

Enhanced Raman scattering by zigzag edges of graphene and spectral analysis using the Bayesian method

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[Summary]

Surface enhanced Raman scattering (SERS) is a phenomenon, in which the Raman scattering of adsorbed molecules is enhanced by a factor of 10^3 – 10^6 through the interaction between the molecules and the substrate. It is attracting attentions as a method to identify and evaluate material from a minute amount. In this study, we focused on the electrons localized at the zigzag (zz) edge of graphene and verified if the Raman scattering is enhanced through the localized electrons. By investigating the Raman scattering of rhodamine 6G (R6G) molecule adsorbed on the zz graphene nano-mesh (zGNM) as a substrate, it is found that zGNM shows stronger enhancement of the Raman scattering than pristine graphene, despite the smaller graphene area. This suggests that the Raman scattering is enhanced on a zz edge. Furthermore, the study about the enhancement dependent on the R6G concentration shows that the R6G molecule is selectively adsorbed on the zz edge. Since the Raman spectrum contains many peaks, the analysis of the Raman spectrum is not straightforward. In this study, the Bayesian method was used to decompose the spectrum into peaks.

1 Introduction

When light is irradiated on a crystal or a molecule, a part of the incident light excites vibrations in the material, and the wavelength of scattered light is shifted from original one by the energy of the excited vibrations. This process is called the Raman scattering. Since the energy of the excited vibration is intrinsic to the molecule, its constituting atom, and the structure of the material, one can identify the material and evaluate its structure from the wavelength difference (Raman shift) between the incident and the Raman-scattered lights. This technique is known as the Raman spectroscopy. It is expected to be applicable to various fields such as chemical process and drug managements, pathological diagnosis, and atmospheric/environmental measurement, because it is a label-free, non-destructive, and non-invasive measurement^{1)–3)}. However, this measurement does not work for a minute amount of molecule, since the intensity of the Raman-scattered light is extremely weak. It is about 10^{-6} order of magnitude smaller than the Rayleigh-scattered light that does not involve vibrational excitations. Surface enhanced Raman scattering (SERS)^{4), 5)} is one of the methods to overcome this problem. It is a phenomenon that the Raman scattering is enhanced by a factor of 10^3 – 10^6 through the interaction between the substrate and the adsorbed molecule, and it enables the Raman spectroscopy even for a minute amount of molecule.

Although the curve fitting by the least-squares method is commonly used for analysis of spectroscopic spectrum such as Raman spectroscopy, this method sometimes overestimates peaks and mis-identifies noise as a peak when the spectrum is complicated. To overcome such problems, an analysis based on the Bayes' theorem (Bayesian method)⁶⁾, which estimates the result based on the measured data under pre-defined conditions, is efficient.

In this study, enhancement of the Raman scattering through the electronic states localized around the zigzag (zz) edge of graphene^{7)–9)} was investigated. The Raman spectra of rhodamine 6G (R6G) molecule, one of the general dyes, adsorbed on a zz graphene nano-mesh (zGNM)^{12), 14)} fabricated by hydrogen plasma etching (HPE)^{9)–13)}, were measured, and it was found that the Raman scattering of R6G molecule is enhanced around the zz edge, and that R6G molecule is selectively adsorbed on the zz edge. Here, the Bayesian method was used to analyze the Raman spectra.

This article introduces the enhancement of the Raman scattering on zGNM as well as the spectral analysis using the Bayesian method. The structure of this article is as follows. Chapter 1 described the Raman scattering and its potential applications. Chapter 2 outlines the mechanism of SERS, and chapter 3 discusses the enhancement of the Raman scattering on zGNM. Finally, in chapter 4, the spectral analysis by the Bayesian method will be introduced.

2 Surface enhanced Raman scattering (SERS)

2.1 SERS

Raman scattering of molecule becomes strong on a specific substrate through the interaction between the molecule and the substrate^{4), 5)}. This effect is called SERS, and the substrate that causes SERS is referred to as a SERS substrate. The following two mechanisms have been proposed as the enhancement mechanism.

1. Electro-magnetic Mechanism (EM)¹⁵⁾
2. Chemical Mechanism (CM)¹⁶⁾

1. EM is the enhancement of Raman scattering by the surface plasmon on the substrate, while 2. CM is that through the charge transfer between the substrate and the adsorbed molecule. Each of these mechanisms is roughly explained in the following sections.

