

Core–Shell Ag–Au Nanoparticles from Replacement Reaction in Organic Medium

J. Yang,[†] Jim Yang Lee,^{*,‡} and Heng-Phon Too^{‡,§}

Departments of Chemical and Biomolecular Engineering and Biochemistry, National University of Singapore, 10 Kent Ridge Crescent, Singapore 119260, and Singapore-MIT Alliance, 4 Engineering Drive 3, National University of Singapore, Singapore 117576

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The replacement reaction between hydrophobized Ag nanoparticles and hydrophobized AuCl_4^- in toluene has been examined in detail. The conclusions obtained under our experimental conditions are different from those reported in the literature in three aspects: (1) a detectable contraction of the Ag nanoparticle sacrificial templates during the course of the reaction is shown; (2) the deposition of Au on the shrunken Ag templates inhibits further Ag oxidation, resulting in the formation of core–shell Ag–Au nanoparticles instead of Au nanoshells; and (3) the significant red-shift in the surface plasmon resonance (SPR) band is more of a consequence of shape and chemical composition changes rather than as an indication of Au nanoshell formation. Solvent and temperature are influential environmental factors that determine the structure and composition of nanoparticles formed by the replacement reaction.

Introduction

After close to a decade of intense effort, many metal nanoparticles can now be prepared with fairly good control of shapes and sizes. A number of nanoparticle geometries including wires,¹ rods,² cubes,³ and prisms⁴ can also be routinely synthesized by solution chemistry methods. The interest now migrates to the synthesis of more complex structures such as core–shell and hollow particles that are perceived to be advantageous to applications in catalysis,⁵ chemical and biological sensing,⁶ and optics.^{2,7}

The Xia group has pioneered a method to prepare hollow metal particles based on a galvanic replacement reaction carried out in aqueous solutions.⁸ They demonstrated the process with the synthesis of Au nanoshells where Ag nanoparticles were used as sacrificial templates to reduce an aqueous HAuCl_4 solution. The Au nanoshells formed were reported to have a hollow interior, smooth and pinhole-free surfaces, as well as homogeneous and highly crystalline walls. The Bai group extended the procedure to Pt and produced Pt hollow nanospheres with rough shells by using sacrificial Co nanoparticles and an aqueous H_2PtCl_6 solution as the reductant and oxidant, respectively.⁹ A more recent refinement of the process came from the work of Sastry and co-workers,¹⁰ who used chloroform as the reaction medium to synthesize Au and Pt nanoshells by the replacement reactions between hydrophobic spherical Ag nanoparticles and hydrophobized AuCl_4^- and PtCl_6^{2-} ions. Synthesis of hollow structures in the organic phase has the advantage of a more amenable subsequent surface modification of the nanoparticles to suit a wide range of applications. From our own experience, the particles produced in the organic phase are also more regular in shapes and sizes than those obtained in the aqueous solutions.

We have previously developed a highly efficient method to transfer metal nanoparticles and metal ions from an aqueous

solution to toluene.¹¹ The method is extensively used in this study to enable the reaction between hydrophobic Ag nanoparticles and hydrophobized AuCl_4^- in toluene. Our room-temperature experiments have generated a number of observations different from those reported in the literature: (1) a significant shrinkage of the Ag templates occurred during the course of the replacement reaction; (2) the deposition of Au atoms on the surface of the shrunken Ag templates inhibited Ag from further oxidation, and a core–shell Ag–Au structure instead of a Au nanoshell was obtained finally; and (3) the red-shift in the surface plasmon resonance (SPR) of the core–shell nanoparticles was caused by shape and composition changes in the particles and is not indicative of the formation of a Au shell. Since our synthesis conditions were different from those used in previous works, there is no intention to generalize the results. However, the formation of nanostructures is most likely kinetically controlled; hence, solvent and temperature are highly influential in the replacement reaction.

