Biosynthesis of Silver and Gold Crystals Using Grapefruit Extract

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Abstract In **this** paper, biological synthesis of silver and gold crystals using grapefruit extract is reported. On treatment of aqueous solutions of silver nitrate and chloroauric acid with grapefruit extract, the formation of stable silver and gold particles at high concentrations is observed to occur. The silver particles formed are quasi-spherical or irregular with sizes ranging from several hundred nanometers to several microns. The gold quasi-spheres with holes on surfaces and with diameters ranging from 1 to 3 microns are obtained. The formation mechanism of silver and gold crystals is discussed, indicating that the soluble biomolecules such as protein(s) and vitamin C in grapefruit extract may play a crucial role in defining the morphology and/or crystal phase of silver and gold crystals.
Keywords: silver, gold, biological synthesis, grapefruit, extract

1 Introduction

Silver, gold and other metal common nanoparticles, nanoclusters, nanowires and related nanostructures have received tremendous attention owing to their unique catalytic, electrical, magnetic and thermal properties[1,2]. Silver nanoparticles have been used in sensor technology[3], biological leveling[4], and many other biomedical applications[5,6]. Gold nanoparticles have been widely employed in medicine[7,8], disease diagnostic and drug delivery systems[9,10]. Currently, there is a growing need to develop environmentally benign material synthesis processes that do not use toxic chemicals in the synthesis protocol. As a result, biological systems are used by many researchers in the field of metal

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nano-materials synthesis[11].

Plant-mediated synthesis of silver and gold nanoparticles has emerged in recent years. For example, silver and gold ions could be reduced to nanoparticles using a leaf extract of *Cinnamomum camphora*[12]. Synthesis of silver nanoparticles using a leaf extract of *Moringa oleifera* was reported by Prasad and Elumalai [13]. Reduction of silver ions to stable and spherically shaped nanoparticles with average size about 10nm using extract of *Desmodium trifolium* was ascribed to the presence of H^+ ions, NAD^+ and ascorbic acid in the extract[14]. Huang et al. reported the formation of gold nanoparticles from the sun-dried leaves of *Cinnamomum camphora*[15]. The extracellular synthesis of gold nanoparticles using the leaf extract of *Coriandrum sativum* has been attempted by Narayanan and Sakthivel[16].

In this paper, we report on the synthesis of silver and gold crystals with sizes of several hundred nanometers to several microns by the reduction of aqueous Ag^+ and $AuCl_4^-$ ions with the grapefruit extract. Grapefruit is one of the most common fruits. This study can provide a new way for green synthesis of functional materials.

2 Materials and methods

Materials used for the synthesis of silver and gold crystals are silver nitrate ($AgNO_3$), chloroauric acid ($HAuCl_4$), and grapefruit extract solution prepared by taking 30 g of grapefruit flesh squeezed and blending the juice obtained with 100 mL of sterile distilled water in a 200-mL beaker.

For reduction of Ag^+ ions, 25 mL of grapefruit extract solution was added to 25 mL of 10^{-2} mol/L aqueous $AgNO_3$ solution. Similarly, 25 mL of grapefruit extract solution was added to 25 mL of 10^{-2} mol/L $HAuCl_4$ solution for reduction of $AuCl_4^-$ ions. The reduction of pure Ag^+ and Au^{3+} ions was monitored by measuring the UV–vis spectra of the solution at regular intervals after diluting a small aliquot (0.2 mL) of the sample 20 times. UV–vis spectra were recorded as a function of time of reaction on a UV-1800 double beam spectrophotometer (Shanghai Mapada Co., Ltd, China).

The silver and gold particles synthesized after 24 hours of reaction of the different salt solutions with the grapefruit extract were centrifuged at 10,000 rpm for 15 min. The precipitates obtained were washed three times with double-distilled water and ethanol, respectively, and then vacuum dried. X-ray diffraction (XRD) measurements of the silver and gold particles were carried out using dry powders on a D8 Advance instrument with CuKα radiation (Bruker, German). The morphologies of the samples were observed by scanning electron microscopy (SEM) (Hitachi S-3400, Japan) with an accelerating voltage of 20 kV.

