Excitation wavelength dependent surface-enhanced Raman spectra of a dipping film of azobenzene-containing long-chain fatty acid on a silver mirror

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Abstract
Surface-enhanced Raman scattering (SERS) of dipping films of azobenzene-containing long-chain fatty acids, nAnH (n = 8, 12, m = 3, 5), on silver mirrors measured with a wide range of excitation wavelengths in the 457.9–1064 nm region is reported. The obtained Raman spectra show great SERS effect even with the 1064 nm excitation, and the excitation with 457.9, 476.5, and 488.0 nm gives surface-enhanced resonance Raman scattering (SERRS) due to the resonance effect of the symmetry-forbidden n–π∗ transition of the azo group. Of particular note in the present study is that the SERS spectra with the excitation in the 532–1064 nm region yield Raman bands whose frequencies are almost identical to those bands in Raman spectra of nAnH in the solid state while the SERRS spectra with the excitation in the 457.9–514.5 nm region show not only a set of bands which correspond to those of nAnH in the solid state but also a set of bands whose frequencies show a significant shift from those of the bands of nAnH in the solid state. These observations lead us to conclude that there are two kinds of molecular aggregates in the dipping films of azobenzene-containing long-chain fatty acid in which azobenzene moieties are condensed to form small bundles.

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1. Introduction
Surface-enhanced Raman scattering (SERS) has been intensively studied for nearly three decades because of its intriguing physical phenomena and a variety of applications to surface science, analytical chemistry, and nanotechnology [1–20]. We have been investigating SERS of azobenzene-containing long-chain fatty acids, nAnH; n = 8, 12, m = 3, 5; Fig. 1) and related compounds because of the following three major reasons [17,18,20]. (1) Azobenzene-containing long-chain fatty acids and related compounds are very suitable targets for SERS. They show very strong SERS effect in various conditions [17,18,20]. Moreover, the azobenzene compounds have absorption bands due to π–π∗ and n–π∗ transitions in the near-UV and visible regions, respectively, so that they may also show surface-enhanced resonance Raman scattering (SERRS) with the excitation in the 400–490 nm region. (2) They easily form aggregates and chemical bonds with a metal surface [17,18,20–24]. (3) Azobenzene-based molecules have been proved to be a potential medium for high-density recording elements and molecular switches. For example, recently, azobenzene-based alkanethiol self-assembled monolayers (SAMs) have attracted much attention not only from the structural point of view but also from that of the photo- and electrochemical characteristics of the azobenzene group [21,23,24].
We have been undertaking the SERS studies of azobenzene-containing long-chain fatty acids and related compounds from various aspects not only for the thin films but also for the colloid systems [17,18,20]. For example, we compared various kinds of active silver surface for SERS of azobenzene-containing long-chain fatty acids, a silver-evaporated glass slide, a nitric acid-etched silver foil and a silver mirror whose surface roughness increases in this order [18]. It was demonstrated from our study on near-infrared (NIR) Fourier-transform (FT) SERS of dipping films of azobenzene-containing long-chain fatty acids that the silver mirror method is very powerful to emerge the strong SERS effect [18]. Using the azobenzene-containing long-chain fatty acids, we also compared silver and gold colloid systems including gold colloid systems with different particle size [20]. It was found that the surface geometry of azobenzene-containing long-chain fatty acids on metal colloids is quite different between gold and silver colloids. It seems likely that the COO\(^{-}\) group is adsorbed directly on the silver colloid surface while one of the phenyl groups is adsorbed directly upon the gold colloid surface with the nearly perpendicular orientation. In addition, it might be possible to observe the trans–cis isomerization of the azo group on the SERS active surface [20].

The purpose of the present study is to investigate SERS of nAmH adsorbed on silver mirrors with a number of excitation wavelengths in the region of 450–1100 nm. In this study, particular attention is paid to the exploration of the excitation wavelength dependencies of SERS spectra of dipping films of 12A3H, 8A3H, and 8A5H on silver mirrors. The contribution of the resonance Raman effect of the forbidden n–π* transition of the azo group to the SERS spectra may also become clear. It is rather rare that SERS is measured using various excitation lines from 457.9 to 1064 nm. The most important finding in the present study is that two kinds of molecular aggregates of nAmH are formed in the dipping films on silver mirrors and that they show quite different SERS effect.

2. Experimental

The azobenzene-containing long-chain fatty acids, nAmH (n = 8, 12, m = 3, 5), were obtained from Dojin Chemical Co. Ltd., Japan and used as received. Other reagents for the present study except for nAmH were purchased from Wako Chemical Co. Ltd., Osaka, Japan. They were used without further purification.

