Blinking surface-enhanced Raman scattering

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1. Introduction

Surface-enhanced Raman scattering (SERS) is sensitive spectroscopy enough to measure a small number of molecules because of localized surface plasmon resonance of a noble metal nanostructure. At a single molecule level, however, blinking SERS, which deteriorates the reproducibility and signal-to-noise ratio of the spectra, is observed in a similar way of fluorescence from a single quantum dot. The blinking SERS may originate from that the molecule randomly enters and leaves an enhanced electromagnetic (EM) field at a few nanometer-sized gap of the nanoparticles (NPs). Thus, a power law can represent the blinking due to the molecular random walk on the metal surface.

2. Results and discussion

From a time-profile of blinking SERS intensity of each spot, probability distributions against duration times of the bright or dark states were obtained by $P(t) = \Sigma_{t'=t}\, n(t')/t$, where $n(t')$ is the number of the bright or dark events against their duration times.

For the bright and dark state, the logarithm–logarithm (log–log) plot shows a line and curve (line truncated at the tail), which given by a power law without and with an exponential function as

$P_{on}(t) = At^{\alpha_{on}}$ and $P_{off}(t) = At^{\alpha_{off}}\exp(-t/\tau)$, respectively.

The large $\alpha_{on,off}$ represents that the line in the log-log plots is sloped more steeply; namely, the probabilities of the long-lived bright or dark SERS state increase. It is noted that α_{on} must be independent of α_{off}, because the $P_{on,off}$ are derived from the total of not both but each events, respectively. However, the α_{on} is increased by a decrease of α_{off} [1]. This result is explained as follows. When the enhanced EM field is strong and wide, the molecule stays in the EM field and thus emits SERS light for long time; namely large α_{on}. Simultaneously, the rest of the surface is narrow, and then the molecule stays in the dark SERS area for short time; namely small α_{off} (steep slope in the log-log plot for the dark state).

Recently, large α_{on} are obtained despite large α_{off} in the system of anisotropic Ag NPs such as rods and triangles. In this case, the enhanced EM field, which can play a role of an optical trapping potential, is strong but narrow at the gap involving an apex of the anisotropic NP. Then, the molecule is optically trapped in the EM field and emits SERS light for long time; namely large α_{on}. On the other hand, the rest of the surface can be wide, and then the molecule can stay in the dark SERS area for long time; namely large α_{off}.

For the dark state, the log-log plot is truncated at the tail. The truncation time is given by $\tau \propto \Gamma/E_a$, where Γ is the time to overcome an energy barrier from the dark to bright state E_a. The energy barrier originates to an enhanced EM field that cannot induce SERS signal via the second enhancement but can optically trap the molecule (metastable state). Without the metastable state, truncation does not occur (τ becomes infinite due to $E_a = 0$; red plot in Fig. 1). If there is the metastable state and the molecule can hardly escape from it, the log-log plot for the dark state shows a gentle slope and hardly truncation (τ is extremely lengthened via long Γ; blue plot in Fig. 1). When the molecule is loosely held in the metastable state, on the other hand, the log-log plot shows mixed behaviors described above, namely truncation (green plot in Fig. 1).

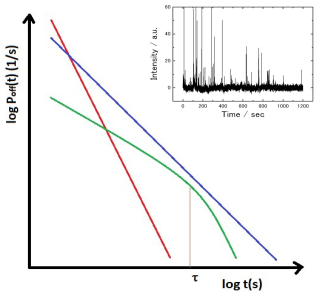

Fig. 1 Time-profile of blinking SERS and schematic log-log plots for probability distributions against duration times of the dark SERS state.

The metastable state may originate from a coupling of multipolar resonance at a gap of the spherical NPs [1]. Recently, it has been observed that the truncation takes place at the middle and tail in the log-log plot. A reason for the step-like truncation may be due to the enhanced EM field at the apex of the anisotropic NP. Even in this case, the molecule sometimes passes through the energy barrier from the apex to the bright state. When the molecule goes to the bright state not from the apex (not via energy barrier), the truncation does not occur. As a result, the step-like truncation can occur. In the former case, on the other hand, the molecule always passes through the energy barrier around the bright state.

3. Conclusions

From the blinking SERS analyzed by the power law, it is revealed that the single molecular behavior on the surface is influenced via plasmon-enhanced optical trapping.

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Reference

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