Microwave-polyol Preparation of Single-crystalline Gold Nanorods and Nanowires

Ying-Jie Zhu* and Xian-Luo Hu
State Key Laboratory of High Performance Ceramics and Superfine Microstructure, Shanghai Institute of Ceramics, Chinese Academy of Sciences, Shanghai 200050, P. R. China

(Received August 1, 2003; CL-030709)

Single-crystalline gold (Au) nanorods and nanowires have been successfully prepared in liquid phase by one-step, seedless and template-free microwave-polyol method. Ethylene glycol (EG) reduced $HAuCl_4$ to form Au by microwave heating at 160 °C. Single-crystalline Au with other morphologies was also produced.

The properties of nanostructured materials show a strong dependence not only on size but also on shape of building blocks.[1–5] Since the discovery of carbon nanotubes in 1991,[6] 1-D nanostructures, such as nanorods, nanowires, and nanotubes, have been intensively studied owing to their potential applications as important components and interconnects in nanodevices.[7–9] Gold nanorods and nanowires in particular may be useful for various optoelectronic devices.[3,4] However, spherical gold nanoparticles are easily produced by the chemical reduction of gold salts.[10,11] To prepare 1-D nanostructures is a challenging task, especially for structurally isotropic metals such as gold with face-centered cubic (fcc) symmetry. There have been several recent reports describing the preparation methods of gold nanorods, including seed-mediated[12–15] and templated[16,17] methods. However, these methods involve the use of the seed or the template, making the preparation complicated and the separation of nanorods from the template difficult. Electrochemical method without using any seed or template for preparation of gold nanorods was also reported.[18]

The microwave-polyol method has recently been used to prepare nanoparticles of Pt and Ag,[19] CdSe,[20] $Cd_{1-x}Zn_xSe$,[21] and TiO_2.[22] However, these nanoparticles prepared were spherical in shape instead of nanorods. In this paper, we demonstrate that the microwave-polyol method can be used to prepare gold nanorods and nanowires without using any seed or template.

Hydrogen tetracholoaurate ($HAuCl_4 \cdot 4H_2O$), ethylene glycol (EG) and surfactants (polyvinylpyrrolidone (PVP) and sodium dodecylsulfate (SDS)) were of analytical grade and used as received without further purification. The mixture of the reagents ($HAuCl_4$, EG, and a surfactant or two surfactants) was placed in a 100 mL round-bottomed flask and microwave-heated to 160 °C and kept at this temperature for a fixed time. The microwave oven used for sample preparation was a focused single-mode microwave synthesis system (Discover, CEM, USA). The unique, circular single-mode cavity focuses the microwave on the reactants, ensuring that the sample was in a homogenous highly dense microwave field. The system was equipped with an in situ magnetic stirring and a water-cooled condenser. Temperature was accurately controlled by automatically adjusting of microwave power. Yellow colloids were obtained after microwave heating. The products were separated by centrifugation, washed with absolute ethanol and distilled water several times, and dried at 80 °C in vacuum.

X-ray powder diffraction (XRD) patterns were recorded using a Rigaku D/max 2550V X-ray diffractometer with high-intensity Cu Kα radiation ($\lambda = 1.54178$ Å) and a graphite monochromator. TEM images were taken with a JEOL JEM-2010 and JEOL JEM-200CX transmission electron microscope, using an accelerating voltage of 200 kV.

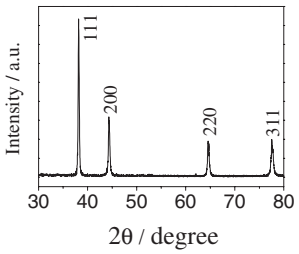

Figure 1. XRD pattern of a typical sample prepared by microwave-heating a mixture of 0.01 M $HAuCl_4$ 3 mL, 0.03 M PVP 3 mL and 20 mL EG at 160 °C for 40 min.

Figure 1 shows XRD pattern of a typical sample prepared by microwave-polyol method. The product was a single phase of well-crystallized elemental Au with a fcc structure. This indicates that EG reduced $HAuCl_4$ to form Au at 160 °C. Samples prepared between 120 and 180 °C have XRD patterns similar to Figure 1. However, no Au was obtained if temperatures were lower than 100 °C, indicating that $HAuCl_4$ could not react with EG below 100 °C.

