Supplemental Information for “Buoyant particulate strategy for few-to-single particle-based plasmonic enhanced nanosensors” by Zhang et al.

Buoyant particulate strategy for few-to-single particle-based plasmonic enhanced nanosensors

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**Supplementary Tables**

**Supplementary Table 1.** Evaporation speed of aqueous and ethanol solvent with 60 μL in volume.

| Heating Temperature | Aqueous solution of CV molecules | Ethanol solution of CV molecules |
|---------------------|---------------------------------|---------------------------------|
| 150°C               | 15 min                          | 3 min                           |
| 120°C               | 19 min                          | 3 min 35 s                      |
| 100°C               | 27 min                          | 4 min 40 s                      |
| 80°C                | 47 min                          | 7 min                           |
Supplementary Notes

Supplementary Note 1: Calculation of solvent and molecules enrichment factor.

The enrichment efficiency of solvent and molecules on the hydrophobic slippery surface was evaluated based on the changes of solvent surface area during evaporation. Firstly, we estimated the surface area of the initial droplet with 60 μL in volume. As shown in Supplementary Fig. 18, the drop was ~5.8 mm in diameter, and thus the surface area $S_1$ could be obtained as following:

$$S_1 = \frac{1}{4} \pi D_1^2 = \frac{1}{4} \times 3.14 \times (5.8)^2 \; mm^2 = 2.5 \times 10^7 \; \mu m^2$$

After the droplets drying on the hydrophobic slippery substrate, almost all solvent and molecules were concentrated on the surface of single particle or into the interface region of dimer particles. In case of single buoyant particle (Supplementary Fig. 18), we assumed that all of solvent and probe molecules were concentrated on the surface region of single particle according to the experiment results. Thus, the surface area $S_2$ could be obtained as following:

$$S_2 = \pi D_2^2 = 3.14 \times (30)^2 \; \mu m^2 = 2826 \; \mu m^2$$

In case of dimer buoyant particle, most solvent and analytes were concentrated into the gaps region according to the fluorescence imaging in Fig.2a. We assumed that all molecules were guided into the marked region shown in Fig. 2c and Supplementary Fig. 7. The surface area $S_3$ could be calculated as following:

$$S_3 = 2 \times (a \times b + b \times c + a \times c) = 2 \times (3 \times 10 + 10 \times 10 + 3 \times 10) \; \mu m^2 = 320 \; \mu m^2$$

Lastly, the enrichment factors of solvent and molecules for single particle and double particles were defined as $\varepsilon_1$ and $\varepsilon_2$, which were calculated by the specific value of surface area before and after evaporation. Therefore, we could obtain the final $\varepsilon_1$ and $\varepsilon_2$ as following:
Supplementary Note 2: Theoretical section

1. To understand the aggregation mechanism of buoyant particulates, we developed an analytical model to describe the influence of floating-particle configurations on droplet evaporation. The model is rooted in the force analysis of the suspended particulate at three phase (air–water-substrate) interfaces (Fig. 3c). For the floating-particle at the final evaporation stage as shown in Fig. 3c, a thin wetting film may be formed between the particle and substrate. The liquid bridge covering particles is formed and the height of liquid surface is close to the particle diameter. Thus the driving force acting on the particle can be written as

\[ F_p = 2\pi\sigma R (\cos\theta_R + \cos\theta_p) \]  

(1)

where \( \theta_p \) is the contact angle between the liquid surface and particle surface, as shown in Fig. 3c, which is a natural parameter about the substrate, solvent, and atmosphere. For the current system, the values of \( \theta_p \) and \( \theta_R \) can be regarded as invariant. Therefore, the driving force acting on the particle is only affected by the particle radius.

