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The adsorption and bonding of ω -mercaptoalkanols on HNO₃ etched copper

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Abstract

 ω -Mercaptoalkanols (HO(CH₂)_nSH, n = 2, 6, 10) could cleave and were chemisorbed in trans and gauche conformation on HNO₃ etched copper foils to form self-assembled monolayers. The orientation of the molecules in the film was characterized by Fourier transform surface enhanced Raman scattering spectroscopy (FT-SERS). In the liquid state the above compounds tend to be in the gauche conformation, however, in the adsorption state they inclined to be in the trans conformation. In the adsorption state the ratio of trans to gauche conformation increased with the chain length.

1. Introduction

Organic compounds containing sulfur, such as ω-substituted alkanethiols $(HS(CH_2)_n X, 21 \ge n \ge 0,$ and $X = CH_3$, CHCH₂, CH₂OH) and disulfide, can form well-defined monolayer films on some metal surfaces [1]. Under some conditions, noble metals such as gold, silver and copper are ready to react with the above compounds. Sandroff and Herschbach investigated the surface products of thiophenol and phenyl disulfide on silver [2]. Whitesides used organic disulfides as anchors for constructing self-assembled organic layers on gold [1]. Nuzzo and Allara showed that dialkyl disulfides form oriented monolayers on metal from solutions [3]. The monolayer had well-oriented microscopic characteristics and endowed the attached metals many special properties such as wetting, adhesion and anti-corrosion. Nuzzo

The first reported SERS study of disulfides and thiols on a surface was by Sandroff and Herschbach

and co-workers have presented data on a monolayer of long-chain alkanethiols adsorbed on gold from solution, using X-ray photoelectron spectroscopy (XPS) and contact-angle measurements [4]. Since then, many other studies have characterized aspects of this monolayer. In many studies surface-enhanced Raman scattering spectroscopy (SERS) was used as the spectroscopic tool [2,5,6]. SERS has played an important part in the field of surface science owing to its high spectral resolution and excellent sensitivity to molecules at composite interfaces. Especially, SERS is ideal for the study of composite interface since it enhances almost exclusively the first monolayer of molecules adjacent to the interface between metal and polymer as long as the polymer films are not so thick that normal Raman scattering from the bulk of the film is more intense than SERS from the interface.

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[2,5]. They found that the surface products of thiophenol and phenyl disulfide on silver are identical. Sobocinski et al. have studied alkanethiols at electrode surfaces using SERS and they have made comparisons between the surface interactions of alcohols and thiols [6]. Meanwhile, some studies indicating the existence of surface-enhanced photochemistry were reported [7]. Most SERS spectra were obtained on noble metals such as silver and gold by metal island films, metal films deposited on guartz or Teflon particles, and chemically reduced metal films on glass slides. The purpose of the above methods involves developing an appropriate roughness on metal surfaces or proper size and shape of metal particles. However, these substrates are not quite stable for long periods of time or at elevated temperature. It is difficult to obtain a reproducible enhancement. This problem hinders a widespread acceptance of SERS as a technique for mechanistic investigations. Recently, a stable substrate prepared by the nitric acid etching method for SERS study has been developed in this laboratory [8]. Copper and silver foils etched with nitric acid exhibit an excellent enhancement factor and show an extraordinary stability under various environmental conditions.

In this study, we have investigated the surface interaction of ω -mercaptoalkanols with copper substrates by FT-SERS. Alkanethiols are of interest as a corrosion inhibitor for metals. However, only a limited number of reports have been published concerning its chemical behavior on metal surfaces [9,10]. We found that the FT-SERS results obtained from ω -mercaptoalkanols adsorbed on HNO₃ etched copper surface showed that they were in a different adsorption state.

