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Surface-Enhanced Raman Scattering of Indigo on a Stable Silver Foil Substrate Prepared by a Nitric Acid Etching Method

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A chemical etching method with HNO_3-prepared silver foils was used for a Raman study. These foils were found to exhibit a strong SERS effect. An SEM image clearly shows that spherical particles exist in an oxidized state, with diameters in the range of 200 nm for oxidized silver. SERS spectrum of Indigo was taken to illustrate the usefulness of this sample preparation technique. HNO_3-roughened silver foils seemed to be more easily prepared substrate systems for SERS studies. There is a high potential that this technique can be used in studies concerning the adsorption, molecular orientation, surface reaction, and surface catalysis at room or elevated temperatures.

When the technique now known as surface-enhanced Raman scattering (SERS) spectroscopy was discovered in 1974, most of the research reported in the following years was devoted to understanding the phenomenon, itself.[1–5] Only recently has there been intense interest in developing of a practically useful sample system for the identification and characterization of adsorbed species. This tendency seems to reveal that it is worth starting analytical or catalytic studies on SERS active surfaces, even without a final understanding of the SERS process.

Practical forms of attractive silver substrates on which the SERS effect is observed most intensely include colloidal silver, silver island films, silver films deposited on quartz or Teflon particles,[6–8] and chemically reduced silver films on glass slides.[9] In each case, the metal can be prepared independently of the sample. The sample can be mixed with a suspension of colloid or coated particles, or spotted on a plate containing silver island films. Colloidal silver has been the most widely employed form of silver, possibly because its preparation requires no specialized apparatus. Since some chemicals do not dissolve in water and many reactions do not occur in aqueous media, this sampling technique is apparently inadequate to adsorption or reaction mechanism studies in other solvent media. Additionally, silver sols are so prone to alter the surface morphological structure that useful SERS spectra can be quenched. In 1984, Wokaun et al. pointed out that pronounced SERS signals could be easily acquired by etching copper foils with concentrated nitric acid.[10] They have demonstrated that the chemical etching method shows its potential to be developed into an analytical tool for routinely preparable substrate system for SERS studies. As an extension of their studies, SERS results are presented in this work for several adsorbates on silver foils.

The reason for using chemically etched silver foils as substrates can be pointed out. First, they are easily prepared by chemical techniques, which are simpler than the generation of properly roughened electrodes or electrochemically deposited surfaces, and even simpler than the generation of metal colloidal particles with a specific size range. Secondly, the costly instrumentation used to produce and characterize vacuum-deposited metal island film is not needed. Thirdly, because a silver foil may suppress undesirable fluorescence, sample purification is sometimes unnecessary. Finally, silver foils provide the possibility of rapid heat conduction under laser irradiation, therefore minimizing sample decomposition and surface morphological instability.

Norrod et al compared five different kinds of SERS substrates for ease of preparation, sensitivity, limit of detection (LOD), reproducibility, and stability.[11] Except for the Ag colloid method, vapor-deposited Ag films, electrochemically roughened Ag electrodes, nitric acid-etched Ag foils, Tollens-produced Ag films, and photo-reduced Ag films on TiO_2 were examined. Of these substrates, vapor-deposited annealed Ag films exhibited the greatest sensitivity and lowest LOD. The easiest substrate to prepare, nitric acid-etched Ag foils, exhibited a good reproducibility and the least-expensive rout to SERS activity. Wu et al prepared for etching a Ag foil by immersing it into a vigorously agitated 3.5 M HNO_3 solution for a few minutes,[12–14] while Perez et al prepared it with dilute HNO_3 (8 : 20 v/v with water) for 1–5 minutes.[15] We prepared for etching a Ag foil much more rapidly than by the above methods. It is now undergoing experiments.

Indigo dyes have long been known and are still used today for several applications. Compared with other mesomeric systems of similar size, light absorption of the indigo occurs at remarkably long wavelengths. The deep color of indigo dye is ascribed to resonance hybrid structures of the carbonyl and zwitter-ionic forms. Numerous groups have investigated the properties of these species.

Schrader[16] reported on the FT-Raman spectrum and a normal coordinate analysis for the solid phase of Indigo. Previous papers reported[17–18] on a Ag foil surface being used to studying molecules containing a sulfur atom or long-chain fatty acids. Those Raman spectra have much noise and fluorescence. In this paper, the SERS spectrum of Indigo containing no sulfur atom is reported. We discuss the nature and orientation of the species adsorbed on silver foil. Especially, the normal Raman spectrum of Indigo in sol could not show a signal.

