Fabrication of Gold Nanosheet and Nanowire by Oxygen Plasma Induced Fusion of Densely Arrayed Nanoparticles

Shin-ya Onoue,[1,2,3] Junhui He,[1] and Toyoki Kunitake*[1]
[1]*The Institute of Physical and Chemical Research (RIKEN), Frontier Research System, Topochemical Design Lab., 2-1 Hirosawa, Wako 351-0198*
[2]*Kyoritsu Chemical & Co., Ltd, R&D Department, 5-1-2 Shiomi, Kisarazu 292-0834*
[3]*PRESTO, Japan Science and Technology Agency (JST)*

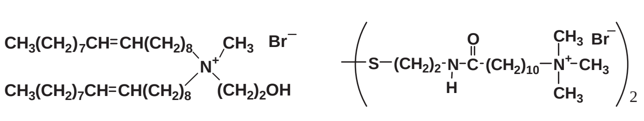
(Received October 11, 2005; CL-051284; E-mail: kunitake@ruby.ocn.ne.jp)

Densely assembled gold nanoparticles were treated by low temperature oxygen plasma to undergo complete fusion due to removal of organic protecting groups. Nanosheet and nanowire of gold with thicknesses of less than 10 nm were formed at room temperature without oxidation. Their sizes reached more than several hundred nanometers, demonstrating the effectiveness of the current method to fabricate nanoscopic architectures of mesoscopic sizes.

Precise morphological control of metallic materials is indispensable for their uses as advanced materials in nanometer to micrometer regimes.[1] Such metallic architectures may be constructed by "build-up" approach as well as by "bulk-down" approach, as in other nano-precision materials. Indeed, metallic mesoscopic architectures have been exploited in chemical and electrical reduction of metal ions on patterned templates,[2,3] and in electro and electroless ion plating techniques. Metallic nanoparticles stabilized by organic molecules are most useful precursors for this purpose, since they can be assembled to designed superstructures with different dimensions.[4–6] Controlled fusion of such nanoparticle assemblies should lead to metallic nano- and microarchitectures. It has been reported that thermal cure at 300–450 °C[7] and laser irradiation[8] caused coalescence of gold nanoparticles to produce partially linked larger particles of spherical and semispherical shapes. Another interesting cases are gradual fusion of densely populated nanoparticles[9a,9b] and rapid fusion due to desorption of short-bulky stabilizer (metastable nanoparticle).[9c] Unfortunately, the resulted structures were quite small.

In this letter, we report a facile and powerful procedure to form gold nanosheet and nanowire by a combination of controlled deposition of gold nanoparticles and removal of organic stabilizers via room temperature oxygen plasma.

Dioleylammonium surfactant (*N*-methyl-*N*-hydroxyethyldi-9-octadecenylammonium bromide (**1**))[10] and disulfide-linked ammonium surfactant (bis(trimethylammonioundecanoylaminoethyl)disulfide dibromide (**2**))[11] were prepared and characterized by TLC-FID, FT-IR, ^{1}H NMR, and elemental analysis, and used as stabilizers of gold nanoparticles (Scheme 1). Two kinds of protected gold nanoparticles were prepared by modified two phase (toluene/water)[12] and one phase (water)[11] reduction procedures. After reprecipitation in poor solvents, good solvents for the stabilizer molecules, the gold nanoparticles were collected and kept as black powders which could be redispersed homogeneously in proper solvents.[11,12] They do not contain free surfactants and stable enough for preservation for at least several months without coagulation. Transmission electron micrograph (TEM) revealed that sizes and standard deviations (SD) of gold nanoparticles protected with **1** and **2** (Au-**1** and Au-**2**) were 6.2 nm (S.D. = 0.8) and 4.6 nm (S.D. = 0.5), respectively.



1 **2**

Scheme 1.

