Facile Fabrication of Caudate Gold Nanoparticles by a Temperature-reducing Seeding Approach

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Caudate gold nanoparticles have been prepared in high yield by a simple temperature-reducing seeding approach, without additional capping agent or surfactant. The added seed colloids, the solution reaction temperature, and the initial concentration of gold ions are critical factors to form the special nanostructures. A possible mechanism is also proposed based on TEM studies.

The shape-controlled fabrication of inorganic nanoparticles has attracted extensive attention since the shape is a critical parameter for the physical and chemical properties of final materials.[1] Many efforts have been made to fabricate nanoparticles with various shapes, such as wires,[2] rods,[3] cubes,[4] belts,[5] and plates.[6] However, the preparation of nanoparticles with novel and controllable shape for promising features is still a challenge for materials scientists. Recently, Hu et al. obtained tadpole-shaped gold nanoparticles using sodium dodecylsulfonate as capping agent in a boiling aqueous solution.[7] This interesting nanostructure, with special optical and electric properties, may have unique applications in second-order nonlinear optics, nanoelectronics and other fields. Herein, we describe a novel preparation method of caudate gold nanoparticles in high yield by a modified seeding approach. In the presence of seed, high-concentration hydrogen tetrachloroaurate is reduced by an insufficient amount of sodium citrate to form caudate gold nanoparticles through a process of temperature reducing, without additional capping agent or surfactant. This simplified synthesis route helps us to propose a possible growth mechanism of the caudate nanoparticles as a kind of aggregation-based growth.

In a typical synthesis, 2.6-nm gold seed colloids were first prepared according to the Brown's method.[8] Then 60-μL seed colloids, together with 0.4 mL of 34 mM sodium citrate, were added to 100 mL of boiling 0.2 mM hydrogen tetrachloroaurate ($HAuCl_4\cdot 4H_2O$) under stirring. Subsequently, the mixture was immediately moved in an ice-water bath (4 °C), still stirring for 10 min, with the temperature dropping gradually (see Supporting Information 1).[12] During the process of temperature reducing, the solution turned from light yellow to violet, and the final temperature is 15 °C. UV–vis spectroscopy was first used to screen these nanostructures (see Supporting Information 2).[12] Obviously, the solution showed a characteristic plasmon peak at ca. 575 nm, with the full width at half-maximum (fwhm) of ca. 200 nm. Then, the morphology of the gold nanostructures was characterized by transmission electron microscopy (TEM). It is interesting that the dispersed nanoparticles exhibit a tadpole-like shape with a maximal head width of ca. 55 nm and a tail length of ca. 120 nm (Figures 1a and 1b). A high-resolution TEM (HRTEM) image taken from the head shows a well developed single-crystalline structure, while that of the tail presents polycrystalline (Figures 1c and 1d). The fringe spacing of the head is measured to be 2.4 Å, which corresponds with the spacing between {111} planes of the fcc gold (JCPDS, file No. 04.0784).

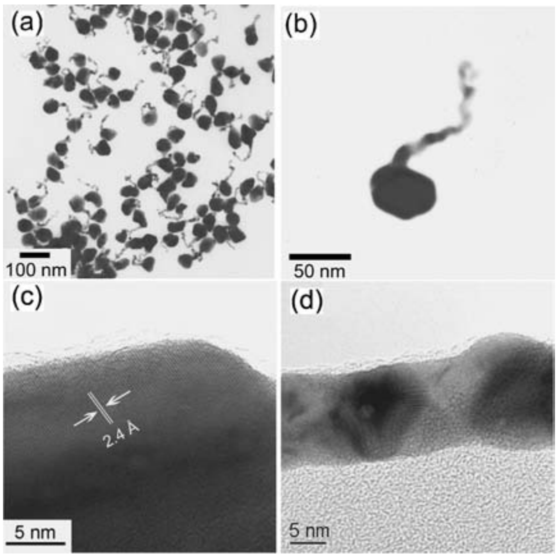

Figure 1. (a) TEM image of as-prepared tadpole-shaped gold nanoparticles, (b) magnified TEM image of a single gold nanotadpole, (c, d) HRTEM images of (c) head and (d) tail of a gold nanotadpole.

