Supplementary Information (SI) for Physical Chemistry Chemical Physics.

Supporting Information

Silver Microplasma-Engineered Nanoassemblies On Periodic Nanostructure for SERS Applications

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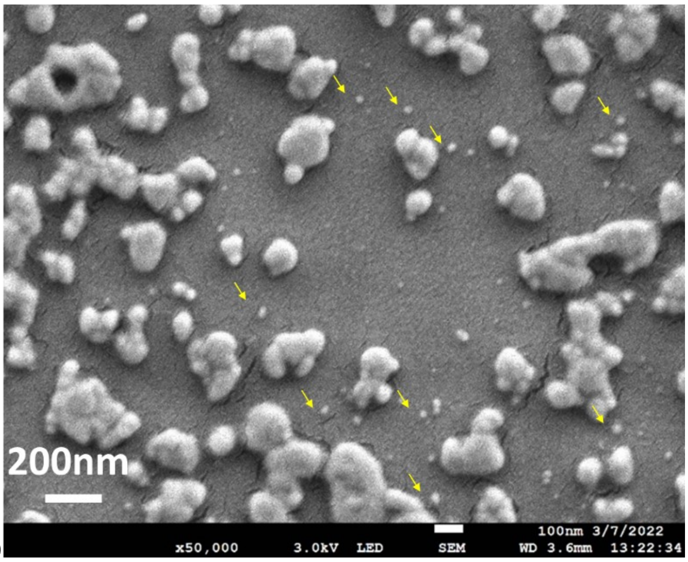
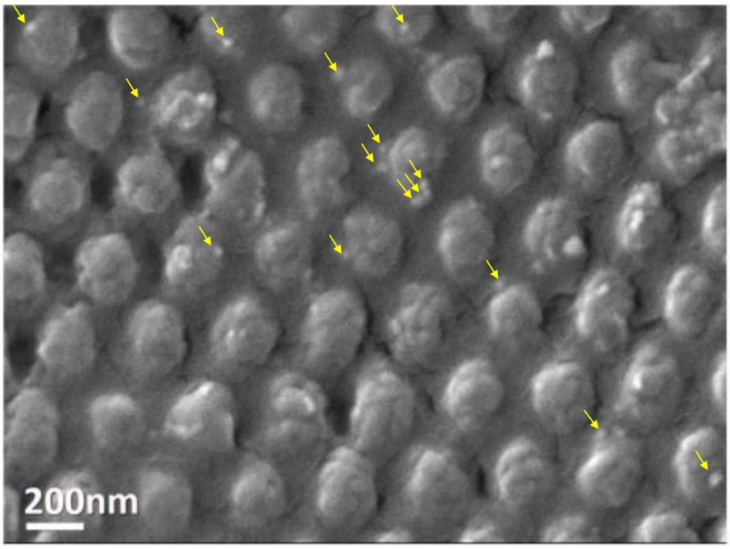
Measure the average diameter of silver nanoparticles by microplasma coating process

The average diameter of silver nanoparticles fabricated by microplasma coating process is about 23.3 nm and 23.5 nm on flat and nanostructured surfaces, respectively.



(a)



(b)

Fig. S1 SEM image microplasma coating process on (a) flat and (b) periodic nanostructure substrates

