Facile synthesis of hollow urchin-like gold nanoparticles and their catalytic activity

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Abstract The galvanic replacement reaction between Ag nanoparticles (NPs) and HAuCl_4 followed by addition of ascorbic acid led to the formation of AuNPs sharing both urchin-like and hollow structures. The AgNPs took as sacrificial templates to guide the hollow structure and the intermediates provided rough surface and active sites for the further deposition of AuNPs, which originated from the reduction of excess HAuCl_4 by ascorbic acid. These unique structured AuNPs presented excellent optical properties and great advantages in catalysis applications.

Keywords Hollow structure · Urchin-like structure · Gold nanoparticles · Catalytic activity

Introduction

Nanostructured gold nanoparticles (AuNPs) have revealed great potential applications in many fields owing to their unique optical and catalytic properties [1–6]. Among them, urchin-like or branched gold particles with a rough surface are of great significance. The high surface area endows them excellent performance in catalysis, surface plasmon resonance (SPR) [7], surface-enhanced Raman spectra (SERS) [8], electronic devices, and biological applications [1, 2,

9]. In particular, owing to the existence of a large electromagnetic field enhancement at the tips of branched particles, a strong SERS activity can be detected with intensity over 10^7 and a relatively high reproducibility [8]. In addition, the urchin-like structure leads to large SPR shift from 500 to 800 nm and tunable SPR enhancement light scattering and absorption, making them novel and highly effective contrast agents for in vivo cancer diagnosis and therapy [10]. Many strategies emerge for the construction of size and branch-controlled urchin-like gold particles [11], mainly through seeding growth approach [12–14], where the preferential deposition of atoms on certain facets is dominant [12]. Besides, various molecules are adapted as stabilizer or capping agent to guide the formation of urchin-like structures, such as thiol-terminated molecules [15], cetyltrimethylammonium bromide [8], and sodium dodecyl sulfate [16].

On the other hand, the hollow metal nanostructures present many potential applications in catalysts, drug delivery, optical imaging, and nano-reactors [17, 18]. In the hollow nanosphere system, SPR peak locations shift over a region of more than 100 nm due to changes of shell thickness [19], rendering them great potential application in optical sensors [17]. As for the generation of NPs with hollow interiors, the sacrificial template approach is the most adaptable one [18–21]. Generally, AgNPs have always been taken as sacrificial templates and their reaction with HAuCl_4 or other metal salts leads to the formation of metal NPs with voids [17, 22–28], in which the morphology of the AgNP seeds directly controls that of the resulting metal shells. These hollow-structured materials have been explored for biomedical and catalytic applications. An improved performance has already been achieved for their use as contrast enhancement agents for both optical coherence tomography and photoacoustic tomography [22, 26].

In this paper, we provided a facile method to prepare gold particles sharing both hollow interior and urchin-like shell.

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Such a unique nanostructure facilitates the access of species to the Au surface and improves their catalytic performance [29].

Experimental

Chemicals

Deionized water was used in all the experimental processes ($18.0 \text{ M}\Omega \text{ cm}^{-1}$). Hydrogen tetrachloroaurate (III) ($\text{Au} \geq 47.8 \%$ on metals basis), silver nitrate, polyvinylpyrrolidone (PVP), sodium borohydride were bought from Sinopharm Chemical Reagent Co. Ltd., ascorbic acid, sodium citrate, and glucose were from Beijing Chemical Works and all these above chemicals were used as received. 4-Nitrophenol (4-NP, Shanghai Chemical Reagent Co. Ltd.) was purified before use.

Synthesis of silver seeds

Typically, 4.5 mg of AgNO_3 was dissolved in 25 mL of water and preheated at 70°C for 10 min. After that, the temperature was increased to 110°C followed by addition of 1.5 mL of sodium citrate (1 % in mass) to initiate the reduction of AgNO_3 . After 1.5 h, the colloidal Ag solution was cooled to room temperature.