Casting of dispersed nanoparticles on solid substrates leads to densely packed monolayers of nanoparticles due to capillary force operating during evaporation of solvents.[4] This monolayer is a convenient system for observation of nanoparticle fusion. Thus, a toluene dispersion of Au-**1** ([Au] = 5 mM) was dropped onto quartz plate for UV–vis–NIR measurement and on silicon monooxide-covered gold grid for TEM observation. A sharpened plasmon band of gold nanoparticles was observed at 552 nm for the as-prepared Au-**1** sample in UV–vis–NIR measurement. When the as-prepared sample was exposed to low temperature oxygen plasma, the surface plasmon band showed red shifts and decreasing intensity with increasing exposure time. At the same time, the absorption increased in the range of 630–2000 nm (Supporting Information I). These spectral changes are typically observed when gold nanoparticles are con-

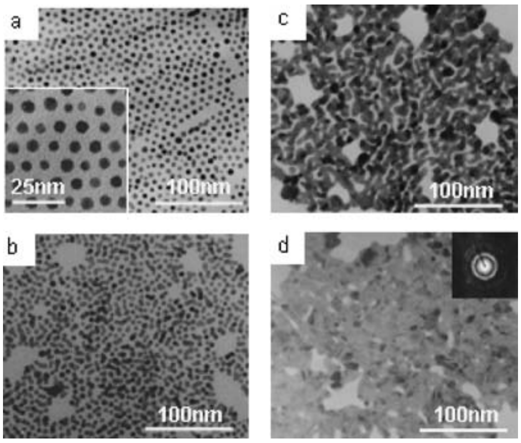


Figure 1. TEM images of a monolayer of Au-**1** (6.2 nm) before (a) and after 2.5 min (b), 15 min (c) and 45 min (d) exposure to oxygen plasma (PE-2000 Plasma Etcher (South Bay Technology), 10 W, 180 mTorr). (d)-inset is the diffraction pattern of image (d). The TEM observation was carried out on a JEOL JEM 2000EX transmission electron microscope at an acceleration voltage of 120 kV.

verted to larger structures.[13] This assumption was verified by TEM observation.

Figure 1a shows TEM images of as-cast gold nanoparticles. Closely packed domains of nanoparticles were readily obtained, where adjacent gold nanoparticles were separated by the steric hindrance of long oleyl chains of stabilizer **1**. When this sample was exposed to oxygen plasma at 10 W for 2.5 min, fusion among a few neighboring gold nanoparticles occurred extensively (Figure 1b). Low temperature oxygen plasma contains a variety of activated species, including radicals, ions, free electrons, and gas molecules. Such plasma states of oxygen can effectively decompose the organic protecting groups without direct thermal fusion of nanoparticles.[14] However, this makes gold nanoparticles more amenable to fusion in order to minimize their surface energy. Additional exposure for 12.5 min led to further fusion of these nanoparticles, but their particle morphology still remained (Figure 1c). After 45-min oxygen plasma treatment, complete fusion of the gold nanoparticles was observed and extended gold sheets were formed in most of the view area with small voids due to initial defects of the nanoparticle array and shrinking (Figure 1d). The gold nanosheet was extended to several hundreds nanometers and possessed a thickness of less than 10 nm, as confirmed by cross sectional TEM observation. In the case of sparsely scattered gold nanoparticles, the extended fusion did not occur. Dense assembly of gold nanoparticles was indispensable for the formation of extended and well fused structures. Since the organic components should be completely decomposed within 15 min,[14] the extended fusion may not be induced simply by removal of the protective organic shell. The atomic diffusion among neighboring may be accelerated under plasma irradiation. Electron diffraction experiments revealed a pattern of five rings that correspond to fcc gold crystals, indicating that gold exists in its metallic state. Interestingly, surface atoms of gold nanosheets were not at all oxidized by oxygen plasma under the experimental conditions employed, as evidenced from XPS investigation (Supporting Information II).

In order to obtain gold nanowire by a similar method, gold nanoparticles should be aligned in one dimension. For this purpose, we employed cationic gold nanoparticles (Au-**2**) that were densely aligned onto anionic λ-DNA molecules as one-dimensional template (Figure 2a).[9c,15] The composite of cationic gold nanoparticles and DNA molecule readily forms bundle structure. The quaternary ammonium groups located densely on the gold nanoparticles will act as a linker between DNA chains. The initial bundle width of the composite was adjustable with the initial concentration of DNA or with the charge ratio of DNA and gold nanoparticles. When the organic moiety (DNA and protecting groups) is removed by oxygen plasma (180 mTorr, 10 W, 60 min), fusion of the gold nanoparticle proceeds along the original DNA chain. Figures 2b and 2c show TEM images of the gold nanoparticles assembled onto λ-DNA molecules after oxygen plasma treatment. Most of the nanoparticles were aligned one-dimensionally and fused to form nanowire. The length of gold nanowires corresponded to that of λ-DNA. The width of the nanowire was 20–30 nm (Figure 2b) and 50–100 nm (Figure 2c), depending on the initial concentration of λ-DNA.