Experimental

An oxidized silver foil was prepared by the following method. A commercial silver foil 1.0 mm in thickness was scratched by sand paper (C-300) (Type I). The scratched silver foil was heated for 2 s by an alcohol lamp and then immersed in a freshly prepared 3% HNO_3 solution at 30 °C for 2 s (Type II), 5 s (Type III), and 10 s (Type IV), respectively. A number of bubbles were formed on the silver surface in the solution. A sponge-type surface with a high degree of roughness was created in about 10 s. The silver foil was etched and then thoroughly rinsed with water. A silver foil roughened with HNO_3 was dipped into an Indigo solution (0.1 mM) for 10 s. The solvent was then evaporated in air.

The FT-Raman spectrum was measured with an IFS-66 spectrometer (Bruker) connected with a Raman module (Bruker, FRA-106). Radiation of 1064 nm from a Nd:YAG laser was used for excitation with a laser power of about 100 mW at the sample. The sample was deposited in a capillary tube. The scattered light was collected at a 180° back-scattering geometry. The SERS spectrum was obtained with a SPEX 1403 scanning double monochromator, an RCA C31034 PMT detector and SPEX DM 3000 software. A Coherent Innova 90-5 argon ion laser ($\lambda = 514.5$ nm) was used as the excitation source. The laser power and the spectral slit widths were 100 mW and 400 μm, respectively. The scattered light was collected at a 90° geometry. All spectra were obtained at room temperature (18 °C). A scanning electron micrograph (SEM) was obtained with a Hitachi H-7100.

Results and Discussion

Figure 1 shows the surface morphology of Ag foils scratched by sand paper (Type I) (a), oxidized by nitric acid for 2 s (Type II) (b), 5 s (Type III) (c), and 10 s (Type IV) (d), respectively. R. P. van Duyne et al.[4] reported that silver nitrate sol reduced with sodium tetrahydroborate consisted roughly spherical of silver particles, each of which was about 200 Å in diameter and with rather narrow size distribution. However, in the HNO_3 -etched silver foil, Type I, Type II, Type III, and Type IV of silver foil taken a stripe, a pillar shape, roughened spherical shape, and smoothened spherical shape with average diameters of 150–200 nm, respectively.

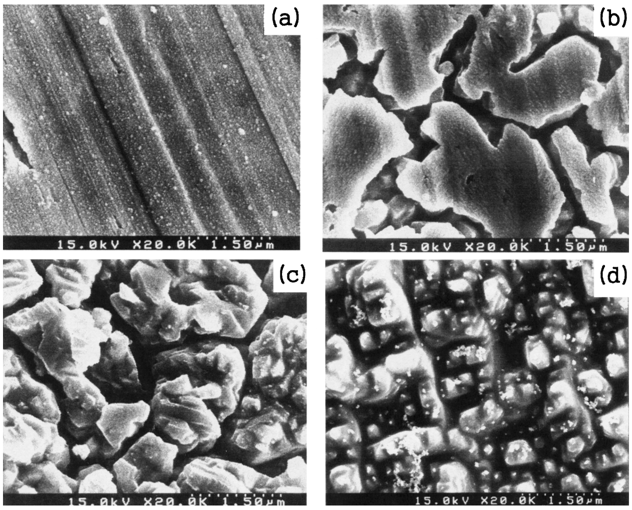

Fig. 1. SEM of type I (a), type II (b), type III (c) and type IV (d) sliver foil.

The characteristics of the SERS spectrum in a published paper[16,17] about SERS at a foil had served as a broad base line, a low resolution, and a low intensity, and target molecule contains a sulfur atom. However the SERS spectrum in this paper had a high resolution, low noise at 0.1 mM, and a highly enhanced intensity. Also the target molecule did not contain sulfur atoms.

Figure 2 illustrates the SERS spectra of various oxidized silver foils. We should point out that the SERS spectra show broad bands in the 500 to 700 cm^{-1} region, which are due to the symmetrically stretched silver oxide. It appears that only a part of the surface was covered with indigo, and the other part was oxides by nitric acid. Also, the SERS spectra show bands at 1400 and 1600 cm^{-1}, which are stretched C–C and C=C of amorphous carbon, respectively. With progressing oxidation, those bands strengthen. If adsorbates such as Indigo could cover the silver surface, the enhancement would be high. In the SERS spectrum of the type III, the Raman signal is stronger and sharper than that of other types, and this spectrum has a baseline. The surface morphology of Type III had a good adsorption site of target molecules. SERS spectrum of Type IV shows only three remaining bands and the surface were covered with silver oxides.

