

Facile green synthesis of gold nanoparticles with gum arabic as a stabilizing agent and reducing agent

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Abstract

A facile, completely green, and cheap route for the synthesis of Au nanoparticles at 25-75°C has been developed by using only hydrogen tetrachloroaurate as the precursor and gum arabic (GA) simultaneously as a reducing agent and a stabilizing agent. No extra reagents are needed. From the analyses of UV/VIS absorption spectra, TEM, HRTEM, SAED, and XRD patterns, the formation of Au nanoparticles with a fcc structure was recognized. The synthesis reaction was usually finished in 2-4 h. Increasing the reaction temperature increased the formation rate but had no significant effect on the optical property and size of Au nanoparticles. With increasing Au(III) ion concentration or GA concentration, the mean diameter of Au nanoparticles slightly increased. Also, the particle size distribution became broader at higher Au(III) ion concentration or lower GA concentration due to the insufficient protection. Although raising the GA concentration was helpful to reduce Au(III) ions completely and stabilize the Au nanoparticles, too high GA concentration was not suitable for the stabilization of Au nanoparticles because the increased intermolecular force of GA might hinder the dispersion of Au nanoparticles. Furthermore, the resultant Au nanoparticles were found to remain highly stable in the NaCl solution.

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Introduction

Among various metal nanoparticles, gold (Au) is the most widespread material used in optics, electrochemistry, catalysis, and biochemical sensing because it is stable, less toxic and biocompatible [1-4]. A lot of techniques have been developed for the synthesis of Au nanoparticles. However, it is inevitable that the interventions of environmentally harmful and toxic chemicals interfere in the synthesis procedures of Au nanoparticles.

Recently, the green synthesis or fabrication of Au nanostructures have been considerably studied by using harmless alternative biocompatible molecules such as proteins, peptides, cellulose, soybeans, gellan gum, vitamin B2, starch, and D-glucose as stabilizing or reducing agents [5-14]. We also developed a facile route for the synthesis of Au nanoparticles by the use of food additives [15].

In this study, we proposed another environmentally benign process for the synthesis of Au nanoparticles using gum arabic (GA) as both the stabilizing agent and reducing agent. GA is known as a natural and harmless polysaccharide derived from acacia trees. Due to its well steric stabilization effect as adsorbing on the surfaces of colloids and its numerous functional groups such as carboxylate and amine groups, it has been widely used as emulsifiers and capping agents [16-22]. In addition, it is also known that GA consists of mainly three distinctive fractions which are referred as arabinogalactan (AG, 88.4% of the total) with a low protein content (0.44% w/w), arabinogalactan-protein (AGP, 10.4% of the total) with a high protein content of 9.18% w/w, and glycoprotein (GP, about 1% of the total) with a protein content of 50% w/w [23-24]. Since the amino acids which are commonly considered as the reducing agents [25-27] are present in AGP and AG fractions, we synthesized Au nanoparticles by the reduction of

Au(III) ions with GA as both the reducing agent and stabilizing agent in the absence of other additives.

Materials and methods

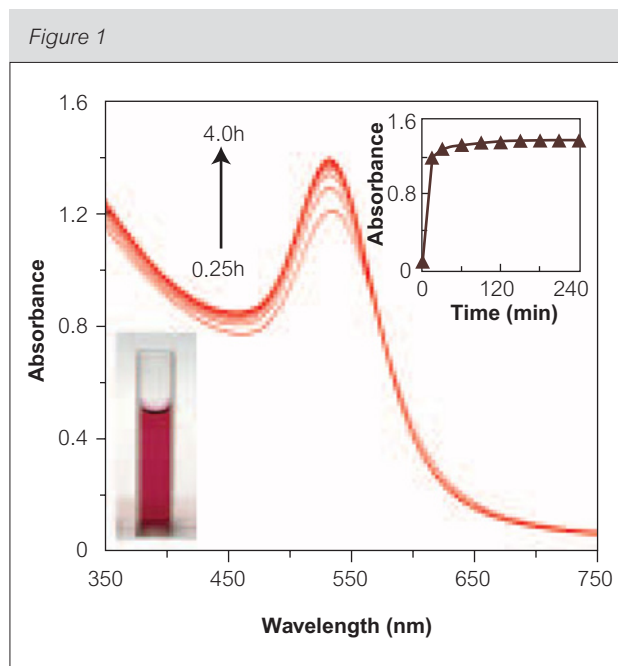
Hydrogen tetrachloroaurate ($\text{HAuCl}_4 \cdot 4\text{H}_2\text{O}$) was purchased from Alfa Aesar (Ward Hill, MA). Gum arabic (molecular weight: $\sim 250,000$) was obtained from Fluka (Buchs). The water used work was the reagent-grade water produced by Milli-Q SP ultra-pure-water purification system of Nihon Millipore Ltd., Tokyo. For the synthesis of Au nanoparticles, hydrogen tetrachloroaurate (0.1, 0.3, 0.5, 0.7, and 0.9 mM) was dissolved in aqueous solutions of GA (1, 5, 10, 15, and 20 mg/ml) at first. Then, the solutions were stirred gently at the desired temperatures (25, 40, 55, and 70°C) to yield Au nanoparticles. The typical sample was obtained at a Au(III) ion concentration of 0.3mM, a GA concentration of 10 mg/ml, a temperature of 55°C, and a reaction time of 4 h.

