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Different behaviour of molecules in dark SERS state on colloidal Ag nanoparticles estimated by truncated power law analysis of blinking SERS

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Abstract

From single colloidal Ag nanoaggregates that covered with a large or small amounts of citrate anions, blinking surface-enhanced Raman scattering (SERS) of anionic thiacyanine were measured and analyzed by a truncated power law. The power law without and with an exponential function reproduces probability distribution for bright and dark SERS events versus their duration times, respectively. On the Ag surface except for junctions of the nanoaggregate with a large or small amount of the citrate anions, two-dimensional fast or one-dimensional slow random walk of the anionic thiacyanine, respectively, is estimated by the exponents and the truncation times in the power law for the dark SERS events. On the other hand, the power law exponents for the bright SERS events were derived to be similar value, indicating the similar molecular random walk nearby the junction, which may be dominated evenly by surface-plasmon-enhanced electromagnetic field on the same-sized Ag nanoaggregate. Thus, not only the bright SERS, but also the dark SERS molecular behaviour on the Ag surface was investigated by the truncated power law analysis.

Keywords: Surface-enhanced Raman scattering, blinking, colloidal silver nanoaggregate, single molecule detection, power law,

Introduction

Molecules adsorbed on noble metal surface cause interesting phenomena related to catalysis and plasmonics;[1,2] for example, their Raman scattering cross-section is enormously enhanced, which is called surface-enhanced Raman scattering (SERS).[3–5] On the nanoparticle, conduction band electrons are resonantly oscillated by excitation light (localized surface plasmon resonance: LSPR), and then an electromagnetic (EM) field is enormously enhanced, especially at a junction of aggregate of the nanoparticles. Thus, SERS is emitted from the localized area rather than the whole nanoaggregate. At the single molecule level, the molecule can enter and exit the enhanced EM field at the nanometer-sized junction, and then blinking SERS are observed.[6–27] The binking hinders application of SERS to single molecule detection, because it deteriorates the reproducibility and signal-to-noise ratio of the spectra, whose sharp peaks of the vibrational modes can provide detailed information about structure and dynamics of the single molecule on the surface.

The blinking SERS have been analyzed recently by using a power law statistics,[6,18–22] which originates from distribution of the first passage time required for a random walker to return to its starting point.[28] The probability distributions of bright and dark SERS events against their duration times are reproduced by a power law and a truncated power law, respectively.[6,19–22] In a different way of blinking fluorescence from a single semiconductor quantum dot (QD),[28–31] the power law exponents for blinking SERS are often deviated from –1.5,[6,19–22] which is derived from one-dimensional random walk model.[28] In our previous study, a truncated power law analysis of blinking SERS from a dye molecule adsorbed on a single Ag nanoaggregate has been given by changing excitation wavelength, the intensity, and LSPR wavelength of the Ag nanoaggregate, which affect the enhanced EM field around the juction.[6,19–22] It is noted that the power law exponents for bright SERS events correlated with those for dark SERS events, although the former are independent of the latter.[6,21,22] Into the junction, a single molecule can be optically trapped by the enhanced EM field,[32] and thus the blinking SERS, both the active and inactive events, are influenced through the photo-dependent behaviour of the molecule around the junction.[6,14–16,20–22] By a super-resolution SERS imaging, the behaviour of the molecule nearby the junction has been revealed precisely.[25–27] However, photo-independent behaviour of a few molecules on the metallic surface in a solution, namely, at a solid-liquid interface, has been hardly investigated. It can play an important role not only in blinking SERS,[6,16,17] but also in catalysis.[1]

In the present study, we used the same-sized colloidal Ag nanoparticles that covered with a large and small amount of citrate anions for measurement of blinking SERS. Colloidal metal nanoparticles have been widely used for not only SERS,[3–5] but also plasmonics and catalysis.[1,2] SERS is strongly influenced by aggregation of the colloidal nanoparticles and adsorption of molecules on the negative-charged metal surface via the stabilizer such as citrate anion.[33–35] From the Ag nanoaggregates with a large and small amount of the citrate anions, the power law exponents for the dark SERS events were derived to be different value, indicating different molecular behaviour on the Ag surface except for the junction, while those for the bright SERS events were similar value. Moreover, the power law for the dark SERS events from the Ag nanoaggregates with a larger amount of the citrate anions was truncated at the shorter tail, suggesting the short passage time of the dark SERS molecules to reach the junction. Thus, the truncated power law analysis can investigate random walk of dark SERS molecule, which can be barely detected even by a super-resolution SERS imaging.[25–27]

