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# Tip-enhanced Raman scattering of glucose molecules

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#### Section 1: Scanning near-field optical microscope (SNOM)

#### **Preparation of SNOM-Holder**

As shown in Fig. S1, the SNOM-Holder consisted of a circuit board and a tuning fork. The circuit board of the SNOM-Holder was prepared using the PCB process: Plate thickness: 6 mm, Material: Fr-4; Gold sinking process. The tuning fork was obtained from a passive crystal oscillator with two resonance frequencies at 32.775 kHz and 190.749 kHz. Finally, the SNOM-Holder was prepared by assembled the tuning fork with the circuit board through the soldering process.



Fig. S1 | Photograph of SNOM-Holder.

#### **Preparation of PFT**

Plasmonic fiber tip (PFT) was batch prepared to ensure the reproducibility of the SNOM-TERS experiment. Thirty optical fibers (Corning, G.652D) with a length of ~1 m was orderly arranged with a home-built fiber holder, and the height of the unjacketed fiber end immersed in the hydrofluoric (HF) acid to 0.5 cm was accurately adjusted using a one-dimensional displacement table. The surface of HF acid (Concentration>40%) was sealed with dimethyl silicone oil (viscosity: 100±8 mPa·s). Due to the effect of the liquid surface tension, the unjacketed fiber end at the junction of the silicone oil and the HF acid will be etched into a cone<sup>\$1</sup>. Selecting silicone oil with different viscosities can adjust the liquid level tension at the interface between the HF acid and the silicone oil, thereby achieving adjustment of the cone angle<sup>\$2</sup>. The etched fiber tip was soaked in the anhydrous ethanol to remove residual impurities on the surface. Next, a 20 nm thick silver film was deposited on the surface of the bare fiber tip using the magnetron coating technology. During the deposition process, a high-purity (99.99%) silver sputtering target was chosen in an argon environment, with a working pressure of 0.6 Pa and a working power of 200 mW.

### Stability of SNOM system

The control module of SNOM system (NT-MDT) can monitor the displacement stability of the scanning head in the *x*-*z* axis. Due to the lateral displacement resolution of the scanning head being in the order of ~10 nm, the piezoelectric sensors use feedback voltage to monitor the displacement stability of the scanning head on the *x* and *y* axis, as shown in Fig. S2(a) and S2(b), respectively. The root mean square (RMS) of the feedback voltage on the *x* and *y* axis are RMS= $3.03 \times 10^{-5}$  and  $1.55 \times 10^{-4}$ , respectively. In addition, the feedback module provides monitoring results of the displacement stability of the scanning head in the *z* axis, as shown in Fig. S2(c), with the displacement range in the *z* axis being of ±1.5 nm.



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Fig. S2 | Stability monitoring of SNOM system in x-z axis.

# Section 2: Calculation of scattering and electric-field enhancement of PFT



Fig. S3 | Scattered far-field distribution of tip hotspot with a tip-silicon substrate distance of *d*=10 nm.



**Fig. S4** | Sketch map of tip-substrate distance under d=15 nm (**a**), 10 nm (**b**), and 5 nm (**c**), respectively. Transverse mode distributions of electric field of tip nanofocusing light source under d=15 nm (**d**), 10 nm (**e**), and 5 nm (**f**), obtained in *x-y* plane of the silicon surface. Horizontal distribution of electric fields (**g**–**i**) through the centers of (**d**–**f**), respectively.

#### Section 3: Resonance frequency response of tuning fork and tuning fork+PFT

The control module of SNOM confirmed the resonance frequency of the tuning fork based on the feedback current, but cannot obtain the absolute value of the transverse vibration displacement of the tuning fork. To solve this problem, an all-fiber optical heterodyne precision measurement device was built to simultaneously obtain the resonance frequency and the absolute value of the transverse vibration displacement of the tuning fork.

