Supporting Information

Semi-permeable membrane stabilized microfluidic plasma chip for continues, tunable synthesis of sub-10 nm nanoparticles

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EXPERIMENTAL SECTION

Materials and preparations. In a typical experiment, the precursor solution was prepared by mixing with gold chloride solution ($HAuCl_4$, 1 ml, 1.214 mM) and sodium citrate (3 ml, 34 mM). $HAuCl_4$ and sodium citrate were purchased from Aladdin. Polydimethylsiloxane (PDMS) was purchased from the Dow Chemical Company. For microchannel fabrication, a mold was initially prepared by 3D printing (Form3, Formlabs). Meanwhile, 2 g of SYLGARD™ 184 Silicone Elastomer Base was well-dissolved in 20 g of SYLGARD™ 184 Silicone Elastomer Curing Agent. After the mixture is defoamed, the PDMS solution is cast onto the mold and solidified at 60 °C for 12 h. PTFE semi-permeable membrane (60 μm, Suzhou Zeyou Fluoroplastic Materials Technology Co., Ltd.) was cut into 20 × 10 mm pieces before use.

For the experimental system, the plasma flow in the channel was activated by an alternating current (AC) power supply (Nanjing Suman Plasma Technology, CTP-2000K, Nanjing, China), in which Helium was used as the working gas. ZnO nanowires substrate was prepared by chemical bath deposition on seed layer coated glass substrate. The seed layer was deposited for 30 nm with atomic layer deposition (ALD, PicoSun RC200, Japan). The growth was carried out at 200 °C for 300 cycles with a flow rate of 150 sccm for diethylzinc (DEZ) and 200 sccm for H_2O. The pulse duration was 0.1 and 0.2 s for DEZ and H_2O, respectively. Afterward, the seed layer coated substrate was immersed in a solution with 0.015 M for both $Zn(NO_3)_2$ (99.8%, Sigma Aldrich, USA) and hexamethylenetetramine (HTMA, 99.9%, Sigma Aldrich, USA). To improve the surface-enhanced Raman Scattering effect on the ZnO substrate, Au nanoparticles from the microplasma reactor were dropping onto a substrate using

a micropipette, followed by drying the substrate at 40°C for 20 min using an oven. This process was repeated 10 times to increase the deposition of Au NPs onto the substrate.

Characterization. The synthesized AuNPs were characterized by a Transmission Electron Microscope (TEM) (FEI, Talos F200X G2, 200 kV) coupled with an energy-dispersive x-ray spectrometer (EDX). The transmittance of the solution after plasma treatment was examined by a Lambda 950 UV-visible spectrometer. SERS spectra were acquired with a con-focal microprobe Raman spectrometer (Renishaw, inVia). The experiments were conducted with a 758 nm laser wavelength.

Yield of Au nanoparticles(Y) calculation.

The yield of Au nanoparticles(Y) can be calculated as the ratio between the actual mass concentration(C_{actual}, mg/mL) and the initial solution concentration ($C_{initial}$, representing 100% yield in mass concentration terms, mg/mL).

$$Y(\%) = \frac{C_{actual}}{C_{initial}} \times 100$$

The particle concentration of nanoparticles(mol/L) can be calculated by the Haiss equation:[1]

$$C_{particle} = \frac{A}{\varepsilon \times L}$$

where A represents the absorbance at the corresponding wavelength, ε is the molar extinction coefficient for nanoparticles, and L is the optical path length. The particle concentration is subsequently converted to the actual mass concentration based on the nanoparticle size and density.

$$C_{actual} = C_{particle} \times \frac{\pi d^3}{6} \times \rho$$

The $C_{initial}$ is calculated as the molar concentration of the gold precursor(mol/L) multiplied by the atomic weight of gold (196.97 g/mol), expressed in mass concentration units (μg/mL).

$$C_{initial} = C_{HAuCl4} \times M_{Au}$$

SERS enhancement factor (EF) calculation.

