Stable SERS Substrates Used for In Situ Studies of the Polymer–Metal Interface at Elevated Temperature

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ABSTRACT: Thermally stable SERS substrates for Raman study of the polymer–metal interface were prepared by etching metal foils with HNO_3. These foils were demonstrated to exhibit a better surface-enhanced Raman scattering (SERS) effect and higher stability at elevated temperature than a vacuum-deposited Ag/CaF_2 substrate. SERS spectra of poly(benzimidazole) and poly(acrylonitrile) have been obtained to illustrate the usefulness of this sample preparation method in the interfacial structure. The order of Raman enhancement effect for different metal substrates was arranged as HNO_3-etched Ag > HNO_3-etched Cu > Ag/CaF_2 at elevated temperature. Comparison of SERS with normal Raman and IR diffuse reflectance spectra for coatings on a roughened metal surface indicates that SERS is highly informative in that the interfacial microstructure can be revealed with much less interference from the polymer bulk.

Introduction

Polymer film cast from solution onto a metal surface usually forms multilayers of macromolecular chains. When the cast solution is very dilute to produce low coverage, the adsorbed polymer is prone to form islands or clumps upon evaporation of the solvent, resulting in an inhomogeneous surface under analysis. So, the film of polymer on metal must be a few hundred angstroms thick in order to cover the surface entirely, while the interfacial region is only related to a few or a few tens of angstroms of polymer adjacent to the metal surface.[1] Thus, it is difficult to measure the interfacial region without the interference of the polymer bulk. Until recently, process technology had developed largely empirically without specific knowledge of the nature of chemical bonding at the interface. With the advent of more sophisticated surface analytical techniques, the polymer/substrate interaction has begun to be studied on a more detailed molecular level. Among the various state-of-the-art tools in surface analysis, X-ray photoelectron spectroscopy (XPS) is used to investigate core level shifts of the polymer components, as well as those of the metal atoms themselves in order to elucidate the nature of the bonding between metal and polymer. But the uncertainties inherent in XPS analysis of polymer/metal interactions stem mostly from differential charging of the sample surface during an XPS measurement.[2] Differential charging leads to artifacts in the XPS spectra, which may be mistaken for chemical bonding effects. Moreover, metals can be studied by the use of electron spectroscopy, but only if the polymer layer is absent or is less than 3–5 nm thick because of the limitation of the mean free paths of the photoemitted electron in the energy range of interest. However, it is difficult in practice to cast synthetic polymers as a uniform monolayer film with thickness less than a few tens of angstroms onto metals. In the manufacture of coatings or adhesives on metals, a "thin layer" may mean a thickness of hundreds of nanometers. Infrared (IR) reflection–absorption and diffuse reflectance spectroscopy could provide rich information about the surface film,[3–6] but mostly from the polymer bulk. Both IR and normal Raman spectroscopy could hardly observe the insight structure of 10–30 Å of polymer near the surface without the interference of the bulk polymer which is at least hundreds of angstroms thick. Because of the difficulty of the experimental measurement of the microstructure at the interface, the specific knowledge of the physical chemistry, such as surface bonding, molecular orientation, catalyzation under various conditions, diffusion of metal ions, and the electrochemical properties in the interfacial region, is still not understood. It is therefore necessary to develop new techniques to investigate the interfacial structure with little interference of the bulk polymer.

The discovery of surface-enhanced Raman scattering (SERS) is probably one of the most important developments in the area of surface science in the last decade.[7–9] Enhanced Raman spectra that are 10^5–10^6 as strong as normal Raman scattering were reported.[10] Boerio pointed out that SERS is good for the study of polymer–silver island interfaces since it enhances almost exclusively the first monolayer of molecules adjacent to the metal. That makes it possible to examine the interfacial region 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.[11]

