

Seeding Method for Three-dimensional Dendritic Growth of Gold Nanoparticles Stabilized by Hexatrimethylammonium Bromide

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Three-dimensional gold dendrites with fractal nanostructure were prepared with HAuCl_4 and l-ascorbic acid via seeding growth method in the presence of hexatrimethylammonium bromide (HTAB) as a protecting agent and architecture soft template. Spherical gold, previously generated, plays as a seed for particle growth. The surfactant HTAB helps to induce various branched nanostructures. The growth of first branches on the seeds leads to the formation of second branches by seed amount.

The formation, evolution, and consequences of fractal structures in metal systems, including metal-polymer or metal-surfactant composites, have been the subject of fruitful research for a long time.¹ The fractal structures are generally observed in a nonequilibrium growth process, and studies of such materials instabilities have important technological applications concerning the formation and control of materials systems with the desired properties.² Because the performance of novel metals in most of the applications ranging from electronics and catalytics to photonics could be significantly enhanced into nanostructures with well-controlled dimensions, numerous methods have been investigated to prepare of novel metal nanostructure with fractal morphologies.³

In the present study, we have approached seeding growth method, to be able to control fractal nanostructures of gold. In seeding growth method, small metal particles are prepared first and later used as seeds for morphological control. Providing the controlled number of preformed seeds and a growth condition that inhibits any secondary nucleation, the particle size and shape can be controlled simply by varying seed amounts.⁴ Novel route has been developed for three-dimensional dendritic gold nanostructures by controlling preadded amounts of hydrogen tetrachloroaurate (HAuCl_4) and l-ascorbic acid solutions in the presence of hexatrimethylammonium bromide (HTAB). A possible growth branching mechanism is proposed. In contrast to previously reported methods of preparing novel metal dendrites, the seeding growth method does not require complex apparatus and techniques.

In an optimized experiment, HTAB (0.0395 M) as a stabilizer and shape controller was dissolved in distilled water (10 mL). When the HTAB solution was preheated at 65 °C under vigorous stirring, the color of the solution was changed into orange. $\text{HAuCl}_4 \cdot 4\text{H}_2\text{O}$ (0.05 M) as a gold precursor and l-ascorbic acid (0.0375 M) as a reducing agent were dissolved in distilled water (2 mL each). HAuCl_4 and l-ascorbic acid starting solutions (50 μL each) were preadded into the preheated HTAB solution. Note that the molar concentrations are values of each solution. After 3 min, the residual starting solutions were poured into the preheated reaction solution. The reaction mixture was

aged and stirred for 15 min at 65 °C. Meanwhile, the reaction mixture exhibited brown color, indicating the formation of gold. The final product was washed several times with distilled water and ethanol to completely remove the supernatant. Finally, the product was redispersed to ethanol for further instrumental analysis.

Figure 1 shows XRD pattern of the product prepared by addition of residual HAuCl_4 and l-ascorbic acid solutions in the presence of gold seeds as formed by initial addition of 50 μL of HAuCl_4 . The reflection peaks can be indexed to the corresponding (111), (200), (220), and (311) facets. All these distinct diffraction peaks correspond to the reflection of face-centered cubic (fcc) crystalline gold without any impurity peaks (JCPDS 04-0784).

Figure 2 shows images of three-dimensional dendrites. Each dendrite consists of a long central backbone and very sharp secondary branches, which preferentially grow along two definite directions rather than random growth. Surprisingly, the secondary branches which emerge at 65° angles with respect to the central backbone have uniform spacing and are parallel

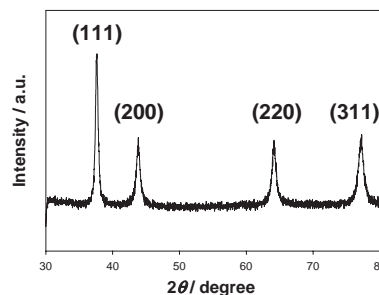


Figure 1. XRD pattern of the product obtained after addition of the residual HAuCl_4 and l-ascorbic acid solutions in the presence of gold seeds.

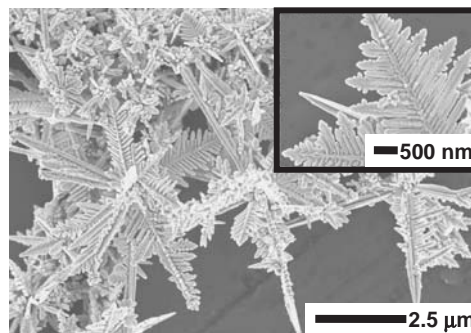


Figure 2. SEM images of the gold products. The inset is high-magnification SEM image of the products.

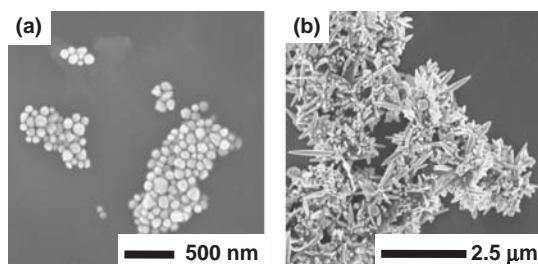


Figure 3. SEM images of gold products, showing different shapes by preadded amount of HAuCl_4 and l-ascorbic acid solutions; (a) 0 and (b) 100 μL (0.05 M HAuCl_4 , 0.0375 M l-ascorbic acid and 0.0395 M HTAB for 15 min at 65 $^\circ\text{C}$).

