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Sum Frequency Generation (SFG) Studies on the Conformational Order of the Self-Assembled Monolayers of Alkanethiols on Silver Surface

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Abstract Sum frequency generation (SFG) spectroscopy measurements showed that the conformational order of the self-assembled monolayers (SAMs) of alkanethiols on silver surface was strongly affected by alkyl chain length and the nature of the terminal group. The SAMs of alkanethiols were densely packed as far as the number of carbon chain (*n*) was more than 5 but significant amount of the gauche defects were formed when *n* was 3. The COOH terminated SAM was less ordered than CH_3 terminated one.

INTRODUCTION

Self-assembled monolayers (SAMs) of thiol derivatives have been widely employed to modify the metal surface to provide novel functions.[1] The formation process, structure and properties of SAMs have been characterized by many methods such as electrochemistry,[1,2] quartz crystal microbalance,[3] infrared spectroscopy,[4-6] Raman scattering,[7] ellipsometry,[4,8] and scanning probe microscopy.[9,10]

Recently, infrared(IR)-visible sum frequency generation (SFG) spectroscopy is attracting much attention because it has extremely high surface/interface selectivity and versatile applicability.[11-13] SFG is a second-order nonlinear optical process in which two photons at frequencies ω_1 and ω_2 generate a photon of sum-frequency at $\omega_3=\omega_1+\omega_2$. The SFG is forbidden in the bulk of a medium with inversion symmetry and is only

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active on the surface or interface where the inversion symmetry is necessarily broken. For IR-visible SFG, if one employs ω_1 in the visible region and ω_2 in infrared region, the ω_2 dependence of the SFG intensity (I_{SFG}) is given by the following equation,

$$I_{SFG} = \left| \sum_n \frac{A_n}{\sqrt{(\omega_2 - \omega_n)^2 + \Gamma_n^2}} e^{-i\delta(\omega_2)} + \left|\chi_{NR}^{(2)}\right| e^{-i\varepsilon} \right|^2 \qquad (1)$$

where $\delta(\omega_2) = \tan^{-1}\frac{\Gamma_n}{\omega_2 - \omega_n}$. χ_{NR}, ε, A_n and Γ_n are second order nonlinear susceptibility corresponding to non-resonant component, phase angle between resonant and non-resonant contribution, strength and damping constant of surface vibration or rotation mode with frequency ω_n, respectively. Thus, I_{SFG} is resonantly enhanced when ω_2 is equal to ω_n. A number of SFG studies on the SAMs have been reported and are converged mainly on alkanethiol molecules with long alkyl chain such as octadecanethiol (ODT).[13-19]

In the present study, SFG spectroscopy was used to evaluate the effect of the alkyl chain length and terminal group on structure and conformation of SAMs of alkanethiol derivatives on silver surface.

EXPERIMENTAL

A passive mode-locked Nd:YAG laser (PL2143B, EKSPLA) generating ~25 ps pulses at a repetition rate of 10 Hz was used as a light source. The optical parametric generation (OPG) and difference frequency generation (DFG) system pumped by the laser can generate infrared output from 2.5 to 8.5 μm. The visible (532 nm) and infrared beams with incident angles of 70 and 50 degrees were overlapped each other on the sample surface. The beam spot of the visible light on the sample surface has an ellipsoidal shape with a size of 2.51×0.86 mm^2 and is larger than that of the infrared light (0.34×0.22 mm^2). The SFG signal was separated from the reflected visible light and was collected by a PMT attached on a monochromator. All SFG spectra were obtained by averaging the signals of 400 pulses and were normalized to the intensities of both the infrared and visible lights. In the present experiment, polarization combinations of SFG, visible and infrared lights were *p*, *p* and *p*, respectively.