Since the original SERS work involving pyridine adsorbed on silver electrodes and sols, most of the reported SERS spectra of polymers were recorded from electrochemical cells, aqueous environments, or in vacuum.[12–15] It was reported that spin-casting of a polymer solution onto Ag island films could be characterized by SERS.[11,16,17] However, we found that the SERS effect of vacuum-deposited Ag island film is not stable at elevated temperature and that copper substrate prepared by this method shows little SERS effect on the adsorbed species. This disadvantage limited the application of SERS as a general tool to analyze the polymer–metal interface, since many composites must be processed or be in use at elevated temperature. Recently, HNO_3-etched silver and copper foils for Raman study of adsorbates were prepared in this laboratory and in others.[18,19] This new sampling technique exhibits a strong SERS effect on surface adsorbates and better thermal stability.[20] In the present study, thin-layer coatings made by solution cast are investigated on the newly-developed Raman enhancing Ag and Cu substrates, in order to elucidate the adsorption and desorption of polymer chain and catalyzation, at the interface and to study the oxidation of metal under the polymer overlayer. For comparative purpose, IR diffuse reflectance spectro-

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scopic investigations from the rough surface were performed in the meantime to elucidate the character of the SERS method in polymer/metal systems. This work is part of a program intended to explore the relationships between the physical chemistry at the interface of the composites and the macroscopic properties, such as mechanical strength, corrosion inhibition, duration of the materials under various environments, etc.

Experimental Section

Preparation of Metal Substrates. Commercial copper foils of 0.025-mm thickness were immersed into 2 M nitric acid solution at 30 °C. After about 10 s, a number of bubbles were formed near the surface of copper. Vigorous agitation was then applied. After 2 min, a sponge-type surface with substantial roughness was created. In the case of etching silver foils, a 5–6 M HNO_3 was used and the etching time was prolonged to 5–10 min until the surface became milky. The roughness of the etched metal surface was about 10–100 nm as measured by electron microscopy.[18] After etching, the metal foils were thoroughly rinsed with water and dried in air. The etched metal foils were then ready for polymer sampling. SERS and XPS were used to exam the newly etched metal foils after they were washed with distilled water. The XPS and SERS spectra provided no evidence for the existence of nitrates on the silver foils. But the Raman lines in the region of 630–400 cm^{-1} of the SERS spectrum of the etched copper substrate gradually increased in intensity due to surface oxidation and the oxide bands reached a new constant after 2 h of exposure. As reported previously, the silver substrates prepared by the nitric acid etching method showed SERS sensitivity 1 order of magnitude higher than the vacuum deposit substrates.[18-20] For the purpose of comparison of the thermal stability, calcium fluoride roughened film overcoated with silver islands (Ag/CaF_2) was prepared for SERS substrate. Calcium fluoride and silver were vapor deposited onto an inch-square glass slide in a cryopumped vacuum system at pressures of approximately 10^{-6} Torr.

Sampling Methods. Poly(benzimidazole), poly(acrylonitrile), and benzotriazole were obtained from Aldrich without any purification before use. The azole compounds were dissolved in DMF to make solutions of concentration 0.03%. A SERS-active substrate and a smooth foil were immersed into a polymer solution at 50 °C for 5 min, and after withdrawal of the sample, the solvent was evaporated slowly. Film thickness on the smooth foil was estimated to be about 300–400 Å based on the weight of polymer film, the density of the sample, and the area of the metal surface.

Raman spectra were recorded with a SPEX-1403 Raman spectrometer. The incident laser excitation was 647.1 nm from a Kr^+ laser source with an output of 40-100 mW. A backscattering geometry in air was used for all samples. The foils were mounted onto a heating cell for the *in situ* Raman measurement at elevated temperature.

FT-IR Diffuse Reflectance Spectrum Measurements. Polymers were coated onto roughened silver foils which had been etched by the same process used to prepare SERS substrates, and the IR reflectance spectra were recorded with a Nicolet 170SX FT-IR spectrometer.

