

Fundamental processes of surface enhanced Raman scattering detected by transient reflecting grating spectroscopy

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Abstract

Ultrafast charge transfer (CT) between gold and crystal violet (CV) molecules in relation with the surface enhanced Raman scattering (SERS) activation was investigated using the transient reflecting grating (TRG) spectroscopic method. A charge transfer between gold and crystal violet was observed only for the SERS-active substrate and it occurred within 200 fs. Since the adsorbed dyes had electronic overlap with the metal substrate at the point of central carbon, considering the difference of the Raman spectra between adsorbed and free dyes, it was suggested that the charge transfer occurred through the central carbon of crystal violet. Furthermore, it was shown that the surface morphology of the substrates is in close correlation with the charge transfer process from its dependence on the preparation method of substrates.

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1. Introduction

The dynamics of photo-excited electrons in the time range from nanoseconds to femtoseconds has attracted much attention, because it is closely related to fundamental processes of photochemical reactions, photoluminescence, and photo-induced effects. Solar cells, photocatalysts and photodevices which utilize these phenomena have been developed for practical use, and surface enhanced infrared absorption [1,2] and surface enhanced Raman scattering (SERS) [3] have often been used as spectroscopic methods for detecting and evaluating adsorbed species on solid surfaces. As a way to clarify fundamental processes of these phenomena, consisting of ultrafast carrier dynamics, researchers have applied time-resolved measurements using an ultrashort pulsed laser for various cases. So far ultrafast processes have been investigated, for example, with regard to titanium oxide [4] and amorphous silicon [5], gallium nitride [6], and gallium arsenide [7] as typical materials of photocatalysts, solar cells and photodevices.

We have developed one of the ultrafast measurement method, the transient reflecting grating (TRG) method with a 200 fs time resolution [8–10], and have investigated

the ultrafast interaction between photo-excited carriers and adsorbed species [11]. Furthermore, the femtosecond time-resolved TRG method was improved to give spectroscopic information by adopting a femtosecond white-light continuum as a probe pulse (TRG spectroscopy) [12]. This improvement has provided detailed information on the excited state of photo-excited carriers. When there are interband transitions in the observed probe wavelength range, carrier density change at an energy state optically coupled to the probe wavelength is selectively detected. Gold has two optical transitions in the observed wavelength range, and the excited carrier density at each state was detected. In a previous article [12], we studied electron–electron and electron–phonon scattering processes at a gold surface. When there are no interband transitions in the observed wavelength range, Drude carrier dynamics is observed for the longer wavelength, while heat dynamics is detected for the shorter wavelength [13].

In this study, we focus on the correlation between photo-excited electron dynamics and the SERS effect. In the SERS effect, Raman intensities of molecules adsorbed on some metals are enhanced to values of 10^4 – 10^6 [14], which have allowed applications to detection of a single molecule [15], new surface scanning method with a spatial resolution of about 100 nm when combined with near-field optical microscopy [16] or atomic force microscopy [17].

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Several reviews on SERS have been published [18,19], but SERS cannot yet be described as a versatile spectroscopic method, mainly because of its low reproducibility. It is well known this is because there are no standardized methods for preparing the metal substrates necessary for the SERS measurement and that their surface structure greatly affects the SERS enhancement. Due to some experimental and theoretical problems including the above-mentioned one, the mechanism is not fully understood, and the enhancement, peak shift, and selectivity of enhanced bands [20] cannot be explained well. Generally, qualitative two mechanisms are proposed as follows [18]. One proposed mechanism is called the electromagnetic (EM) effect, which is caused by conditions of substrates [21]. The nano-scale roughness of a metal surface is coupled with the incident light to excite surface plasmon, resulting in a local enhancement of the electromagnetic field. The other proposed mechanism is called the charge transfer (CT) effect [22,23], which has an explanation analogous to that for the resonant Raman (RR) mechanism [24]. The CT effect is induced by the resonant charge transfer between chemically adsorbed molecules and photo-excited electrons at metal surfaces. Presently, both of the above-mentioned mechanisms are considered to work mutually for the SERS effect. The dynamics of photo-excited electrons is closely related to the SERS effect in both mechanisms, but direct observation of the dynamics is lacking. To deduce the carrier dynamics directly related to the SERS effect, we measured the photo-excited carrier dynamics directly at each energy state for SERS-active and -inactive substrates. We found that ultrafast charge transfer occurred only for SERS-active substrate using a pyridine/gold sample [25]. In this study, we investigated a crystal violet (CV)/gold sample to elucidate more general description in the fundamental processes of the SERS effect by applying a typical dye as adsorbed species, including the consideration of the structure of the adsorbed species. Furthermore, the contribution of the charge transfer in the SERS effect was investigated from the dependence on the substrate preparation method.