In contrast, when we kept the same-prepared mixture boiling for 10 min, only polyhedral nanoparticles were formed (see Supporting Information 3),[12] implying that the process of temperature reducing is crucial for the formation of the tadpole-shaped nanoparticles.

What leads to the different morphologies of the products? TEM studies on the intermediate stage have been carried out. At the initial stage, small spheres (10 nm) aggregated

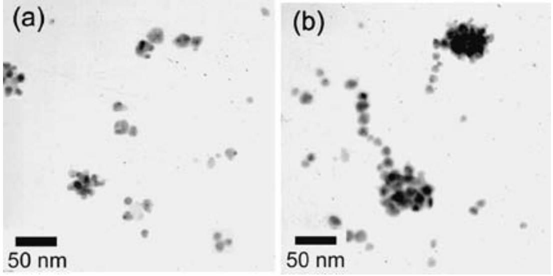

Figure 2. Typical TEM images of nanoparticles obtained (a) at the initial boiling temperature and (b) at 45 s after dropping solution temperature.

(Figure 2a). When temperature dropped, several other small spheres attached the boundary of the aggregate, almost arraying linearly (Figure 2b). These help us to hypothesize the formation of tadpole-shaped nanoparticles as a kind of aggregation-based growth, including spherical aggregation and linear aggregation. Firstly, at the boiling temperature, the seeds act as nucleation centers and grow to primary particles (small spheres) by the reduction of metal ions at their surfaces. With the lower molar concentration ratio of citrate to gold ions, these primary particles are unstable because of the insufficient capping of citrate. Favored by thermodynamics, they aggregate spherically. And these aggregations further melt to form secondary particles (heads of the tadpole-shaped nanoparticles). When temperature reduced, kinetic control becomes dominant, which is usually responsible for formation of highly anisotropic structures.[9] As a result, spherical aggregation is restrained when a primary nanoparticle attaches the boundary, other thermodynamically unstable ones have a tendency to assembly linearly by the dipole interaction to form the tail of a tadpole-shaped nanoparticle.[10] This embryonic tadpole-shaped nanoparticle evolves into a full-grown one with newly formed gold atoms by autocatalytic reduction depositing on the concave regions of the connected particles through capillary phenomenon, a kind of locatized Ostwald ripening, similar as the fabrication of gold nanowires with a 2-D network structure.[2]

It is worth mentioning that the presence of seed colloids in the solution is also an important factor in determining the morphology of the final gold nanoparticles. Under otherwise identical conditions, the solution without the addition of seed colloids can hardly produce uniformly shaped nanoparticles (see Supporting Information 4).[12] This suggests that seeds may direct uniform growth to form the small gold spheres.

Otherwise, the morphology of the caudate nanoparticles still strongly depends on the initial concentration of gold ions. The caudate nanoparticles can become kite-shaped following the same procedure used to prepare tadpole-shaped nanoparticles unless the initial concentration of $AuCl_4^-$ is increased to 0.3 mM. The kite-shaped nanoparticles consist of a triangular or truncated triangular platelike head and a tail with the maximal length of ca. 1 µm (Figures 3a and 3b). The selected-area electron diffraction (SAED) pattern of an individual nanokite in the inset of Figure 3b presents a hexagonal symmetry of the diffracted spots, indicating a single-crystalline structure. The shape change from nanotadpoles to nanokites can be attributed to the increscent concentration of gold ions, favoring a growth of single-crystalline planar nanoparticles.[11] On the contrary, when the initial concentration of $AuCl_4^-$ is decreased to 0.03 mM, nearly no caudate nanoparticles but polyhedral ones have obtained (see Supporting Information 5). It can be indicated that the high molar concentration ratio of gold ions to citrate is important for the caudate shape.