Experimental Procedures

$\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$, AgNO_3 , and dodecylamine (98%) from Aldrich, sodium borohydride (98%) from Fluka, sodium citrate (98%) and ethanol (99%) from Merck, and toluene from JT Baker were used as received. Deionized water was distilled by a Milli-Q water purification system. All glassware and Teflon-coated magnetic stir bars were cleaned in aqua regia, followed by copious washing with distilled water before drying in an oven.

A JEOL JEM2010 microscope was used to obtain TEM images of the nanoparticles. For TEM measurements, a drop of the nanoparticle solution was dispensed onto a 3 mm copper grid covered with a continuous carbon film. Excess solution was imbibed by an adsorbent paper, and the sample was dried under vacuum at room temperature. UV–vis spectroscopy of the nanoparticle solution was performed on a Shimadzu UV-2450 spectrophotometer.

EDX and XPS analyses were carried on a JEOL MP5600 SEM and a VG ESCALAB MKII spectrometer, respectively. The nanoparticles used for EDX and XPS analyses were those

* Corresponding author. Fax: 65 6779 1936; tel.: 65 6874 2899; e-mail: cheleejy@nus.edu.sg.

[†] Department of Chemical and Biomolecular Engineering.

[‡] Singapore-MIT Alliance.

[§] Department of Biochemistry.

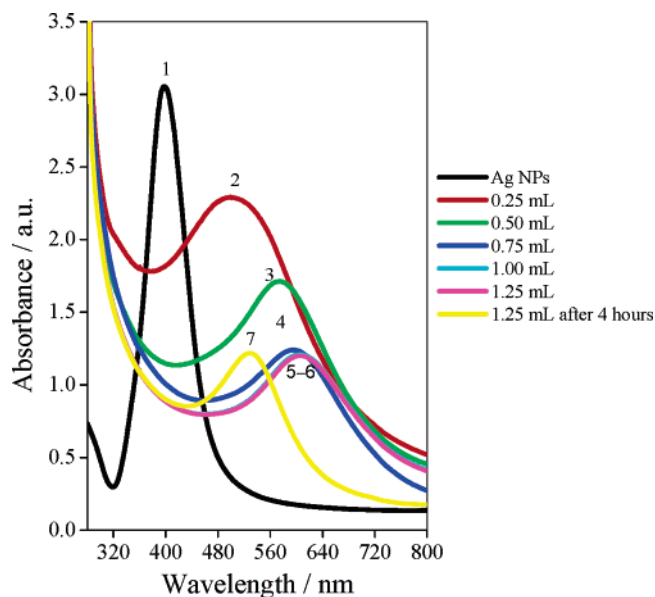


Figure 1. UV-vis spectra at different stages of the replacement reaction between dodecylamine-stabilized Ag nanoparticles and hydrophobized AuCl_4^- in toluene: 1 h: as-prepared dodecylamine-stabilized Ag nanoparticles; 2–6 h: after the addition of 0.25, 0.5, 0.75, 1, and 1.25 mL of hydrophobized AuCl_4^- ions, respectively; and 7–4 h: after the addition of 1.25 mL of hydrophobized AuCl_4^- ions.

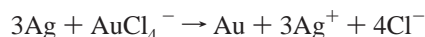
recovered from toluene by centrifugation and washed with ethanol several times to remove nonspecifically bound dodecylamine. The nanoparticles were also dried at room temperature in a vacuum.

