

Sputter deposition onto ionic liquids: Simple and clean synthesis of highly dispersed ultrafine metal nanoparticles

Tsukasa Torimoto,^{a)} Ken-ichi Okazaki, and Tomonori Kiyama

Graduate School of Engineering, Nagoya University, Chikusa-ku, Nagoya 464-8603, Japan

Kaori Hirahara and Nobuo Tanaka

EcoTopia Science Institute, Nagoya University, Chikusa-ku, Nagoya 464-8603, Japan

Susumu Kuwabata

Graduate School of Engineering, Osaka University, Suita, Osaka 565-0871, Japan

(Received 22 August 2006; accepted 1 November 2006; published online 14 December 2006)

Sputter deposition of gold (Au) onto ionic liquids (ILs) resulted in the formation of highly dispersed Au nanoparticles without additional chemical species, such as reducing and/or stabilizing agents. The Au nanoparticles in 1-ethyl-3-methylimidazolium tetrafluoroborate had an average diameter (d_{av}) of 5.5 nm with a standard deviation (σ) of 0.86 nm, while sputter deposition onto *N,N,N*-trimethyl-*N*-propylammonium bis(trifluoromethanesulfonyl)imide resulted in the formation of much smaller Au nanoparticles with d_{av} of 1.9 nm and σ of 0.46 nm. Prolongation of sputtering time results in a higher concentration of Au nanoparticles in ILs, but did not cause a remarkable change in their size. © 2006 American Institute of Physics. [DOI: 10.1063/1.2404975]

Ultrafine metal nanoparticles of a few nanometers in diameter exhibit size-dependent photonic and electronic properties that are of interest for applications such as biosensors, catalysts, optics, and electronics.¹⁻⁵ In most cases of nanoparticle preparation in solution, reduction of the corresponding metal ions or metal complexes is conducted in the presence of additional stabilizing agents (e.g., thiol compounds and polymers).⁶⁻¹³ As a result, the prepared suspension contains byproducts, remaining substrates, and stabilizing agents. Since species other than metal nanoparticles are sometimes obstructive for utilization of the prepared nanoparticles, their removal is needed. On the other hand, metal-vapor-deposition techniques have been developed for the clean preparation of metal nanoparticles dispersed in organic solvents without formation of byproducts. For example, metal particles were vacuum deposited on running liquid substrates of organic solvents with a very low vapor pressure, such as alkylnapthalene and silicone oils.^{14,15} Stoeva *et al.* have developed the solvated metal atom deposition technique, where gold was vaporized under vacuum followed by deposition on the inside walls of a liquid-nitrogen-cooled vacuum chamber simultaneously with acetone vapor.¹⁶ However, these methods required complicated apparatuses equipped with rotary reactors or cooled traps to collect metal vapor, and furthermore, deposited particles generally made large aggregation unless suitable stabilizing agents, such as thiol compounds or surfactants, were added.

Ionic liquids (ILs) have attractive features such as high ionic conductivity and capability to dissolve many kinds of substances.¹⁷⁻¹⁹ The extremely low vapor pressure of ILs has enabled x-ray photoemission spectroscopy²⁰ and scanning electron spectroscopy²¹ measurements under a high vacuum condition. This property of ILs also enables vacuum deposition of solid materials onto ILs, though such attempts have never been made. Here we report an extremely clean method to synthesize gold (Au) nanoparticles in ILs using the sputter

deposition technique without any additional stabilizing agents. The simple sputter deposition onto ILs resulted in the formation of a solution containing highly dispersed Au nanoparticles whose size was dependent on the kind of IL used.

ILs of 1-ethyl-3-methylimidazolium tetrafluoroborate (EMI-BF4) and *N,N,N*-trimethyl-*N*-propylammonium bis(trifluoromethanesulfonyl)imide (TMPA-TFSI) were purchased from Kanto Chemical Co., Inc., and dried for 3 h at 378 K under vacuum. An IL (0.60 cm³) was spread on a glass plate (20 cm²) that was horizontally set in a sputter coater (Eiko, IB-3). It was located at a distance of 35 mm from the gold (99.99% in purity) foil target. Sputter deposition onto ILs was carried out with a current of approximately 4.0 mA under an air pressure of approximately 20 Pa at room temperature. The structure and size distribution of nanoparticles were examined using a JEOL 2010 transmission electron microscope (TEM) operated at 120 kV acceleration voltage. TEM samples were prepared by dropping the IL solution onto a copper TEM grid with amorphous carbon overlayers, followed by the removal of excess amount of solution with a filter paper.

