Photoinduced Deposition of Size-Controlled Gold Nanoclusters onto the Self-Assembled Monolayer of 1,9-Nonanedithiol

Takayuki Sumida, Kei Murakoshi,# and Shozo Yanagida*
Material and Life Science, Graduate School of Engineering, Osaka University, Suita, Osaka 565-0871

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Gold nanoclusters are formed photochemically in organic solvent to give nanometer-scale islands on the self-assembled monolayer (SAM) of 1,9-nonanedithiol. The size and shape are variable by choosing electron-donating organic solvents. In ethanol, the plate-like nanoclusters are produced with layer-by-layer growth to give atomically flat top. The nano-structures are formed in *N, N*-dimethylformamide to give larger size than those in ethanol under comparable conditions.

Construction of size and shape controlled metal nano-structure onto various surfaces has attracted considerable interest because the techniques would be applicable to fabrication of mesoscopic architecture for optical or electronic nano-devices.[1] Efforts now gradually become to be focused on the techniques using chemical synthetic / surface modifying method,[2] because their dimensions are much smaller than those using ordinary lithographic techniques. Thus, the chemical technique to prepare size- and shape- controlled metal clusters onto various surfaces should be developed. The deposition of nano-sized metal is generally achieved adapting the method of underpotential deposition (UPD)[3] and the deposition using a tip of a STM.[4] In both cases, substrates must contact directly to metal ions in solution to induce electron transfer for the metal ion reduction, and thus these electrochemical techniques are not appropriate to fabricate metal nano-structure onto various surface of insulating materials, such as oxides and self-assembled monolayer, which would work as electron tunneling barrier of nano-devices. Novel approach to deposit metal nanoparticles onto chemically modified surface should be worth investigation. In this letter, we report a novel photoinduced deposition method of gold nanoparticles onto self-assembled organic monolayer on Au(111) in acetonitrile, ethanol, or *N, N*-dimethylformamide solution containing $AuCl_4^-$. Gold nanoparticles can be deposited onto the surface by photoreduction of $AuCl_4^-$. Size and shape of the particles are variable by changing the choice of solvents and photo-irradiation time.

A gold single-crystal with Au (111) facets was prepared by flame annealing of a gold wire (diameter = 0.8 mm) in gas-oxygen flame. The resulting single crystal with diameter of *ca.* 3 mm was annealed and quenched by Milli-Q water just before use. In order to obtain Au(111) covered with 1, 9-nonanedithiol as a self-assembled monolayer (SAM), the gold single-crystal was immersed into ethanol solution containing 5 mM of 1, 9-nonanedithiol for 17 h at room temperature. Photoinduced deposition of gold nanoparticles onto the SAM was carried out by irradiation of an acetonitrile, ethanol or *N, N*-dimethylformamide solution (4 mL) containing 4 x 10^{-6} M $HAuCl_4 \cdot 4H_2O$ in a 1-cm quartz cell using a 500 W xenon lamp ($\lambda > 200$ nm) after putting the single-crystal into the cell. Each solution was purged by Ar gas for 20 min before the irradiation. STM observation was carried out in air after washing out excess ions on the surface.

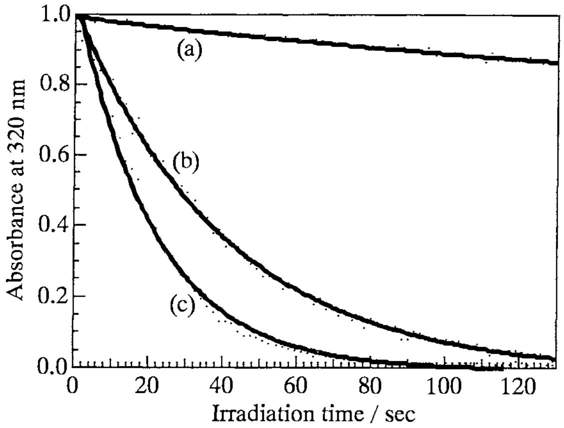

Figure 1. Time-dependence of absorbance at 320 nm in each solvent; (a) acetonitrile, (b) ethanol, (c) N,N-dimethylformamide.

Figure 1 shows time dependence of the absorption at 320 nm, which is assigned to $AuCl_4^-$, using three kinds of solvent under photo-irradiation. In acetonitrile, the decrease was slower than that in ethanol. The rate in DMF was much faster than ethanol, leading to complete disappearance of the absorption after 80-sec irradiation. Similar photoinduced decrease in absorption was previously observed in the $AuCl_4^-$ solutions, which was attributed to reduction of $AuCl_4^-$.[5] The present decrease in absorption could be also explained as due to reduction of $AuCl_4^-$. In fact, the formation of gold nanoparticles during the irradiation of $AuCl_4^-$ in ethanol and DMF was confirmed by dynamic light scattering measurement or TEM.[6] Formation of gold nanoparticles was not observed in acetonitrile. In the systems of ethanol and DMF, gold nanoparticles were dispersed relatively stable without further coagulation under the present conditions. Therefore, solvent molecules of ethanol and DMF should work as coordinating ligands as well as electron donor to reduce gold ions. Thus, not only redox potentials of solvent molecules but also the donor properties reflect the difference in rate. Considering more positive redox potential of DMF than ethanol[7] and the recovery of the absorbance at 320 nm caused by addition of HCl to DMF solution after 60-sec irradiation, faster decrease of the absorption should be partially attributed to the ligand exchange reaction of $AuCl_4^-$ giving $Au^{3+}(DMF)_n$.[8]