3 Results and discussion

Formation of the silver and gold particles by reduction of the aqueous metal ions during exposure to the grapefruit extract may be easily followed by UV–vis spectroscopy. It is well known that silver and gold particles exhibit yellowish-brown and ruby red colors, respectively, in water, these colors arising due to excitation of surface plasmon vibrations in the metal particles.

Figs. 1 and 2 show the UV–vis spectra recorded from the aqueous solutions $AgNO_3$-grapefruit extract and $HAuCl_4$-grapefruit extract reaction medium as a function of time of reaction. It is observed from Fig.1 that the silver surface plasmon resonance band occurs at about 450 nm and steadily increases in intensity as a function of time of reaction without any shift in the peak wavelength. In the case of gold ion reduction, the band corresponding to the surface plasmon resonance occurred at about 550 nm as shown in Fig. 2. The reduction of the two noble metal ions occurs fairly rapidly; more than 90% of reduction of Ag^+ and Au^{3+} ions is complete within 5 hours, respectively, after addition of the grapefruit extract to the metal ion solutions (Figs. 1 and 2).

Fig. 3a and b show the XRD patterns obtained for silver and gold particles synthesized using grapefruit extract. A number of Bragg reflections corresponding to the (111), (200), (220), (311), and (222) sets of lattice planes are observed which may be indexed based on the fcc structures of silver and gold. The XRD pattern thus clearly shows that the silver and gold particles formed by the reduction of Ag^+ ions and $AuCl^-$ by grapefruit extract are crystalline in nature.

Fig. 4 shows representative SEM images of the silver and gold particles synthesized by treating $AgNO_3$ or $HAuCl_4$ solutions with grapefruit extract for 24 hours. From Fig. 4a, it can be seen that the silver particles formed were quasi-spherical or irregular with sizes ranging from several hundred nanometers to several microns. We speculate the large particles are formed by aggregation of small particles. Fig. 4b indicates that the gold particles formed were quasi-spherical with diameters in the range of 1 to 3 microns. If seen clearly, there are holes on surfaces of the particles can be identified.

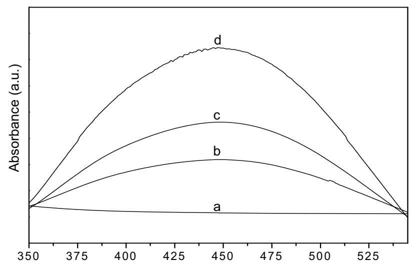

Fig. 1. UV–vis spectra recorded as a function of time of reaction of 0.01mol/L $AgNO_3$ aqueous solutions with grapefruit extract. (a: 2 min; b: 1h; c: 2h; d: 5h)

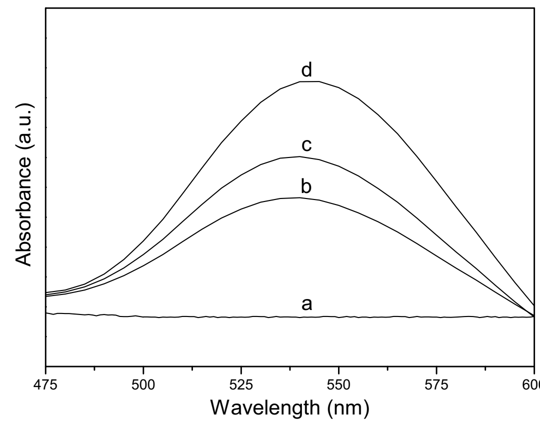

Fig. 2. UV–vis spectra recorded as a function of time of reaction of 0.01mol/L $HAuCl_4$ aqueous solutions with grapefruit extract. (a: 2 min; b: 1h; c: 2h; d: 5h)

