Surface-Enhanced Raman Scattering of Azobenzene-Containing Long-Chain Fatty Acids Adsorbed on Metal Colloids

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We have investigated the surface geometry of azobenzene-containing long-chain fatty acids (nA_{m}H; n = 8, 12, m = 3, 5) adsorbed on silver and gold colloids as well as the interaction between nA_{m}H and the two kinds of metal colloidal surface by means of near-infrared and visible surface-enhanced Raman scattering (SERS). The 488.0 and 514.5 nm excited Raman spectra of nA_{m}H adsorbed on silver colloid and the 1064 nm excited Fourier transform (FT)-Raman spectrum adsorbed on gold colloid show a marked SERS effect. The lowest concentration at which the SERS signals were observed was 10^{-18} and 10^{-8} M for the silver and gold colloids, respectively, in the present study. The 488.0 nm excited SERS spectrum of 12A_{3}H adsorbed on silver colloid is very similar to a Raman spectrum of 12A_{3}H in chloroform, while the 1064 nm excited SERS spectrum of 12A_{3}H adsorbed on gold colloid is quite different; a number of new bands appear, and the relative intensity of bands changes markedly in the 1064 nm excited SERS spectrum. Probably, a chemical mechanism contributes significantly to the emergence of the SERS effect for 12A_{3}H on gold colloid. Particularly striking in the SERS spectrum of 12A_{3}H adsorbed on gold colloid is the observation that bands at 1586, 1166, and 834 cm^{-1} due to the phenyl ring modes show remarkable enhancement. It seems likely that the COO group is adsorbed directly on the silver colloid surface, while one of the phenyl groups is adsorbed directly on the gold colloid surface. The effect of the particle size on the SERS intensity has been explored for 12A_{3}H on gold colloid. It was found from the frequency of the –N=–N stretching band that 12A_{3}H assumes a cis conformation on the gold colloid with the smaller particle size.

Index Headings: SERS; Surface-enhanced Raman scattering; Metal colloids; Azobenzene; Adsorption.

INTRODUCTION

A number of recent studies have demonstrated the great utility of surface-enhanced Raman scattering (SERS) for investigating the structure of adsorbed molecules and exploring the interactions between the molecules and metal surface.1–26 The SERS effect, in general, yields enormous enhancement of the Raman cross section, and fluorescence is markedly quenched in SERS spectra.1–35 The mechanism of SERS may be divided into so-called “electromagnetic” and “chemical” effects.1–28–35 The electromagnetic mechanism is induced by the enhancement of the local electromagnetic field near rough metal surface; if the frequency of the incident light matches with the frequency at which the extinction by the metal is maximal, surface plasmon (sp) resonance occurs. On the other hand, the enhancement of selective vibrations is usually explained in terms of the chemical or charge-transfer (CT) model, which involves interaction of the adsorbed molecules with the metal surface. Both electromagnetic and chemical SERS theories predict that, although the enhancement of Raman bands depends strongly on surface roughness features such as the size, shape, and distributions of particles and clusters of the metal colloids, they are in very different size dimensions for electromagnetic and chemical enhancement.

We have been involved in near-infrared (NIR) SERS studies of Langmuir–Blodgett (LB) and dipping films of long-chain molecules with an azo group.25,26 The combination of SERS with NIR excitation has recently become increasingly important to avoid fluorescence and photodecomposition and to explore the excitation profile of SERS.11,12,16–18,24–27 It was found in our study on the dipping films of azobenzene-containing long-chain fatty acids (nA_{m}H; n = 8, 12, m = 3, 5; Fig. 1) on silver mirror that the silver mirror method yields a pronounced SERS effect even with 1064 nm excitation.26,27

The purpose of the present study is to expand our study on SERS of metal colloid systems to amphiphilic long-chain molecules with a functional group. Studies of SERS of the amphiphilic long-chain molecules with a functional group (nA_{m}H in the present case) on metal colloid are very important for three major reasons. First, the amphiphilic long-chain molecules with a functional group have, in general, hydrophilic and hydrophobic parts along with the functional group; thus, it is very interesting to investigate which part directly interacts with the metal colloid surface. It is very likely that different parts of the molecules adsorb directly on the gold and silver surface.6,16,24 Second, since the length of the alkyl tail and that of the spacer of the long-chain molecules may be controlled, one can examine the effects of the lengths on the nature of adsorption on the colloidal surface. Third, comparison of the interaction of the long-chain molecules with the metal surface between the metal colloidal systems and metal substrates is also of particular importance.