In a CCA evaporation mode, it is reasonable to assume that the sliding friction force of the particle is approximately the friction force at the contact line, which is proportional to the value of \( (\cos\theta_R - \cos\theta_e) \) from the unbalanced Young’s stress.\(^2\)\(^3\) \( \theta_e \) is the static contact angle, which is affected by the nature of the substrates and solvent. Thus, when the driving force \( F_p \) is equal to the friction force, the critical particle radius \( R_c \) for particulate aggregating inwards can be derived as,

\[ R_c \propto \frac{(\cos\theta_e - \cos\theta_R)}{(\cos\theta_R + \cos\theta_p)} \]  

(2)
From Eq. 1 and 2, we note that the critical particle size is determined by $\theta_e$, $\theta_p$ and $\theta_R$. For the given system, $\theta_e$, $\theta_p$ and $\theta_R$ are constant parameters. Hence, a critical particle size, $R_c$ exists. When the size of floating-particle exceeds this value, the liquid capillary attraction $F_p$ may dominate during the aggregating process.

2. The effect of gravity on the capillary bridge, formed in the gap between two spherical particles (Supplementary Fig. 26) in the micron scale, is neglected because the Bond number is approximately 0 ($10^{-5}$), i.e., significantly less than 1. The bond number (Bo = $\rho g R^2/\sigma$) is a dimensionless number measuring the importance of gravitational forces compared with surface tension forces. The surface tension, $\sigma$, between the gas and liquid is constant, indicating a constant mean curvature along the gas-liquid surface. The pendular ring is assumed to be axisymmetric about the connecting center line of two equally sized spheres. The shape of a pendular ring can be described by the Young-Laplace equation in two-dimensional cylinder coordinate (Supplementary Fig. 26) by $r(x)$,

$$\frac{1}{r(1 + r'^2)^{3/2}} - \frac{r''}{(1 + r'^2)^{3/2}} = -2k$$

(3)

where $r' = \partial r/\partial x$, $r'' = \partial^2 r/\partial x^2$. $k = \Delta p/(2\sigma)$, is the characteristic parameter for the shape of the pendular ring, where $\Delta p$ is the pressure difference across the gas-liquid interface.

The pendular ring is constrained on the particle surfaces with two boundary conditions:

$$r = r_p, \quad x = 0;$$

(4)

$$r' = \cot(\theta_p + \beta), \quad x = x_c$$

(5)

where $\theta_p$ is the contact angle, $\beta$ the filled-angle between the $x$-axis and the line contacting the contact point and center of the circle, $x_c$ the $x$-coordinate of the contact point, $r_p$ the $r$-coordinate with $r' = 0$. Eqn. (3) is transformed to
\[
\frac{1}{rr'} \frac{d}{dx} \left[ \frac{r}{(1 + r^2)^{1/2}} \right] = -2k \tag{6}
\]

Integrating with the boundary condition of Eq. (5), Eq. (6) can be rewritten as

\[
\frac{r}{(1 + r^2)^{1/2}} = -kr^2 + c_o \tag{7}
\]

where \(c_o = r_c \sin(\theta_p + \beta) + k r_c^2\), \(r_c\) is the \(r\)-coordinate of the contact point. The following result is obtained using the geometrical relationship

\[
\frac{1}{(1 + r^2)^{1/2}} = -kr + \frac{R \sin \beta \sin(\theta_p + \beta) + k R^2 \sin^2 \beta}{r} = f(r) \tag{8}
\]

For a given \(k\) and \(\beta\), further integration results in the following:

\[
x = \int_{r_c}^{r} f(r) \left[ 1 - f^2(r) \right]^{-1/2} dr + x_c \tag{9}
\]

Solutions of the profile equation can be obtained as a combination of standard elliptic integrals.

Combining Eq. (4) and (7), \(r_p\) can be represented as

\[
r_p = \left( \sqrt{1 + 4kc_o} - 1 \right)/(2k) \tag{10}
\]

The volume of the residual pendular ring is given by

\[
V = 2\pi \int_{r_p}^{r_c} r^2 f(r) \left[ 1 - f^2(r) \right]^{-1/2} dr - 2\pi \left( R - x_c/3 \right) x_c^2 \tag{11}
\]