Citrate stabilized Ag nanoparticles (the sacrificial templates) were prepared from the NaBH_4 reduction of AgNO_3 . Briefly, 20 mL of a 1 mM aqueous AgNO_3 solution was mixed with 1.6 mL of a 40 mM aqueous sodium citrate solution used as stabilizer. A total of 0.4 mL of a 112 mM aqueous NaBH_4 solution was then added dropwise under vigorous stirring, giving rise to a yellowish brown Ag hydrosol. The Ag hydrosol was aged for 24 h to decompose residual NaBH_4 before it was used in subsequent steps. The transfer of Ag nanoparticles and HAuCl_4 (aqueous solution, 1 mM) from water to toluene followed a previous procedure developed by us.¹¹ Typically, 20 mL of the Ag hydrosol (or a 1 mM aqueous HAuCl_4 solution) was mixed with 20 mL of ethanol containing 400 μL of dodecylamine. After 1 min of stirring, 20 mL of toluene was added, and stirring continued for 3 more min. Phase transfer of the dodecylamine stabilized Ag nanoparticles (or chloraurate ions) from water to toluene would then occur quickly and completely, as evidenced by the complete bleaching of color in the aqueous phase. The chloraurate ion concentration in toluene assuming complete transfer of the ions from water was therefore 1 mM. The hydrophobized Ag nanoparticles and chloraurate ions in toluene were separated from the aqueous phase and saved for further experiments. The replacement reaction between the chloraurate ions and the Ag nanoparticles in toluene was carried out by adding different volumes of a 1 mM AuCl_4^- solution in toluene to five 3 mL dodecylamine-stabilized Ag nanoparticles in toluene. In all cases, the Ag nanoparticle solutions in toluene gradually changed color from yellowish brown to different shades of pink, indicating the reduction of chloraurate ions by the oxidation of Ag atoms.

Results and Discussion

Curve 1 of Figure 1 shows the UV-vis absorption spectrum of dodecylamine-stabilized Ag nanoparticles in toluene. The

strong absorption at 397 nm is due to the excitation of surface plasmon resonance (SPR) in the Ag nanoparticles. The TEM image of dodecylamine-stabilized Ag nanoparticles before the replacement reaction with AuCl_4^- ions is shown in Figure 2A. The Ag nanoparticles obtained from the NaBH_4 reduction of AgNO_3 are nearly spherical and uniform in size with an average diameter of 9.6 nm. The addition of hydrophobized AuCl_4^- ions (in various quantities) to the dodecylamine-stabilized Ag nanoparticle solution in toluene resulted in a significant reduction in the intensity of the Ag SPR (Figure 1, curves 2–6). All analytes were diluted with toluene to the same total volume before UV-vis measurements, which also progressively redshifted with the amount of chloraurate ions added, to finally an absorption band at ca. 609 nm. The changes in SPR were caused by changes in the shape and composition of the initial Ag nanoparticles due to their reaction with hydrophobized AuCl_4^- ions. The presence of only a single SPR band indicates the formation of bimetallic Ag–Au nanoparticles instead of a mixture of gold and silver nanoparticles.¹² The absorption due to the chloraurate ions under the experimental conditions was too weak to cause any interference effect. The reaction between hydrophobic Ag nanoparticles and hydrophobized chloraurate anions may be represented categorically as a replacement reaction between the two⁸



The previous redox reaction provides the mechanism for forming a gold shell on the silver core. As the replacement reaction progresses and more deposited Au atoms are accumulated in the nanoshell, shell densification occurs leading eventually to a pinhole-free structure that insulates the underlying Ag core from further reaction, and the growth of the core–shell structure is terminated. On the basis of reaction stoichiometry, the complete oxidation of Ag nanoparticles in 3 mL of toluene solution would require 1 mL of AuCl_4^- ions of the same concentration (metal basis). However, Figure 1 shows that the SPR of the bimetallic nanoparticles ceased to grow after the addition of only 0.75 mL of a 1 mM AuCl_4^- solution, suggesting that a pinhole-free Au shell had already been established by that time, which inhibited the further oxidative dissolution of the core. In this case, the replacement reaction between hydrophobized AuCl_4^- ions and dodecylamine-stabilized Ag nanoparticles in toluene could only produce core–shell Ag–Au nanoparticles instead of Au nanoshells on completely hollowed-out Ag cores.