Experimental setup

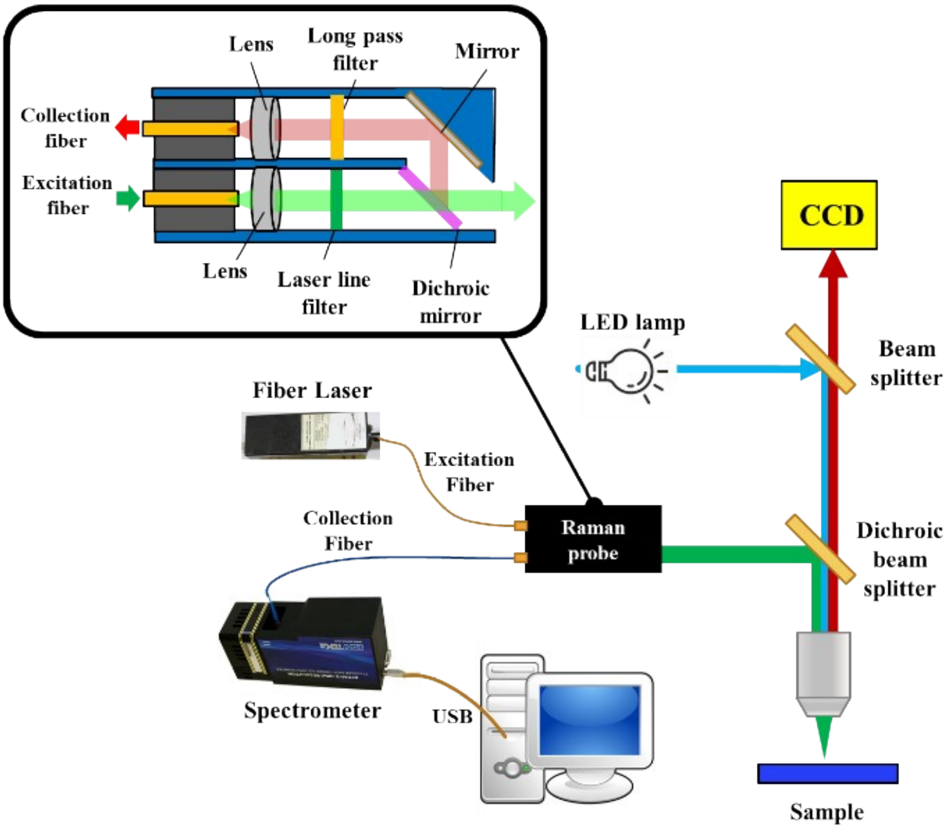


Fig. S2 Schematic diagram of the home-built Raman measurement system

Estimation of the Limit of Detection (LoD)

Based on Fig. 7(d), the equation of the regression line in the liner region is：

$y = 2 \times 10^{9}x - 1456.6$

Moreover, the noise level (σ) of the blank sample is about 72 counts, the signal-to-noise ratio should be larger than 3σ to distinguish the signal from the noise.

Therefore,

$$72 \times 3 \leq 2 \times 10^{9}x - 1456.6$$

$\rightarrow \text{LoD} = x \geq 8.4\ x\ 10^{-7}\ (M)$

Calculation of SERS enhancement factor

The enhancement factor (EF) is an essential index to judge the performance of SERS, representing the comparison of enhancing Raman signal of molecules with and without plasmonic nanostructure interactions. The EF of the SERS substrate could be calculated by the following formula:

$$EF = \frac{I_{SERS}/N_{SERS}}{I_{RS}/N_{RS}} = \frac{I_{SERS}/(C_{SERS} \times V_{SERS})}{I_{RS}/(C_{RS} \times V_{RS})}$$

$$= \frac{(1018\ \text{counts/s})/(10^{-6}\ \text{M} \times 0.25\pi \times (151.42\mu\text{m})^2 \times 1\ \mu\text{m})}{(90.2\ \text{counts/s})/(10^{-3}\ \text{M} \times 0.25\pi \times (165.38\mu\text{m})^2 \times 200\ \mu\text{m})} = 2.69 \times 10^6$$

where

I_{SERS} and I_{RS} are Raman intensities of adenine measured from SERS substrate and flat silver substrate.

N_{SERS} and N_{RS} are the number of analyte molecules which is coated on the SERS substrate and flat silver film, respectively.

C_{SERS} and C_{RS} are concentrations of analyte for SERS and bulk Raman measurement.

V_{SERS} and V_{RS} are the volume of analyte calculated for SERS and bulk Raman by volume of laser spot.

