

Inner Shell Excitation Spectroscopy of Gold Nanoparticles Coated with Aromatic Molecules

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Gold nanoparticles have been used commercially since the 4th century B.C. Gold nanocolloid solutions have a reddish purple color [1]. On the research front, it was found that organic molecules with thiol groups chemisorb onto the gold surface to form self-assembled monolayers (SAMs) in 20th century [2]. In recent years, next-generation materials and in vivo sensors based on gold nanoparticles modified with organic molecules have been developed. A lot of knowledge has been obtained about aliphatic SAMs. On the other hand, aromatic SAMs, which are expected to be applied as conductive materials, have not been fully understood. In this study, we compared the core excitation spectra of aromatic SAMs adsorbed on gold with different surface geometries and investigated the molecular states of the nanoparticle surface.

In this experiment, methyl 4-mercaptobenzoate (MP0) molecules with a methyl ester group (CH_3COO^-) were used (Figure 1a). MP0-coated gold substrates (MP0S, Figure 1b) were prepared by immersing gold substrates in MP0 solution. The gold nanocolloid solution prepared with pulsed laser ablation in liquid (PLAL) technique. MP0-coated gold nanoparticles (MP0N, Figure 1c) were produced by adding MP0 to gold nanocolloid solution. Field emission scanning electron microscopy (SEM) image (Figure 2) and surface plasmon resonance (SPR) absorption spectrum (Figure 3) were used to evaluate the size of gold nanoparticles. Near-edge X-ray absorption fine structure (NEXAFS) spectra and X-ray photoelectron spectra (XPS) have been observed at HiSOR BL-13. In the NEXAFS measurements, the incident angle of the soft X-rays was varied from normal (90°) to grazing (40°) incidence with respect to the sample surface.

The size of gold nanoparticles was determined at 7 nm from the SPR peak wavelength shown in Figure 3 based on the analytical equation by Haiss et al [3]. The XPS spectrum of the carbon 1s peak consisted of four peaks, (i) C=C, (ii) H-C-O, C-S-Au, (iii) C=O, and (iv) $\pi-\pi^*$ shake off satellite (Figure 4), and the peak intensity ratio (i)/(ii)/(iii) = 5/2/1 was corresponded to the carbon number ratio of MP0. Since the same result was obtained MP0N, it was found that MP0 molecules were densely chemisorbed onto the nanoparticles regardless of their surface shapes.

We have succeeded to observe the polarization dependence of the carbon K-edge NEXAFS spectra of MP0S (Figure 5a, b). From the fitting analysis of the first π^* peak (~ 285 eV) based on Stohr's analytical formula

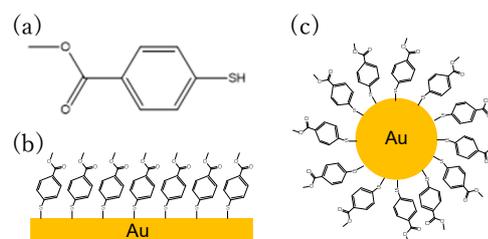


FIGURE 1. (a) Molecular structure of MP0. Schematic drawings of (b) MP0S and (c) MP0N.

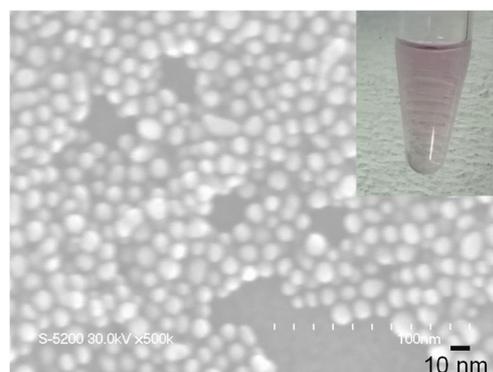


FIGURE 2. SEM image of MP0N. Inset shows the photograph of obtained MP0N nanocolloid solution.

[4], the tilting angle of MP0 molecule from the surface normal have been determined. On the other hand, the polarization dependence of MP0N was not observed in the carbon K-edge NEXAFS spectra (Figure 5c, d), because the gold nanoparticles synthesized in this study were confirmed to be spherical by SEM images (Figure 2). Recently, time-of-flight mass spectrometry was performed at Photon factory BL-2B, and different CH_n^+ ion fragment distribution was obtained between MP0S and MP0N, which are being analyzed from the view point of surface morphology.