The UV-VIS absorption spectra of the resultant colloid solutions were monitored by a JASCO model V-570 UV/VIS/NIR spectrophotometer. The particle size analysis by transmission electron microscopy (TEM) was done using a Hitachi model HF-2000 field emission transmission electron microscope with a resolution of 0.1 nm. The electron diffraction pattern and lattice image were performed by a Jeol model JEM-2100F electron microscope operated at 200kV. X-ray diffraction (XRD) measurement was performed on a Shimadzu model RX-III X-ray diffractometer at 40 kV and 30 mA with $\text{CuK}\alpha$ radiation ($\lambda = 0.1542$ nm). Fourier transform infrared (FTIR) spectrum was recorded on a Varian FTS 1000 FT-IR Spectrometer. The samples for XRD and FTIR measurements were washed twice with water, collected by centrifugation, and vacuum dried overnight. The measurement of hydrodynamic diameter distribution by dynamic light scattering (DLS) was conducted on a Malvern Autosizer model 4700/PCS100 spectrometer equipped with an Ar ion laser operating at 488 nm. All the colloidal solutions obtained at various parameters were found to have a pH value around 4 and used for DLS analysis without pH adjustment.

Results and discussion

Characteristics of GA-stabilized Au nanoparticles

Fig. 1 shows the UV-VIS absorption spectra of the resultant Au colloid solutions obtained at a Au(III) ion concentration of 0.3mM, a GA concentration of

