Supplementary Information

Direct Observation of Nanoparticle Multiple-Ring Pattern Formation during Droplet Evaporation with Dark-Field Microscopy

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1. SUPPLEMENTARY EXPERIMENTAL SECTION

Chemicals and materials. $HAuCl_4$, sodium citrate, were purchased from Sinopharm Chemical (Shanghai, China). 2-mercaptosuccunic acid (MSA) and (3-aminopropyl) triethoxysilane (APTES) were obtained from Sigma-Aldrich. Ultrapure water with a resistivity of 18.2 MΩ was produced using a Millipore Milli-Q apparatus and used in all the experiments.

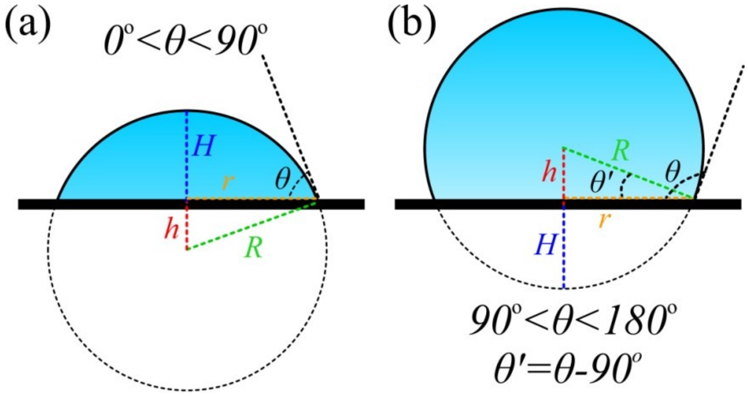
GNP seed synthesis. 1.03 mL of 24.28mM $HAuCl_4$ mixed with 98.97 mL of DI H_2O was added to a 250 mL round-bottom flask, and the solution was heated to boil for 30 min under vigorous stirring. Then 588 μL of 0.2 M sodium citrate solution was rapidly injected into the boiling solution. The solution was vigorously stirred and refluxed for 30 min. After the color of the solution changed to wine red, the colloidal solution was kept stirring at room temperature for another 20 min. The GNP seeds prepared by this protocol have an average size of about 18 nm.

GNP preparation. The 50 nm GNPs were synthesized using a seed-mediated method from 18 nm GNP seeds. In brief, 4 mL of 18 nm GNP seeds, 1.320 mL of 24.28 mM $HAuCl_4$, and 1.920 mL of 0.01 M MSA were sequentially added into 100 mL of DI water. Then the solution was stirred in room temperature for 2 h to accomplish the over-growth.

Preparation of hydrophilic substrates. The coverslips were first immersed in piraha solution (30% concentrated H_2SO_4 : 70 % H_2O_2) for 2 h. Then successively ultra sonication in and rinsing by DI water were repeated until the glass surface was very clean. After drying in the oven at 110℃ for 1 h, the coverslips were immersed in ethanol solution of APTES (1% v/v) for 30 min to finish the silanization reaction. The hydrophilic dispose of the slides surface were completed by washing with ethanol, deionized water and drying in an oven at 110℃for 1 h.

2. SUPPLEMENTARY FORMULA DERIVATION

When a droplet was put onto a wettable substrate, its shape was present to be a hemisphere. The following figure shows the cross-section diagram of the droplet located on hydrophilic (a) and hydrophobic (b) substrate respectively.



