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Fluorescence and Fourier Transform Surface-Enhanced Raman Scattering Measurements of Methylene Blue Adsorbed onto a Sulfur-Modified Gold Electrode

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Surface enhanced Raman scattering (SERS) and molecular fluorescence are used to probe the structure of a methylene blue monolayer adsorbed onto a sulfur-modified polycrystalline gold electrode. Changes in the wavelength of fluorescence for methylene blue on the gold electrode as compared to dilute solution indicate that the dye molecules' state of aggregation and electronic structure have been modified upon adsorption to the surface. An increase in the molecular fluorescence is observed on the sulfur-modified gold electrodes, and is attributed to the intervention of the sulfur between the methylene blue and the metal surface. To avoid interference from the methylene blue fluorescence, *ex situ* SERS spectra were obtained with a Fourier transform (FT) spectrometer that utilized an excitation wavelength of 1064 nm. The FT-SERS spectra from methylene blue on sulfur-modified and bare gold surfaces exhibit differences that can be ascribed to the interactions of the dye molecules with the sulfur monolayer.

Introduction

The adsorption of dye monolayers onto metal and semiconductor substrates has been employed extensively as a method of monitoring and controlling electrochemical processes at electrode surfaces. For example, the fluorescence spectrum of dye molecules adsorbed onto metal electrodes has been used to probe the static electric fields at the interface.[1] Another large area of application is the chemical modification of electrode surfaces with thin films of electroactive dyes to form a variety of photogalvanic cells, electrochromic devices, photoelectrocatalytic surfaces, and chemical sensors.[2–5] In particular, electrodeposited films of dyes belonging to the phenothiazine, phenoxazine, and phenazine families are particularly easy to form.[2,5]

In a recent series of papers[6–8] we have studied the adsorption of the phenothiazine dye methylene blue (MB) onto bare and sulfur-modified gold and platinum surfaces. Our interest in this system originally stemmed from a series of papers by Clavilier et al.,[9–12] who demonstrated electrochemically that the modification of a gold electrode with an adsorbed sulfur monolayer enhanced the chemisorption of the methylene blue. Barner and Corn studied the formation of leucomethylene blue multilayers coadsorbed onto gold surfaces with long chain alkyl sulfides,[8] and Saez and Corn[6] studied the formation of leucomethylene blue multilayers *in situ* with the technique of polarization-modulation Fourier transform infrared (PM-FTIR) spectroscopy. Unfortunately, we were unable to obtain either the *in situ* or *ex situ* FTIR spectrum of the adsorbed MB monolayer. Further studies by Campbell et al.[7] demonstrated that MB adsorption onto platinum electrodes can also be enhanced by the presence of a zerovalent sulfur monolayer. The orientation of an adsorbed MB monolayer on the sulfur-modified platinum surface was measured spectroscopically using the surface-selective technique of optical second harmonic generation.[7]

For both the gold and platinum surfaces, the enhanced chemisorption in the presence of sulfur has been attributed to a sulfur–sulfur interaction between the sulfur adatoms of the monolayer and the ring sulfur atom of methylene blue.[9,12] However, at the present time no spectroscopic evidence exists to further clarify the sulfur–sulfur interaction. Verification of this interaction requires a vibrational spectroscopy sensitive enough to detect single monolayers. For roughened surfaces, the technique of surface enhanced Raman spectroscopy (SERS) possesses sufficient sensitivity. Over the past decade, SERS has become a powerful probe of the orientation and structure of dye molecules adsorbed onto roughened silver and gold electrodes.[2,13–21] In this paper we examine the fluorescence and SERS spectra of methylene blue monolayers adsorbed onto roughened gold surfaces that have been modified with an adsorbed sulfur monolayer.

Experimental Considerations

Gold foils (99.99+%, D. F. Goldsmith, 0.010 in. thickness) and a 7 mm diameter silver rod (Aesar, puratronic grade) were used as substrates for the SERS measurements. The surfaces were first polished to a mirror finish with 0.05-μm alumina, rinsed

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thoroughly with triply-distilled water, and then sonicated for 15 min before use. Electrochemical roughening of the electrodes was performed with an electrochemical cell and apparatus described elsewhere.[8] All potentials are reported versus a saturated calomel electrode (SCE). The gold electrodes were roughened in 0.1 M KCl solution by scanning between −0.800 and 1.900 V at a sweep rate of 100 mV s^{-1} for 10 min.[22] The silver electrode was roughened in 0.1 M KCl with five to seven oxidation–reduction cycles between 0.2 and −0.5 V at 15 mV/s.[23] After roughening, the gold electrodes were exposed to a 0.02 M sodium sulfide solution (Fluka, puriss grade) for 15 min to form a sulfur monolayer on the surface,[8] rinsed with triply distilled water, and dried with nitrogen. The electrodes were then exposed to a 1.0×10^{-4} M methylene blue (Kodak, twice recrystallized from ethanol–water[7]) solution for 2 h and subsequently removed from solution, rinsed with triply-distilled water, and dried.

