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Fabrication of Nanoframe Structures by Site-selective Assembly of Gold Nanoparticles on Silver Cubes in an Ionic Liquid

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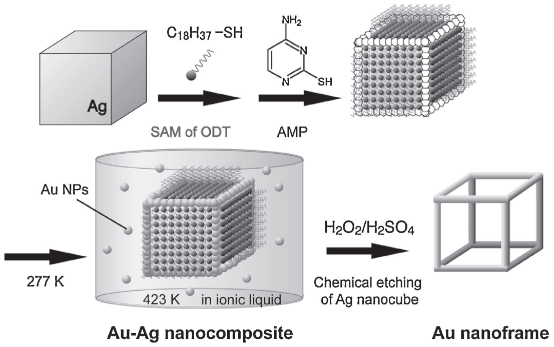
Gold nanoparticles (Au-NPs) prepared by sputter deposition of Au in an ionic liquid were selectively assembled at the edges and vertices of Ag nanocubes, the surfaces of which were modified with a self-assembled monolayer of 1-octadecanethiol and 4-amino-2-mercaptopyrimidine. Chemical etching of Ag from the resulting Au–Ag binary nanocomposites resulted in the formation of Au nanoframes.

Nanostructured metal particles, such as gold (Au) and silver (Ag), have attracted much attention because of their unique optical and electromagnetic properties depending on their shape and size.[1,2] These particles exhibit a localized surface plasmon resonance (SPR) peak in the region from visible to near-infrared light. Photoexcitation of the SPR peak induces a localized electric field near the particles and enables wide applications such as surface-enhanced Raman scattering (SERS),[3] photochemical reaction,[4] and photothermal destruction of cancer cells.[5,6] Recently, anisotropic nanoparticles such as rods,[7] cubes,[8] and prisms[9] have been successfully prepared using a chemical reduction of the corresponding metal ions and have been promising materials for plasmonic applications, because an electric field induced by SPR excitation is significantly enhanced at sharp edges and vertices of metal nanostructures.[10] Hollow gold structures, such as cubic nanoshells with hollow interiors (Au nanoboxes and nanocages) and cubic framework structures (Au nanoframes), have been fabricated by a galvanic replacement reaction[10–12] or an electrochemical deposition[13] using Ag nanocubes as a template.

We have developed an extremely clean method to synthesize metal nanoparticles, such as Au, Ag, and AuAg alloy, in ionic liquids (ILs) using a sputter deposition technique without additional chemical species, such as reducing agents and/or stabilizing agents.[14–16] The extremely low vapor pressure enabled sputter deposition of Au in ILs under high vacuum, resulting in the formation of Au nanoparticles (Au-NPs) dispersed in ILs with diameters of several nanometers. Furthermore, the thus-prepared Au-NPs could be densely immobilized on the flat surface of highly oriented pyrolytic graphite (HOPG)[16] and a silane-coupling-agent-modified quartz substrate[17] by heating an Au-NPs-dispersed IL solution spread on the substrates. Novel metal nanoarchitectures could be fabricated using Au-NPs as a building block if the particles in ILs are site-selectively accumulated on metal particles having anisotropic shapes, but this has not been attempted.

In this paper, we demonstrate a homogeneous preparation of the anisotropic nanostructures of Au nanoframes via thermally induced site-selective assembly of Au-NPs on Ag nanocubes in an IL, in which Ag nanocubes were surface-modified with a self-assembled monolayer (SAM) of two molecules having different affinities for Au-NPs. A schematic illustration of the preparation strategy is shown in Scheme 1.



Scheme 1. Illustration of the procedure to prepare the Au nanoframe via thermal assembly of Au-NPs onto Ag nanocubes in an ionic liquid.

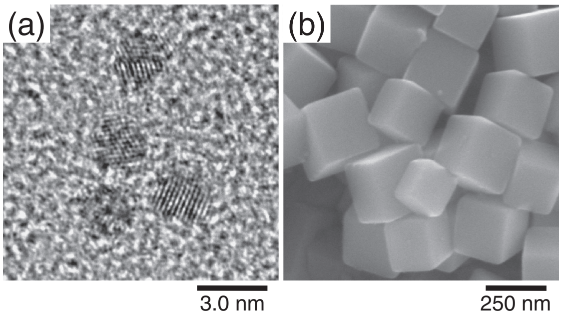


Figure 1. (a) TEM image of as-prepared Au-NPs by sputter deposition in BMI-PF_6. (b) SEM image of as-prepared Ag nanocubes.