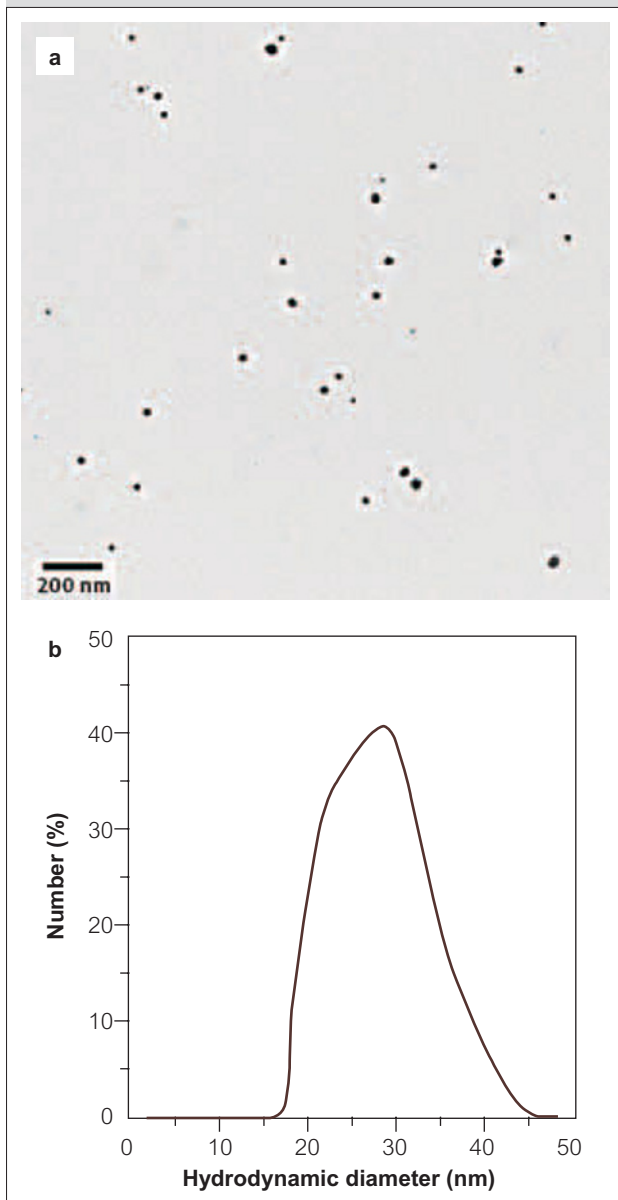


UV-VIS absorption spectra of the resultant Au colloid solutions obtained at a Au(III) ion concentration of 0.3mM, a GA concentration of 10 mg/ml, and a temperature of 55°C for various time intervals. The bottom left inset shows that the resultant colloid solution is wine red and transparent. The top right inset indicates the time-dependence of the absorbance at 532.5 nm

10 mg/ml, and a temperature of 55°C for various time intervals. The characteristic absorption band of Au nanoparticles was clearly observed at 534.5–532.5 nm, slightly blue shifted with time. Also, as indicated in the bottom left inset of Fig. 1, the colloid solution was wine red and transparent, consistent with the UV-VIS absorption spectra and revealing that the Au nanoparticles were well dispersed. Both results suggested that Au nanoparticles have been successfully synthesized. In addition, the top right inset of Fig. 1 shows that the absorbance at 532.5 nm increased sharply within 0.25 h and approached a constant after about 2 h, implying the synthesis reaction was finished at this time.

The TEM image for the typical sample obtained at a Au(III) ion concentration of 0.3 mM, a GA concentration of 10 mg/ml, a temperature of 55°C, and a reaction time of 4 h was shown in Fig. 2(a). It is obvious that the resultant Au nanoparticles were discrete completely with a mean diameter of 21.1 ± 4.6 nm, revealing that GA could protect Au nanoparticles from aggregation effectively. The hydrodynamic diameter distribution of GA-stabilized Au nanoparticles in water was shown in Fig. 2(b). The hydrodynamic diameters were mostly in the ranges

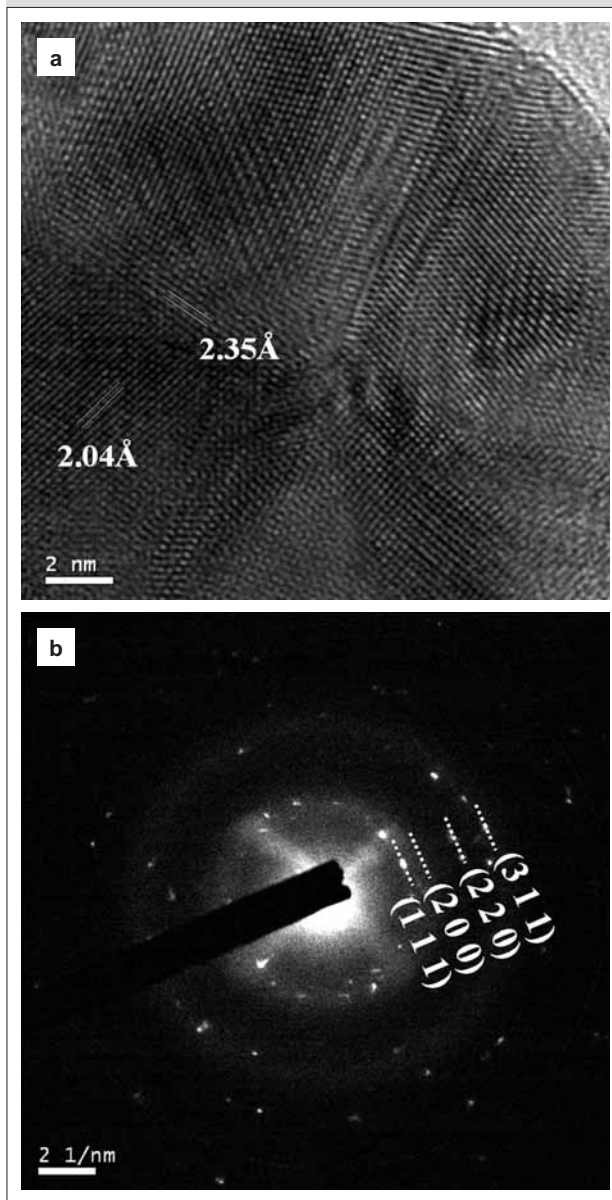
Figure 2



TEM image (a) and hydrodynamic diameter distribution (b) for the typical sample obtained at a Au(III) ion concentration of 0.3mM, a GA concentration of 10 mg/ml, a temperature of 55°C, and a reaction time of 4h

