pH-Dependent Surface-enhanced Raman Scattering Analysis of Maleimide and Succinimide on Ag Nanocolloidal Surfaces

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The adsorption structure and binding of maleimide (MI) and succinimide (SI) on silver nanocolloidal surfaces have been comparatively investigated by means of pH-varied surface-enhanced Raman scattering (SERS). The two molecules appeared not to adsorb onto Ag surfaces at pH values below 5. The appearance of a ring ν(C-H) band at ~3100 cm^{-1} denoted the standing geometry of MI's aromatic ring on Ag. The absence or weakness of in-plane vibrational modes of MI and SI also supported a perpendicular orientation of MI and SI on Ag from the electromagnetic selection rule. Density functional theory (DFT) calculations were employed to examine the vibrational frequencies of MI's and SI's neutral and anionic states.

Key Words : Silver nanoparticles, Adsorption, Maleimide, Succinimide, SERS

Introduction

Recently interest in bioconjugations of oligonucleotides or proteins on surfaces has increased due to their potential applications in analytical chemistry.[1,2] One of the most versatile methods of bioconjugating them may be using imide derivatives such as maleimide (MI) or succinimide (SI) esters.[3] MI and SI are industrially and biologically useful compounds.[4] SI is used as an analgesic of human leukocytes and as a corrosion inhibitor.[5] MI's versatility arises from its ability to react either via dienophile in Diels-Alder reactions or by polymerization of double bonds.[6]

Structural order has been one of major concerns in most applications of self-assembled thin films because packing and orientating adsorbates affect the monolayers' surface chemistry.[7,8] Vibrational spectroscopy has played a significant role in chemical analysis.[9] Ever since its discovery,[10] the surface-enhanced Raman scattering (SERS) phenomenon has become one of the most sensitive techniques for monitoring adsorbates on metal substrates at the submonolayer coverage limit.[11,12] The quantum chemistry community has regarded density functional theory (DFT) as a general procedure for studying molecules' physical properties and confirming their vibrational assignments.[13]

Few reports have explored the direct chemisorption of MI or SI on metal surfaces.[14] MI's adsorption characteristics on gold and silver surfaces were studied by Raman spectroscopy. The edge-on orientation of MI was inferred from the SERS data on Ag and Au by Aroca *et al.*[14] Although MI and SI derivatives' structures have been investigated by means of vibrational spectroscopic tools,[5,14,15] no comparative study on the interfacial structures of MI and SI has been experimentally reported on metal surfaces. To compare the binding of aromatic-containing and non-aromatic imide self-assembled monolayers, a SERS study of MI and SI was performed on Ag nanocolloidal surfaces. The purpose of this study was to examine the structure and binding of simple aromatic and non-aromatic imides on silver surfaces at different pH values.

Experimental

MI (99%) and SI (> 98%) were purchased from Sigma Aldrich. They were used without further purification. The molecular structures of MI and SI are depicted in Figure 1. For Ag nanocolloids, a portion of AgNO$_3$ (~90 mg) was dissolved in ~500 mL of distilled water, brought boiling and a solution of ~1% sodium citrate (10 mL) was added, and kept on boiling for *ca.* 1 h.[16] All the chemicals otherwise specified were reagent grade and triply distilled water, of resistivity greater than 18.0 MΩ·cm was used in making aqueous solutions. Raman spectra were obtained using a Renishaw Raman confocal system model 1000 spectrometer equipped with an integral microscope (Leica DM LM). The 633 nm irradiation from a 25 mW air-cooled HeNe laser (Melles Griot Model 25 LHP 928) with the plasma line rejection filter were used as the excitation sources for the Ag SERS experiments.[17,18] For the Ordinary Raman (OR) spectra of MI and SI, near infrared irradiation at 1064 nm from a Bruker RFS 100/S FT-Raman spectrometer was used to avoid a strong fluorescence. An appropriate holographic notch filter was set in the spectrometer depending on the excitation source. Raman scattering was detected with 180° geometry using a peltier cooled (–70 °C) CCD camera (400 × 600 pixels). The holographic grating (1800 grooves/mm), and the slit allowed the spectral resolution to be ~1 cm^{-1}. The Raman band of a silicon wafer at 520 cm^{-1} was used to calibrate the spectrometer, and the accuracy of the spectral measurement was estimated to be better than ~1 cm^{-1}. To 1 mL of Ag colloidal solution was added a 0.05 M aqueous
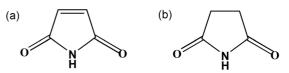

Figure 1. Structures of (a) maleimide (MI) and (b) succinimide (SI).

solution of MI or SI to a final concentration of ~10^{-3} M using a micropipet. A glass capillary with an outer diameter of 1.1 mm was used as a sampling device. The pH values of Ag nanoparticle solutions were measured by using a Thermoelectron Orion 3 star bench top pH meter. All *ab initio* molecular orbital calculations were carried out using the Gaussian '03 suite of programs.[19] The geometry optimizations were converged to one structure.

