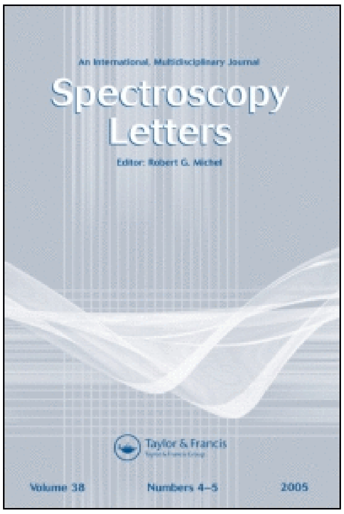

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SERS Studies of the Ring Opening Reaction of an Epoxy Compound on the Top of Chemisorbed Cystamine

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SERS Studies of the Ring Opening Reaction of an Epoxy Compound on the Top of Chemisorbed Cystamine

Keywords: Silver, adsorption, surface enhanced Raman scattering, cystamine, styrene oxide.

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ABSTRACT

Silver foils for Raman scattering were prepared by HNO_3 etching method. These foils were found to exhibit a SERS effect and excellent thermal stability. SERS spectra of

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4,4′-dipyryl and cystamine have been taken to illustrate the usefulness of this sample preparation method in the studies of chemisorption. The ring opening reactions of an epoxy compound have been observed on the top of chemisorbed cystamine on silver foils.

INTRODUCTION

Although the high information content of Raman spectra from adsorbates on metal surface has long been recognized, practical application has been impeded by poor sensitivity. The discovery of enormously enhanced cross section for Raman scattering from molecules adsorbed on an electrochemically roughened silver surface was first reported by Fleischmann et al. [1] Subsequent reports by Van Duyne and by Albrecht and Creighton showed that such a scattering spectrum represented as much as a millionfold increase in Raman intensity as compared to liquid or solution spectra. [2] These reports renewed considerable interest in the filed of Raman spectroscopy and caused an explosion of experimental and theoretical research activities in this area.

In addition to the electrochemically roughened silver on which the remarkable phenomenon was first observed, the surface enhanced Raman scattering (SERS) effect has been tested on various forms of metal surfaces. These efforts were mainly for better theoretical understanding and to pursue the applicability of the technique in the study of surface chemistry. Surface enhancement depends critically on the creation of surface roughness; as mentioned in many reports, particles in the 10-100 nm size range give the strongest electromagnetic enhancement contribution. [3] Vacuum depositing calcium fluoride onto CaF_2 surface to form Ag/CaF_2 substrate may yield quite strong enhancements in the case of Ag and Au [4]. However, these substrate are not stable at room or elevated temperature. A variety of other procedures are known to produce such roughness as colloidal metal particles, [5] matrix-isolated metal clusters, iodine-roughened silver in ultra-high vacuum, tunnel junction structure, metal-capped polymer posts, and holographic gratings.[6] However, in order to develop SERS into a general-analytical tool, it is necessary to devise more routinely prepared substrate systems which exhibit Raman enhancement with reasonable stability in air. We describe in this report a very effective, easy-to-prepare and less cost substrate system for obtaining SERS effect. Silver films etched with a HNO_3 solution are shown to exhibit reproducible strong SERS effects. SERS spectra of 4,4′-dipyryl and cystamine adsorbed on silver foils respectively are presented. The chemical reaction of styrene oxide on the chemisorbed cystamine was demonstrated to show the usefulness of this method in the studies of surface reactions.