2.2 Electro-magnetic Mechanism (EM)

EM is an enhancement mechanism of Raman scattering by the localized surface plasmon (LSP). Figure 1 shows a schematic diagram of this mechanism. Plasmon is a collective vibration of electrons in a solid, and a plasmon that appears on a solid surface is particularly called surface plasmon. This surface plasmon usually appears locally at nanostructures on surfaces. When light irradiates metal surfaces (particularly particles and rough surfaces), LSP is excited and resonates with the incident light that results in the enhancement of the optical field 10^2 – 10^5 times larger than the incident light. This enhanced optical field increases the frequency of Raman scattering. In addition, the Raman-scattered light is also enhanced by resonating with LSP. As a result, the Raman scattering is enhanced in both incident and scattered processes. The enhancement is particularly strong in a few nm gaps between metal nanoparticles (hot spots), at where the enhancement factor of the Raman scattering reaches 10^9 ⁵⁾.

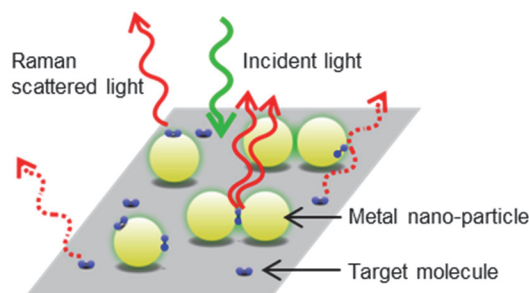


Figure 1 Schematic view of the enhancement of the Raman scattering of molecules by LSP at metal nanoparticles. The green arrow represents the incident light, while the red arrows represent the Raman-scattered light. The enhancement is stronger at gaps between nanoparticles than on nanoparticles.

Surfaces covered with silver or gold nanoparticles are often used as an EM-based SERS substrate, with which enhancement factor of 10^5 – 10^6 is achieved in average. Since this mechanism is applicable to all molecules in principle, the enhancement can be expected regardless of the molecular species. However, the enhancement factor depends on the hot spot, and the resonance with LSP may generate a large amount of heat, which may cause oxidation of the substrate and alteration of the sample molecules. Furthermore, since the substrate is not uniform, it is unclear how and where the molecule adsorbs on the substrate. Therefore, EM-based SERS has disadvantages in terms of reproducibility, uniformity, biocompatibility, etc¹⁷⁾.

2.3 Chemical Mechanism (CM)

CM is the enhancement mechanism by the charge transfer resonance between the substrate and the molecule. In the conventional Raman scattering of molecule, as shown in figure 2(a), electrons in the highest occupied molecular orbital (HOMO) are excited to a virtual state by the incident light (process ①), and then the electrons transit to excited state of molecular vibration by emitting the Raman-scattered light (process ②). When the energy of the incident light is the same as the energy difference between HOMO and lowest unoccupied molecular orbital (LUMO), the Raman scattering becomes strong because electrons are excited to an actual electronic state rather than to a virtual state (figure 2(b)). It is called resonance Raman scattering. On the other hand, in the case of the Raman scattering through the charge transfer resonance, i.e., the CM of SERS, the electrons in the substrate are excited to LUMO by the incident light, and then transit to the vibrational excited state by emitting the

Raman-scattered light (figure 2(c)). The change of the polarization of molecule caused by adsorption to the substrate is also considered to be a cause of CM²⁾.

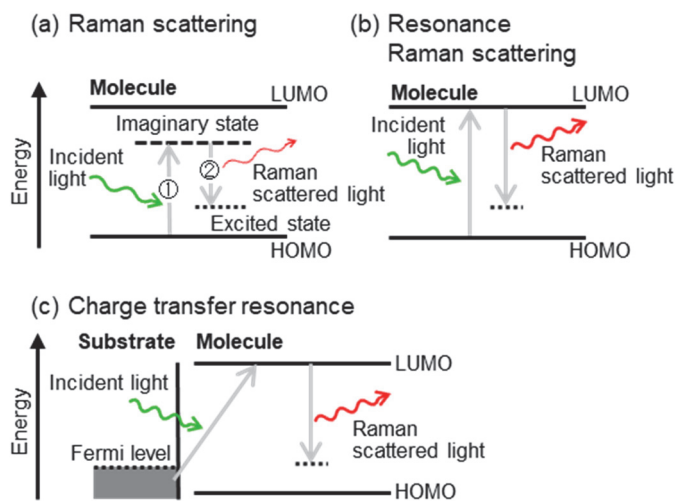


Figure 2 Schematic diagrams of (a) conventional Raman scattering process, (b) resonance Raman scattering process and (c) Raman scattering process by the charge transfer resonance.