11-mercaptoundecanoic acid ($HOOC(CH_2)_{10}SH$) was synthesized according to the procedure reported previously.[20] Alkanethiols ($CH_3(CH_2)_nSH$, n=17, 14, 11, 9, 5, 3) and other chemicals were purchased from Wako Pure Chemicals and were used without further purification. The substrates were prepared by vacuum evaporation of 200 nm silver on a slide glass at 150℃ at an evaporation rate of ca. 0.1 nm/s. The SAMs were constructed by immersing the freshly prepared silver substrate into ethanol solutions containing 1mM thiol for over night. After the adsorption treatment, the surface was rinsed by ethanol and then by Milli-Q water and finally was dried by N_2.

RESULTS AND DISCUSSIONS

Figure 1 shows an SFG spectrum (black circles) of ODT monolayer on a silver surface measured in air. Intensities of visible and infrared lights were approximately 200 μJ/pulse and 250 μJ/pulse, respectively. The SFG spectrum showed a rather complicated shape and was fitted to Eq. 1 (solid line) with five resonance bands (dotted lines). The phase angle (ε) was determined to be approximately −125 degree. The shape of this spectrum was different from the SFG spectra reported by Bain *et al.* and the phase angle of their spectra was −45 degree.[13,15,18] These differences were caused by the difference in the experimental arrangement. In the present experiment, visible and infrared beams come from the same side while Bain *et al.* use a counter-

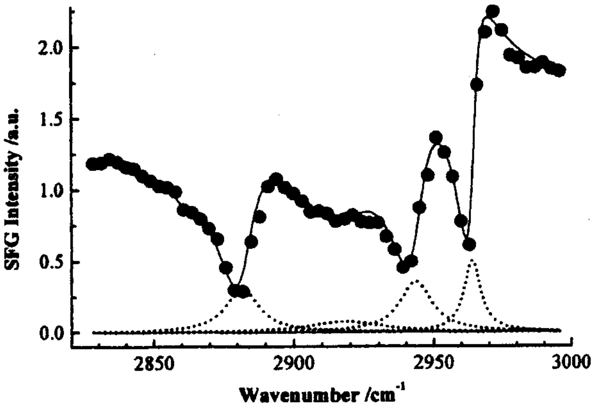

FIGURE 1 SFG spectrum of ODT on silver surface.

propagating geometry.[13] The difference in the laser configuration makes ε different, resulting in the SFG spectra of different shape. The peaks at 2881 cm^{-1} and 2964 cm^{-1} were assigned to the symmetric (r^+) and the asymmetric (r^-) C-H stretching of the CH_3 group.[21] The peak at 2943 cm^{-1} was attributed to the Fermi resonance ($r_{FR}{}^+$) between r^+ and a CH_3 bending overtone. A very small peak observed at 2860 cm^{-1} was assigned to the symmetric C-H stretching (d^+) of the CH_2 group. A broad peak around 2920 cm^{-1} was attributed to the asymmetric C-H stretching (d^-) of the CH_2 group and the Fermi resonance ($d_{FR}{}^+$) between d^+ and a CH_2 bending overtone.[21] This broad band was also reported by Potterton *et al.* in the SFG study of ODT on silver and gold surfaces.[18] One of the possible reasons for the broad peak width is the partial band overlapping between d^- and $r_{FR}{}^+$.[4,22] Hence, we will only refer to the d^+ band in the following discussion. Compared to the relatively strong bands of the CH_3 group, d^+ band of the CH_2 group was very weak. The CH_2 groups in the monolayer become SFG inactive when CH_2 groups are in a perfect *all-trans* conformation as it has the inversion symmetry. The SFG spectrum shown in Fig. 1 clearly demonstrates that the gauche defects in the ODT monolayer hardly exist and an well-ordered ODT monolayer is formed on the silver surface.

