Surface-enhanced Raman scattering study of polymer on metal: 1. A new sampling technique using HNO_3 etched metals as the substrates

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Silver and copper foils for Raman study of the interfacial structure of polymer–metal composites were prepared by chemical etching with HNO_3. These foils were found to exhibit a strong surface-enhanced Raman scattering (SERS) effect on polymer samples. Three different sample doping methods were compared. By slowly evaporating the solvent, polymer chains deposited on metal to form an ordered arrangement on the surface, resulting in an excellent SERS effect. The HNO_3-etched metal foils show a better enhancement factor and higher thermal stability than vacuum-deposited silver island film.

(Keywords: metal; composite; interface; surface-enhanced Raman scattering; surface)

INTRODUCTION

Polymer–metal composites are of great interest both in science and in technology. An understanding of the structure and role of composite interfaces is critical to control chemical and physical properties of the composites. There are a number of instrumental analysis techniques which can be used to investigate thin films of polymer on metal[1]. 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. It is known that a monolayer of polystyrene, about 4 nm thick forms on gold in the presence of non-polar solvent[2]. In practice, it is difficult to cast synthetic polymers as a uniform monolayer film on to metals. In the manufacture of coatings on metal, a 'thin layer' may mean a thickness of hundreds of nanometres. On the other hand, polymer film on metal can be studied with Raman or infra-red (i.r.) spectroscopy. However, it provides information mainly from the bulk polymer; the composite interfacial region only involves a few nanometres near the metal surface[3]. It is therefore necessary to develop new techniques to investigate the interfacial structure without the 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 few years[4–6]. SERS is ideal for the study of polymer–metal composites since it enhances almost exclusively the first monolayer of molecules adjacent to the surface. 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[7]. However, most SERS studies have been performed in electrochemical cells, aqueous environments, or in a vacuum[8]. Proteins adsorbed on electrodes have also been investigated by SERS[9]. While the high information content of Raman signals from adsorbed species on metal has long been recognized, practical applications have so far been impeded by poor sensitivity. Raman measurements for composites pose greater difficulties than test systems in fundamental SERS studies. First, most synthetic polymers do not dissolve in water. Secondly, the polymer chain is bonded to the surface only at a few points along the chain with the remainder coiled about surface voids. 'Monolayer' coverage of polymer probably provides only 'sub-monolayer' active sites for SERS effect. Thirdly, vacuum-deposited silver island film, which was reported to show a SERS effect on polystyrene, is not stable at high temperatures or for long periods of storage, as will be discussed. This instability of the vacuum-deposited silver island substrate limits its practical application in SERS study of composite interfaces. In order to develop SERS into a general analytical tool for polymer–metal composite study, it is necessary to devise a more routine sampling technique which can yield the SERS effect under various environments. In this paper we describe a very effective and easily prepared sampling technique for obtaining the SERS effect on a composite interface. By slowly evaporating solvent from a very dilute polymer solution spread on HNO_3-etched metal foils, a well ordered polymer film can be formed on the surface, resulting in a good SERS effect. This work is part of a programme of surface chemistry intended to explore the relationships between the microscopic structure of the interface in polymer–metal composites and the macroscopic properties, such as mechanical strength, corrosion at high temperatures or under radiation, etc.

EXPERIMENTAL

Preparation of metal substrates

Commercial silver foil of 0.025 mm thickness was immersed in a freshly prepared 3.5 M HNO_3 solution at

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30°C. Vigorous agitation was applied. After about 2–3 min, a sponge-like surface with much roughness was formed. After etching, the silver foil was thoroughly rinsed with water and dried with nitrogen. The etched silver foil was ready for polymer sample doping. In the case of copper foil, the same procedure was performed except that the concentration of etching solution was 2 M HNO_3. Two other surface morphologies were used for the purpose of comparison: smooth silver foil and calcium fluoride overcoated with silver island film. CaF_2 and Ag were deposited by evaporation onto a glass slide with a base pressure of 0.267 mPa.