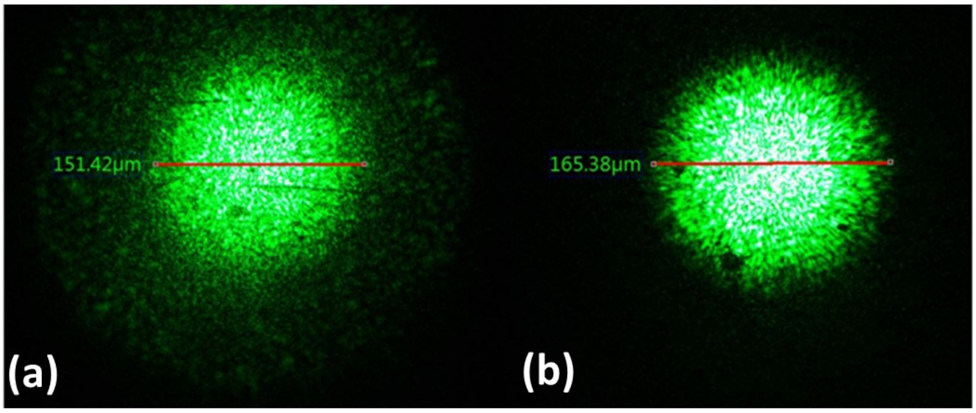


Fig. S3 The spot size of laser of (a) SERS and (b) Bulk Raman measurements.

Compared with FDTD simulations

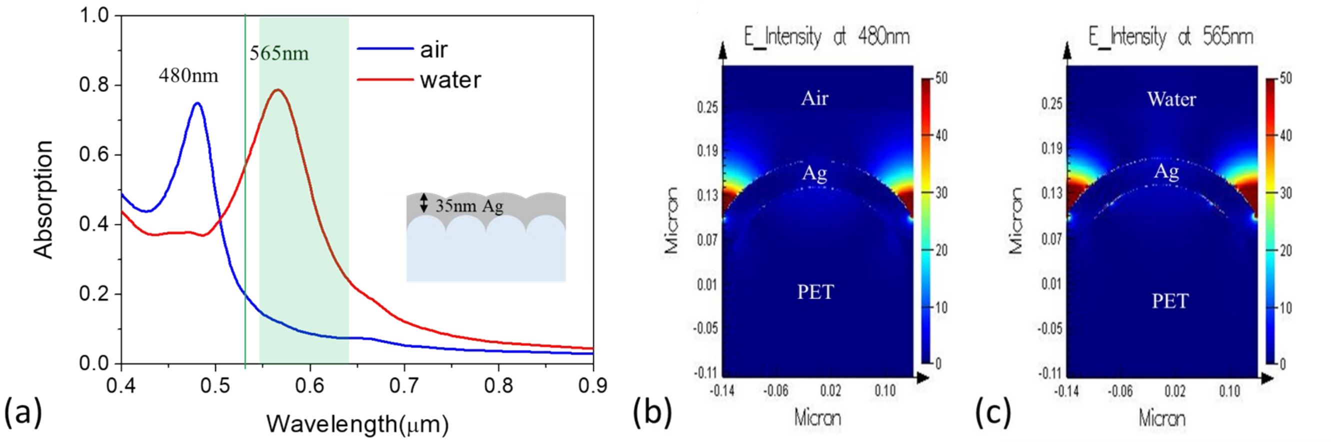


Fig. S4 (a) FDTD simulation absorption spectra of 35nm silver overlay coating on the motheye substrate under air and water environment conditions. The corresponding electric field distribution at the absorption peak wavelength of (b) air and (c) water condition.

Estimation of effective silver film thickness by microplasma-engineered nanoassembly process

Since Ag-MEN is not a conventional physical vapor deposition process and the coated samples are composed of nanoparticles that are not uniform on the microscopic scale, we estimate the film thickness using the concept of effective silver thickness. We used the property of the LSPR spectrum dependence to the silver film thickness by spttering to estimate the effecitve silver film thickness of our optimal SERS substrate by Ag-MEN process is close to 35nm, as shown in Fig. S5.