The calculation of the EF is based on the following formula:[2]

$$EF = \frac{I_{SERS}}{I_{Raman}} \times \frac{N_{Raman}}{N_{SERS}}$$

where I_{SERS} is the SERS intensity of a specific Raman vibrational line in the R6G spectrum on Au-modified ZnO nanorods, I_{Raman} is the R6G Raman intensity measured on pristine ZnO nanorods. N_{Raman} and N_{SERS} represent the estimated average numbers of adsorbed molecules generating the reference Raman signal and SERS signal, respectively.

The value of N_{Raman} can be estimated by the number of molecules within the laser focal volume:[3]

$$N_{Raman} = C_{R6G} \times V \times NA$$

where C_{R6G} is the concentration of R6G (10^{-3} M), V is the laser focal spot volume, and NA is Avogadro's number.

The laser focal spot volume can be approximated as a cylinder, calculated as the product of the spot size (d) and the depth of focus (DOF). Both the spot size and depth of focus can be estimated using the numerical aperture (NA = 0.4) and laser wavelength (λ = 758 nm):

$$V = d \times DOF = \frac{2\lambda}{NA^2} \times \frac{1.22\lambda}{NA}$$

N_{SERS} can be estimated by the number of molecules adsorbed on the focal plane within the laser spot area:[4]

$$N_{SERS} = (4\pi r^2) \times C \times A \times D \times (\pi dh) \times N$$

Here, r, C, A, D, d, h, and N represent the average radius of Au NPs, the surface density of R6G monolayer, the laser spot area, the areal density of nanorods (rods/μm^2), diameter of nanorods, average length of nanorods, and surface coverage of Ag NPs (particles/μm^2), respectively.

The final calculations yield: $I_{SERS} = 1.29 \times 10^4$; $I_{Raman} = 1.03 \times 10^2$; $N_{Raman} = 2.41 \times 10^7$; $N_{SERS} = 4.56 \times 10^5$; $EF = 6.63 \times 10^3$.

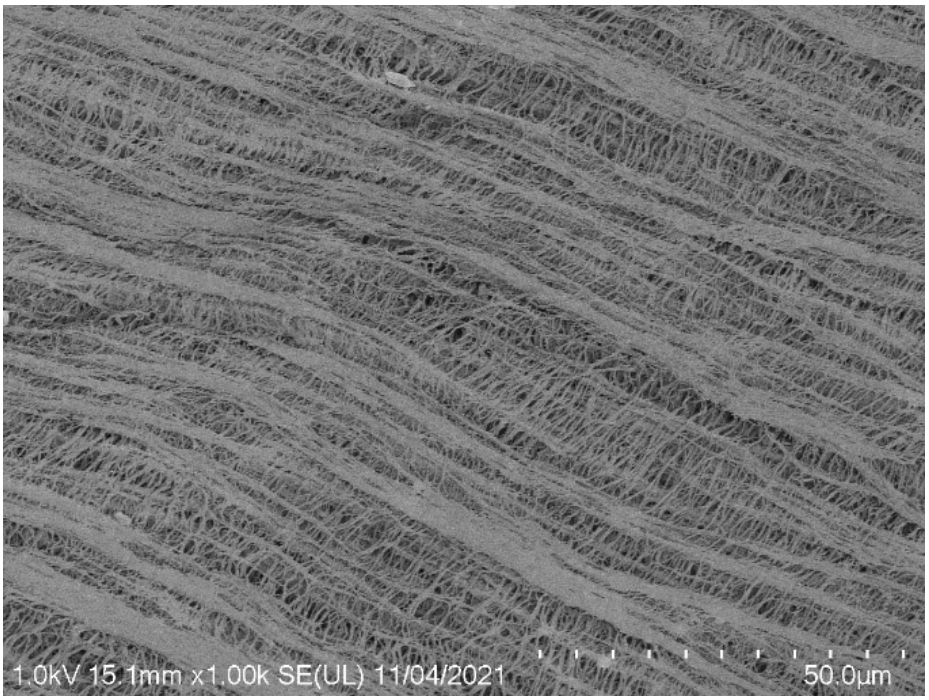

Figure S1. FE-SEM image of the PTFE semi-permeable membrane.