2.4 Graphene as a SERS substrate

Although both EM and CM coexist for SERS in general, study about CM has been limited. This is because, in addition to the fact that the enhancement by EM is dominant, it is difficult to prepare a SERS substrate based only on CM, i.e., a flat substrate in nanometer scale, on which LSP is not excited. However, the SERS based only on CM is re-evaluating since the discovery of graphene, an atomically flat two-dimensional material. It has been confirmed that the Raman scattering of molecules such as rhodamine 6G (R6G)^{18), 19)}, phthalocyanine¹⁸⁾, and protoporphyrin IX^{18), 20)} is enhanced by using graphene as a substrate, and that their enhancement factor dependent on the electronic state and the energy of the incident light can be explained by the CM²¹⁾. Although the enhancement factor of the Raman scattering using graphene as a substrate is $\sim 10^3$, which is smaller than that of SERS based on EM, there is no heat generation because of the LSP. Moreover, molecules can be adsorbed on the substrate homogeneously, since graphene is flat in atomic scale. In such senses, graphene can overcome the disadvantages of SERS using metal nanoparticles as a substrate.

3 Raman scattering enhanced on zigzag edges

3.1 Zigzag edge state of graphene

Graphene consists of a honeycomb lattice with hexagons,

in which a carbon atom sp^2 -bonds to other three carbon atoms, as shown schematically in figure 3(a). Reflecting this crystal structure, two atomic structures, i.e., zz and armchair, can be considered for the edge of graphene. The electronic state of graphene is characterized by linear energy dispersion crossing at one point (Dirac point) (black line in figure 3(b)), while a dispersion-free (flat) energy band appears at the Dirac point around the zz edge (red line in figure 3(b)). This is due to the breaking of the honeycomb symmetry of graphene at the zz edge, and the band structure indicates that a localized electronic state appears around the zz edge (zz edge state)⁷⁾⁻⁹⁾. As mentioned in the previous chapter, the electronic state of the substrate plays an important role in the CM-based SERS. Therefore, the enhancement of the Raman scattering through these localized electrons around the zz edge can be expected.

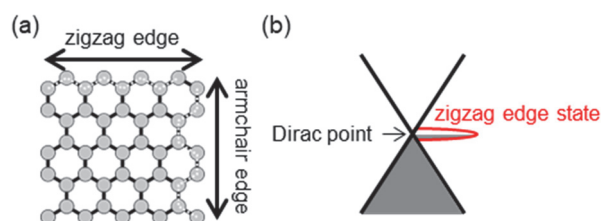


Figure 3 Schematic diagrams of (a) crystal structure of graphene and its edges, (b) the electronic state of graphene. The red line indicates the zigzag edge state.

3.2 Experimental

We have established a technique to create hexagonal nanopits terminated by zz edges on graphene at desired positions^{12), 14)} by hydrogen plasma etching (HPE)⁹⁾⁻¹³⁾. Figure 4 shows an optical microscope image (figure 4(a)) and an atomic force microscope (AFM) image (figure 4(b)) of a graphene device, as an example. In this paper, tri-layer graphene flakes obtained by exfoliating graphite on a SiO_2/Si substrate were used. In this case, high-quality graphene with less defects can be obtained, although the area is limited to $10 \mu m^2$ at most. Both pristine and zGNM regions were fabricated in one flake as shown in figure 4, and the Raman scattering from both regions was obtained in one spectral mapping. This makes it possible to ignore uncertainties such as variation of laser intensity in each measurement, surface contamination, and contact condition between graphene and the substrate. To investigate the enhancement of the Raman scattering by the zz edge state, as long zz edge as possible is

desired within a Raman laser spot ($\sim\phi 500$ nm). Therefore, hexagonal nanopits of ~ 100 nm diagonal length triangularly arranged with 200 nm interval were prepared as a zGNM. Hexagonal holes in the zGNM region shown in figure 4(b) are those fabricated by HPE, and the substrate SiO_2 is exposed inside the nanopits. The edges of the nanopit are the zz edges of graphene.