Where θ, r *are* contact angle and contact radius between droplet and substrate. If $0° < \theta < 90°$, the substrate is hydrophilic and the parameters in (a) can be defined as

The radius of the whole sphere R:

$$R = \frac{r}{sin\theta} \qquad (1)$$

The distance from the center of the sphere to substrate h:

$$h = \frac{r}{tan\theta} \qquad (2)$$

The hemisphere height H:

$$H = R - h = \frac{r}{sin\theta} - \frac{r}{tan\theta} = r\frac{(1 - cos\theta)}{sin\theta} = rtan\left(\frac{\theta}{2}\right) \qquad (3)$$

Then we can know the volume of the droplet on hydrophilic substrate based on hemisphere volume:

$$V = \frac{\pi H}{6}(3r^2 + H^2) = \frac{\pi r^3}{6}\left(3\left(\frac{1 - cos\theta}{sin\theta}\right) + \left(\frac{1 - cos\theta}{sin\theta}\right)^3\right)$$

$$= \frac{\pi r^3}{6}\left(3 + tan^2\left(\frac{\theta}{2}\right)\right)tan\left(\frac{\theta}{2}\right) \qquad (4)$$

If $90° < \theta < 180°$, the substrate is hydrophobic and the several parameters in (b) can be defines as

The included angle between R and substrate $\theta^{'}$:

$$\theta' = \theta - \frac{\pi}{2} \qquad (5)$$

The radius of the whole sphere R:

$$R = \frac{r}{cos\theta'} = \frac{r}{sin\theta} \qquad (6)$$

The distance from the center of the sphere to substrate h:

$$h = r|tan\theta'| = -rcot\theta \qquad (7)$$

The complementary height of the hemisphere H:

$$H = R - h = \frac{r(1 + cos\theta)}{sin\theta} \qquad (8)$$

So the volume of the droplet on hydrophobic substrate can be written as:

$$V = \frac{4}{3}\pi R^3 - \frac{\pi H}{6}(3r^2 + H^2) = \frac{\pi r^3}{6}\left(\frac{8}{sin^3\theta} - \frac{3(1 + cos\theta)}{sin\theta} - \frac{(1 + cos\theta)^3}{sin^3\theta}\right)$$

$$= \frac{\pi r^3}{6}\left(3 + tan^2\left(\frac{\theta}{2}\right)\right)tan\left(\frac{\theta}{2}\right) \qquad (9)$$

By comparing, we found formula (4) and (9) are equal. So the volume of the droplet on substrate can be expressed as:

$$V = \frac{1}{6}\pi r^3\left(3 + tan^2\left(\frac{\theta}{2}\right)\right)tan\left(\frac{\theta}{2}\right) \qquad (10)$$

3. SUPPLEMENTARY FIGURES

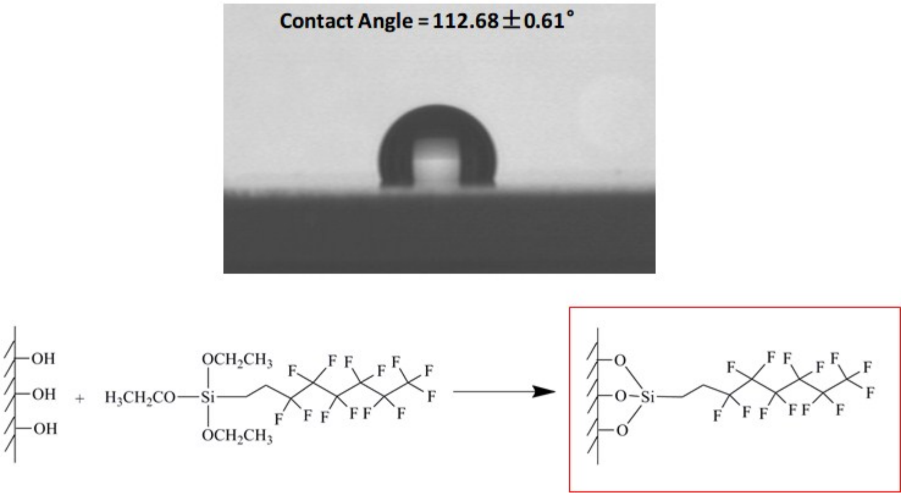


Fig. S1 The contact angle between water-drop and the hydrophobic substrate, with an average angle about 112.7±0.6°.