In this paper, we report on a comparison of the interaction of nA_{m}H with the metal surface between the gold and silver colloid and the effects of the lengths of the tail and spacer and of the particle size of the gold colloid on the SERS effect. In addition, the SERS spectra of nA_{m}H...
**EXPERIMENTAL**

**Samples.** $nA_mH$ (Fig. 1) was purchased from Dojin Chemical Co. Ltd., Kumamoto, Japan and used without further purification. $nA_mH$ was dissolved in acetonitrile obtained from Wako Chemical Co. Ltd., Osaka, Japan.

**Preparation of Colloids.** Silver colloid was prepared by a method similar to that reported by Creighton et al. A solution of 150 mL of sodium borohydride ($2 \times 10^{-3}$ M) was mixed with a solution of 50 mL of silver nitrate ($5 \times 10^{-3}$ M) with strong stirring in an ice-cold bath, yielding a greenish yellow-colored silver colloid with an absorption maximum of 395 nm.

Gold colloid was prepared by the method proposed by Frens. A solution of 50 mL of gold chloride acid (10 wt %) was mixed with a solution of 0.16, 0.21, 0.30, and 0.50 mL of sodium citrate (1 wt %) in an aqueous solution. The gold colloids had a red-violet color depending upon the particle size and showed an absorption maximum near 530 nm. Commercial colloidal gold solution (Polysciences Inc, Warrington, PA) was also used for the present study. It contained isolated, nearly spherical, gold particles with a diameter of about 40 nm and a narrow size distribution. A NaCl solution of $10^{-1}$ M was added to the commercial colloidal gold solution to induce special colloidal aggregation.

**Spectroscopy.** Raman spectra were measured at 4 cm$^{-1}$ resolution with a JASCO NRS-2100 Raman system equipped with a liquid nitrogen-cooled charge-coupled device (CCD) detector (LN/CCD-1100PBUVAR, Princeton Instruments). The 488.0 nm line from an argon-ion laser (Spectra-Physics 2016) was used as an excitation source for the Raman spectra. A Nicolet Magna 860 Fourier transform (FT-Raman) spectrometer equipped with an InGaAs detector was used to obtain FT-SERS spectra with 4 cm$^{-1}$ resolution. Continuous-wave (CW) NIR excitation at 1064 nm was provided by a diode laser-pumped Nd:YAG laser (Spectra-Physics).

**RESULTS AND DISCUSSION**

Figure 2a and 2b show the 488.0 nm excited Raman spectrum of an acetonitrile solution of $12A_3H$ ($1 \times 10^{-3}$ M) adsorbed on silver colloid and the 1064 nm excited FT-Raman spectrum of $12A_3H$ ($1 \times 10^{-3}$ M) adsorbed on gold colloid. Of note in Fig. 2 is the observation that $12A_3H$ on silver and gold colloids shows a significant SERS effect. In all the cases, the intensities of bands at 1375 and 923 cm$^{-1}$ due to acetonitrile remain constant. Thus, one can normalize the intensities of SERS signals with reference to those of the acetonitrile bands. The lowest concentration at which the SERS effect can be obtained was found to be $1 \times 10^{-10}$ M and $1 \times 10^{-8}$ M for the silver and gold colloids, respectively, in the present study. The assignments of bands observed in the spectra in Fig. 2a and 2b are listed in Table I.