EXPERIMENTAL

Commercial silver foil of 0.025 mm thickness was immersed into an agitated 3.5 M HNO_3 at ambient temperature, for about 2-3 minutes until the foil displayed a milky surface. This procedure created a sponge-type surface with plentiful roughness features on a 10-100 nm size scale, as shown by electron micrographs. After etching, the foil was ready for sample doping. It was reported that HNO_3 with a concentration of 2 M could create surface roughness on copper. [7] We found that only concentrated HNO_3 (>3.5 M) could roughen silver effectively. Another surface morphology was used for the purpose of comparison: CaF_2 roughened films overcoated with silver. Calcium fluoride and silver were vapor deposited onto a glass slide in a cryopumped vacuum system at pressures of 10^{-6} torr. The adsorbates were intially dissolved in methanol to make a 0.001 M soultion. A silver foil roughened with HNO_3 was dipped into the adsorbate solution for approximately 3 minutes. AS reported by Garoff et al, this method results in rather uniform coverage of the adsorbates on these foil controlled by the concentration of the adsorbate in solution.[8] After withdrawing, the excess liquid was blown off with nitrogen. It was found that the saturated surface was attained with a doping solution concentration of 0.001 M. This method appeared to provide good SERS spectrum for adsorbates that could be dissolved in volatile solvents.

Surface Reaction: After the HNO_3 roughened Ag foil was doped with monolayer of cystamine, it was immersed into the styrene oxide liquid for 20 minutes at 80°C. After withdrawing, the physisorbed styrene oxide was rinsed away with benzene, the excess benzene was blown off with nitrogen. Raman spectra were recorded with a SPEX-1403 Raman spectrometer. The incident laser excitation wavelength was 632.8 nm.

RESULTS AND DISCUSSION

A SERS spectrum was obtained from monolayer 4,4'-dipyryl on HNO_3 roughened Ag foil as shown in Figure 1(B).

For comparison, a SERS spectrum of 4,4'-dipyryl adsorbed on Ag/CaF_2 substrate is presented in Figure 1(A), and its normal Raman spectra in methanol solution (1 M) is illustrated in figure 1(C). Following the procedure reported by D. A. Weitz et al. [9], the enhancement factor for the sharp ring mode near 1615 cm^{-1} was estimated as per molecule of 1.5×10^6 on the HNO_3 roughened Ag foil and was 0.9×10^6 on the vacuum deposited Ag/CaF_2 substrate respectively.

Figure 2 shows the SERS spectrum of cystamine ($NH_2(CH_2)_2S\text{-}S(CH_2)_2NH_2$) on HNO_3-roughened silver foil and its normal Raman spectrum in aqueous solution. The C-S stretches occur in Raman spectrum as two bands at 640 and 730 cm^{-1}, while the S-S band appears at 510 cm^{-1}. The 510 cm^{-1} band disappeared in the SERS spectrum, indicating the breakage of S-S bond. This is consistent with the previous findings that disulfides could chemically react with silver to form mercaptides [10]. The most significant enhancements have occurred for the bands centered at 640 and 730 cm^{-1} in

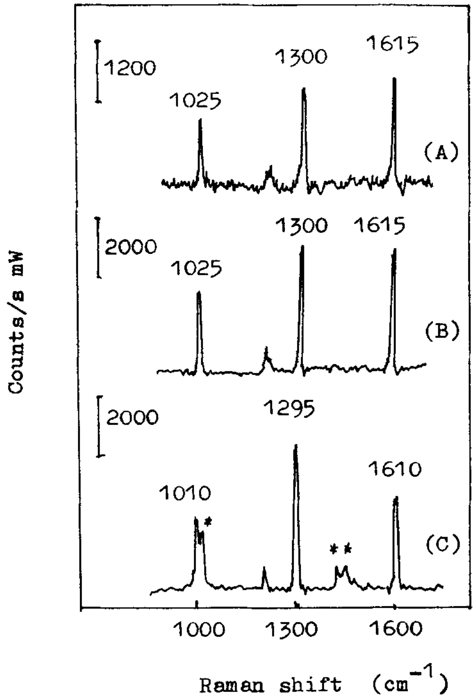

Figure 1. Raman spectra of 4,4′-dipyridyl: (A) SERS on solver island film; (B)SERS on nitric acid etched Ag film; (C) a normal Raman spectrum.

the SERS spectrum, indicating that the C-S band is probably perpendicular to the surface. The enhancement for the 640 and 730 cm^{-1} bands was estimated by comparing the SERS intensity to that of cystamine in aqueous solution. We obtained an average enhancement per molecule of 8×10^5. Hence, our HNO_3-roughened silver foil appears to be as good as the electrochemically roughened electrode in SERS study.