A laser Raman microscope²²⁾ with a 532 nm laser was used for the Raman scattering measurement. To compare the spectra obtained at different measurements, all Raman spectra are normalized by the intensity of the Si-originated signal that appears at ~ 950 cm^{-1} . Accordingly, the spectral intensity shown in this paper can be considered as the intensity per unit area of a device. The R6G molecule, which is commonly used in the study of SERS, was adopted as a probe molecule to evaluate the enhancement. R6G molecule was adsorbed onto graphene devices by immersing the devices in an R6G solution with a concentration of 0.1, 1, 10, 100 μM ²³⁾ (which corresponds to approximately 0.05, 0.5, 5, 50 ppm, respectively).

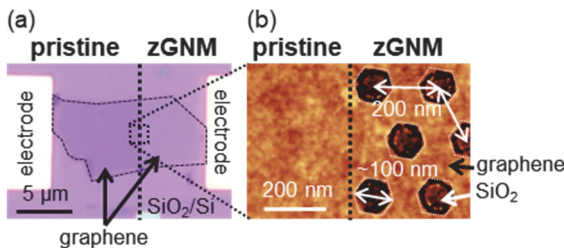


Figure 4 (a) An optical microscope image and (b) an atomic force microscope image of a graphene device.

3.3 Results and discussion

Figure 5 shows the Raman spectra obtained on (a) pristine graphene and on (b) zGNM modified by R6G molecule of 10 μM concentration. The gray dots are the measured data, the colored solid lines are the spectral peaks decomposed by the Bayesian method, which will be introduced in the next chapter, and the black solid line is the sum of the decomposed peaks. In all cases, the spectra are decomposed into peaks named a–m originated from R6G molecule together with the G and D bands of graphene. Since G band is related to the honeycomb structure of graphene, its intensity is proportional to the graphene area. Therefore, G-band is smaller for the mesh structure of zGNM than for pristine graphene. On the other hand, D-band is related to the intervalley scattering inside the crystal, and is proportional to the amount of

defects in the honeycomb structure. As a result, D-band is negligible on pristine graphene, while it appears on zGNM which is micro-fabricated.

Raman scattering of R6G molecule is hardly enhanced on the SiO_2 surface, and any peaks originated from R6G molecule are not observed on the SiO_2 substrate. Therefore, the fact that the peaks originated from R6G molecule are observed on pristine graphene and zGNM indicates that both surfaces have an effect to enhance the Raman scattering of R6G molecule. Among several peaks originated from R6G molecule, a peak named “g” (g-peak) at ~ 1500 cm^{-1} will be focused on in this paper. Figure 6(a) shows the R6G concentration dependence of the g-peak intensity. The peak intensity on pristine graphene (P_g) is shown by an open circle, while that on zGNM (M_g) is shown by a filled circle. Each point is slightly shifted along the horizontal axis to make the graph easier to see. It shows that both P_g and M_g increase with increasing the R6G concentration, and that M_g is larger than P_g at any concentration, namely, the Raman scattering is enhanced stronger on zGNM than on pristine graphene. Considering that no peaks originated from R6G molecule are obtained on the SiO_2 substrate, it is noteworthy that zGNM shows stronger spectral intensity per device area than a substrate fully covered by graphene, even though zGNM has smaller area that contributes to enhance the Raman scattering of R6G molecule. It suggests that there is a strong Raman scattering enhancement at the zz edge around the nanopits, which zGNM has but pristine graphene doesn't.

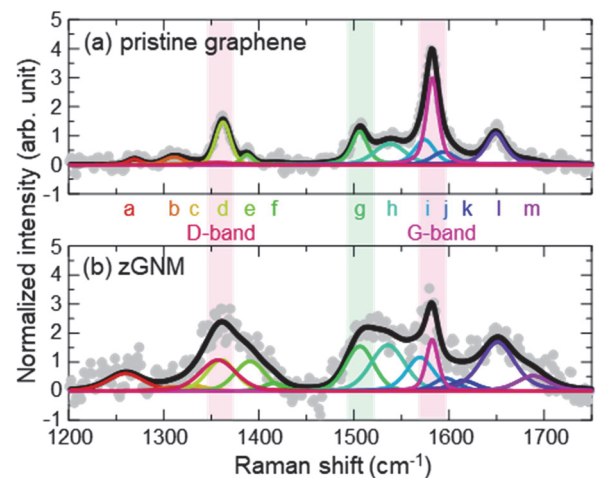


Figure 5 Raman spectra of R6G molecule of 10 μM concentration measured on (a) pristine graphene and on (b) zGNM. The G and D bands originated from graphene and the g-peak among the a–m peaks originated from R6G molecule are marked by red and green, respectively.