Figure 1(a) shows changes in the absorption spectra of EMI-BF4 with the sputter deposition of Au. Spectra showing onset around 800 nm and a shoulder around 520 nm assigned to the surface plasmon resonance (SPR) peak of Au nanoparticles developed with elapse of sputtering time. The concentration of Au in the IL was proportional to the sputtering time, as shown in the inset of Fig. 1(a). It is well known that the SPR peak becomes remarkably sharp with an increase in the size of spherical Au nanoparticles from 2 to 9 nm.^{22,23} However, the peak shape of the spectra shown in Fig. 1(a) seemed to be invariable even when the Au concentration reached as high as 33 mmol dm⁻³ after 120 min of sputtering. This indicates that the successive sputtering did not cause any significant change in the size as well as size distribution of Au nanoparticles. Hence, a desired concentration of Au nanoparticles was simply obtained by adjusting the sputtering time.

^{a)}Electronic mail: torimoto@apchem.nagoya-u.ac.jp

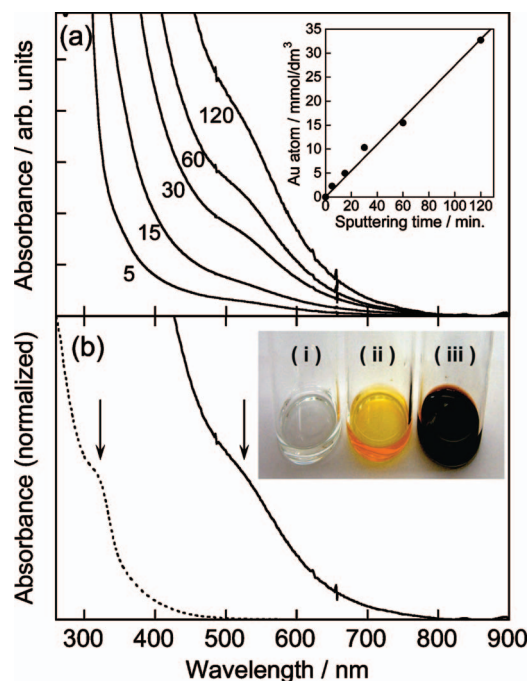


FIG. 1. (Color) (a) Changes in the absorption spectra of EMI-BF4 with sputter deposition of Au. Sputtering time is shown in the unit of minutes in the figures. (Inset) Concentration of Au in EMI-BF4 as a function of sputtering time. (b) Normalized absorption spectra of EMI-BF4 (solid line) and TMPA-TFSI (dotted line). The spectra were obtained by the sputter deposition of Au for 30 min and normalized in absorbance at arrows. (Inset) Photographs of original TMPA-TFSI (i) and Au-deposited ILs of TMPA-TFSI (ii) and EMI-BF4 (iii).

The colorless solutions of TMPA-TFSI and EMI-BF4 turned yellow and dark red, respectively, after the sputter deposition of Au [inset of Fig. 1(b)], and their absorption spectra were greatly dependent on the kind of IL used, as shown in Fig. 1(b). The sputtering of Au into TMPA-TFSI gave an absorption spectrum exhibiting onset around 500 nm and an absorption shoulder around 320 nm, which were apparently blueshifted compared with the spectrum of nanoparticles in EMI-BF4. It has been reported that in the case of Au nanoparticles prepared by the chemical reduction of Au ions, the SPR peak around 520 nm disappeared when the particle size was less than 2 nm.²² Instead, absorption peaks in the range of 300–450 nm were observed in spectra of synthesized Au clusters.^{24,25} These facts suggest that our sputtering method would be useful even for preparation of metal clusters. The nanoparticles dispersed in both ILs were very stable; no recognizable change in their absorption spectra was observed for several months under an N₂ atmosphere in the dark.

To verify the above-described characterization of Au-deposited ILs, TEM observations of Au-deposited ILs were conducted. Highly dispersed nanoparticles with no aggregation were seen in both ILs. Sputter deposition onto EMI-BF4 resulted in the formation of spherical nanoparticles that had clear lattice fringes with interplanar spacing of 0.24 nm assigned to the (111) plane of the face-centered-cubic (fcc) crystal structure of gold, as shown in Fig. 2(a). The electron diffraction patterns of these particles consisted of seven clear diffraction rings that were assignable to diffractions from (111), (200), (220), (311), (222), (420), and (422) planes of the fcc crystal structure. On the other hand, much smaller Au nanoparticles having clear lattice fringes with interplanar