Au-NPs were sputter-deposited in an IL of 1-butyl-3-methylimidazolium hexafluorophosphate (BMI-PF_6) using a previously reported method.[17] A 0.60 cm^3 portion of BMI-PF_6 was spread on a glass slide (5.7 cm^2) that was horizontally set in a sputter coater (JEOL, JFC-1300). 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 for 5 min with a current of 40 mA under an air pressure of 20 Pa at room temperature. A TEM image of the as-prepared Au-NPs in BMI-PF_6 is shown in Figure 1a. The average diameter of the Au-NPs was 2.5 nm.

Colloidal Ag nanocubes with sharp edges were prepared by reducing $AgNO_3$ with ethylene glycol in the presence of poly(vinylpyrrolidone) (PVP, $M_w = 40000$) as reported in our

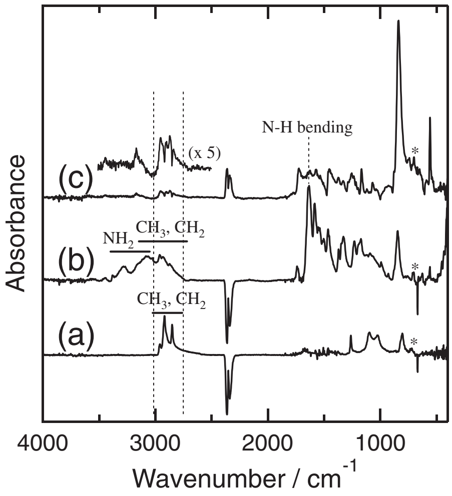


Figure 2. FTIR spectra of Ag nanocubes modified with (a) ODT, (b) AMP, and (c) both ODT and AMP.

previous paper.[13] Figure 1b shows an SEM image of the as-prepared Ag nanocubes used as a structural template in this study. The average edge length and its standard deviation were 240 and 34 nm, respectively.

The surfaces of Ag nanocubes were successively modified with two different thiol compounds, 1-octadecanethiol (ODT) and 4-amino-2-mercaptopyrimidine (AMP). A 5.0 $\mathrm{cm^3}$ portion of the suspension of Ag nanocubes (0.52 $\mathrm{mmol\,dm^{-3}}$ Ag) was mixed with 2.0 $\mathrm{mmol\,dm^{-3}}$ ODT ethanol solution (5.0 $\mathrm{cm^3}$) and left standing for 40 min in the dark. Thus-obtained ODT-modified Ag (ODT–Ag) nanocubes were washed with ethanol and then resuspended in 5.0 $\mathrm{cm^3}$ of 4.0 $\mathrm{mmol\,dm^{-3}}$ AMP ethanol solution and left standing for 6.5 h in the dark. The resulting Ag nanocubes modified with both ODT and AMP (ODT–AMP–Ag) were washed with ethanol and resuspended in acetonitrile (6 $\mathrm{cm^3}$).

Figure 2 shows FT-IR spectra of thiol-modified Ag nanocubes. Though PVP was adsorbed on the surface of as-prepared Ag nanocubes as reported in our previous paper,[13] no C=O stretching vibration at around 1630 $\mathrm{cm^{-1}}$, assigned to the PVP, was observed in the ODT–Ag nanocubes (Figure 2a). Absorption bands originating from $-\mathrm{CH_2}$ and $-\mathrm{CH_3}$ vibrations were observed at 2849 and 2918 $\mathrm{cm^{-1}}$, respectively. Furthermore, a very weak absorption attributed to C–S stretching appeared at around 720 $\mathrm{cm^{-1}}$ (peaks marked with asterisks) without showing a peak assigned to S–H vibration at 2560 $\mathrm{cm^{-1}}$.[18] These results indicated that PVP attached on the surface of as-prepared Ag nanocubes was completely replaced by ODT. Absorption bands of N–H bending vibration[19] and stretching vibrations of N–H and C–H were observed at 1635, 3170, and 2850–2950 $\mathrm{cm^{-1}}$, respectively, in the spectrum of AMP–Ag nanocubes (Figure 2b). On the other hand, the ODT–AMP–Ag nanocubes exhibited absorption bands originating from both AMP and ODT; the N–H stretching peak of AMP appeared at 3170 $\mathrm{cm^{-1}}$ and absorption peaks of $-\mathrm{CH_2}$ and $-\mathrm{CH_3}$ in ODT were observed at 2868 and 2949 $\mathrm{cm^{-1}}$, respectively, as shown in Figure 2. These results indicated that the surface of Ag nanocubes was successfully modified by both ODT and AMP after the sequential modification of individual thiol compounds.