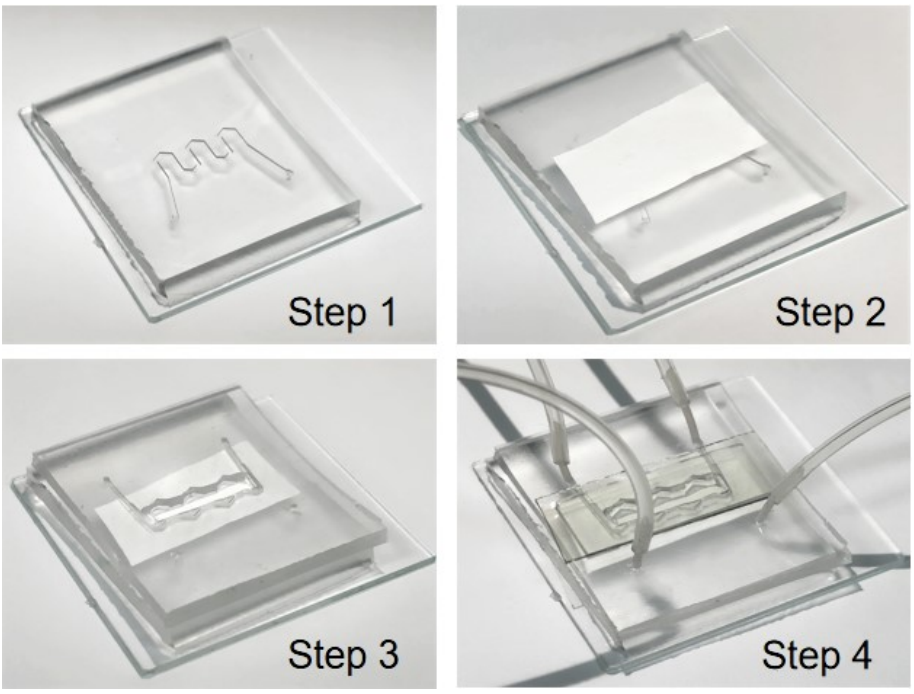

Figure S2. Fabrication process of microfluidic plasma chip.

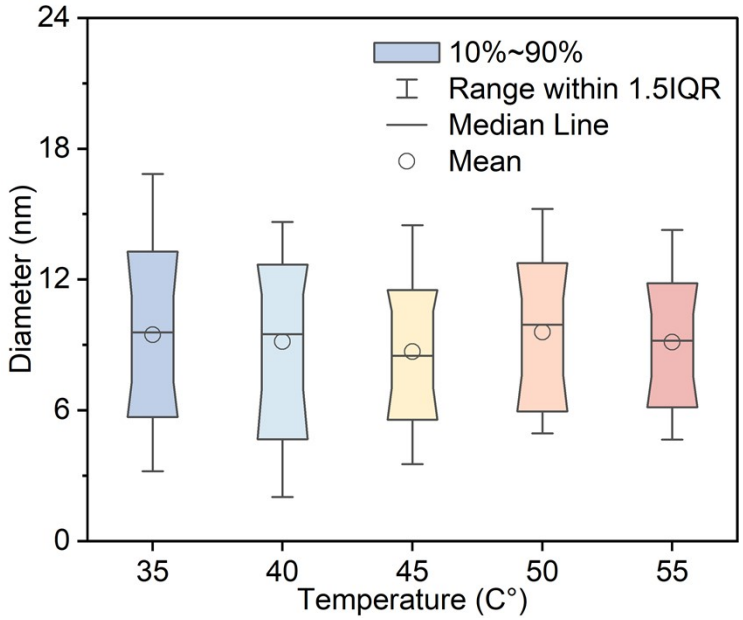

Figure S3. Notched box chart displaying the summarized diameter distribution under different temperatures, indicating the 90th, 75th, 25th, and 10th percentile diameters from top to bottom of each box.

