

Diffuse Reflectance Infrared Fourier Transform Spectroscopic (DRIFTS) Study of Self-Assembled Monolayers of 4-Mercaptobenzoic Acid on Ag Powder

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The self-assembled monolayers (SAMs) of various organic molecules on metal surfaces have attracted considerable attention in both basic understanding of metal-adsorbate interaction and practical applications.¹⁻³ There is the selectivity between the metal and the adsorbate head group for the formation of SAMs: Au for thiols^{4,5} and Al for alkanolic acids^{6,7} are well known examples. On the other hand, Ag is known to produce SAMs with both thiols^{8,9} and alkanolic acids.¹⁰⁻¹² However, the competitive adsorption of a thiol and a carboxylic acid on Ag surface was not reported yet. In a previous study, we observed that mercaptoacetic acid, containing both a thiol group and a carboxylic acid group in the same molecule, adsorbed on Ag powder as the thiolate exposing the carboxylic acid group to the air.¹³ This showed that a thiol was preferred to a carboxylic acid for the adsorption on Ag powder.

The structure of SAM is dependent on the interchain interaction between the adsorbates as well as the head group-metal interaction. In this respect, aromatic compounds might behave differently compared to their aliphatic counterparts. Monolayers of aromatic compounds, in spite of interesting properties such as relatively high electrical conductivity and reactivity for derivatization, have been less studied compared to their aliphatic counterparts.

Here, we present a study of the SAM on Ag powder of 4-mercaptobenzoic acid (4-MBA) which is the simplest aromatic compound containing both a thiol group and a carboxylic acid group. The structure of the resulting monolayer would answer which group of the compound predominantly adsorbs on Ag powder. We also studied SAMs of 4-nitrobenzoic acid (4-NBA) and 4-nitrothiophenol (4-NTP) on Ag powder for comparison. Since the DRIFT spectrum of 4-NBA on Ag powder has been reported previously,¹⁴ it can be used as criteria for the proper fabrication of SAMs on Ag powder.

Since we used Ag powder as a substrate, DRIFT spectroscopy was used as the characterization tool. This technique has proved to be very effective in characterizing SAMs on metal powders.¹³⁻¹⁷

Experimental Section

4-Mercaptobenzoic acid (Aldrich), 4-nitrobenzoic acid (Aldrich), 4-nitrothiophenol (Aldrich), absolute ethanol (Carlo Erba), *n*-hexane (Mallinckrodt), and sodium hydroxide (Ald-

rich, >99.9%) were used as received. Ag powder (2-3.5 μm , >99.9% purity) was purchased from Aldrich and kept in a nitrogen atmosphere prior to use.

Prior to the fabrication of monolayers, Ag powder was cleaned with *n*-hexane and absolute ethanol successively in an ultrasonic cleaner. The powder was filtered on a glass filtration assembly with a nylon membrane filter (Gelman, pore size 0.20 μm), then was dried by blowing nitrogen gas. The cleaned Ag powder was immersed in the absolute ethanol solution containing 1.0 mM of the appropriate adsorbate for 10 h. An absolute ethanol solution containing both 0.05 mM 4-NBA and 0.05 mM 4-NTP was used for preparing a mixed monolayer. The solution was stirred with a magnetic stirrer for the efficient adsorption. The treated Ag powder was filtered and rinsed with absolute ethanol on a glass filtration assembly, then dried by blowing nitrogen gas. The sample was transferred to a DRIFTS sampling cup (Grasby Specac) and analyzed by an infrared spectrophotometer.

Infrared spectra were taken with a Mattson Research Series FT-IR spectrophotometer equipped with a liquid nitrogen cooled MCT detector. DRIFT spectra of SAMs were obtained with a diffuse reflection accessory (Grasby Specac). For measuring background spectra, either KBr powder or Ag powder was used depending on the case. The KBr powder to be used as a background material and a diluent for solid samples was made by grinding KBr chunks (Spectra-Tech) with a Wig-L-Bug grinder. The Ag powder used for measuring background spectrum of monolayers was freshly cleaned with *n*-hexane and absolute ethanol successively just before measurement. Each spectrum was measured with 512 scans coadded at 4 cm^{-1} resolution with Happ-Genzel apodization. The DRIFT spectrum of neat 4-MBA diluted with KBr powder was reported as Kubelka-Munk unit.¹⁸ However, the DRIFT spectra of the monolayers on Ag powder were reported as absorbance, $-\log(R/R_0)$, where R was the reflectivity of the sample and R_0 was the reflectivity of cleaned Ag powder.¹⁴