Results and Discussion

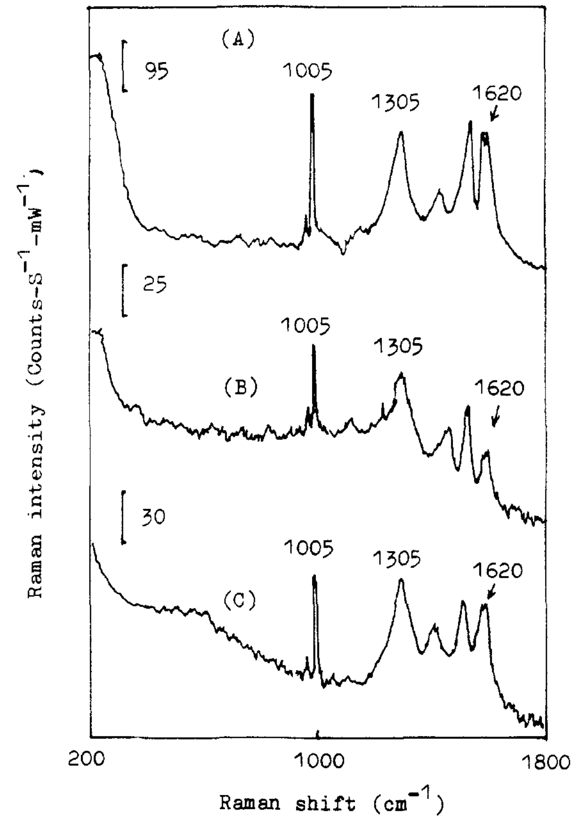

Figure 1. *In situ* SERS spectra of poly(benzimidazole) at 100 °C (A) on HNO_3-etched silver foil, (B) on vacuum-deposited Ag/CaF_2, and (C) on HNO_3-etched copper foil.

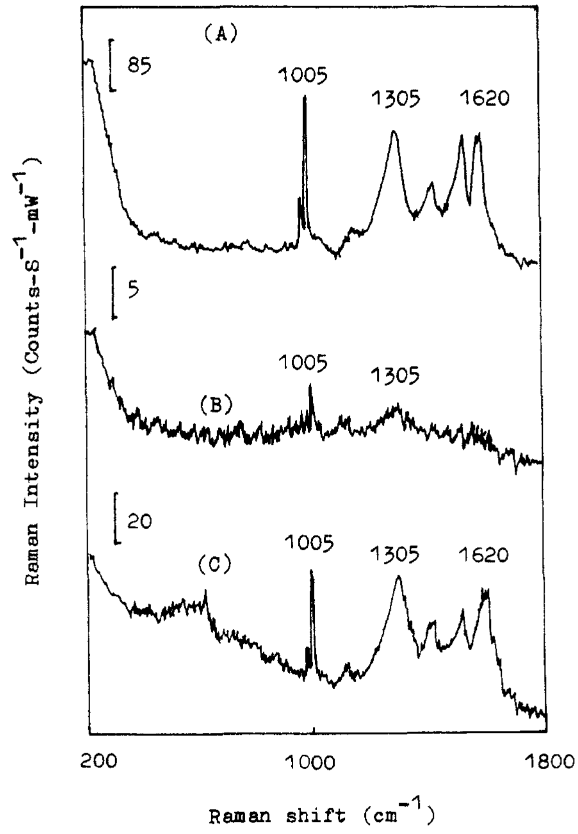

Figure 2. *In situ* SERS spectra of poly(benzimidazole) at 200 °C (A) on HNO_3-etched silver foil (B) on vacuum-deposited Ag/CaF_2, and (C) on HNO_3-etched copper foil.

1. Thermal Stability of SERS Substrates Covered with Polymer Film. Figures 1 and 2 compare the thermal stability of the surface enhancement factors of the nitric acid etched silver and copper foils and the vacuum deposited silver island film. The Raman band intensities are reported in counts S^{-1} mW^{-1} to account for the different laser power and integration times. In order to ensure that there is no laser-induced change in the SERS spectra, the foil was spun during the spectrum measurement. Spinning can also average the detecting adsorbate thickness. By comparison of the Raman line intensities and the signal-to-noise ratio of spectra at Figures 1 and 2, one can find out that the HNO_3-etched silver or copper foils could still produce good SERS spectra for poly(benzimidazole) at elevated temperature, while the vacuum-deposited silver island film lost most of its enhancement. The order of Raman enhancement factor at elevated temperature can