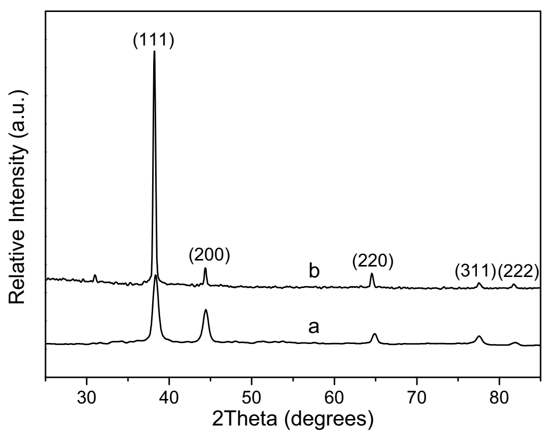

Fig. 3 XRD patterns of silver (a) and gold (b) crystals synthesized by treating grapefruit extract with $AgNO_3$ and $HAuCl_4$ aqueous solutions.

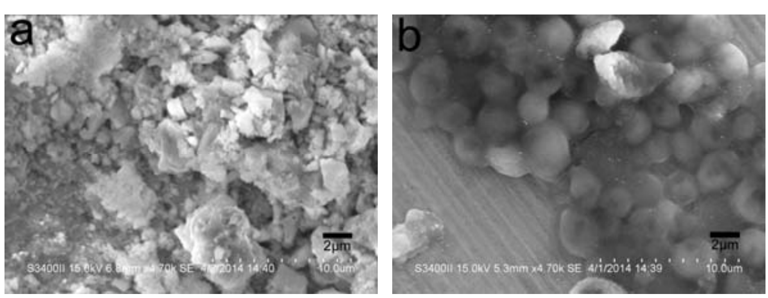

Fig. 4. SEM images of silver (a) and gold (b) particles synthesized by treating grapefruit extract with $AgNO_3$ and $HAuCl_4$ aqueous solutions.

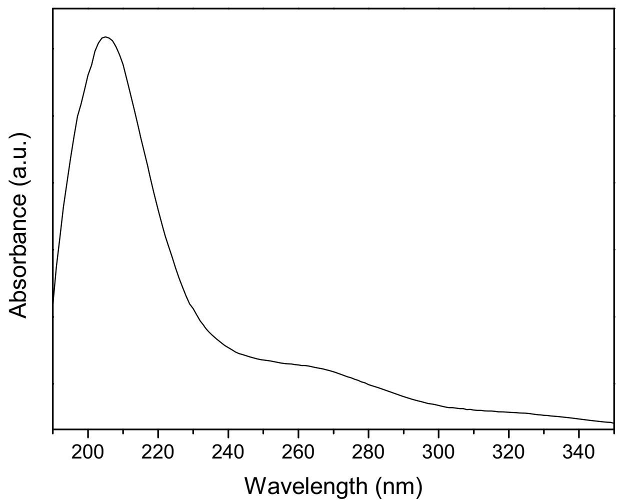

Fig. 5. UV-vis spectrum of grapefruit extract aqueous solution

Fig. 5 shows the related UV-vis spectrum of grapefruit extract solution. The peak at 210 nm is assigned to the strong absorption of peptides bounds of protein(s) in the extract, which rose owing to the stemming from n-π* transition of C=O group. The absorption at 280 nm is belonged to the π-π* transition of tyrosine, tryptophan, or phenylalanine residues of protein(s). It suggests that the protein(s) in grapefruit extract contains tyrosine, tryptophan, or phenylalanine residues.

To our best knowledge, grapefruit extract also contains reductive biomolecules such as vitamin C, etc. Here, we speculate that the soluble biomolecules such as protein(s) and vitamin C in grapefruit extract play a crucial role in defining the morphology and/or crystal phase of silver and gold crystals.

4 Summary

In summary, a process for the biological synthesis of stable silver and gold crystals using grapefruit extract was demonstrated. Quasi-spherical or irregular silver particles with sizes ranging from several hundred nanometers to several microns, as well as quasi-spherical gold particles in the range of 1 to 3 microns were produced in aqueous solution containing grapefruit extract and $AgNO_3$ or $HAuCl_4$. The soluble biomolecules such as protein(s) and vitamin C in grapefruit extract may play a crucial role in defining the morphology and/or crystal phase of silver and gold crystals. This study can provide a new way for green synthesis of functional materials.