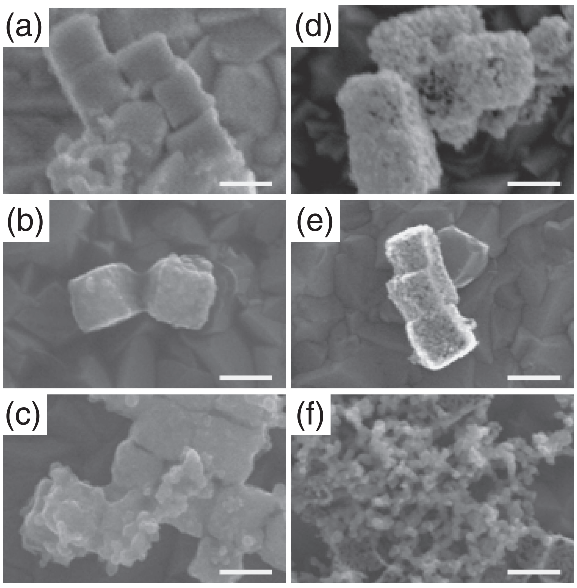


Figure 3. SEM images of Au–Ag binary nanocubes obtained by heat treatment at 423 K in BMI-$\mathrm{PF_6}$ solution containing sputter-deposited Au-NPs (a–c) and the Au nanostructures obtained after chemical etching of the corresponding Au–Ag nanocomposites (d–f). Template nanocubes used were as-prepared (a and d), AMP-modified (b and e), and ODT-modified Ag nanocubes (c and f). The bar in each image represents the scale of 250 nm.

Thermally induced self-assembly of Au-NPs was performed on thiol-modified Ag nanocubes. A 0.15 $\mathrm{cm^3}$ portion of the acetonitrile solution containing thiol-modified Ag nanocubes was mixed with a 0.30 $\mathrm{cm^3}$ portion of BMI-$\mathrm{PF_6}$, followed by stirring for 3 h at 378 K. After vacuum evaporation of acetonitrile, the BMI-$\mathrm{PF_6}$ solution containing the thiol-modified Ag nanocubes was kept standing in the dark at 277 K for 12 h and mixed with a 15 $\mathrm{mm^3}$ portion of Au-sputter-deposited BMI-$\mathrm{PF_6}$. The resulting solution was heat-treated at 423 K with stirring for 30 min under vacuum.

Heat treatment at 423 K induced the accumulation of Au-NPs over the entire surfaces of both as-prepared Ag cubes and AMP-modified Ag cubes, as shown in Figures 3a and 3b, respectively. Thus-obtained Au–Ag binary particles were chemically etched with an $\mathrm{H_2O_2/H_2SO_4}$ (3:1 v/v) mixture solution to selectively remove Ag cubes used as a template. The treatment of Au–Ag binary composites with $\mathrm{H_2O_2/H_2SO_4}$ solution caused selective dissolution of Ag metal, resulting in the formation of nanostructures composed of only Au metal as reported in our previous paper.[13] As shown in Figures 3d and 3e, the cubic particles etched with an $\mathrm{H_2O_2/H_2SO_4}$ had several pores at the surfaces, through which Ag surface could not be observed. It has been reported in our previous paper[13] that cubic Au nanoshells with hollow interiors prepared by an electrochemical method had similar surface structures, in which the pores were formed in the Au shell by the chemical etching. Furthermore, the EDX analysis of these particles revealed that the nanocomposites having cubic shapes were made of only Au. Therefore, these facts indicated that in both cases, the chemically etched particles had cubic hollow structures composed of Au-NPs (nanoboxes or nanocages).