Results and Discussion

It has been well known that both aromatic thiols¹⁹ and aromatic acids^{14,20,21} produced well packed monolayers on Ag surface. Figure 1 shows the schematic diagrams of 4-NBA, 4-NTP, 4-MBA adsorbed on Ag surface. Since it is well known that carboxylic acids are adsorbed as carboxylates with two oxygen atoms attached on Ag surface,^{12,14} 4-NBA would have structure shown in Figure 1(a). 4-NTP would adsorb as a thiolate with S atom on Ag surface as shown in

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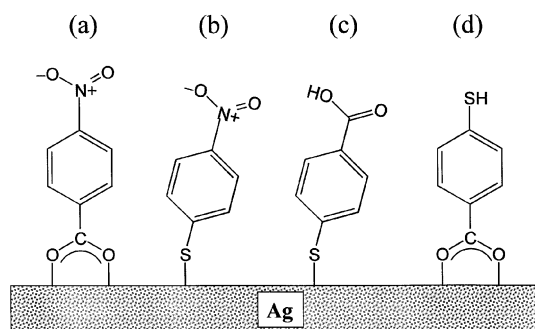


Figure 1. Schematic diagrams of the adsorbed molecules on Ag. (a) 4-NBA, (b) 4-NTP, (c) 4-MBA adsorbed as a thiolate, and (d) 4-MBA adsorbed as a carboxylate.

Figure 1(b), 4-MBA, which has both a thiol group and a carboxylic acid group, can be adsorbed as either a thiolate shown in Figure 1(c) or a carboxylate shown in Figure 1(d). Another possibility is that 4-MBA would adsorb with both groups on Ag surface especially in low-coverage monolayers. The head group-metal interaction would play a key role in determining the structure of SAM in this case. To compare the relative binding strength of the two functional groups on Ag, we measured DRIFT spectra of SAMs of 4-NBA and 4-NTP. We would not discuss all the spectroscopic details. Instead, only those peaks relevant for structural elucidation would be explained.

The monolayer spectrum of 4-NBA shown in Figure 2(a) is almost identical to those reported previously.¹⁴ We could not observe any peak corresponding to $\nu(\text{C}=\text{O})$ mode that would normally show up at around 1700 cm^{-1} . It supports the monolayer structure shown in Figure 1(a). In this structure, the molecule adsorbed symmetrically with two oxygen atoms on Ag surface. The adsorption occurs as a carboxylate, so there is no carbonyl group left in the structure. Among two peaks for carboxylate stretching modes, only that for $\nu_s(\text{CO}_2^-)$ mode appears at 1397 cm^{-1} . The usual surface selection rule has been successfully applied to the metal powders previously.¹⁴ According to the rule,²² only the

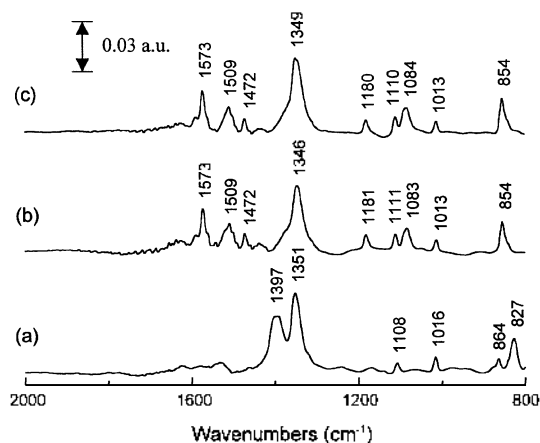


Figure 2. DRIFT spectra of the monolayers adsorbed on Ag powder of (a) 4-NBA, (b) 4-NTP, and (c) the mixed monolayer of 4-NBA and 4-NTP.

vibrational modes with dipole moment perpendicular to the metal surface would give absorption peaks. Since the dipole moments of $\nu_{\text{as}}(\text{CO}_2^-)$ mode lies parallel to the metal surface, the absorption peak for that would not show up in the spectrum. The presence of a strong peak for $\nu_s(\text{NO}_2)$ mode at 1351 cm^{-1} and the absence of a peak for $\nu_{\text{as}}(\text{NO}_2)$ mode at around 1510 cm^{-1} indicate that the nitro group is perpendicular to the metal surface.