Figure 2B,C,D is typical TEM images of nanoparticles in toluene after 0.25, 0.5, and 1.25 mL of chloraurate ions were added to 3 mL of a Ag nanoparticle solution. The deposition of Au atoms on the Ag nanoparticle cores to form core–shell bimetallic particles is discernible by the brightness difference between inner and outer regions of the particles. According to the TEM characterization of core–shell Ag–Au nanoparticles by Srnova-Sloufova and co-workers,¹³ and to the STEM characterization of multi-shell bimetallic Au–Ag nanoparticles,¹⁴ the lighter regions are invariably a feature of Ag. For further confirmation of the composition and structure of the nanoparticles formed by the replacement reaction in toluene, the sample in Figure 2D was analyzed by EDX and XPS independently. The Ag to Au atomic ratio was about 0.7:1 according to EDX measurements, indicating the substantial presence of residual Ag in the bimetallic nanoparticles. On the contrary, almost no Ag presence was detected by XPS, indicating that the surface of the particles was Au rich.¹⁵ The compositional difference between XPS (a surface analysis

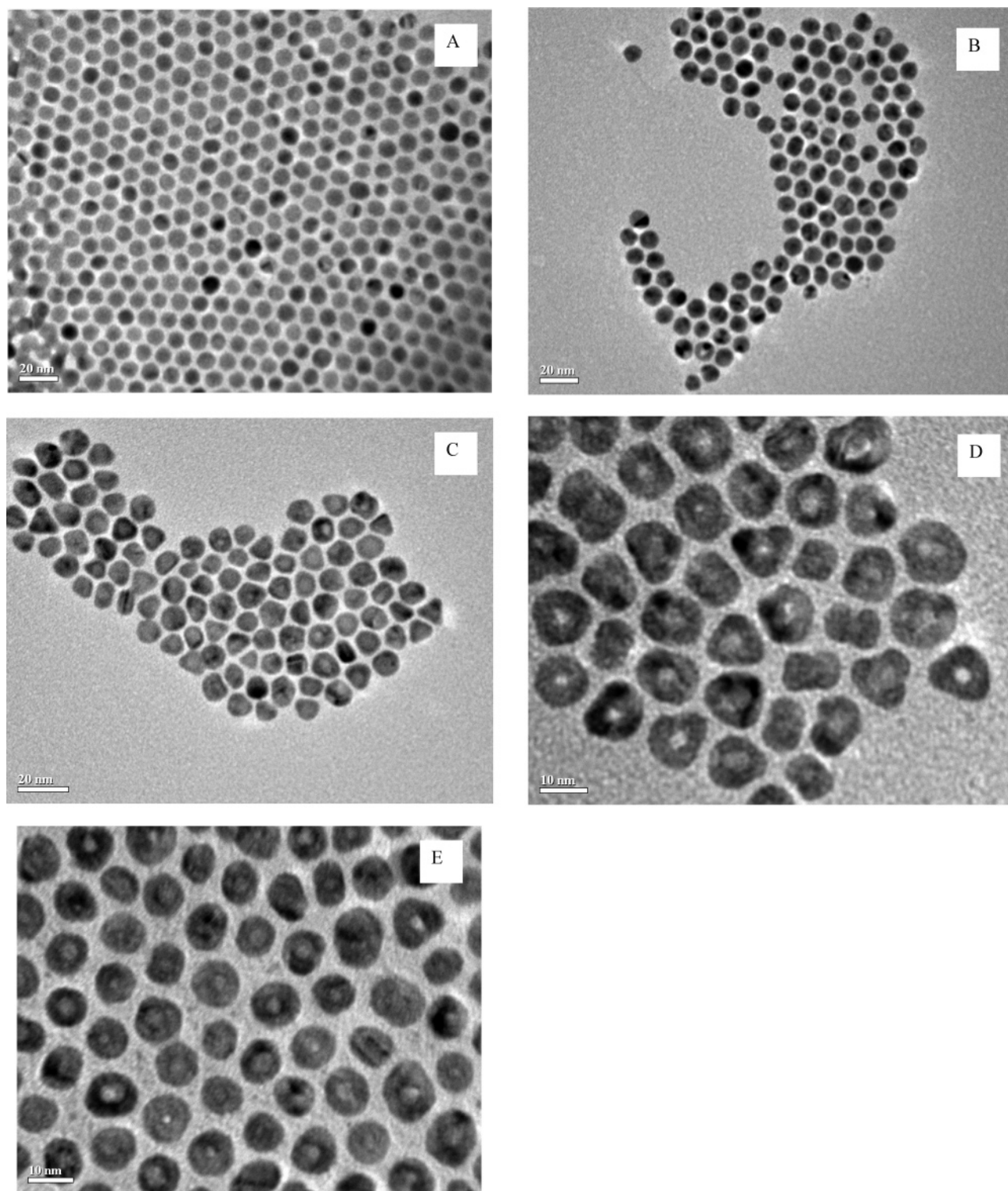


Figure 2. Representative TEM images of (A) dodecylamine-stabilized Ag nanoparticles; (B–D) after the addition of 0.25, 0.5, and 1.25 mL of hydrophobized AuCl_4^- ions, respectively; and (E) 4 h after the addition of 1.25 mL of hydrophobized AuCl_4^- ions.