Fluorescence spectra were recorded *ex situ* with 595-nm laser excitation for the gold surfaces using a conventional 0.75-m double monochromator and experimental geometry described elsewhere.[8] All spectra were recorded with a slit width of 100 μm, which roughly corresponds to 2 cm^{-1} resolultion at 600 nm. Fourier transform (FT)-SERS spectra of the gold electrodes were obtained at an excitation wavelength of 1064 nm using a Nicolet FT-Raman System 800 spectrometer at Nicolet Instrument Corp. (Madison, WI). The FT-SERS spectra were recorded at a resolution of 2 cm^{-1} with a zero-angle backscattering geometry and have been normalized to a background spectrum of an unroughened gold surface. For comparison, an additional SERS spectrum of methylene blue on a silver electrode was obtained with 514.5-nm excitation using the scanning monochromator.

Results and Discussion

A. Electrochemical Measurements. The adsorption of a monolayer of methylene blue (MB) onto sulfur-modified polycrystalline gold electrodes was accomplished following the procedure outlined previously for evaporated gold films by Barner and Corn.[8] As shown originally by Clavilier et al.,[12] the presence of an irreversibly chemisorbed zerovalent sulfur monolayer enhances the adsorption of the first monolayer of methylene blue. This enhancement results in the formation of a well-defined adsorption postwave in the cyclic voltammogram (CV) of the electrode in an 80 μM MB solution (Figure 1). Integration of this current peak for polycrystalline gold films leads to a surface charge density of 29 μC cm^{-2} and a MB surface coverage of 1.50×10^{-10} mol cm^{-2}. If the gold electrode was removed from the MB solution, rinsed with water, and returned to a buffer solution that did not contain MB, a subsequent CV demonstrated that MB remained on the electrode with approximately the same surface coverage.[8] Similar surface coverages were observed for MB monolayers prepared on SERS-active electrochemically roughened surfaces. The leucomethylene blue species formed upon reduction of the MB is not strongly adsorbed onto the gold surface, so that repeated reduction and reoxidation of the MB in the absence of solution species eventually desorbs the entire monolayer. In addition, the adsorbed MB is in equilibrium with a small amount of solution species. Due to this equilibrium, all attempts at obtaining an *in situ* SERS spectrum resulted in only the observation of fluorescence from MB in solution. Thus, both the SERS and surface fluorescence measurements were obtained *ex situ* after emersion and rinsing of the electrode.

B. Fluorescence Spectra. Figure 2a plots the molecular fluorescence spectrum obtained with 595-nm excitation from a MB monolayer on a roughened sulfur-modified gold surface (MB–S–Au). Note that even after emersion and thorough rinsing, fluorescence attributable to the adsorbed molecules is still observed. Some SERS bands can be discerned in the fluorescence spectrum, as the efficiency of surface enhancement for Raman scattering is expected to be much higher than that of the fluorescence process.[24]

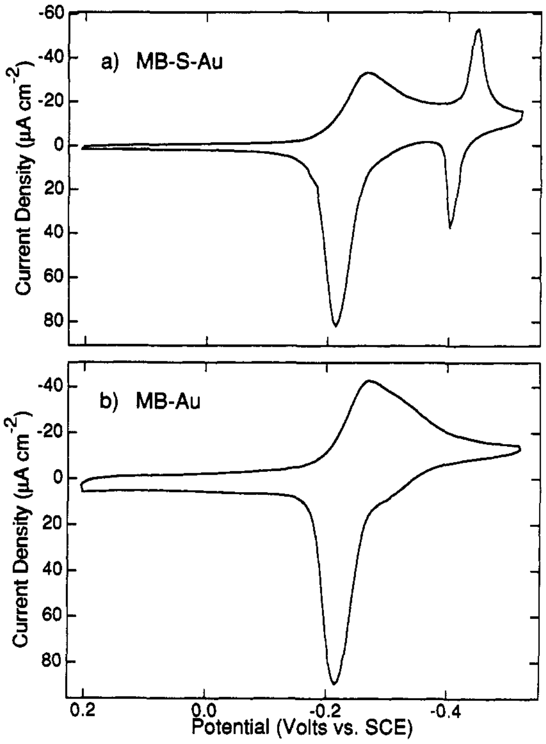

Figure 1. Cyclic votammograms (CVs) of an 80 μM methylene blue (MB) solution (a) at a sulfur-modified gold electrode (MB–S–Au) and (b) at a bare gold electrode (MB–Au). The main oxidation–reduction peaks in both CVs are due to solution species. The sharp adsorption postwave for the sulfur-modified electrode at −0.45 V is due to the sulfur enhancement of the MB adsorption. Both CVs are taken from ref 8.