Sample doping methods

Poly(4-vinyl pyridine) and polybenzimidazole were obtained from Aldrich, and were dissolved in DMF to make solutions with concentrations of 0.04%, 0.08% and 0.12% respectively. Three sample doping methods were used in this work. In the first method, solution spreading, 20 μl of solution was spread onto a 2 cm foil and placed into a container to evaporate the solvent slowly. The thickness of polymer film is about 40 nm. The second method involves dipping a foil into a solution at 60°C for 5 min, and then evaporating the solvent slowly after withdrawing the foil from solution. The third method is solution casting in a vacuum system. In the first and second methods, the solvent was evaporated for 8 h by adjusting the vapour pressure of the solvent in the evaporating cell, while in the third method the solvent was evaporated quickly, in a few minutes. SERS spectra recorded from samples prepared by different methods were compared.

Raman spectra measurements

Raman spectra were recorded with a SPEX-1403 Raman spectrometer. The incident laser excitation was 647.1 nm laser from a Kr^+ laser source, with output of 20–200 mW. A back scattering geometry in air was used for all samples.

RESULTS AND DISCUSSION

Figure 1 illustrates SERS spectra of poly(4-vinyl pyridine) on HNO_3-etched silver foils prepared from DMF solution of concentration 0.04% using three different sampling methods. The thickness of polymer on silver is calculated to be about 40 nm based on the amount of solution applied, the concentration and the area of silver foil. Poly(4-vinyl pyridine) was used as a probe macromolecule to study the surface-enhanced phenomenon of Raman scattering. This polymer was chosen because the SERS study of pyridine has been investigated extensively, and the SERS spectrum of poly(4-vinyl pyridine) on a silver electrode from aqueous solution has been reported recently[10]. Thus it is convenient to make a comparison of different sampling techniques. Spin-casting the polymer onto the foil by fast evaporation of the solvent did not yield significant SERS effect, as shown in spectrum A (*Figure 1*). Normal Raman scattering from a smooth foil coated with 40 nm of the polymer could not give Raman bands either. Increasing the thickness of the polymer film was found to create strong fluorescence. However, spectra B and C show obvious SERS bands with good signal-to-noise ratio. We propose that slow evaporation of the solvent may allow polymer chains sufficient time to arrange themselves on the surface so that more points along the chains are bonded to the metal.

Another interesting feature of *Figure 1* is that there are remarkable differences between SERS spectra B and C, which were recorded from the same polymer solution by different sampling techniques. The spectral differences indicate surface geometry changes of polymer chains. A successful basis for analysing SERS spectra with regard to orientation of adsorbate is in the form of 'surface selection rules' proposed by Moskovits and co-workers[11–14] and others[15–17]. These rules are based on the electromagnetic theory of SERS intensity which indicates that, via resonance interaction with surface plasmons of the metal, incident light increases the electromagnetic field at the surface of small metallic particles, which in turn amplifies both the Raman excitation intensity and the scattered intensity. Since the local fields are highest normal to the surface, normal modes of the adsorbed molecule involving changes in molecular polarizability with a component normal to the surface are subject to the greatest enhancement. This same type of analysis has been succesfully applied by others[18–20]. The SERS spectrum B of *Figure 1* shows an intensive band at 500 cm^{-1}, which is almost absent in spectrum C, while spectrum C shows a strong band at 1600 cm^{-1}, which is Raman-inactive in spectrum B. In the Raman spectrum of 4-methyl pyridine, the band near 500 cm^{-1} is due to out-of-plane ring deformation, while the band at 1600 cm^{-1} is ring stretching vibration[21,22]. Based on the surface selection rules, we propose that in the sample of spectrum B (*Figure 1*) the ring of pyridine is lying down flat on the surface since the out-of-plane vibration is enhanced and the stretching band is absent, and that in the sample of spectrum C (*Figure 1*) the ring is standing up on the surface because the stretching

