Damage-free tip-enhanced Raman spectroscopy for heat-sensitive and soft materials

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Raman enhancement in an AM mode

Raman enhancement at different amplitudes of cantilever oscillation is calculated from the profile of scattering light intensity as a function of the probe-substrate separation. The profile has an exponential character, and its decay length, λ in water with a non-gap mode configuration is estimated to be 5.5 nm.[1] By assuming that the position of the tip apex can be described by a simple sinusoidal function, the Raman enhancement was obtained by integrating the scattering intensity as a function tip-substrate separation over a cycle of the oscillation as following:

$$\text{Raman enhancement} = \frac{1}{2\pi}\left\{\int_0^{2\pi} \exp\left[\frac{-(A+A\sin t)}{\lambda}\right] \mathrm{d}t\right\} \tag{1}$$

where A, λ, and t are oscillation amplitude of the cantilever, decay length, and time, respectively.

Figure S1 shows the normalized Raman enhancement as a function of amplitude of the cantilever. All data were normalized by the intensity at the amplitude of 0 nm. The Raman enhancement is 0.81 at the amplitude of 1.2 nm (set point for the feedback in the AM mode in Fig. 5).

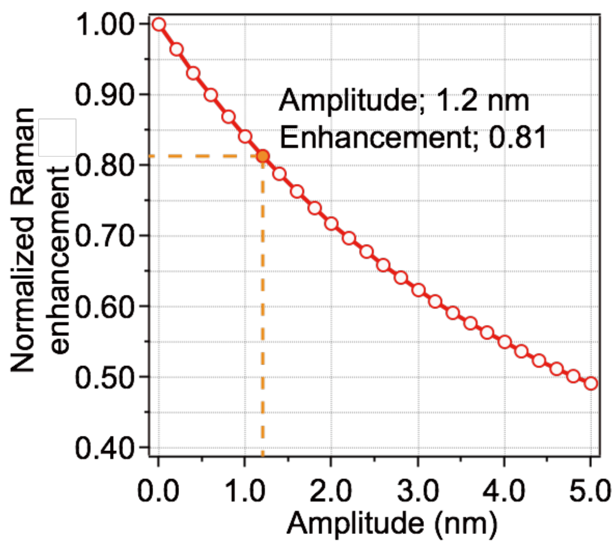

Fig. S1 Normalized Raman enhancement as a function of amplitude of the cantilever under an AM feedback in water.

TERS measurement of biological samples

We summarized the experimental conditions employed in previous works on TERS measurements of biological samples.

Table 1 Experimental conditions of biological samples by TERS

Tip coating	Excitation wavelength (nm)	Laser power ($mW/\mu m^2$)	Exposure time (sec)	NA of objevtive lens	Focus spot (μm^2)	Sample	Reference
Silver	530	3.84	5	1.45	0.156	Hemozoin	[2]
Silver	568	11.1	100	1.45	0.179	DNA	[3]
Silver	568	8.36	10	1.45	0.179	Bacteria	[4]
Silver	532	0.474	10, 30	1.4	0.169	Cytochrome C	[5]
Silver	868.2	3.19	10	1.45	0.419	Tabacco Mosaic virus	[6]
Silver	530.9	4.02	1	1.4	0.157	Lipid	[7]
Silver	532	11.8	20	1.4	0.169	Virus strain	[8]
Silver	530.9	5.42	2, 5, 10	1.45	0.156	Protein Glycosylation	[9]
Silver	530	2.69	10	1.45	0.156	Amyloid fibrils	[10]
Silver	532	2.35	10	1.49	0.149	Phospholipid	[11]

Dissipation of heat by oscillating of cantilevers in air and water

Figure S2 shows temperature of a bare Si probe as a function of oscillation amplitude. Note that the experimental condition here is different from that used to obtain the results in Fig. 6(b) (NA of the objective = 0.55 and laser power density = 18.3 $mW/\mu m^2$). The result clearly shows that cantilever oscillation effectively promotes dissipation of heat from the probe to surrounding media of both air and water. We expect that the difference in temperature between in air and water is due to the difference in their thermal conductivities.

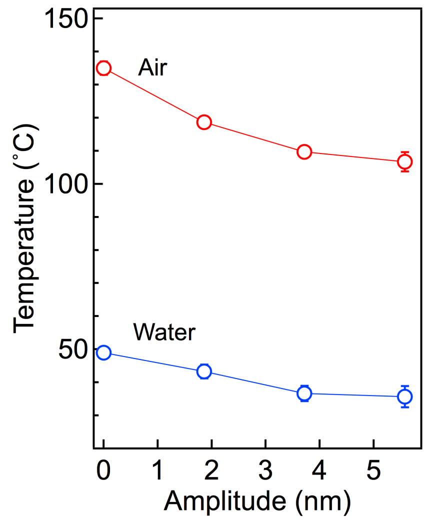

Fig. S2 Temperature of the bare silicon probe in water calculated with Eq. 2 plotted as a function of the amplitude of the cantilever oscillation under laser illumination

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