

Supplementary information for

# Study on Transport of Molecules in Gel by Surface-Enhanced Raman Spectroscopy

*Samir Kumar, Taneichi Taiga, Takao Fukuoka, Kyoko Namura, Motofumi Suzuki*

Department of Micro Engineering, Graduate School of Engineering, Kyoto University, Katsura,  
Nishikyo, Kyoto, 615-8540, Japan

## A. Molecular structure of Raman probe molecules used in this study.

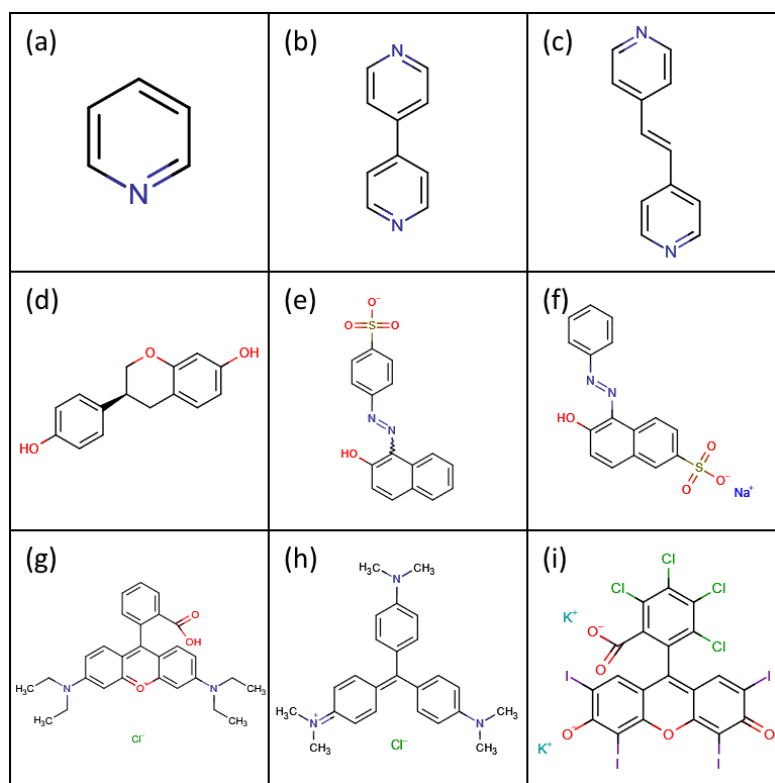


Figure S1. Molecular Structure of (a) Pyridine, (b) 4,4'-Bipyridine, (c) 4,4'-Viylenedipyridine, (d) (S)-Equol, (e) Acid Orange 7, (f) Acid Orange 12, (g) Rhodamine 6G, (h) Crystal Violet, and (i) Rose Bengal.

## B. Detailed derivation of the fitting model for diffusion in gel

We will deduce a function that indicates the time change of the SERS spectral intensity and will be used for fitting the experimental data. Diffusion of solutes in homogeneous solvents on a macro scale can be described using the diffusion equation [8]. According to Fick's first law, a solute's diffusion flux is proportional to its concentration gradient. At this time, if the concentration is  $C(z, t)$  as a function of the coordinates  $z$  in the vertical direction and the time  $t$ , and the amount of solute transported through the unit area in the unit time is  $J$ , then

$$J = -D \frac{\partial C(z,t)}{\partial z} \quad (1)$$

Where  $D$  is the diffusion coefficient of the solute molecule. Simultaneously, the mass flowing into the region of height  $z$  and  $z + \Delta z$  during time  $\Delta t$  is expressed as

$$J(z)\Delta t - J(z + \Delta z)\Delta t = -\frac{\partial J}{\partial z} \quad (2)$$

Since this is equal to the increase in solute concentration  $\Delta C(z, t)$  during the time  $\Delta t$ , the following equation satisfies the continuity equation.