Silver mirrors as substrates for the SERS experiments were prepared by the Tollen’s test, which is widely used for the identification of aldehyde compounds [25]. The detailed procedure for preparing the silver mirrors was described in our previous paper [17]. Scanning electron microscopy (SEM) image of the silver mirrors (not shown) showed that the silver particle size was about 300 nm. The silver mirrors were immersed in a chloroform solution (0.001 M) of nAmH for approximately 30 s to yield dipping films with a reproducible coverage of the monolayer range. The obtained films were rinsed thoroughly with chloroform after withdrawing from the solution, and then dried in the air.

Visible and NIR excited Raman spectra were measured at a 4 cm\(^{-1}\) resolution with a JASCO NRS-2100 Raman system equipped with a liquid nitrogen-cooled CCD detector (LN/CCD-1100PBUVAR, Princeton Instruments). An argon ion laser (Spectra-Physics 2016) and an Nd:YAG laser pumped electrically turned Ti:sapphire laser (Ushiwaka-maru, Photon Turning Co.) operating in the 700–1000 nm region were used as excitation sources for the Raman spectra. A Nicolet Magna 560 FT-IR/FT-Raman spectrometer equipped with an InGaAs detector was used to obtain the FT-SERS spectra with a 4 cm\(^{-1}\) resolution. UV-Vis absorption spectra were measured with a Shimadzu UV-Vis 3101 PC spectrophotometer.

3. Results and discussion

Fig. 2(a)–(c) show UV-Vis absorption spectra of dipping films of 8A3H, 8A5H, and 12A3H on silver mirrors, respectively. In Fig. 2 an UV-Vis spectrum of a silver mirror itself is also shown for comparison (Fig. 2(d)). Of particular interest in Fig. 2 is that the absorption spectrum of the dipping film of 12A3H on the silver mirror shows a very broad band in the 380–500 nm region due to the n–π* transition with a clear shoulder near 500 nm, while those of 8A5H and 8A3H show a less broad feature near 400 nm. It should be noted that there are clear differences in the 380–500 nm regions of the UV-Vis spectra between 12A3H and 8AmH (m = 3 and 5).

Raman spectra of a dipping film of 12A3H on a silver mirror with various excitation wavelengths are shown in Fig. 3. Note that the Raman spectra of the dipping film of 12A3H on the silver mirror develop intense bands with a high signal-to-noise ratio owing to the SERS effect even with the 1064 nm excitation. Band assignments for the spectra in Fig. 3 were made by referring to references.
A band at 1411 cm$^{-1}$ in the spectra is due to the $\sim\text{N=N}$ stretching mode while that at 1606 cm$^{-1}$ is assigned to the $\sim\text{N=N}$ stretching mode coupled to the phenyl ring mode. The frequency of the $\sim\text{N=N}$ stretching band reveals that 12A3H assumes a trans conformer in the dipping film [26–29]. The spectra in Fig. 3 yield a weak feature at 1554 cm$^{-1}$ and a shoulder near 1400 cm$^{-1}$ due to antisymmetric and symmetric stretching modes of COO$^-$ group, and there is no band assignable to a C = O stretching mode of the COOH group. Accordingly, it seems likely that the 12A3H molecules are adsorbed on the silver mirrors via chemisorption as carboxylate, as one would certainly expect. Thus, the azobenzene moieties assume nearly perpendicular orientations with respect to the silver mirror surface. This is consistent with the conclusions reached by the previous studies [18,24]. Moreover it seems to preclude the possibility of the azobenzene groups forming parallel stacks of face-to-face azobenzene dimmers. Thus, it is very likely that the azobenzene groups are packed in a herringbone pattern [21,23,24]. The interesting point in Fig. 3 is doublet appearances of the bands at 1460, 1411, and 1141 cm$^{-1}$. We will discuss this point later.

We also tried to measure Raman spectra of cast films of 12A3H on silver and gold-evaporated glass slides, but the observed spectra did not show so great SERS effect as the spectra of the dipping films, the formers showed weak fluorescence. It is confirmed again that the silver mirror method is powerful for emerging SERS effect [18].