In the discussion below, it is assumed that the peak intensity obtained on zGNM is the sum of the contribution of the graphene area and that of the zz edge. By denoting the peak intensity per unit area of pristine graphene and zGNM as P and M , respectively, the peak intensity due to the zz edge per unit edge length as E_0 , the ratio of graphene area in the unit area as r , and the total zz edge length in the unit area as L , above assumption can be expressed as follows.

$$M = r \cdot P + L \cdot E_0 \quad (1)$$

From this equation, contribution of the zz edge to the g-peak (E_{0g}) can be calculated using the g-peak intensities (P_g, M_g) obtained from Raman spectra and r, L measured from AFM images. The resultant E_{0g} depending on the R6G concentration is shown in figure 6(b). It shows that E_{0g} is almost constant at concentrations below 10 μM , and then increases at between 10 and 100 μM . This suggests that the amount of R6G molecule adsorbed on the zz edge is already saturated at a concentration of 0.1 μM . It can be concluded that R6G molecule is adsorbed on basal plane of graphene after selectively adsorbing on the zz edge, and that the second and higher layer promotion starts at a concentration between 10 and 100 μM .

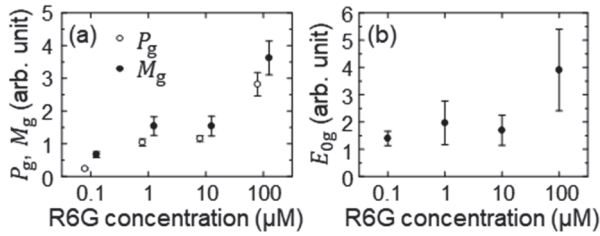


Figure 6 R6G concentration dependence of (a) g-peak intensity on pristine graphene and zGNM (P_g, M_g), and (b) contribution of the zz edge to the g-peak (E_{0g}).

4 Raman spectrum analysis by the Bayesian method

4.1 The Bayesian method

The analysis of spectroscopic data is a trial to reproduce the measured data $y = (y_1, y_2, \dots, y_n)$ for variables $x = (x_1, x_2, \dots, x_n)$ using an estimated value e obtained by a specific function $f(x; \theta)$ under conditions of a certain parameter set θ . Considering that the error d is the difference between the estimated value e and the data y , e and y can be expressed as follows.

$$e = f(x; \theta) \quad (2)$$

$$y = e + d \quad (3)$$

Three methods are generally discussed to find the appropriate parameter set θ . Those are the least-squares method, the maximum-likelihood method, and the Bayesian method.

In the least-squares method, θ is evaluated so that the error d (square-root of d , precisely speaking) is minimized. Here, estimated value e obtained from the parameter set θ is unique, and the difference between e and the measured data y is evaluated. On the other hand, the maximum-likelihood and the Bayesian methods introduce a concept of probability, that is to say, “the probability to take *this* value is the highest”. In the maximum-likelihood method, the error d is thought to be a random variable that follows a specific probability distribution, and it considers the probability $p(y|\theta)$ to obtain measured data y as $f(x; \theta) + d$ for given parameter set θ . Namely, it is a method to find the parameter set θ that maximizes $p(y|\theta)$ (“maximum likelihood”). Since $p(y|\theta)$ is the probability to take the value y under the condition θ , it is called “conditional probability”. It is also called “likelihood” or “likelihood function” depending on the field of research. The least-squares and the maximum-likelihood methods are similar in the sense that both of them evaluate the error d . In fact, their solutions are essentially the same if the error d follows a Gaussian distribution²⁴⁾.

