Supplementary materials

Broadband field enhancement in disordered plasmonic hybrid aggregates

Peng Mao[1,2], Changxu Liu[2,3]*, Qiang Chen[4]*, Min Han[4], Stefan A. Maier[3]*, and Shuang Zhang[2]*

1 College of Electronic and Optical Engineering & College of Microelectronics, Nanjing University of Posts and Telecommunications, Nanjing 210023, P. R. China

2 School of Physics and Astronomy, University of Birmingham, B15 2TT, United Kingdom

3 Chair in Hybrid Nanosystems, Nanoinstitut München, Fakultät für Physik, Ludwig Maximilians-Universität München, 80539 München, Germany

4 Key Laboratory of Intelligent Optical Sensing and Integration, College of Engineering and Applied Sciences, Nanjing University, Nanjing, 210093, P. R. China.

Peng Mao and Changxu Liu equal contribution

Fabrication of 3D-Ag HNA structure

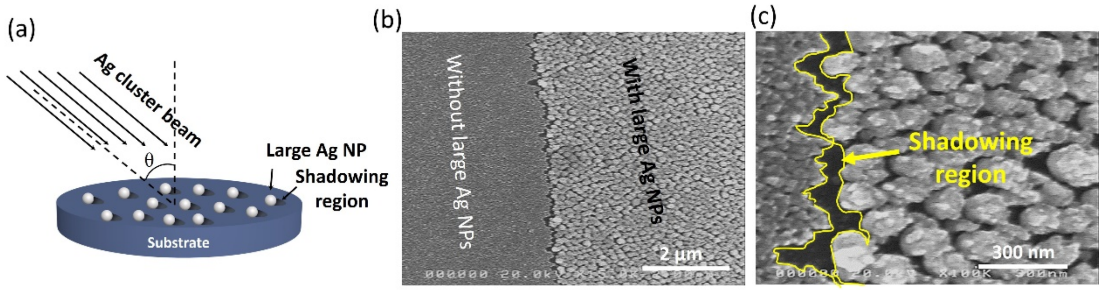

Figure S1. (a) Sketch illustrating the oblique-angle cluster beam deposition process; θ is the cluster beam incident angle measured from the substrate norm. (b) Low magnification and (c) high magnification SEM image of the Ag cluster assembles (left part) and the 3D-Ag HNA structure (right part). The shadow region was marked in the image by the yellow lines. In the oblique cluster beam deposition process, the large-size Ag NPs produced shadow regions that the incident Ag cluster flux could not reach. On the non-shadow regions (tops of the Ag NPs) the incident cluster flux deposited preferentially. As a result, the Ag clusters piled up and formed a columnar 3D hierarchical nanostructure.

Caculation of the speed of the cluster beam

The principle of the cluster generation can be schematically demonstrated in Figure 2a in the main text. The supersonic expansion process occurs when the cluster beam passes through the nozzle. For the sake of simplicity, considering the isentropic expansion of an ideal gas of mass m. Based on the conservation of energy:

$$C_{P_0}T_0 = \frac{1}{2}mu^2 + C_{P_b}T_b$$

Where subscript b indicates beam. $T_b < T_0$. The speed of the beam is:

$$\nu = (\frac{\gamma RT}{m})^{1/2}$$

Where $\gamma = C_P C_V$. Define Mach number:

$$M = \frac{u}{\nu} = c(x/D)^{1/\gamma}$$

Where x is the distance between the beam and the front end of the nozzle, c is the characteristic constant of the gas beam.

In the process of supersonic expansion, M will increase until it reaches a certain value M_t. M_t can be estimated by:

$$M_t \approx 1.17K^{-0.4} \approx (p_0 D)^{0.4}$$

Where K is Knudsen number, $K = \lambda_0/D$, λ_0 is mean free path and D is the diameter of nozzle. In our cluster source, the diameter of nozzle D is 3 mm. Therefore, the speed of cluster beam can be calculated around 1000 m/s.