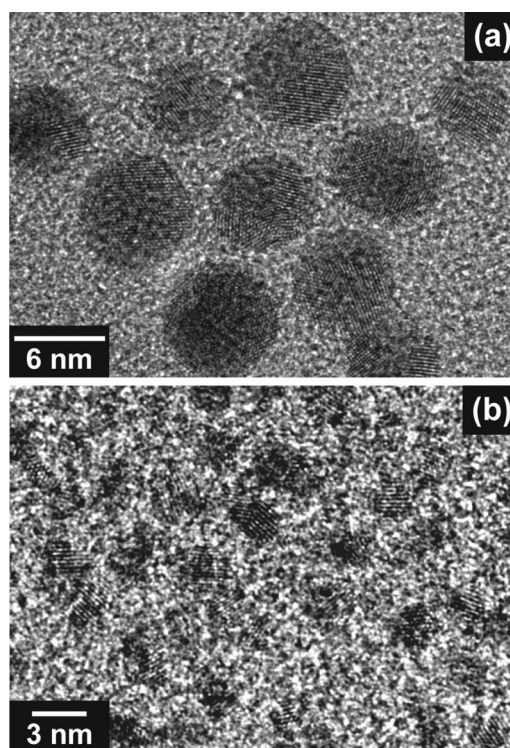


FIG. 2. TEM images of Au nanoparticles prepared by sputter deposition onto EMI-BF4 (a) and TMPA-TFSI (b).

spacing of 0.24 nm were formed in TMPA-TFSI, as shown in Fig. 2(b).

The size distribution of Au nanoparticles was determined by measuring the sizes of individual particles in TEM images (more than 100 particles). The Au nanoparticles in EMI-BF4 had an average diameter (d_{av}) of 5.5 nm with a standard deviation (σ) of 0.86 nm, while sputter deposition onto TMPA-TFSI resulted in the formation of much smaller Au nanoparticles with d_{av} of 1.9 nm and σ of 0.46 nm. In the latter case, we noticed some coalescence of nanoparticles during TEM observation, which should give a larger d_{av} value. The dependence of size variation on the kind of IL in TEM images roughly agreed with that expected from the absorption spectra in Fig. 1(b), though the precise crystal shape could not be determined in the present observations of Au clusters in TMPA-TFSI. It is well known that in sputter deposition, the bombardment of Au foil surface with energetic gaseous ions causes the physical ejection of surface atoms and/or small Au clusters.²⁶ Though sputtered species were assumed not to considerably suffer gas-phase collisions in the space between Au foil and IL solution because of low gas pressure, their injection into IL solution could make high concentration enough to coalesce with each other, resulting in the formation of larger particles. Metal nanoparticles formed by chemical reduction have been reported to be stable in ILs even in the absence of additional stabilizing agents, where the high dispersibility of nanoparticles was attributed to the prevention of coalescence between particles both by the strong adsorption of IL species on the surface and by the electrostatic repulsion between the resulting particles.^{27–31} Considering these facts, the coalescence of the sputtered species would proceed until Au nanoparticles were stabilized by the adsorption of ions of IL; the degree being dependent on the kind of IL. Furthermore, it is well known that TFSI anion makes a coordination bond with metal

ions.³² If this coordination ability works for its adsorption on nanoparticle surface, it is expected that strong adsorption of TFSI suppresses the growth and/or coalescence of particles.

In conclusion, an extremely clean way to synthesize Au nanoparticles in IL was demonstrated using the sputter deposition technique. The deposited nanoparticles were very stable in the absence of any additional stabilizing agents, and the size of nanoparticles was found to depend on the kind of IL. This could not be achieved by the vacuum deposition onto conventional organic liquids, in which the surface of metal particles must be modified with stabilizing agents to prevent the aggregation. Although the preparation of only Au nanoparticles is described in this letter, nanoparticles of various solid materials, such as semiconductors, polymers, and organic compounds, can be prepared in ILs by using strategies for the preparation of thin films in vacuum, such as thermal evaporation, pulsed laser deposition, and chemical vapor deposition. Furthermore, this technique will also enable the preparation of alloy nanoparticles with simultaneous evaporation of different kinds of pure materials. Study along this line is currently in progress.

This research was partially supported by a Grant-in-Aid for Scientific Research (B) (No. 16350095) from the Japan Society for the Promotion of Science and by a Grant-in-Aid for Scientific Research on Priority Areas (417) and on Priority Area (452) "Science of Ionic Liquids" from the Ministry of Education, Culture, Sports, Science and Technology (MEXT) of Japan.

¹G. Schmid, *Chem. Rev. (Washington, D.C.)* **92**, 1709 (1992).

²A. C. Templeton, M. P. Wuelfing, and R. W. Murray, *Acc. Chem. Res.* **33**, 27 (2000).

³N. R. Jana, L. Gearheart, and C. J. Murphy, *Chem. Mater.* **13**, 2313 (2001).

⁴C. Burda, X. B. Chen, R. Narayanan, and M. A. El-Sayed, *Chem. Rev. (Washington, D.C.)* **105**, 1025 (2005).

