Synthesis and Properties of Tadpole-Shaped Gold Nanoparticles

ARTICLE *in* JOURNAL OF THE AMERICAN CHEMICAL SOCIETY · SEPTEMBER 2004

Impact Factor: 12.11 · DOI: 10.1021/ja049738x · Source: PubMed

9 AUTHORS, INCLUDING:


Bo Liu
Xiamen University


Jinxuan Liu
Dalian University of Technology

Zhilin Yang
Xiamen University


Zhong-Qun Tian
Xiamen University

J|A|C|S
COMMUNICATIONS

Published on Web 06/08/2004

Synthesis and Properties of Tadpole-Shaped Gold Nanoparticles

Jianqiang Hu, Yong Zhang, Bo Liu, Jinxuan Liu, Haihui Zhou, Yunfeng Xu, Yuxiong Jiang, Zhilin Yang, and Zhong-Qun Tian*

State Key Laboratory for Physical Chemistry of Solid Surfaces and Department of Chemistry, Xiamen University, Xiamen 361005, China

Received January 15, 2004; E-mail: zqtian@xmu.edu.cn

Metal building blocks with dimensions on the nanometer scale exhibit a wide range of unique electrical and optical properties associated with both their structures and shapes,[1] and thus they have potential for fabricating electrical devices,[2] biological labels,[3] optical devices,[4] magnetic data storage systems,[5] and biological sensors.[6] However, a major barrier for the applications of the blocks is to fabricate nanoparticles with novel structures and shapes because they display novel properties and have wider applications in comparison to nanostructures with the more common shape.[3] Now, spherical or one-dimensional metal nanostructures with controllable size or aspect ratio have been successfully synthesized.[7,8] However, the challenge of synthesizing these nanoparticles with novel structures and shapes has been met with limited success. Yet, some metals have effectively been processed into nanoparticles having unusual and controllable shapes, such as tetrahedrals, polyhedrals, irregular prismatics, cubics,[9] triangles,[10] ribbons,[11] prismatics,[3] disks,[12] triangular nanoframes and nanoplates,[13] nanodisks,[14] etc. Recent promising work in this field is the synthesis of silver nanocubes that were also used as sacrificial templates to prepare case-shaped gold nanoparticles.[15] Here we report the synthesis of gold nanoparticles with a tadpole shape in single, dispersed, and high yield using a simple aqueous-phase chemical procedure.

Well-defined, single, dispersed, structurally unusual, tadpole-shaped gold nanoparticles were synthesized by the reduction of chloroauric acid with tri-sodium citrate in the presence of a capping agent such as sodium dodecylsulfonate (see Supporting Information 1). Transmission electron microscopic (TEM) and atomic force microscopic (AFM) images show a clear view of its three-dimensional (3D) stereographic-structure (Figure 1 A,B). The nanoparticles possess a well-defined shape with a maximal head width of ~25.0 nm and a tail that tapers along its longitudinal axis of ~115.0 nm. Figure 1 C,D gives two typical high-resolution TEM (HRTEM) images of the head and tail of a gold nanotadpole synthesized using this method described, and the insets show their respective Fourier transform (FT) patterns. It can be easily inferred from these images that the head and tail of the nanotadpole possess different structures (poly- and single-crystalline, respectively), but the tadpole-shaped object as a whole maintains polycrystalline (see Supporting Information 2).

Figure 2 shows a typical 3D stereograph of the tadpole that is marked with an arrow in Figure 1B. It can be clearly seen from magnified Figure 1A and Figure 2 that the width of the tadpole gradually broadens (from ~5.0 to ~25.0 nm) from the head to the tail along the longitudinal axis, and then narrows (from ~25.0 to ~5.0 nm); its height regularly increases (from ~3.0 to ~8.3 nm), and then decreases (from ~8.3 to ~3.1 nm) (see Supporting Information 3). Interestingly, the highest point (~8.3 nm) of the tadpole corresponds to its greatest width (~25.0 nm). Furthermore, the height at any one point of the tadpole is smaller than its corresponding width. As a result, a vertical section at any one point