The morphologies of samples were investigated with TEM. Figure 2 shows TEM micrographs of three typical samples prepared by the microwave-polyol method. One can see that Au nanorods and nanowires as well as Au with various morphologies were produced. The aspect ratio of a shape is defined as the length of the major axis divided by the width of the minor axis. Nanorods are defined as structures that have a width of 1–100 nm and aspect ratios greater than 1 but less than 20; and nanowires are analogous structures that have aspect ratios greater than 20.[23] Figure 2a shows an Au nanorod (aspect ratio is ca. 7.5) with a diameter of ca. 55 nm and a length of ca. 410 nm. The longest nanorod in Figure 2b has a diameter of ca. 42 nm and a length of ca. 480 nm (aspect ratio ca. 11.4). Electron diffractions on different positions of a given single nanorod/nanowire and on different nanorods/nanowires were the same, indicating that they were single crystalline. Figure 2c shows a TEM image of a randomly chosen individual Au nanorod (Sample 1) with a diameter of ca. 40 nm and a length of ca. 380 nm, its corresponding electron diffraction pattern is shown in the inset of Figure 2c. It can be indexed with the fcc Au symmetry, which is consistent with the result obtained from XRD. Other morphologies of Au nanostructures observed include spherical, triangular, hexagonal, polyhedral shapes, etc. Electron diffractions of these Au nanostructures with various morphologies were single crystal-

line, too. Typical nanowires observed are shown in Figures 2d and 2e. Two nanowires shown in Figure 2d have a diameter of ca. 55 and 100 nm and an aspect ratio of ca. 36 and 27, respectively. The nanowire shown in Figure 2e is much longer, with a diameter of ca. 50 nm and a length of ca. 7 μm, thus having a very high aspect ratio of ca. 140. The relative ratio of number of Au nanorods and nanowires to total number of Au nanostructures was around 10%. The yield of Au nanorods and nanowires is higher than that reported (4%).[13]

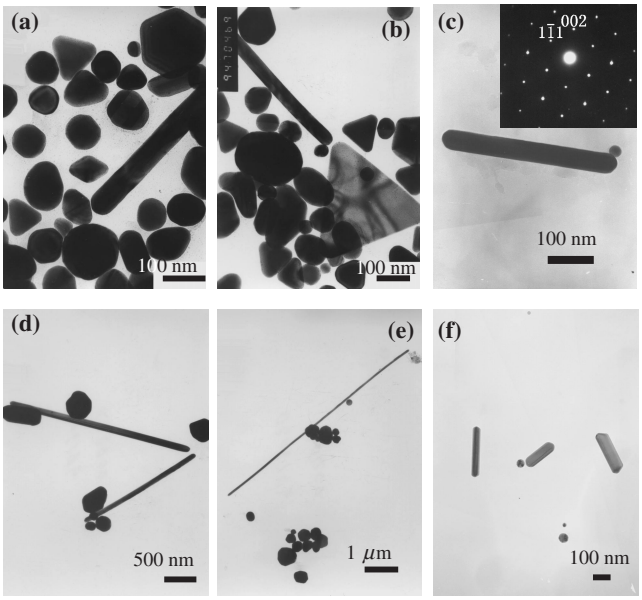

Figure 2. TEM micrographs of Au prepared by the microwave-polyol method. (a), (b), and (c) are for Sample 1 prepared by microwave-heating of a mixture of 0.01 M $HAuCl_4$ (3 mL), 0.03 M SDS (1.5 mL), 0.03 M PVP (1.5 mL) and 20 mL EG at 160 °C for 1 h. SDS and PVP were added rapidly and simultaneously. The inset of (c) is the electron diffraction pattern of the nanorod in (c). (d) and (e) are for Sample 2 prepared by microwave-heating a mixture of 0.01 M $HAuCl_4$ (3 mL), 0.03 M PVP (3 mL) and 20 mL EG at 160 °C for 30 min. PVP was added rapidly. (f) is for Sample 3 prepared by microwave-heating a mixture of 0.01 M $HAuCl_4$ (3 mL), 0.03 M PVP (3 mL) and 20 mL EG at 160 °C for 60 min (including the PVP addition time). PVP was added at a rate of 0.15 mL min^{-1}.