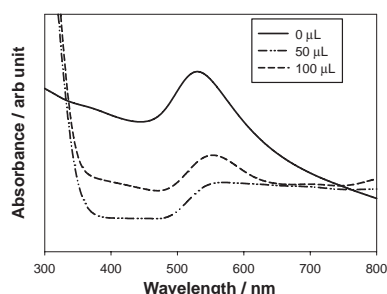


Figure 4. UV-vis absorption spectra of gold products at different preadded amount of HAuCl_4 and l-ascorbic acid solutions.

to each other. These secondary branches resemble needle crystal very much, which are the extreme case of anisotropic growth.

Figure 3 shows SEM images of gold products with different morphologies by different preadded amount of HAuCl_4 and l-ascorbic acid solutions. When the seeding solution was not added, no morphological evolution was appeared. Quasi-spheres with diameter ca. 160 nm were solely formed as shown in Figure 3a. However, when the seeding solution was 100 μL , the shape was flower-like-branched product with an average size of 1.3 μm as shown in Figure 3b. Note that some gold products did not develop into branch and kept growing into quasi-sphere with large size, conjugated on the flower-like product. These products could not make a secondary branch on the central part of the flower-like product owing to growth restriction in the presence of large amount of seeds.

Figure 4 shows UV-vis absorption spectra of gold products at different preadded amounts of the starting solutions. Gold nanoparticles exhibit surface plasmon resonance absorption that is strongly dependent on the particle morphology. For spherical gold nanoparticles, the absorption band was formed typically between 520 and 535 nm.⁵ Likewise, when the preadded amount was 0, maximum absorption band for the spherical gold was at 530 nm. As the preadded amount increased to 100 μL , the flower-like gold showed the absorption band at 560 nm. The absorption spectrum was red-shifted remarkably and show slightly broad band. When the preadded amount of the starting solutions was 50 μL , a more significant red shift in the absorption band occurs in the dendrites with a band maximum at 570 nm. Surface plasmon band is strongly dependent on length of branches of gold products. It is well known that absorption spectra are red-shifted, as spherical particles elongate into rod

or wire.⁶ The branches of the flower-like and dendritic products may have a similar effect as rod or wire.

The rapid seeding growth method allows secondary small particles to diffuse and stick to the gold seed. When the residual solution was poured into the reaction solution, the small gold nanoparticles, formed through second nucleation, might start to dissolve into the solution and grow onto the seed gold nanoparticles through Ostwald ripening. Gold seed amount is very important for crystal growth to dendritic nanostructure. Small amount of gold seed results in the formation of dendritic particles. Conversely, when much amount of seed exists in the solution, the flower-like products without the secondary branches were formed. For the role of HTAB, the surfactant molecules (HTA^+) probably act as protecting agent and structure directing agent.⁷ On the other hand, the coadsorbed Br^- ions could act as a bridge for the adsorption of HTA^+ on gold surface. HTAB can kinetically control the growth rates of various facets of gold by interacting with these facets through adsorption and desorption.⁸ The faceted growth of gold-induced the formation of the anisotropic gold covered by HTAB. Consequently, the branched structures are formed.

The formation of branched structures requires a relatively small amount of gold seed, and then the evolution of branches is determined by the seed amount and the surfactant effect.

In summary, a simple but practical method, so called seeding growth method, has been developed to attain the fractal nanostructures. Three-dimensional growth of the dendritic gold can be well controlled through preadded amount of the starting solutions. It was found that both the seed amount and the use of the surfactant HTAB play important roles in controlling the preparation of gold nanoparticles with different branched structures. From a technological point of view, these obtained the dendritic and flower-like gold particles may have important applications in microelectronic devices or nanometer-scaled electrodes.

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References

1. L. M. Sander, *Nature* **1986**, 322, 789; E. Ben-Jacob, P. Garik, *Nature* **1990**, 343, 523.
2. M. Moseler, U. Landman, *Science* **2000**, 289, 1165; J. Zhu, X. Liao, H. Chen, *Mater. Res. Bull.* **2001**, 36, 1687.
3. S. T. Selvan, T. Hayakawa, M. Nogami, M. Moller, *J. Phys. Chem. B* **1999**, 103, 7441; J. P. Xiao, Y. Xie, R. Tang, M. Chen, X. B. Tian, *Adv. Mater.* **2001**, 13, 1887; F. Favier, H. Liu, R. M. Penner, *Adv. Mater.* **2001**, 13, 1567.
4. C. J. Murphy, N. R. Jana, *Adv. Mater.* **2002**, 14, 80; N. R. Jana, L. Gearheart, C. J. Murphy, *J. Phys. Chem. B* **2001**, 105, 4065.
5. N. R. Jana, L. Gearheart, C. J. Murphy, *Langmuir* **2001**, 17, 6782.
6. Y. W. Jun, S. M. Lee, N. J. Kang, J. Cheon, *J. Am. Chem. Soc.* **2001**, 123, 5150; Y. Sun, B. Gates, B. Mayers, Y. Xia, *Nano Lett.* **2002**, 2, 165.
7. Y. H. Chen, C. S. Yeh, *Colloids Surf., A* **2002**, 197, 133.
8. V. V. Yaminsky, *J. Adhes. Sci. Technol.* **2000**, 14, 187; M. Knag, J. Sjöblom, E. Gulbrandsen, *J. Dispersion Sci. Technol.* **2005**, 26, 207.