The relative intensities of bands at 1460, 1411, 1190, and 1141 cm$^{-1}$ in Fig. 3 change markedly with the excitation wavelength; when the exciting wavelength approaches to the contour of the n-$\pi^*$ transition of azo group, the intensities of two bands at 1460 and 1411 cm$^{-1}$ and their shoulders at 1448 and 1406 cm$^{-1}$ increase. Thus we attribute the wavelength dependences of these Raman bands to the resonance Raman effect of the n-$\pi^*$ transition. Okamoto et al. [30] studied resonance Raman excitation profiles of several totally symmetric modes of trans-azobenzene in the low-energy side of symmetry-forbidden n-$\pi^*$ absorption maximum at $\approx$ 450 nm. They concluded from the resonance Raman excitation profiles that the contribution of the forbidden n-$\pi^*$ transition to the Raman intensities is significant [26]. The same conclusion may be reached in the present case. It is worth noting that the bands at 1460 and 1141 cm$^{-1}$ due to vibrations involving the $\sim\text{N=N}$ stretching mode show much more significant resonance Raman effect than the bands at 1600 and 1190 cm$^{-1}$ due to $\nu_{\text{as}}$ (C=C-C=) and $\nu_{\text{as}}$(N-Pb) stretching modes, respectively. Careful inspection of Fig. 3 reveals that shoulder bands at 1448, 1406, and 1138 cm$^{-1}$ and a weak feature at 922 cm$^{-1}$ increase their intensities with the increase in the excitation energy. This indicates that the Raman spectra excited with 721.5, 766.0, and 1064 nm are SERS spectra while those excited with the excitation lines below 532.0 nm are SERRS spectra.

Fig. 4(a)–(c) compare the 488 nm excited Raman spectra of the dipping films of 12A3H, 8ASH, and 8ASH on silver mirrors, while Fig. 5(a)–(c) depict the corresponding 457.9 nm excited Raman spectra. Particularly striking in Fig. 4 is that the Raman spectrum of the dipping film of 12A3H shows four shoulders at 1586, 1445, 1401, and 1138 cm$^{-1}$ while those of 8ASH and 8ASH show only sharp bands at 1603, 1458, 1410, and 1141 cm$^{-1}$. There are notable spectral changes in the Raman spectra between the 457.9 and 488 nm excitation. The dipping films of 8ASH and 8ASH show much more marked differences than that of 12A3H between the two excitation wavelengths. For
example, all the bands in the 1650–1000 cm$^{-1}$ region of the films of 8A3H and 8A5H are sharp in the 488.0 nm excited SERS spectra while they all consist of two sets of bands in the 457.9 nm excited spectra. New bands appear at 1586, 1460, 1448, 1406, 1190 and 1138 cm$^{-1}$ in the latter spectra. It can be seen from Figs. 4 and 5 that the SERRS spectra of these dipping films of 12A3H, 8A3H, and 8A5H consist of two component spectra. One has peaks at 1606, 1460, 1411, 1188, and 1141 cm$^{-1}$ and another has those at 1586, 1448, 1406, 1190 and 1138 cm$^{-1}$ in the latter spectra.

It is known that azobenzene groups are very favorably condensed to form a close-packed structure (bundles) on a substrate [21,23,24]. Recently, Han et al. [24] investigated SAMs of azobenzene-based alkanethiol on a gold surface and proposed “bundle model” where azobenzene moieties are condensed to form small bundles. It is very likely that similar bundles are formed also in the present case and the interactions of azo moieties are quite different between the inside and shell of bundles. The marked differences in the excitation profiles between 12A3H and 8A4H may be explained by the differences in the formation of molecular aggregates in the dipping films. The UV-Vis spectra shown in Fig. 2 suggest that the structure of aggregates is significantly different between 12A3H and 8A4H. Upon going from 488.0 nm excitation to the 457.9 nm excitation, the SERRS spectra change more largely for the dipping films of 8A4H than that of 12A3H (Figs. 4 and 5). These observations are consistent with the results that the UV-Vis spectra of 8A4H vary more significantly than that of 12A3H (Fig. 2). Kawai et al. [31] reported that 12A3H is more perpendicular than 8A3H and 8A5H in the LB films from the calculation of molecular orientation in LB films of azobenzene-containing long-chain fatty acids and their salts based upon their infrared transmission and reflection-absorption spectra. Therefore, it seems that the length of the alkyl chain is a key factor that determines the molecular orientation and aggregation.

4. Conclusions

SERS of the dipping films of azobenzene-containing long-chain fatty acids on the silver mirrors measured with the excitation wavelengths in the range from 450 to 1100 nm have elucidated that molecules adsorbed on the silver mirrors via chemisorption as carboxylate and that the symmetry-forbidden n$\rightarrow$n* transition of the azo group is responsible for the SERRS effect. Furthermore, the present study has clearly demonstrated that the two kinds of molecular aggregates coexist in the dipping films of 12A3H, 8A5H, and 8A3H on the silver mirrors: one aggregate (Aggregate A) shows the SERS effect through the 450–1100 nm region while the other one (Aggregate B) yields the effect...
only in the 450–500 nm region. It is very likely that in the dipping films, azobenzene moieties are condensed to form small bundles and that the interaction of molecules in the dipping film on the silver mirror surface is quite different between the inside and shell of bundles. It is also of interest to note that 12A3H and 8A2H provide largely different excitation profiles. Probably, the difference in the chain length brings about significantly different molecular aggregation.

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