Figure 2a shows SFG spectra of the SAMs of alkanethiol of various chain lengths ($CH_3(CH_2)_nSH$, n=17, 14, 11, 9, 5, 3) on silver surface (black circles). These SFG spectra were fitted well to Eq. (1) (solid lines). Figure 2b shows the intensity of d^+ band of CH_2 group determined from the fitting as a function of the number of CH_2 group (n). The intensity of d^+ band was rather low as far as n was more than 5 but was very high when n was 3. This result suggests that the SAM was less ordered and contained many gauche defects when n was 3. This is in good agreement with the previous findings that the SAMs of long alkyl chain are highly ordered with *all-trans* conformation but those of short alkyl chain are less well ordered.[4,5] It must be mentioned here, however, that the symmetry of $CH_3(CH_2)_nSH$ itself decreases with the

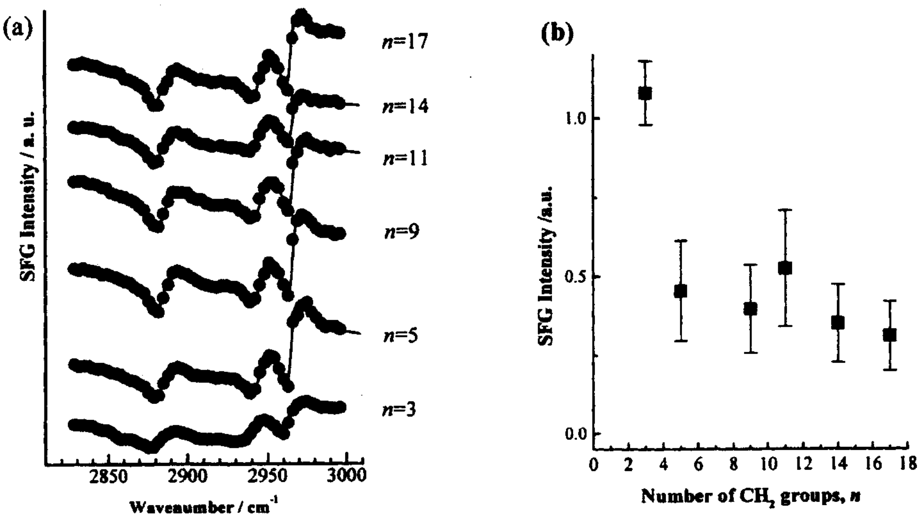

FIGURE 2 (a) SFG spectra of $CH_3(CH_2)_nSH$ on silver surface, (b) Intensity of $\nu_{ss}(CH_2)$ as a function of n.

decrease of n. This must also contribute to the increase of SFG intensity of the d^+ band of the CH_2 group.

We also found that the terminal group of the thiol molecules affects the order of the SAM very significantly. Figure 3 shows an SFG spectrum of $HOOC(CH_2)_{10}SH$ monolayer on silver surface. The existence of the symmetric C-H stretching band of CH_2 (d^+) at 2860 cm^{-1} was clearly visible as indicated by an arrow in the SFG spectrum (Fig. 3), suggesting the COOH terminated SAM is much less ordered than the CH_3 terminated SAM. This conformation change can be attributed to the increase of the size of the terminal group which reduces the van der Waals interaction between the molecules in the SAM.

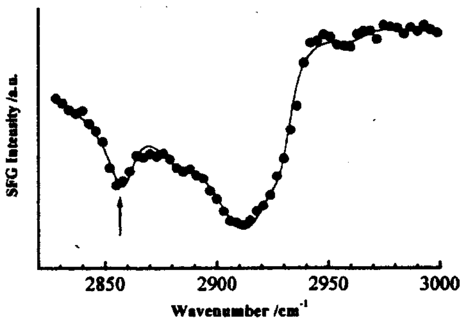

FIGURE 3 SFG spectrum of $HOOC(CH_2)_{10}SH$ on Ag.

In conclusion, we have demonstrated that the conformational order of the SAMs is strongly affected by the alkyl chain length and the nature of the terminal group. This information is difficult to be obtained by other techniques including infrared spectroscopy.

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