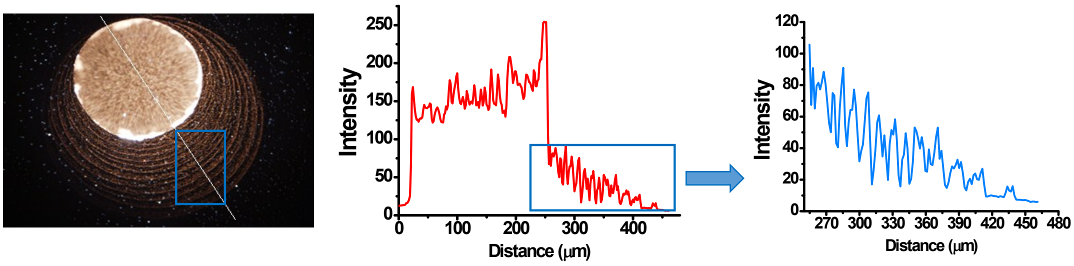


Fig. S2 The scattering intensity of the particles in the field of the view along the cross section marked by the white line. The disk in the center presents much stronger intensity than the surrounding rings due to the higher density of the accumulated GNRs. The obvious intensity fluctuation indicated the variation of the local densities of the GNRs in each ring.

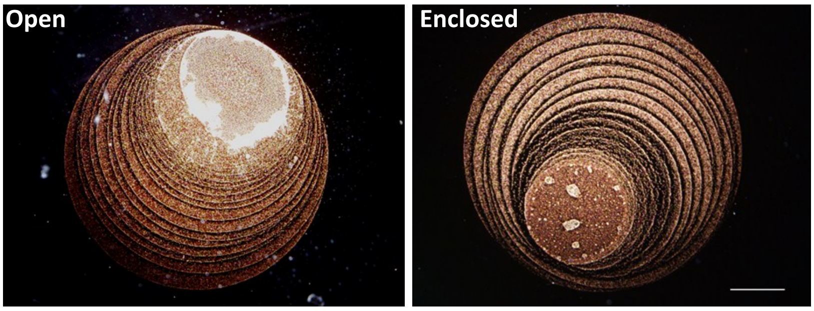


Fig. S3 The dried pattern of GNRs suspension at 5 pM in an open environment (A) and (B) enclosed environment. There were both multiple-ring formed. Scale Bar 300 μm.

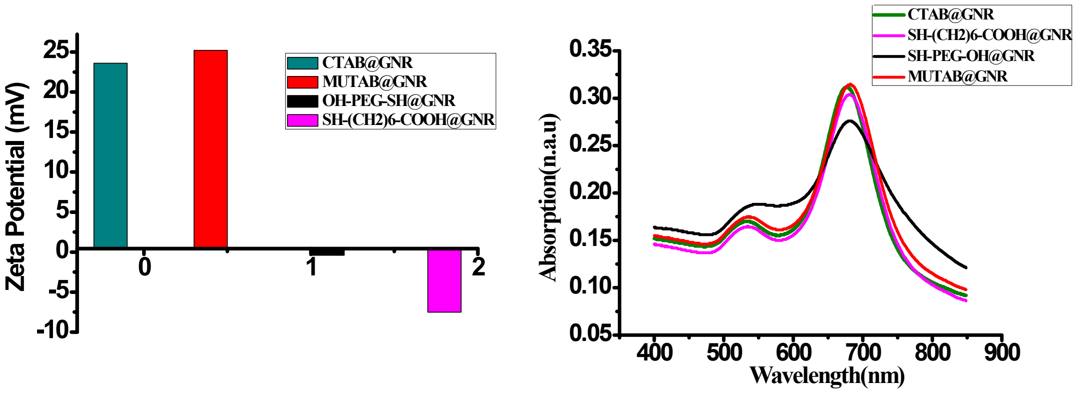


Fig. S4 The Zeta potential and UV-Vis absorption variation after different surface modifications.