Results and Discussion

Ordinary Raman and SERS spectra of MI. Figure 2(a) and (b) shows the ordinary Raman spectrum of MI in a neat solid state and the Ag SERS spectrum, respectively. Obtaining information on the surface structure requires analyzing spectral changes according to the adsorption process. A correct vibrational assignment is prerequisite in this respect. We performed a density functional theory (DFT) calculation to obtain a reliable assignment, as shown in Figure 2(c) and (d). Consulting the earlier vibrational assignments,[14,15] we analyzed Raman spectra in Figure 2. The peak positions of MI are listed in Table 1 along with the appropriate vibrational assignments. The concentrations of MI in the Ag nanocolloids were estimated to be ~10^{-3} M. According to the transmission electron microscopy (TEM) and dynamic light scattering (DLS) measurements, silver particles' average diameters were ~30 nm. This implies that the SERS spectra shown in Figure 2(b) should be higher than that needed to cover the silver particles' total surface area.[18]

As shown in Figure 2(b), it is noteworthy that the aromatic ring CH stretching band is identified at ~3100 cm^{-1}. It is well documented in the literature that the presence of a ring CH stretching band in an SERS spectrum indicates a vertical (or at least tilted) orientation of the aromatic ring moiety on a metal substrate.[18] MI's aromatic ring band in silver nanocolloids appeared at 1574 cm^{-1}, and at 1583 cm^{-1} in the solid state. These results suggest a vertical orientation of the

Table 1. Spectral Data and Vibrational Assignment of MI[a]

OR	DFT (Neutral)[b]	Ag SERS	DFT (Anion)[b]	Assignment[c,d,e]
3165	3107	3152	3059	Sym C-H stretch (i.p.)
3102	3087	3088	3021	Asym C-H stretch (i.p.)
1757	1748	1685	1663	Sym C=O stretch (i.p.)
1710	1710			Asym C=O stretch (i.p.)
1583	1558	1574	1559	C=C stretch (i.p.)
1364	1282	1355		Sym C-N-C bend (i.p.)
1300	1254	1279	1235	C-H, N-H bend (i.p.)
1068	1027	1061w	988	Asym C-N-C bend (i.p.)
901	864	924	817	Ring def (i.p.)
643	608	667	618	Sym C=O bend (i.p.)
407w		461w		Asym C=O bend (i.p.)
		246		Ag-N

[a]Unit in cm^{-1}. [b]Scale factor: 0.9500. Abbreviations: w; weak. [c]Based on refs. 14, 15. [d]i.p.; in-plane; [e]o.p.; out-of-plane.

Figure 3. pH-dependent SERS spectra in ~10^{-3} M MI in aqueous silver nanocolloids at various pH values.

aromatic ring in MI on silver. Most ring modes were found to be in-plane modes. The absence or weakness of out-of-plane bands supported the notion that the adsorbate should have a vertical structure.[12] The C=O stretching band at 1757 cm^{-1} was redshifted to 1685 cm^{-1}. The present DFT calculation, predicted the frequency positions to be 1748 and 1663 cm^{-1}, respectively, as shown in Figure 2(c) and (d). This result suggests that MI should bind to the Ag surfaces in a deprotonated form. To examine pH dependent adsorption behaviors, we obtained SERS spectra at various pH values.

Figure 3 shows pH-dependent SERS spectra in ~10^{-3} M MI in aqueous silver nanocolloids at various pH values. We observed that the SERS spectral intensities weakened considerably at pH values below 5. This result also supports the assertion that MI should adsorb onto Ag in a deprotonated form. Considering that the pKa value of MI is 9.5,[20] our pH-dependent results indicate that MI should adsorb on Ag as a deprotonated form.

Ordinary Raman and SERS spectra of SI. Figure 4 shows the ordinary Raman spectrum in a neat solid state and the Ag SERS spectrum of SI, respectively. It was rather
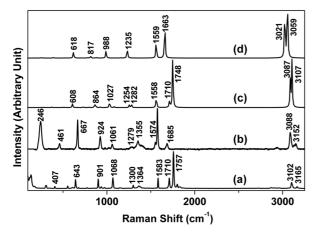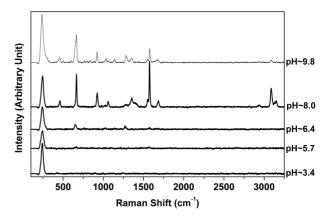

Figure 2. OR spectrum of MI in (a) neat solid state and SERS spectrum of (b) ~10^{-3} M MI in aqueous silver nanocolloids at pH ~8 in 100-3250 cm^{-1}. Simulated spectra of (c) neutral and (d) anionic states of MI from the DFT calculation. Peak intensities are normalized for a better comparison.
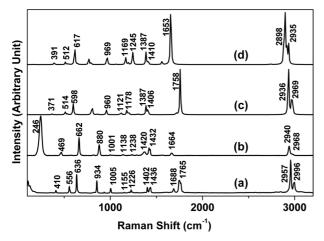
Figure 4. OR spectrum of SI in (a) neat solid state and SERS spectrum of (b) ~10^{-3} M SI in aqueous silver nanocolloids at pH ~8 in 100-3250 cm^{-1}. Simulated spectra of (c) neutral and (d) anionic states of SI from the DFT calculation. Peak intensities are normalized for a better comparison.