In contrast, the Bayesian method considers the parameter set θ as a random variable. Here, an assumption that “ θ follows the Gaussian distribution centered at $\hat{\theta}$ with a standard deviation of σ ” is given in advance, and then the parameter set θ is re-evaluated using the probability to reproduce the measured value from the estimated value based on the assumption. In other words, compared to the least-squares and maximum-likelihood methods that estimate the result from pre-conditions, the Bayesian method estimates the next result using the experiences. Since this process is essentially the same as a learning process and is easy to handle mathematically, this method is often used in the field of machine learning.

As can be found from this concept, the Bayesian method requires a starting probability distribution $p(\theta)$ for the parameter set θ . This $p(\theta)$ is called “prior (probability) distribution”. By reflecting the measured data on this $p(\theta)$, “posterior (probability) distribution” of the parameter set θ is obtained. Since the posterior distribution is the probability distribution of the parameter set θ based on the measured

data y , it is denoted as the conditional probability $p(\theta|y)$ and expressed as follows (the Bayes' theorem).

$$p(\theta|y) = \frac{p(y|\theta)p(\theta)}{p(y)} \quad (4)$$

Here, the denominator $p(y)$ is the probability that measured data y occurs, and it is obtained by integrating the numerator over all θ .

$$p(y) = \int p(y|\theta)p(\theta)d\theta \quad (5)$$

Equation (4) means that, " $p(\theta|y)$, which is the probability distribution of parameter set θ based on the measured data y , is the probability that the measured data y occurs when a certain parameter set θ is realized ($= p(y|\theta)p(\theta)$) under a condition that y occurs ($= p(y)$)". Incidentally, the maximum-likelihood method is the way to estimate parameters only from the likelihood by considering that the prior distribution is uniform²⁵⁾.

4.2 The Markov chain Monte Carlo (MCMC) method

As mentioned in the previous section, the Bayesian method calculates the posterior distribution $p(\theta|y)$ using equation (4). In this calculation, although the prior distribution $p(\theta)$ and the likelihood $p(y|\theta)$ can be handled relatively easily, the evaluation of the integral of their multiple (equation (5)) is not straightforward. To overcome this difficulty, some methods are known to simulate the posterior distribution using random numbers, and one of the methods is the Markov chain Monte-Carlo (MCMC) method. This is a method to generate random numbers from an arbitrary probability distribution, and it is based on two ideas. One is the concept of Markov chain that the i -th generated random number θ_i is influenced only by the previous one θ_{i-1} . And the other is the Monte-Carlo method that uses another random number for the random number generation²⁴⁾. The value and the overall feature of $p(y|\theta)p(\theta)$ for each θ can be obtained by substituting N parameter sets $\theta_1, \theta_2, \dots, \theta_N$ generated by MCMC method into $p(y|\theta)p(\theta)$. Furthermore, the integral of $p(y|\theta)p(\theta)$ can also be calculated using a method called Monte-Carlo integration. As a result, the posterior distribution $p(\theta|y)$ can be obtained from equation (4). The simulation can be performed efficiently by using this MCMC method, since parameter sets of higher posterior probability distribution are generated more intensively²⁴⁾.

4.3 Raman spectrum analysis by the Bayesian method

In general, a spectroscopic spectrum can be expressed as a convolution of the Lorentzian distribution, that is inherent in the electro-magnetic waves, and the Gaussian distribution such as the random thermal vibration of crystals and molecules. In this study, a peak in a Raman spectrum is considered as a pseudo-Voigt function $V(x; \theta)$ ²⁶⁾, which is the sum of the Lorentzian and the Gaussian functions. Therefore, the intensity of the Raman spectrum (measured data) y at Raman shift x (cm^{-1}) is expressed as the sum of M peaks, that is, the M pseudo-Voigt functions $\sum V(x; \theta_i)$ and the error d .

$$y = \sum_{i=1}^M V(x; \theta_i) + d = f(x; \theta) + d \quad (6)$$

Here, the parameter set θ_i for the i -th peak includes the spectrum peak intensity I_i , peak position μ_i , full width at half maximum (FWHM) Γ_i , and Gaussian ratio a_i . The Gaussian ratio a is the mixing ratio of the Gaussian and the Lorentzian functions, and $a = 0$ (1) makes the pseudo-Voigt function the Lorentzian (Gaussian) function. The error d is assumed to be a Gaussian distribution with a mean of 0 and a standard deviation of σ .