The AgNPs in (ethylene) glycol (EG) system were prepared based on the previous report [30]: 0.025 g of AgNO_3 and 0.10 g of PVP were dissolved in 10 mL of EG at room temperature. After that, the solution was heated at 160°C in an oil bath for 3 h under stirring.

Synthesis of hollow urchin-like gold nanoparticles

Four milliliters of Ag colloid was centrifuged at 4,000 rpm for 5 min and the concentrated Ag deposits were dropped into 1 mL of HAuCl_4 aqueous solution (2.94 mM). Right after that, 1 mL of ascorbic acid (10 mM) was added. The solution turned dark blue in a short period of time. Five minutes later, 400 μL of PVP (50 mM in monomer concentration) was mixed with the product solution to avoid the possible aggregation in the further purification process. A control experiment was conducted with the same conditions in the absence of Ag seeds. The morphology of the products was investigated by a high-resolution transmission electron microscopy (HRTEM, JEOL-2100F) operated at 200 kV and scanning electron microscopy (SEM, XL-30 ESEM FEG). The optical spectra of the samples were recorded on a UV2400PC UV–vis spectrometer.

Catalytic reaction for degradation of 4-NP

Three hundred microliters of as-prepared solution was concentrated to a total of 10 μL by centrifugation at 6,000 rpm for 4 min. After removal of the supernatant, the isolated AuNPs

were immediately added to a freshly prepared reaction mixture (3 mL) containing 4-NP (0.15 mM) and NaBH_4 (5.5 mM). The optical property of the reaction system was analyzed by using a UV–vis spectroscopy (UV-2550) at every 5-min interval.

Electrocatalytic oxidation of glucose

A piece of indium–tin–oxide (ITO)-coated glass ($1 \times 5 \text{ cm}$) was firstly pre-cleaned with acetone and immersed into a solution of H_2O_2 : $\text{NH}_3 \cdot \text{H}_2\text{O}$ /H₂O (1:1:5 v/v) for 30 min. After that, the ITO glass was rinsed with deionized water and dried at 40°C .

The cleaned ITO glass was treated with aqueous 3-aminopropyltriethoxysilane (0.25 wt%) for 15 min. After washing, the glass was immersed in a purified hollow urchin-like AuNPs solution for 30 min, washed with water, and dried in air.

The electrocatalytic oxidation of glucose was performed on a CHI 852C electrochemical workstation (CH Instruments, Chenhua Co., Shanghai, China). A conventional three-electrode cell was utilized with a saturated Ag/AgCl electrode as the reference electrode, a platinum plate as the counter electrode, and the Au-loaded ITO glass as the working electrode. A potential scan in the range of -0.6 – 0.85 V with a scan rate of 50 mV s^{-1} was implemented to explore the electrochemical behavior of glucose in stirred 0.1 M NaOH aqueous solutions containing 1.33 mM glucose.

The estimation of the electrochemically active surface area of the hollow urchin-like and spherical gold electrodes were carried out using cyclic voltammetry (CV) and the Randles-Sevcik equation for a reversible redox couple, which at 25°C is [31]

$$I_p = (2.69 \times 10^5) n^{3/2} A D^{1/2} \nu^{1/2} C_\infty$$

where I_p is the peak current (ampere), n is the number of electrons transferred, A is the electrode area (square centimeter), D is the diffusion coefficient of the electroactive species (square centimeter per second), ν is the scan rate (volt per second), and C_∞ is the bulk concentration of the same electroactive species (moles per cubic centimeter). Here, we used 5 mM $\text{K}_3\text{Fe}(\text{CN})_6$ in 0.1 M KCl aqueous solution for this purpose, and $\text{K}_3\text{Fe}(\text{CN})_6$ has a diffusion coefficient of $1.0 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ at 25°C . The scan rate kept at 50 mV s^{-1} in the measurement.