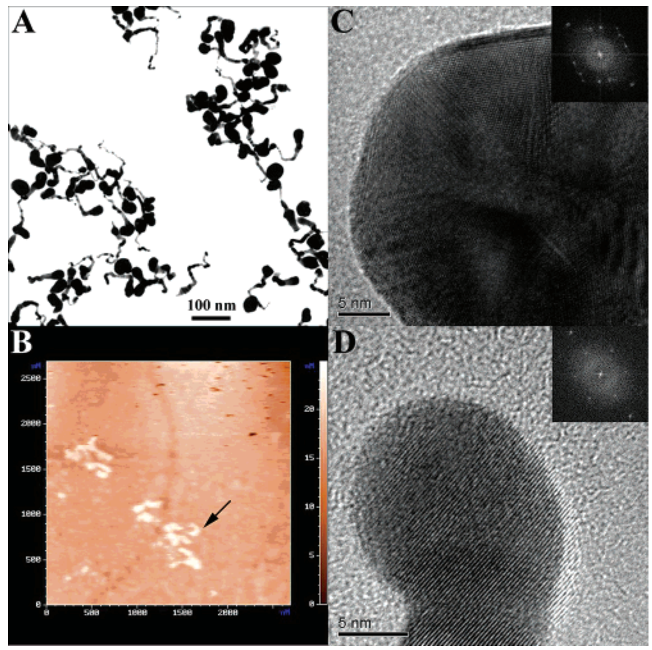

Figure 1. (A) TEM and (B) AFM images of tadpole-shaped gold nanoparticles. (C) Head and (D) tail HRTEM images of a gold nanotadpole, and their insets are the corresponding Fourier transform (FT) patterns.

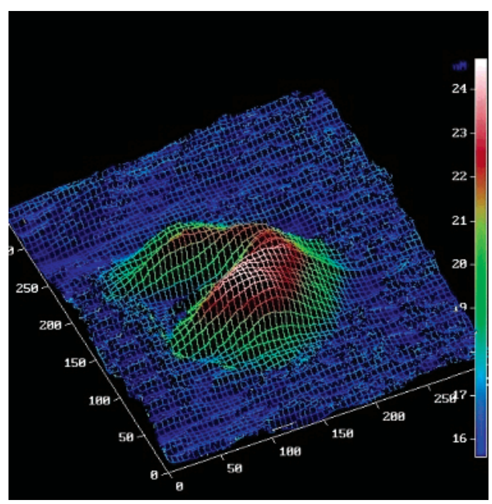

Figure 2. Three-dimensional (3D) stereograph of the tadpole at the point of the arrow marked in Figure 1B.

of the tadpoles is not round, but oblate; thus, they have a "real" tadpole-like appearance.

The optical properties of metallic nanoparticles depend on shape.[16] For example, the nanospheres with a diameter of ~25 nm prepared by the method described (see Supporting Information 1

10.1021/ja049738x CCC: $27.50

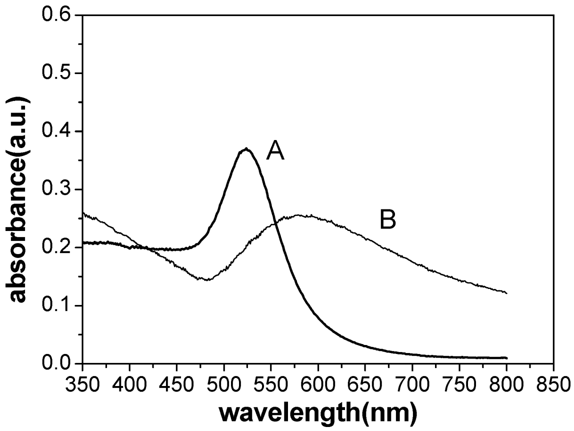

Figure 3. UV−visible images of differently shaped gold colloids synthesized by the method described. (A) Sphere. (B) Tadpole.