As shown in Fig. S5, a laser beam was output from a tunable laser and then amplified via an erbium-doped fiber amplifier (EDFA). The laser beam was divided into two beams via a fiber splitter, and then two acousto-optical frequency shifters (AOFS) shifted the frequency of two laser beams to make the two coherent laser beams with frequencies of  $A_1 cos(2\pi f_1 + \varphi_1)$  and  $A_2 cos(2\pi f_2 + \varphi_2)$ , respectively. The light beam with a frequency of  $f_1$  was led out from Port 2 of the collimator to collect the vibration information of the tuning fork. The vibration could change the light path in the arm, and the reflected beam with the vibration information of the tuning fork was led out from the Port 3 of the circulator and then it was combined with the laser beam with a frequency of  $f_2$  via the splitter. Thus, the carrier signal was generated and then detected by a photodetector. After the carrier signal was discretized by a data acquisition card, it was input into a demodulation software based on the LabVIEW platform.

The carrier signal generated by two coherent light beams with different frequencies was written as<sup>\$3,\$4</sup>

$$S(t) \propto \cos(2\pi f t + \delta \varphi)$$
, (S1)

where  $f=f_1-f_2$ ,  $\delta \varphi = \varphi_1 - \varphi_2$  were the frequency and phase difference of two coherent light beams, respectively.  $\delta \varphi$  was eliminated to be zero by a phase delay line to improve the signal-to-noise ratio (SNR) of the carrier signal. The vibration u(t) of the tuning fork could modulate the phase of the carrier signal, thus the resultant phase modulation signal was written as



Fig. S5 | Measurement of vibrational displacement of tuning fork and tuning fork+PFT based on home-built all-fiber optical heterodyne configuration.

$$V(t) \propto \cos\left[2\pi f t + \frac{4\pi}{\lambda}u(t)\right]$$
, (S2)

with  $\lambda$  being the light wavelength of the carrier signal. By modulating the phase modulation signal, the vibration information u(t) of the tuning fork was obtained including the vibration frequency and the absolute values of vibrational displacement.

The blue and red curves in Fig. S6(a) are the frequency response of the tuning fork measured via the control module of SNOM and the all-fiber optical heterodyne configuration, respectively. Note that, compared with the SNOM control module, the optical heterodyne configuration can provide a more accurate frequency response of the tuning fork. The low (Fig. S6(b)) and high (Fig. S6(c)) resonance frequencies of the tuning fork obtained by the all-fiber optical hetero-dyne configuration were consistent with the SNOM measurement results, and the *Q*-factor of the low and high frequency resonance modes were 2185 and 438, respectively. Furthermore, the absolute value of the transverse vibrational displacement of the tuning fork were given by the all-fiber optical heterodyne configuration, as shown in Fig. S6(d) and S6(e), respectively. The transverse vibration displacement of the high frequency resonance mode was about an order of magnitude smaller than that of the low frequency resonance mode.

With the PFT being of bonded to the shaft of the tuning fork, the frequency response of the tuning fork+PFT were measured using the control module of SNOM and the all-fiber optical heterodyne configuration, as shown the blue and black curves shown in Fig. S7(a), respectively. Note that, the low (Fig. S7(b)) and high (Fig. S7(c)) resonance frequencies of the tuning fork decreased to 30.027 kHz and 189.649 kHz, respectively. Furthmore, the Q-factor of the low and high frequency resonance modes decreased to 182 and 329, respectively. The absolute value of the transverse vibrational displacement of the tuning fork+PFT were also obtained by the all-fiber optical heterodyne configuration, as shown in Fig. S7(d) and S7(e), respectively. The transverse vibration displacement of the high frequency resonance mode. The introduction of PFT has little effect on the transverse vibration displacement of the low frequency resonance modes, but further reduces the transverse vibration displacement of the high frequency resonance modes.

Summary, when the PFT was attached to the shaft of the tuning fork, the high-frequency resonance mode not only has a higher *Q*-factor, but also has a smaller transverse vibration displacement, proving a stronger ability of the PFT to resist external environmental disturbances. Therefore, when performing the SNOM-TERS experiments, a more stable TERS signal can be obtained.

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**Fig. S6** | (a) Frequency response of tuning fork measured via control module of SNOM (blue curve) and all-fiber optical heterodyne configuration (red curve). Low (b) and high (c) frequency resonance modes measurement of tuning fork obtained via control module of SNOM (blue curve) and all-fiber optical heterodyne configuration (red dotted curve), and red curves were Lorenz fitting for red dotted curve. Transverse vibrational displacement of tuning fork working at low (d) and high resonance frequency (e).