The spectrum shown in Figure 2(b) is for the monolayer of 4-NTP. Two peaks at 1573 cm^{-1} and 1472 cm^{-1} are for aromatic ring stretching modes. The peak for $\nu_s(\text{NO}_2)$ mode appears at 1346 cm^{-1} . The presence of the peak for $\nu_{\text{as}}(\text{NO}_2)$ mode appeared at 1509 cm^{-1} indicates that the nitro group is tilted a little bit. If the main axis of the molecule were perpendicular to the Ag surface, the peak would not show up. Although the exact tilt angle was not calculated here, the tilt was due to the bent nature of Ag-S-C bond as shown in Figure 1(b).

Figure 2(c) shows the spectrum of a mixed monolayer of 4-NBA and 4-NTP on Ag surface. This spectrum is almost identical to the monolayer spectrum of 4-NTP alone. The absence of the peak for $\nu_s(\text{CO}_2^-)$ at 1397 cm^{-1} assures that there is no 4-NBA on the Ag surface. This is due to the stronger adsorption of a thiolate on Ag surface than that of a carboxylate.

To confirm the fact, we studied the monolayer structure of 4-MBA on Ag powder. Figure 3(a) is the DRIFT spectrum of neat 4-MBA diluted with KBr powder. The molecule is randomly oriented in this environment. The monolayer spectrum of the same compound adsorbed on Ag powder is presented in Figure 3(b). The spectrum is quite similar to that of neat solid in Figure 3(a) and supports the thiolate structure shown in Figure 1(c). If the monolayer would have the carboxylate structure shown in Figure 1(d), the presence of a strong absorption peak for $\nu(\text{C}=\text{O})$ mode at 1705 cm^{-1} could not be explained. To make sure that the carboxylic acid group is on the tail (far from the metal), we treated the monolayer with an aqueous 0.5 M NaOH solution for 20 min. The monolayer spectrum shown in Figure 3(c) is for the NaOH treated monolayer. We observed the complete dis-

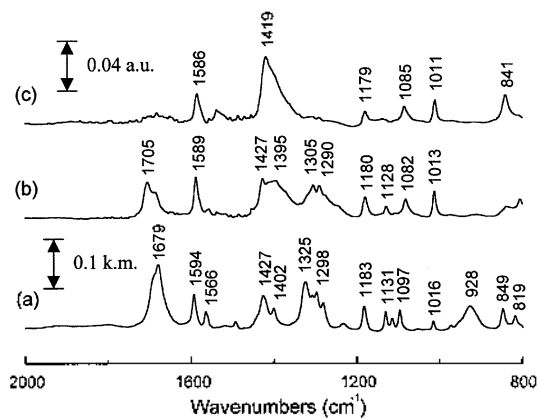


Figure 3. DRIFT spectra of (a) neat 4-MBA diluted with KBr powder, (b) the monolayer of 4-mercaptopzoic acid, and (c) NaOH treated monolayer of 4-MBA on Ag powder.

appearance of the peaks for $\nu(\text{C}=\text{O})$ mode at 1705 cm^{-1} and for $\nu(\text{C}-\text{O})$ mode at around 1300 cm^{-1} as well as the appearance of the intense peak for $\nu_s(\text{CO}_2^-)$ mode at 1419 cm^{-1} . This means that the monolayer remains on the Ag surface, but the carboxylic acid group is converted to the corresponding carboxylate salt. Similar behavior of exposed carboxylic acid group was reported for mercaptobenzoic acid adsorbed on gold.²³

All these experimental facts indicate that the thiolate-Ag interaction is stronger than the carboxylate-Ag interaction. Consequently, a thiol group would adsorb preferentially when there are both a thiol group and a carboxylic acid group present either in the same molecule or in different molecules.

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