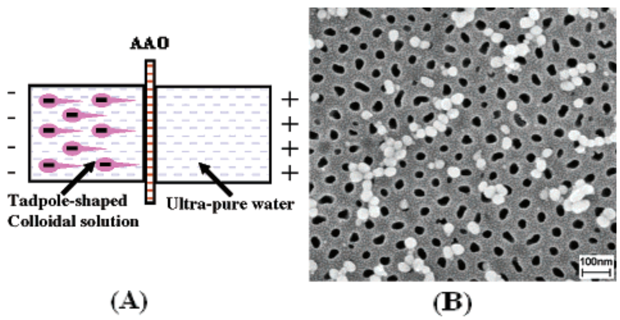

Figure 4. (A) Schematic illustration of the electrophoresis process for tadpole-shaped nanoparticles. (B) SEM image of AAO template packed by the tadpoles. Scale bar: 100 nm.

and 4) present a narrow absorption band at ∼525 nm (Figure 3A). In comparison, the nanotadpole solution shows a broad peak at ∼583 nm with the full width at half-maximum (fwhm) of ∼150 nm (Figure 3B). Such a large difference could neither be explained by regarding the tadpole as a sum of a sphere and a tapered rod nor by a somewhat imperfect sphere configuration (see Figure 3A). It suggests that the tadpole has the integral structure of a quantum confinement due to the big disparity in size from the maximum width of the head (∼25 nm) to the tip of the head and tail (∼5 nm).[17] Therefore, the electron oscillation corresponding to a plasmon absorption along the long axis is retarded and/or on a reflective path.

The tadpole-shaped nanoparticles have an unusual structure with an interesting optical property. These nanoparticles are also expected to exhibit some original electric properties. Colloidal nanoparticles are well-known to possess uniformly positive or negative charges on their surfaces.[18] Figure 4A shows a typical schematic illustration of an electrophoresis process for the tadpole-shaped nanoparticles, with an anodic aluminum oxidation (AAO) template in the middle with an average aperture of ∼30 nm that divides the electrophoresis device into two parts. The left (cathode) of this device is filled with tadpole-shaped colloid, the right (anode) with ultrapure water. When an electrical circuit is connected, the violet color of the tadpole-shaped colloidal solution appears on the anode side, indicating that the tadpoles migrate through the AAO template and are negatively charged with electricity. Figure 4B shows a typical SEM image of the AAO template packed with the tadpoles. The fact that only the heads are visible in the image suggests that the tails are protruding into the pores of the AAO template. This, in turn, implies that the tails of the tadpoles contain a higher negative charge than their heads and thus leads to its orderly moving morphology during the course of electrophoresis (as shown in Figure 4A). This point may be especially helpful for the assembly of nanodevices or joint biochips.[18]

In summary, we synthesized single, dispersed, and tadpole-shaped gold nanoparticles in a large quantity by a simple aqueous-phase chemical method. Its novel three-dimensional and crystallized structures were demonstrated by TEM, AFM, and HRTEM methods. The SEM and UV−visible absorption measurements and electrophoresis experiments revealed that the tadpoles had unusual optical and electrical properties. These attractive structures and properties may have applications in a variety of areas such as biomaterials, nanodevices, and electrochemistry.

Acknowledgment. We thank Prof. D. L. Denlinger for editing the English. This work was supported by Ministry of Science and Technology (Grant No. 2001CB610506) and Natural Science Foundation of China (Grant No. 20021002).

Note Added after ASAP Publication: There were errors in authorship and the designation of corresponding author in the version published on the Web June 8, 2004. The version published July 13, 2004, and the print version are correct.

