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Conformational Order of Octadecanethiol (ODT) Monolayer at Gold/Solution Interface: Internal Reflection Sum Frequency Generation (SFG) Study

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Sum frequency generation (SFG) spectroscopy using internal reflection geometry was employed to investigate the conformational order of octadecanethiol (ODT) monolayer on gold thin films in an electrolyte solution. This approach is convinced to be useful to study the molecular structure on the electrode/solution interface under electrochemical condition.

1. Introduction

Sum frequency generation (SFG) spectroscopy is becoming a powerful tool in the research on surface science because of its high surface/interface selectivity and versatile applicability [1-6]. SFG is a second-order nonlinear optical process in which two photons at frequencies ω_1 and ω_2 generate one photon of sum-frequency at $\omega_3=\omega_1+\omega_2$. The SFG is forbidden in the bulk of a cetrosymmetric medium and is only active on the surface or interface where the inversion symmetry is necessarily broken. For IR-visible SFG, a pulsed visible laser at a fixed frequency ω_1 and a pulsed infrared laser with a tunable frequency ω_2 are used. SFG signal is resonantly enhanced when ω_2 matches vibrational modes (ω_n) on the interface as:

$$I_{SFG}=\left|\sum_n \frac{A_n}{\sqrt{(w_2-w_n)+i\Gamma_n}}+\left|c^{(2)}_{NR}\right|e^{-ie}\right|^2 \qquad (1)$$

where I_{SFG} is the intensity of SFG signal, ω_n A_n and Γ_n are the resonant frequency, strength and damping constant of the vibration modes, respectively, and $c^{(2)}_{NR}$ and ε are the non-resonant contribution and its phase angle, respectively. Therefore, SFG spectroscopy can be regarded as an interface specific vibrational spectroscopy.

When SFG spectroscopy is applied to the solid/aqueous solution interface, the input energy of infrared laser pulse is significantly reduced before reaching the electrode surface by the aqueous solution layer between the electrode and the optical window even its thickness is minimized by pressing the electrode against the window [6,7]. Recently, Williams *et al.* proposed to obtain SFG spectra of molecules adsorbed on the gold ultra-thin films in solution using total internal reflection geometry [8]. The attenuation effect of input infrared by the aqueous solution layer can be avoided and a large enhancement of surface electric field is expected in this geometry. The films used in their study were, however, too thin (<10 nm) to be used in electrochemical application because of their low electric conductivity [8].

In the present work, we obtained SFG spectra of octadecanethiol (ODT: $CH_3(CH_2)_{17}SH$) monolayers adsorbed on gold thin films with various thickness, which were prepared by sputtering of gold on a fused quartz surface, using an internal reflection geometry. It was found that the optimum thickness of the gold film to obtain a high-quality SFG spectrum of ODT monolayer both in air and in electrolyte solution was 40~60 nm. The gold film of this thickness has a good electric conductivity and can be used as an electrode for *in situ* SFG measurement under potential control.

2. Experimental

The SFG system employed in this study is schematically shown in Figure 1. A picosecond Nd:YAG laser (PL2143B, EKSPLA) was used to pump an optical parametric generation and amplification (OPG/OPA) system. The output from the OPG/OPA was mixed with 1064 nm laser output in a nonlinear infrared crystal, Ag_2GaS_2, to generate a tunable infrared output between 2.3 and 8.5 μm. The second harmonic generation output (532 nm) from the laser was used as visible light [9, 10].