Results and discussion

Figure 1a, b present a typical TEM image of the resulting AuNPs. All observed particles are urchin-like with hollow interiors. The average particle size is $104 \pm 11 \text{ nm}$ and the interior size ranges from 23 to 45 nm. The interior turns smaller compared to the AgNP seeds ($d_{av} = 65 \text{ nm}$, Fig. 1c), which may originate from the balance between the diffusion of the Ag^+ ions (or Ag atoms) and the shrinkage of Au

Fig. 1 **a, b** TEM images of hollow urchin-like AuNPs at low and high magnification; **c** TEM image of Ag seeds obtained with centrifugation speed of 4000 rpm for 5 min; **d** EDS of the hollow urchin-like AuNPs; **e** TEM image of spherical AuNPs obtained in the absence of Ag seeds; **f** SEM image of hollow urchin-like AuNPs

atoms. The galvanic replacement reaction between Ag and HAuCl_4 leads to the dissolution of Ag atoms and their following migration to the outside [32]. Meanwhile, HAuCl_4 is reduced to Au atoms and they deposit on the original Ag surface. Along with the disappearance of the AgNPs, AuNPs tend to shrink in order to minimize the surface energy. The diffusion rate of silver may be faster than that of the shrinkage of gold atoms; therefore, after the complete dissolution of Ag, the shrinkage process may stop, leaving the center part unoccupied. In comparison, only spherical AuNPs ($d_{\text{av}}=33$ nm) are obtained in the absence of Ag seeds (Fig. 1e). The SEM image of the products confirms that all the particles present rough surface with sharp tips (Fig. 1f).

The UV–vis spectra verify the structure evolution process (Fig. 2). Initially, the SPR peak of Ag colloid is observable at 420 nm (curve 1). Upon mixing the AgNPs with HAuCl_4 solution, the original Ag peak red-shifts to 550 nm (curve 2). This indicates the beginning of the galvanic reaction between Ag seeds and HAuCl_4 and partial formation of the nanoshells. After addition of ascorbic acid into the above system, the peak continues red-shifting to nearly 830 nm (curve 3), which derives from the combination of formation of the nanoshells and the growth of the Au branches onto their surface. In this sense, this structured NP can be found in application in optics and clinical diagnostics [22].

The ratio of HAuCl_4 to AgNP seeds plays an important role in the formation of uniform hollow urchin-like AuNPs. Decreasing the amount of AgNP seeds by half results in the free growth of spherical AuNPs in bulk solution (Fig. 3a). Onto the AgNPs surface, only limited HAuCl_4 is consumed

to generate the aimed gold structures. The excessive HAuCl_4 relative to the typical usage will be reduced into spherical AuNPs coexisting with the hollow ones. On the other hand, if we decrease the HAuCl_4 content to half, less uniform structure is achieved (Fig. 3b), which should result from the incomplete dissolution of Ag or AgCl on the surface (vide post).

The selection of reductant appears significant for the generation of well-structured hollow urchin-like AuNPs. If NaBH_4 was applied instead of ascorbic acid, no uniform urchin-like products were observed (Fig. 3c). Only small NPs with average diameter of 7 nm are distributed around

Fig. 2 UV–vis spectra of synthetic mixture. Curve 1: Ag colloid; curve 2: addition Ag seeds into HAuCl_4 aqueous solution; curve 3: addition of ascorbic acid into the above solution

Fig. 3 TEM images of AuNPs obtained from a system **a** with less Ag seeds; **b** with lower HAuCl_4 concentration; **c** with NaBH_4 as reductant instead of ascorbic acid; **d** operated at 100°C

the as-obtained hollow gold structures. This indicates that a very fast reaction (NaBH_4 is a stronger reductant than ascorbic acid) does not benefit the further deposition of gold on the preexisting hollow gold surface.

