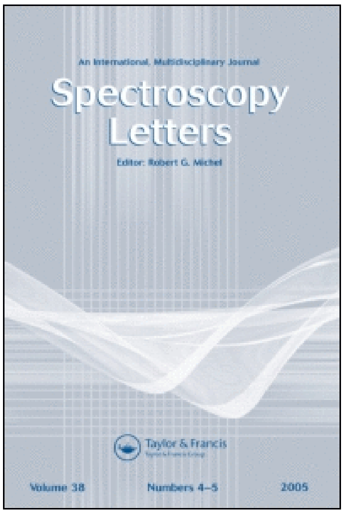

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pH Dependence of Surface Enhanced FT-Raman Scattering of Ω-Mercaptoalkanols on Silver Surface

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PH DEPENDENCE OF SURFACE ENHANCED FT-RAMAN SCATTERING OF ω-MERCAPTOALKANOLS ON SILVER SURFACE

Keywords: self-assembled monolayer film, Fourier transform surface enhanced Raman scattering (FT-SERS), ω-mercaptoalkanols, conformation, silver surface.

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Abstract Fourier transform surface enhanced Raman spectrometer is used to characterize ω-mercaptoalkanols ($HO(CH_2)_nSH$, n=2, 6) chemisorption on silver surface from their aqueous solution of different pH values.

INTRODUCTION

Since the pioneering works by Fleischmann[1], Van duyne[2], Creight and their co-workers[3], surface enhanced Raman scattering (SERS) has

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found widely application in the characterization of a monolayer or submonolayer of adsorbed molecules on metal surface. In addition to the electrochemically roughened silver electrode, on which this phenomenon was first discovered, metal surfaces prepared by various processes have been employed for the measurements of the SERS spectra. Up to now, there are a lot of manners to obtain SERS-active substrate, which include metal sols[4], vacuum-deposited metal island films[5], and HNO_3 etched metal foils[6].

Organic sulfur derivatives coordinate strongly to some metal surfaces and form monomolecular film. Nuzzo and Allara showed that dialkyl disulfides formed oriented monolayer on metal from solutions[7]. The monolayer was well-organized microscopic characteristics and endowed the metals attached many special properties such as wetting, adhesion, anti-corrosion. Many other studies have characterized aspects of this monolayer. Nuzzo, et al. have presented data on monolayer on long-chain alkanethiols adsorbed on gold from solution, using X-ray photoelectron spectroscopy (XPS) and contact-angle measurement[8]. Yuichi Yamamoto studied the anti-corrosion property of $HO(CH_2)_{11}SH$ on the copper electrode in a spectroelectrochemical cell[9].

In this study we used silver film as substrate to investigate the chemical adsorption of 2-mercaptoethanol and 6-mercaptohexanol in different pH value aqueous solution with a fluorescence-free Fourier transform Raman spectrometer.

EXPERIMENTAL

Materials 2-mercapto-ethanol is obtained as high-grade commercial reagent and was used without further purification (purity 99.9%). 6-Mercapto-hexanol can be easily synthesized according to reports described previously[10]. All other chemicals are analytical reagent.

Sampling methods of ω-mercaptoalkanols Formaldehyde and silver ammonia complex are used to prepare fresh silver surface according to the procedure described previously[11]. In brief, at room temperature, we mix 10 ml 0.1-0.2 M silver ammonia complex and 5 ml 5% formalhydrde in a beaker, which contains a few of piece of clean glass plate (10-mm×10-mm×1-mm). A few of seconds later, the solution turns to gray and silver ions are reduced onto the plate to form a fine silver film. The thickness of silver film can be adjusted by controlling reaction time or temperature. Higher temperature and longer reaction time favor thicker silver film. After withdrawing, the silver film is washed with distilled water and then dipped in 0.001 M ω-mercaptoalkanols aqueous solution. The pH value of solution is adjusted by HCl or NaOH aqueous solution. The spectra are recorded 5 min later after the change of pH value.

FT-Raman and FT-SERS spectroscopy measurement The spectra are recorded with a Bruker model RFS 100 Fourier Raman spectrometer with an air-cooled diode pumped Nd-YAG laser, and Ge-detector, cooled to liquid nitrogen temperature. The incident laser excitation is 1064 nm. The outputs are 30 and 350 mW for normal FT-Raman and FT-SERS measurement. The resolution is 4.0 cm^{-1}. The FT-SERS samples are dipped in the solution and recorded. There is a distance of 1 mm solution between the SERS sample surface and sample cell wall to ensure that there is fast adsorption equilibrium. The scattered light is collected at the angle of 180°. The ω-Mercaptoalkanols liquids are sealed in glass capillaries and determined.