The likelihood $p(y|\theta)$ and the prior distribution $p(\theta)$ are considered based on the above assumptions. Since the measured data y follows the Gaussian distribution with a mean value of $f(x; \theta)$ and a standard deviation of σ according to equation (6), the likelihood is expressed as

$$p(y|\theta) = \prod_{i=1}^n \frac{1}{\sqrt{2\pi\sigma^2}} \exp\left(-\frac{(y_i - f(x_i; \theta))^2}{2\sigma^2}\right). \quad (7)$$

On the other hand, the prior distribution $p(\theta)$ must be considered for all parameters. In this study, the peak intensity I and the Gaussian ratio a are considered to be a uniform distribution with the range of $0 \leq I \leq A$ and $0 \leq a \leq 1$, respectively. Here, A is a sufficiently large peak intensity. Fifteen peaks in total were considered as the peaks which constitute the Raman spectrum. Those are the R6G molecule originated 13 peaks named a–m referred to the previous researches^{19), 27), 28)}, and the G and D bands of graphene. Their peak position μ (cm^{-1}) is assumed to be a Gaussian distribution with a mean of $\hat{\mu}$ (cm^{-1}) referred to previous research²⁷⁾ and a standard deviation of 5 (cm^{-1}). The FWHM Γ (cm^{-1}) is assumed to be a Gaussian distribution with a mean of 30 (cm^{-1}) and a standard deviation of 10 (cm^{-1}) based

on our own experience. Afterwards, the prior distribution $p(\theta)$ can be written as

$$p(\theta) = \prod_j \frac{1}{\sqrt{50\pi}} \exp\left(-\frac{(\mu_j - \hat{\mu}_j)^2}{50}\right) \cdot \frac{1}{\sqrt{200\pi}} \exp\left(-\frac{(\Gamma_j - 30)^2}{200}\right) \cdot \frac{1}{1} \cdot \frac{1}{A}. \quad (8)$$

Now, since the prior distribution and the likelihood function are defined, the posterior distribution can be estimated using the MCMC method. No-U-Turn-Sampler implemented in PyMC, that is a Python MCMC library, was used to execute the MCMC method.

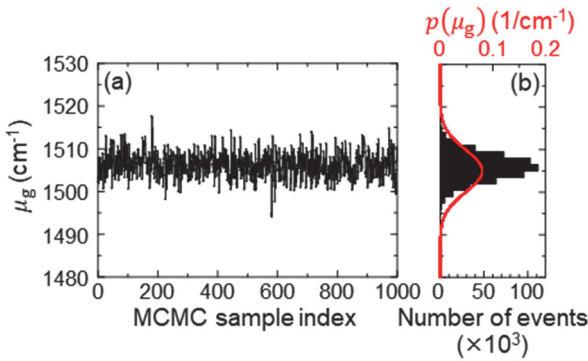


Figure 7 (a) 1,000 of μ_g obtained using the MCMC method. (b) Histogram of μ_g (black) and its prior distribution (red).

Figure 7 shows the g-peak position μ_g among 100,000 parameter sets θ obtained using the MCMC method for Raman spectrum of zGNM modified with R6G molecule of 10 μM concentration (figure 5(b)). Figure 7(a) shows 1000 of μ_g out of them, and the histogram of all 100,000 is shown by black lines in figure 7(b). It can be seen that μ_g takes various values probabilistically and converges within a certain range. In comparison with the prior distribution $p(\mu_g)$ shown by the red line in figure 7(b) (center at 1505 cm^{-1} with $\sigma = 5 \text{ (cm}^{-1})$), the posterior distribution obtained using the measured data is found to have smaller variance, and the center value is shifted from $p(\mu_g)$.

Although the posterior distribution of each parameter can be estimated using the Bayesian method in such way, it is not straightforward to choose an optimal value of the distribution. In general, the maximum a posteriori (MAP) estimate, which is the value most frequently appears in the posterior distribution, and the expected a posteriori (EAP) estimate, which is the mean value of the posterior distribution, are discussed²⁵⁾. In this study, the EAP estimate is adopted.

4.4 Evaluation of the Raman spectrum analysis

Finally, the validity of the spectrum analysis performed in this study is evaluated. Figure 8 compares the Bayesian method (figure 8(a)) and the least-squares method (figure 8(b)). Note that figure 8(a) is reiteration of figure 5(b). At first glance, the least-squares method also fits the data well. However, some peaks are overestimated, the peak positions are shifted significantly, and obvious noise is evaluated as a peak. In contrast, such mis-analysis does not occur and the spectrum seems to be decomposed more appropriately in analysis using the Bayesian method.

