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Raman Fingerprinting of Single Dielectric Nanoparticles in Plasmonic Nanopores

Sarp Kerman[a,b], Chang Chen[a,b], Yi Li[b,c], Wim Van Roy[a], Liesbet Lagae[a,b], Pol Van Dorpe[a,b]

Supporting Information

Forces Acting On a 20 nm Polystyrene Particle In Nanopore and Contact Mechanics

We mainly considered the electrostatic force, van der Waals force and optical force acting on the particle and compared their orders of magnitude. All forces are calculated for a particle in the middle of the long axis of nanopore. Optical force is calculated by FDTD simulations.

The electrostatic force is calculated by assuming that the metal surface of the nanopore is an infinite planar surface due to the large curvature of nanopore and the vicinity of the particle. Another assumption we made is that the Debye length of the deionized water is much longer than the distance of the particle to the nanopore's wall. Therefore, the force acting on the particle from one wall of the nanopore is[1]

$$F_e = \frac{Q^2}{16\pi\varepsilon_0\varepsilon_w d^2}$$

where, Q is the total charge of the particle, calculated from the carboxyl charge titration data provided with the particle solution as 2.73x10^{-16} C , ε_0 is the vacuum permittivity, ε_w is the water's relative permittivity[2] taken as 80.4, and d is the distance from nanoparticle's center to nanopore's wall. We sum the electrostatic force acting on the nanoparticle for both sides of the nanopore's wall to calculate the total electrostatic force. It should be noted that we didn't take the local changes into account such as the change in permittivity of water due to high electric field[2] or the shape deformation of the particle.

The van der Waals force acting on the particle is also calculated by assuming that the gold surface is an infinite plane and the particle stays as a perfect sphere, therefore, the force is[3]

$$F_{vdW} = \frac{A\,r}{6(d-r)^2}$$

Where $A = 2.75 \times 10^{-20}$ is the Hamaker constant of polystytrene-gold in water[4] , r is the radius of the particle.

The force required to create plastic deformation at the contact of the polystyrene nanoparticle with gold surface is calculated by the Hertzian contact theory[5]. Where the contact pressure exceeds the compressive strength of polystyrene[6], $p_{pl} \cong 100\,MPa$, the contact becomes elastoplastic. Therefore, the force required for plastic deformation as $F_{pl} = 48\,pN$ using

$$F_{pl} = \frac{p_{pl}{}^3\pi^3 r^2}{6E^{*2}}$$

$$\frac{1}{E^*} = \frac{1-v_1{}^2}{E_1} + \frac{1-v_2{}^2}{E_2}$$

where $v_1 = 0.34$ and $v_2 = 0.42$ are the Poisson ratios, $E_1 = 3GPa$ and $E_2 = 79\,GPa$ are the elastic moduli of polystyrene and gold.

Dwell Time of Particle Trapping Events

Fig. S1 shows the dwell times histogram of the SERS events for different powers. We didn't observe any significant change of the particle dwell times with increasing laser power. Despite the optical force acting on the particle increases, the temperature increases as well, which makes the particles more mobile. Those two counter-acting effects prohibits a trend of dwell time dependence on laser power.

[a.] imec, Kapeldreef 75, Leuven, B3001, Belgium
[b.] Department of Physics and Astronomy, KU Leuven, Celestijnenlaan 200D, 3001 Leuven, Belgium
[c.] Department of Electrical Engineering, KU Leuven, Kasteelpark Arenberg 10, 3001 Leuven, Belgium
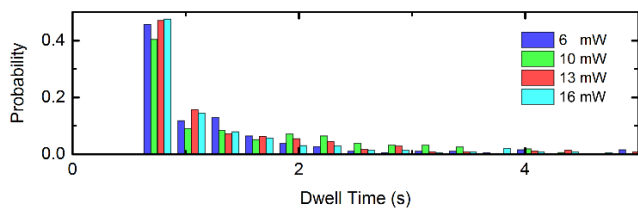See DOI: 10.1039/x0xx00000x