Experiments

A citrate-reduced Ag colloidal suspension was prepared by Lee-Meisel method.[36] After the heating of 150 mL of the precursor for an hour, we had kept 10 and 140 mL of the same suspension in iced water and at room temperature (25 ºC) overnight, respectively. We used 3,3′-disulfopropylthiacyanine (TC) triethylamine as purchased from Hayashibara Biochemical Laboratories (Japan). A stock aqueous solution of the anionic TC dyes (25 μM), a NaCl aqueous solution (100 mM), and the Ag colloidal suspension were mixed at a volume ratio of 1:1:2 at room temperature. In this stage, it was roughly estimated that the Ag adsorbs 0.46 μM of the TC dyes by an absorption spectrum of the sample after centrifugation (for more details, see Fig. S1 and the text in the ESI). The sample solution was spin-coated on a glass plate and rinsed with water and acetone. Then the dyes are washed off the glass plate, while the adsorbates on the Ag may be further decreased. An aliquot of a 1 M NaCl solution was dropped on the glass plate to immobilize the sample Ag nanoaggregates on the surface. In the solution, a drastic change of LSPR of the Ag nanoaggregates was not observed by a dark-field observation for 20 min (for more details, see Fig. S2 and the text in the ESI) unlike the report on effect of the surrounding.[37] This glass plate was covered with another glass plate to prevent the solution from evaporating. The details of the experimental setup are described elsewhere.[21] In brief, the Ag nanoaggregates with adsorbed TC on an inverted microscope (Olympus, IX-70) were excited using a 458 nm line of an Ar ion laser whose intensity of 8—10 mW corresponding to power density of 80—100 W cm^{-2}. The SERS emissions of a single Ag nanoaggregate with adsorbed the TC were collected with an objective lens (Olympus, LCPlanFl 60×, NA 0.7) and led to a polychromator (Acton, Pro-275) coupled to a thermoelectrically cooled CCD (Andor, DV434-FI) through a notch filter and a pinhole. Movies of the blinking SERS were taken for 20 min by the inverted microscope coupled with a cooled digital CCD camera (Hamamatsu, ORCA-AG), which has a time resolution of 61 ms. Absorption spectra of the Ag colloidal suspension were acquired by a UV-Vis spectrometer (Shimadzu, UV-3101PC). Size and zeta potential of the Ag colloidal nanoparticles in the suspension were measured by a light scattering photometer (Otsuka Electronics, ELSZ-2KG). The Ag nanoaggregates were observed by a scanning electron microscope (SEM) (JEOL, JSM-6700FZ).

Results and Discussion

Figure 1 shows that absorption spectra of the Ag colloidal suspension had been kept in iced water and at room temperature overnight are almost the same. Also averages of the Ag nanoprticle sizes, which affect their LSPR wavelengths,[34,38,39] in the suspensions are measured to be the same within their standard errors as expressed in Table 1. Figure 2 displays typical SEM images of Ag nanoaggregates that consists of a small number of the nanoparticles in the colloidal suspension had been kept in iced water and at room temperature overnight. There was no difference between two kinds of the Ag nanoaggregates in terms of their size, shape, and so on. Thus, the Ag nanoparticles in two kinds of suspension have the same LSPR property, because we divided the same suspension after the synthesis by the heating for an hour. On the other hand, Table 1 indicates that zeta potential of the Ag colloidal nanoparticles had been kept at room temperature is more negative than that in iced water; namely, the former are covered with a larger amount of citrate anions than the latter. The reason is that the citrate anions as stabilizers of colloid, which chemisorbed onto the Ag surface,[34,35] are increased at higher temperature, because chemisorption takes place through transition state.

Figure 3a exhibits SERS spectrum of the anionic TC adsorbed on the single Ag nanoaggregate like Figure 2. The prominent peaks appeared at similar wavenumbers to those in a conventional Raman spectrum of the TC powder as shown in Figure 3b. It was observed and has been already reported that some SERS peaks disappear and slightly shift from the corresponding Raman peaks.[6–24] Thus, the blinking SERS likely originate not from amorphous carbon formed by photo- and thermo-degradation,[40] but from the anionic TC molecules. In the report on SERS spectra from various kinds of single molecule, there is the difference in the blinking behaviour between totally and nontotally symmetric modes due to vibronic coupling.[24]

On the other hand, there is no cross correlation between them of Fe-protoporphyrin IX, and their power law exponents for the dark SERS events are derived to be similar values.[18,22] Thus, also the mode dependence of blinking SERS by a truncated power law analysis is interesting. However, time-resolved SERS spectra cannot have high time resolution for an accurate fitting by a truncated power law in log-log plot. Indeed, the dark events in the blinking SERS of the each mode were analyzed by a power law without an exponential function in semi-logarithm plot.[18] Therefore we have used the integrated total emission intensity, which has enough time resolution for the truncated power law analysis.

