Electronic Supplementary Information

Highly reproducible SERS arrays directly written by inkjet-printing

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1. Experimental Section

Materials

Silicon substrates were purchased from Tianjin Institute of Semiconductors. Hydrogen tetra-chloroauric acid ($HAuCl_4 \cdot 4H_2O$, gold content ≥47.8%) was purchased from Shenyang Jinke Reagent Co., Ltd. Trisodium citrate (ca. 98%) was supplied by Beijing Chemical Plant. Polyvinylpyrrolidone (PVP, $M_w = 4\times10^4$ g mol^{-1}) was purchased from Sigma-Aldrich. Rhodamine 6G (R6G, ca. 99%) was purchased from J&K Scientific. Decyltrichlorosilane (ca. 97%) and 1*H*, 1*H*, 2*H*, 2*H*-perfluorodecyltriethoxysilane (97%) were obtained from Alfa Aesar China (Tianjin) Co., Ltd. All other reagents used were of AR grade. Ultrapure water (Milli-Q, 18.2 MΩ cm) was used through this experiment.

AuNPs ink preparation

PVP-capped AuNPs were synthesized according to Frens'[1] and Liu'[2] methods. Briefly, 0.048 g PVP was added into 50 mL aqueous solution of $HAuCl_4 \cdot 4H_2O$ (50 mg) and heated to boiling. Then 10 ml of trisodium citrate solution (1%) was added and the solution was refluxed for 15 min. 150 mL of acetone was added into the reaction solution and was separated by centrifugation (3000 rpm for 5 min). The AuNPs ink was prepared by dissolving the PVP-capped gold nanoparticles in the mixed solution of ethylene glycol and deionized water to a concentration of 50 mg mL^{-1}.

Silicon substrates preparation

Six different silicon substrates (five smooth and one structured silicon substrates) were used for investigating the dewetting and assembly behavior of AuNPs droplets. Five smooth substrates were cleaned sequentially by ethanol, ultrapure water and piranha solution (volume ration H_2O_2:H_2SO_4=1:3) before using. The subtrates with contact angles of 30°, 60°, 80°, 100° were obtained by immersing the cleaned silicon wafers into methylbenzene solution with 10 ppm octyltrichlorosilane for 5, 10, 20, 30 seconds respectively. The substrates with contact angle of 120° were obtained by modifying the cleaned silicon wafers in vacuum by chemical vapour deposition (CVD) of 1H, 1H, 2H, 2H-perfluorodecyltriethoxysilane (PFDTS). The superhydrophobic substrates were obtained by modifying structured silicon wafers in vacuum by CVD of PFDTS. The structured silicon wafers were prepared by Ag-assisted chemical etching in HF solution, which were reported by some literatures.[3]

Inkjet printing AuNPs microarray patterns

The microarrys was printed by Dimatix Materials Printer (DMP-2831, Inc. Santa Clara, CA). During printing, a custom wave form was used. The effects of substrates wettability and assembly behavoir of AuNPs droplet were investigated.

As for the effect of wettability, 10 pL AuNPs were inkjet printed on silicon substrates with contact angles of 30°, 60°, 80°, 100°, 120°, and 150°. The hydrophobic SERS microarray chip with a 3 × 3 matrix was printed on hydrophobic substrates with contact angle of 117°. The spots spacing was set to 100 μm.

Characterization

FE-SEM images were obtained by a scanning electron microscope (JSM-6700F, JEOL, JPN) at 3.0 kV. Microscope images were obtained by an Olympus microscope (BX51, Olympus, JPN). Contact angles were measured on a contact-angle system (OCA20, Dataphysics Co., GER). SERS spectra were measured from a laser Raman microscope (inVia plus, Renishaw, UK).

