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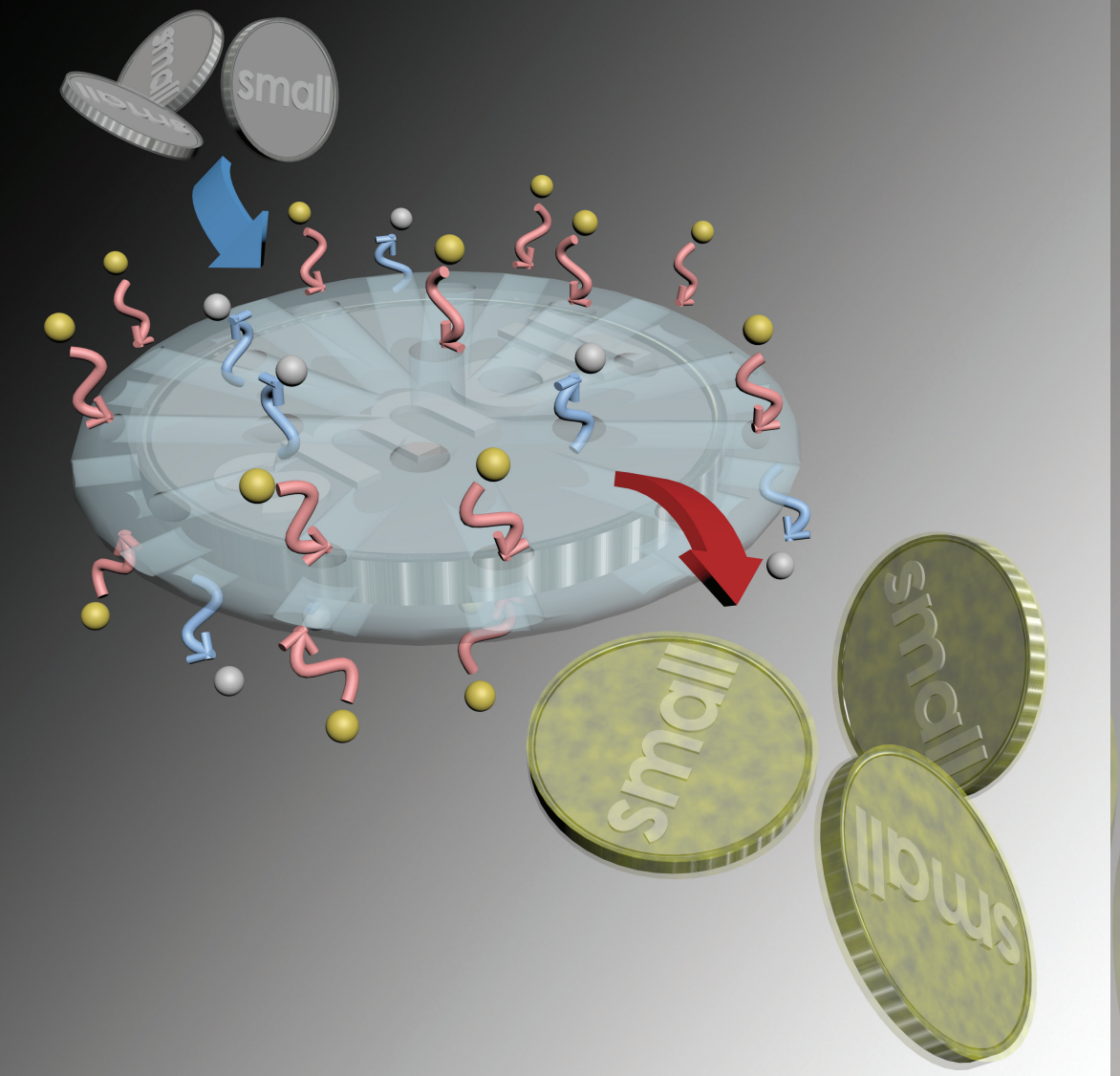

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Shape-Persistent Replica Synthesis of Gold/Silver Bimetallic Nanoplates Using Tailored Silica Cages