Figure 4a displays a time profile of the integrated total emission intensity from a single Ag nanoaggregate with adsorbed the anionic TC. It is rationalized that the time-profile as Figure 4a represents the blinking SERS intensity by following reasons. The background emission, which may originate from surface-enhanced fluorescence and so on, coincides with SERS signal.[16,41] Moreover, fluorescence is hardly emitted, because molecules on a metallic surface take place an energy transfer to the metal,[42] and this TC molecule barely absorbs this excitation light at 458 nm.[23] Even if fluorescence is emitted, it may be too weak compared with SERS or continuous because of absence of surface-enhancement for a few molecules or many fluorophores, respectively. The continuous change of the baseline in Figure 4a was subtracted by a polynominal function. Figure 4b exhibits the log-log plot for probability distributions of the bright and dark SERS events against their duration times. Probability distribution for a duration time *t* of bright or dark SERS event is represented by

$$P_{\mathrm{on,off}}(t) = \sum_{t'=t} n_{\mathrm{on,off}}(t')/t, \qquad (1)$$

where $n_{\mathrm{on,off}}(t')$ are the number of bright or dark SERS events against their duration times, respectively.[22] For the bright SERS events, the log-log plot yields a line and is given by

$$P_{\mathrm{on}}(t) = At^{\alpha_{\mathrm{on}}}. \qquad (2)$$

On the other hand, the probability distributions of dark SERS events against their duration are reproduced by a truncated power law as

$$P_{\mathrm{off}}(t) = At^{\alpha_{\mathrm{off}}}\exp(-t/\tau), \qquad (3)$$

where $P_{\mathrm{on,off}}(t)$ are probability distributions of the bright and dark SERS events, $\alpha_{\mathrm{on,off}}$ are power-law exponents for the bright and dark SERS events, respectively, τ is a truncation time in the power law, and A are coefficients for normalization.

Figure 5 shows histograms of the exponents in the power law that reproduces probability distributions of the bright and dark SERS events against their duration for TC adsorbed on single Ag nanoaggregates with various sizes and shapes. The power law exponents were derived from 135 and 213 single Ag nanoaggregates had been kept in iced water and at room temperature overnight, respectively. For the bright SERS events, the maxima of the histograms of the power law exponents, α_{on}, appear at the same value, and the averages are almost the same value within their standard errors as expressed in Table 2. On the other hands, α_{off} of the Ag nanoaggregates from the colloidal suspension had been kept at room temperature overnight are smaller than those in iced water as expressed also in Table 2. It is noted that the present result is different from the opposite trend of α_{on} to α_{off} in the previous reports; namely, the α_{on} and α_{off}

were simultaneously increased and decreased, respectively, by an approach of LSPR peaks of the Ag nanoaggregates to the excitation wavelength or as the excitation light becomes stronger.[6,21,22] The deeper and wider optical trapping potential well due to the surface-plasmon-enhanced EM field (the latter means narrower dark SERS area) lead the molecules to stay in bright and dark SERS state for long and short time, which represented by the large α_{on} and small α_{off}, respectively.[21]

In the present case, the similar α_{on} (Figure 5a) may be induced by the same LSPR property of two kinds of the Ag colloidal suspension (Figure 1) due to the same averaged sizes of the nanoparticles (Table 1). In the histogram of α_{off} from the Ag colloidal nanoparticles had been kept in iced water and at room temperature overnight (Figure 4b), the maxima appear at –1.7 and –1.1, respectively. The power law exponents are derived to be –1.5 and –1 from one- and two-dimensional random walk model, respectively.[28] On the Ag colloidal nanoparticles had been kept in iced water and then adsorbed a small amount of the citrate anions, the TC molecules may be attracted one-dimensionally by the surface-plasmon-enhanced optical trapping potential well. On the other hand, the anionic TC, which has one positive-charged nitrogen atom and two -SO_3^-, can jump around two-dimensionally via a large amount of the citrate anions on the Ag colloidal nanoparticles had been kept at room temperature.

Figure 6 shows histograms of the truncation times in the power law for the dark SERS events. The truncation times were derived from 96 and 194 single Ag nanoaggregates had been kept in iced water and at room temperature overnight, respectively. The maximum of the histograms of the Ag nanoaggregates from the colloidal suspension had been kept at room temperature overnight appears at a shorter truncation time than that in iced water. Also the medians of the truncation times show this trend as summarized in Table 3. Though the averages of the truncation times are similar within their standard errors as expressed in Table 3, the probability distributions of dark SERS events from the Ag colloid had been kept in iced water overnight cannot be reproduced more often than those at room temperature by the truncated power law (Table 3); namely, the percentage of very long truncation times, which were not used for derivation of the average, of the Ag colloid had been kept in iced water are higher than that at room temperature. Thus, we conclude that the truncation times of the Ag nanoaggregates had been kept at room temperature overnight are shorter than those in iced water.