RESULTS AND DISCUSSION

Alkanethiols were first reported to form monolayer on silver surface by the chemisorption of the S head group to the metal substrate, resulting the formation of Ag-S bond. FIG.1 shows the normal FT-Raman spectra of 6-mercapto-hexanol (A) and its FT-SERS spectra on silver film from pH 7 aqueous solution (B). FIG.1A exhibits strong vibration of S-H bond at 2575 cm^{-1}. In its FT-SERS spectrum B, a few spectral changes take place, following the its adsorption on the silver surface. First, the 2575 cm^{-1} band assigned to S-H vibration disappears in FT-SERS spectrum. This observation indicates that it is chemisorbed dissociatively on the silver surface by the split of its S-H bond. In addition, the absence of S-H intensity in the self-assembled monolayer film suggests that there is no

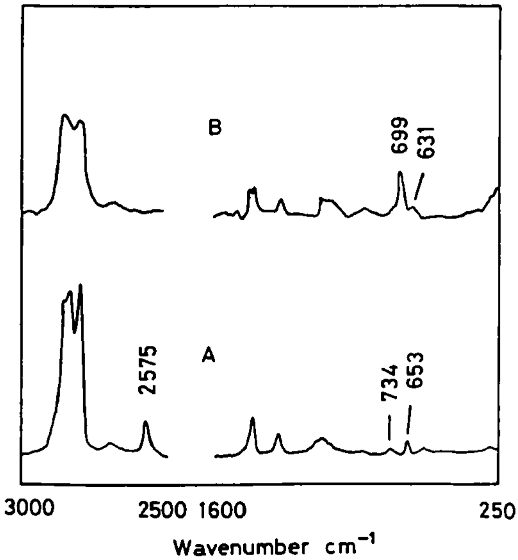

FIG.1 FT-Raman spectrum of 6-mercaptohexanol(A) and FT-SERS spectrum of its thiolate adsorbed on silver surface from pH 7 aqueous solution.

free 6-mercaptohexanol on silver surface. The bands at 734, 653 cm^{-1} in FIG.1A, which are assigned to the trans and gauche C-S stretching vibration have shifted to 699, 631 cm^{-1} in FIG.1B[9]. Therefore we can conclude that the 6-mercaptohexanol is chemisorbed on the silver and changed into 6-hydroxylhexanothiolate.

FIG. 2A and 2B, respectively, present the normal spectrum of liquid 2-mercaptoethanol and the SERS spectrum on silver surface dipped in 0.001 M 2-mercaptoethanol aqueous solution of pH 7. The disappearance of S-H band at 2565 in FIG. 2B, and great red shifts of C-S bands are also observed in the SERS spectrum of 2-mercaptoethanol adsorbed on silver surface. Comparing FIG.2A and 2B, we think that the trans (T) and gauche (G) C-S vibration red shifts in its FT-SERS spectra are caused by the Ag-S bond. In the previous SERS investigation

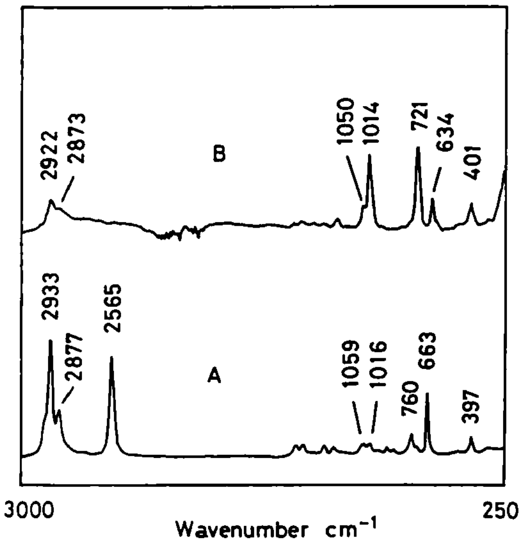

FIG.2 FT-Raman spectrum of 2-mercaptoethanol (A) and FT-SERS spectrum of its thioate adsorbed on silver surface from pH 7 aqueous solution.

of $HO(CH_2)_{11}SH$, similar results were obtained about thiolate on the copper electrode in a spectroelectrochemical cell [9]. Because of electrodonation from sulfur to silver the C-S bond weakened, resulting the red shift of their stretching frequency.