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For several decades, Au and Ag have been known as plasmonic metals and consequently have been studied in various fields such as in electrical devices,[1] medical devices,[2] sensors,[3,4] and surface enhanced Raman spectroscopy[5] due to their strong surface plasmon resonance (SPR) property.[6] SPR results in new electrical, chemical, and optical phenomena, which depend on the shape, size, and component of a material.[6,7] Accordingly, methods for tuning SPR properties have been developed by many researchers.[8–11] One approach is the synthesis of binary and multi component structures such as bimetal or alloy, cluster, and core/shell. The properties of the resulting multicomponent structures can be tuned by changing the composition and atomic structures.[12,13] The properties of the structures depend on material composition, and these structures are not only capable of SPR tuning, but also display various synergistic effects in mixed materials, such as electrochemical, magnetic, and anticorrosion effects.[12–16]

Au and Ag bimetallic nanostructures have been synthesized by sol–gel and template methods, and their properties were reported to be dependent on the atomic ratio between Au and Ag. The sol–gel method can generate various shapes of nanoparticles by reduction and growth but it is to achieve uniform shape.[14–17] The template method is a relatively simple process to deliver the uniform shape by the use of predetermined geometrical structures such as anodic aluminum oxide, nanotubes, and mesoporous materials. However, the limitation of this method is that it can generate particles of simple geometry including sphere and rod in shape.[18–20]

To circumvent these restrictions, we devised a tailored silica cage in which particle synthesis generates a replica particle resembling a seed. Advantage of this method is that we can vary the shape of replicated nanoparticles through initial choice of shape of the seed particles, largely to say, without limits. Extremely large number of micro and nanopores on silica, coupled with its high chemical/physical stability, allows various small materials, such as ions and molecules, to diffuse through silica.[21–24] The materials that diffuse to the silica can react with the contents of the core.[25–27] With the development of these processes, shape-persistent replica of Au/Ag bimetallic nanoplates can be synthesized in a tailored silica cage.

A scheme for the replica synthesis is shown in **Figure 1**. Ag nanoplates were used as the initial materials onto which the silica cage was grown via the Stöber method.[29–31] Subsequently, galvanic reactions took place between the Ag nanoplates and the Au precursors ($AuCl_4^-$), which led to the formation of a replicated nanoplate in the tailored silica cage. As $AuCl_4^-$ diffused into the silica cage, galvanic reactions occurred with the Ag nanoplates in silica cage.[32,33] Because the standard reduction potential of $AuCl_4^-/Au^o$ (0.99 V vs SHE) is higher than that of Ag^+/Ag^o (0.80 V vs SHE), the galvanic reaction could proceed according to the following equation[33] $3Ag^o + AuCl_4^- \rightarrow Au^o + 3Ag^+ + 4Cl^-$. While reactants having lower reduction potential than the Ag, such as Cu^{2+}/Cu^o (0.34 V vs SHE) and Fe^{2+}/Fe^o (–0.44 V vs SHE), do not progress to the galvanic reaction (Figure S1, Supporting Information). At this moment, Ag nanoplates were oxidized and released as Ag^+ and small Ag seeds, while $AuCl_4^-$ was reduced to Au^o. Through this reaction, Au^o, Ag^+, and small Ag seeds were generated in the remaining space of the core. A reducing agent (ascorbic acid) was then added to the silica cage to cause confined growth of Au and Ag to fit the initial shape in the tailored silica cage. Finally, by treating the silica cage with an etchant (hydrofluoric acid, HF), the Au/Ag bimetallic nanoplates were harvested.

Figure 2 and **Figure 3** show the variation of morphological and optical properties with each reaction step. The Ag nanoplates, used initial materials, had truncated triangular shapes with a size of ≈46.7 ± 5.2 nm as given in Figure 2a and Figure S2 (Supporting Information). According to the Mie theory, a plasmonic nanoparticle possesses a unique absorption spectrum that is related to its shape.[6,10,28] The Ag nanoplates had three absorption peaks, which were ascribed to the plasmon vibration modes of the nanoplates: out-of-plane quadrupole (338 nm), in-plane quadrupole (404 nm), and in-plane dipole (544 nm) plasmon resonance as given in Figure 3a. In addition, Ag nanoplates have been observed to exhibit hexagonal crystal structures on the $[0001]_H$ zone axis (JCPDS NO. 87-0598) as given in Figure S3 (Supporting Information).

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