Table 2. Spectral Data and Vibrational Assignment of SI[a]

OR	DFT (Neutral)[b]	Ag SERS	DFT (Anion)[b]	Assignment[c,d,e]
2996	2969	2968	2935	Asym CH$_2$ stretch (i.p.)
2957	2936	2940	2898	Sym CH$_2$ stretch (i.p.)
1765	1758			Sym C=O stretch (i.p.)
1688		1664	1653	Asym C=O stretch (i.p.)
1436	1406	1432	1410	Sym CH$_2$ scissor (i.p.)
1402	1387	1420	1387	Asym CH$_2$ wag (o.p.)
1226	1198	1238 w	1245	Asym CH$_2$ twist (o.p.)
1155	1178	1138	1169	CC or CN stretch (i.p.)
1005	1121	1001	1064	Asym CH$_2$ rock (i.p.)
934	960	880	969	Ring bend (i.p.)
636	598	662	617	Asym C=O bend (i.p.)
556	514	469	512	Sym C=O bend (i.p.)
410	371		391	C=O bend (o.p.)
		246		Ag-N

[a]Unit in cm^{-1}. [b]Scale factor: 0.9500. Abbreviation: w; weak. [c]Based on ref. 5. [d]i.p.; in-plane. [e]o.p.; out-of-plane.

straightforward to correlate the ordinary Raman bands with the SERS bands. Their peak positions are listed in Table 2 along with the appropriate vibrational assignments. SI's concentration in the colloidal solution was ~10^{-3} M, implying that the SERS spectra shown in Figure 4 should also correspond to SI on silver at a concentration far above the full-coverage limit. We did not attempt to perform a concentration-dependent SERS study due to the poor spectral quality at other concentrations.

Figure 5 shows pH-dependent SERS spectra in ~10^{-3} M SI in aqueous silver nanocolloids at various pH values. We observed that the SERS spectral intensities weakened considerably at pH values below 5. This result also supports the notion that SI should adsorb onto Ag in an anionic form. Considering that SI's pKa value is 9.4-9.6,[21] our pH-dependent results indicate that SI should adsorb onto Ag in a
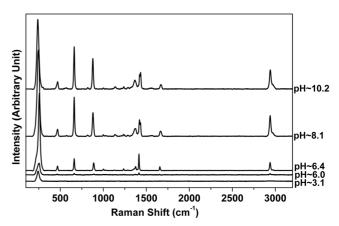

Figure 5. pH-dependent SERS spectra in ~10^{-3} M SI in aqueous silver nanocolloids at various pH values.

deprotonated form.

Adsorption Structures of MI and SI on Ag. According to the electromagnetic (EM) surface selection rule,[11,12] the vibrational mode perpendicular to the surface is more enhanced than the parallel mode. For MI and SI, the absence of out-of-plane bands in the Ag SERS spectra suggests that the adsorbates should have a vertical structure on silver. Regarding aromatic ring geometry, the appearance of the C-H stretching band identified at ~3100 cm^{-1} suggests that MI has an upright orientation on Ag surface as discussed.[18] It is not absolutely certain whether MI and SI may have different adsorption structures or tilt angles on metal surfaces in response to the presence or absence of aromatic property due to the equivocal SERS selection rules. It is intriguing that the SERS peak intensities at pH~6 appeared to be somewhat different for MI and SI. Due to its aromatic ring structure, MI may not change flexibly as in the case of SI. It is not absolutely certain that this may influence somewhat different SERS intensity changes between MI and SI depending on pH values. Since the interfacial pKa values on metal surfaces should not be the same as those in the solution as in the previous report,[22] it seems understandable that the adsorption changes of MI and SI occurred at much lower pH values in the present SERS study than their intrinsic pKa values of 9.5. Thermodynamic, electrochemical, and theoretical studies shall also be beneficial to explain the adsorption characteristics of MI and SI on Ag surfaces.

Summary and Conclusions

The adsorption behaviors of maleimide (MI) and succinimide (SI) on silver surfaces have been comparatively investigated by means of surface-enhanced Raman scattering (SERS). The strong enhancements of the in-plane vibrational modes indicate that MI and SI should adsorb vertically onto silver. The two molecules appeared not to adsorb onto Ag surfaces at pH values below 5.

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