2. Experimental

The principle of the TRG spectroscopic method was described previously [12]. The main feature of this method is that the number density of excited electrons in the surface region of solids can be measured selectively at each excited state because the each excited state is resonant with the each probe wavelength. Regarding equipment, we used a regeneratively amplified titanium sapphire laser (CPA-1000: Clark-MXR Inc.) as a light source. The pulse train wavelength was 800 nm, with a repetition rate of 1 kHz and an autocorrelation pulse width of 200 fs in full width at half maximum. The pulse was separated into pump and probe pulses using a partial reflective mirror. The pump pulses were frequently doubled to a wavelength of 400 nm (3.1 eV),

and then further divided into two pulses by a half mirror. The two pump pulses were crossed and irradiated onto the same spot of the sample surface, to coincide in time to form an interference pattern. The probe pulse was focused into heavy water to generate a femtosecond white-light continuum after passing through a computer-controlled optical delay line. Wavelengths used ranged from 450 nm (2.75 eV) to 800 nm (1.58 eV). The white pulse was irradiated at the center of the pump-irradiated spot on the sample surface. The reflected diffracted light was spread like a fan due to the diffraction conditions. It was collected and focused to the entrance of the optical fiber end. The diffraction spectrum was detected using the PMA-11 (Hamamatsu) with the wavelength resolution of 2 nm. As a matter of fact, the probe pulses arrive at the sample at different timing according to the wavelength due to dispersion of the used optical elements. Before the TRG experiments, the difference of the arrival time at the sample for each wavelength was measured using the Kerr effect of a glass. Then, the time 0 of the detected TRG responses for each wavelength were adjusted after data acquisition. From the Kerr measurement, the width of the cross-correlation between the pump and probe pulses was obtained and it was approximately 200 fs at every probe wavelength. A part of the white-light continuum was detected as a reference of the spectral profile, and the TRG spectra were obtained by dividing the diffraction intensity by the reference intensity at each wavelength.

Gold substrates (30 mm × 20 mm, 40 nm thick) were prepared by vapor-deposition on a glass. Generally, a vapor-deposited gold film has a structure with a lot of islands with an average diameter of several tens of nanometers laid on the surface. Two kinds of substrates were prepared by changing the vacuum pressure in the vacuum chamber during deposition at a deposition speed of 0.3 nm/s. Higher pressure deposition makes the island-like structure rougher and such nano-sized roughness induces the SERS effect. In this experiment, one of the substrates was deposited at 2 Pa as a typical SERS-active substrate, while the other was deposited at 1.7×10^{-3} Pa as a typical SERS-inactive substrate. The AFM image of each substrate is shown in Fig. 1. The SERS-active gold film had more islands with an average height of 10 nm in the AFM images than the SERS-inactive one had. CV molecules were adsorbed on the surface by dipping each of the substrates into CV solution for 15 min, and the substrate was washed with pure water to remove impurities and non-adsorbed CV. The SERS effect was confirmed using a Raman spectrometer with argon laser excitation (488 nm). To prepare several different SERS-active substrates with different morphology, we prepared the substrates at different deposition speed (0.1, 0.3, 0.5, 1, 2 nm/s), fixing the vacuum pressure in the chamber to 2 Pa. It is supported that electron dynamics related to both chemical (charge transfer) and electromagnetic effects (localized plasmon) are included in the TRG spectra. But in this experiment, we used the pump wavelength of 400 nm, which is quite away from the excitation wavelength of