$$\frac{\partial C(z,t)}{\partial t} + \frac{\partial J}{\partial z} = 0 \quad (3)$$

The following equation is obtained from equations (1) and (2).

$$\frac{\partial C(z,t)}{\partial t} = D \frac{\partial^2 C(z,t)}{\partial z^2} \quad (4)$$

Equation 4 is called the diffusion equation. The coefficient  $D$  is called the diffusion coefficient and has the dimension of (distance)<sup>2</sup>/time. From kinetic theory, it is known that the diffusion coefficient is proportional to the inverse square root of the molecular weight. The larger the diffusion coefficient, the faster the diffusion. By using initial conditions and boundary conditions to the diffusion equation, the transport phenomena of solutes in various states can be described using the solution of the diffusion equation, and the diffusion of substances can be evaluated using the diffusion coefficient. The diffusion equation of Eq. (4) is modeled in one dimension for the sample cell as shown in Figure S2(a), with the initial conditions.

$$C(z, 0) \Big|_{0 < z \leq a} = 0 \quad (5)$$

and boundary conditions

$$C(0, t) = C_0 = \text{Const.} \quad (6)$$

$$\left. \frac{\partial C(z, t)}{\partial z} \right|_{z=a} = 0 \quad (7)$$

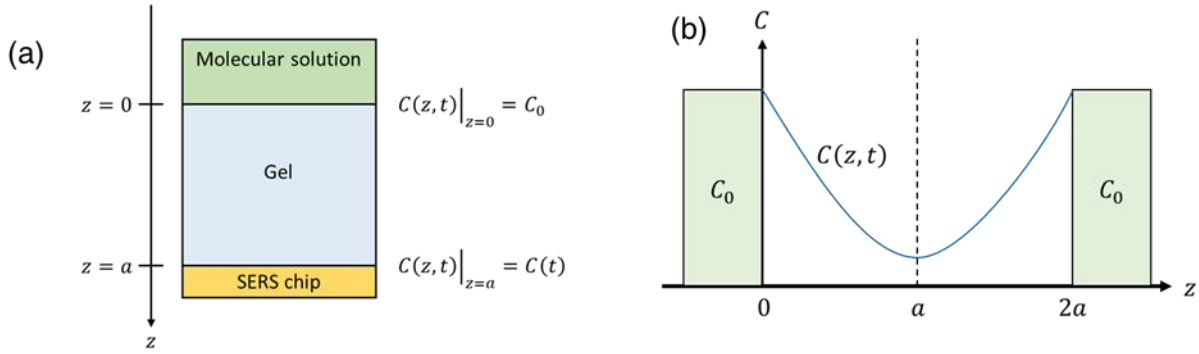


Figure S2. (a) Schematic diagram and coordinate settings in a sample cell. (b) Schematic diagram replaced using mirror image for simplifying the calculations.

From the boundary condition of Eq. (7), the schematic diagram was replaced as shown in Figure S2(b) using the mirror image method. To obtain the special solution, the concentration  $C(z, t)$  was replaced as the product of the function of  $t$  and the function of  $z$  by the separation of variables method.

$$C(z, t) = g(t)h(z) \quad (8)$$

After, substituting it into the Eq. (4) and reorganize it.

$$\frac{1}{Dg(t)} \cdot \frac{dg(t)}{dt} = \frac{1}{h(z)} \cdot \frac{d^2h(z)}{dz^2} \quad (9)$$

Then, since the left side is a function of  $t$  and the right side is a function of  $z$ , both sides can be regarded as equal to a certain constant. Let the constant be  $-\gamma$  and considering the LHS of Eq. (9)

$$\frac{1}{Dg(t)} \cdot \frac{dg(t)}{dt} = -\gamma \quad (10)$$

After solving

$$g(t) = \delta \exp(-\gamma Dt) \quad (11)$$

Let us now consider the RHS of Eq. (9)

$$\frac{1}{h(z)} \cdot \frac{d^2 h(z)}{dz^2} = -\gamma \quad (12)$$

After solving Eq. 12

$$h(z) = \beta \cos\{\sqrt{\gamma}(z - \epsilon)\} \quad (13)$$

From this, as a solution to the diffusion equation  $\beta, \epsilon$

$$C(z, t) = A \exp(-\lambda^2 Dt) \cdot \cos\{\lambda(z - \epsilon)\} \quad (14)$$