Figure 3 shows the SERS spectrum of type III and the FT-Raman spectrum of Indigo. Table 1 shows the assignments[16] and the relative intensity. In the FT-Raman spectra, the six C–C stretching vibrations of the benzene rings give rise to three bands that can be assigned to 1625, 1475, and 1443 cm^{-1}. Vi-

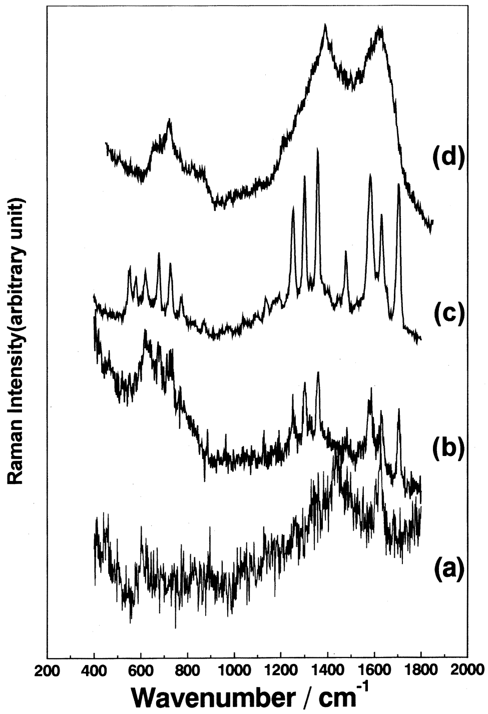

Fig. 2. SERS spectrum of Indigo on type I (a), type II (b), type III (c) and type IV (d) sliver foil at 0.1 mM.

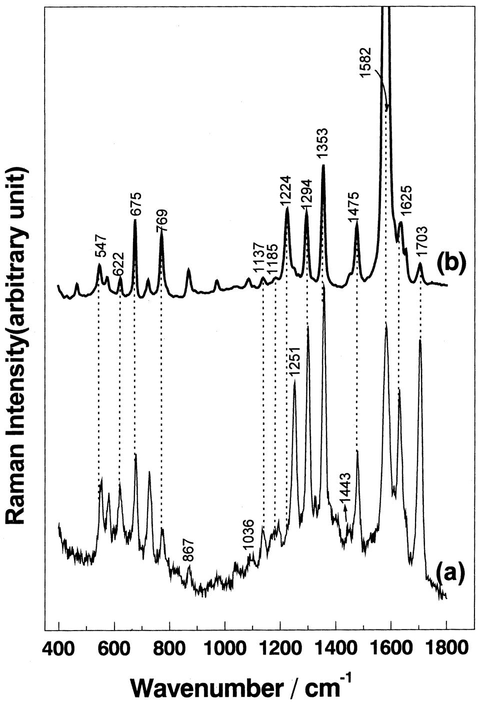

Fig. 3. SERS spectrum on type III (a) and FT-Raman spectrum in solid (b) of indigo.

Table 1. Peak Assignment and Relative Intensity (RI) Factor of Raman Spectra of Indigo

Peak Position	R I (I/I_{1475})		Assignment[a)]
	FT-Raman	SERS	
468		0.34	Bg, γC–C
547	0.20	0.34	Ag, δC=C–CO–C
574		0.72	Ag, δC=O, δC–H, δC–NH–C
622	0.27	0.77	Bg, γN–H
675	1.08	0.98	Ag, δC–C
722	0.25	0.87	
769	0.88	0.48	Ag, δC–H, δC–N–C
867	0.38	0.23	Ag, νC–N
970	0.24	0.16	Bg, γC–H
1036		0.26	Bu, δC–H
1085	0.26	0.32	Bg, γC–H
1137		0.47	Ag, δC–C
1185		0.52	νC–C ring
1251	1.21	1.46	Ag, δC–H, δC=O
1294	1.15	1.84	Bu, δC–C
1353	1.83	2.10	Ag, δN–H, δC–H
1443		0.50	Bu, νC–C, δC–H
1475	1.00	1.00	Bu, νC–C, δC–H
1582	8.13	0.45	Ag, νC=C, νC=O
1625	1.03	1.41	Ag, νC=C, δC–H
1703	0.46	1.74	Ag, νC=C, νC=C

a) assigned on the basis of E. Tatsch and B. Schrader, *J. Raman Spectrosc.*, **1995**, 26, 467.

