Fabrication of Silica Nanocapsules Containing Ag/Au Alloy Nanoparticles by Galvanic Replacement Reaction

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A straightforward method has been developed to generate silica nanocapsules containing Ag/Au alloy nanoparticles (Ag/Au@silica) by in-situ galvanic replacement reaction between the silica-coated silver (Ag@silica) nanoparticles with aqueous chloroauric acid (HAuCl₄). Ag/Au@silica exhibits an optical absorbance derived from the surface Plasmon resonance of the encapsulated Ag/Au alloy nanoparticle. The behaviour of chemical diffusion across the silica shells of Ag/Au@silica is also investigated. It is worthy to noting that this facile synthetic strategy could be amenable to the other systems that involve the use of different combination of materials for the core (Pd/Ag, Pt/Ag alloy nanoparticles) and for the shell (titania).

Keywords: Ag/Au Alloy, Chemical Diffusion, Galvanic Replacement Reaction, Nanoparticles, Silica Nanocapsules.

1. INTRODUCTION

Nanocapsules with modified interior have received considerable attention due to their potential utility as confined nano-reaction vessels, drug carriers, catalyst carriers, and biosensors.¹-⁴ As one of promising interior modifier of nanocapsules, metal nanoparticles could endow the nanocapsules with fascinating optical, magnetic, electronic and catalytic properties and extend the application of nanocapsules greatly.

Recently, despite the fact that several nanocapsules, such as poly(benzyl methacrylate), carbon and zirconia, containing gold nanoparticles have been fabricated by templating against modified silica nanoparticles,⁵-⁷ the preparation of silica nanocapsules containing bimetallic alloy nanoparticles has still remained few exploration. silica nanocapsules possess the intrinsic hydrophilicity, biocompatibility, functionalizable surface and the excellent protection for the internal payload, which make them perfect candidates for biomedical application.⁵ In addition, bimetallic nanostructures, as a new type of materials, exhibit excellent physical and chemical properties and can be extensively utilized as catalysis, optoelectronics, biological and chemical sensing, and contrast agent.⁹ Therefore, the fabrication of silica nanocapsules containing alloy nanoparticles is of scientific and technological interest.

Ag/Au alloy nanostructures, as one of the most important alloy materials for their interesting optoelectronic properties, have achieved extensive attention.¹⁰-¹² The recent studies demonstrated that a galvanic replacement (GR) reaction between a bare Ag nanoparticles (Ag NPs) and aqueous HAuCl₄ could generate hollow Ag/Au alloy nanostructures with controllable optical properties depending on shapes and chemical compositions. More interestingly, by means of simple increase the ratio of aqueous HAuCl₄ to Ag, the resulting alloy structure could finally collapse into small Ag/Au alloy fragments, which offered an alternative way to create Ag/Au nanoparticles.¹³,¹⁴

Herein, we describe a new and facile route to generate the silica nanocapsules containing Ag/Au alloy nanoparticles (Ag/Au@silica) by means of in-situ GR reaction between the silica coating Ag nanoparticle (Ag@silica) and aqueous HAuCl₄. The preparation procedure is shown in Scheme 1. The first step involves the conformal coating of silver nanoparticles (~20 nm in diameter) with amorphous silica shells derived from the tetraethyl orthosilicate (TEOS) precursors by Stöber method.¹⁵,¹⁶ The resulting silica shell is generally porous,¹⁷ which allows the aqueous HAuCl₄ solution to diffuse through the silica shell and react with Ag core (step 2). Accompanying with the proceeding of GR reaction, the single Ag core can be converted into multiple Ag/Au alloy nanoparticles, and the silica capsule structures also be generated simultaneously.
Fabrication of Silica Nanocapsules Containing Ag/Au Alloy Nanoparticles by Galvanic Replacement Reaction

Li et al.

Scheme 1. Schematic procedures for generating silica nanocapsule containing Ag/Au alloy nanoparticles (Ag/Au@silica) by galvanic replacement reaction between silica coating Ag (Ag@silica) nanocomposite and aqueous HAuCl₄.