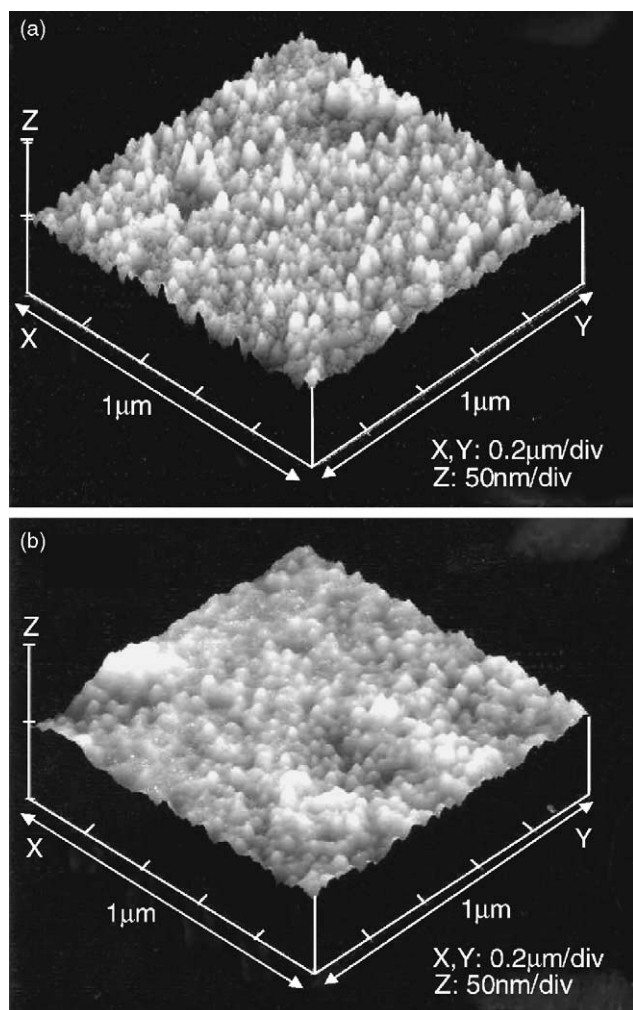


Fig. 1. AFM images of vapor-deposited gold films (40 nm thick) used as substrates for inducing and not inducing the SERS effect. Two kinds of gold films were prepared by changing the vacuum pressure during deposition. One of them was deposited at 2 Pa, and was SERS-active, (a), while the other was deposited at 1.7×10^{-3} Pa, and was SERS-inactive, (b).

localized plasmon, and so only the chemical effect can be measured.

3. Results and discussion

Following the same procedure of the previous study on the gold/pyridine, four kinds of samples, SERS-active gold substrates with adsorbed CV, without it, and SERS-inactive gold substrates with it, and without it were prepared. As expected, no enhancement of the CV spectrum was observed for only the substrates, and the CV-adsorbed SERS-inactive substrate. Only the SERS-active substrate with CV clearly showed an enhancement of the Raman intensity of CV.

Before comparison of the TRG spectra among the samples, a TRG spectrum for only a substrate, that is, a gold film, was observed. The decay profile of the spectrum and