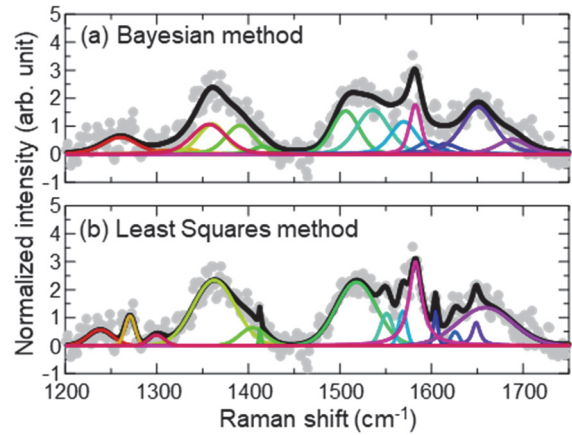


Figure 8 Results of peak decomposition of the Raman spectrum (gray dot) of R6G molecule of 10 μM concentration on a zGNM substrate using (a) the Bayesian method and (b) the least-squares method.

The validity of the analysis can also be confirmed by considering the ratio of the graphene area in the pristine and the zGNM regions. As mentioned before, the peak intensity of the G-band in Raman spectrum is roughly proportional to the area of graphene. The G-band intensities of pristine and zGNM regions, and the ratio of them, extracted from the data in figure 8, and the areal ratio of graphene per unit device area evaluated from AFM images are shown in table 1. It can be confirmed that the areal ratio estimated from the G-band intensity is within about ± 0.1 of the actual value before modifying the substrate with R6G molecule (w/o R6G). The ratio of the G-band intensity between the pristine graphene and the zGNM is expected to take a similar value as far as the graphene area does not change by R6G modification (w/ R6G). Actually, the G-band intensity ratio obtained using the Bayesian method after R6G modification is almost the same as the actual areal ratio. On the other hand, in the case of the least-squares method, the intensity ratio changes

significantly, and the zGNM shows larger G-band intensity than the pristine graphene, although the zGNM is a mesh structure. This also suggests that the analysis using the least-squares method is not valid, while the Bayesian method is appropriate, at least, in this study.

Table 1 The G-band intensity in the Raman spectra shown in figure 5 and 8 and their ratio, together with the areal ratio of graphene per unit device area evaluated from AFM images of the device.

G-band intensity		Pristine graphene (P_G)	zGNM (M_G)	ratio (M_G/P_G)
w/o R6G		3.96	1.58	0.42
w/ R6G	Bayesian method	3.00±0.63	1.78±0.41	0.59±0.19
	Least Squares method	2.91	3.02	1.04
Graphene area ratio of zGNM estimated from AFM images				0.52

5 Summary

In this study, we focused on the SERS by the chemical mechanism (CM) based on the charge transfer, and investigated the enhancement of the Raman scattering via electrons localized at the zz edge of graphene. By measuring the Raman spectra of R6G molecule adsorbed on pristine graphene and zGNM with zz edges, it was found that the intensity of the Raman scattering originated from the R6G molecule is stronger on zGNM than on pristine graphene at any R6G concentration. This suggests that the Raman scattering is enhanced on zz edges of zGNM. It was also found by evaluating the contribution of the zz edge to the Raman scattering that the R6G molecule is selectively adsorbed on the zz edge.

Since the R6G molecule shows many peaks within the measurement range in the Raman spectrum, the least-squares method, which is often used in spectrum analysis, does not always decompose the spectrum into peaks appropriately. Therefore, the Bayesian method, which is commonly used in the field of the machine learning, was used in this study.

This study reveals that the Raman scattering is enhanced through the zz edge states of graphene. Since the SiO₂ substrate, which is exposed inside the nanopits, does not enhance the Raman scattering, zGNM loses the area that

contributes to enhance the Raman scattering. If zGNM could be transferred onto pristine graphene, stronger enhancement of the Raman scattering can be achieved because Raman scattering is enhanced inside the nanopits, too. Furthermore, more practical enhanced Raman scattering substrate could be expected, if chemically grown graphene with large surface area could be fabricated into zGNM and transferred onto graphene on a flexible transparent film.

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