

A Simple Approach to Control the Growth of Non-spherical Gold Nanoparticles

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Abstract: A simple method to prepare the non-spherical gold particles was developed. The result solution included trigonal, truncated trigonal, hexagonal layers, and a pseudo-pentagonal shaped gold nanocrystals. The key factor is to control the relative rates of nucleation and cluster growth in this method. These attributes make seeding growth method as a useful tool in the fabrication of colloidal metal materials. A longitudinal plasmon resonance of 866 nm was observed, which is in the near-IR spectral regions (600-1000 nm). The excellent optical properties as near-IR labels are used to develop highly sensitive analysis method.

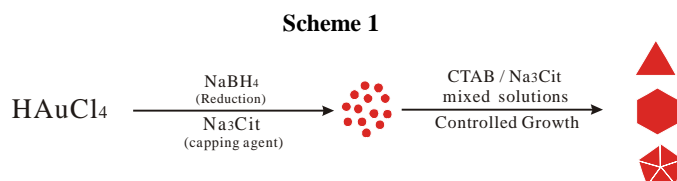
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In the past decade, attention has been paid to the formation of super-lattices of size-controlled metal nanoparticles. The common approach for controlling the size of nanoparticles is the relatively easy solution-phase chemical methods. Lastly the seeding growth methods were developed to prepare larger metal nanoparticles¹. Thus, the improved monodispersity was achieved for colloidal particles with diameters (d) ranging from 10 to 150 nm. It is predicted and confirmed that in some cases unique and improved properties are possible with anisotropic nanomaterials compared to spheres. Some methods for obtaining shaped-control nanoparticles have investigated, for example photochemical method², and electrochemical method³. The shape of metal nanoparticles was found to strongly affect the spectral position of the surface plasmon band²⁻⁴. The longitudinal plasmon resonance shifts to higher wavelengths with increasing aspect ratio or size of the particles³ and also the nanoparticles with a high aspect ratio exhibit a strong fluorescence enhancement⁴. Two distinct quadrupole plasmon resonances of anisotropic particles are observed and the Ag nanoprisms exhibit Rayleigh scattering in the red, unlike the spherical particles scattering in the blue². The key to the preparation of shape-controlled metal nanoparticles, such as tetrahedral, cubic, and rod particles, is to control specifically the growth rate of the different planes.

In the present work, a simple, alternative method according to a seeding growth

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approach is developed to yield shape-controlled gold nanocrystals as well as trigonal, truncated trigonal, hexagonal layers, and a pseudo-pentagonal gold nanocrystals (**Scheme 1**).



Firstly, the gold seeds were prepared by borohydride reduction of gold salt according to Ref 5. 50 mL aqueous solution containing 1.0×10^{-3} mol/L HAuCl_4 and 2 mL of 38.8×10^{-3} mol/L trisodium citrate was mixed in a conical flask. One minute later, 1.00 mL of fresh 0.075% NaBH_4 in 38.8 mmol/L sodium citrate was added. The solution turned pink immediately after adding NaBH_4 . The colloidal solution was stirred for an additional 10 min. The diameter of gold nanoparticles is about 5 nm. Then small nanoparticle seeds serve as nucleation centers to grow gold nanoparticles *via* reduction of a gold salt. A 10 mL aqueous solution of 1.0×10^{-3} mol/L HAuCl_4 mixed with 1 mL of 40 mmol/L NH_2OH was prepared. In the presence of CTAB and sodium citrate, 50 μL seed particles were added to the stirred growth solution. While the color of the growth solution changes from pale yellow to burgundy, the shaped gold nanoparticles were formed. Nucleation during the growth stage was inhibited by carefully controlling the growth conditions. As NH_2OH cannot act as a nucleating but only as a growth agent in slightly acidic conditions, the particle size of the existing particles is steadily increased. The CTAB can control the growth of non-spherical gold nanoparticles. The factors that selectively control the growth of Au particles is the formation of ion pairs between AuCl_4^- and cationic surfactant, and the different adsorbability of CTAB⁶. Two control experiments provide additional insight into the shaped formation of colloidal nanoparticles in order to confirm how they affect the growth of non-spherical particles. The colloidal gold was prepared in the present of CTAB or of sodium citrate only. Neither gave good results.