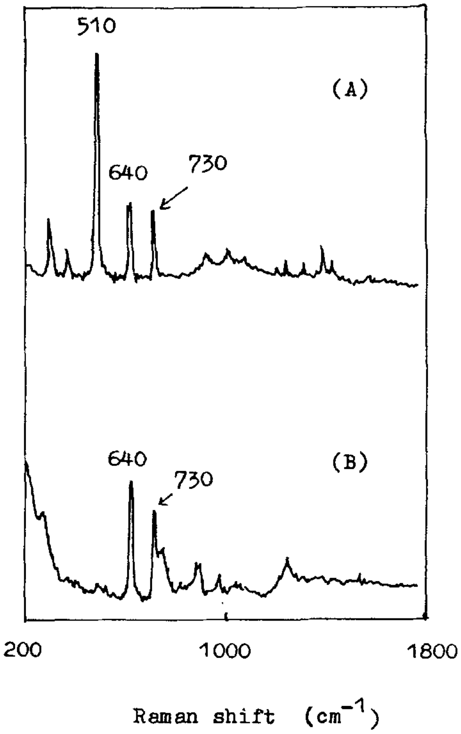

Figure 2. (A) Normal Raman spectrum of cystamine in solid state and (B) SERS spectrum of cystamine on Ag foil.

A successful basis for analyzing SERS spectra with to orientation of adsorbates has been reported in the form of "surface selection rules" by Moskovist et al. [11]. These rules are based on the electromagnetic theory of SERS intensity, which says that, via resonance interaction with surface plasmons of the metal, incident light increases in the electromagnetic fields are highest normal to the surface; normal modes of the adsorbed molecule involving changes in molecular polarizability with a component perpendicular to the surface are subject to the greatest enhancement. This same type of analysis has been successfully applied by Ni and Cotton [12] and by Strekas and Diamandopoulos.[13] Based on these "surface selection rules" and the relative intensity changes in Figure 2, we conclude that (1) C-S bond sit perpendicular to the surface, and (2) S-S bond is breaken to form S-Ag interfacial bonding.

It is believed that the high degree of structural order on the metal surface will make cystamine on metal a system of wide utility for studies in the chemical, physical, and biological fields. One possibility is that, the NH group of cystamine sitting on the top of the chemisorbed molecules, may induce that ring opening reaction of an epoxy compound. Styrene oxide is used as a model compound to investigate this surface reaction. Its reaction with cystamine on HNO_3 roughened Ag foil surface was followed by SERS spectra, and shown in Figure 3 and 4.

As can be seen in Figure 3 and 4, interaction on Ag foil surface caused variation in spectra. In Figure 3(A), the peaks at 620, 1005 and 1615 cm^{-1} are due to the monosubstituted benzene ring deformation, in-plane-deformation and ring stretching of benzene ring respectively; the peaks at 815, 880 cm^{-1} are related to the in-plane-ring deformation of epoxy ring. Figure 3(B) is the SERS spectra of styrene oxide on cyctamine-pretreated Ag