of 16-45 nm with a mean hydrodynamic diameter of 26.8 ± 5.3 nm, which was roughly consistent with that from TEM observation. Furthermore, the high-resolution TEM (HRTEM) image as shown in Fig. 3(a) revealed that Au nanoparticles had a high crystallinity and the lattice spacings of 2.04 and 2.35 Å related to the (200) and (111) planes of face centered cubic (fcc) Au. The selected-area electron diffraction (SAED) pattern was shown in Fig. 3(b), in which the radii of four main fringe

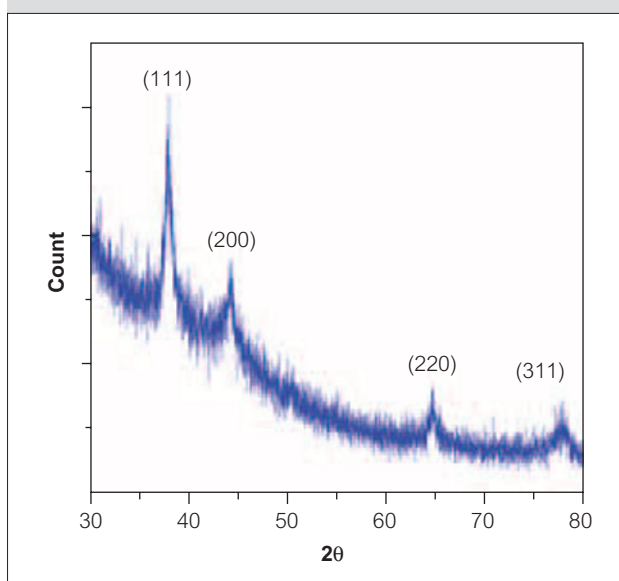
Figure 3



HRTEM image (a) and SAED pattern (b) for the typical sample obtained at a Au(III) ion concentration of 0.3mM, a GA concentration of 10 mg/ml, a temperature of 55°C, and a reaction time of 4h

patterns were in the ratio of $\sqrt{3}:2:\sqrt{8}:\sqrt{11}$. They related to the (111), (200), (220), and (311) planes of fcc Au. Fig. 4 indicates the XRD pattern of Au nanoparticles. Four characteristic peaks at $2\theta = 38.1, 44.3, 64.5,$ and 77.4° which were corresponding to the (111), (200), (220), and (311) planes confirmed that the resultant Au nanoparticles had the fcc structure. The above results all demonstrated the formation of Au nanoparticles.