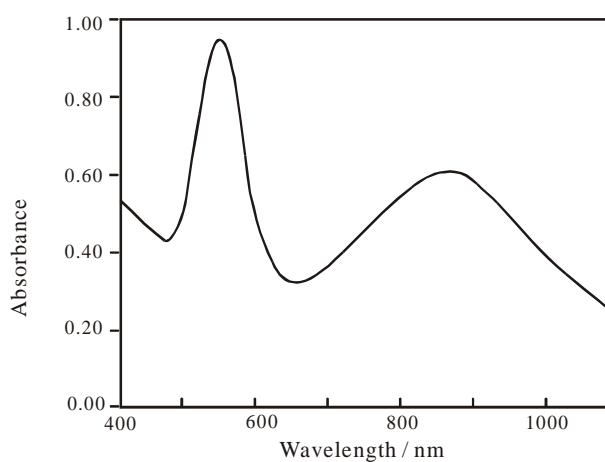
A representative TEM image is shown in **Figure 1**. Gold nanoparticles with several different shapes are formed, including trigonal, truncated trigonal, hexagonal layers, and pseudo-pentagonal shaped gold nanocrystals. The lower contrast observed for the polygons suggests that they are flat, unlike the spherical NPs around them. The electron diffraction analysis confirmed the trigonal structure lying flat on the TEM grid. It is shown from the image that the pentagonal nanoparticles form the spatial structure not as flat structure. Such a flat geometry imposes strong restrictions for the oscillation frequency of the free conduction electrons, which is directly reflected on the optical properties of the dispersion.

Figure 1 TEM photographs of shaped Au nanoparticles



The UV-visible spectrum shown in **Figure 2** was measured from a dilute sol containing the particles. The spectrum shows two distinct plasmon absorption bands centered at 540 nm and 866 nm. The band at higher energy is located at typical values for Au spheres, with a certain distortion with respect to the spherical shape. However, the band at 866 nm may only correspond to a resonance over much larger distances (observed for the longitudinal resonance). The band is broad because of the relatively high polydispersity, both in size and shape. The 866 nm band is attributed to the surface plasmon band in flat gold particles of triangular and related shapes seen in **Figure 1**. The optical properties of shaped gold nanoparticles are similar to that of the silver nanoprisms².

Figure 2 UV-visible spectrum measured from a dilute sol containing the particles



Besides Natan¹ reported the control of growth into larger particles of a predetermined size and surface-confined Au nanoparticles. The seeding approach to the synthesis of non-spherical colloidal Au nanoparticles is noteworthy in several respects. (i) The chemical reduction offers a variety of parameters that can influence the physical and chemical properties of the resulting particles. Under similar growth conditions, varying either the volume of CTAB or that of trisodium citrate will result in additional shape control of the gold nanocrystals. The choice of a capping agent is a key factor of control growth of shaped nanoparticles. The selective growth of metal nanoparticles can be achieved by varying such reaction conditions as type and concentration of the metal reactions, or depending on the different adsorbability of capping reagents for various lattice facets of metal nucleus. (ii) The particle size and shape in colloidal dispersions are strongly governed by the interplay between two processes, which occur during preparation, nucleation and cluster growth. In principle the particle size and shape can be determined by influencing the relative rates of nucleation and cluster growth. The formation of non-spherical nanoparticles must be a process that is not simply limited to an accelerated growth in one dimension but to reduce the growth rate in the other axial direction.

We have shown that the controlled growth of colloidal gold nanoparticles occurs in CTAB / sodium citrate hybrid solutions. The synthetic conditions required to prepare them are more inhomogeneous, short time and easy operation than others that have been reported². Further experiments are needed to determine the different lattice facets of non-spherical gold nanoparticles so that we can unambiguously understand the fabricative effect of cationic surfactants in synthesis of colloidal gold. It was found that the wonderful optical properties of shaped gold particles are different from that of spherical gold particles. The shaped nanoparticles are used as luminescent probes and near-IR labels.

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References

1. K. R. Brown, M. J. Natan, *Langmuir*, **1998**, *14*, 726.
2. R. C. Jin, Y. W. Cao, C. A. Mirkin, K. L. Kelly, G. C. Schatz, J. G. Zheng, *Science*, **2001**, *294*, 1901.
3. Y. Ying, S. S. Chang, C. L. Lee, C. R. C. Wang, *J. Phys. Chem. B*, **1997**, *101*, 6661.
4. M. B. Mohamed, V. Volkov, S. Link, M. A. El-Sayed, *Chem. Phys. Lett.*, **2000**, *317*, 517.
5. N. R. Jana, L. Gearheart, C. J. Murphy, *Chem. Mater.*, **2001**, *13*, 2313.
6. Z. L. Wang, R. P. Gao, B. Nikoobakht, M. A. El-Sayed, *J. Phys. Chem. B*, **2000**, *104*, 5417.

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