The formation of the hollow urchin-like gold nanostructure can be induced by two separated steps (Fig. 4): (1) upon introducing concentrated AgNPs into the HAuCl_4 aqueous solution, a galvanic replacement reaction occurs on the original AgNPs surface. After that, the Au atoms are generated and AgNPs simultaneously transfer into Ag^+ ions (or Ag atoms) followed by migration to the bulk solution (vide ante). Attention should be paid that no heat treatment is conducted, which allows for the fast diffusion of the newly formed Au, forming alloy with the coexisting Ag atoms and constructing to seamless shell [24]. (2) Owing to the rough surface provided via the presence of undissolved AgCl [27], an urchin-like structure is readily produced when ascorbic acid is added to reduce the excessive HAuCl_4 . This occurs because the reduced gold has great tendency to nucleate on the surface of preexisting NPs for lowering the energy cost. In the case of NaBH_4 system, a kinetic process may dominate in the second step. In addition, AgCl taking as anchoring sites can be coordinated or dissolved via the excess addition of HAuCl_4 , and no Cl signal is detected in energy-dispersive spectrometer (EDS, Fig. 1d, the Cu peaks come from the TEM grid). Finally, such interesting structured AuNPs are achieved. A control experiment was done by carrying out the reaction at 100°C . As mentioned in the previous reports, such condition helps for the generation of

Fig. 4 Scheme for the fabrication of hollow urchin-like AuNPs

seamless and smooth metal shell without the presence of AgCl. As a result, introducing ascorbic acid does not lead to

Fig. 5 TEM images of the hollow urchin-like AuNPs at different intervals. **a** 10 s; **b** 30 s; **c** 1 min

Fig. 6 TEM image of the hollow urchin-like AuNPs via adding HAuCl_4 to concentrated AgNPs

the urchin-like structure (Fig. 3d). Temporal evolution of the hollow urchin-like structure was studied and it showed that the formation of these unique structured NPs is a fast process. Upon addition of all the ingredients, the galvanic replacement reaction occurs in 10 s, resulting hollow-structured NPs with rough surface. After 30 s, the tips grow around the hollow NPs via the reduction of HAuCl_4 by ascorbic acid. No apparent difference is observed in the later incubation time except a structure optimization from the diffusion process and Oswald ripening (Fig. 5). Attention should be paid that the feeding order of the reactants slightly makes effects on the formation of the hollow urchin-like AuNPs. If HAuCl_4 is added to the concentrated Ag NPs, similar structure can be obtained; however, the NPs show less uniform distribution (Fig. 6), which may originate from the uneven galvanic replacement reaction between the seeds and HAuCl_4 because of the limited HAuCl_4 available at the initial stage.

The morphology of the AgNP seeds controls the shape and size of the resulting AuNPs. Changing the AgNP size can effectively tune the diameter of the corresponding gold structures. After centrifugation at lower speed, the supernatant of the Ag colloid is further centrifugated at higher speed, thereby AgNPs with smaller size were roughly obtained (inset in Fig. 7a).

Using these AgNP seeds ($d_{\text{av}} = 46 \text{ nm}$), we synthesized hollow urchin-like AuNPs with average diameter of $95 \pm 15 \text{ nm}$

Fig. 7 **a** SEM image and **b** UV-vis spectrum of hollow urchin-like AuNPs obtained by using smaller AgNPs as seeds. *Inset:* TEM image of AgNPs with smaller average diameter

Fig. 8 TEM images of **a** AgNPs obtained from (ethylene) glycol system and **b** hollow urchin-like AuNPs via using the above AgNPs as seeds. *Inset:* A larger view for the AuNPs in **b**

(Fig. 7a). Their SPR peak can thus be regulated to 800 nm owing to the morphology change (Fig. 7b), and the shoulder peak at around 560 nm (also observable in curve 3, Fig. 2) is related to the gold tips, which is always detectable in previous reports [33, 34]. Additionally, in Figs. 1f and 7a, some fiber-like structured particles are also observable, which should originate from the similar morphological AgNPs (inset in Fig. 7a). To exclude the presence of Ag nanofibers and the broad distribution of the AgNPs, we applied AgNPs obtained from EG system as seeds for the formation of hollow urchin-like NPs. As expected, similar structures were generated except for a more compact tips configuration (Fig. 8), which may result from the different surface properties of the Ag seeds.