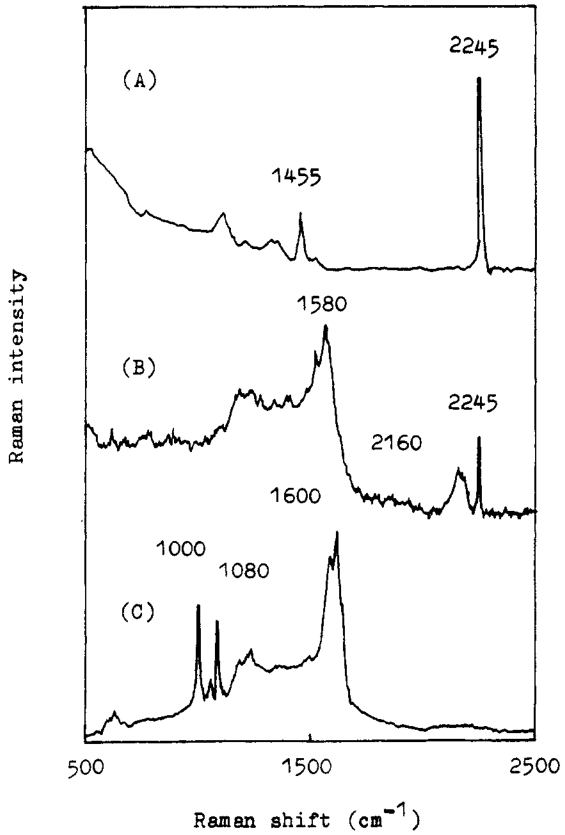

Figure 3. (A) Normal Raman spectra of poly(acrylonitrile) (PAN) on smooth silver foil. (B) SERS spectrum of PAN on rough silver foil. The film was prepared by fast evaporation of the solvent. (C) SERS spectrum of PAN on rough silver foil. The film was prepared by slow evaporation of the solvent.

be arranged as HNO_3-etched Ag > HNO_3-etched Cu > Ag/CaF_2. The good enhancement factor and high stability of the HNO_3-etched metal foils indicate that SERS has a good potential for use as an *in situ* analytical tool for the study of interfacial structure at elevated temperature.

2. Observation of Adsorption and Surface-Catalyzed Reaction of Polyacrylonitrile on Silver. The interaction of the cyanide side group of poly(acrylonitrile) with metal surfaces is important from both theoretical and practical (catalytic) points of view. However, only recently detailed studies of CN surface chemistry have appeared.[22-27] In the IR spectrum, The C≡N stretching vibration of chemisorbed sample on Cu/SiO_2 was appreciably shifted to lower frequency regions in comparison with that in liquid state, suggestive of a component coordination of the cyano group in acrylonitrile with the Cu surface site.[28] Our SERS studies of the polymer on silver foil provided information concerning adsorption-induced cyclization under room temperature. Figure 3A shows a normal Raman spectrum of poly(acrylonitrile) coatings of about 3000 nm thickness on a smooth silver foil by "spin-casting". Figure 3B and C shows SERS spectra recorded from poly(acrylonitrile) coatings on HNO_3 etched surfaces where the samples were prepared by spreading 20 μL of a 0.3% solution on 2 cm^2 foils followed by fast and slow evaporation of the solvent, respectively. The band at 2245 cm^{-1} in Figure 3B, having the same position and band width as that in Figure 3A, can be assigned to freely dangling CN groups of poly(acrylonitrile). A broad band centered at 2160 cm^{-1} of Figure 3B is also attributed to the C≡N stretching mode. The substantial shift (85 cm^{-1}) and band broadening upon adsorption indicate the direct interaction (side-on coordination) between the cyano groups and the silver surface atoms. Here, the presence of side-on coordination of CN groups of poly(acrylonitrile) on Ag corroborates Kim's proposal that this fashion is favored when the CN group is not conjugated with an unsaturated group.[29] A similar phenomenon has been observed in the case of aliphatic dinitriles adsorbed on Cu surfaces in SERS studies.[30] Therefore, the 2160 cm^{-1} band implies that the coordination of Ag surface atoms to the cyano groups brings about back-donation of electrons from the metal to the CN antibonding orbitals, therefore reducing the CN triple-bond order. Such a favorable adsorption on the roughened surface weakened the CN triple bond and facilitated the adsorption-catalyzed cyclization under mild conditions. The SERS spectrum of Figure 3C is typical of aromatic ring vibrations and correlates well with the FTIR spectra of degraded PAN.[31] The bands at 1600 and 1580 cm^{-1} can be assigned to —(C=C)— or —(C=N)— conjugation ring stretching vibration, implying that the adsorbed PAN has been turned into a fused ring structure at the interfacial region. This is consistent with the signal intensity of the 2245-cm^{-1} band. The bands at 1080 and 1000 cm^{-1} can be ascribed to in-plane ring C–H deformation frequencies. Because of their strong intensity, it is reasonable to propose that the aromatic ring structure is sticking up to the metal surface via its N atoms or at least the fused rings are tilted off the surface as long as the electromagnetic theory on the SERS selection rule is applied.[32]

