

Fabrication of Au Fine Structures of Nanoparticles by Anodization of Purple Gold (AuAl₂)

Kazuyuki Nishio,^{*1,2} Toshiaki Kondo,² and Hideki Masuda^{1,2}

¹*Division of Applied Chemistry, Tokyo Metropolitan University, 1-1 Minamiosawa, Hachioji, Tokyo 192-0397*

²*Kanagawa Academy of Science and Technology (KAST), 5-4-30 Nishi Hashimoto, Sagamihara 229-1131*

(Received September 15, 2009; CL-090830; E-mail: k-nishio@ecom.metro-u.ac.jp)

The anodization of purple gold (AuAl₂) in oxalic acid at low voltage (5 V) generated uniformly sized Au nanoparticles on the substrate. The surface of the sample showed a characteristic color after the anodization, which originated from the localized surface plasmon (LSP) of Au nanoparticles. The samples with Au nanoparticles could be applied as a substrate for the measurement of surface-enhanced Raman scattering of molecules.

The fabrication of uniformly sized metal nanoparticles has attracted increasing interest owing to their applicability to various applications, such as catalyst,¹ magnetic devices,² or functional optical devices.³ A functional optical device based on the localized surface plasmon (LSP) is one of the promising applications of nanoparticles. In the present report, we describe a new process for the preparation of Au nanoparticles based on the anodization of purple gold (AuAl₂) and its application to the substrate for surface-enhanced Raman scattering (SERS) measurement.^{4,5} AuAl₂ is known as a typical intermetallic compound, which is characterized by its unique purple color. The anodization of AuAl₂ in oxalic acid solution was found to generate the Au nanoparticles on substrate. Although fabrication of Au nanostructures by chemical or electrochemical etching of Au alloy has been examined,⁶ the formation of a surface having nanoparticles has not been reported so far. In the present work, the applicability of the obtained structure for the SERS substrate was also examined.

AuAl₂ alloy was prepared by melting high-purity Au (99.95%) and Al (99.99%) at the atomic ratio of 1:2. The mixture was melted by resistive heating in a vacuum environment. After cooling, the surface of the sample was polished using alumina paste (0.1 μm). The anodization of AuAl₂ alloy was conducted in 0.3 M oxalic acid under constant voltage using Al cathode. The morphology of the anodized samples was observed by scanning electron microscopy (SEM, JEOL JSM 6700F). The optical property in the visible wavelength range was measured using a spectrophotometer equipped with an integrating sphere (Hitachi U-3500). Raman scattering spectra were obtained with JASCO NRS-2000.

Figure 1 shows SEM images of AuAl₂ alloys after anodization in 0.3 M oxalic acid at 5 V. Figure 1a shows the surface of AuAl₂ after anodization at 5 V for 30 min. From the image, it can be seen that fine particles emerged from a flat surface. The particles were uniformly dispersed on the sample and isolated from each other. After anodization for 90 min (Figure 1b), a layer of larger nanoparticles was clearly observed. Enlarged image (insertion in Figure 1b) revealed that the nanoparticles covered ca. 50% of the surface, although the coagulation of nanoparticles partially occurred. Mean size of the nanoparticles was ca. 30 nm. Anodization at higher voltage (20 V) resulted in the formation of macroscopically rough and microscopically porous surface.

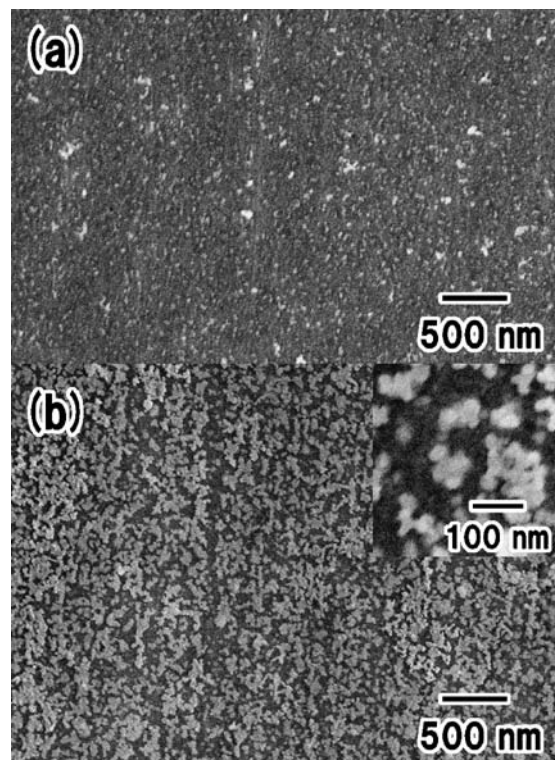


Figure 1. SEM images of AuAl₂ surface after anodization in 0.3 M oxalic acid at 5 V for (a) 30 min, (b) 90 min. Insert in (b) is an enlarged image.