technique) and EDX (a bulk analysis technique) measurements is strong evidence for the formation of core-shell Ag–Au nanoparticles. The EDX and XPS results also rule out the formation of Ag–Au alloy nanoshells with hollow interiors, which were the product reported for the replacement reaction between AuCl_4^- and Ag nanoparticles in aqueous solutions.^{8a,e}

The average diameter of core-shell Ag–Au nanoparticles at the end of the replacement reaction in toluene was ca. 12.8 nm (Figure 2D). The preformed Ag nanoparticle cores had contracted significantly from 9.6 nm (Figure 2A) initially to

5.4 nm finally. The formation of core-shell nanoparticles was dependent on the size of the seed particles. For small Ag seed nanoparticles, the probability of a complete etching of the Ag cores to form solid Au nanoparticles became increasingly higher. Experimentally, we have detected a small number of particles without cores by TEM (ca. 7%, from Ag seed particles ≤ 4 nm in Figure 2A).

Interestingly, when the UV–vis spectrum of the sample from adding 1.25 mL of hydrophobized AuCl_4^- to 3 mL of a Ag nanoparticle solution in toluene was reexamined after 4 h of

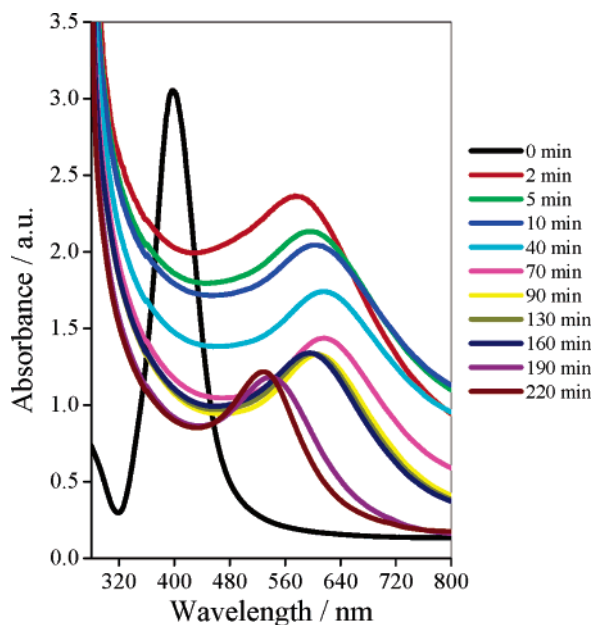
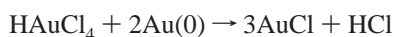


Figure 3. Time course of UV-vis absorption of a Ag nanoparticle solution in toluene after the addition of 1.25 mL of hydrophobized AuCl_4^- .