Once the shape of the pendular ring is determined for a certain particle radius \(R\), the filled-angle \(\beta\), surface tension \(\sigma\), relative volume of liquid with respect to the solid sphere volume, and the capillary force arising from the interaction between the solid and liquid surface can be obtained. The capillary force comprises two parts: the surface tension term acting at the wetting perimeter, tangent to the meniscus at the intersection with the solid surface; the pressure difference term across the curved gas-liquid interface, which is computed over the axially projected wetting area of each particle.
To identify the capillary rise of the liquid, which locates the void that formed among the landed-particles and substrate, the vertical component of the capillary force is quantified. The vertical component of the capillary force \( F_r \) can be expressed as

\[
F_r \approx -2 \pi r_c \sigma \cos (\theta_p + \beta) + \Delta p \cdot 2 x_c r_p
\]  

(12)

where the first item corresponds to the wetting force arising from the contact line and the second one to the Laplace force. The projected area in the vertical direction is assumed as an approximately rectangular projected area of the pendular ring with width \( 2x_c \) and length \( r_p \). Furthermore, the vertical capillary force can be represented with independent variables as

\[
F_r \approx -2 \pi \sigma R \sin \beta \cos (\theta_p + \beta) + 2 \sigma R (1-\cos \beta)(\sqrt{1+4 k c_0} - 1)
\]  

(13)

Obviously, with a given filled-angle \( \beta \), the wetting force (first item) is proportional to the particle radius. The unknown parameter in the second item is \( k c_0 \). From the above equations, \( k c_0 = k R \sin \beta \sin (\alpha + \beta) + (k R \sin \beta)^2 \), and the decisive parameter is \( k R \). However, \( k R \) is constant at a given filled-angle. Under a given filled-angle \( \beta \), the profile of the liquid ring is coaxial parallel at various radii. Considering the pressure difference, \( k R = (1/r_1 + 1/r_2)R/2 \), where \( r_1 \) and \( r_2 \) are two principle curvature radii that are both proportional to the particle radius with the coaxial parallel profile. Then, the Laplace force (second item) is also proportional to the particle radius with a given filled-angle \( \beta \).

\[
F_r \propto \sigma R \sin \beta \left[ -\pi \cos (\theta_p + \beta) + K(\beta)(1-\cos \beta) \right]
\]  

(14)

where \( K(\beta) = k R \) is the function of the filled-angle \( \beta \). From Eq. (14), \( F_r \) increases with the particle radius for a certain filled-angle. Therefore, the liquid will be promoted to rise under vertical capillary force with a larger particle.

However, the vertical capillary force reduces along with the particle radius decrease. The appearance of liquid lifting is conditional for the micron scale particle. The vertical capillary force should be larger than zero for lifting the solvent liquid. Then, the critical radius for zero-\( F_r \) is
derived as

\[
R_{\text{crit}} = \frac{-\sin(\theta_p + \beta) + \cos(\theta_p + \beta)\sqrt{\left(\frac{\pi \sin \beta}{1 - \cos \beta} + \frac{1}{\cos(\theta_p + \beta)}\right)^2 - 1}}{2k \sin \beta}
\]  

(15)

Considering the situation in this work, the void between particles and substrate is filled with solvent liquid. The critical radius at this situation is corresponding to the radius of the appearance of liquid lifting from the substrate, which can be represented as following with \(\beta = \pi/2\),

\[
R_i = \frac{\sigma}{\Delta p} \left[ \cos \theta_p + \sin \theta_p \sqrt{\left(\pi - 1/\sin \theta_p\right)^2 - 1} \right]
\]  

(16)

The particles used in this paper are hydrophilic particles with contact angles less than 90°. The relationship between the nondimensional radius \(R_i\Delta p/\sigma\) and the contact angle is shown in Supplementary Fig. 27. As can be seen that, the critical lifting radius \(R_i\) is inversely related to the contact angle when the contact angles are less than 27.8°. Within this range, a larger particle radius is needed to lift the liquid for the more hydrophilic particle. For this reason, the liquid will not be lifted for some hydrophilic particles that the size is less than \(R_i\). Then the signal of CV molecules will be observed on the substrate. Therefore, the size of the particle selected as an aggregate medium should be larger than \(R_i\).
Supplementary Fig. 26 | The model of residual pendular liquid ring between spherical particles.

Supplementary Fig. 27 | The relationship between nondimensional radius and contact angle for the liquid lifting of Eqn. (16).
Supplementary References

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