Figure 4



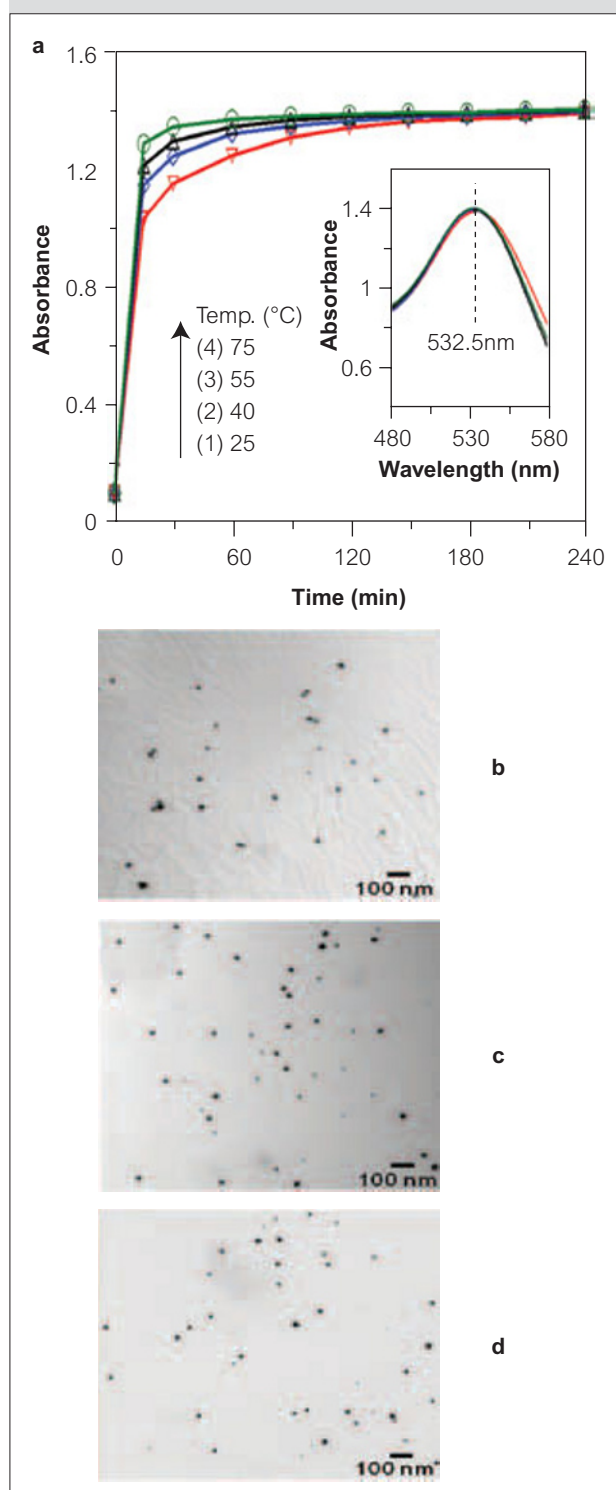
XRD pattern for the typical sample obtained at a Au(III) ion concentration of 0.3mM, a GA concentration of 10 mg/ml, a temperature of 55°C, and a reaction time of 4hrs

Effects of reaction temperature and Au(III) ion and GA concentrations

Fig. 5(a) shows the time-dependence of the absorbance at 532.5 nm for the resultant Au colloid solutions obtained at various temperatures with a Au(III) ion concentration of 0.3 mM, a GA concentration of 10 mg/ml, and a reaction time of 4 h. It was found that, with increasing the temperature, the formation rate of Au nanoparticles increased but the characteristic absorption band had no significant shift as shown in the inset of Fig. 5(a), implying the resultant Au nanoparticles had similar size in the examined temperature range. This could be confirmed by the TEM analysis as shown in Figs. 2(a) and 5(b)-(d).

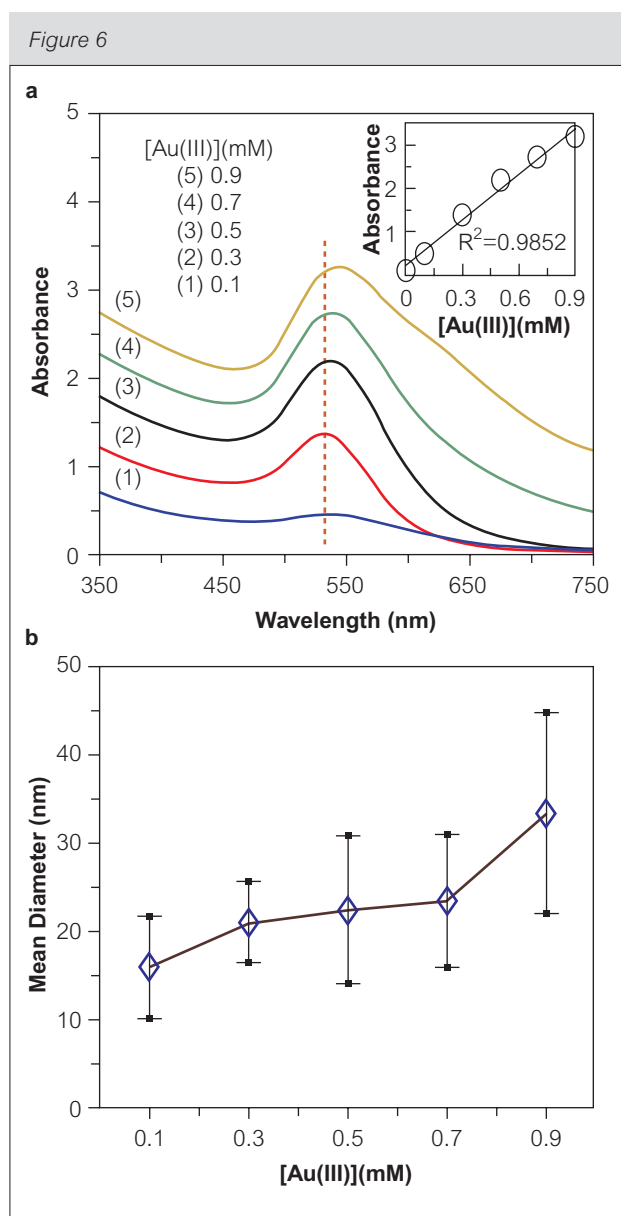
Fig. 6(a) shows the UV-VIS absorption spectra of the resultant Au colloid solutions obtained at various Au(III) ion concentrations (0.1-0.9 mM) with a GA concentration of 10 mg/ml, a temperature of 55°C, and a reaction time of 4 h. It was obvious that, with increasing the Au(III) ion concentration, the absorbance at 532.5 nm increased linearly (the inset in Fig. 6(a)) but the characteristic absorption band was slightly red-shifted. Also, when Au(III) ion concentration was 0.9 mM, a longitudinal plasmon which might be resulted by the larger particle size or particle aggregation was observed around 620 nm. By further TEM analysis, the effect of Au(III) ion concentration on the mean diameter of Au

