Fabrication of Octahedral Gold Nanostructures Using an Alcoholic Ionic Liquid

Lanzheng Ren, Lingjie Meng, and Qinghua Lu*
School of Chemistry and Chemical Technology, Shanghai Jiao Tong University, 800 Dongchuan Road, Shanghai 200240, P. R. China

(Received October 29, 2007; CL-071195; E-mail: qhlu@sjtu.edu.cn)

Octahedral gold nanocrystals have been fabricated in an alcohol ionic liquid by a one-step method in the absence of any extra capping agent. The method is based on a reaction of $HAuCl_4 \cdot 4H_2O$ in 1-(3-hydroxylpropyl)-3-methylimidazolium tetrafluoroborate ($C_3OHmimBF_4$) by microwave heating. Upon adjusting $HAuCl_4 \cdot 4H_2O$ concentration and reaction temperature, nanoplates and micrometer-sized particles have also been obtained.

Metal nanomaterials, owing to their unique chemical and physical properties such as catalytic, electronic, optical, and other properties, have attracted intensive study in extending their structures and applications in the past decade.[1–3] Among these metal nanomaterials, gold nanoparticles are of particular interest because of their many potential applications.[2] As we know, the physical and chemical properties of nanostructures are closely related to their size and shape.[1,3] Many papers describing the controlled growth of gold nanostructures using a wide range of approaches have been published, mostly focusing on rods,[4] wires,[4,5] and plates.[6] However, there remain some shapes such as octahedron that are difficult to obtain by existing methods. It is interesting to note that only very recently, octahedral metal nanocrystals have been reported.[7,8] As surface capping agents or templates, polymers are usually needed in the previous studies.

Ionic liquids (ILs) have received increasing attention in recent years.[9] They are liquid organic salts at ambient temperature and are regarded as "green solvent" for their nonflammability, high specific solvent abilities, etc.[9] Recently, ILs have been used as excellent media for the preparation and stabilization of transition-metal nanoparticles.[10] It has been suggested that both the electrostatic and coordination effects of ILs contribute to nanoparticles stabilization.[11]

Here, we describe the novel and facile fabrication of gold nanostructures, octahedral gold nanocrystals in particular, by microwave irradiation of $HAuCl_4 \cdot 4H_2O$ in 1-(3-hydroxypropyl)-3-methylimidazolium tetrafluoroborate ($C_3OHmimBF_4$). Alcohol is one of the best reducing agents for preparation of metal nanomaterials.[5,6] Thus, $C_3OHmimBF_4$ can serve as solvent, reducing agent, and stabilizer in this procedure, and polymer surfacing capping agent is not required. In addition, ILs are also excellent microwave-absorbing agents owing to their high ionic conductivity and polarizability. Thus may result a high heating rate and a significantly shortened reaction time by introducing microwave heating.[5] $C_3OHmimBF_4$ was synthesized according to the literature.[12] In a typical experiment for preparing octahedral gold nanocrystals, $HAuCl_4 \cdot 4H_2O$ (50 mg) was dissolved into 1 mL of $C_3OHmimBF_4$ in a 10-mL tube. After homogenization of the mixture, the tube was put into the microwave reactor (Apex, Shanghai EU Microwave Chemistry Technology Co., Ltd.) for a desired time. The system was equipped with a built-in magnetic stirring, and the temperature of the reaction mixture was accurately controlled by automatically adjusting microwave power output with the aid of a thermocouple sensor. The mixture was allowed to cool to room temperature, and the products were separated by centrifugation and washed with anhydrous ethanol and distilled water several times.

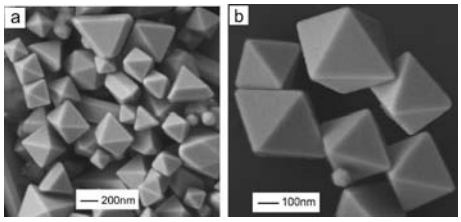

Figure 1. SEM images of the octahedral gold nancrystals obtained via 50 mg of $HAuCl_4 \cdot 4H_2O$ in 1 mL of $C_3OHmimBF_4$ at 300 °C for 1 min. (a) Low magnification, and (b) high magnification.