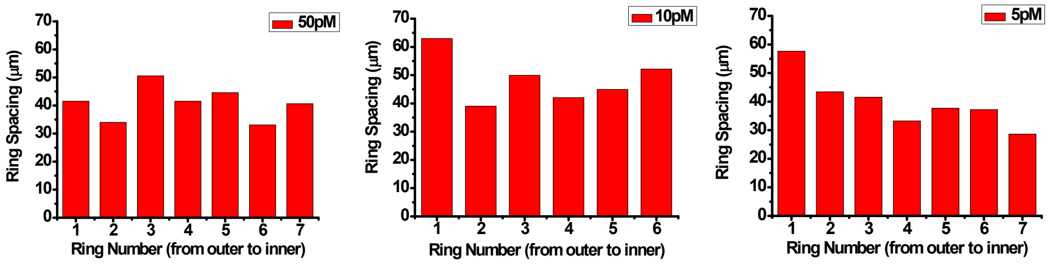


Fig. S5 The ring spacing of the multiple-ring patterns formed with GNR droplets of 50 pM, 10 pM, and 5 pM, respectively.

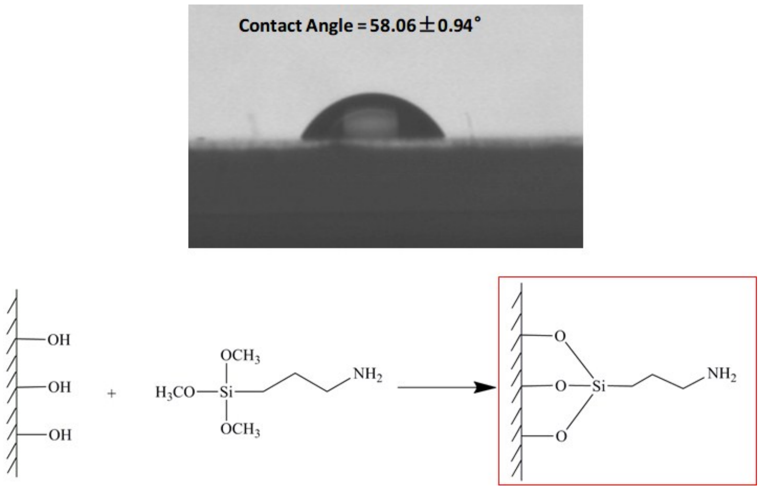


Fig. S6 The contact angle between water-drop and the hydrophilic substrate with an average angle of 58.06±0.94°.

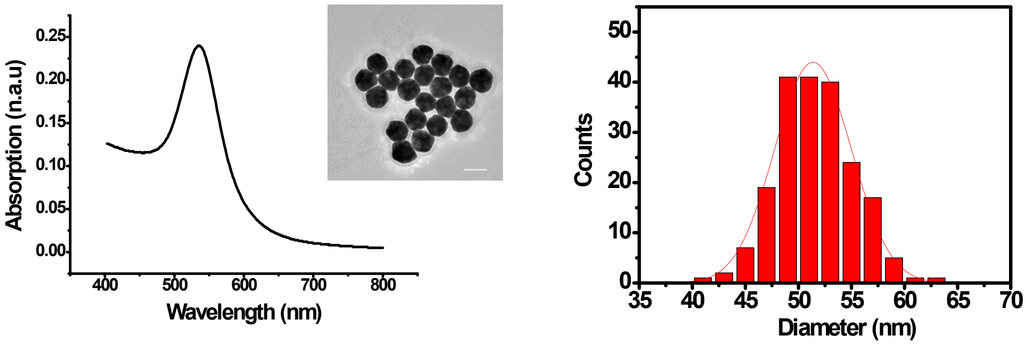


Fig. S7 (left) The UV-vis absorption spectra and TEM image of the GNP. Scale bar 50 nm. (right) The size distribution of the GNPs. Their mean diameter is 54 nm.

