Electronic Supplementary Material (ESI) for Lab on a Chip

Supplementary Information

Optofluidic SERS chip with plasmonic nanoprobes self-aligned along microfluidic channels

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< The impact of plasma treatment on silver film >

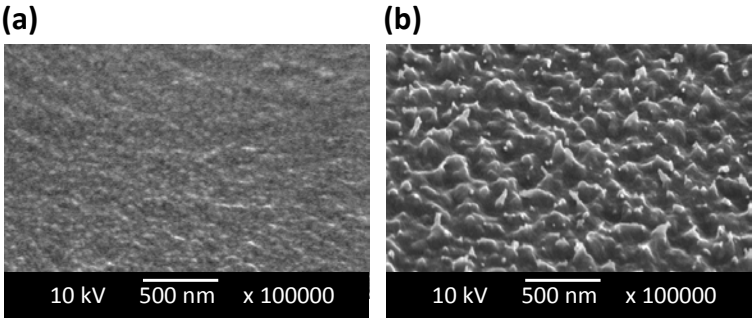

Figure S1. (a) SEM image of the microfluidic channel wall covered with 30 nm thick silver film. (b) SEM image of the microfluidic channel with plasmonic nanoprobes (after plasma treatment, 30 nm in initial silver thickness). The plasma treatment transformed silver film into roughened nanotextures with nanotips and nanodots.

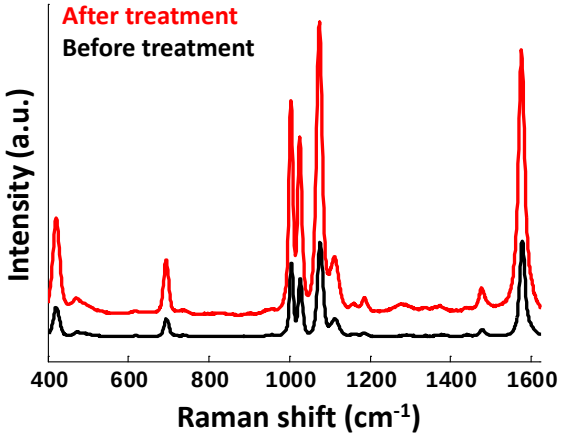

Figure S2. SERS spectra of benzenethiol on silver film (30 nm) and plasmonic nanoprobes made by plasma treatment. The plasmonic nanoprobes with nanotips and nanodots provide more than three times stronger signal than that from the silver film before treatment.

< SERS enhancement factor calculation >

The SERS enhancement factor was calculated in a similar way to the previous work (Y.-J. Oh and K.-H. Jeong, *Adv. Mater.*, 2012, **24**, 2234-2237).

The average enhancement factor of $\boldsymbol{EF_{ave}}$ of the substrate (plasmonic nanoprobes) is defined as

$$\boldsymbol{EF_{ave}} = (\boldsymbol{I_{SERS}} / \boldsymbol{N_{SERS}}) / (\boldsymbol{I_{Raman}} / \boldsymbol{N_{Raman}})$$

$\boldsymbol{I_{SERS}}$: SERS intensity, $\boldsymbol{N_{SERS}}$: number of probed molecules in SERS,

$\boldsymbol{I_{Raman}}$: Raman intensity, $\boldsymbol{N_{Raman}}$: number of probed molecules in Raman measurements.

* The excitation wavelength was 632.8 nm, and the laser beam spot radius was about 2.5 μm.

* The $\boldsymbol{I_{SERS}}$ is 7205.3 (the calculation is based on 1075 cm^{-1} peak).

* Surface area of silver is about 3.5 times increased compared to the flat layer. The surface coverage of benzenethiol on silver is assumed to be $3.3*10^{14}$ cm^{-2}, and then the $\boldsymbol{N_{SERS}}$ is about $2.2*10^{8}$.

* $\boldsymbol{I_{Raman}}$ is 38.3 (1094 cm^{-1} peak). The excitation power and the acquisition time are compensated for both $\boldsymbol{I_{SERS}}$ and $\boldsymbol{I_{Raman}}$.

* $\boldsymbol{N_{Raman}}$ is about $1.3*10^{13}$ (collection depth 110 μm, density of the benzenethiol 1.073 g/ml, and the molecular weight 110.18 g/mol).

From the above values, we obtain $\boldsymbol{EF_{ave}} \approx 1.1*10^{7}$.

< Silver structure oxidation >

	Wt %			Ratio
Sample	Si K	O K	Ag L	O K / Ag L
Ag 30 nm	90.55	1.39	8.05	0.17
Plasma treated	83.38	3.39	13.22	0.26

Table S1. Electron dispersive X-ray spectroscopy (EDS) analysis of silver film (30 nm) before and after oxygen plasma treatment. Increase in oxygen ratio after plasma treatment indicates the oxidation of the silver structure. The silicon substrate was used for fabrication and EDS analysis to minimize the effect of oxygen in substrate material (note that the PDMS have abundant oxygen components).