An interesting phenomenon is the conformation change of 2-hydroxyethanethiolate attached to silver surface with the variation of pH value. FIG. 3 displays the normal Raman spectrum of 2-mecaptoethanol liquid and FT-SERS spectra of 2-hydrosyethanethiolate adsorbed on silver surface from different pH solution in the range of 400-1200 cm^{-1}. 2-Hydroxyethanethiolate can be in eight conformations, they are TTT, TTG, TGT, TGG, GTT, GTG, GGT, GGG (the first signal denote the conformation of C-S, the second C-C, and the third C-O, T represents trans, G represents gauche). The relative intensity of C-S or C-O bands

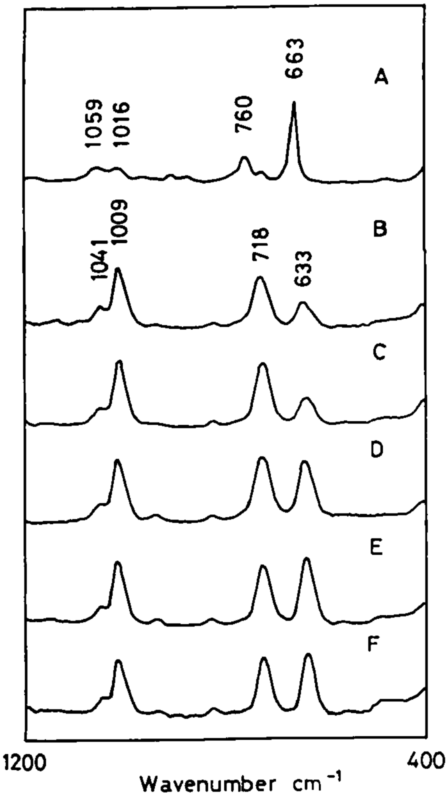

FIG.3 FT-Raman spectrum of 2-mercaptoethanol (A) and FT-SERS spectra of its thioate adsorbed on silver surface from different pH values aqueous solution, pH values are 12(B), 9(C), 6(D), 3(E), 1(F) respectively.

can be taken as a measure of trans rotamers or gauche rotamers in adsorbed molecules. The bands at 718, 633 cm^{-1} in FIG. 3, except FIG. 3A , are assigned to the trans and gauche C-S stretching vibration. The bands at 1041 cm^{-1} and 1009 cm^{-1} are perhaps caused by the vibration of C-C or C-O bonds. With decrease of pH value most of trans C-S conformers alter to gauche conformers, so that C-C bonds will adjust their conformation, in other words, the C-C bond will parallel to the silver surface, which would lead to the intensity decrease of C-C bands and it becomes non-discriminating. We find no intensity change of the bands at 1041 cm^{-1} and 1009 cm^{-1}. The C bonds and C-C bond all in gauche conformation, the end group C-O bond can in trans and gauche form, and most of C-O bond has component perpendicular to the surface whether they in either forms. Therefore the intensity of C-O bands does not vary.

Therefore we propose that these bands are due to the stretching vibration of C-O bonds. The difference of these two band intensities is caused by the number gap of trans and gauche conformers. These bands intensities get little affect from pH value change perhaps due to the coordination between oxygen and silver to some extent. Because of multiplicity of the conformation, we can conclude that 2-mercaptoethanol can attach chemically to silver surface by sulfur atom and by the coordination between oxygen of hydroxyl and silver. The pH value affects the conformation of thiolate. In higher pH value range, above 7, most of C-S bonds are in trans form, with decrease of pH value, these bonds alter to gauche form. The C-O and C-C conformation gain little effect from the variation of acidity. Theseconformation changes of 2-hydroxylethanothiolate on silver surface indicate that the monolayer film is defect, and there is enough space for them to adjust their conformation when being subject to different environments.

From the FT-SERS spectra of 6-mercaptohexanol, however, we did not observe this phenomenon except the ratio increase of trans rotamers over gauche. These results suggest that the conformation of long chain molecule is more ordered than the short one and they are not interfered by the contacting medium. This is in agreement with the results found by Porter, et al[12], that the long chain alkanethilos adsorbed on gold surface from solution could form a crystalline structure. We suggest that the crystalline structure of 6-hydroxyhexanethiolate on silver surface is not easily interfered by the pH change of solution. The conformation change implies that the assembled-film of 2-mercaptoethathiolate on the silver surface is not ordered as that of long-chained thiols adsorbed on silver surface. The conformation of 2-hydrogethanethiolate is reversible to pH. It can undergo continuous conformation transformation.

CONCLUSION

Fourier transform surface enhanced Raman scattering spectroscopy (FT-SERS) was used to characterized ω-mercaptoalkanols self-assembled monolayer on silver surface. The normal FT-Raman and FT-SERS spectra lead the conclusion that by the split of S-H bond, above compounds can be adsorbed on the silver surface to form monolayer of their thiolates. The thiolates are ordered in trans and gauche conformation. For the 2-hydroxyethnethiolate on the surface, the ratio of trans over gauche conformation increased with pH value, while, the conformation of 6-hydroxyhexathiolate is not interfered by pH due to its closed-packed structure.

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