SERS measurement

Analytes solution with a volume of 5 μL were injected on each spot. After dried, the SERS spectra of analytes were recorded. The sensitivity and detection limit were achieved by analyzing the SERS signals with R6G conentration ranging from 10^{-4} M to 10^{-10} M. The reproducibility was charaterized by recording SERS signals with at least 5 sites in one spot and 9 spots randomly selected from the chip. The stability was tested once a week for 12 weeks. SERS testing conditions: The excitation wavelength was 633 nm, the laser power is 0.5 mW on the sample through a ×50 objective, the integral time is 5 seconds.

2. AuNPs characterization

The as-prepared AuNPs utilizing in the SERS-active substrates were characterized by TEM and UV-vis spectroscopy.

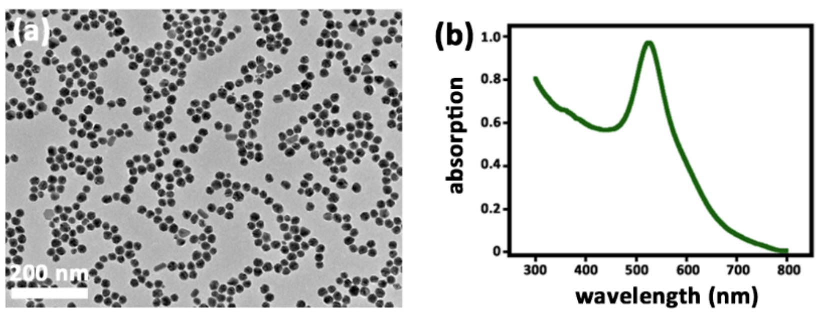

Fig. S1 (a) TEM image of AuNPs which showed the monodispersity was excellent. (b) UV-vis spectrum for the AuNPs dispersion.

3. Theoretical calculating diameters of droplets

When a droplet was dropped or printed on a substrate, the wetted area would be influenced by the wettability of substrates. On these substrates (Fig. S2), a ball-lacking type will formed and its volume (V) can be calculated by its contact angle (θ) and diameter (d) of the wetted area.

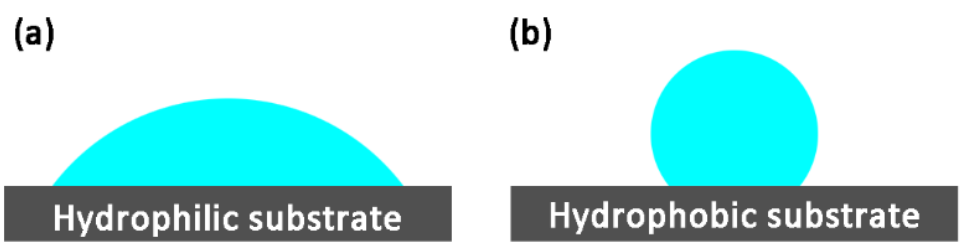

Fig. S2 Schematic illustration for the droplets on hydrophilic (a) and hydrophobic (b) substrates.

On the hydrophilic substrates (Fig. S2a), the volume of the ball segment was smaller than that of a half ball. As we know, the volume (V) of ball segment have below relationship with the contact angle and diameter.

$$V = \frac{1}{6}\pi h(3r^2 + h^2) \tag{1}$$

Where V is the volume of the ball segment, h represents the height of the ball segment, r means the radius of the ball segment.

The relationship between r and h can be demonstrated in below.

$$h = \frac{r(1 - cos\theta)}{sin\theta} \tag{2}$$

where θ is the contact angle of the segment ball.

And we know that

$$r = \frac{d}{2} \tag{3}$$

where d is the diameter of the segment ball.