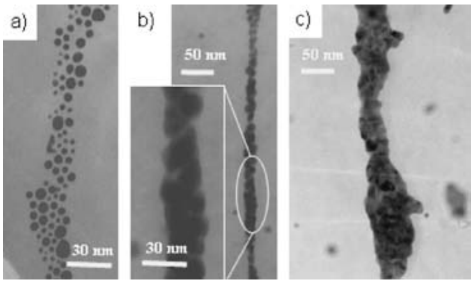


Figure 2. TEM images of one-dimensionally aligned Au-**2** (4.6 nm) on λ-DNA (a) and of fused structures after 60 min oxygen plasma treatment (b) and (c). Nanowire widths: (b) 20–30 nm (mixed with 7.2 µg/l λ-DNA), (c) 50–100 nm (mixed with 72 µg/l λ-DNA).

We have shown that extensive fusion converted one- and two-dimensionally assembled gold nanoparticles to gold nanosheet and nanowire by oxygen plasma treatment. Low temperature plasma irradiation can lead to controlled fusion of nanoparticle assemblies due to suppression of less-controlled thermal fusion. Its additional advantage is the use of tailor-made organic stabilizers. The stabilizer molecule may be removed not only by oxygen plasma but also by light of specific wavelengths, by specific chemical reactions, if properly designed stabilizers are used. Thus, accelerated fusion of unstabilized metal nanoparticles under moderate conditions will offer new possibilities in the fabrication of nanoprecision materials.

The authors thank Ms. A. Nakao in beam application team, RIKEN for XPS measurement and fruitful discussions.

References

1 *Nanoparticles and Nanostructured Films. Preparation, Characterization and Application*, ed. by J. H. Fendler, Wiley-VCH, Weinheim, **1998**.
2 S. Hoeppener, R. Maoz, S. R. Cohen, L. Chi, H. Fuchs, J. Sagiv, *Adv. Mater.* **2002**, *12*, 1036.
3 a) E. Braun, Y. Eichen, U. Sivan, G. Ben-Yoseph, *Nature* **1998**, *391*, 775. b) J. Richter, R. Seidel, R. Kirsch, M. Mertig, W. Pompe, J. Plaschke, H. K. Schackert, *Adv. Mater.* **2000**, *12*, 507.
4 M.-C. Daniel, D. Astruc, *Chem. Rev.* **2004**, *104*, 293.
5 T. Yonezawa, S. Onoue, N. Kimizuka, *Adv. Mater.* **2001**, *13*, 142.
6 B. A. Korgel, D. Fitzmaurice, *Adv. Mater.* **1998**, *10*, 6613.
7 a) S. Fullam, D. Cottel, H. Rensmo, D. Fitzmaurice, *Adv. Mater.* **2000**, *12*, 1430. b) J. He, T. Kunitake, T. Watanabe, *Chem. Commun.* **2005**, 795.
8 Y. Niidome, A. Hori, T. Sato, S. Yamada, *Chem. Lett.* **2000**, 310.
9 a) C. J. Kiely, J. Fink, M. Brust, D. Bethell, D. J. Schiffrin, *Nature* **1998**, *396*, 444. b) T. Hassenkam, K. Nørgaard, L. Iversen, C. J. Kiely, M. Brust, T. Bjørnholm, *Adv. Mater.* **2002**, *14*, 1126. c) T. Yonezawa, S. Onoue, N. Kimizuka, *Chem. Lett.* **2002**, 1172.
10 T. Kunitake, Y. Okahata, *Chem. Lett.* **1977**, 1337.
11 T. Yonezawa, S. Onoue, T. Kunitake, *Chem. Lett.* **1999**, 1061.
12 M. Brust, D. Bethell, C. J. Kiely, D. J. Schiffrin, *J. Chem. Soc., Chem. Commun.* **1994**, 801.
13 *Absorption and Scattering of Light by Small Particles*, ed. by C. F. Bohren, D. R. Huffman, **1998**.
14 J. Huang, I. Ichinose, T. Kunitake, *Chem. Commun.* **2002**, 1910.
15 a) T. Yonezawa, S. Onoue, T. Kunitake, *Kobunshi Ronbunshu* **1999**, *56*, 855. b) M. G. Warner, J. E. Hutchison, *Nat. Mater.* **2003**, *2*, 272.

Published on the web (Advance View) January 21, 2006; DOI 10.1246/cl.2006.214