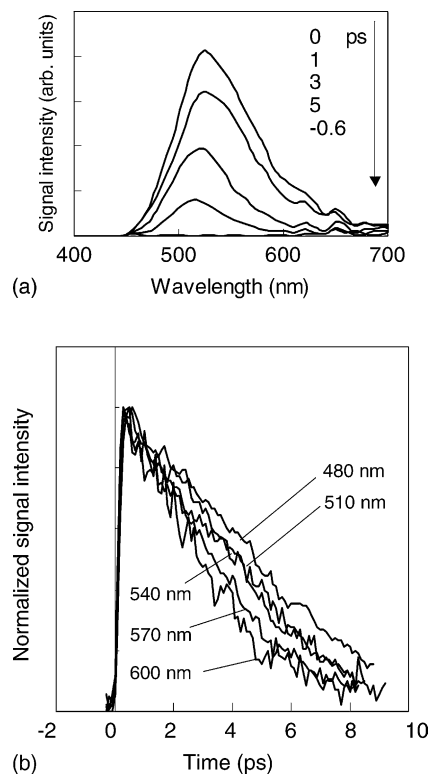


Fig. 2. A transient reflecting grating (TRG) spectrum only for the gold film which was used as a substrate. The gold film was prepared by vapor-deposition and had a thickness of 40 nm. The decay of the TRG spectrum intensity is shown in (a), and the normalized TRG responses at various probe wavelengths are shown in (b).

the normalized temporal responses at various probe wavelengths are shown in Fig. 2. The TRG spectrum had a main peak around 520 nm and a shoulder around 600 nm just after photo-excitation, and the signal intensity decayed about 3–5 ps according to the probe wavelength, defining the decay time as the time when the signal intensity is reduced to the half of the maximum. We previously found that the peak and shoulder corresponded to the number of photo-excited electrons at L and X in the band structure of gold, respectively [12], because the main interband transition from the d-band to E_F at 520 nm (2.5 eV) and the minor interband transition at 600 nm (1.9 eV) [25–27] are in good agreement with the position of the peak and shoulder in the TRG spectrum. The temporal response showed a linear decay [28–30]. The dependence of the decay time on the probe wavelength shows that excited electrons decayed for different decay times according to the excited energy states. The decay curve corresponded to the decrease of photo-excited electron density due to the electron temperature decrease process caused by electron–phonon scattering. It has been proved using the two-temperature model that this component decays linearly, when the gold film is thinner than 100 nm and the temperature of photo-excited electrons is much higher than that of phonons [31]. The SERS-active and SERS-inactive gold substrates showed no differences

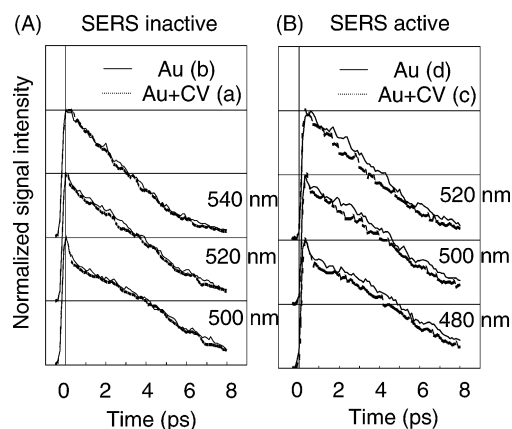


Fig. 3. The normalized TRG responses at various probe wavelengths for the four samples; SERS-inactive substrates with CV (a) and without it (b), shown in Fig. 3A; and SERS-active substrates with CV (c) and without it (d) shown in Fig. 3B.

in the intensity profiles and decay times of the TRG spectra. The result indicates that both substrates have the same electronic property, though each of them showed different surface structure for roughness, as seen from the AFM images.

For each of the substrates, we compared normalized TRG responses between the presence and absence of adsorbed CV. The sets of transient responses for the SERS-inactive substrates with the presence (a) and absence (b) of CV are shown in Fig. 3A, and those for the SERS-active substrates with the presence (c) and absence (d) of CV are shown in Fig. 3B. No difference in the TRG spectra for SERS-inactive substrates was observed between (a) and (b), but there was a slight difference in the decay time between (c) and (d), where the TRG signal of (c) decayed a little faster than those of (d) for every wavelength. This result indicates that the number of excited electrons decreases faster for the SERS-active gold substrate with CV than without it, while there was no difference in the electron dynamics for the SERS-inactive gold substrate, whether there were adsorbed species or not. The decrease of the decay time was also observed for the pyridine/gold sample [25]. When the carrier dynamics for CV is the same with that for pyridine, it can be considered that the initial density had already decreased before the process of electron–phonon scattering began. This interpretation means there is another relaxation channel between gold and adsorbed CV in the faster time range. For gold, electron–electron scattering occurs within several hundred femtoseconds before electron–phonon scattering, [12,30,32] and so the SERS-related new channel is competing with electron–electron scattering. To confirm the validity of the interpretation, a TRG spectrum intensity at the delay time of zero was investigated because a TRG spectrum intensity reflects the density of excited electrons at each energy state and so we can reason the behavior of excited electrons before the electron–phonon scattering by examining the TRG spectra just after photo-excitation [25]. Fig. 4