Supporting Information Available: Synthetic and characteristic procedures of spherical and tadpole-shaped gold nanoparticles, Electrical diffraction (ED) pattern of the whole nanotadpole. Length-dependence height plot of the tadpole marked with an arrow in Figure 1B and length-dependence width plot of a tadpole in Figure 1A. TEM image of spherical gold nanoparticles synthesized by the method described. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) (a) El-Sayed, M. A. *Acc. Chem. Res.* **2001**, *34*, 257. (b) Li, J.; Wang, L. W. *Nano Lett.* **2003**, *3*, 1357.
(2) Fissan H.; Kennedy M. K.; Krinke T. J.; Kruis F. E. *J. Nanopart. Res.* **2003**, *5*, 299.
(3) Jin, R.; Cao, Y.; Mirkin, C. A.; Kelly, K. L.; Schatz, G. C.; Zheng, J. G. *Science* **2001**, *294*, 1901.
(4) Maier, S. A.; Kik, P. G.; Atwater, H. A.; Meltzer, S.; Harel, E.; Koel, B. E.; Requicha, A. A. G. *Nat. Mater.* **2003**, *2*, 229.
(5) Sun, S.; Murray, C. B.; Weller, D.; Folks, L.; Moser, A. *Science* **2000**, *287*, 1989.
(6) (a) Yu, L.; Banerjee, I. A.; Matsui, H. *J. Am. Chem. Soc.* **2003**, *125*, 14837. (b) Bruchez, M. Jr.; Moronne, M.; Gin, P.; Weiss, S.; Alivisatos, A. P. *Science* **1998**, *281*, 2013. (c) Storhoff, J. J.; Elghanian, R.; Mucic, R. C.; Mirkin, C. A.; Letsinger, R. L. *J. Am. Chem. Soc.* **1998**, *120*, 1959.
(7) (a) Jana, N. R.; Peng, X. *J. Am. Chem. Soc.* **2003**, *125*, 14280. (b) Jana, N. R.; Gearheart, L.; Murphy, C. J. *Langmuir* **2001**, *17*, 6782.
(8) (a) Hu, J.; Chen, Q.; Xie, Z.; Han, G.; Wang, R.; Ren, B.; Zhang, Y.; Yang, Z.; Tian, Z. *Adv. Funct. Mater.* **2004**, *14*, 183. (b) Mayers, B.; Jiang, X.; Sunderland, D.; Cattle, B.; Xia, Y. *J. Am. Chem. Soc.* **2003**, *125*, 13364. (c) Jana, N. R.; Gearheart, L.; Murphy, C. J. *J. Phys. Chem. B* **2001**, *105*, 4065.
(9) Ahmadi, T. S.; Wang, Z. L.; Green, T. C.; Henglein, A.; El-Sayed, M. A. *Science* **1996**, *272*, 1924.
(10) Bradley, J. S.; Tesche, B.; Busser, W.; Maase, M.; Reetz, M. T. *J. Am. Chem. Soc.* **2000**, *122*, 4631.
(11) Puntes, V. F.; Krishnan, K. M.; Alivisatos, A. P. *Science* **2001**, *291*, 2115.
(12) Chen, S.; Fan, Z.; Carrol, D. L. *J. Phys. Chem. B* **2002**, *106*, 10777.
(13) Métraux, G. S.; Cao, Y. C.; Jin, R.; Mirkin, C. A. *Nano Lett.* **2003**, *3*, 519.
(14) (a) Sun, Y.; Xia, Y. *Nano Lett.* **2003**, *3*, 1569. (b) Maillard, M.; Huang, P.; Brus, L. *Nano Lett.* **2003**, *3*, 1611.
(15) Sun, Y.; Xia, Y. *Science* **2002**, *298*, 2176.
(16) Murphy, C. J.; Jana, N. R. *Adv. Mater.* **2002**, *14*, 80.
(17) Ishikawa, H.; Tamaru, H.; Miyano, K. *J. Opt. Soc. Am. B* **2001**, *18*, 762.
(18) (a) Tsai, S. W.; Loughran, M.; Suzuki, H.; Karube, I. *Electrophoresis* **2004**, *25*, 494. (b) Gessner, A.; Lieske, A.; Paulke, B. R.; Muller, R. H. *Eur. J. Pharm. Biopharm.* **2002**, *54*, 165.

JA049738X