⁵Y. Sawai, B. Takimoto, H. Nabika, K. Ajito, and K. Murakoshi, *Faraday Discuss.* **132**, 179 (2006).

⁶C. B. Murray, D. J. Norris, and M. G. Bawendi, *J. Am. Chem. Soc.* **115**, 8706 (1993).

⁷T. Teranishi, M. Hosoe, and M. Miyake, *Adv. Mater. (Weinheim, Ger.)* **9**, 65 (1997).

⁸V. M. Cepak and C. R. Martin, *J. Phys. Chem. B* **102**, 9985 (1998).

⁹P. Mulvaney, L. M. Liz-Marzan, M. Giersig, and T. Ung, *J. Mater. Chem.* **10**, 1259 (2000).

¹⁰T. Torimoto, H. Kontani, Y. Shibusaki, S. Kuwabata, T. Sakata, H. Mori, and H. Yoneyama, *J. Phys. Chem. B* **105**, 6838 (2001).

¹¹P. V. Kamat, *J. Phys. Chem. B* **106**, 7729 (2002).

¹²Y. G. Sun and Y. N. Xia, *Science* **298**, 2176 (2002).

¹³N. Malikova, I. Pastoriza-Santos, M. Schierhorn, N. A. Kotov, and L. M. Liz-Marzan, *Langmuir* **18**, 3694 (2002).

¹⁴I. Nakatani, T. Furubayashi, T. Takahashi, and H. Hanaoka, *J. Magn. Magn. Mater.* **65**, 261 (1987).

¹⁵M. Wagener and B. Gunther, *J. Magn. Magn. Mater.* **201**, 41 (1999).

¹⁶S. Stoeva, K. J. Klabunde, C. M. Sorensen, and I. Dragieva, *J. Am. Chem. Soc.* **124**, 2305 (2002).

¹⁷T. Welton, *Chem. Rev. (Washington, D.C.)* **99**, 2071 (1999).

¹⁸M. Antonietti, D. B. Kuang, B. Smarsly, and Z. Yong, *Angew. Chem., Int. Ed.* **43**, 4988 (2004).

¹⁹M. J. Earle, J. Esperanca, M. A. Gilea, J. N. C. Lopes, L. P. N. Rebelo, J. W. Magee, K. R. Seddon, and J. A. Widegren, *Nature (London)* **439**, 831 (2006).

²⁰E. F. Smith, I. J. V. Garcia, D. Briggs, and P. Licence, *Chem. Commun. (Cambridge)* **2005**, 5633.

²¹S. Kuwabata, A. Kongkanand, D. Oyamatsu, and T. Torimoto, *Chem. Lett.* **35**, 600 (2006).

²²M. M. Alvarez, J. T. Houry, T. G. Schaaff, M. N. Shafiqullin, I. Vezmar, and R. L. Whetten, *J. Phys. Chem. B* **101**, 3706 (1997).

²³J. H. Hodak, A. Henglein, and G. V. Hartland, *J. Chem. Phys.* **112**, 5942 (2000).

²⁴G. H. Woehrle, M. G. Warner, and J. E. Hutchison, *J. Phys. Chem. B* **106**, 9979 (2002).

²⁵Y. Negishi and T. Tsukuda, *J. Am. Chem. Soc.* **125**, 4046 (2003).

²⁶W. O. Hofer, in *Sputtering by Particle Bombardment III*, edited by R. Behrisch and K. Wittmaack (Springer, Berlin, 1991), 64, p. 15.

²⁷G. T. Wei, Z. S. Yang, C. Y. Lee, H. Y. Yang, and C. R. C. Wang, *J. Am. Chem. Soc.* **126**, 5036 (2004).

²⁸W. Wojtkow, A. M. Trzeciak, R. Choukroun, and J. L. Pellegatta, *J. Mol. Catal. A: Chem.* **224**, 81 (2004).

²⁹M. A. Gelesky, A. P. Umpierre, G. Machado, R. R. B. Correia, W. C. Magno, J. Morais, G. Ebeling, and J. Dupont, *J. Am. Chem. Soc.* **127**, 4588 (2005).

³⁰L. S. Ott, M. L. Cline, M. Deetlefs, K. R. Seddon, and R. G. Finke, *J. Am. Chem. Soc.* **127**, 5758 (2005).

³¹D. B. Zhao, Z. F. Fei, W. H. Ang, and P. J. Dyson, *Small* **2**, 879 (2006).

³²D. B. Williams, M. E. Stoll, B. L. Scott, D. A. Costa, and W. J. Oldham, *Chem. Commun. (Cambridge)* **2005**, 1438.