Preparation and Characterization of Gold Nano-Particles Chemisorbed by π-Radical Thiols

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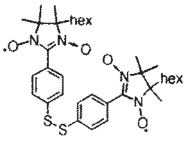
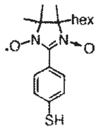
π-Radical thiol-derivatized gold nano-particles with the average diameter of 4.1 nm were isolated, and about one hundred π-radical ligands were found to be chemisorbed on the nano-particle. The solid sample of the nano-particles showed an extremely broadened ESR signal with the peak-to-peak derivative line width (ΔH_{pp}) of 30 mT at 300 K.

Urgent demand in the field of spin-electronics has prompted us to develop nano-structured magnetic composites with a characteristic electronic structure.[1] Gold nano-particles chemisorbed by alkanethiols, in particular, have drawn much attention from the viewpoint of the size effect on its electronic structure.[2] However, magnetic properties of gold nano-particles derivatized by magnetically active ligands have not been exploited yet.[3] Since the plasmon resonance absorption of gold nano-particles with diameters larger than 3 nm is observed,[4] it may be extremely interesting if the electronic structure of a gold nano-particle is spin-polarized by chemisorbed π-conjugated radical thiols.[5] Based on the success of the construction of a π-radical thiol SAM (self-assembled monolayer) on a gold substrate,[6] we planned to prepare a gold nano-particle chemisorbed by π-radical thiols as an organic and inorganic magnetic nano-composite.



DSPN-hex



SPN-hex

Gold nano-particles chemisorbed by π-radical thiols were prepared using a diphenyl disulfide derivative (**DSPN-hex**) carrying a nitronyl nitroxide group (NN) at the *para*-position of each phenyl ring.[6a] The preparative procedure was as follows. To a 50 ml toluene solution of gold nano-particles (11.25 mM) stabilized by surfactants,[7] such as tetra-*n*-octylammonium bromide, or methyl-tri-*n*-octylammonium chloride, was added 25 mg (0.03 mmol) of **DSPN-hex**, and the mixture was stirred for 1 day at room temperature (Figure 1). After evaporation of the solvent, the slurry of the nano-particles chemisorbed by **SPN-hex** was dissolved in 10 ml of dichloromethane to give a wine-red solution. Then, 300 ml of hexane was added to precipitate the nano-particles. These processes were repeated several times and the purified nano-particles were isolated by filtration through a membrane filter (mesh of 0.1 μm); The isolation yield was 60%.

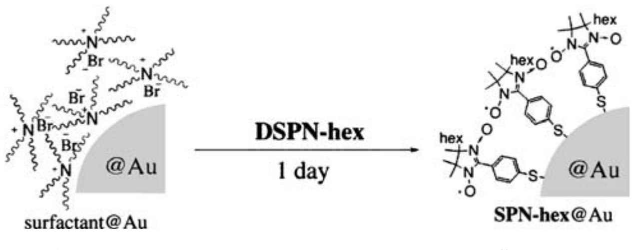


Figure 1. Reaction of surfactant@Au with **DSPN-hex**.

Elemental analysis data[8] of the obtained nano-particles showed that the ratio of Au atom and the ligand was 14 : 1. The average diameter of the obtained gold nano-particles were examined by transmission electron microscopy (Figure 2(a) and (b)). A histogram of the size distribution of the gold nano-particles is shown in Figure 2(c). Since the diameter of the maximum distribution was 4.1 nm, the average number of gold atoms was estimated to 1750, taking the magic number of gold atoms corresponding to 4.1 nm into account; The representative chemical formula was presented as $Au_{1750}(\textbf{SPN-hex})_{125}$. The average area per each ligand is calculated to be ca. 40 Å^2, because the surface area of the gold nano-particle with the diameter of 4.1 nm is ca. 5000 Å^2. This area is nearly the closest packing value for SPN on gold 111 surface.[9] The average distance between particles was also evaluated to be 1.8 nm from the TEM image (Figure 2(b)). This value corresponds well to the twice of the length of 0.9 nm for the rigid part of **SPN-hex**. Thus, the obtained sample was safely assigned to the self-assembly of the gold nano-particles coated by **SPN-hex**.

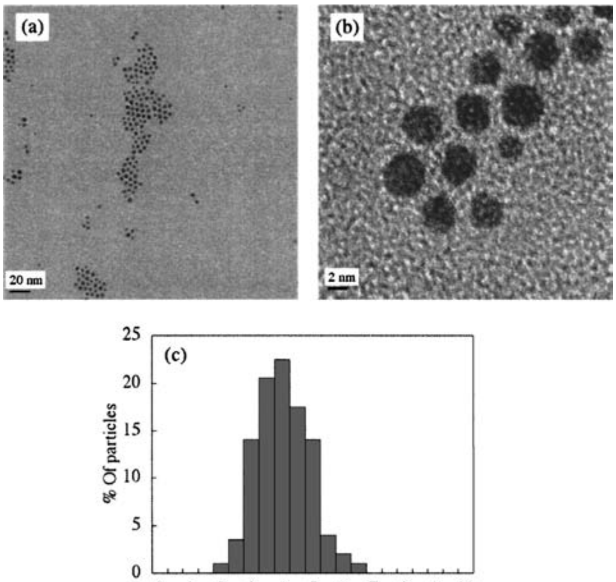


Figure 2. (a) TEM image of the gold nano-particle chemisorbed by π-radical thiol. (b) HRTEM image of the gold nano-particle chemisorbed by π-radical thiol. (c) Histogram showing the size distribution.