We studied the effect of the heating method, the addition rate of the surfactant and reaction temperature on the formation of Au nanorods and nanowires. We performed the experiment under the same conditions as Sample 1 except using the conventional heating (oil bath) method instead of microwave heating. For the sample (Sample 1) prepared by the microwave heating method, Au nanorods and nanowires were observed, as shown in Figures 2a, 2b, and 2c. In contrast, no nanorods or nanowires were observed for the sample prepared by the conventional heating method. Furthermore, by increasing the conventional heating time to 3 h at 160 °C, there were still no nanorods or nanowires observed. Sample 2 was prepared by rapid addition of PVP at 160 °C, Au nanowires were produced (Figures 2d and 2e). If PVP was added slowly at a rate of 0.15 mL min^{-1}, Au nanorods with much shorter lengths of ca. 100 to 300 nm were produced (Figure 2f). If PVP was added at a rate of 0.03 mL min^{-1}, no Au nanorods or nanowires were observed. Reaction temperature is another crucial parameter for producing Au nanorods and nanowires. Our experiments showed that Au nanorods and nanowires could only be produced in the temperature range of ca. 130 to ca. 170 °C.

In summary, we have demonstrated successful synthesis of single-crystalline Au nanorods and nanowires as well as Au nanostructures with various other morphologies by the microwave-polyol method. The reduction of $HAuCl_4$ by EG to form Au was achieved by microwave-heating at 160 °C. No seed or template was needed in the preparation.

Financial support from Chinese Academy of Sciences under the Program for Recruiting Outstanding Overseas Chinese (Hundred Talents Program) is gratefully acknowledged. We also thank the Innovation Research Fund from Shanghai Institute of Ceramics, Chinese Academy of Sciences and a Science Research Start-up Fund from the Ministry of Education of China.

References

1 "Colloidal Gold: Principles, Methods, and Applications," ed. by M. A. Hayat, Vol. 1, Academic Press, New York (1989).
2 J. A. Creighton and D. G. Eadon, *J. Chem. Soc., Faraday Trans.*, **87**, 3881 (1991).
3 J. T. Hu, T. W. Odom, and C. M. Lieber, *Acc. Chem. Res.*, **32**, 435 (1999).
4 S. Link and M. A. El-Sayed, *J. Phys. Chem. B*, **103**, 8410 (1999).
5 M. A. El-Sayed, *Acc. Chem. Res.*, **34**, 257 (2001).
6 S. Iijima, *Nature*, **354**, 56 (1991).
7 S. Frank, P. Poncharal, Z. L. Wang, and W. A. de Heer, *Science*, **280**, 1744 (1998).
8 X. Duan, Y. Huang, Y. Cui, J. Wang, and C. M. Lieber, *Nature*, **409**, 66 (2001).
9 H. M. Huang, S. Mao, H. Feick, H. Yan, Y. Wu, H. Kind, E. Weber, R. Russo, and P. Yang, *Scinece*, **292**, 1897 (2001).
10 G. Frens, *Nature*, **241**, 20 (1973).
11 D. V. Leff, P. C. Ohara, J. R. Heath, and W. M. Gelbart, *J. Phys. Chem.*, **99**, 7036 (1995).
12 C. J. Johnson, E. Dujardin, S. A. Davis, C. J. Murphy, and S. Mann, *J. Mater. Chem.*, **12**, 1765 (2002).
13 N. R. Jana, L. Gearheart, and C. J. Murphy, *J. Phys. Chem. B*, **105**, 4065 (2001).
14 B. D. Busbee, S. O. Obare, and C. J. Murphy, *Adv. Mater.*, **15**, 414 (2003).
15 B. Nikoobakht and M. A. El-Sayed, *Chem. Mater.*, **15**, 1957 (2003).
16 M. Wirtz and C. R. Martin, *Adv. Mater.*, **15**, 455 (2003).
17 S. Fullam, D. Cottell, H. Rensmo, and D. Fitzmaurice, *Adv. Mater.*, **12**, 1430 (2000).
18 Y. Y. Yu, S. S. Chang, C. L. Lee, and C. R. C. Wang, *J. Phys. Chem. B*, **101**, 6661 (1997).
19 S. Komarneni, D. S. Li, B. Newalkar, H. Katsuki, and A. S. Bhalla, *Langmuir*, **18**, 5959 (2002).
20 O. Palchik, R. Kerner, A. Gedanken, A. M. Weiss, M. A. Slifkin, and V. Palchik, *J. Mater. Chem.*, **11**, 874 (2001).
21 H. Grisaru, O. Palchik, A. Gedanken, V. Palchik, M. A. Slifkin, M. Weiss, and Y. R. Hacohen, *Inorg. Chem.*, **40**, 4814 (2001).
22 T. Yamamoto, Y. Wada, H. B. Yin, T. Sakata, H. Mori, and S. Yanagida, *Chem. Lett.*, **2002**, 964.
23 C. J. Murphy and N. R. Jana, *Adv. Mater.*, **14**, 80 (2002).

Published on the web (Advance View) November 17, 2003; DOI 10.1246/cl.2003.1140