2. Experimental

2.1. Preparation of ω -mercaptoalkanols

2-Mercaptoethanol was obtained as high-grade commercial reagent and was used without further purification. 6-Mercapto-1-hexanol and 10-mercapto-1-decanol were synthesized according to the following reactions [11,12]:

$$HO(CH_2)_n OH + HBr \rightarrow HO(CH_2)_n Br,$$
 (1)

$$HO(CH_{2})_{n}Br + (NH_{2})_{2}CS$$

$$\rightarrow HO(CH_{2})_{n}SCBr(NH)NH_{2}HBr, \qquad (2)$$

$$2HO(CH_{2})_{n}SCBr(NH)NH_{2}HBr + 2NaOH$$

$$\rightarrow 2HO(CH_{2})_{n}SH + NH_{2}C(NH)NHCN$$

$$+ NaBr + 2H_{2}O, \qquad (3)$$

where n = 6 or 10. 1,6-Hexanediol and 1,10-decanediol (reagent grade) were purchased from Fluka and used as received. 0.03 mmol alkanediol were mixed with 7 g 40% HBr and 0.2 g H₂SO₄ (98 wt.%). The solution was heated to refluxing and maintained for two hours. Then it was cooled and washed with 5% Na₂CO₃ solution. The oil product was separated. The above raw product was then heated to refluxing for two hours with 20 ml alcohol and 0.033 mmol thiourea followed by two more hours refluxing with 10 g 20% NaOH. The resulting volume of the aqueous solution was reduced by about 20 ml. The upper oil was separated and washed with 2% HCl until neutral and was then purified by silica gel column chromatography.

2.2. Sampling methods of chemicals

Copper foils of 0.025 mm thickness were used as commercially supplied (Aldrich; purity 99.999%) and were cut into pieces of 3 mm \times 10 mm and immersed into a 3–5 M HNO₃ solution at room temperature. After several seconds, a number of tiny bubbles were formed near the surface of copper. A red and sponge-type surface with substantial roughness was created a few minutes later. The etched copper foils were thoroughly rinsed with water and dried in air and were ready for sampling chemicals instantly.

First, ω -mercaptoalkanols were dissolved in ethanol to obtain a solution with a concentration of 0.001 M. The etched copper substrates were then dipped into the solution at room temperature for 5 min. After withdrawing, the excess liquid was washed with alcohol. The treated samples were ready for SERS spectroscopy. The liquids were sealed in glass capillaries and measured.

2.3. Instrument

All of the FT-SERS and normal FT-Raman spectral measurements were performed 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 was 1064 nm. The outputs were 30 and 50 mW for FT-SERS and normal FT-Raman measurement, respectively. Spectra were obtained with a resolution of 4.0 cm⁻¹ and 100 scans. The scattered light was collected at an angle of 180°.

3. Results and discussion

n-Alkanethiols were supposed to form a monolayer on the copper surface by the chemisorption of the S head group to the metal substrate. Copper and silver proved to be more reactive to alkanethiols and more sensitive to attributes of the alkanethiols than gold. On copper, the metal-sulfur bonds were stronger than those on gold, but the formation of metal sulfides and the different spacing of the head groups induced numerous defects in the film. Evidence for this bonding is the disappearance and appearance of the Cu-S bond in the FT-SERS spectra of their films. Fig. 1 shows the normal FT-Raman



Fig. 1. The normal FT-Raman spectra of neat ω -mercaptoalkanols (HO(CH₂)_nSH). (A) n = 2, (B) n = 6, (C) n = 10.



Fig. 2. The FT-SERS of ω -mercaptoalkanols (HO(CH₂)_nSH) adsorbed on HNO₃ etched copper. (A) n = 2, (B) n = 6, (C) n = 10.

spectra of (A) 2-mercaptoethanol, (B) 6-mercapto-1hexanol and (C) 10-mercapto-1-decanol. Fig. 1A-C exhibits strong vibration of S-H bond at 2566, 2574 and 2575 cm^{-1} , respectively. Fig. 2 shows the SERS spectra of (A) 1-mercaptoethanol, (B) 6-mercapto-1hexanol and (C) 10-mercapto-1-decanol on copper foils. A few spectral changes have occurred, following the adsorption of $HO(CH_2)_n SH$ on the copper surface. First, the bands assigned to the S-H vibration have all disappeared in Fig. 2. This observation indicates that they were chemisorbed dissociatively on the copper surface by the capture of their S-H bonds. In addition, the absence of S-H intensity in the self-assembled monolayer films suggests that there was no free ω -mercaptoalkanol present. Once bonded to the copper surface through the S atom, the ω-hydroxyalkanethiolates would interact through the van der Waals forces and were ordered in different conformations. According to the 'surface selection rules' by Moskovits and others [13-15], the vibration signals of adsorbed molecules, which have a component perpendicular to the surface, would be enhanced. The enhancing factor was directly proportional to the perpendicular component. From the bands and enhancing effect, we can determine the conformation of the molecules in the films. Of these signals, the most informative about the molecular conformation are the C-S stretching modes (600-750 cm⁻¹) [16,17].