It was reported in our previous paper[17] that Au-NPs sputter-deposited in ILs had bare surfaces and then heating ILs

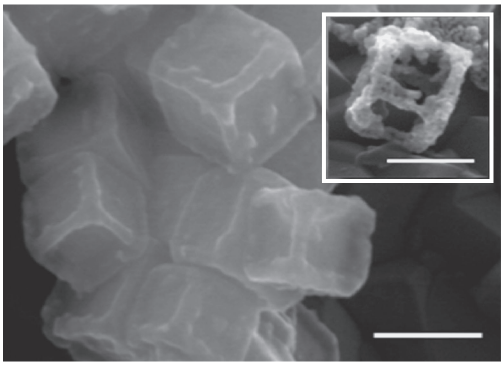


Figure 4. SEM images of ODT–AMP–Ag nanocubes obtained after deposition of Au-NPs. (Inset) Corresponding Au nanoframe prepared by chemical etching of Ag nanocube. The bar in each image represents the scale of 250 nm.

containing nanoparticles easily induced coalescence between Au-NPs to form larger particles. The results shown in Figures 3a and 3d, therefore, suggest that the heat treatment induced coalescence between Au-NPs and as-prepared Ag cubes having PVP-adsorbed surfaces, resulting in the formation of an Au shell layer on the Ag surface. On the other hand, since amino groups have been reported to show high affinity for metal nanoparticles,[20] Au-NPs were immobilized on the surfaces of AMP–Ag nanocubes during the heat treatment, with AMP-modified on the Ag cubes acting as a crosslinking agent.

In contrast, Au-NPs were rarely deposited on the surfaces of ODT–Ag nanocubes and simply coalesced with each other into large particles in BMI-PF_6 during heating at 423 K. As shown in Figure 3c, the coalesced Au particles were randomly scattered on the surfaces of ODT–Ag nanocubes. Consequently, chemical etching of Ag from thus-obtained binary composites could not produce cubic structures (Figure 3f). These facts indicated that the surface of the Ag cube was completely covered with an ODT monolayer without exposing a bare surface and that the ODT monolayer acted as a blocking layer to prevent the deposition of Au-NPs on Ag cubes, because of no affinity of the alkyl group of ODT for the Au surface.

Figure 4 shows an SEM image obtained after Au-NP deposition on ODT–AMP–Ag nanocubes by heat-treating at 423 K in BMI-PF_6. The edges and vertices of the Ag nanocubes were selectively swollen, indicating that Au-NPs were assembled and sintered to each other at the edges and vertices of Ag nanocubes. This was supported by the selective removal of Ag from thus-obtained Au–Ag binary nanocomposites by treatment with H_2O_2/H_2SO_4. The chemical etching produced cubic Au framework structures as shown in the inset of Figure 4. Thus-obtained Au nanoframes have an edge length of 270 nm, corresponding to that of Ag nanocubes, and the average width of frames was 14 nm. It has been reported that thiol molecules bound on the surfaces of Au or Ag could be replaced with other thiol molecules in a solution at the defect sites, such as terrace edges or corners on the metal surface and the boundary between domains in the self-assembled monolayer.[21,22] Therefore, the selective deposition of Au-NPs on the edges and vertices implies that ODT molecules attached on Ag cubes were partially replaced by AMP molecules, especially at the defect sites of the ODT-self-assembled monolayer on Ag cubes,[13] that is, at the edges and vertices of Ag nanocubes, on which Au-NPs were thermally deposited because of the high affinity of amino group of AMP for Au-NPs.

