Synthesis of Gold Nanoparticles and Hollow Gold Nanostructures

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Abstract

Mercaptopranoic acid (MPA) capped gold (Au) nanoparticles have been synthesized in aqueous medium using a citrate reduction method. Size dependent properties of the phase transfer agent, tetraoctylammonium cations (TOA⁺) was investigated. Au hollow structures have been fabricated in aqueous medium by using the Galvanic replacement method in which Ag nanostructures served as the sacrificial templates. Prior to Galvanic replacement of Ag template by HAuCl₄, three sets of Ag nanoparticles were synthesized by varying the surfactant and reducing agent used. MPA-capped Ag nanoparticles reduced by different reducing agent resulted in different of sizes and crystal faces. It was found that the corresponded shape and size of the fabricated hollow nanostructures rely closely on the crystal planes and the size of the sacrificial Ag templates.

Introduction

Modified surface of colloidal gold nanoparticles with thiolates have been extensively studied because of their potential applications in many fields [1-3]. Recently, it has been focused on the control of the size of nanoparticles. In this regard, the use of tetraoctylammonium cations that capable are of transferring carboxylate-ω-functionalized alkanethiolate-modified Au nanoparticles have been studied [5]. The size-dependent properties of transferring processes lead to an alternative methodology for size selective separation of nanoparticles. The tuning of the intrinsic properties of metal nanostructures have been concerned in the past and this could be done by controlling shape as well as structure (hollow vs solid) [6]. Hollow nanostructures could improve performance over filled nanostructures due to their relatively lower densities and higher surface areas. Synthesis of hollow nanostructures via Galvanic Replacement using Ag nanoparticles as sacrificial templates were developed in which the hollow structures is strongly dependent on the morphologies, size and the crystal faces of the sacrificial template.

Materials and methods

Chemicals and instrumentation. Silver Nitrate (Sigma Aldrich, 99.50%), Hydrogen tetrachloroaurate(III) trihydrate (Sigma Aldrich, 99.90%), Mercaptopropanoic acid (Sigma Aldrich, 99.90%), Tetraoctylammonium bromide (Sigma Aldrich, 99.90%), Tri-sodium citrate (Sigma Aldrich, 99%), and Sodium Hydroxide (Sigma Aldrich, 99.50%). All UV spectra were obtained from UV-2450 spectrometer by using quark cell. The scanning range was set from 800 nm to 300 nm. The TEM images (JEOL-2010 or JEOL-3010) were taken of direct sampling of the solution on carbon-coated copper grids.

Synthesis of MPA-capped Au NP. Synthesis was carried out as reported [8]. Briefly, 95 mL deionized water containing HAuCl₄ (2.94 x 10⁻⁴ M) and Na-MPA (1.47 x 10⁻⁴ M) in a round-bottom-flask, rbf, was stir vigorously and heated at ~80°C. 5 mL of 1% aqueous trisodium citrate was added.
dropwise to the heated solution over a period of 10 min. The reaction mixture was further refluxed for 60 min.

**Phase transfer using TOABr in toluene.** One step phase-transfer experiment was carried out as reported [8]. 50 mL of toluene containing TOABr (3.88 x 10^{-4} M) was added to 50 mL of the reaction mixture containing synthesized MPA capped Au NP. The biphasic mixture was stirred vigorously for 30 min. The colored toluene layer was collected for characterization. Step-wise phase-transfer experiments were carried out as above while using five portions of 10 mL instead of one portion of 50 mL of toluene that containing TOABr (3.88 x 10^{-4} M) for extracting the synthesized MPA capped Au NP.

**Synthesis of MPA capped Ag NP using citrate as reducing agent.** MPA-capped Ag NP was synthesized using a citrate reduction method similar to the one for MPA-capped Au NP while using AgNO_3 in place of HAuCl_4. The synthesized nanoparticles were washed twice by centrifugation (4000 rpm, 30 min) followed by redispersing in deionized water.

**Synthesis of MPA capped Ag NP using sodium borohydride as reducing agent.** While 30 mL deionized water containing AgNO_3 (1 x 10^{-4} M) and Na-MPA (2 x 10^{-4} M) in rbf was being stirred vigorously, 5 mL of cold aqueous NaBH_4 (1.2 x 10^{-3} M) was added dropwise to the solution over a period of 10 min. The synthesized nanoparticles were washed twice by centrifugation (4000 rpm, 30 min) followed by redispersing in deionized water.

**Synthesis of citrate capped Ag NP using trisodium citrate as reducing agent.** 50 mL deionized water containing AgNO_3 (1 x 10^{-4} M) and trisodium citrate (5 x 10^{-4} M) in a rbf was stirred and refluxed for 150 min and cooled to room temperature. The synthesized nanoparticles were washed once by centrifugation (4000 rpm, 30 min) followed by redispersing in deionized water.