The truncation at a tail of the power law for the blinking is originated from random walk on parabolic potential surfaces against reaction coordinate for emissive and non-emissive states.[43] According to the differential equation for classical diffusion on a harmonic potential of a diffusion-controlled electron-transfer model for a single QD,[43] the truncation time is given by

$$\tau = \frac{\Gamma}{E_a / 2k_B T}, \qquad (4)$$

where Γ is the random walk time to overcome the energy-barrier between emissive and non-emissive states, E_a; namely, the truncation requires the high energy-barrier and a fast random walk to overcome the energy-barrier. In the case of a QD, the energy-barrier between emissive (electron–hole pair) and non-emissive states (photo-ionized state) derives from Marcus theory.[43] In blinking SERS, the energy-barrier may be attributed to a periodic enhanced EM field around the junction due to coupling of multipollar surface plasmon resonance, which is accelerated by an excitation at a shorter wavelength.[22,44,45] The energy-barrier is not likely influenced by the amount of the citrate anions. Thus, the short truncation time suggests fast random walk of the anionic TC molecules on the Ag surface with a large amount of the citrate anions. This may be consistent with the previous result, in which the truncation times were shortened at lower concentration of the anionic TC,[22] in terms of a ratio of the stabilizer to the adsorbate.

In the present study, the behaviour of the anionic TC molecules on the Ag nanoparticles, which is influenced by the amount of the citrate anions, is estimated by the power law analysis of the blinking SERS. Recently, a super-resolution SERS imaging has revealed precise behaviour of the molecule nearby the junction of the Ag nanoaggregate.[25–27] However, it is difficult to detect the molecular behaviour on the Ag surface except for the junction using a super-resolution SERS imaging, although centroid positions of SERS and luminescence on an Ag nanoaggregate have been revealed.[26] Even by averages of duration times of dark SERS events in a similar way of those of bright SERS events,[6,16,20] behaviour of molecules in dark SERS state cannot be investigated. The reason is that the averages cannot be derived; namely, total duration times of dark SERS events on the single Ag nanoaggregates are decreased by an increase in the number of the events, while total duration times of bright SERS events are increased.[6]

Conclusion

The Ag colloidal nanoparticles that covered with a small and large amounts of the chemisorbed citrate anions were prepared by they had been kept in iced water and at room temperature overnight after the heating, respectively. The Ag colloids show the same averaged sizes and LSPR wavelengths. From the nanoaggregates had been kept in iced water and at room temperature, the power law exponents for the dark SERS events, α_{off}, were derived to be –1.7 and –1.1, which are similar values of –1.5 and –1 and attributed to one- and two-dimensional random walk of the anionic TC molecules via a small and large amounts of the citrate anions, respectively. Thus, the molecular random walk on the Ag surface except for the junction is influenced by the amount of the citrate anion. On the other hand, the similar molecular behaviour at the junction of the nanoaggregate with a small and large amount of the citrate anions is indicated by the similar α_{on}. Thus, the molecules that differently behave in the dark SERS state are evenly dominated by the surface-plasmon-enhanced EM field through the optical trapping potential well at the junction of the same-sized nanoaggregate. The truncation times in the power law for the dark SERS events from the Ag colloids had been kept at room temperature are shortened. This suggests that the anionic TC molecules on the Ag surface reach the junction more quickly via a larger amount of the citrate anions. It is noted that the truncated power law analysis of the blinking SERS can estimate the behaviour of molecules on the metal surface even in dark SERS state, which can be barely investigated even by a super-resolution SERS imaging and the averaged duration times.

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Table 1 Averaged sizes and zeta potential of the citrate-reduced colloidal Ag nanoparticles in the suspension had been kept in iced water and at room temperature (R.T.) overnight. The values in parentheses are their standard errors.

	Size	**ζ-potential**
Iced water	54.7 (0.1) nm	–47.4 (0.2) mV
R.T.	54.8 (0.4) nm	–55.8 (2.3) mV

Table 2 Averaged exponents in the power law for the bright and dark SERS events (α_{on} and α_{off}, respectively) of TC adsorbed on 135 and 213 single Ag nanoaggregates from the colloidal suspension had been kept in iced water and at room temperature (R.T.) overnight, respectively. The values in parentheses are their standard errors.

	α_{on}	α_{off}
Iced water	–2.52 (0.03)	–1.72 (0.02)
R.T.	–2.51 (0.02)	–1.44 (0.02)

Table 3 Medians and averages of truncation times in the power law for the dark SERS events of TC adsorbed on 96 and 194 single Ag nanoaggregates from the colloidal suspension had been kept in iced water and at room temperature (R.T.) overnight, respectively. The values in parentheses are their standard errors. The

right column shows percentages of the dark SERS events whose probability distribution cannot be reproduced by a truncated power law.

	Median	**Average**	**Fail in the reproduction**
Iced water	42 s	63 (6) s	39/135 = 29 %
R.T.	36 s	64 (5) s	19/213 = 9 %

Figure captions

Figure 1 Absorption spectra of the citrate-reduced Ag colloidal suspension had been kept in iced water and at room temperature (R.T.) overnight.

Figure 2 Scanning electron microscope images of Ag nanoaggregates that consists of a small number of the nanoparticles in the citrate-reduced colloidal suspension had been kept (a) in iced water and (b) at room temperature overnight.

Figure 3 (a) SERS and (b) conventional Raman spectra of 3,3′-disulfopropylthiacyanine adsorbed on single Ag nanoaggregate and the powder, respectively. Inset: chemical structure of 3,3′-disulfopropylthiacyanine triethylamine.