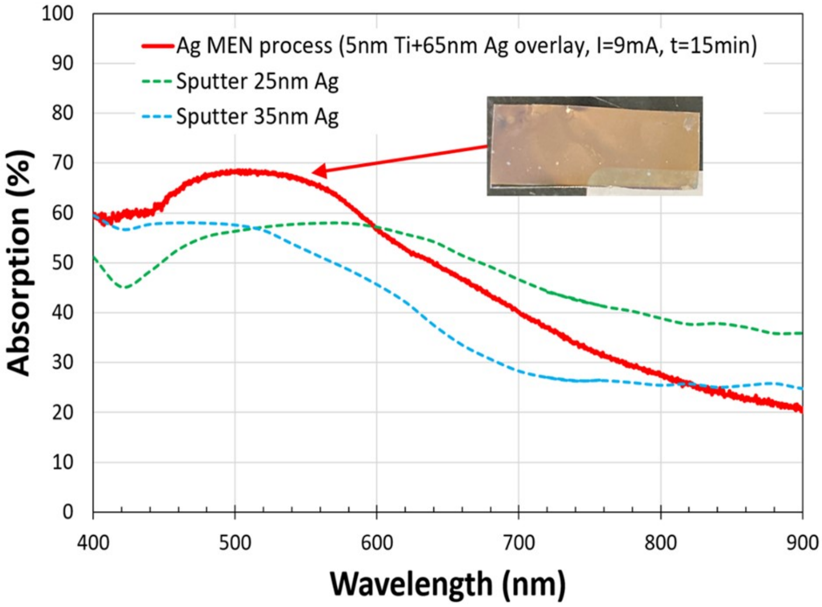
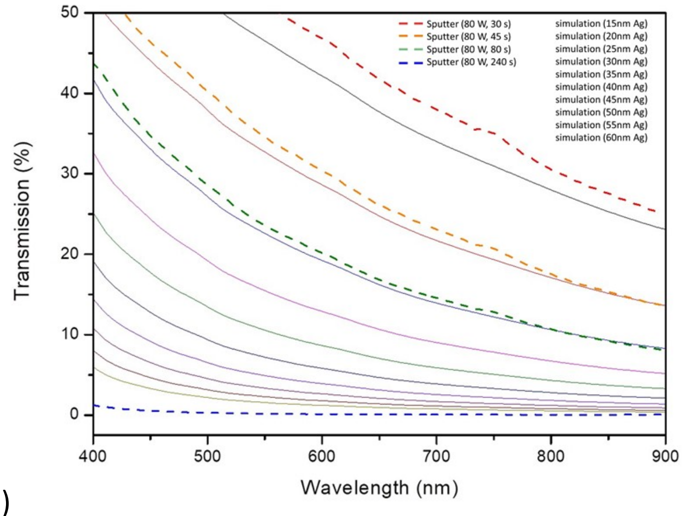


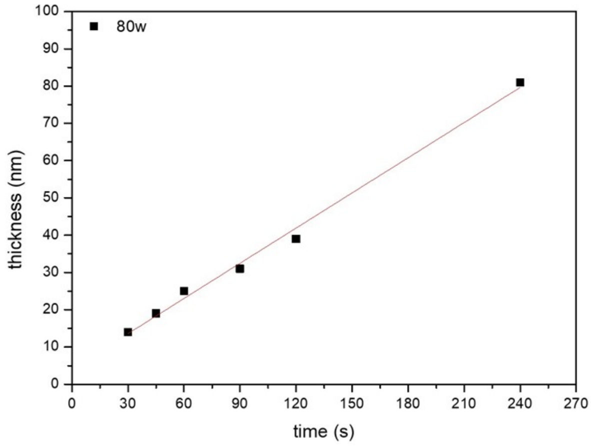
Fig. S5. Measurements of the absorption spectra of the motheye template after Ag-MEN and sputtering process (25 and 35nm). The result indicates the effective silver thickness of Ag-MEN is between 25 and 35 nm.

Analysis of the actual thicknesses of silver/titanium films

The simulated spectra for silver films of varying thickness were generated using Gsolver software, employing the silver dielectric constant from a table model. During each sputtering process, a blank glass substrate was used to monitor film thickness. The actual thickness was determined by interpolating the relationship between the measured and simulated transmission spectra of silver films with different thicknesses, as shown in Fig. S6. The first time of actual silver film thickness was rechecked by AFM or surface profiler measurements. Once the relationship is confirmed, subsequent film thicknesses can be measured using transmission spectra quickly.



(a)



(b)

Fig. S6. (a) The simulated and measured transmission spectra of different silver film thickness. (b) The relation of sputtering time to the silver film thickness at the power condition of 80 W.