Particularly striking is the fact that the SERS spectrum...
of 12A3H adsorbed on gold colloid is markedly different from that of 12A3H adsorbed on silver colloid; the former shows many more bands than the latter. New bands appear at 1245, 1166, 1087, 1001, and 834 cm\(^{-1}\) in the SERS spectrum of 12A3H on gold colloid (Fig. 2b). These observations suggest that the interaction between 12A3H and the metal colloidal surface is quite different between the two kinds of colloids. In order to investigate the band assignments for the 1064 nm excited SERS of 12A3H on gold colloid, we measured FT-IR and FT-Raman spectra of 12A3H in a solid state (Fig. 3). The new bands at 1245, 1087, and 1001 cm\(^{-1}\) have their counterparts in the FT-IR and FT-Raman spectra, while those at 1166 and 834 cm\(^{-1}\) do not have their counterparts in these spectra. Table I also summarizes assignments for infrared and Raman bands of 12A3H in the solid state.\(^{38-41}\)

The 488.0 nm excited SERS spectrum of 12A3H adsorbed on silver colloid is very similar to the Raman spectrum of 12A3H in chloroform (Fig. 3a), while the 1064 nm excited SERS spectrum of 12A3H adsorbed on gold colloid is quite different; a number of new bands appear, and the relative intensity of the bands changes markedly in the 1064 nm excited SERS spectrum, as shown in Fig. 2b. It appears that a chemical mechanism plays a significant role in the emergence of the SERS effect for 12A3H on the gold colloid.

The most characteristic feature of the 1064 nm excited SERS spectrum of 12A3H on gold colloid is prominent enhancement of bands at 1586, 1166, and 834 cm\(^{-1}\), assignable to \(\nu_{1h}\) and breathing modes of the two phenyl rings. It is also of note in Fig. 2b that the relative intensities of the –N=N– stretching bands at 1454 and 1409 cm\(^{-1}\) decrease significantly compared with those in the spectrum of 12A3H on silver colloid. Thus, it seems likely that the molecular axis of 12A3H is tilted largely with respect to the colloid surface normal or nearly parallel to the surface. There is little doubt that the COO\(^{-}\) group is attached to the silver colloid, because the silver colloid has positive charge.\(^{25,38}\) The marked differences in the spectral features between the spectra of 12A3H on silver and gold colloid suggest that the molecular orientation of 12A3H is quite different between the two kinds of colloid surface. Since the gold colloid surface has a negative charge,\(^{16,24}\) the COO\(^{-}\) group cannot adsorb directly on the gold colloid surface. We infer that one of the phenyl groups is adsorbed on the gold colloid surface, because some of the phenyl ring bands show remarkable enhancement. SERS spectra of 12A3H silver and gold colloid show marked dependence on the citation wavelength. The 488.0 nm excitation does not show any SERS signal for 12A3H on the gold colloid, while the 1064 nm excitation does not include the SERS effect for 12A3H on the silver colloid.

Figure 4 shows the 1064 nm excited FT-SERS spectra of 12A3H adsorbed on gold colloids with different particle sizes. Many properties of colloids depend on the particle size.\(^{37}\) Probably, the different surface potential of the gold particles is responsible for the size dependence shown in Fig. 4. The reduction of gold chloride with sodium citrate in an aqueous solution yields a series of monodisperse gold suspensions with widely different particle sizes depending upon the relative amounts of gold chloride; when a solution of 50 mL of gold chloride acid (10\(^{-2}\) wt %) was mixed with a solution of 0.16 and 0.30 mL of sodium citrate (1 wt %) in an aqueous solution, the particle size of the gold colloids was 120 and 75 nm, respectively.\(^{37}\) We have used such series of gold colloids with different particle size, gold colloids with 120 and 75 nm particle size, and commercial gold colloid with 40 nm particle size to investigate the particle size effect on SERS spectra. The spectra in Fig. 4 demonstrate that the SERS effect depends sharply upon the particle size.

In Fig. 4, there are notable spectral changes between spectrum \(a\) and the rest. It is noted for spectrum \(b\) and \(c\) that the intensities of the bands at 1454 and 1409 cm\(^{-1}\) due to the –N=N– stretching mode with the contribution from the phenyl ring mode and –N=N– stretching mode, respectively, decrease and, instead, a new band appears
at 1535 cm\(^{-1}\). There is correlation between the intensities of two bands at 1535 and 1454 cm\(^{-1}\); if the intensity of the former increases, that of the latter decreases, and vice versa. Thus, we assign the band at 1535 cm\(^{-1}\) to an \(-\text{N} = \text{N}-\) stretching mode of the cis azo group.\(^{41}\) It seems that the cis conformer is induced upon the adsorption of 12A3H on the gold colloid with smaller particle size. A band at 1141 cm\(^{-1}\) due to the phenyl–N stretching mode also shows a shift downward by 4 cm\(^{-1}\) upon going from spectrum \(a\) to the rest.

