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Controlled formation of gold nanoflowers by reduction of tetrachloroauric acid with thermally treated glucose in alkaline solution

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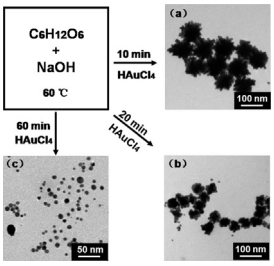
HIGHLIGHTS

- Gold nanoflowers were successfully prepared by using glucose as reductant.
- Size of the nanoflowers was tunable in the range of 50–520 nm.
- The nanoflowers showed excellent surface enhanced Raman scattering activity.

GRAPHICAL ABSTRACT



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ABSTRACT

Herein, thermally treated glucose in alkaline solution at 60 °C for 10 min was used to reduce tetrachloroauric acid for the preparation of gold nanoflowers within the size range of 50–520 nm. The use of the glucose activated for a longer period of time led to the formation of gold nanoparticles with less anisotropic characteristics. The degradation of glucose in alkaline solution results in enediols and carboxylates. It was suggested that the product has stronger reduction ability and limited protection effect for tetrachloroauric acid and gold nanoparticles, respectively, contributes to the controlled formation of gold nanoflowers. The as-prepared gold nanoflowers showed better surface enhanced Raman scattering (SERS) activity than citrate or PVP coated ones when rhodamine 6G (R6G) was used as probe molecule.

1. Introduction

Highly branched metal nanoparticles have attracted great attention owing to their unique structures and properties. They may serve as a very good candidate in surface enhanced Raman scattering (SERS), catalysis and energy conversion due to strong electromagnetic field located around the tips of the branched nanoparticles [1–12]. In solution-phase syntheses, face-centered-cubic (fcc) gold tends to form spherical or polyhedral nanoparticles, and its anisotropic growth is induced to form branched structures when additives such as cetyltrimethylammonium bromide (CTAB) and poly-N-vinylpyrrolidone (PVP) were introduced [13–20]. Usually, the strong interaction of the branched nanoparticles with the additives depresses the SERS and catalytic activity due to the competitive adsorption of the target molecules with the additives on the particles.

With an increased emphasis on green chemistry, a biocompatible and weak ligand, glucose, has also aroused great interest in the preparation of gold nanoparticles [21–23]. Glucose has very limited reducing ability at common ambient condition because of its predominant cyclic structure in aqueous solution, external heating or base catalyst is necessary to activate the glucose by opening the cycle [24–32]. Pal and co-workers prepared spherical gold nanoparticles by heating the mixed solution of glucose

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and tetrachloroauric acid at 70 °C for 30 min [26]. Liu and coworkers obtained spherical gold nanoparticles with average size of ~8.2 nm at room temperature by continuously adding NaOH into the mixed solution of glucose and tetrachloroauric acid [31]. One dimensional Ag nanowires [25] and Au nanobelts [28] were successfully prepared in glucose under hydrothermal and sonochemical treatments, respectively. To date, there is still no report on the syntheses of branched three dimensional metal nanoparticles by glucose reduction.

Herein, we reported a facile approach to synthesize gold nanoflowers by reduction of tetrachloroauric acid ($HAuCl_4$) with thermally treated glucose in alkaline solution at 60 °C. Glucose possesses a limited reducing ability in neutral aqueous solution while its reducing ability is improved to some extent after thermally treated in alkaline solution for chemical reduction of $HAuCl_4$. The untreated glucose usually resulted in the formation of spherical gold nanoparticles, and the thermally treated glucose led to the formation of gold nanoflowers. By changing the time for activating glucose or the volume of the activated glucose added, the size of the nanoflowers was tuned in a wide range from 50 to 520 nm. Both the appropriate reduction rate and limited protection effect of the thermally treated glucose play important roles in formation of the nanoflowers. The as-prepared nanoflowers presented much better SERS activity than those capped by PVP.

2. Experimental

2.1. Materials

Tetrachloroauric acid ($HAuCl_4{\cdot}4H_2O$) and glucose ($C_6H_{12}O_6$) was purchased from Shanghai Chemical Reagent Co. Int. Sodium hydroxide (NaOH) was purchased from Bio Basic Inc. Rhodamine 6G (R6G), poly-N-vinylpyrrolidone (PVP) and sodium citrate tribasic dihydrate was purchased from Sigma–Aldrich. Mercaptoacetic acid was purchased from Acros. All the chemicals were of analytical grade and used without further purification. High purity Water (Pall Purelab Plus) with a resistivity of 18.2 ΩM cm was used in all the experiments. All the glassware were cleaned by freshly prepared aqua regia solution (HCl/HNO_3, 3:1) and then rinsed thoroughly with water prior to use.