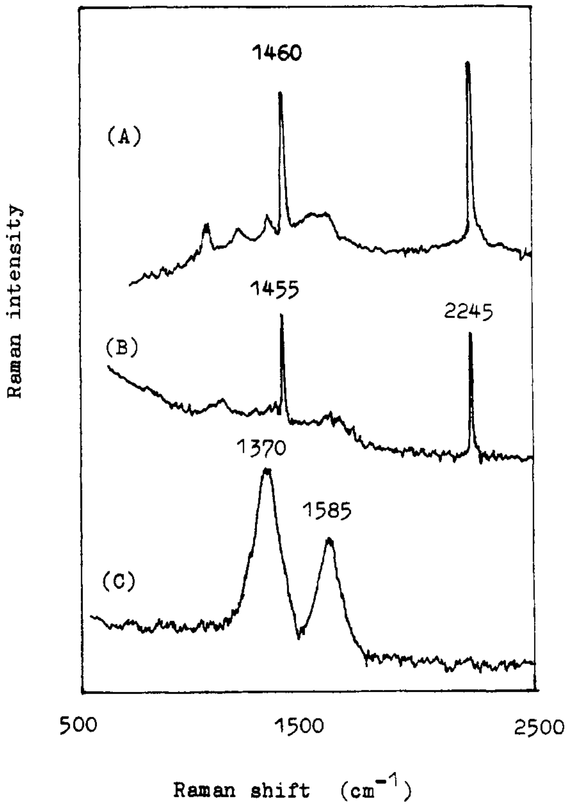

Figure 4. (A) IR diffuse reflectance spectrum of PAN on rough silver foil after heating at 80 °C for 24 h. (B) Normal Raman spectrum of PAN on smooth silver after heating at 80 °C for 24 h. (C) SERS spectrum of PAN on rough silver foil after heating at 80 °C for 6 h.

Figure 4C shows the SERS spectrum of the adsorbed polymer sample on rough Ag after heating at 80 °C for 6 h. The spectrum reveals that PAN at the interfacial region has further been converted to a graphite-like structure on heating. This spectrum is exactly identical to the reported SERS spectra obtained by evaporating silver on carbon fiber or graphite fiber as well as the ordinary Raman spectra of graphite or PAN-based graphite fiber.[33,34] In contrast, the diffuse reflectance IR spectrum recorded from the

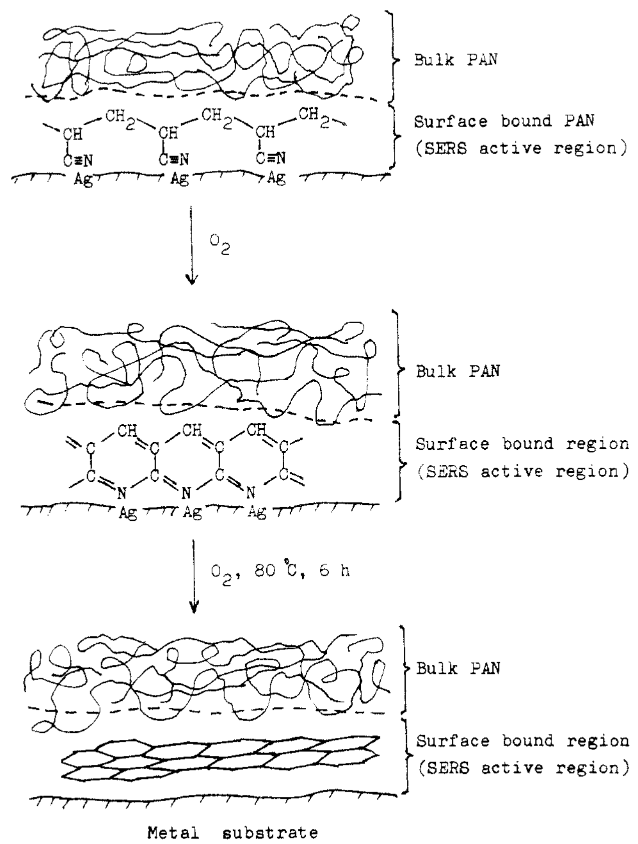

Figure 5. Schematic diagram of the structural change at the interfacial region of PAN/Ag: (A) initial desorption, (B) cyclization of PAN, and (C) graphitization of PAN.

same sample and the normal Raman spectrum shown in Figure 4A and 4B indicate that PAN bulk film underwent only partial cyclization even after it had been heated for 24 h, with little graphitization.