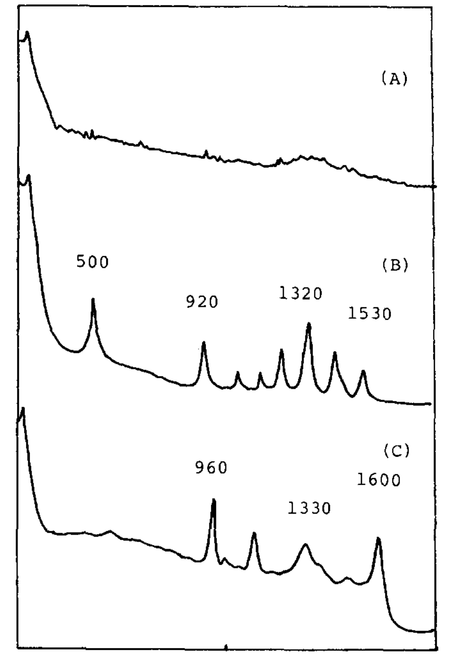

Figure 1 SERS spectra of poly(4-vinyl pyridine) on HNO_3-etched Ag foils applied by different sampling techniques: A, spin-casting; B, spreading the solution onto Ag and evaporating the solvent slowly; C, dipping Ag into a hot polymer solution and evaporating the solvent slowly after withdrawing the foil

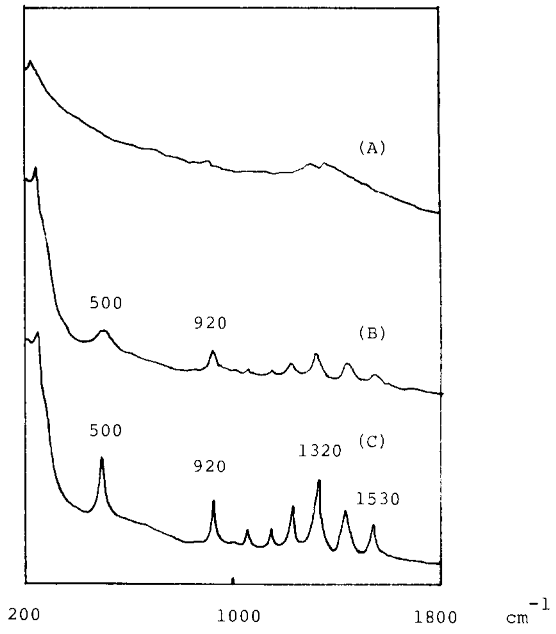

Figure 2 SERS spectra of poly(4-vinyl pyridine) on HNO_3-etched Ag foil applied from DMF solutions of different concentration: A, 0.12%; B, 0.08%; C, 0.04%

vibration is enhanced and the out-of-plane vibration is almost absent. Comparison of the SERS spectra in *Figure 1* clearly indicates the importance of the sampling method on the SERS effect. Spin-casting of polymer solution on silver foil gave little SERS effect and probably a random orientation of the polymer chains on the surface. Slow evaporation of the solvent from the solution spread on the foil produced a flat orientation of pyridine side groups of the polymer on the surface, resulting in a good SERS effect. Dipping the film in a warm solution produced a perpendicular orientation of pyridine side groups on the surface as well as a good SERS effect. Although the SERS spectra B and C of *Figure 1* show the same quality as one measured on an electrode[10], the present spectra contain richer information about the surface geometry.

Figure 2 shows a 'dilution effect' on SERS of poly(4-vinyl pyridine) on metal. A solution of concentration 0.12% was spread on Ag foil. After evaporation the SERS spectrum was taken and is shown in *Figure 2A*. The spectrum gives few bands. However, as the solution was diluted to 0.04%, and then coated onto the Ag foil by the same method, an excellent SERS spectrum was obtained, as shown in *Figure 2C*. Other polymers, such as polybenzimidazole, polyhistidine, polyvinylimidazole, polyacrylonitrile, etc., were found to show a similar dilution effect on the SERS phenomenon. It should be kept in mind that more than one mechanism may be responsible for the enhancement phenomenon and that the observed enhancement factors resulted from a combination of several contributions. One may not exclude the possibility that surface interactions, e.g. formation of charge transfer states of the metal–adsorbated molecule complex, are effective at close range[23]. As the solvent was removed, the polymer coils collapsed against the surface of the metal. If the solution was thicker, polymer chains would have more difficulty arranging themselves, resulting in a more random orientation on the surface. When the solution was very dilute (less than 0.05%), polymer chains would have more chance to interact with the metal and arrange themselves by thermodynamic movement, if the solvent was evaporated slowly, resulting in more contact points along the chain bonded to the surface and thus a better SERS spectrum.