The maximum of the fluorescence from the MB monolayer in Figure 2a occurred at approximately 660 nm. For comparison, fluorescence obtained from a MB monomer in dilute solution was found to have a maximum at 678 nm. At a concentration of 10^{-3} M, where it is known that MB dimers exist in solution,[25] the fluorescence reached a maximum at 710 nm. Since this red shift due to dimerization was not observed from the MB monolayer, it can be safely assumed that the MB molecules are not adsorbing onto the surface as dimers from solution. Instead, the blue-shift by 18 nm of the MB fluorescence when on the surface can be attributed to either (i) interactions of the MB monolayer with the metal surface or (ii) interactions between the adsorbed MB molecules that are different than the interactions observed in solution due to the geometric constraints of adsorption. In support of this latter mechanism, the position of the fluorescence maximum shifted slightly as a function of the concentration of the methylene blue solution in which the foil had been dipped. However, the fluorescence from all of the MB monolayers was found to be blue-shifted from the dilute solution spectrum.

Figure 2b plots the molecular fluorescence spectrum obtained with 595-nm excitation from a MB monolayer on a roughened gold surface that has not undergone sulfur

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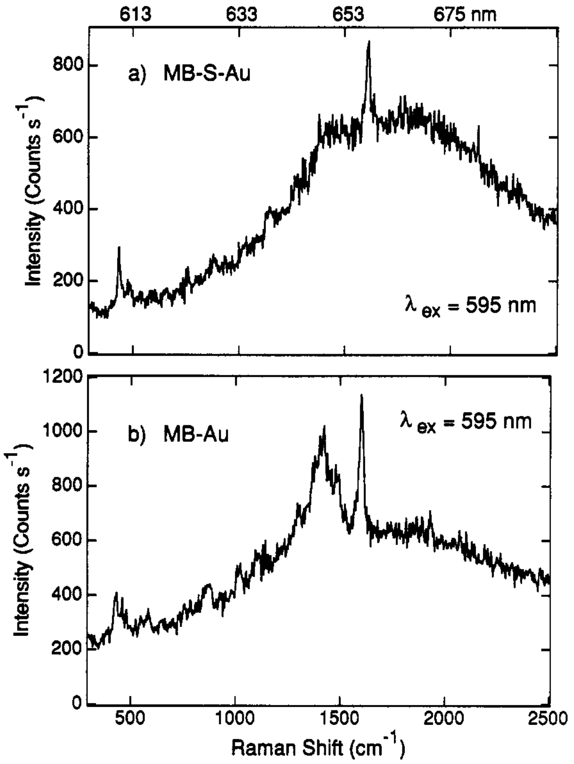

Figure 2. Molecular fluorescence and SERS spectrum obtained with a laser excitation wavelength of 595 nm for a MB monolayer (a) adsorbed onto a sulfur-modified roughened gold surface (MB–S–Au) and (b) adsorbed to bare roughened gold electrode (MB–Au). For the MB–S–Au surface, only the ring stretch and CNC skeletal deformation are clearly visible. The rest of the peaks are obscured by MB fluorescence. In the MB–Au spectrum the relative intensity of fluorescence to Raman peaks has decreased, leaving a few more peaks visible, but much of the Raman spectrum is still obscured.

modification (MB-Au). Within experimental error, the wavelength of the fluorescence maximum for surfaces prepared without sulfur was the same as that observed on the sulfur-modified surfaces. This similarity suggests that the chemical differences in the MB monolayers adsorbed with and without sulfur are small in comparison to the changes that occur upon going from the solution to the adsorbed state.

Although the fluorescence wavelength does not shift between modified and unmodified gold surfaces, the intensity of the fluorescence is altered significantly. As can be seen in Figure 2b, the major Raman peaks of the unmodified surface can be clearly identified above the fluorescence. The MB fluorescence on the unmodified surfaces relative to the Raman signal was typically 3 to 4 times less than that observed on the sulfur-modified surfaces (the fluorescence intensity relative to the SERS intensity was used since the absolute magnitude of fluorescence from the adsorbed MB depended upon the degree of surface roughening). In all cases, of course, the level of fluorescence from the MB monolayer was orders of magnitude less than that obtained in solution.