Figure 4 (a) A time-profile of the SERS intensity from the single Ag nanoaggregate. (b) Probability distributions of the bright and dark SERS events against their duration times.

Figure 5 Histograms of exponents in the power law for the (a) bright and (b) dark SERS events (α_{on} and α_{off}, respectively) of TC adsorbed on single Ag nanoaggregates from the citrate-reduced Ag colloidal suspension had been kept in iced water and at room temperature (R.T.) overnight. The bin widths are 0.2.

Figure 6 Histograms of truncation times, τ, in the power law for the dark SERS events of TC adsorbed on single Ag nanoaggregates from the citrate-reduced Ag colloidal suspension had been kept in iced water and at room temperature (R.T.) overnight. Inset: the enlargement. The bin widths are 10 s.

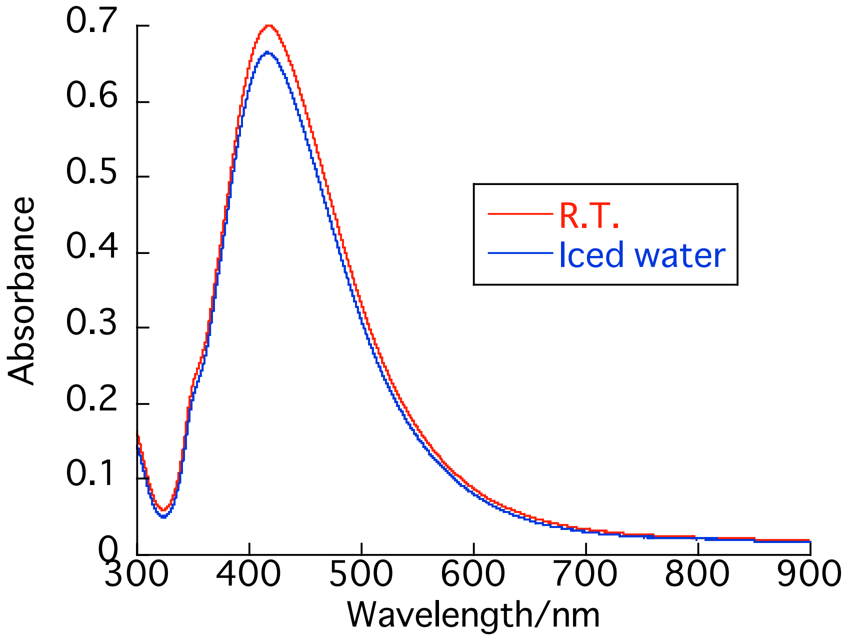


Figure 1 Y. Kitahama et al.

