

# Charge Transfer in Gold Substrates and Nanoparticles Coated with Methyl Ester Substituted Aromatic Thiol Molecules

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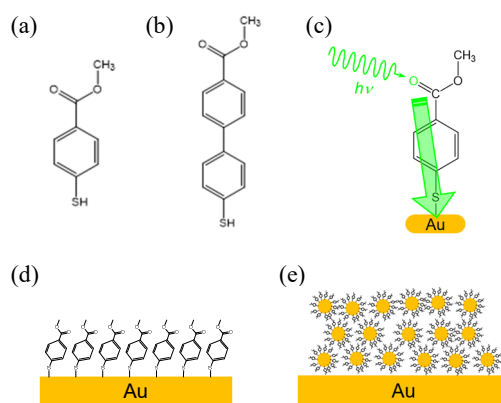
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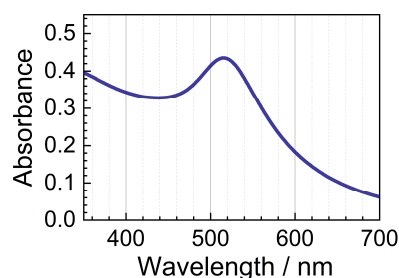
Charge transfer between molecules and metal surfaces is a crucial process with implications for molecular electronics, energy storage, and catalysis. Particularly in nanoparticle films deposited on substrates, where organic molecules coat gold nanoparticles (AuNPs), charge transfer between  $\pi$ -conjugated molecules and metal plays a pivotal role in determining the photoelectric conversion efficiency of dye-sensitized solar cells. In this study, we focused on oligophenyl molecules, which have different molecular lengths, and directly measured the charge transfer time using soft X-rays (Figure 1 (a)–(c)) [1]. Subsequently, we elucidated the electronic properties of the nanoparticle films by comparing the charge transfer dynamics from molecules to flat metal surfaces.

Monophenyl and biphenyl self-assembled monolayers (MP and MBP SAMs, Figure 1 (a), (b)) were prepared on two different metal surfaces. The first SAMs were formed on two-dimensional flat gold substrates (2D SAMs, Figure 1 (d)). The second SAMs were formed on three-dimensional AuNPs, which were drop-cast onto the substrates (3D SAMs, Figure 1 (e)). AuNPs were synthesized by pulsed laser ablation in liquid. The size of the AuNPs was determined to be 7 nm from the surface plasmon resonant peak wavelength, as shown in Figure 2, based on the analytical equation.

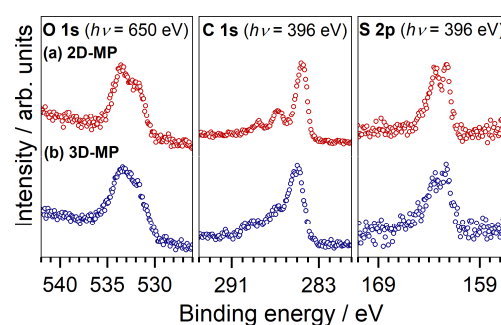
Near-edge X-ray absorption fine structure (NEXAFS) spectra and X-ray photoelectron spectra (XPS) were collected at the HiSOR BL-13. The XPS results for the 2D-MP and 3D-MBP SAMs are presented in Figure 3. An important observation from XPS is the similarity in chemical shifts, with no clear discrepancy in the energy position between 2D and 3D SAMs. Any slight variations were attributed to the inhomogeneity of the NP surfaces; nevertheless, the electronic structures of the 2D and 3D SAM remained identical. Figure 4 shows the C and O K-edge NEXAFS spectra. The dominant peaks included  $\pi^*(C=C)$  at  $\sim 285$  eV for the C K-edge and  $\pi^*(C=O)$  at 532.0 eV for the O K-edge. Polarization angular



**FIGURE 1.** Molecular structures of (a) MP and (b) MBP. Images of (c) charge transfer process, and (d) 2D-MP, and (e) 3D-MP SAMs.



**FIGURE 2.** UV-VIS spectrum of AuNP colloids.



**FIGURE 3.** XPS of 2D-MP and 3D-MP SAMs.

dependence was observed in 2D-MP, and the subsequent fitting analysis suggested that the molecules adsorbed in an upright orientation to the surfaces [2]. In contrast, this phenomenon was not observed in 3D SAMs, likely due to the averaging of the transition dipole moment of molecules on spherical particles. The energy level of the  $\pi^*(\text{C}=\text{O})$  peaks exceeded the binding energy of the  $\text{C}=\text{O}$  peaks at 531.7 eV in the O 1s XPS spectra, indicating that it was suitable for subsequent resonant Auger electron spectroscopy experiments.