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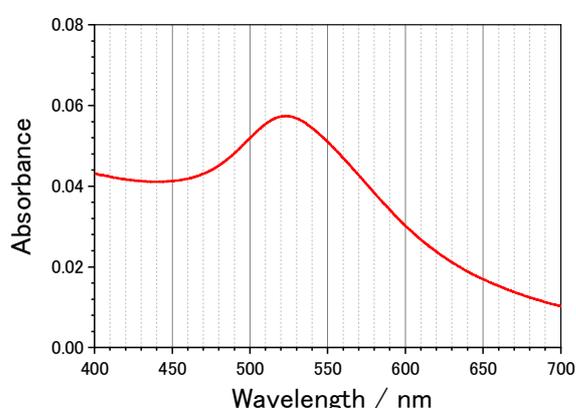


FIGURE 3. Visible spectrum of gold nanocolloid solution. The wavelength of SPR peak was 521 nm.

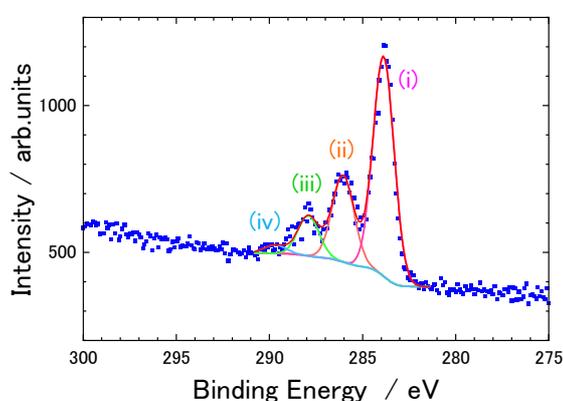


FIGURE 4. Carbon 1s XPS of MP0S. The four peaks were assigned to (i) C=C, (ii) H-C-O, C-S-Au, (iii) C=O, and (iv) π - π^* shake off satellite, respectively.

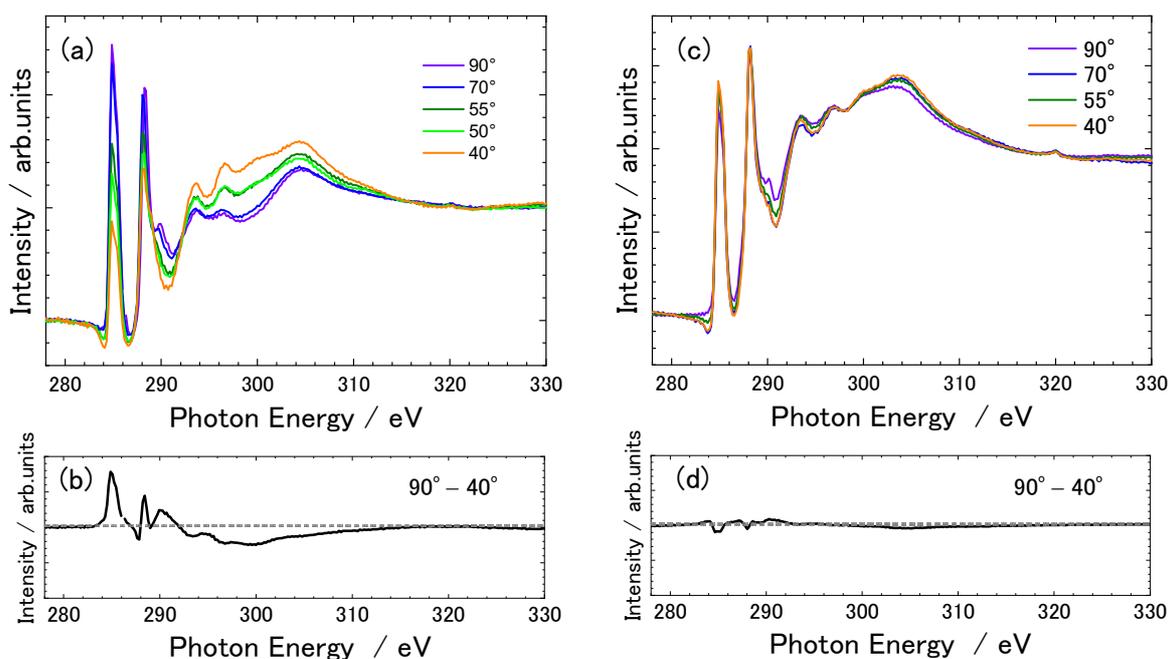


FIGURE 5. Carbon K-edge NEXAFS spectra of (a) MP0S and (c) MP0N, and difference spectra between the normal (90°) and grazing (40°) incidence spectra of (b) MP0S and (d) MP0N. The energy positions of the resonance peaks were consistent between MP0S and MP0N.