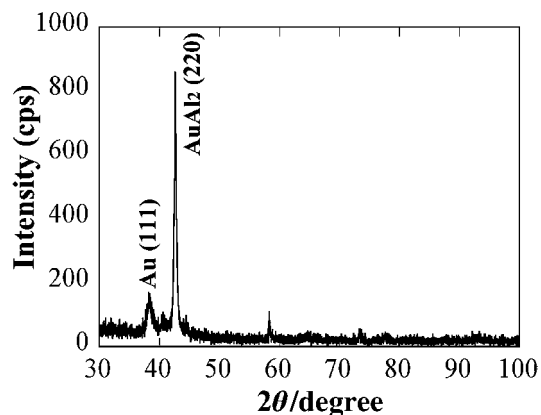


Figure 2. XRD pattern of anodized AuAl₂ in 0.3 M oxalic acid at 5 V for 90 min.

Figure 2 shows the X-ray diffraction pattern of the sample after the anodization. The strong peak at $2\theta = 42.6^\circ$ was assigned to the diffraction from (220) of AuAl₂ ($d = 0.5998$

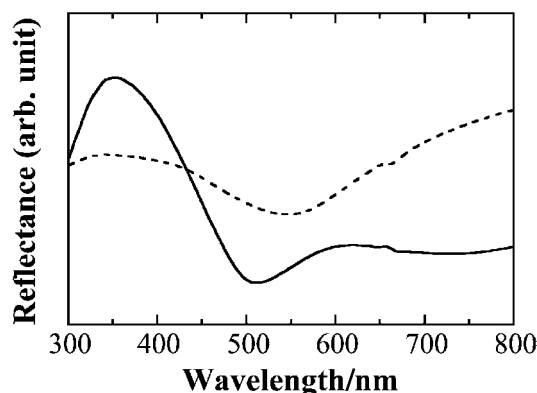


Figure 3. Reflection spectra of polished AuAl₂ (dashed line) and anodized AuAl₂ in 0.3 M oxalic acid at 5 V for 90 min (solid line). The reflectance of the anodized AuAl₂ was multiplied by 10.

nm).⁷ The small peak at 38.2°, which was not observed before the anodization (Figure S1),⁸ was assigned to the (111) plane of cubic Au ($d = 0.4079$ nm). This result indicates that the nanoparticles on the surface were crystalline Au. The detailed mechanism of the formation of Au nanoparticles is not clear at present. However, it is assumed from these results that Au atoms, which remained on the surface through the selective anodization of Al, were rearranged and form nanoparticles on the surface to reduce the surface energy.

The formation of Au nanoparticles on the AuAl₂ substrate led to a distinct color change. Figure 3 shows the reflection spectra of the sample before and after the anodization. The spectrum before the anodization corresponded to the characteristic purple color of the AuAl₂ alloy, whereas after the anodization, the decrease in the reflectance was observed at wavelengths longer than ca. 500 nm. This decrease in the reflectance was attributed to the absorption of the incident light by the LSP of Au nanoparticles on the substrate.

The formation of the surface with the LSP of Au nanoparticles could be applied to a substrate for the measurement of the Raman scattering of molecules. Figure 4 shows the Raman scattering spectrum of pyridine molecules adsorbed on the anodized AuAl₂. The clear peak at 1014 cm⁻¹ was assigned to the ring stretching band of the adsorbed pyridine molecules, while such a peak was not observed on the surface of the AuAl₂ before the anodization and chemically dealloyed AuAl₂ (Figure S2).⁸ This means that the efficiency of the Raman scattering was enhanced on the small Au particles. On the basis of this result, it can be concluded that the substrate with Au nanoparticles formed by the anodization of AuAl₂ alloy can be applied to the substrate for the SERS measurement. It has been also reported that nanoporous gold can be applied to SERS substrate.⁹ However, Au nanoparticles formed by the anodization of AuAl₂ in oxalic acid show distinct LSP adsorption in visible range. The process presented here has the possibility to enormously enhance the electric field intensity^{5,10} if the distance between the Au nanoparticles was precisely controlled by optimization of anodization conditions and composition of Au–Al alloy.