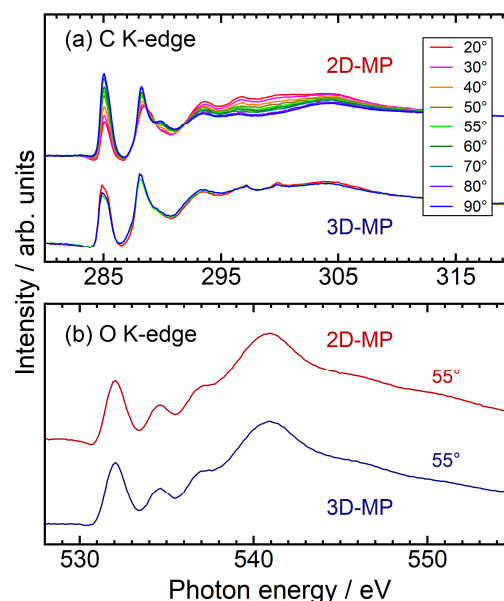
We conducted time-of-flight mass spectrometry (TOF-MS) at Photon Factory BL-2B and utilized the data obtained to construct near-edge X-ray absorption mass spectra (NEXAMS), as shown in Figure 5. The total ion yield (TIY) and partial ion yield (PIY) spectra for both 2D and 3D SAMs exhibited a primary peaks corresponding to  $\sigma^*(\text{O}-\text{CH}_3)$  at 288.9 eV. This observation indicates that 3D SAMs form monolayers similar to those formed by 2D SAMs. The presence of a single sharp peak at 288.9 eV for  $\text{CH}_n^+$  ( $n = 0-3$ ) ions suggests site-selective desorption of  $\text{CH}_n^+$  ions from the methoxy group of SAMs [3].

Resonant Auger electron spectra (RAES) were measured at HiSOR BL-13, and the charge transfer times of the 2D and 3D SAMs were determined using the core-hole-clock (CHC) approach. In Figure 6, RAES at O  $1s \rightarrow \pi^*(\text{C}=\text{O})$  excitation is presented, with peaks corresponding to spectator Auger decay processes observed at  $\sim 486$  eV and  $\sim 511$  eV. The RAES at  $\pi^*(\text{C}=\text{O})$  excitation was fitted with the RAES at post-edge excitation and  $\pi^*(\text{C}=\text{O})$  excitation of 2D-aliphatic SAMs, which exhibit insulation properties. Using the fitting coefficient and core hole lifetime of O 1s, the charge transfer time for each 2D and 3D SAMs were determined. The charge transfer time of 3D SAMs decreased with increasing chain length, similar to that of 2D SAMs. Furthermore, the charge transfer time between the 2D and 3D SAMs remained unchanged.

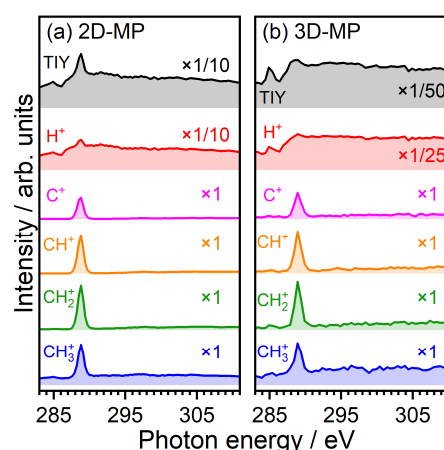
Our results suggest that the spectroscopic and electrical properties of 3D SAMs closely resemble those of 2D SAMs. This similarity can be attributed to the fact that the AuNPs synthesized in our study had a diameter of  $\sim 7$  nm, predominantly comprising  $\{111\}$  terraces on their surfaces [4]. Notably, unique absorption features at the corners and edges of the NPs were not observed in the spectra. In essence, this study serves as a crucial link, extending the applicability of insights into the charge transfer times obtained from diverse molecules observed in 2D to the context of 3D SAMs.

## REFERENCES

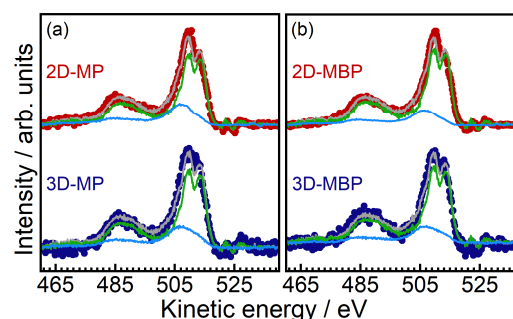
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**FIGURE 4.** (a) Polarization dependence spectra of C K-edge NEXAFS spectra of 2D and 3D-MP. (b) O K-edge NEXAFS spectra of 2D and 3D-MP.



**FIGURE 5.** C K-edge NEXAMS spectra of (a) 2D-MP and (b) 3D-MP. Total ion yield spectra and partial ion yield spectra of major products.



**FIGURE 6.** RAES of (a) MP and (b) MBP under  $\pi^*(\text{C}=\text{O})$  excitation after Shirley background subtraction (dotted lines). The reproduced spectra (gray lines) were obtained by fitting with the normal Auger spectra of each MP or MBP SAM (green lines) and the spectator Auger spectra of 2D-aliphatic SAM (light blue lines).