The typical scanning electron microscopy (SEM, JSM-7401F, operating voltage of 5 kV) images of octahedral gold nanocrystals are shown in Figure 1. It can be seen from Figure 1a that the as-prepared products consist of octahedral nanocrystals with an edge length of ca. 150–500 nm (ca. 61%), coexisting with particles of other shapes (ca. 39%). Figure 1b demonstrates the high-magnification image of the octahedral particles, from which one can clearly resolve the exact shape. It clearly demonstrates that each octahedron has eight equilateral triangle faces.

To further characterize the octahedral gold nanocrystals, transmission electron microscopy (TEM, JEOL-2010, operating voltage of 200 kV) and energy-dispersive X-ray spectrography (EDS, Oxford INCA) have also been used to illustrate the products. Figures 2a and 2b demonstrate the typical TEM image of a single octahedral gold nanocrystal as well as its corresponding geometrical model. The size of the octahedral nanocrystal is in agreement with the results of the SEM characterization. The EDS (Figure 2c) obtained from the octahedral gold nanocrystal only shows the peaks corresponding to Au, thus demonstrating that the octahedral gold nanocrystal consists only of metallic Au and that there are no residues on its surface (the peaks of Cu come from Cu grid).

The high crystalline nature of the gold nanocrystals was also confirmed by the corresponding X-ray diffraction (XRD, D/max-2200/PC, Rigaku) spectrum in Figure 3. The five sharp peaks can be assigned to the {111}, {200}, {220}, {311}, and {222} diffraction peaks of pure crystalline Au with face-centered cubic (fcc) structure. Note that the intensity ratio between the {111} and other peaks is much higher than the conventional bulk intensity ratio (JCPDS, file no. 04-0784). This observation indicates that the surfaces of the particles are primarily dominat-

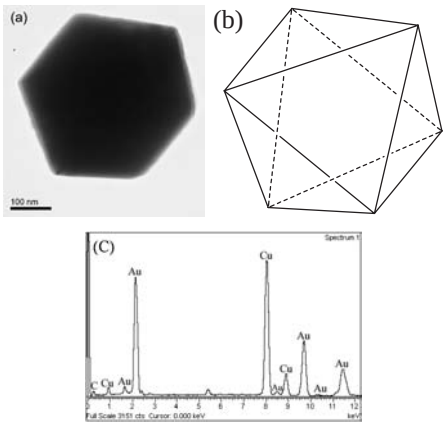

Figure 2. TEM (a) image of the octahedral gold nanocrystal and (b) its cogeometrical structure; (c) EDS spectrum of the gold nanocrystal.

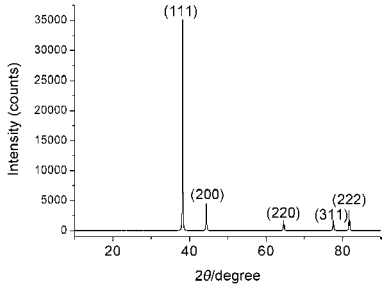

Figure 3. X-ray diffraction pattern of the octahedral gold nanocrystals.

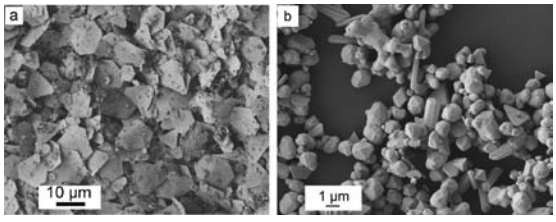

Figure 4. SEM images of the gold products prepared via microwave heating of (a) 1 mg of $HAuCl_4 \cdot 4H_2O$ in 1 mL of $C_3OHmimBF_4$ at 300 °C for 1 min, and (b) 50 mg of $HAuCl_4 \cdot 4H_2O$ in 1 mL of $C_3OHmimBF_4$ at 120 °C for 5 min.

ed by {111} facets. It is consistent with the previous report that octahedron is one of the Platonic solid shapes and covered with the {111} family of planes.[13]

It is found that both the reaction temperature and the $HAuCl_4 \cdot 4H_2O$ concentration are important factors in fabricating the gold octahedra. It can be seen from Figure 4 that, while other experimental conditions were the same as Figure 1, lower concentration of $HAuCl_4 \cdot 4H_2O$ result in micrometer-sized plates, and only micrometer-sized particles can be obtained at lower temperature. These results indicate that it is possible to tune the shape of the gold nanocrystals by simply controlling the reaction temperature and the concentration of $HAuCl_4 \cdot 4H_2O$.

