Scalable and controlled self-assembly of aluminum-based random plasmonic metasurfaces

Supplementary Information

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Figure S1 Angle-resolved goniometric scattering measurement. Angle-resolved goniometric scattering measurements of blue, green and red sample show the angle-independent scattering properties of the metasurfaces. The dotted lines show the shift of peak scattering wavelength.

Figure S2 Effect of native aluminium oxide (Al₂O₃) on proposed random metasurfaces is shown with FEM simulation. There is a small red shift of 3 nm in the scattering behaviour observed due to the additional 3 nm insulating layer of Al₂O₃ (refractive index, $n = 1.768$) is considered.
for simulation). However, it does not significantly alter overall optical scattering.

**Figure S3** Plasmonic random metasurfaces lift-off. A lift-off technique is employed to prove the separation between the plasmonic elements by dissolving the PMMA layer, so the upper Al nanohole layer is removed and the Al disks keep remaining on the surface (a). (b) 3D surface topography confirms the height and homogeneity of the evaporated Al metal film.
**Figure S4** (a) 3D FEM Simulation of individual nanohole-disk is shown considering 5 nm gap for different diameters of hole. Enhanced coupling of optical fields within the nanocavities is observed in the electric field norm distribution at broad scattering peak wavelengths in the...
near field leading to broadband scattering. The thickness of the PMMA layer used in the
calculation is 70 nm, while the thickness of the Al layer is 65 nm to maintain a gap of 5 nm.
(b) Photograph of a sample (right) with 5 nm gap between nanohole and nanodisk appears
whitish compared to the one with a gap of 40 nm (middle). In both cases, average diameter of
holes is maintained to be 80 nm, only the Al thickness is varied. For a comparison, a flat
aluminium film is shown on the left.

SERS ENHANCEMENT CALCULATIONS

SERS enhancement factors (EFs) were calculated by \( EF = \frac{I_{\text{SERS}}/N_{\text{SERS}}}{I_{\text{RAMAN}}/N_{\text{RAMAN}}} \). First, the Raman scattering spectrum of 20 mM BPT in ethanol was measured.
The signal strength was extracted at 1584 cm\(^{-1}\) and normalized to the mode volume following the
1/e\(^2\) method for Gaussian beams\(^{\text{(ref.2)}}\), thus obtaining \( I_{\text{RAMAN}} \) and \( N_{\text{RAMAN}} \). The numbers of
molecules contributing to the SERS signal \( N_{\text{SERS}} \) was calculated by assuming a molecular surface
coverage of 80 Å\(^2\) per molecule\(^{\text{(ref.3)}}\). The SERS intensity was extracted from the spectra shown
in Figure 6a-b.

Approximated spot size: \( d = 2\omega_0 = 2\times\lambda/(\pi\times NA) \) and area of interest: \( A = \pi\times\omega_0^2 \).

| Wavelength (nm) | Spot diameter (nm) | Area \( A \times 10^{-15} \text{m}^2 \) |
|-----------------|--------------------|----------------------------------------|
| 488             | 414                | 1.35                                   |
| 532             | 451                | 1.60                                   |
| 633             | 537                | 2.27                                   |
| 785             | 666                | 3.49                                   |

BPT density on substrate\(^{\text{(ref.4)}}\): \( \rho_{\text{BPT}} = 1.25 \times 10^{18} \text{molecules/m}^2 \)

SERS signal measurements, \( N_{\text{SERS}} = A \times \rho_{\text{BPT}} \):

| Wavelength (nm) | \( N_{\text{SERS}} \times 10^5 \) | Signal per molecule (Al) | Signal per molecule (Au) |
|-----------------|----------------------------------|--------------------------|--------------------------|
| Wavelength (nm) | $I_{SERS}^{Al}/N_{SERS}^{Al}$ | $I_{SERS}^{Au}/N_{SERS}^{Au}$ |
|----------------|-----------------------------|-----------------------------|
| 488            | 1.7                         | 19.7 E-3                    |
| 532            | 2                           | 7.8 E-3                     | 0.19 E-3 |
| 633            | 2.8                         | 1.6 E-3                     | 1.2 E-3 |
| 785            | 4.7                         | 1.2 E-3                     | 3.0 E-3 |

Raman signal measurements:

| Sample                  | Wavelength (nm) | $N_{RAMAN}$ (counts / (mW*s)) |
|-------------------------|-----------------|-------------------------------|
| BPT on Al SERS substrate| 488             | 3347                          |
|                         | 532             | 1553                          |
|                         | 633             | 450                           |
|                         | 785             | 570                           |
| BPT on Au SERS substrate| 488             | -                             |
|                         | 532             | 37                            |
|                         | 633             | 332                           |
|                         | 785             | 1433                          |
| BPT on flat Au          | 488             | - (no signal)                 |
|                         | 532             | -                             |
|                         | 633             | -                             |
|                         | 785             | -                             |

Calculated Raman enhancement, EF = $(I_{SERS}/N_{SERS})(I_{RAMAN}/N_{RAMAN})$:

| Wavelength (nm) | EF ($\times 10^6$) (Al) | EF ($\times 10^6$) (Au) |
|-----------------|--------------------------|--------------------------|
| 488             | 1.5 (7.3)                | -                        |
| 532             | 2.6                      | 0.6                      |
| 633             | 3.4                      | 2.5                      |
| 785             | 15                       | 38                       |
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