The decrease in MB monolayer fluorescence upon adsorption is due to the well-known fluorescence quenching of the metal surface. Interactions between the fluorescing molecule and the free electrons in the metal permit the rapid transfer of energy and relaxation, even at a considerable distance.[24] Additional fluorescence quenching is observed for the first monolayer of adsorbed molecules due to the overlap of the molecular wavefunctions with those of the electrons at the surface of the metal. The increase in fluorescence from the MB monolayer of the samples prepared with the sulfur monolayer suggests that the sulfur modification prevents direct adsorption of methylene blue onto the gold surface. The simultaneous enhancement of adsorption and decoupling from the metal surface by the adsorbed sulfur leads one to suspect a specific chemical interaction exists between the adsorbed sulfur monolayer and the MB.

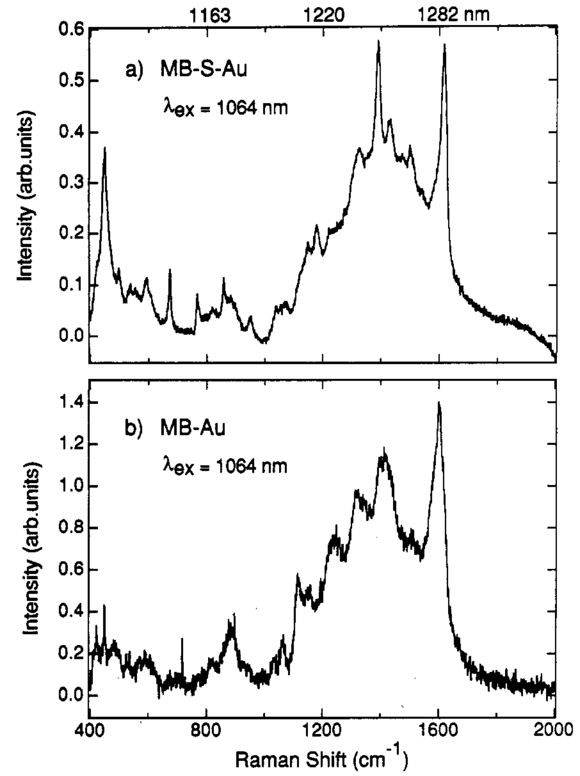

Figure 3. FT-SERS spectrum at an excitation wavelength of 1064 nm for (a) MB adsorbed onto a sulfur-modified roughened gold electrode (MB–S–Au) and (b) MB adsorbed onto a bare roughened gold electrode (MB–Au). No MB fluorescence background was observed in either spectrum. The vibrational frequencies are listed in Table I.

C. SERS Spectra. To avoid the MB fluorescence, SERS spectra were obtained utilizing an excitation wavelength of 1064 nm. In this wavelength region, FT spectrometers have been developed for Raman spectra with shifts greater than 400 wavenumbers.[26–29] The FT-SERS spectra of the MB monolayer on sulfur-modified and bare gold surfaces are shown in parts a and b of Figure 3, respectively. Theoretically, SERS is expected to occur on gold surfaces at a wavelength of 1064 nm if the proper length scale of roughening is present on the surface,[30–32] and it is not surprising that the electrochemically treated surfaces would produce a sufficiently large variety of roughness to include the appropriate length scale.[33,34] For comparison, a SERS spectrum of MB was obtained at a roughened silver electrode (without sulfur) using 514.5-nm excitation (Figure 4). The use of 514.5-nm excitation on the silver electrode shifted the SERS spectrum away

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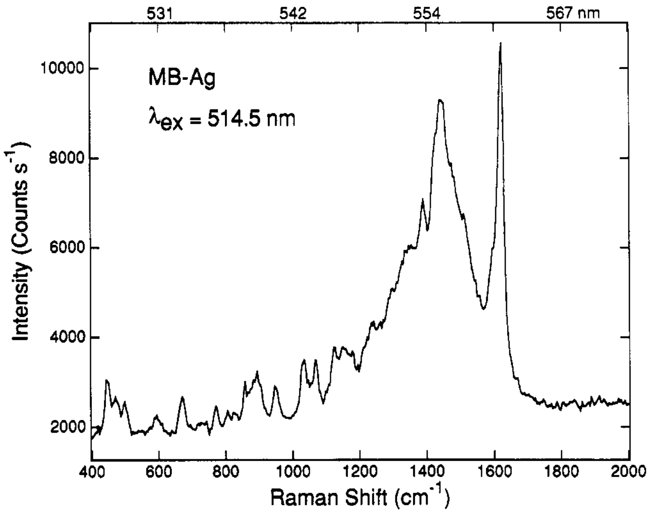

Figure 4. SERS spectrum of MB on bare roughened silver electrode with an excitation wavelength of 514.5 nm. Many vibrational bands are the same as in the MB–S–Au system; new bands are probably due to different MB–Ag interactions.