Is obtained. Where,  $A = \beta\delta$  and  $\lambda^2 = \gamma$ . Using the initial condition in Figure S2(a).

$$C(z, 0) \Big|_{0 < z < 2a} = 0 \quad (15)$$

and boundary conditions

$$C(z, t) \Big|_{z=0, 2a} = C_0 = \text{Const.} \quad (16)$$

The form of Fourier series expansion is

$$C_0 \left[ 1 - \frac{4}{\pi} \sum_{n=0}^{\infty} \frac{1}{2n+1} \sin \left\{ \frac{(2n+1)\pi}{2a} z \right\} \right] \quad (17)$$

Therefore,

$$\lambda = \frac{(2n+1)\pi}{2a} \quad (18)$$

$$\epsilon = \frac{a}{2n+1} \quad (19)$$

Then, Eq. (14) becomes

$$C(z, t) = A \cdot \exp \left\{ - \left( \frac{(2n+1)\pi}{2a} \right)^2 Dt \right\} \cdot \sin \left\{ \frac{(2n+1)\pi}{2a} z \right\} \quad (20)$$

and when  $t = 0$

$$C(z, 0) = A \cdot \sin \left\{ \frac{(2n+1)\pi}{2a} z \right\} \quad (21)$$

Equation (17) can be treated as  $C(z, 0)$  because it is obtained by multiplying the infinite sum of Eq. (21) by a constant and adding a constant term. Therefore

$$C(z, 0) = C_0 \left\{ 1 - \frac{4}{\pi} \sum_{n=0}^{\infty} \frac{1}{2n+1} \sin \frac{(2n+1)\pi}{2a} z \right\} \quad (22)$$

Multiplying equation (20) by a coefficient to obtain an infinite sum,

$$C(z, t) = C_0 \left\{ 1 - \frac{4}{\pi} \sum_{n=0}^{\infty} \frac{1}{2n+1} \cdot \exp \left[ - \left\{ \frac{(2n+1)\pi}{2a} \right\}^2 Dt \right] \cdot \sin \left[ \frac{(2n+1)\pi}{2a} z \right] \right\} \quad (23)$$

When  $t = 0$ , it agrees with Eq. (21), so Eq. (23) is a special solution of the diffusion equation because of the existence and uniqueness of the solution. If  $z = a$  in this equation,

$$C(a, t) = C(t) = C_0 \left\{ 1 - \frac{4}{\pi} \sum_{n=0}^{\infty} \frac{(-1)^n}{2n+1} \cdot \exp \left[ - \left\{ \frac{(2n+1)\pi}{2a} \right\}^2 Dt \right] \right\} \quad (24)$$

and becomes  $C(t)$ . Since the SERS spectral intensity of a molecule is proportional to its concentration,<sup>1,2</sup> the SERS spectral intensity  $S(t)$  can be written as

$$S(t) = S_0 \left\{ 1 - \frac{4}{\pi} \sum_{n=0}^{\infty} \frac{(-1)^n}{2n+1} \cdot \exp \left[ - \left\{ \frac{(2n+1)\pi}{2a} \right\}^2 D't \right] \right\} \quad (25)$$

C. The SEM images of the SERS chip utilized for this study. The SERS chip with elongated Au nanorod arrays (AuNRAs) was developed by Suzuki et al.<sup>3,4</sup> and is now commercially available as Wavelet.