Figure 5



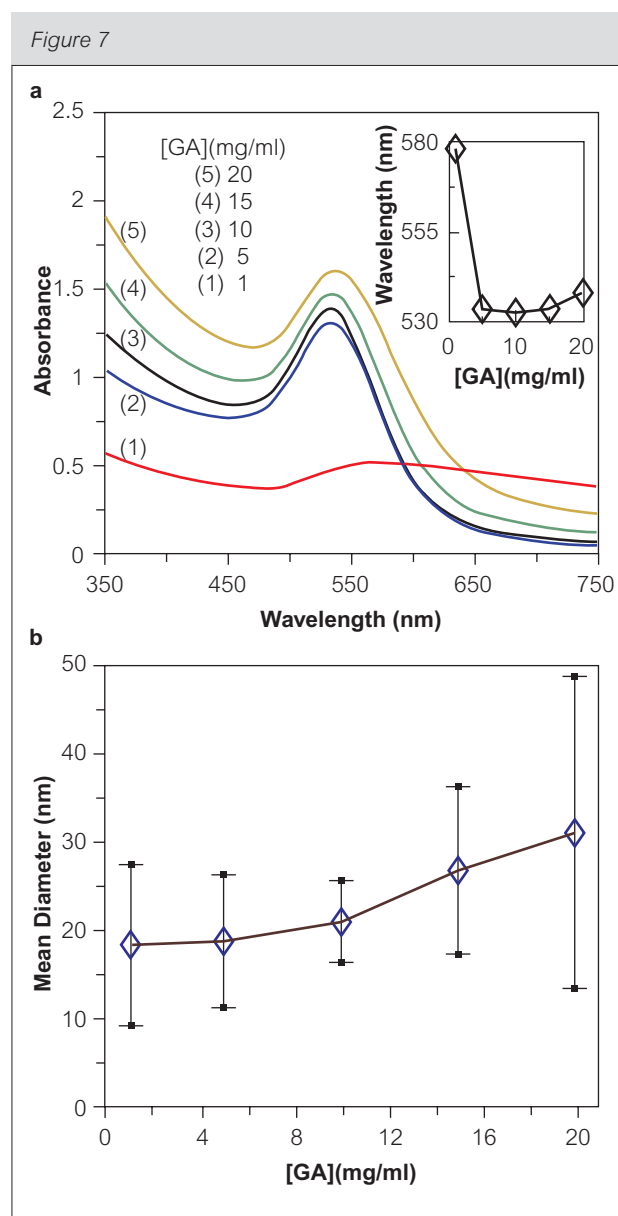
Time-dependence of the absorbance at 532.5 nm for the resultant Au colloid solutions obtained at various reaction temperatures (a) and the corresponding TEM images obtained at 25 (b), 40 (c), and 75 (d) °C. The inset in (a) indicates the UV-VIS absorption spectra focused around 532.5nm. The reaction time was 4 h and the Au(III) ion and GA concentrations were 0.3mM and 10 mg/ml, respectively

nanoparticles could be illustrated in Fig. 6(b). It was found that the mean diameter increased slightly with the increase in Au(III) ion concentration. This could be due to the higher collision frequency among Au atoms or nuclei. When Au(III) ion concentration was 0.9 mM, significantly larger particle size and size distribution were observed. This might be referred to the less protective effect by GA and could account for the longitudinal plasmon around 620 nm as shown in Fig. 6(a).