Figures 1 and *2* show that excellent SERS spectra could be obtained by proper sample doping methods on a HNO_3-roughened silver foil. Vacuum-deposited silver island film has been recognized as an effective substrate for SERS study. In our previous study, we found that HNO_3-roughened silver foil shows an even better enhancement factor and thermal stability[24]. *Figure 3* shows two SERS spectra of poly(4-vinyl pyridine) applied on vacuum-deposited Ag/CaF_2 substrate using two doping methods. Both spectra in *Figure 3* show less enhancement factor than those illustrated in *Figures 1* and *2*.

Figures 4 and *5* compare the thermal stability of the surface enhancement factors. After heating, the HNO_3-

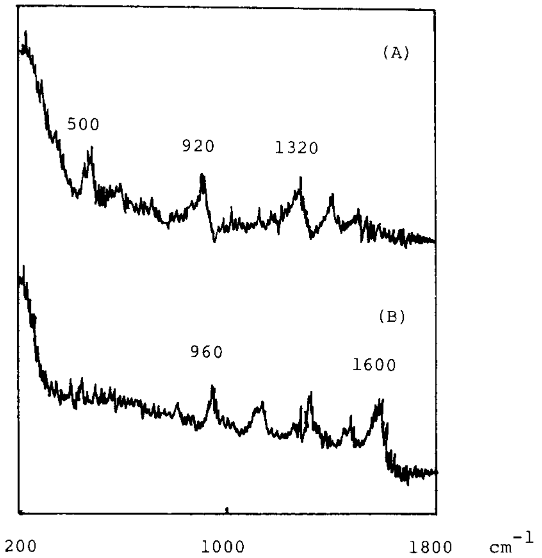

Figure 3 SERS spectra of poly(4-vinyl pyridine) on vacuum-deposited Ag/CaF_2 substrate: A, by spreading the solution on the substrate; B, by dipping the substrate into the solution

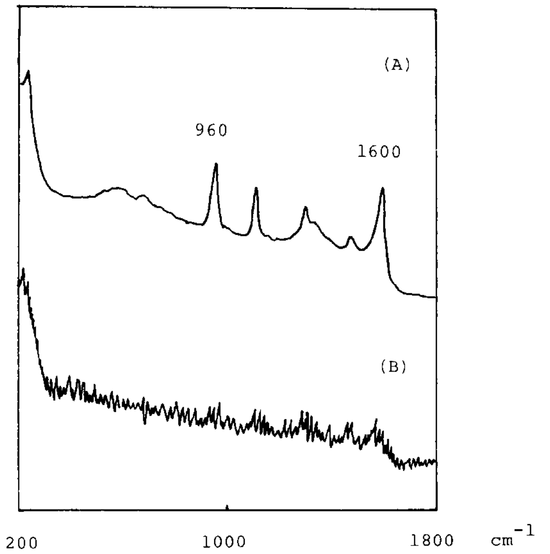

Figure 4 SERS spectra of poly(4-vinyl pyridine) after heating at 130°C for 12 h: A, on HNO_3-etched Ag foil; B, on a vacuum-deposited Ag/CaF_2 substrate

Figure 5 SERS spectra of polybenzimidazole on metals after heating at 130°C for 8 h: A, on HNO_3-roughened copper foil; B, on a vacuum-deposited Ag/CaF_2 substrate

roughened silver or copper foil could still produce good SERS spectra for poly(4-vinyl pyridine) or polybenzimidazole, while the vacuum-deposited silver island film lost almost all of its enhancement. The good enhancement factor and high stability of the HNO_3-etched metal foils indicate that SERS has a good potential for use as a general analytical tool for the study of interfacial structure under various conditions.

CONCLUSION

We have demonstrated that HNO_3-etched silver and copper foils show excellent SERS effect on polymers. SERS study indicates that spreading a dilute polymer solution onto the foil and then slowly evaporating the solvent produced a flat orientation of poly(4-vinyl pyridine) on metal, and dipping the foil in a warm solution produced a perpendicular orientation of this polymer on the surface. The HNO_3-etched silver and copper foils show a better enhancement factor and higher thermal stability than the vacuum-deposited silver island film.

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