In conclusion, a novel temperature-reducing seeding approach has been developed for fabrication of two kinds of caudate gold nanoparticles, nanotadpoles, and nanokites. The method requires only a relatively short preparation time and does not need the use of any additional capping agent or surfactant. The added seed colloids, the solution reaction temperature, and the initial concentration of gold ions are critical factors to form the special nanostructures, which opens up new possibilities for the shape control of nanoparticles.

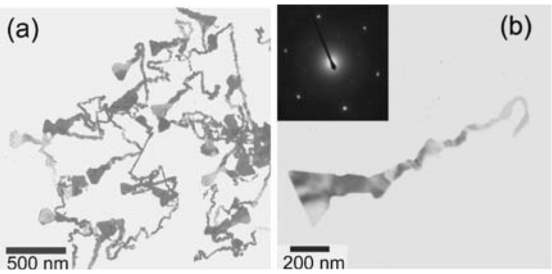

Figure 3. (a) TEM image of as-prepared kite-shaped gold nanoparticles, (b) magnified TEM image of an individual nanokite and its corresponding SAED pattern in the inset.

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References and Notes

1 B. Wiley, Y. Sun, J. Chen, H. Cang, Z. Li, X. Li, Y. Xia, *MRS Bull.* **2005**, *30*, 356.

2 L. Pei, K. Mori, M. Adachi, *Langmuir* **2004**, *20*, 7837.

3 a) C. J. Murphy, N. R. Jana, *Adv. Mater.* **2002**, *14*, 80. b) F. Kim, J. Song, P. Yang, *J. Am. Chem. Soc.* **2002**, *124*, 14316. c) B. D. Busbee, S. O. Obare, C. J. Murphy, *Adv. Mater.* **2003**, *15*, 414.

4 a) F. Kim, S. Connor, H. Song, T. Kuykendall, P. D. Yang, *Angew. Chem., Int. Ed.* **2004**, *43*, 3673. b) Y. Sun, Y. Xia, *Science* **2002**, *298*, 2176.

5 Y. Sun, B. Mayers, Y. Xia, *Nano Lett.* **2003**, *3*, 675.

6 a) S. Chen, D. L. Carroll, *Nano Lett.* **2002**, *2*, 1003. b) Y. Shao, Y. Jin, S. Dong, *Chem. Commun.* **2004**, 1104. c) L. X. Sun, S. Dong, E. Wang, *Angew. Chem., Int. Ed.* **2004**, *43*, 6360. d) L. Wang, X. Chen, J. Zhan, Y. Chai, C. Yang, L. Xu, W. Zhuang, B. Jing, *J. Phys. Chem. B* **2005**, *109*, 3189. e) C. Li, W. Cai, F. Cao, B. Sun, Y. Li, C. Kan, L. Zhang, *Adv. Funct. Meter.* **2006**, *16*, 83.

7 J. Hu, Y. Zhang, B. Liu, J. Liu, H. Zhou, Y. Xu, Y. Jiang, Z. Yang, Z. Tian, *J. Am. Chem. Soc.* **2004**, *126*, 9470.

8 K. R. Brown, D. G. Walter, M. J. Natan, *Chem. Mater.* **2000**, *12*, 306.

9 Y. Xiong, J. M. McLellan, J. Chen, Y. Yin, Z. Li, Y. Xia, *J. Am. Chem. Soc.* **2005**, *127*, 17118.

10 a) J. Y. Chang, J. J. Chang, B. Lo, S. H. Tzing, Y. C. Ling, *Chem. Phys. Lett.* **2003**, *379*, 261. b) J. Liao, Y. Zhang, W. Yu, L. Xu, C. Ge, N. Gu, *Colloids Surf., A* **2003**, *223*, 177.

11 C. S. Ah, Y. J. Yun, H. J. Park, W. Kim, D. H. Ha, W. S. Yun, *Chem. Mater.* **2005**, *17*, 5558.

12 Supporting Information is available electronically on the CSJ-journal Web site, http://www.csj.jp/journals/chemlett/index.html.