(a) UV-VIS absorption spectra of the resultant Au colloid solutions obtained at a GA concentration of 10 mg/ml, a temperature of 55°C, and a reaction time of 4 h for various Au(III) ion concentrations. The inset indicates the effect of Au(III) ion concentration on the absorbance at 532.5 nm. (b) Variation of mean diameter with Au(III) ion concentration

Fig. 7(a) shows the UV-VIS absorption spectra of the resultant Au colloid solutions obtained at various GA concentrations (1-20 mg/ml) with a Au(III) ion concentration of 0.3 mM, a temperature of 55°C, and a reaction time of 4 h. When GA concentration was as low as 1 mg/ml, it was found that the resultant Au colloid solution was purple-blue. Also, its absorption band became weak and broad with a red shift to about 578 nm (the inset in Fig. 7(a)). This suggested that the low GA

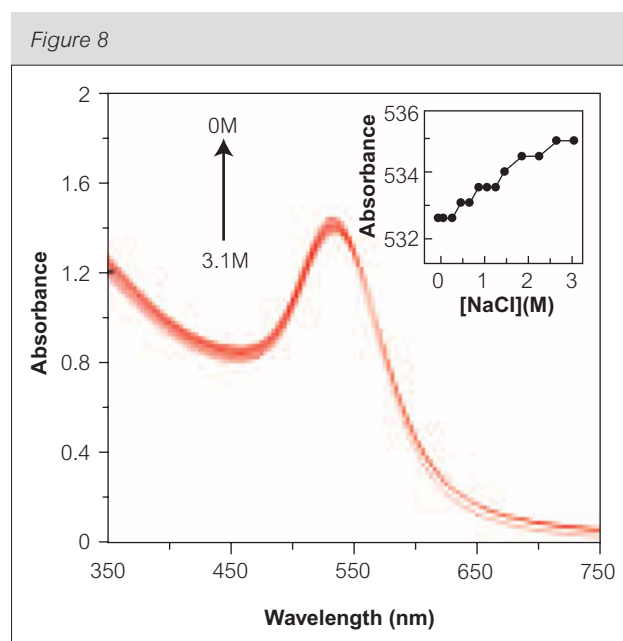


(a) UV-VIS absorption spectra of the resultant Au colloid solutions obtained at a Au(III) ion concentration of 0.3 mM, a temperature of 55°C, and a reaction time of 4 h for various GA concentrations. The inset indicates the effect of GA concentration on the characteristic absorption band. (b) Variation of mean diameter with GA concentration

concentration was not sufficient to reduce all Au(III) ions and stabilize the Au nanoparticles effectively. When the GA concentration was in the range of 5-20 mg/ml, the characteristic absorption band of the resultant Au colloid solutions was red-shifted slightly with the increase in GA concentration (inset in Fig. 7(a)). The variation of optical property might be due to the difference in their particle size and size distribution. By TEM analysis, the effect of GA concentration on the mean diameter of Au nanoparticles was obtained as Fig. 7(b). It was found that the mean diameter of Au nanoparticles increased slightly with the increase in GA concentration. Furthermore, it was noteworthy that the particle size distributions were broader at lower and higher GA concentrations. The broad particle size distribution at lower GA concentration might be due to the insufficient protection by GA. At high GA concentration, the broad particle size distribution might be resulted by the increased intermolecular force of GA molecules which may hinder the dispersion of Au nanoparticles. Thus, insufficient or excess GA were unfavorable for the stabilization of Au nanoparticles. In this study, the optimal GA concentration was 10 mg/ml.