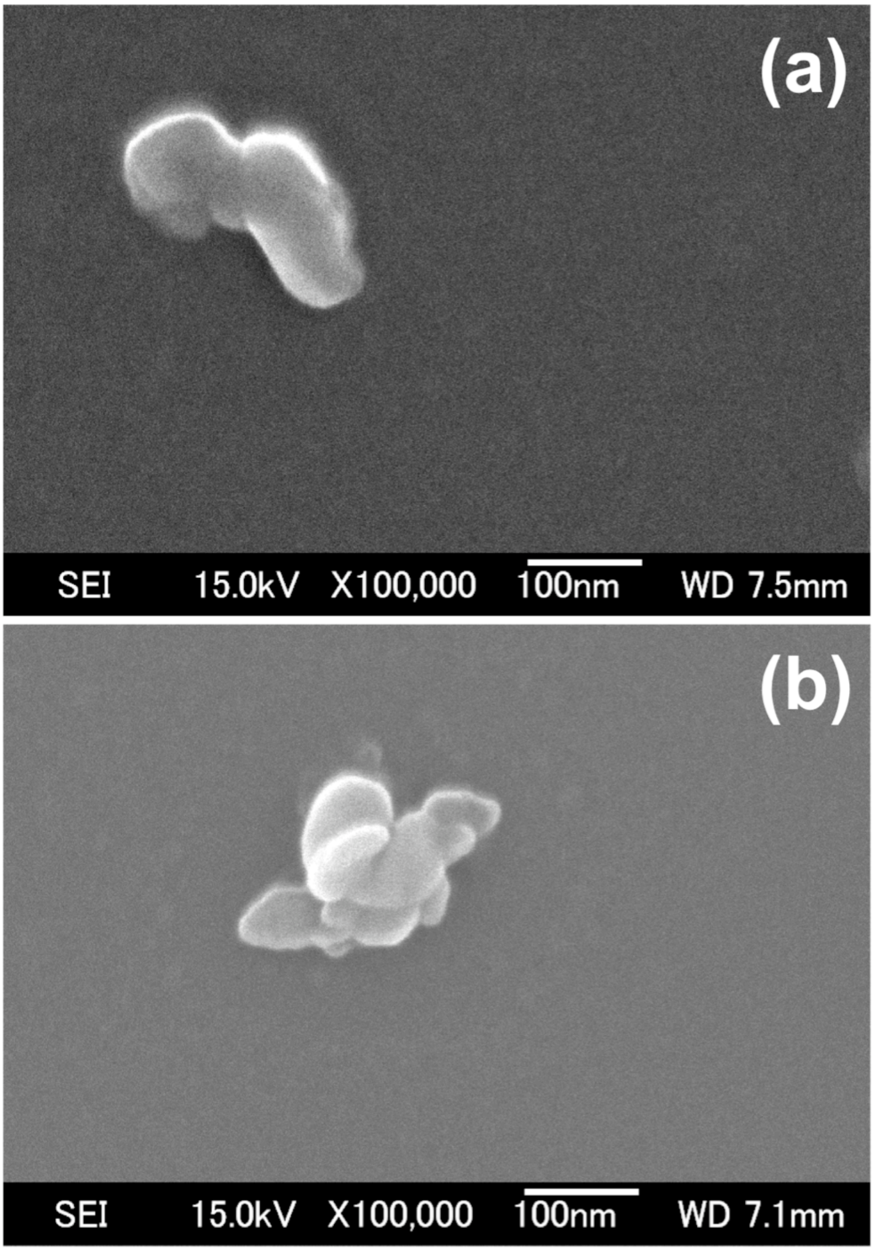


Figure 2 Y. Kitahama et al.

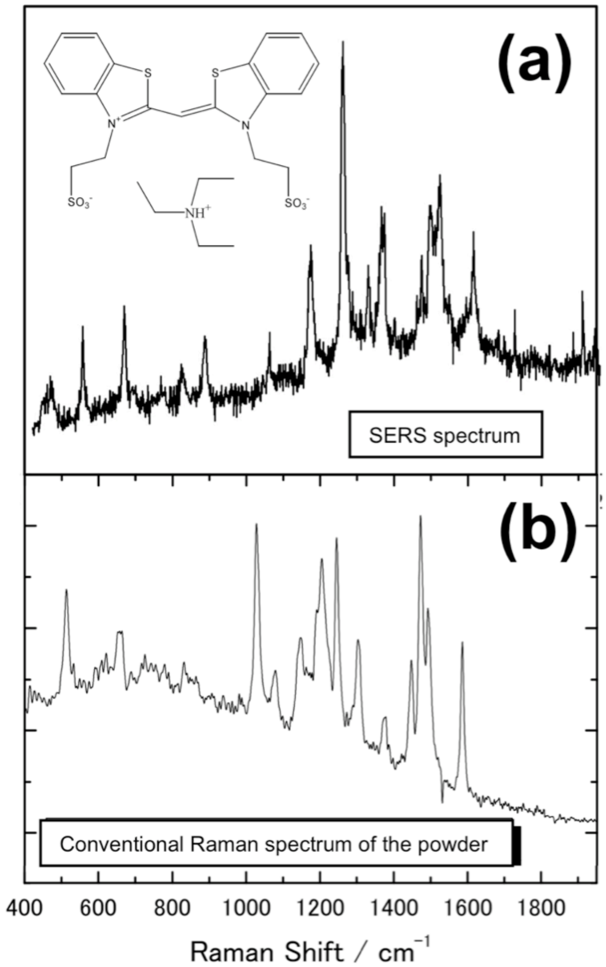
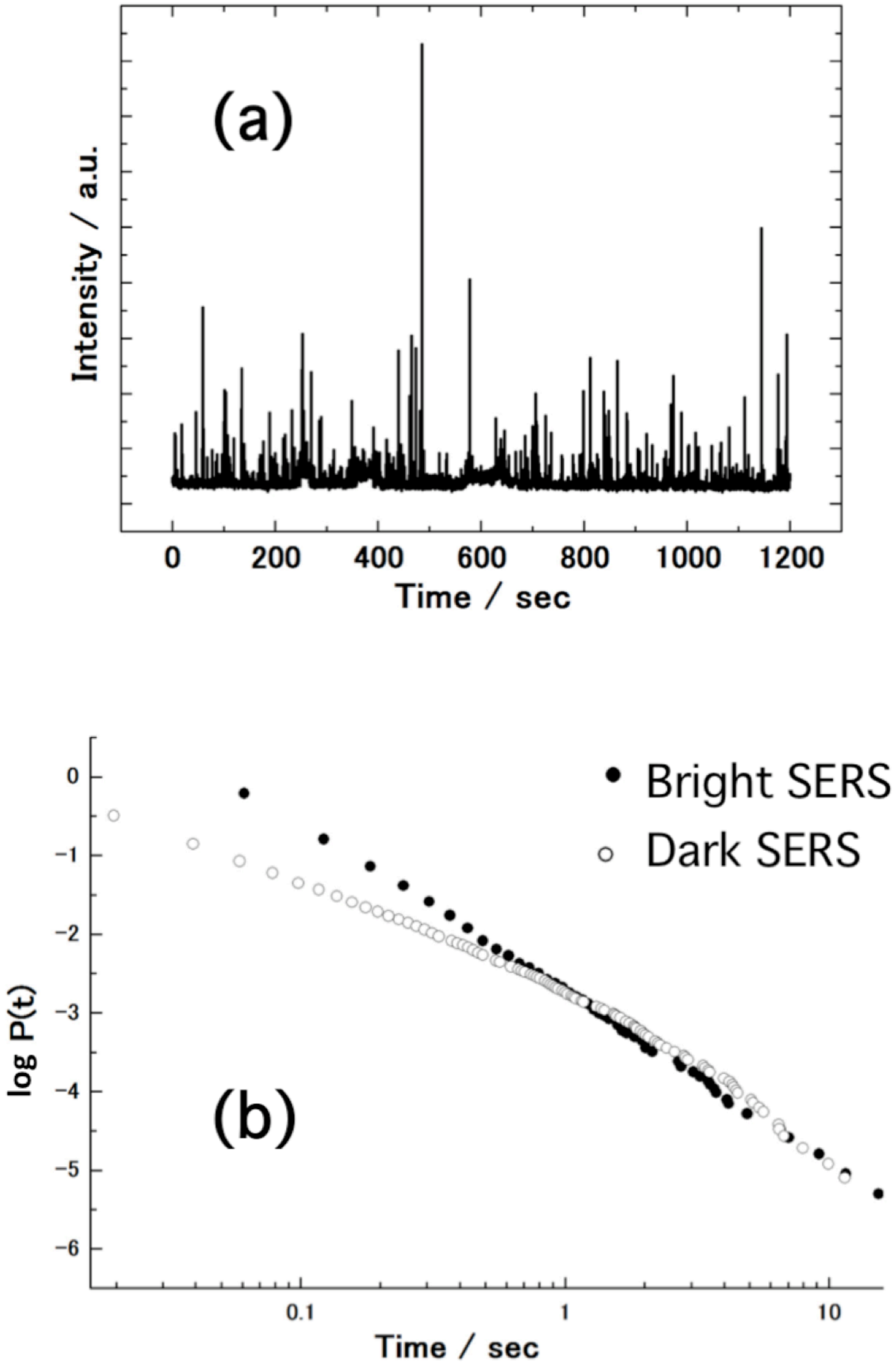