Table I. Major Bands (cm^{-1}) and Assignments of the SERS Spectra of a MB Monolayer on Sulfur-Modified Gold (MB–S–Au), Gold (MB–Au), and Silver (MB–Ag)

MB–S–Au^a	MB–Au^a	MB–Ag^b	assignment^c
1617 ± 2	1600	1617	ν(CC) ring
1430	1414	1442	ν_{asym}(CN)
1390	1390	1390	ν_{sym}(CN)
1151	1151	1150	β(CH)
1030	1030	1030	β(CH)
858	858	860	
675	675	670	γ(CH)
449	449	442	δ(CNC)

^{a} 1064 nm excitation. ^{b} 514.5 nm excitation. ^{c} Assignments are based on thionine spectra of Hutchinson et al.[2]

from the MB fluorescence at 660 nm. Table I lists the major bands observed in the three SERS spectra. The assignments in the table are based on the analysis of the SERS spectrum of thionine by Hutchinson et al.[2] The most intense peaks in the three spectra are the ring stretch (ν(CC)) at 1600 cm^{-1}, the symmetric and asymmetric CN stretches (ν_{sym}(CN) and ν_{asym}(CN)) at 1390 and 1414 cm^{-1}, respectively, and the C–N–C skeletal deformation mode δ(CNC) at 449 cm^{-1}.

Several of the bands in the SERS spectrum change in intensity and position in the presence of a sulfur sublayer. The ring stretch at 1600 cm^{-1} shifts to 1617 cm^{-1}, and ν_{asym}(CN) shifts from 1414 cm^{-1} to 1430 cm^{-1}. The frequencies of these two bands on the sulfur-modified surfaces are actually closer to those observed for MB on silver. The positions of these Raman bands were found to be independent of the concentration of the MB dipping solution. Notice also that the intensity of ν_{sym}(CN) at 1390 cm^{-1} is much larger than ν_{asym}(CN) at 1430 cm^{-1} in the MB spectra of sulfur-modified samples, but in the absence of sulfur (on gold and on silver), the reverse is true. This relative intensity pattern was found to hold at all surface concentrations. In addition to the δ(CNC) band at 449 cm^{-1}, some other minor peaks increase in intensity on the sulfur-modified surfaces.

The differences in the FT-SERS spectra from the two gold surfaces (MB–S–Au and MB–Au) provide some spectroscopic evidence as to the nature of the changes in MB chemisorption that occur when the sulfur monolayer is present. Since the FT–SERS spectra did not depend upon the MB surface coverage, the changes in vibrational frequencies for the sulfur-modified surface can be ascribed to changes in the interactions with the sulfur-coated electrode surface, as opposed to different interactions between the molecules. A more quantitative discussion of the nature of the changes in the FT-SERS spectra in the presence of the sulfur monolayer unfortunately requires a detailed normal coordinate analysis of the MB band frequencies and intensities. However, it is worth noting that the large increases in band intensities of ν_{sym}(CN) and δ(CNC) are not observed in the MB–Ag SERS spectrum, further suggesting that these changes are specifically linked to the effect of the sulfur monolayer on the MB molecule as opposed to changes in the electronic structure of the metal surface.

Summary and Conclusions

Examination of the FT-SERS and fluorescence spectra from MB monolayers adsorbed onto sulfur-modified roughened gold electrodes demonstrates that the chemisorbed sulfur monolayer indeed enhances and alters the nature of the dye molecule adsorption by intervening between the MB molecules and the gold surface. The fluorescence spectra show that the electronic structure of MB changes significantly upon adsorption both with and without a chemisorbed sulfur monolayer due to the interactions with the gold electrode. The presence of a sulfur monolayer on the surface further modifies the environment of adsorbed MB monolayer by lessening the interaction of dye molecules and the gold substrate (as evidenced by the changes in fluorescence intensity) and by altering the vibrational spectrum of the MB (as evidenced by the FT-SERS spectra). These effects indicate a strong sulfur–methylene blue interaction, but a more quantitative statement of how these two species are interacting (e.g., by formation of a sulfur–sulfur bond) requires a detailed normal coordinate analysis of the MB dye molecule's vibrations.

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