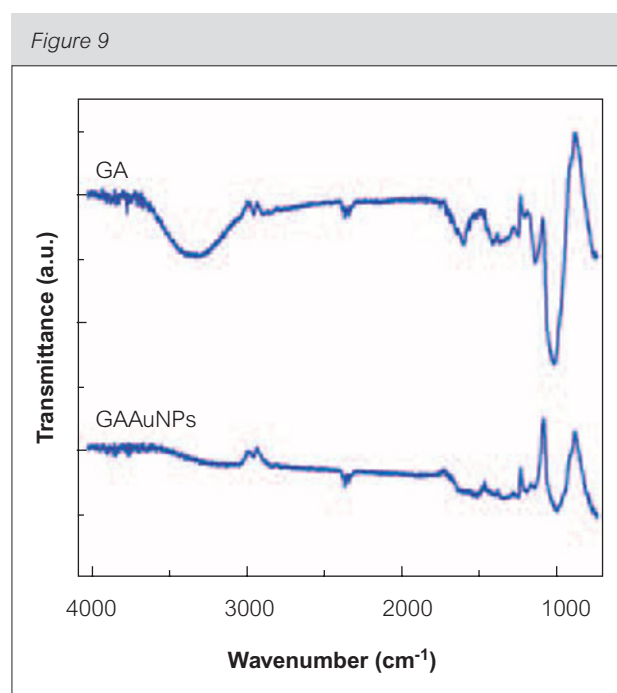
Stability of GA-stabilized Au nanoparticles

The stability of the resultant Au nanoparticles was



UV-VIS absorption spectra of the resultant Au colloid solutions obtained at a Au(III) ion concentration of 0.3mM, a GA concentration of 10 mg/ml, a temperature of 55°C, and a reaction time of 4 h in the presence of various concentrations of NaCl. The inset indicates the effect of NaCl concentration on the characteristic absorption band

examined by a conventional electrolyte introducing method. It was found that the Au colloid solution remained quite stable in the presence of NaCl. As shown in Fig. 8, when NaCl concentration increased from 0 to 3 M, the UV-VIS absorption spectra had no significant change and the characteristic absorption band shifted only slightly from 532.5 to 535 nm (inset in Fig. 8). Fig. 9 indicates the FTIR spectra of GA and the resultant Au nanoparticles. Both the spectra showed the main characteristic peaks of GA at 1049 and 1413 cm^{-1} (C-O stretch), 1612 cm^{-1} (C-O stretch and N-H bending), 2914 and 2995 cm^{-1} (C-H stretch), and 3000-3600 cm^{-1} (O-H stretch). Their similarity demonstrated the presence of GA on the surface of Au nanoparticles. Thus, the highly stability of Au nanoparticles could be reasonably attributed to the well protection of GA on the particle surface.



FTIR spectra of GA and the typical GA-stabilized gold nanoparticles (GAAuNPs) obtained at a Au(III) ion concentration of 0.3mM, a GA concentration of 10 mg/ml, a temperature of 55°C, and a reaction time of 4hrs

Conclusions

Highly stable Au nanoparticles with a fcc structure have been successfully synthesized at room temperature to a slightly elevated temperature by using GA simultaneously as a reducing agent and a stabilizing agent. The typical product obtained at a Au(III) ion concentration of 0.3mM, a GA concentration of 10 mg/ml, a temperature of 55°C, and a reaction

time of 4 h exhibited a characteristic absorption at 532.5 nm and had a mean diameter of 21.1 ± 4.6 and a mean hydrodynamic diameter of 26.8 ± 5.3 nm. The synthesis reaction was usually finished in 2-4 h. With increasing the temperature from 25 to 75°C, the formation rate increased but the resultant Au nanoparticles had similar optical property and particle size. Increasing Au(III) ion concentration led to slightly larger particle size or particle aggregation if GA was insufficient relatively. Lower GA concentration was not sufficient to reduce Au(III) ions completely and stabilize the Au nanoparticles, but too high GA concentration was also unfavorable for the stabilization of Au nanoparticles due to the increased intermolecular forces. In addition, the resultant Au nanoparticles were found to be quite stable even in the presence of NaCl up to 3 M owing to the protection of GA on the particle surface. This work provides a facile, green, and cheap route for the synthesis of Au nanoparticles.

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Dr. Dong-Hwang Chen is a distinguished professor of Chemical Engineering Department at National Cheng Kung University (Taiwan). His research works include the synthesis of nanoparticles, the fabrication of composite nanoparticles and thin films, the development of nanomaterials for electromagnetic wave absorption, as

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