Full graphitization of PAN usually needs a temperature of about 2000 °C. On Ni, Al, and Cu surfaces, dehydrogenation did not start until 300 °C. The extremely low cyclization and carbonization temperature at 80 °C implies several responsible mechanisms. The catalytic action of the metal is, of course, one possible explanation for the observed lowering of temperature. A schematic diagram for the structural changes at the interfacial region is proposed in Figure 5, based on the SERS, IR, and the normal Raman spectra.

The diffuse reflectance IR and normal Raman spectra reveal that physisorbed PAN on silver only partially cyclized after heating, as shown in Figure 5A and 5B. Signals from the microstructure at the very interfacial region of PAN/Ag systems were greatly interfered with by those from the physisorbed PAN. The above reactions occur exclusively at the SERS-active region and are undetected by IR and normal Raman spectroscopy, indicating that SERS spectra recorded from HNO_3-roughened silver is highly informative in that the interfacial thermal reactions can be revealed with much less interference from the polymer bulk.

3. Observation of Oxidation of Copper under the Polymer Film Overlayer. The thermal oxidation of copper covered with polymeric films can be monitored with SERS. Benzotriazole is reported to react with the copper surface forming a polymeric films which is supposed to prevent the surface from further oxidation.[35] No observable signals of copper oxides in the region of 630–400 cm^{-1} can be detected in the initial spectrum of benzotriazole-treated copper. But after exposure at 200 °C for a few hours, the oxide bands appeared quickly, as shown on the left side of Figure 6. This allows us to utilize polymer to overcome this weakness so long as its degradation does not commence under the applied temperature. Poly(benzimidazole) is well known for its heat resistance. However, the appearance of oxide bonds in the Cu SERS spectrum of the poly(benzimidazole)-covered surface implies that this polymer does not possess substantial resistance to oxygen permeation, as illustrated by the spectra on the right side of Figure 6. Oxygen permeability could be reduced by decreasing the chain mobility and by increasing the density of molecular packing. Rigid as the poly(benzimidazole) chain is, it cannot suppress oxidation even at room temperature. This may be due to the fact that there are pinholes on the metal surface that are not covered by the polymer. Upon heating to 200 °C for 8 h, the oxide band intensity became more prominent as shown on the right side of Figure 6, indicating the acceleration of surface oxidation. It is noticeable that the SERS effect remains so strong at this temperature that Raman signals originating from adsorbed poly(benzimidazole) are still of high quality. Preliminary work on nitric acid etched silver foils showed that this kind of SERS-active substrates possesses satisfactory thermal stability under relatively high temperatures; SERS on nitric acid etched metal foils seems to be a very promising technique for mechanistic studies of the reactions. Figure 7 illustrates in situ SERS spectra of poly(benzimidazole) and benzotriazole coadsorbed from a solution of their mixture. The oxide film formation did not occur even when the treated copper had been heated to 200 °C for 20 h. This property is very important since copper surfaces treated with either poly(benzimidazole) or benzotriazole alone oxidized in a few hours at 200 °C, as illustrated in Figure 6. We therefore conclude that the surface loci left by poly(benzimidazole) have been filled with benzotriazole. This corrosion inhibition effect on the copper surface of coadsorbed poly(benzimidazole) and benzotriazole is synergetic and may be explained by the physicochemical mechanism of corrosion protection by organic coatings.[36] The physicochemical mechanism consists of blocking diffusion of corrosive agents, like water and oxygen, and of corrosion stimulants. This barrier action of organic coatings may be enhanced significantly by fillers, pigments, or extenders which greatly increase the length of diffusional pathways through the cross section of the coating films. Our previous work found that benzotriazole could react with metallic