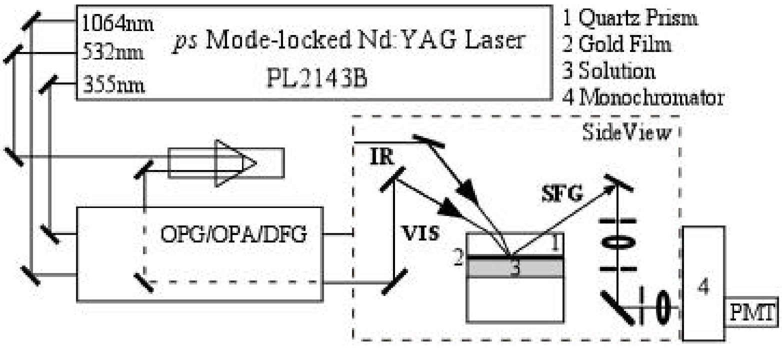

Figure 1. The SFG system and an experimental arrangement for SFG measurement

An IR-grade fused quartz circular plate (d=31.75 mm, l=3.18 mm, Esco Products) was used as a substrate. The quartz plate was thoroughly cleaned by chromic acid solution and then rinsed with Milli-Q water several times. Gold thin films of various thickness were prepared on the fused quartz substrate by gold sputtering using a fine coater (JFC-1200, JEOL) with a deposition rate of 10 nm/min. A gold single crystal Au(111) surface prepared by Clavilier's method [11] was also used a substrate. ODT was used as received from Wako Pure Chemicals. ODT monolayers were constructed by immersing the fresh gold films or annealed Au(111) electrode into a 1mM ODT ethanol solution overnight.

An experimental arrangement for the SFG measurement with internal reflection geometry is also shown in Fig. 1. Electrolyte solution was exposed to the face of gold film in a homemade cell and the infrared and visible beams were incident from quartz side with incidence angle of 50 and 70 degrees, respectively. The two beams were overlapped at the interface between gold and quartz. The SFG signal was collected by a photomultiplier (Hamamatsu R630-10) after passing through a holographic SuperNotch filter (HSPF-532-1.0, Kaiser Optical System) and a monochromator.

Polarizations of SFG, visible and infrared lights were all *p*. Each data point was obtained by averaging the SFG signals corresponding to 100 pulses and was normalized against the intensities of the infrared and visible inputs.

3. Results and Discussions

Figure 2 shows an SFG spectrum (circles) of ODT monolayer on Au(111) surface in air by using normal external reflection geometry, i.e., both visible and infrared beams were incident from the gold side. The SFG spectrum was fitted to Eq. 1 (top, solid line) with five resonance components (bottom, solid lines). The SFG spectrum is in agreement with that previously reported [3,12,13]. Three dominant peaks attributed to CH_3 group of ODT monolayer were observed. The peak at 2886 and 2972 cm^{-1} were assigned to the symmetric and asymmetric C-H stretching of CH_3 group. The peak at 2948 cm^{-1} was attributed to the Fermi resonance between symmetric C-H stretching of CH_3 and CH_3 bending overtone. Compared to the relatively

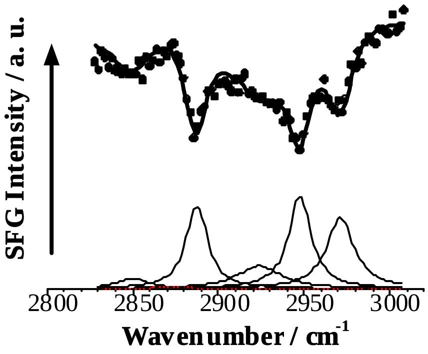

Figure 2. SFG Spectrum of ODT adsorbed on Au(111). Top: data and fitted curve; Bottom: deconvoluted resonance bands.

strong C-H bands corresponding to the CH_3 group, bands of symmetric (2848 cm^{-1}) and asymmetric (2924 cm^{-1}) C-H stretching of CH_2 group were very weak. This result confirmed that the ODT monolayer was densely packed on the gold surface with very small number of gauche defects, which results in the CH_2 peak in the SFG spectrum.

Figure 3 shows SFG spectra (circles) of the ODT monolayer adsorbed on gold films of various thickness in contact with 0.1 M H_2SO_4 solution obtained by using internal reflection geometry. Solid lines correspond to the results fitted to Eq. (1). Figure 3 shows that the SFG spectra of ODT monolayer essentially depend on the thickness of the gold films. When the gold film was thin (Figs. 3(a)~1(b), 20~30 nm), three small peaks attributed to CH_3 groups of ODT monolayer were observed and peaks attributed to CH_2 groups were hardly observed. These features are similar to that in Fig. 2 where external reflection geometry was used, although the intensities of these peaks were much less than those in Fig. 2. Although Williams et al. reported that total internal reflected SFG spectra of ODT monolayer was only observed on the gold thin films with thickness less than 10 nm by using their nanosecond laser system [8], the high quality SFG spectra were not obtained on such thin films in the present work. Furthermore, the surface of the gold thin layer was easily damaged by laser illumination during the SFG measurement.