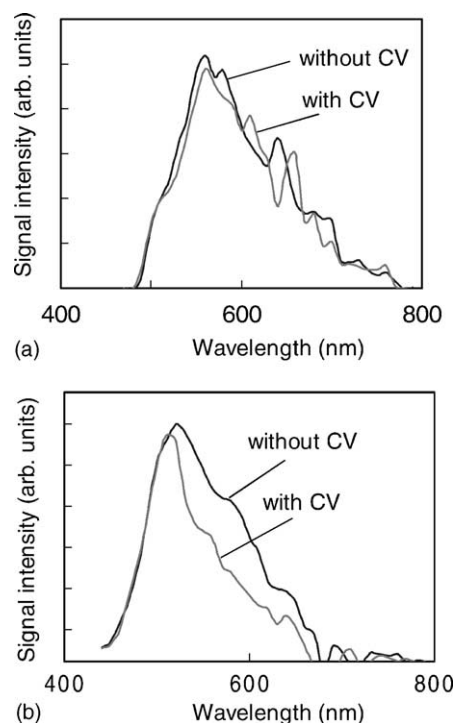


Fig. 4. TRG spectra just after photo-excitation by pump pulses for (b) SERS-active substrates with and without CV and for (a) SERS-inactive substrates with and without CV.

compares TRG spectra just after photo-excitation for only gold and CV-adsorbed gold for the SERS-active substrate. In the wavelength range from 500 to 650 nm, the spectrum intensity for the CV-adsorbed gold was greatly reduced only for the SERS-active substrate. This indicates that the density of excited electrons has been reduced through some energy states within the time resolution of the apparatus. Thus, we conclude that the electronic interaction between gold and CV occurred within 200 fs, as is the same with the pyridine.

To speculate which part of the CV molecules is involved in the ultrafast charge transfer, the Raman shift of each band was investigated in detail, and it was found that several specific peaks showed remarkable shifts in comparison with the Raman spectrum of only CV [33]. The wave number of their peaks are summarized in the Table 1, in comparison with those of the resonant Raman spectrum. Mainly shifted peaks

Table 1

The wave numbers of the Raman shift of crystal violet which were different for the surface enhanced Raman scattering (SERS) and resonant Raman (RR) scattering

Assignment	RR (cm ⁻¹)	SERS (cm ⁻¹)
In-plane Ph–C–Ph bend	334	344
N-phenyl stretching	1377	1366
	1390	1395
Ring C–C stretching + ring deformation	1489	1482

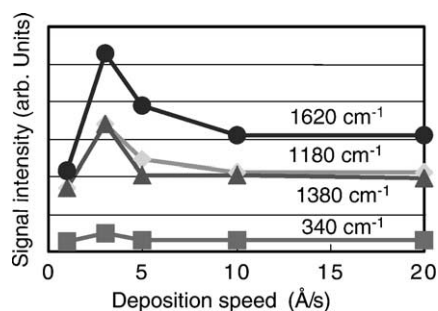


Fig. 5. Intensity dependence of several peaks of CV on the various substrates which were prepared under different deposition speed (0.1, 0.3, 0.5, 1.0, 2.0 nm/s) at constant vacuum pressure, 2 Pa in the chamber.

were related with the central carbon and three nitrogens at the end of the phenyl group. This result indicates that the charge of the central carbon and the lone pair of each nitrogen had some interaction with the gold substrates. Then, CV molecules are assumed to be adsorbed on the gold substrates with a flat structure. Since the places of the nitrogens had originally excess charges, photo-excited electrons might be transferred through the central carbon which had originally the positive charge.