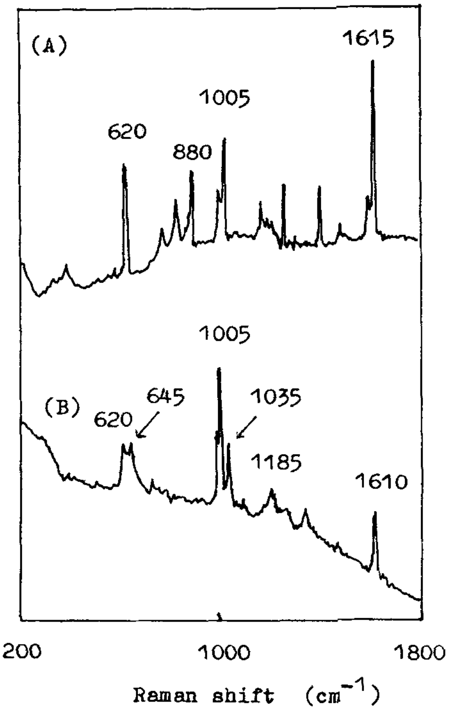

Figure 3. (A) Normal Raman spectrum of styrene oxide and (B) SERS spectrum of styrene oxide on Ag foil pretreated with cystamine.

foil surface. There is also occurring the peaks at 620, 1005 and 1605 cm^{-1} which are attributed to benzene ring vibration. The peaks which disappeared at 815 and 880 cm^{-1} result from the ring opening of epoxy ring. The new peaks at 1035 and 1185 cm^{-1} are characteristics of other group (C-O-C) vibration. According to these results, we may conclude that styrene oxide can chemically react with

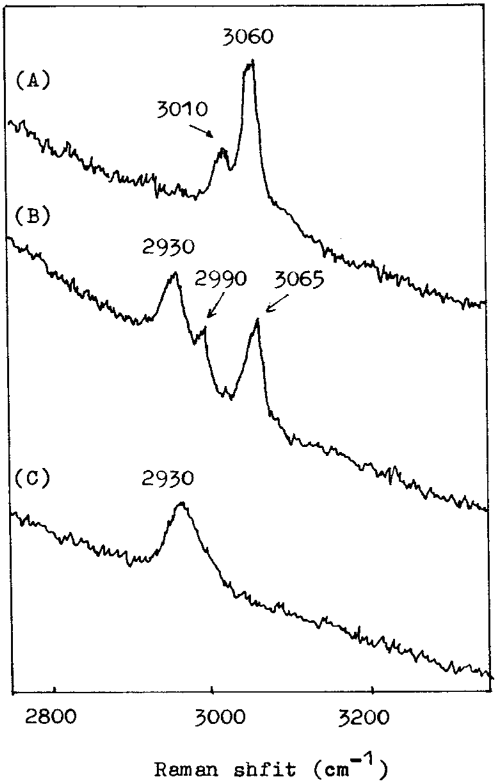

Figure 4. (A) Normal Raman spectrum of styrene oxide; SERS spectrum of styrene oxide on Ag foil pretreated with cystamine; (C) SERS spectrum of Ag foil pretreated with cystamine.

cystamine adsorbed on Ag foil, its epoxy group is initiated by -NH group of cystamine, then polymerize through C-O-C bonds.

Figure 4 shows the Raman spectra of various samples at high wavenumber region. Figure 4(A) is the normal Raman spectra of styrene oxide. The peaks at 3010 and 3060 cm^{-1} in Figure 4(A) are due to CH stretching vibration of epoxy ring and benzene ring respectively; The peaks at 2930, 2293, 3065 cm^{-1} in Figure 4(B) are related to CH stretching vibration oh cystamine, $-CH_2-O-CH_2-$, benzene ring in the order mentioned. The peak at 2930 cm^{-1} in Figure 4(C) is attributed to the CH stretching vibration of cystamine. The peak at 3010 cm^{-1} that appears in Figure 4(A) and disappeared in Figure 4(B) further confirms that cystamine which was absorbed on Ag foil surface is still able to initiate the epoxy ring into polymerization. Based on above results, cystamine was adsorbed on Ag foil surface with self-assembled, well-oriented monolayer. The NH_2 group sitting on the top of cystamine could open the epoxy ring. So it may be used as a coupling agent between metal and epoxy compounds.

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