In conclusion, Au nanoparticles were fabricated on the substrate by the anodization of AuAl₂ alloy in oxalic acid at 5 V.

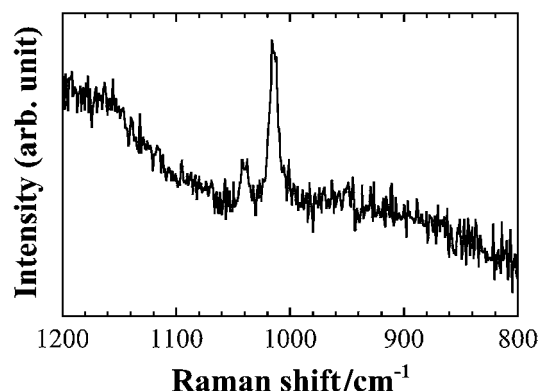


Figure 4. Raman scattering spectrum of pyridine molecules adsorbed on Au nanoparticles formed on AuAl₂ by anodization in 0.3 M oxalic acid at 5 V for 90 min. Excitation wavelength was 633 nm.

The average size of the nanoparticles was ca. 30 nm after the anodization for 90 min. The obtained sample with small Au particles was applied to the substrate for the SERS measurement. The simple process described in this work can be applied in various applications that require uniformly sized Au nanoparticles on the surface.

References and Notes

- G. Schmid, *Chem. Rev.* **1992**, 92, 1709; M. Haruta, *Chem. Rec.* **2003**, 3, 75; T. Ishida, M. Haruta, *Angew. Chem., Int. Ed.* **2007**, 46, 7154.
- K. S. Suslick, M. Fang, T. Hyeon, *J. Am. Chem. Soc.* **1996**, 118, 11960; S. Sun, C. B. Murray, D. Weller, L. Folks, A. Moser, *Science* **2000**, 287, 1989.
- A. Henglein, *Langmuir* **1999**, 15, 6738; P. V. Kamat, *J. Phys. Chem. B* **2002**, 106, 7729; K. L. Kelly, E. Coronado, L. L. Zhao, G. C. Schatz, *J. Phys. Chem. B* **2003**, 107, 668.
- M. Fleischmann, P. J. Hendra, A. J. McQuillan, *Chem. Phys. Lett.* **1974**, 26, 163; J. A. Creighton, C. G. Blatchford, M. G. Albrecht, *J. Chem. Soc., Faraday Trans. 2* **1979**, 75, 790.
- S. Nie, S. R. Emory, *Science* **1997**, 275, 1102; Y. Sawai, B. Takimoto, H. Nabika, K. Ajito, K. Murakoshi, *J. Am. Chem. Soc.* **2007**, 129, 1658.
- J. P. Candy, P. Fouilloux, M. Keddah, H. Takenouti, *Electrochim. Acta* **1981**, 26, 1029; J. Erlebacher, M. J. Aziz, A. Karma, N. Dimitrov, K. Sieradzki, *Nature* **2001**, 410, 450; M. B. Cortie, A. I. Maarroof, G. B. Smith, *Gold Bull.* **2005**, 38, 14.
- H. Büchler, K.-J. Range, *J. Less Common Met.* **1990**, 160, 143.
- Supporting Information is available electronically on the CSJ-Journal Web site, <http://www.csj.jp/journals/chem-lett/index.html>.
- S. O. Kucheyev, J. R. Hayes, J. Biener, T. Huser, C. E. Talley, A. V. Hamza, *Appl. Phys. Lett.* **2006**, 89, 053102; L. H. Qian, X. Q. Yan, T. Fujita, A. Inoue, M. W. Chen, *Appl. Phys. Lett.* **2007**, 90, 153120.
- K. Ueno, S. Juodkazis, T. Shibuya, Y. Yokota, V. Mizeikis, K. Sasaki, H. Misawa, *J. Am. Chem. Soc.* **2008**, 130, 6928.