Figure 3 Y. Kitahama et al.



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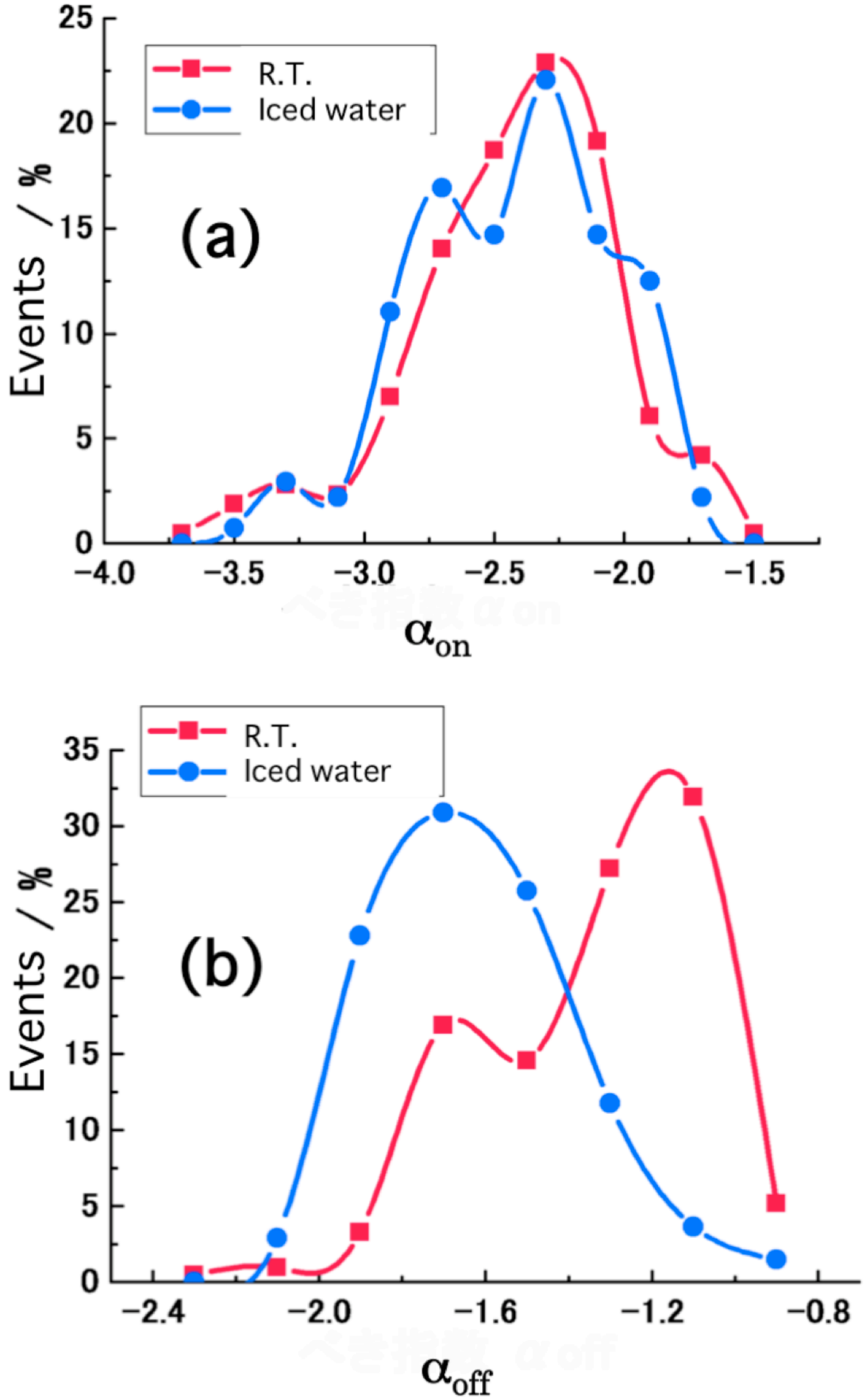