The UV spectrum of the gold nano-particles chemisorbed by π-radical thiols showed a plasmon resonance peak at 533 nm. The maximum of the peak position was shifted by 15 nm towards the bathochromic side compared with that of the nano-particle coated by surfactants. The reason for the bathochromic shift may be ascribed to the fact that the surfactants which covered the nano-particles were replaced by the arylthiol(**SPN-hex**) with a larger dielectric constant. Observation of the plasmon resonance absorption band of the gold nano-particle suggests that the gold nano-particle exhibits the metallic conductivity even when the particle was chemisorbed by π-radical ligands.

The magnetic susceptibility was measured on the solid sample of nano-particles chemisorbed by **SPN-hex** by SQUID magnetometer. Basically, it behaves paramagnetically with Weiss temperature of -0.9 K. The Curie constant of the nano-particle is as large as 36.4 emu·K·mol^{-1} and this value indicates that about one hundred molecules of π-radical thiols are chemisorbed on the particle. The result is consistent with the chemical formula determined by the elemental analysis.

While the peak-to-peak derivative line width (ΔH_{pp}) of the ESR spectrum of the solid **DSPN-hex** was only 0.6 mT at 300 K, that of the solid sample of nano-particles chemisorbed by **DSPN-hex** was as wide as 30 mT, the spectral extent reaching to 360 mT (Figure 3).[10] A sharp peak observed in the middle of the broad peak may be ascribed to **SPN-hex** which was not chemisorbed on the gold surface but merely dissolved in the layer of ligands. Since the integrated intensity of the sharp peak was less than 0.1%, its contribution to the composition of the nanoparticle would be negligibly small. The ΔH_{pp} of the broad peak was tremendously broadened to 180 mT at 11.5 K. The extreme broadening of the line width was presumably derived from the rapid relaxation of the localized spins of the radical units due to the interaction with conduction electrons of the gold nano-particle.[11] This interaction may be caused through the following mechanism. While SOMO localizes at the NO-groups of the ligand, HOMO spreads over the entire molecule. Therefore, the unpaired electron in SOMO must interact with conduction electrons of gold nano-particles through the delocalizing π-electrons in HOMO of which coefficients distribute over to the sulfur atom attached with the gold atom.[2,12]

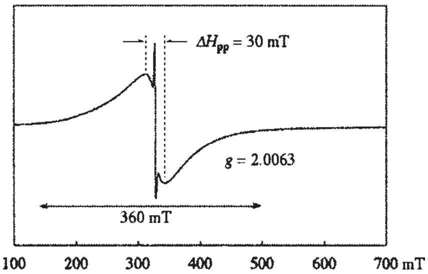


Figure 3. ESR spectrum of **SPN-hex**@Au at 300 K.

In summary, we have established the method of preparing the magnetic nano-composite consisting of a gold nano-particle with the average diameter of 4.1 nm and about one hundred π-radical thiols chemisorbed on it. The UV absorption spectrum showed the metallic nature of the nano-particle chemisorbed by π-radical thiols. Magnetic susceptibility and ESR measurement indicated that the unpaired electrons on the π-radical ligands behave paramagentically but that they interact electronically with the electrons of the gold nano-particle. This nano-composite has opened the interesting possibility to investigate the spin-electronic function, especially when the nano-particles are connected by conducting molecular wires.

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8 The elemental analysis data for Au_{1705}(**SPN-hex**)$_{125}$: Found: C, 6.77; H, 0.84; N, 0.82; S, 1.03%. Calcd for $Au_{1705}(C_{18}H_{26}N_2O_2S)_{125}$: C, 6.98; H, 0.85; Au, 89.18; N, 0.90; O, 1.03; S, 1.03%.

9 The area of gold surface per *p*-(nitronyl nitroxide) phenylthiol in the closely packed self-assembled monolayer on a gold thin plate was evaluated to be 42 Å^2 as discussed in reference 6a).

10 The significance of π-conjugated thiol was certified by the following result. When alkanethiol with an NN head group or *p*-NN-substituted benzylthiol was chemisorbed on gold nano-particles, the broad ESR peak was not detected at all. The detail will be published elsewhere.

11 Power dependence of the peak intensity showed that the saturation tendency of the signal was significantly smaller than that of regular organic radicals in the solid state. While power dependence of the peak intensity of the solid **DSPN-hex** was saturated at 9 mW at room temperature, that of the gold nano-particles chemisorbed by **SPN-hex** was not saturated up to 100 mW. At 4.2 K, the saturation occurs at 4 μW for **DSPN-hex** and at 25 μW for the gold nano-particle.

12 Facile relaxation of the unpaired electron of the π-radical thiol on the gold nano-particle is presumably derived from the spin-orbit coupling between the unpaired electron and electrons of gold atoms at the surface.