**Fig. S7** | (a) Frequency response of tuning fork+PFT measured via control module of SNOM (blue curve) and all-fiber optical heterodyne configuration (black curve). Low (b) and high (c) frequency resonance modes measurement of tuning fork+PFT obtained via control module of SNOM (blue curve) and all-fiber optical heterodyne configuration (red dotted curve), and red curves were Lorenz fitting for red dotted curve. Transverse vibrational displacement of tuning fork+PFT working at low (d) and high (e) resonance frequency.

#### Section 4: SNR of far-filed Raman of SWNT

#### **Samples preparation**

Ultra-high purity single wall nanotube (SWNT, 25 mg/100 mL, Diameter: 1.2–1.7 nm) was purchased from NanoIntegris. Ultra-high purity SWNT aqueous solution was diluted 200 times with water, and then a small amount (5 mL) of the diluted solution was dropped onto the silicon wafer. The silicon wafers were placed in a fume hood to naturally air dry, and a layer of invisible carbon tubes was deposited on the silicon wafer.

# Far-filed Raman spectrum of SWNT

A linearly polarized beam at  $\lambda$ =632.8 nm and *P*=0.1 mW was focused via a micro-objective (MO, *NA*=0.42) and then illuminated the SWNT deposited on silicon used in Fig. 2(e). Figure S8 is the normalized far-field Raman spectrum of SWNT. Taking the Raman peak at 1556 cm<sup>-1</sup> for example, the signal-noise ratio (SNR) of the far-field excited Raman spectrum of SWNT was estimated to be SNR=6.7.



Fig. S8 | Normalized far-field Raman spectrum of SWNT.

#### Section 5: Shear-force topography via SNOM-Holder with PFT

A commercialized atomic force microscope (AFM, Bruker, Dimension fastScan) was adopted to scan the standard metal grating (NT-MDT, Height: 20-30 nm, Tip curvature radius: 50 nm). The multilayer WSe<sub>2</sub> and monolayer MoS<sub>2</sub> samples were grown on the single crystal silicon using the vapor deposition method<sup>85,86</sup>.



**Fig. S9** | AFM image of a standard metal grating (**a**) provided by NT-MDT and its enlarged view of one tip apex (**b**). (**c**) Shear-force topography for one tip apex of the metal grating obtained by SNOM-holder integrated with a PFT. (**d**) Optical microscope image of the multilayer WSe<sub>2</sub> grow on silicon substrate. Inset is shear-force topography of one multilayer WSe<sub>2</sub> unit. (**e**) Three-dismission topology of one WSe<sub>2</sub> unit with height of 40 nm shown in the inset. (**f**) Shear-force topography of one monolayer MoS<sub>2</sub> unit with height of 1.2 nm shown in the inset, proving that the longitudinal spatial resolution of SNOM is in the order of ~1 nm.



Fig. S10 | Chemical structures of (a) chain glucose molecule and (b) D-(+)-glucose molecule.

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No	DFT	TERS	Assignment	No	DFT	TERS	Assignment
	(cm⁻¹)	(cm <sup>-1</sup> )			(cm <sup>-1</sup> )	(cm⁻¹)	
1	485	485	O3–C2–C4 bending	18	1181	1177	C1,2,3-H, O1-H wagging
2	517	506	O3–H wagging	19	1207	1198	C4,5-H, O6-H wagging
3	558	555	C1–C2–O3 bending O5,6–H wagging	20	1234	1221	C1,2-H, O3-H wagging
4	623	616	C3–C4–C5 bending	21	1278	1275	C3-H, O5-H wagging
5	639	639	O2–H wagging	22	1288	1286	C3,4,5,6-H, O5, 6-H wagging
6	726	726	C4–C5–O6 bending	23	1310	1315	C3,5-H, O3-H wagging
7	795	795	C3–C4–C5 stretching	24	1374	1384	C2,3-H, O3,6-H wagging
8	840	824	C5–C6 stretching	25	1392	1398	C5-H, O6-H wagging
9	872	888	C1–C2–O3 stretching	26	1406	1410	C1,3,4-H, O5-H wagging
10	914	922	C4,5–H wagging	27	1433	1447	C3-H, O5-H wagging
			C4–C5 stretching				
11	968	953	C5–C6 stretching	28	1483	1499	C1-H scissoring
			C6–H wagging				
12	1001	994	O4–C1–C2 stretching	29	1753	1775	C6-O1 stretching
13	1041	1030	O4–C1 stretching	30	2856	2851	C6-H stretching
14	1046	1043	C2–C3 stretching	31	2877	2877	C3-H, C4-H stretching
15	1061	1070	C2–O3, C3–C4 stretching	32	2901	2906	C1,2,3,4,5-H stretching
16	1094	1117	C3–C4–C5 stretching C1–C2 twisting	33	2917	2926	C2-H stretching
17	1132	1147	C3–C4–C5 bending	34	2967	2957	C1-H stretching