It is anticipated that such structured AuNPs behave excellent catalytic performance. We selected the reduction of 4-NP to 4-aminophenol by NaBH_4 in aqueous media as a model reaction. The catalytic properties of the hollow

Fig. 9 Time-dependent evolution of UV–vis spectra for the reduction of 4-NP by NaBH_4 using **a** hollow urchin-like and **b** spherical AuNPs as catalysts. *Inset*: The relationship between $-\ln(C_t/C_0)$ versus time (t) in **a** hollow urchin-like and **b** spherical AuNPs system

urchin-like AuNPs and spherical AuNPs synthesized in the similar system without AgNPs as seeds were compared based on their respective degrade effects. When hollow urchin-like AuNPs were used as catalysts, the complete degradation was detected in 30 min; however, using equivalent spherical AuNPs as catalysts accomplished the degradation in 55 min (Fig. 9a, b). Furthermore, in Fig. 9b, the first two curves nearly overlap, indicating that a longer period of time is required for the 4-NP to adsorb onto the surface of the spherical AuNPs due to their lower activity [24].

Considering this reaction a first-order reaction, the rate constant is determined by the slope of the linear fit of $-\ln(C_t/C_0)$ versus time, where C_t/C_0 represents the ratio of 4-NP concentration at time t and 0 as calculated based on their corresponding absorbance intensity in the kinetic UV–vis spectra. The rate constants are 0.124 and 0.073 min^{-1} for the reaction by using hollow urchin-like and spherical AuNPs as catalysts, respectively (insets in Fig. 9a, b). Following the previous discussion on the catalyst, a relatively large surface permits the oxidation and reduction reaction occurring together while a small particle size is essential to keep its high activity [24]. The hollow urchin-like AuNPs fit this point well. The sharp tips and thin shell not only render them high activity, but keep linked to avoid separating the two half

reactions. Therefore, a higher catalytic activity was achieved for the hollow urchin-like AuNPs.

The catalytic property of the hollow urchin-like AuNPs was further evaluated by exploiting the NPs in the electrocatalytic oxidation of glucose. The CV curves of the glucose oxidation using gold as catalyst are documented in previous reports [33, 35, 36]. Typically, using the spherical AuNPs electrode (Fig. 10), an oxidation potential located at 0.21 V is corresponding to the electrosorption of glucose to form adsorbed intermediate, which releases one proton per glucose molecule. These intermediates accumulated and occupied on the active sites of the electrode surface, inhibiting the direct oxidation of glucose. As a more positive potential is attained (0.48 V), the intermediates are catalytically oxidized by the formed adsorbed OH, leaving free Au active sites to directly oxidize the glucose. However, the formation of the gold oxide at a higher potential blocks the glucose to adsorb onto the active sites. As the negative potential is carrying on, the peak at -0.07 V is observed, relating to the formation of intermediates on the electrode surface again. Compared to the result by using spherical AuNPs, a much higher current density is achieved for the direct oxidation of glucose around 0.32 V for the hollow urchin-like gold system, indicating a much faster electron transfer on the electrode surface and thus higher catalytic performance [37]. During the negative potential sweep, glucose can be oxidized again when the Au surface is free from oxides, leading to the cathodic reoxidation peak at 0.66 V. This peak along with the peak located at 0.76 V are rarely detected for the spherical AuNPs, which probably results from the special hollow urchin-like structure and needs further detailed investigation.

In summary, we successfully synthesized hollow urchin-like gold nanoparticles by using silver nanoparticles as sacrificial seeds followed by reduction of excessive HAuCl_4 with ascorbic acid. This unique structure makes them excellent application in optics and catalysis fields. Similar strategies will be adopted for generation of other hollow urchin-like metal nanoparticles to dig their wider application.

Fig. 10 CVs for the oxidation of glucose (1.33 mM) at hollow urchin-like (curve 1) and spherical (curve 2) AuNPs electrodes in 0.1 M NaOH at 50 mV s^{-1} . *Inset*: A magnified view for curve 2

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