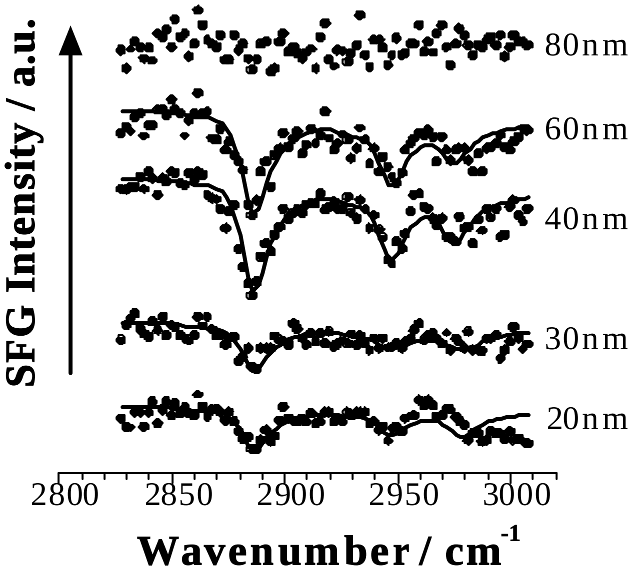

Figure 3. Internal reflection SFG spectra of ODT adsorbed on Au films with various thickness in contact with 0.1 M H_2SO_4.

As the thickness of the gold films increased to 40-60 nm (Figs. 3(c)-1(d)), the signal/noise (S/N) ratio of the SFG spectra improved and the three peaks attributed to CH_3 group were observed clearly. The gold films were more tolerant to the laser illumination. These SFG spectra were almost the same as that in Fig. 2. It should be mentioned here that the gold films with the thickness of 40~60nm show a good electric conductivity and can be used in electrochemical measurement. In fact, this gold film is using as the substrate for *in situ* SFG measurement under electrochemical condition.

When the gold film was thicker than 80 nm, no peak was observed (Fig. 3(e)).

The intensity of light decreases exponentially with thickness of the gold films as:

$$\boldsymbol{E} = \boldsymbol{E}_0 \boldsymbol{e}^{-\alpha \boldsymbol{d}} = \boldsymbol{E}_0 \boldsymbol{e}^{-\frac{4\pi\kappa}{\lambda}\boldsymbol{d}} \qquad (2)$$

where α is the absorption coefficient, κ is the imaginary part of refractive index, λ is wavelength and *d* is the thickness of the film. The penetration depths, where light intensity is decreased to 1/e (36.8%), for visible (532 nm) and infrared (3.4 μm) were estimated to be 17 nm and 11 nm, respectively [14]. Since the penetration depths were much smaller than the optimum thickness for internal reflection SFG measurement shown in Fig. 3, the intensities of both visible and infrared lasers are expected to be attenuated significantly by the gold thin films. A strong SFG signal from ODT monolayer on gold surface was, however, observed clearly as that in normal external reflection SFG spectra (Figs. 2 and 3). Thus, another enhancement factors should be considered here. It is well known that the intensity of the Raman scattering signal for a surface adsorbed species is enhanced by 10^5-10^6 when a grained metal thin layer is used [15]. The strong electromagnetic (EM) field associated with the surface plasmon polariton and the collective electron resonance are considered as major reasons for the surface enhanced Raman scattering (SERS). Similar surface enhanced phenomenon associated with surface roughness of the evaporated metal thin layer was reported for IR absorption [16]. Surface structure and morphology of the gold thin film should play an important role also in the thickness dependent SFG spectra shown in Fig. 3.

One should be able to reduce the light loss within the gold films by illuminating the visible and observing SFG output both from the water side because the absorption of visible and SFG lights by water are negligible. This study is now in progress.

In conclusion, we have demonstrated that internal reflection SFG spectroscopy is useful in determining conformational order of ODT monolayer on gold films in electrolyte solution. The internal reflection SFG spectroscopy can be used as an efficient tool to study the electrochemical interface.

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