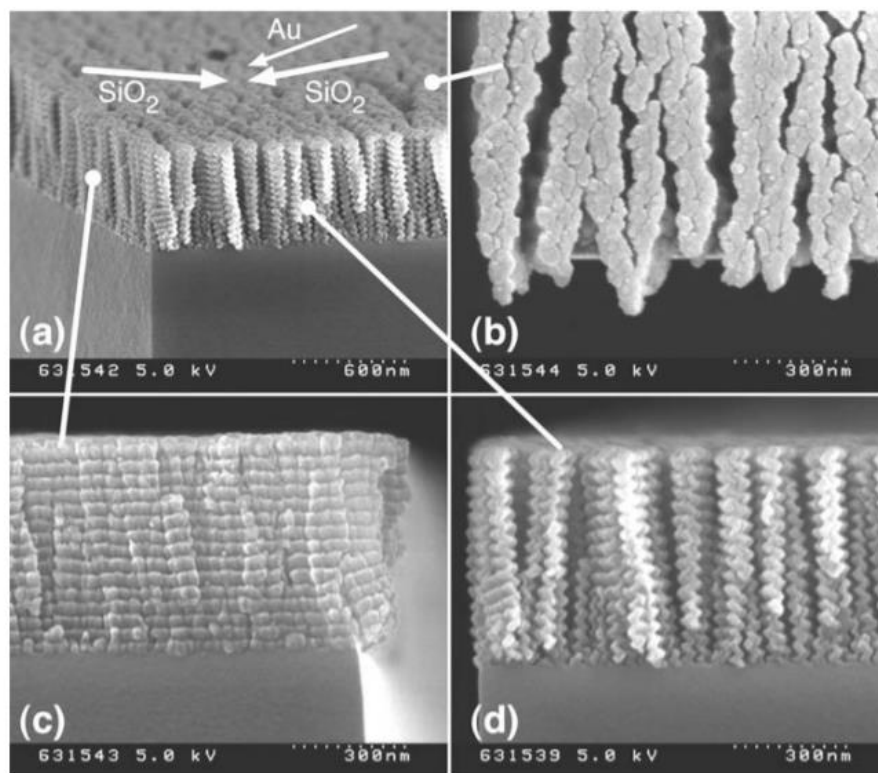


Figure S3. SEM images of a typical SiO<sub>2</sub> template layer. (a) Bird's-eye view, (b) surface with cross sections fractured, (c) perpendicular or (d) parallel to the deposition plane. Thick arrows in (a) indicate the deposition directions of SiO<sub>2</sub>. The incident direction of Au deposition is also indicated for providing a better understanding of the sample preparation method.<sup>3</sup>

- (1) Wang, Y. Y.; Jiang, J.; Yin, J.; Li, N.; Yu, K.; Quan, S. F.; Yue, X. F.; Zhong, B. Determination of Concentration of Adsorbed Molecules by Raman Spectroscopy and Optical Imaging. *J. Appl. Phys.* **2019**, *125* (24), 244305.
- (2) Salemmilani, R.; Mirsafavi, R. Y.; Fountain, A. W.; Moskovits, M.; Meinhart, C. D. Quantitative Surface-Enhanced Raman Spectroscopy Chemical Analysis Using Citrate as an in Situ Calibrant. *Analyst* **2019**, *144* (5), 1818–1824.
- (3) Suzuki, M.; Nakajima, K.; Kimura, K.; Fukuoka, T.; Mori, Y. Au Nanorod Arrays Tailored for Surface-Enhanced Raman Spectroscopy. *Anal. Sci.* **2007**, *23* (7), 829–833.
- (4) Kumar, S.; Kanagawa, M.; Namura, K.; Fukuoka, T.; Suzuki, M. Multilayer Thin-Film Flake Dispersion Gel for Surface-Enhanced Raman Spectroscopy. *Appl. Nanosci.* **2020**. <https://doi.org/10.1007/s13204-020-01562-0>.