2. EXPERIMENTAL DETAILS

2.1. Preparation of Silver Nanoparticles

A polyol process was used to synthesize Ag NPs with average diameter of 20 nm. Silver nitrate was reduced by ethylene glycol (EG) which also served as the reaction solvent. Poly(vinylpyrrolidone) (PVP, MW:55000) was used as protecting agent to prevent the aggregation of Ag NPs. In a typical experiment, 2 g of PVP was added slowly into 15 mL of EG solution containing 80 mg of silver nitrate under vigorous stirring. This reaction mixture was then heated to 120 °C at a rate of 1 °C/min, followed by a reaction proceeding for 1 h at 120 °C. Subsequently, the reaction mixture was cooled down to ambient temperature and acetone (>200 mL) was added to dilute the reaction mixture. The resulting Ag NPs colloids were collected and redispersed in 100 mL ethanol.

2.2. Preparation of Silica Coated Ag NPs (Ag@Silica)

The Ag@silica composite nanoparticles were prepared by Stöber method. 1 mL of the resulting AgNPs colloids was added to a reactor containing 25 mL of ethanol, 4 mL of deionized water and 0.02 mL of TEOS, followed by adding 2 mL of ammonia water (28%) consecutively. After the reaction had proceeded for 1 h, the resulting Ag@silica was collected and redispersed in 10 mL of deionized water.

2.3. Fabrication of Ag/Au@Silica

To synthesize Ag/Au@silica, deionized water was used as the solvent for the galvanic replacement reaction. In a typical synthetic procedure, 5 mL of the as-prepared Ag@silica colloids was diluted with 10 mL of deionized water and heated to boiling temperature. Subsequently, 1.2 mL of aqueous HAuCl₄ (1 mM) was added dropwise under vigorous stirring. After continuous reaction for another 60 min, Au/Ag@silica composites were generated.

2.4. Characterization

For the transmission electron microscopy (TEM) examination of nanoparticles, a small drop of suspension was applied to a carbon-coated copper grid. A MODEL H-7600 (HITACHI) was used to observe the structure and determine the particle size. The concentration of gold and silver in the alloy nanoparticles were analyzed using an atomic emission spectrophotometer equipped with a Jarrell Ash 955 inductively coupled plasma system. All the UV-vis absorption spectra of the nanoparticles suspension were recorded at room temperature on a UV-1650PC apparatus (SHIMADZU).

3. RESULTS AND DISCUSSION

In a typical GR reaction, since the standard reduction potential of AuCl₄⁻/Au pair (0.99 V vs. standard hydrogen electrode) is higher than that of the Ag⁺/Ag pair (0.88 V versus standard hydrogen electrode), Ag is inclined to be oxidized into Ag⁺ and AuCl₄⁻ is reduced into Au simultaneously. This general reaction included in GR reaction can be described as follows:

\[
3\text{Ag}^{+} + \text{AuCl}_{4}^{-} (\text{aq}) \rightarrow \text{Au}^{0} (\text{aq}) + 3\text{Ag}^{+} (\text{aq}) + 4\text{Cl}^{-} (\text{aq})
\]

In this process, accompanying with the formation of Au, the silver chloride (AgCl) is also produced. In order to eliminate the effect of solidified AgCl on the characterization results of the resulting Ag/Au@silica, the AgCl was removed using a saturated sodium chloride (NaCl) solution prior to the characterizations. The absence of AgCl could be evidenced by the energy-dispersive X-ray (EDX) spectroscopy (Fig. 1). The resulting alloy nanoparticles were subjected to EDX analysis after removal of silica shell using hydrofluoric acid. The EDX spectrum exhibits strong Au and Ag intensities, while no signals indicating the existence of chlorine atom were observed. The exact concentration of Au and Ag in the alloy nanoparticles was analyzed using an atomic emission spectrometer equipped with an inductively coupled plasma (ICP) system. The corresponding result shows that the molar fraction of Au in alloy nanoparticles is 64.8%.

Figures 2(a and b) show the transmission electron microscope (TEM) images of silver nanoparticles with average diameter of 20 nm and the resulting Ag@silica...
Li et al. Fabrication of Silica Nanocapsules Containing Ag/Au Alloy Nanoparticles by Galvanic Replacement Reaction

Fig. 2. TEM images of (a) Ag nanoparticles, (b) silica coating Ag composite nanoparticles and (c) silica nanocapsules containing Ag/Au alloy nanoparticles.

nanoparticles with an amorphous silica shell 35 nm in thickness. The size of the composite nanoparticles is quite uniform. TEM image of the resulting Ag/Au@silica is shown in Figure 2(c). As expected, it is clearly observed that the single Ag nanoparticle encapsulated in silica shell is replaced by several Ag/Au alloy nanoparticles after in-situ GR reaction, and the contrast in inset shows the existence of nanocapsule structure. The resulting Ag/Au nanoparticles are in irregular shapes, and the size is less than 5 nm by calculation over 100 Ag/Au@silica nanoparticles.