Figure 5 compares the 488.0 nm excited SERS spectra of 12A3H, 8A5H, and 8A3H adsorbed on silver colloid, while Fig. 6 compares the 1064 nm excited SERS spectra of the three compounds on gold colloid with a particle size of 40 nm. The solvent band at 923 cm\(^{-1}\) is used as an internal intensity standard to compare the degree of enhancement. For the 488 nm excited Raman spectra, the SERS effect of 8A3H adsorbed on silver colloid is significantly stronger than that of 8A5H, probably because the distance of the phenyl azo group of 8A3H from the colloidal surface is shorter than that of 8A5H. In the 1064 nm excited SERS spectra, the relative intensities of the bands at 1457 and 1411 cm\(^{-1}\) are stronger for 8A5H and 8A3H than for 12A3H. Thus, it seems that 8A5H and 8A3H predominantly assume the trans conformer even on the gold colloids with the smaller particle size.

We have been investigating the 1064 nm excited SERS spectra of LB and dipping films of \(n\text{AMH}\) on silver substrates prepared by silver mirror and nitric acid-etched silver foil methods.\(^{25,26}\) It is of particular interest to compare the present results for \(n\text{AMH}\) on metal colloids with the previous results for the same compounds on the silver substrates. The 1064 nm excitation yielded a pronounced SERS effect for \(n\text{AMH}\) on the silver substrates, but \(n\text{AMH}\) on silver colloid did not show any SERS signal with the 1064 nm excitation. Thus, the silver substrates are much more efficient than the silver colloid in the appearance of the SERS effect of 12A3H with the 1064 nm excitation.

**CONCLUSION**

The present study on the SERS spectra of 12A3H adsorbed on gold and silver colloids has demonstrated that the molecular orientation of 12A3H and the interaction between 12A3H and the metal colloidal surface are quite different between the silver and gold colloids. The SERS spectra of 12A3H on silver colloid are close to its normal Raman spectrum in terms of both the frequencies and the relative intensities. It has been concluded in the present study that the COO\(^{-}\) group is directly adsorbed on the silver colloid. In contrast to 12A3H on silver colloid, 12A3H on gold colloid yielded a number of new bands, some of which have their counterparts in the FT-IR and/or FT-Raman spectra of the solid sample and some of which do not. It appears that a chemical effect contributes significantly to the SERS of 12A3H on gold colloid. The remarkable SERS effect of the three bands at 1586, 1166, and 834 cm\(^{-1}\) in the 1064 nm excited spectrum has led us to conclude that one of the phenyl groups is adsorbed directly upon the gold colloid surface.

Both the SERS spectra of 12A3H on silver and gold colloid show prominent excitation wavelength dependence. The 488.0 nm excitation did not show any SERS effect for the gold colloid solution, while the 1064 nm excitation did not result in SERS signals for the silver colloid solution.

We have also investigated the particle size effect on the SERS spectra of 12A3H on the gold colloid. It was found that 12A3H assumes a cis conformation on the gold colloid with the smaller particle size. Comparison among the SERS spectra of 12A3H, 8A5H, and 8A3H on the gold colloid has shown that the population of the cis conformation is much less for 8A5H and 8A3H than for 12A3H.

**ACKNOWLEDGMENTS**

The authors thank Dr. K. Kneipp (Technical University Berlin, Germany and Massachusetts Institute of Technology, USA), Prof. K. Tash-
iro (Osaka University, Japan), and Prof. N. Tamai (Kwansei-Gakuin University, Japan) for valuable discussions. The authors also thank Dr. E. Nishio and Mr. A. Nara (Nicolet Japan Co.) for the FT-Raman measurements. This study was supported by Special Coordination Funds for Promotion Science and Technology of the Science and Technology Agency of the Japanese Government.

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