2.2. Synthesis of gold nanoflowers

In a typical preparation, an aqueous solution of 0.1 M glucose (10 mL) was mixed with 1 M NaOH (0.5 mL) in a 50 mL glass vial at room temperature, and then the mixture was immediately placed in a water bath at 60 °C. During the incubation, pre-determined volumes of the mixture were withdrawn at different reaction time, and added into an aqueous solution of $HAuCl_4$ (0.25 mM, 3.9 mL) at room temperature under magnetic stirring at 300 rpm. During the reaction, aliquots of the solution were taken out and cooled by ice water to quench the reaction prior to UV–vis spectral and transmission electron microscope (TEM) measurements. To get the TEM images of the particles formed at the initial stage of the reaction (1–10 s, Fig. 2), excess amount of mercaptoacetic acid (6 μL, 0.25 M) was added rapidly into the reaction solution to stop the growth of the nanoparticles [33,34].

2.3. Detection of $AuCl_4^-$ concentration in the formation of gold nanoflowers

A procedure reported previously was adopted to determine the consumption of $AuCl_4^-$ in the reaction [35,36]. Aliquot (250 μL) of the above reaction solution was taken out at a given time interval and then quenched immediately by adding it into 1 mL solution containing 0.9 M NaCl and 0.1 M HCl (pH = 1). After being kept at room temperature for 24 h, the absorbance of the supernatant at 314 nm was measured by UV-Vis spectrophotometer to determine the concentration of $AuCl_4^-$ according to the standard curve.

2.4. Measurements

UV–vis spectra were measured on a SHIMADZU UV-1800 spectrophotometer. Temporal evolution of the UV–vis spectra in Fig. S2 were collected on an Ocean Optics HR4000CG-UV–NIR high-resolution spectrophotometer. TEM images were acquired by using a JEOL JEM-2010 electron microscope with an operating voltage of 100 kV. High-resolution TEM (HRTEM) images were characterized by a JEOL JEM-3010 electron microscope operated at an acceleration voltage of 300 kV. TEM and HRTEM samples were prepared by dropping the solution onto Formvar- and carbon-coated copper grids respectively. XRD patterns of the samples were recorded on a Rigaku D-Max 2550 diffractometer equipped with a graphite monochromator using Cu Kα radiation (λ = 1.5418 Å). The scanning angle (2θ) ranged from 20° to 90° in steps of 3°. SERS measurements were conducted on a BWTEK MiniRam instrument equipped with a 785 nm excitation laser and acquired each spectrum for 30 s (accumulation time). Fourier transform infrared (FTIR) spectra were collected on a Perking-Elmer Spectrum One FT-IR spectrophotometer. To prepare the KBr pellets, the alkaline solution of glucose was dried frozenly under vacuum to get the powders.

2.5. SERS measurement

Three sets of 4 mL aqueous dispersions of the gold nanoflowers synthesized by using glucose activated for 10 min as shown in Fig. 1 were centrifuged for 5 min at 3000 rpm. After taking the supernatants away carefully by pipette, one set of the precipitates was re-dispersed in 4 mL water. The other two sets of the precipitates were first re-dispersed in 4 mL sodium citrate (2.5 mM) and PVP (2.5 mM) respectively, and then kept under magnetic stirring (200 rpm) at room temperature to carry out the ligand exchange reaction [37]. After 12 h, the dispersions were centrifuged for 5 min at 3000 rpm and re-dispersed in 4 mL water. For the SERS measurements, 11.5 μL of the probe solution (R6G, 10^{-3} M) was added into 100 μL of the dispersions modified by different ligands.

3. Results and discussion

As schematically illustrated in Fig. 1, 0.1 M glucose (10 mL) was first mixed in 1 M NaOH solution (0.5 mL) followed by heating at 60 °C for 10 min, and a pre-determined volume of the mixed solution (105 μL) was then added into $HAuCl_4$ (3.9 mL, 0.25 mM) at room temperature for the preparation of gold nanoflowers. Fig. 1a gives the temporal evolution of UV–vis spectra of the gold nanoflowers prepared by using the thermally treated glucose. In the 1 min, the broad absorption peak at 650 nm indicates the rapid formation of gold nanoparticles. In the following 7.5 h, this peak experienced a slow red-shift to 708 nm, indicating the increased anisotropic character of the nanoparticles [38]. After that, the peak underwent a slow blue-shift, and a narrow peak at 547 nm was observed after 24 h, suggesting the particles became nearly spherical-like in shape as a result of the intraparticle ripening [39,40].

TEM observations were carried out to further understand the size and shape evolution of the gold nanoparticles. Gold nanoflowers with an average size of 92 nm (±9.3%) were observable after 1 min of the reaction (Fig. 1b), which was consistent with the pronounced absorption peak at 650 nm appeared in the UV–vis spectra. After 7 h, there was no obvious change in size of the flowers. It was noted that branches of the flowers became thicker and less regular at this time (Fig. 1c), which contributed to the red-shift of the