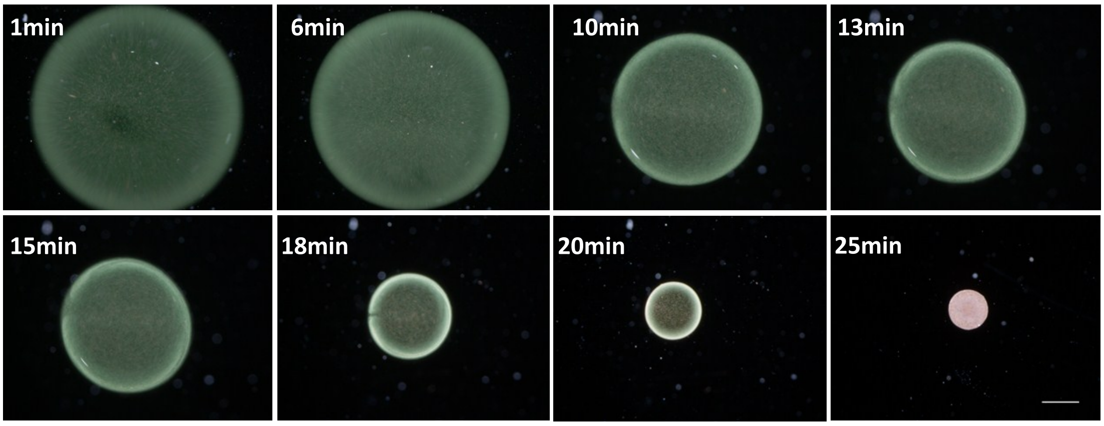


Fig. S8 The drying process of 5 pM spherical GNPs solution on a hydrophobic substrate. There was no multiple-ring formation. Scale Bar 300 μm.

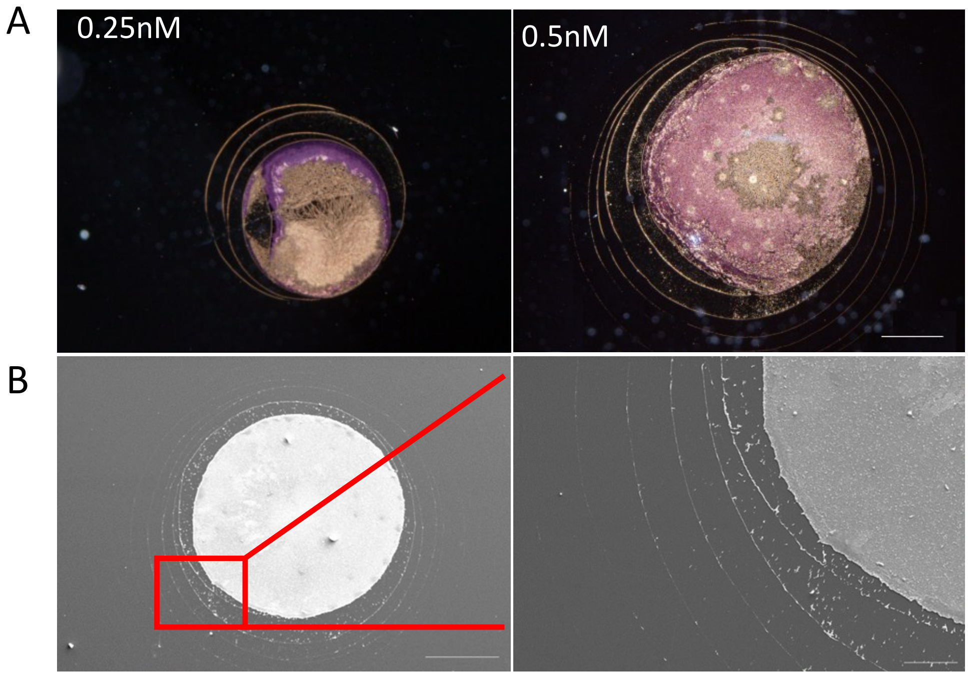


Figure S9. (A) The spherical gold nanoparticle can assembled into multiple-ring structure when the original GNPs solution was concentrated to be higher than 0.25 nM. Scale Bar 300μm. (B) The SEM images of multiple-ring pattern formed from spherical gold nanoparticles. Scale Bar 300μm (left), 50μm (right).