A common point in many different reports highlights the important role of polymers or surfactants as templates or capping agents for achieving anisotropic growth. To our knowledge, only spherical gold particles are obtained in the traditional solvent ethylene glycol via the microwave heating of $HAuCl_4$ without the presence of polymer surfactant (PVP).[5] Thus, it can be speculated that ions of $C_3OHmimBF_4$ play important roles like the "capping agents" directing the crystal growth and consequently determine its final shape. It has been well demonstrated that the octahedra and plates mainly bounded with {111} facets and that the surface free energy of cubic crystal is in the order of $\gamma_{\{110\}} > \gamma_{\{100\}} > \gamma_{\{111\}}$.[14] When the reduction performs at high temperature, the $AuCl_4^-$ is reduced by $C_3OHmimBF_4$ to generate Au^0 atoms at a sufficiently high rate, and the final products will take the thermodynamically favored shapes which have the lowest surface free energy. Thus, the octahedra and plates which mainly bounded with {111} facets are formed at high temperature. While the reduction becomes substantially slow at low temperature, the nucleation and growth will be turned into kinetic control and the final product can take a range of shapes deviated from the thermodynamic ones. Therefore, micrometer-sized particles with various shapes were obtained at low temperature. On the basis of above results, it demonstrates that reaction temperature, $HAuCl_4 \cdot 4H_2O$ concentration and special properties of $C_3OHmimBF_4$ play important roles in the formation of gold nanostructures. It is still unclear about the role of each reaction parameter in detail, and the crystal evolution mechanism needs further research.

In conclusion, octahedral gold nanostructures were fabricated in an alcoholic ionic liquid by microwave heating without any extra surfactant or polymer. By adjusting $HAuCl_4 \cdot 4H_2O$ concentration and reaction temperature, nanoplates and micromter-sized particles were obtained. This environmentally friendly fabrication procedure is a rapid and one-pot reaction route. The simple and facile procedure may be extended to the fabrication of other metal nanocrystals of different size.

This work was supported by the NSFC (No. 60577049) and Shanghai Municipal Science and Technology Commission (Nos. 034319224 and 0652nm017).

References

1 M. A. El-Sayed, *Acc. Chem. Res.* **2001**, *34*, 257.
2 M. C. Daniel, D. Astruc, *Chem. Rev.* **2004**, *104*, 293.
3 C. Burda, X. Chen, R. Narayanan, M. A. El-Sayed, *Chem. Rev.* **2005**, *105*, 1025.
4 C. J. Murphy, N. R. Jana, *Adv. Mater.* **2002**, *14*, 80.
5 M. Tsuji, M. Hashimoto, Y. Nishizawa, M. Kubokawa, T. Tsuji, *Chem.—Eur. J.* **2005**, *11*, 440.
6 M. Tsuji, M. Hashimoto, Y. Nishizawa, T. Tsuji, *Chem. Lett.* **2003**, *32*, 1114.
7 Y. Chen, X. Gu, C.-G. Nie, Z.-Y. Jiang, Z.-X. Xie, C.-J. Lin, *Chem. Commun.* **2005**, 4181.
8 P. Raveendran, A. Goyal, M. A. Blatchford, S. L. Wallen, *Mater. Lett.* **2006**, *60*, 897.
9 R. D. Rogers, K. R. Seddon, *Science* **2003**, *302*, 792.
10 M. Antonietti, D. Kuang, B. Smarsly, Y. Zhou, *Angew. Chem., Int. Ed.* **2004**, *43*, 4988.
11 P. Migowski, S. R. Teixeira, G. Machado, M. C. M. Alves, J. Geshev, J. Dupont, *J. Electron Spectrosc. Relat. Phenom.* **2007**, *156–158*, 195.
12 L. C. Branco, J. N. Rosa, J. J. M. Ramos, C. A. M. Afonso, *Chem.—Eur. J.* **2002**, *8*, 3671.
13 F. Kim, S. Connor, H. Song, T. Kuykendall, P. Yang, *Angew. Chem., Int. Ed.* **2004**, *43*, 3673.
14 Z. L. Wang, *J. Phys. Chem. B* **2000**, *104*, 1153.

Published on the web (Advance View) December 15, 2007; doi:10.1246/cl.2008.106