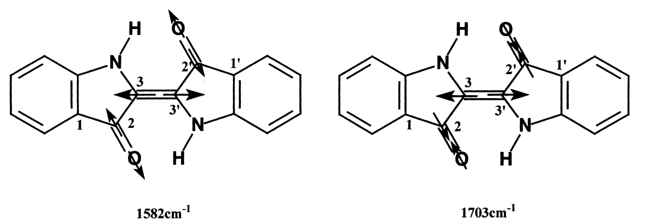

Fig. 4. Typical vibrations of the C=O/C=C system in indigo.

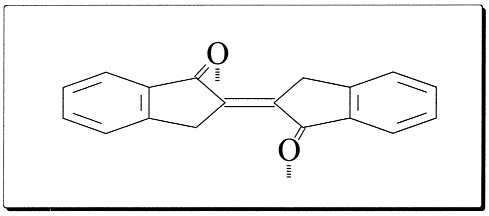

Fig. 5. Plausible orientation of indigo on silver foil.

brations involving the C–H in-plane bending are attributed to 1251, 1224, and 1036 cm^{-1}. The five-member ring bands of the Indigo molecule are assigned to 1185, 769, 622, and 574 cm^{-1}. There are three typical vibrations of the C=O/C=C system shown in Fig. 4. In the infrared spectrum already discussed by Wille and Luttke,[19] the out-of-phase vibrations of the ν(C=O) bonds at 1627 cm^{-1} are observed as the strongest band; however, the FT-Raman spectrum shows two in-phase ν(C=O) vibrations, 1582 and 1703 cm^{-1}. When a carbonyl group is hydrogen bonded and resonance can occur, which puts a partial negative charge on the oxygen accepting the hydrogen bond and a positive charge on the donating atom, the C=O wavenumbers lie in a lower region. The band at 1703 cm^{-1} in the Raman spectrum is therefore attributed to a symmetric ν(C=O) stretch. The strongest line in the FT-Raman spectrum is vibration where the C=C bond also vibrates in-phase at 1582 cm^{-1}. If Indigo could bind to the surface via oxygen lone-pair electrons, the 1582 cm^{-1} band in Fig. 4(a) would be decreased because the vibration of a synchronized shrinking mode of C2 and C3 atom at 1582 cm^{-1} was difficult, and the 1703 cm^{-1} band in Fig. 4(b) would be increased because of surface-enhanced scattering.

The SERS spectrum features very enhanced bands at 1251 and 1703 cm^{-1}, which are δ(C=O) and ν(C=O), respectively, and very weakened bands at 1224 and 1582 cm^{-1} which δ(C–N) and ν(C=C), respectively, compared with the FT-Raman spectrum. In the SERS spectrum, the out-of-plane ring deformations of indigo occur at 675, 1137, 1185 and 1294 cm^{-1}, but are relatively weak in the FT-Raman spectrum. The two bands at 1137 and 1185 cm^{-1}, which are δ(C–C) and ν(C–C), respectively, upshifted to 2–3 cm^{-1} and are significantly enhanced compared with the FT-Raman spectrum. We therefore suggest that the Indigo ring is oriented flat to the surface.

In Table 1, the relative intensity of I/I at 1475 cm^{-1} of the indigo is ca 8.1–0.2. The relative intensity of a mode containing an oxygen became greater than that of a mode doing not contain an oxygen. We therefore postulate that the oxygen related to this band connects to silver atom(s) through the electron pair in oxygen.

The SERS spectra of indigo on a type III foil are very similar to the FT-Raman spectrum, except for the fact that the SERS spectrum has a little noise because of the spectral noise at 10^{-4}

M. The SERS spectrum shows only very small wavenumber shifts and no change in the relative intensities. This means that molecules may be physisorbed and do not react chemically with the silver foil. On the basis of the spectral changes, we propose that the geometry of indigo physisorbed on the surface silver is as shown in Figure 5.

Conclusion

In the present work evaluated the use and performance of a simple (takes only 7 seconds) and inexpensive silver substrate system for Raman studies, which could significantly increase the applicability of the SERS techniques. We have also performed SERS measurements with this substrate system on molecules containing no sulfur atom. The results show that molecules containing no sulfur atom can easily be detected by the SERS technique using solid silver media etched by concentrated HNO_3. The results of this work also show that our SERS sampling method is particularly efficient. We have also shown that the surface orientation can be observed on silver foils. Therefore, we have postulated that the oxygen related to this band connects to silver atom(s) through the electron pair in oxygen. Hence, SERS seems to be a rather general phenomenon observable from a properly roughened metal surface.

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