In summary, we have demonstrated thermally induced site-selective deposition of Au-NPs on Ag nanocubes surface-modified with both ODT and AMP to produce Au-framed Ag cubes. The resulting Au–Ag nanocomposites could be used as a precursor to form Au nanoframes via chemical etching of Ag. The sputter deposition of metals in ILs enables preparation of various kinds of metal and alloy nanoparticles. Since Ag nanoparticles with various anisotropic shapes have been successfully prepared,[2] the present technique has much potential for preparation of more complicated three-dimensional nanostructures having unique plasmonic, magnetic, or catalytic properties, by self-assembly of metal/alloy nanoparticles on Ag nanoparticles. Furthermore, since the resulting nanostructures can be obtained as dispersion, they can be easily assembled to form a desired structure on various substrates such as quartz, silicon, or graphite. Study along this line is currently in progress.

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References

1 C. J. Murphy, T. K. Sau, A. M. Gole, C. J. Orendorff, J. X. Gao, L. Gou, S. E. Hunyadi, T. Li, *J. Phys. Chem. B* **2005**, *109*, 13857.
2 B. Wiley, Y. G. Sun, B. Mayers, Y. N. Xia, *Chem.—Eur. J.* **2005**, *11*, 454.
3 C. J. Orendorff, L. Gearheart, N. R. Jana, C. J. Murphy, *Phys. Chem. Chem. Phys.* **2006**, *8*, 165.
4 C. W. Yen, M. A. Mahmoud, M. A. El-Sayed, *J. Phys. Chem. A* **2009**, *113*, 4340.
5 J. Y. Chen, D. L. Wang, J. F. Xi, L. Au, A. Siekkinen, A. Warsen, Z.-Y. Li, H. Zhang, Y. N. Xia, X. D. Li, *Nano Lett.* **2007**, *7*, 1318.
6 J. Chen, B. Wiley, Z.-Y. Li, D. Campbell, F. Saeki, H. Cang, L. Au, J. Lee, X. Li, Y. Xia, *Adv. Mater.* **2005**, *17*, 2255.
7 S. Link, M. A. El-Sayed, *J. Phys. Chem. B* **1999**, *103*, 8410.
8 Y. G. Sun, Y. N. Xia, *Science* **2002**, *298*, 2176.
9 R. C. Jin, Y. C. Cao, E. C. Hao, G. S. Metraux, G. C. Schatz, C. A. Mirkin, *Nature* **2003**, *425*, 487.
10 M. A. Mahmoud, M. A. El-Sayed, *Nano Lett.* **2009**, *9*, 3025.
11 X. M. Lu, L. Au, J. McLellan, Z.-Y. Li, M. Marquez, Y. N. Xia, *Nano Lett.* **2007**, *7*, 1764.
12 L. Au, Y. C. Chen, F. Zhou, P. H. C. Camargo, B. Lim, Z.-Y. Li, D. S. Ginger, Y. N. Xia, *Nano Res.* **2008**, *1*, 441.
13 K. Okazaki, J. Yasui, T. Torimoto, *Chem. Commun.* **2009**, 2917.
14 T. Torimoto, K. Okazaki, T. Kiyama, K. Hirahara, N. Tanaka, S. Kuwabata, *Appl. Phys. Lett.* **2006**, *89*, 243117.
15 K. Okazaki, T. Kiyama, K. Hirahara, N. Tanaka, S. Kuwabata, T. Torimoto, *Chem. Commun.* **2008**, 691.
16 T. Suzuki, K. Okazaki, T. Kiyama, S. Kuwabata, T. Torimoto, *Electrochemistry* **2009**, *77*, 636.
17 T. Kameyama, Y. Ohno, T. Kurimoto, K. Okazaki, T. Uematsu, S. Kuwabata, T. Torimoto, *Phys. Chem. Chem. Phys.* **2010**, *12*, 1804.
18 X.-H. Zhang, S.-F. Wang, N.-J. Sun, *Bioelectrochemistry* **2004**, *65*, 41.
19 X. M. Lu, H.-Y. Tuan, J. Y. Chen, Z.-Y. Li, B. A. Korgel, Y. N. Xia, *J. Am. Chem. Soc.* **2007**, *129*, 1733.
20 A. R. Morrill, D. T. Duong, S. J. Lee, M. Moskovits, *Chem. Phys. Lett.* **2009**, *473*, 116.
21 V. Chechik, *J. Am. Chem. Soc.* **2004**, *126*, 7780.
22 B. Wrzosek, J. Bukowska, A. Kudelski, *Vib. Spectrosc.* **2005**, *39*, 257.