The bands related to trans and gauche conformations can be observed at 760 and 663, 733 and 654, and 737 and 653 cm^{-1} in the normal Raman spectra in Fig. 1A-C, respectively. As in the liquid state molecules move easily and are in disorder, the gauche conformation corresponding to the bands at 663, 654 and 653 cm^{-1} dominate the spectra. Comparing Fig. 1 with Fig. 2, we find that the trans (T) and gauche (G) C-S vibration bands of above liquid compounds have shifted to 722 and 633, 704 and 632, and 693 and 621 cm⁻¹, respectively in the FT-SERS spectra. In the previous SERS investigation of $HO(CH_2)_{11}SH$, similar results were obtained from the thiolate adsorbed on the copper electrode in a spectroelectrochemical cell [18]. Because of electrodonation from sulfur to copper, the C-S bond weakened, resulting in a red shift of their stretching frequency.

For ω -hydroxyalkanethiolate adsorbed on copper surface, the extent of ordering appeared to be somewhat different. The ratios of the intensity of T (C–S) to G (C–S) were calculated and are listed in Table 1. The significant increase in the intensity ratio of the SERS spectra to the liquid spectra suggests that the C–S bonds have a significant component perpendicular to the surface and they are ordered on the surface in more trans conformations than they are in the liquid form. With increasing chain length, the molecules would be more ordered. These results are consistent with work published previously on an n-alkylthiol monolayer on gold [19].

The bands at 1291 cm⁻¹ in Fig. 1A, 1302 cm⁻¹ in B and 1299 cm⁻¹ in C are due to the CH_2 wagging mode. They have become weak in their respective SERS spectra at 1277, 1276, and 1279

Table 1

The ratios of integr	al areas of trans,	/gauche C–S	conformers
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Compound	Liquid state trans/ gauche	Adsorbed state trans/ gauche
$\overline{n=2}$	0.15	0.083
n = 6	0.44	0.85
<i>n</i> = 10	0.91	1.69

Fig. 3. The FT-SERS of ω -mercaptoalkanols (HO(CH₂)_nSH) adsorbed on HNO₃ etched copper after seven-day keeping. (A) n = 2, (B) n = 6, (C) n = 10.

 cm^{-1} in Fig. 2A-C. The bands at 1458 and 1426 cm^{-1} in Fig. 1A and at 1446 and 1418 cm^{-1} in Fig. 2A are caused by the HC1H and HC2H in-plane deformation (C1 is the first C adjacent to the surface). The environments of C1 and C2 are different, therefore they represent two different kinds of HCH deformations. The bands at 1437 cm⁻¹ in Fig. 1B and C, and 1424 and 1455 cm⁻¹ in Fig. 2B and C are due to the HCH in-plane deformation. No further effort was made to assign the residual weak peaks. During the keeping of samples, their FT-SERS spectra showed strong bands within the range of 600-660 and $510-550 \text{ cm}^{-1}$ due to copper oxide [20,21]. Fig. 3 shows the FT-SERS spectra of ω -mercaptoalkanols adsorbed on copper surface in air after seven days. In Fig. 3A, as the copper oxide band overlaps the trans C-S band, it is difficult to identify this band. The C-S bands are very weak in the FT-SERS spectra so that they are covered by the strong CuO bands (see Fig. 3B and C).

4. Conclusion

FT-SERS was used to characterize a self-assembled monolayer of ω -mercaptoalkanols on a HNO₃



etched copper surface. The normal FT-Raman and FT-SERS spectra led the conclusion that by splitting of the S-H bond, the above compounds could be adsorbed on the metal surface to form their thiolates and exhibit a relatively large Raman enhancement. The thiolates were ordered in trans and gauche conformations. The ratio of trans to gauche conformation increased with increasing alkyl chain length. The trans conformation was conjectured to be more favorable on the basis of a closed-packed structure.

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