Furthermore, the dependence of the charge transfer process on the surface morphology of the gold substrates was investigated. Gold substrates were prepared at 2 Pa under various deposition speeds because it is well known that vapor-deposited films have different morphology according to the speed. Each surface was measured by AFM, and clear differences of the surface structure were not observed for the island size. However, the Raman intensity of CV for each substrate showed a dependence on the deposition speed, shown in Fig. 5. The Raman intensity showed a maximum at the deposition speed of 0.3 nm/s. It was supposed that the deposition speed changed the surface structure on the smaller scale than the island size. The TRG spectra for each substrate for the presence and absence of CV were shown in Fig. 6. The partial reduction of the spectrum intensity, corresponding to the charge transfer, was increased in the order of the Raman signal intensity. From this result, three conclusions can be made. First, the charge transfer detected by the TRG spectroscopy is directly related to the SERS enhancement. Second, the SERS enhancement increases with the quantity of the charge transfer. Finally, though it is apt not to be noticed, the SERS enhancement was observed due to EM enhancement even for the substrate with the lowest enhancement, prepared at 2 nm/s. However, the TRG spectra for 2 nm/s did not show any difference for the presence or absence of CV. This result shows that the charge transfer detected by the TRG spectroscopy is purely related to the CT enhancement. So, it can be said that the TRG spectroscopy has a possibility of separating the EM and CT enhancements which have been difficult to be separated, especially about the CT enhancement due to smaller enhancement than the EM enhancement.

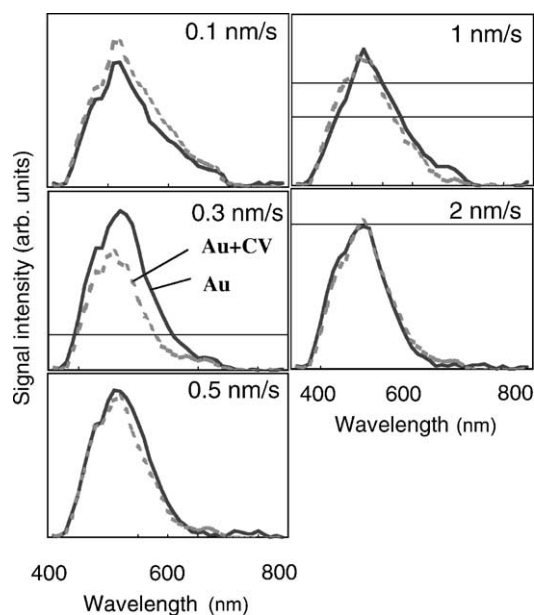


Fig. 6. TRG spectra just after photo-excitation by pump pulses for the presence and absence of CV for various substrates prepared as the same method with Fig. 5.

4. Conclusion

A charge transfer from the SERS-active substrate to the chemisorbed dyes was detected, and the process was almost the same as the case for the SERS-active substrate and pyridine. Although it is too much to make a conclusion from the results only for CV and Py molecules, no clear dependence of the spectra on the chemisorbed species indicates that the SERS related charge transfer has a close correlation with the property of substrates. On the other hand, these dyes may accidentally have a similar adsorption energy state in the wavelength range from 500 to 650 nm. Similar experiments are necessary for other dyes to confirm the dependence of the adsorption state on the kind of dyes or the property of SERS-active substrates. As a support of the interpretation, it was found that the SERS related charge transfer depended on the preparation method of the substrates. The TRG spectroscopy, one of the ultrafast spectroscopic method, can deduce only the charge transfer process directly, and so such studies will make a prospect for the SERS mechanism, which has been a controversial problem for more than 20 years.

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