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References

1. Y. Xia, Y. J. Xiong, B. Lim, S. E. Skrabalak, Shape-controlled synthesis of metal nanocrystals: simple chemistry meets complex physics? Angew. Chem. Int. Ed. 48(2009) 60-103.
2. R. J. White, R. Luque, V. L. Budarin, J. H. Clark, D. J. Macquarrie, Supported metal nanoparticles on porous materials. methods and applications, Chem.Soc.Rev. 38(2009) 481-494.
3. P. Gomez-Romero, Hybrid organic−inorganic materials: In of synergic activity, Adv. Mater. 13 (2001) 163-174.
4. H. Qiu, B. Rieger, R. Gilbert, R. Jerome, C. Jerome, PLA coated gold nanoparticles for leveling of PLA biocarriers, Chem. Mater. 16 (2004) 850−856.
5. P. V. Asha Rani, G. L. K.Mun, M. P. Hande, S. Valiyaveettil, Cytotoxicity and genotoxicity of silver nanoparticles in human cells, ACS Nano. 3 (2009) 279−290.
6. W. R. , X. B. Xie, Q. S. Shi, S. S. Duan, Y. S. Ouyang, Y. B. Chen, Antibacterial effect of silver nanoparticles on Staphylococcus aureus, Biometals 24 (2011) 135−141.
7. R. Bhattacharya, P. Murkherjee, Biological properties of “naked”metal nanoparticles. Adv. Drug. Delivery Rev. 60 (2008) 128−1306.
8. P. Puvanakrishnan, J. Park, D. Chatterjee, S. Krishnan, J. W. Tunnel, In vivo tumor targeting of gold nanoparticles: Effect of particle type and dosing strategy, Int. J. Nanomed.7 (2012) 1251-1258.
9. D. R. Bhumkar, H. M. Joshi, M. Sastry, V. B. Pokharkar, Chitosan reduced gold nanoparticles as novel carriers for transmucosal delivery of insulin. Pharm. Res. 24 (2007) 1415−1426.
10. E. Torres-Chavolla, R. J. Ranasinghe, E. C. Alocilja, Characterization and functionalization of biogenic gold nanoparticles for biosensing enhancement. IEEE Trans. Nanobiotechnol. 9 (2010) 533−538.
11. L. Castro, M. L. Blázquez, J. Á. Muñoz, F. G. González, A. Ballester,. Mechanism and applications of metal nanoparticles prepared by bio-mediated process. Reviews in

Advanced Sciences and Engineering 3(2014) 199-216.
12. J. Huang, Q. Li, D. Sun, Y. Lu, Y. Su, X.Yang, Biosynthesis of silver and gold nanoparticles by novel sundried cinnamomum camphora leaf. Nanotechnology 18(2007) 202-207.
13. TNVKV Prasad, E. Elumalai, Biofabrication of Ag nanoparticles using Moringa oleifera leaf extract and their antimicrobial activity. Asian. Pac. J. Trop. Biomed. 1(2011) 439–442.
14. N. Ahmad, S. Sharma, V. Singh, S. Shamsi, Fatma A., B. Mehta, Biosynthesis of silver nanoparticles from Desmodium triflorum: a novel approach towards weed utilization. Biotechnology Research International (2090-3138) (2011) 454090.
15. J. Huang, L. Qingbiao, D. Sun, Y. Lu, Y. Su, X. Yang, H. Wang, Y. Wang, W. Shao, N. He, J. Hong, C. Chen, Biosynthesis of silver and gold nanoparticles by noval sundried Cinnamomum camphora leaf, Nanotechnology 18 (2007) 105−106.
16. K. B. Narayanan, N. Sakthivel, Coriander leaf mediated biosynthesis of gold nanoparticles, Mater. Lett. 62 (2008) 4588−4590.