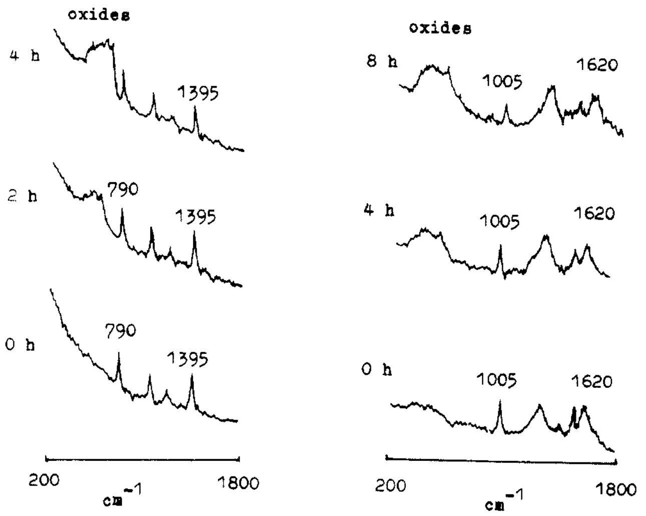

Figure 6. *In situ* SERS studies of oxidation of copper at 200 °C under film overlayers. Left: the foil was pretreated with benzotriazole. Right: the foil was pretreated with poly(benzimidazole). (Heating time is adjacent to each spectrum.)

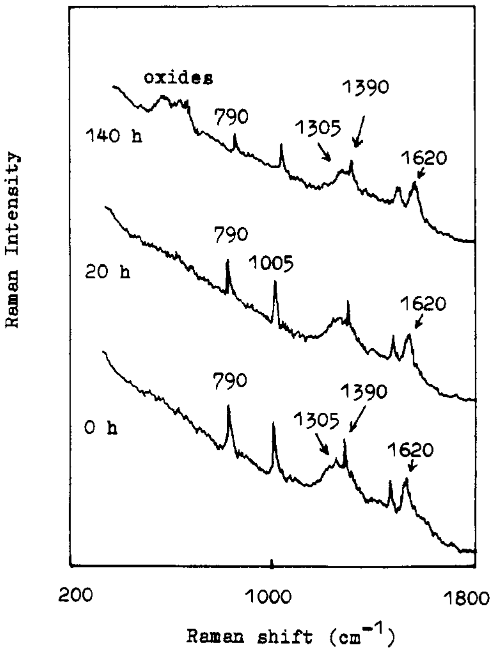

Figure 7. *In situ* SERS studies of oxidation of copper foil at 200 °C under poly(benzimidazole)–benzotriazole overlayers. (Heating time is adjacent to each spectrum.)

copper under mild conditions forming cuprous benzotriazolate.[37] We now propose that this surface reaction product filled up the pinholes left by poly(benzimidazole) and acted as a barrier to greatly retard the oxidation. This point was ascertained by a prolonged heating test in which oxide bands were ultimately observable after heating at 200 °C for 140 h, as shown in Figure 7. In order to confirm this proposal, copper was coated with poly(benzimidazole) first from its DMF solution. Before drying, the coated specimen was immersed into a benzotriazole–ethanol solution at 60 °C for 10 min. Since poly(benzimidazole) does not dissolve in ethanol, the film remained on the metal surface when it was immersed in ethanol solution, while benzotriazole could diffuse into the film. As it makes contact with the metal surface, benzotriazole reacts with copper or copper oxide at 60 °C to form copper benzotriazolate, filling up the pinholes left by poly(benzimidazole).[37] SERS studies for such a specimen indicated that it shows a anticorrosion effect similar to the sample treated with mixture solution. This synergetic effect could be also obtained from a two-component anticorrosion system of poly(vinylimidazole) and 2-mercaptobenzimidazole.

Conclusions

We believe that the present results provide a novel and potentially important demonstration of the use of metal foils etched with HNO_3 as a means of generating *in situ* SERS spectra for polymer/metal interface at room and elevated temperatures or after heat treatment. Polymer species adsorbed at the very interface show critical adsorption, catalyzation, and oxidation which cannot be revealed by normal Raman scattering under the same conditions. We therefore anticipate that the principles outlined here might be transposed to the *in situ* studies of physical chemistry of polymer/metal systems at elevated temperature or after the heating process.

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