aging, the SPR band was blue-shifted to 528 nm (curve 7 in Figure 1), and the color of the nanoparticle solution also changed from pink into light red. The observation is similar to that reported by Xia and co-workers previously, although the reaction medium in that work was purely aqueous.^{8e} However, we could not find evidence for the collapse of the core-shell structure as described by the Xia group in their work.^{8a,c} The TEM image of the particles after 4 h aging is shown in Figure 2E, where the core-shell structure is still clearly visible. Nevertheless, a comparison with Figure 2D (which shows the particles before aging) identifies the following evolutions in morphology: (1) the average size of the core-shell Ag–Au nanoparticles had decreased from 12.8 nm (Figure 2D) to 10.2 nm (Figure 2E) and (2) the particles were more spherical after aging. In view of the fact that there were no apparent changes in the core size of the particles after aging, the decrease in the overall size of the particles must be due to a reaction between the shell component and the environment. We postulate the occurrence of the following reaction only as a pedagogical explanation for the moment.



For the sample obtained by reacting 1.25 mL of hydrophobized AuCl_4^- solution with 3 mL of Ag nanoparticle solution, the changes in the UV-vis spectra with time were also recorded (Figure 3). It took approximately 70 min to form a completely pinhole-free Au shell on preformed Ag nanoparticles (as shown by the cessation of the SPR red-shift), which inhibited the further oxidation of Ag atoms. The time-dependent UV-vis spectra in Figure 3 show that the replacement reaction between hydrophobized Ag nanoparticles and AuCl_4^- ions in toluene was not as fast as that occurring in aqueous or chloroform solutions, where the reactions were reported to be instantaneous.^{8,10} The SPR of the core-shell Ag–Au nanoparticles began to blue-shift after 70 min, and there was no further spectral evolution after 220 min.

The SPR blue-shift was caused by the respherification of the nanoparticles and the change in the core-shell composition to a lesser Au content in the aging process. It was primarily a shape

and chemical composition effect since the accompanying change in the particle size was not large enough to produce a significant SPR shift (as inferred from the comparison of UV-vis spectra of 5, 13, and 17 nm Au nanoparticles used in a control experiment). On the other hand, the absorption maxima in curves 4–6 of Figure 1 are located at wavelengths longer than what is typical for spherical Au nanoparticles (ca. 520 nm). Previously, such shift anomaly was used to infer the formation of Au nanoshells,^{10,16} but the experimental evidence provided here suggests that variations in chemical composition (from initially Ag to progressively more Au in Ag–Au) and shape changes from spherical nanoparticles into less spherical and more irregular particles by the replacement reaction could be a better explanation since the evidence for nanoshell formation is lacking in this case.

The experimental evidence gathered in this work points collectively to the formation of core-shell Ag–Au nanoparticles, and not Au or Ag–Au alloy nanoshells as in previous studies,^{8,10} when the replacement reaction between Ag nanoparticles and AuCl_4^- ions is carried out in toluene. The significantly different conclusions may be traced to the different experimental conditions (toluene vs water or chloroform¹⁰ as the reaction medium and room temperature vs reflux at 100 °C), which suggest that the structure and the geometry of the particles formed in replacement reactions are determined by reaction kinetics, which can be altered by temperature and the choice of solvent. Hence, there is good opportunity to sculpture nanoparticles of different shapes, sizes, compositions, and structures through replacement reactions carried out in different solvent environments.

Conclusion

In summary, the replacement reaction between Ag nanoparticles and AuCl_4^- ions in toluene was carefully studied. The nanoparticles that remained after the cessation of the replacement reaction were not the same as those obtained in an aqueous reaction environment. Core-shell Ag–Au nanoparticles, and not Au or Ag–Au alloy nanoshells, were formed under the experimental conditions. Contraction of the preformed Ag nanoparticle seeds was observed during the replacement reaction in toluene. In addition, we found that the shift in the surface plasmon resonance (SPR) associated with the formation of core-shell Ag–Au nanoparticles correlated better with the progressive variations in chemical composition and the despherification of the nanoparticles than the assumption of nanoshell formation. The observation that the outcome of the replacement reaction can be significantly altered by temperature and solvent choice indicates kinetics control and the possibility for sculpturing more intricate nanostructures through controlled manipulation of the reaction environment.

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