The formation of Ag/Au@silica structure might be attributed to the alloying and de-alloying process during the GR reaction between the Ag nanoparticles and aqueous HAuCl₄ solution. In the alloying process, the GR reaction is initiated locally in the form of formation of some “pits” rather than over the entire surface. These “pits” act as active sites for the further GR reaction. The Ag atoms diffuse continuously from the bulk to the active sites and react with HAuCl₄ to generate Au atoms, which will be deposited on the surface of Ag templates. Since pure Ag is more reactive than the alloyed Ag, HAuCl₄ reacts only with the pure Ag template rather than the alloyed Ag unless the pure Ag was digested. Therefore, accompanying this reaction process (termed as confined alloy process), the alloy nanostructures with hollow interior can be generated. When the suitable amount of aqueous HAuCl₄ solution was employed, the complete de-alloying process will happen. In this process, the AuCl₄⁻ ions etch the Ag/Au alloy nanostructures by selectively removing the Ag atoms. According to the stoichiometric relationship described in Eq. (1), one Au atom can be produced at the expense of three Ag atoms. Thus with de-alloying reaction proceeded, numerous lattice vacancies are created, resulting in the increase of surface energy. In order to reduce the total surface energy, the holes onto the surface of alloy nanostructures can be generated via Ostwald ripening process and finally lead the alloy nanostructures to collapse into Ag/Au alloy fragments. Simultaneously, the remained lattice vacancies further widen the interior of silica nanocapsules.

The UV-vis analysis of the Ag, Ag@silica composite and are shown in Figure 3(a). In comparison, it was observed that there is a red-shift of 9 nm in the maximum absorption peak (422 to 431 nm) after Ag nanoparticles are covered with a silica layer, which caused by an increase in the local refractive index of surrounding medium (ethanol to silica, 1.36 to 1.46). The Ag/Au@silica sample presents a quite broad absorption peak with a maximum situated at 525 nm, which is attributed to the surface plasmon resonance peak of Ag/Au alloy nanoparticles. It is

Fig. 3. UV-vis absorption spectra of (A) Ag, silica coating Ag nanoparticles (Ag@silica) and silica nanocapsules containing Ag/Au alloy nanoparticles (Ag/Au@silica) as well as (B) Ag/Au@silica after they had been added into quinoline for different period of time. Inset in (B) is the plot for dependence of maximum plasmon peak on time.
worthy to noting that the encapsulated alloy nanoparticles endows Ag/Au@silica with optical absorbance, which make Ag/Au@silica a promising novel materials utilized as bioimaging, diagnostics, targeted drug delivery and controlled release. Because of the porous structure of silica shell\textsuperscript{17}, the Ag/Au@silica can be allowed to act as a unique system for investigating the diffusion of chemicals across the silica shells. Figure 3(b) shows UV-vis absorption spectra of Ag/Au@silica nanocapsules (obtained from redispersion of Ag/Au@silica in ethanol, with interior of the shell still filled with ethanol) after they had been redispersed in quinoline for different periods of time. Because quinoline has a refractive index higher than that of ethanol (1.62 vs. 1.36), the surface plasmon resonance peak of Ag/Au nanoparticles was shifted to longer wavelength as quinoline diffused into and ethanol diffused out of the silica shells. The dependence of maximum plasmon peak on time was plotted and shown in inset of Figure 2(b). It was observed that the maximum plasmon peak of Ag/Au@silica quickly shifted from 525 nm to 628 nm after quinoline was added, and then the peak position kept unchanged. It indicated that quinoline could diffuse through the silica shell quickly and caused the quick increase of refractive index of medium around the Ag/Au nanoparticles, which was attributed to the good solubility of quinoline and ethanol, as well as the relatively narrow free space remained in the interior of silica nanocapsules.

4. CONCLUSION

In summary, based on Ag@silica composite nanoparticles, a novel and simple rout has been demonstrated to generate the silica nanocapsule containing multiple Ag/Au nanoparticles by means of in-situ GR reaction. Monitored by UV-vis spectra, the resulting Ag/Au@silica nanocapsules exhibited rapid diffusion and response for quinoline. In addition, this facile method should be amenable to the other systems that involve the use of different combination of materials for the core (Pd/Ag, Pt/Ag alloy nanoparticles) and for the shell (titania). The relative works are in process.

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References and Notes


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