**Synthesis of Hollow Au NP by galvanic replacement.** Synthesis was carried out as reported [9]. Briefly, 5 mL of aliquot of the as-obtained dispersion of Ag nanostructures was stirred vigorously and refluxed in a round-bottom-flask before a specific volume of HAuCl_4 (5 x 10^{-4} M) was added dropwise with the rate of ~0.1mL/min.

**Results and Discussion**

MPA-capped Au nanoparticles were synthesized successfully by using citrate-reduction method. The size of the particles varied from ~5 nm to ~30 nm as shown in fig. 1.

In one step separation, colored aqueous layer and water-toluene interface indicated not all nanoparticles were transferred to toluene layer and TEM images in fig. 2 showed that only particles
with diameter < 10 nm were transferred by TOA$^+$. In 5 steps successive extraction process, it was determined that the smaller particles will first be coordinated by TOA$^+$ for transferring process. In fig. 3, intensity of SPR absorption of Au NP decreased with each extraction process implied that upon 1$^{st}$ extraction, only minor particles with diameter <10 nm left in aqueous layer. Water-toluene interface is attributed to the particles with diameter of ~10 nm and >10 nm nanoparticles will remain in the aqueous layer.

Au hollow structures were synthesized via galvanic replacement in which Ag nanoparticles served as sacrificial template as it is relatively stable from oxidation due to high reduction potential of Ag$^+/Ag$ pair while it is still lower than reduction potential of AuCl$_4^-/Au$ pair. Equation (3) shows that overall reaction is thermodynamically favorable in aqueous medium.

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\begin{align*}
\text{Ag}^+(aq) + e^- & \rightarrow \text{Ag}(s) = +0.8 \text{ V} & (1) \\
[\text{AuCl}_4^-](aq) + 3e^- & \rightarrow \text{Au}(s) + 4\text{Cl}^-(aq) = +0.99 \text{ V} & (2) \\
3\text{Ag}(s) + \text{AuCl}_4^- (aq) & \rightarrow \text{Au}(s) + 3\text{Ag}^+(aq) + 4\text{Cl}^-(aq) = +0.19 \text{ V} & (3)
\end{align*}
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Three sets of Ag templates shown in Figure 7, 8 and 9 were synthesized for galvanic replacement with HAuCl$_4$. It was observed that the synthesized MPA-capped Ag template using citrate as reducing agent have a larger diameter (~50 nm) than that of NaBH$_4$ (~20 nm). NaBH$_4$ is a strong reducing agent and will form a lot more nucleation sites compared to citrate which resulted in formation of relatively smaller particles. Majority of the citrate-capped Ag templates have spherical morphologies while a minority formed rod shapes. The spherical particles have the diameter of ~40 nm to ~70 nm and have irregular crystal faces while the nanorods have inconsistent length ranges from ~60 nm to >150 nm with a diameter of ~40 nm shown in fig. 9.

As shown in fig. 10, 11 and 12, upon addition of HAuCl$_4$, the reacted Ag templates have different morphologies, thickness and surface. In general, the size of the hollow structures was observed to be slightly larger than its Ag template. In fig. 10, the synthesized hollow structures have relatively smooth surface and the difference of thickness is due to irregular replacement rate. This is because the Ag atoms located at the crystal plane that has higher energy will first be oxidized and diffuse to solution, followed by deposition of the Au atoms on the Ag template. This is best illustrated in fig 12 as the hollow structures have appreciably difference in thickness of wall and “rough” surface. It was observed that its corresponding Ag template consists of “branched” surfaces. During the replacement process, there were probably a lot of faces with higher energy involved in the replacement process with irregular replacement rate which further contributed to the difference in the surface energy and morphologies of the Ag template. Subsequently, this will lead to irregular thickening of the wall due to non-homogeneous deposition of Au atom on the Ag template and hence leads to the formation of hollow structures with irregular thickness of wall. In fig. 11, it was observed that there are mixture of hollow structures and “ring” structures. One of the proposed explanation is that the Ag template involved consist of appreciable high energy crystal plane on both end and during the replacement, Ag atoms was oxidized from both of these end while the Au atoms were deposited on the other place which resulted in the “ring” structures.

Fig. 4, 5 6 show the UV-vis spectra of Ag templates upon addition of HAuCl$_4$. It was observed that the prepared Ag template exhibit the typical SRP absorption peak at ~410 nm to ~420 nm. Moreover, red-shift of the absorption maxima was observed with increased amount of addition of HAuCl$_4$. This is due to the deposition of the Au atoms to form Au-Ag alloys which exhibit longer wavelength of absorption peak.
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References