Table S1 | Comparison of DFT-calculation and SNOM-TERS of Raman vibrational modes of glucose molecule and its assignment.<sup>57</sup>

#### Section 6: Raman spectra examination of glucose molecules using different illumination methods

As shown in Fig. S11(a), a focused linearly polarized beam (LPB) at  $\lambda$ =632.8 nm was illuminated on the glucose powder, and Fig. S11(d) is the obtained far-field Raman spectrum of glucose molecules.

As shown in Fig. S11(b), a silver film with a thickness of 100 nm was deposited on the silicon wafer by the magnetron sputtering method. As shown the AFM imaging in Fig. S12, the surface morphology of the silver film exhibited an island-like structure with a height of ~10 nm, which was adopted as the substrate of surface-enhanced Raman spectroscopy (SERS)<sup>S8-S11</sup>. The SERS substrate was immersed in a glucose aqueous solution with a concentration of  $10^{-1}$  mol/L for 24 hours, then it was removed and dried with nitrogen gas. Figure S11(e) is the obtained SERS spectrum by focusing a LPB at  $\lambda$ =632.8 nm on the SERS substrate.

Figure S11(c) is the sketch map of the tip-enhanced Raman spectroscopy (TERS)<sup>S12–S16</sup>. The PFT with a tip curvature radius of 20 nm (Fig. 1(c)) was integrated to the STM holder. Glucose molecules were deposited on the Au (111) substrate. The tip-substrate distance of 1 nm was maintained via the STM feedback. Figure S11(f) is the STM-TERS spectrum by a focused LPB at  $\lambda$ =632.8 nm side illuminating on the tunneling junction. Note that, the STM-TERS could detect more vibrational modes of the glucose molecules than that of the conventional Raman and SERS.



Fig. S11 | Glucose molecules examination using (a) conventional far-field Raman, (b) SERS and (c) TERS, respectively. (d–f) Raman examination results corresponding to (a–c).



Fig. S12 | AFM imaging of surface morphology of silver film deposited on silicon wafer.

#### Section 7: Position-dependence of SNOM-TERS spectra

Experimentally, we can obtain SNOM-TERS spectra at different locations of the glucose molecules cluster (Fig. S13(a) by adjusting the spatial position relationship between the tip hotspot and the glucose molecules. When the tip hotspot was positioned at Point 2, the SNOM-TERS spectrum is only background noise, as shown in Fig. S13(b). Furthermore, the tip hotspot was positioned at Point 3, and the obtained TERS spectrum is shown in Fig. S13(c). Therefore, by adjusting the position relationship between the tip hotspot and the glucose molecule (Point 1), we can obtain the SNOM-TERS spectrum (Fig. 3(f)) which is more consistent with the DFT calculation results (magenta curve in Fig. 3(g)).



Fig. S13 | (a) Shear-force topography of glucose molecules cluster dispersed on a silicon substrate. SNOM-TERS spectra obtained by positing the tip hotspot at Point 2 (b) and Point 3 (c).





**Fig. S14** | (a) Time-series of SNOM-TERS spectra of glucose molecule at ~2906 cm<sup>-1</sup>, integration time was 120 s for each cycle. (b) Illustrations for Raman vibrational mode at ~2906 cm<sup>-1</sup>. Gray, red, and white atoms indicate carbon, oxygen, and hydrogen, respectively. (c) Time variation of SNOM-TERS signal intensity.



Fig. S15 | Raman spectra of silicon (black curve) and hydrophilic silicon (red curve).

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