross-section is a truncated square/rectangle with four {110} facets as the dominant sides. This interesting growth mode results from the balance of strong stabilization of CTAB molecules to the {110} facets of Ag and thermodynamically driven growth. Moreover, due to the well-defined facets, we can follow the growth behavior of the different facets and the shape evolution of the metal nanocrystals quite.
well. Finally, considering the limited success in making various Ag nanostructures using seed-mediated techniques, we present here a very simple procedure with a high controllability.

**Acknowledgment.** The work was supported by the National Natural Science Foundation of China (Grants 20773032 and 10334060) and “973” National Key Basic Research Program of China (2006CB932602, 2006CB705600, 2006AA03Z326, and 2005CB623602). Z. Y. Li thanks the National Natural Science Foundation of China for financial support (10525419).

**Supporting Information Available:** Five figures. This material is available free of charge via the Internet at http://pubs.acs.org.