Fig. S1 The histogram of trapping event dwell times for different laser powers

Thermal Simulations

We performed finite element method simulations by using Comsol v3.4 in order to quantify the temperature change and distribution, which the details have been described before[7]. Fig. S2 shows the temperature distribution inside the nanopore for the highest intensity used in our experiments. The room temperature is defined as 293.15 K and the temperature change we estimate from the simulations is 0.418 K/mW . It should be noted that the distribution is close to isothermal state inside the nanopore.
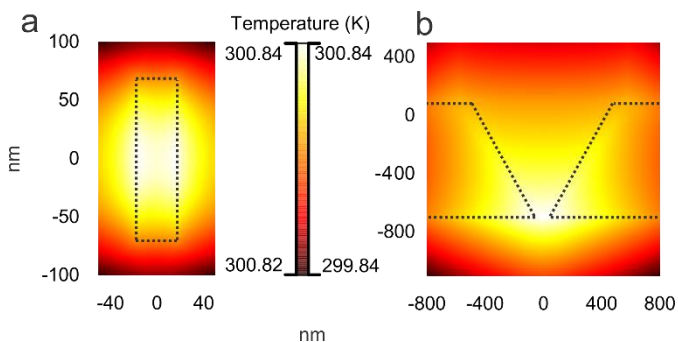

Fig. S2 The temperature distribution for the plasmonic nanopore illuminated by 16 mW of 785 nm laser wavelength. (a) The top view of the temperature profile of the nanopore (b) The side view of the temperature profile of the nanopore. The dashed lines indicate the contour of the nanocavity pore.

FDTD Simulations

The enhancement factor is simulated for the case where there is a polystyrene nanoparticle inside the nanopore. Fig. S3 shows the enhancement factor distribution inside the particle in the presence of a 20 nm polystyrene nanoparticle from the top in cases where it's in the middle, Fig. S3 a, and its closest interface is 0.5 nm apart from the gold surface, Fig. S3 b. The top view, shows that the enhancement is mostly localized at the interface of the particle due to refractive index contrast between water and polystyrene.

In order to estimate the effect of the enhancement factor on the SERS signal in cases where the particle is in the middle of the nanopore and 0.5 nm away from the nanopore's surface, the enhancement factor is integrated over the particle for Fig. S3 a and Fig. S3 b. The integrated enhancement factor increases 14.8% when the particle is 0.5 nm away from the gold surface

compared to the case where it's in the middle of the nanopore. However, as the SERS signal is mostly generated from the particle/water interface, we integrated the enhancement factor for a 2 nm shell inside the particle and 0.3 nm shell outside. The integrated factor increases 17.1% for 2nm shell inside and 19.1% for 0.3 nm shell outside the particle when the particle is in the vicinity of the gold surface. Therefore, according to the FDTD simulations, we don't expect a considerable change in amplitude when the particle is touching the nanopore's wall.
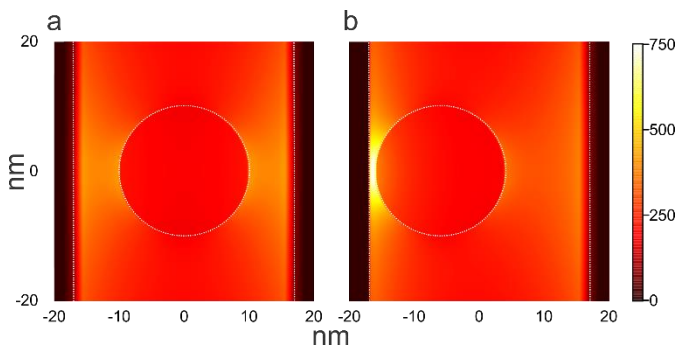

Fig. S3 The FDTD simulation results of the enhancement factor, the top view of the optical intensity distribution in the nanopore with a polystyrene nanoparticle inside. (a) The polystyrene nanoparticle in the middle of the nanopore (b) The polystyrene nanoparticle close to the left side of nanopore's wall. The dashed lines indicate the contour of the nanocavity pore and the polystyrene nanosphere.

Reproducibility: Experiments with another nanopore

We tested the reproducibility of the shift of polystyrene SERS peak around 785 cm-1 by performing the experiment on a different nanopore with 28x110 nm2 size. Fig. S4 shows the probability distribution of the peak position for a different nanopore at 2 different laser powers. We observed that the shift is reproducible for different nanopores around the same dimensions.
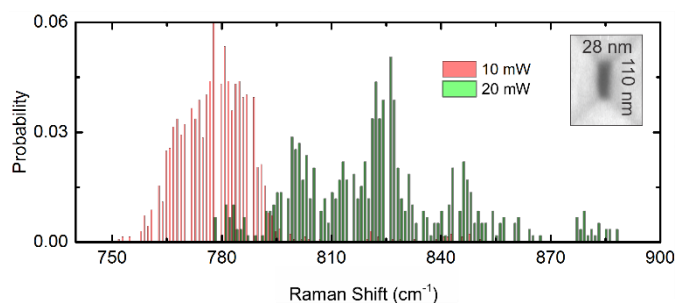

Fig. S4 The histogram of the peak positions of polystyrene nanoparticle in a different nanopore inset: SEM picture of the nanopore used.

Notes and references

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