Combining the equations above together, we can get the relationship between V and d with θ.

$$V = \frac{1}{24}\pi d^3 \frac{(2 + cos\theta)(1 - cos\theta)^2}{\sin^3\theta} \tag{4}$$

As for the hydrophobic substrates (Fig. S2b), the relationship can be illustrated:

$$V = \frac{1}{6}\pi d^3 - \frac{1}{24}\pi d^3 \frac{(2 - cos\theta)(1 + cos\theta)^2}{\sin^3\theta} \tag{5}$$

In our work, the volume of ink drop is 10 pL, the relationship between d and θ is showed below:

$$d = \begin{cases} \sqrt[3]{\dfrac{24V sin^3\theta}{\pi(2 + cos\theta)(1 - cos\theta)^2}}, & \theta < \dfrac{\pi}{2} \\ \sqrt[3]{\dfrac{24V}{\pi\left(4 - \dfrac{(2 - cos\theta)(1 + cos\theta)^2}{\sin^3\theta}\right)}}, & \theta > \dfrac{\pi}{2} \end{cases} \tag{6}$$

According to Equation (6), the diameters of printed spots can be calculated and showed in below with the drop volume of 10 pL.

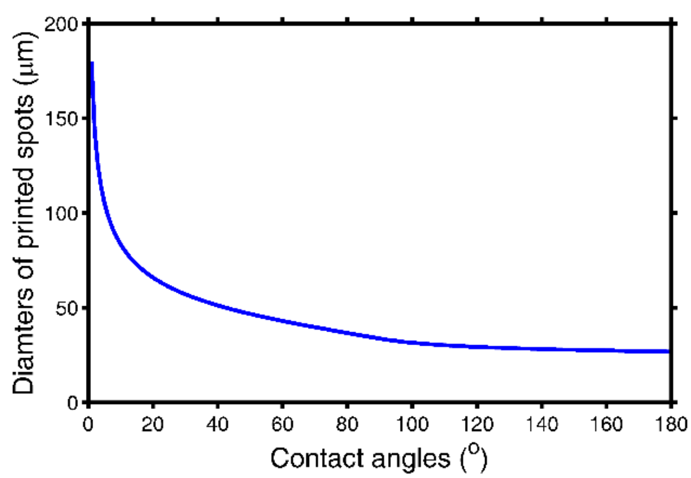

Fig. S3 The theoretical calculated diameters of printed droplets with respected to different contact angles.

The drying processes of inkjet printed droplets on substrates with different wettability were recorded by the microscopy on the inkjet printer. The processes showed in Fig. S4 proves the reasonability of the proposed drying processes in Fig. 2e.

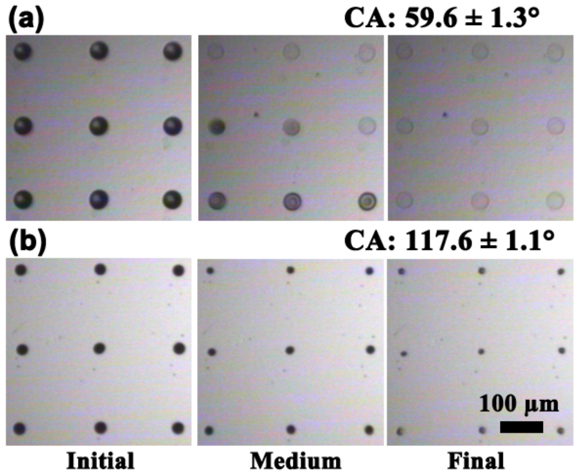

Fig. S4. The drying processes of inkjet printed droplets on hydrophilic (a, CA: 59.6 ± 1.3°) and hydrophobic (b, CA: 117.6 ± 1.1°) substrates, respectively

References

1 G. Frens, *Nat. Phys. Sci.*, 1973, **241**, 20.

2 W. X. Tu and H. F. Liu, *J. Mater. Chem.*, 2000, **10**, 2207.

3 a) K. Q. Peng, J. J. Hu, Y. J. Yan, Y. Wu, H. Fang, Y. Xu, S. T. Lee and J. Zhu, *Adv. Funct. Mater.*, 2006, **16**, 387; b) K. Peng, Y. Wu, H. Fang, X. Zhong, Y. Xu and J. Zhu, *Angew Chem Int Ed Engl*, 2005, **44**, 2737.