Figure 5 Y. Kitahama et al.

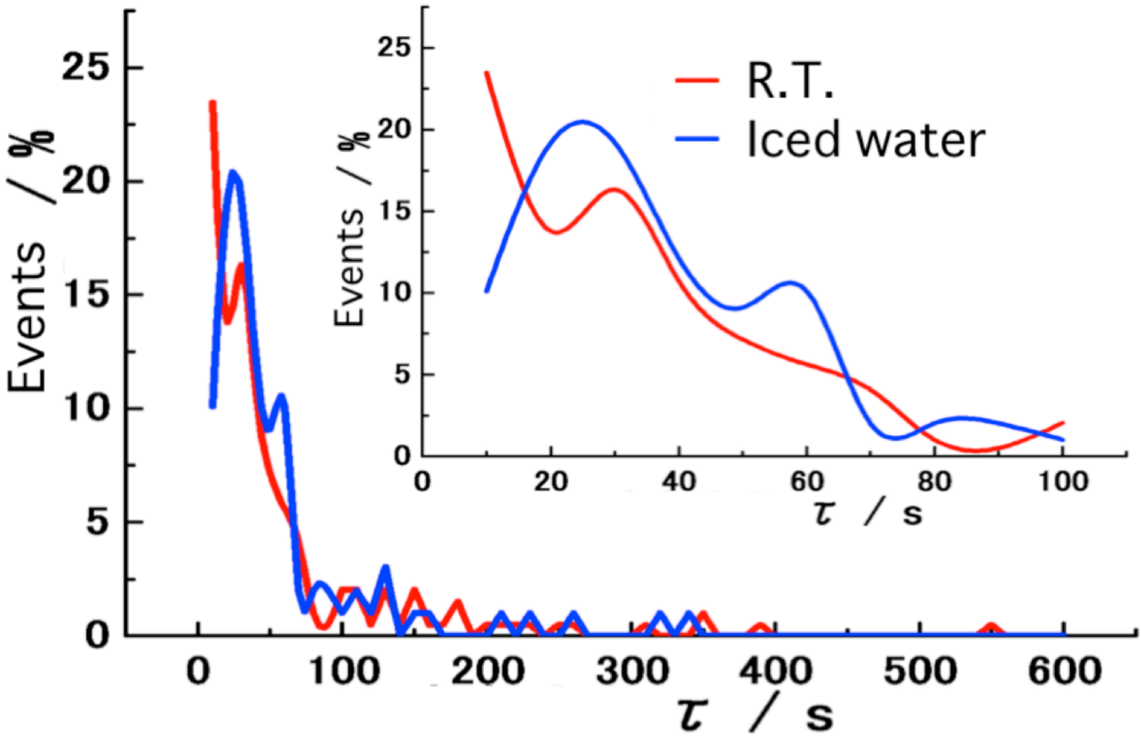
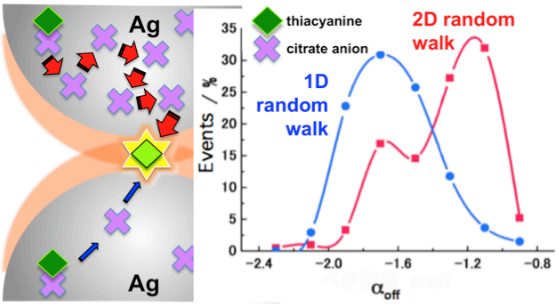


Figure 6 Y. Kitahama et al.

TOC graphic



Power law analysis of blinking SERS can estimate behaviour of thiacyanine in dark SERS state on the Ag surface with a large or small amount of citrate anions.