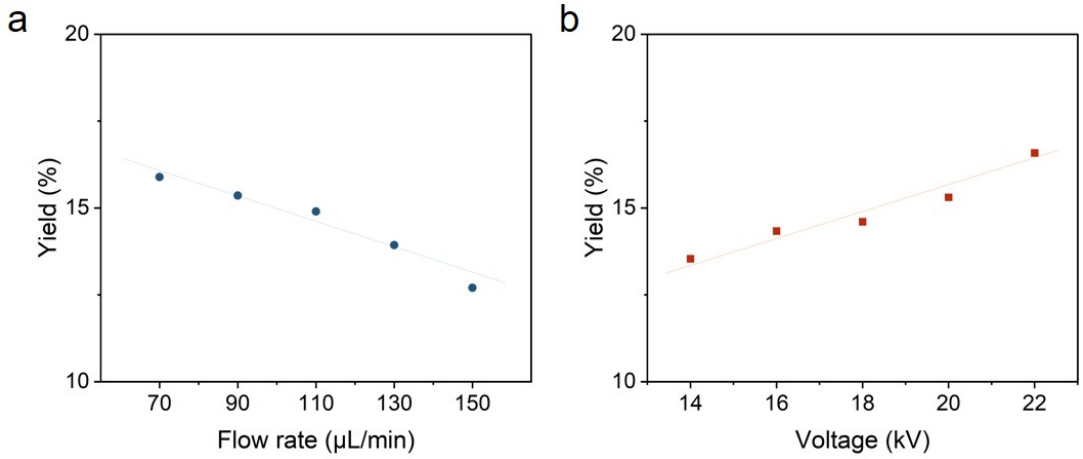

Figure S4. Yield of the Au nanoparticles versus (a) flow rate and (b) voltage.

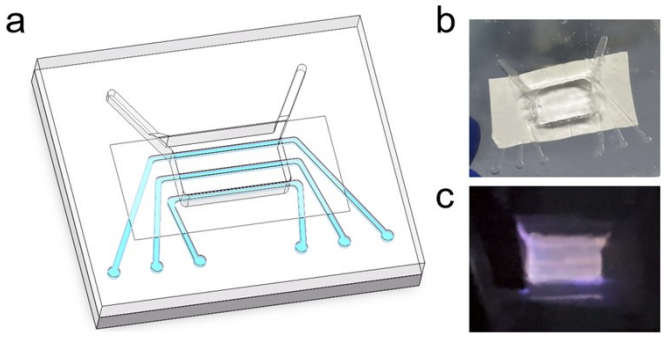

Figure S5. a). Schematic illustration of the three parallel liquid channel(blue) microfluidic plasma chip. b). PDMS assembled chip and c). three microplasma glow lines in the gas/plasma channel.

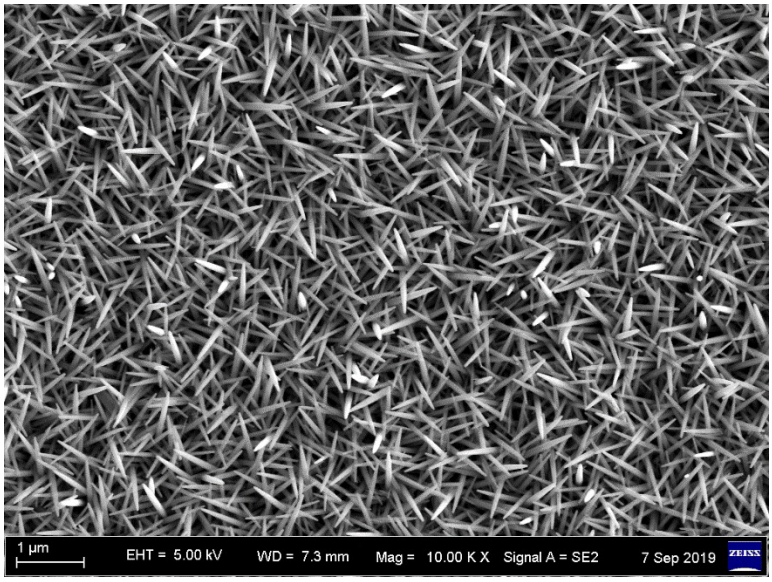

Figure S6. FE-SEM image of the ZnO nanowires substrate.

Reference

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