Figures 2a-c show the surface of Au(111) modified with 1,9-nonanedithiol after gold photodeposition for 5 min in acetonitrile, ethanol, and DMF, respectively.

In acetonitrile, typical feature of Au(111) facet was not changed during the irradiation, suggesting no deposition of gold nanoparticles. In ethanol, the formation of the nano-sized gold island was observed, and the top structure was atomically flat (Figure 2d). The islands grew two-dimensionally to form plate-like structure and covered more than half of the surface. Further deposition of second layer of the plate also occurred partially.

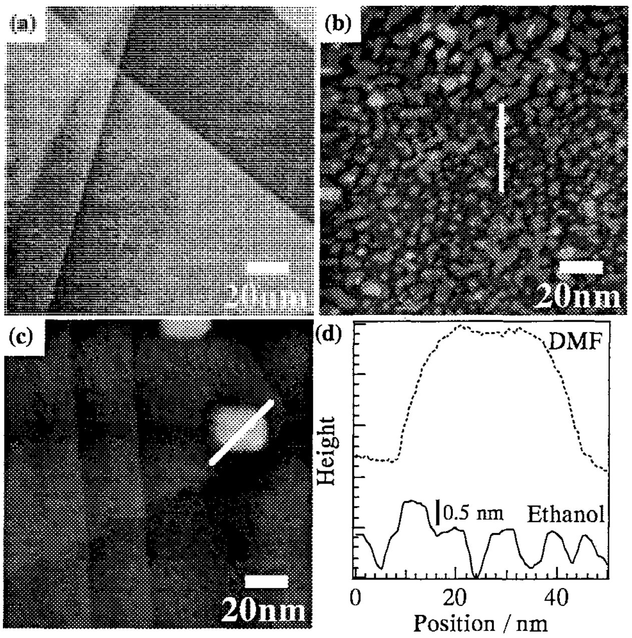

Figure 2. STM images of 1, 9 - nonanedithiol / Au (111) surface at irradiation time for 5 min in each solvent; (a) acetonitrile, (b) ethanol, (c) N, N-dimethylformamide, (d) Cross - sectional profiles along the lines indicated in (b), (c).
[Tunneling parameters : Bias voltage = 0.5 V, Tunneling current = 0.5 nA]

The island should grow via immobilization due to affinity of Au for the thiol group and aggregation of photo-formed species on the substrate. In the present system, anions such as Cl^- and the solvent molecules should adsorb on deposited gold atoms on SAM of 1, 9-nonanedithiol layer to induce such structure. The formation of the plate-like structure would be caused by similar mechanism in the layer-by-layer growth of Pd / Au(111)[9] in solution. In DMF, the deposition of nanoparticles was also observed although the size and shape were completely different from those obtained in ethanol. Figures 2c and 2d show the appearance of larger nanostructure with *ca.* 30 nm wide and 3 nm thick. As further irradiation time passed, the size, i.e., height and width of the larger nanostructure was not changed significantly. Such structural evolution was only confirmed under irradiation. Pits structure of the surface, which are the characteristic of self-assembling layer composed of thiol molecules with long alkyl chain, are also observed in Figure 2b.

Gold nanoparticles prepared by photoreduction of $AuCl_4^-$ can be deposited on Au(111) modified with a SAM of 1, 9-nonanedithiol in organic solvents of ethanol and DMF. The island size is enlarged with increasing irradiation time in ethanol and the shape depends on the choice of organic solvent. Direct photodeposition of gold nanoparticles onto the surface of insulating layer without any synthetic procedure was achieved for the first time.

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Present address: PRESTO, Japan Science and Technology Corporation; Graduate School of Engineering Science, Osaka University.

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6 Average diameters of the gold nanoparticles in ethanol and DMF solution after irradiation for 300 sec were determined to be 4.2 nm (±0.6 nm) using dynamic light scattering measurement and 10.1 nm (±5.0 nm) using TEM, respectively.

7 Electrochemical oxidation potentials of ethanol, DMF, and acetonitrile are ca. 0.4 V, 1.4 V, and 2.7 V (vs. SCE), respectively.

8 The addition of HCl to the DMF solution containing $AuCl_4^-$ after 60-sec irradiation induces the recovery of the absorbance at 320 nm. This result indicates that ligand exchange reaction is dominant rather than the reduction of gold ions at early stage of irradiation.

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