A comparison between vertical and oblique deposition

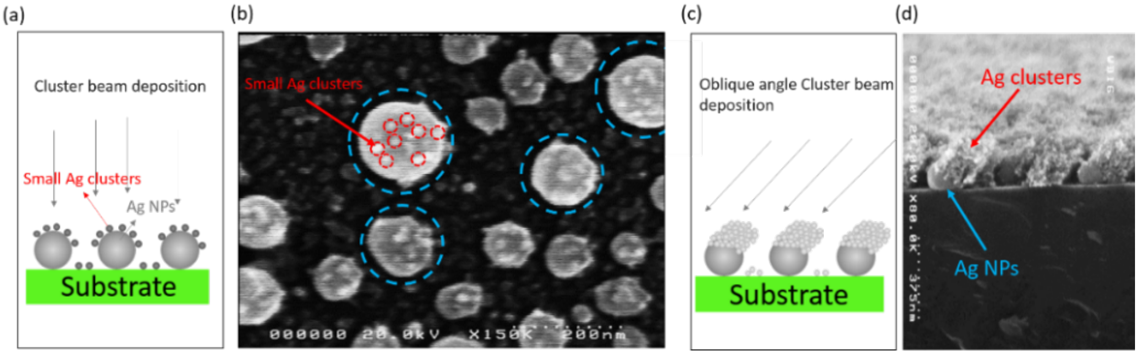

Figure S2 (a-b) Schematic and SEM image of Ag cluster/Ag NPs hierarchical nanostructure under vertical cluster beam deposition (without oblique angel). (c-d) Schematic and cross-sectional SEM image of the 3D-Ag-HNA with oblique depostion.

SERS spectra of R6G on the R6G-treated 3D-Ag-HNA substrate at 50 different locations.

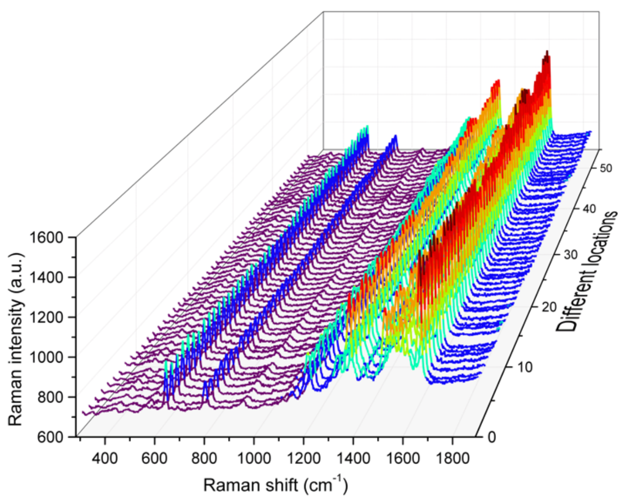

Figure S3. SERS spectra of R6G measured from a R6G-treated 3D-Ag-HNA substrate.

SERS spectra measured from the 3D-Ag-HNA substrates of different batches

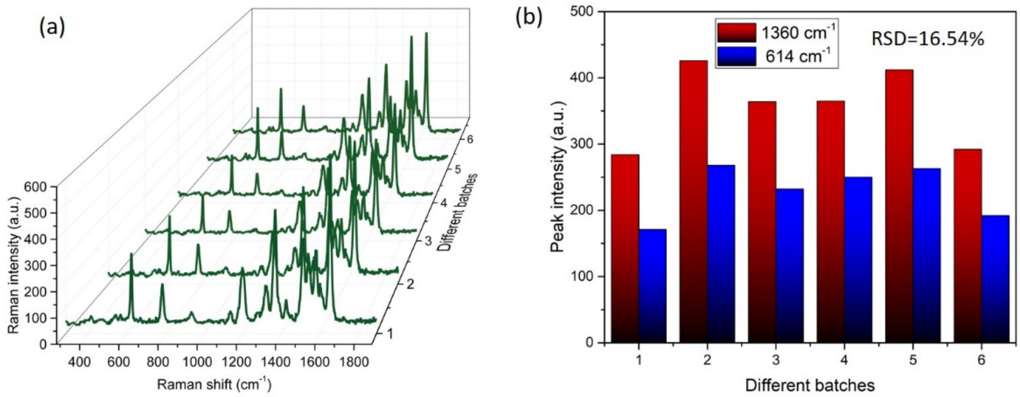

Figure S4. (a) SERS spectra of 10^{-7} M R6G collected from six 3D-Ag-HNA substrates of different batches. (b) The corresponding histograms of selected SERS spectral intensities on the 3D-Ag-HNA SERS substrates with different batches. The relative standard deviation (RSD) of the average 1360 cm^{-1} intensity for the SERS spectra collected from six 3D-Ag-HNA substrates of different batches was 16.54%, confirming good substrate-to-substrate reproducibility of SERS signal.

Raman signal mapping and calculated RSD of R6G at different Raman peaks.

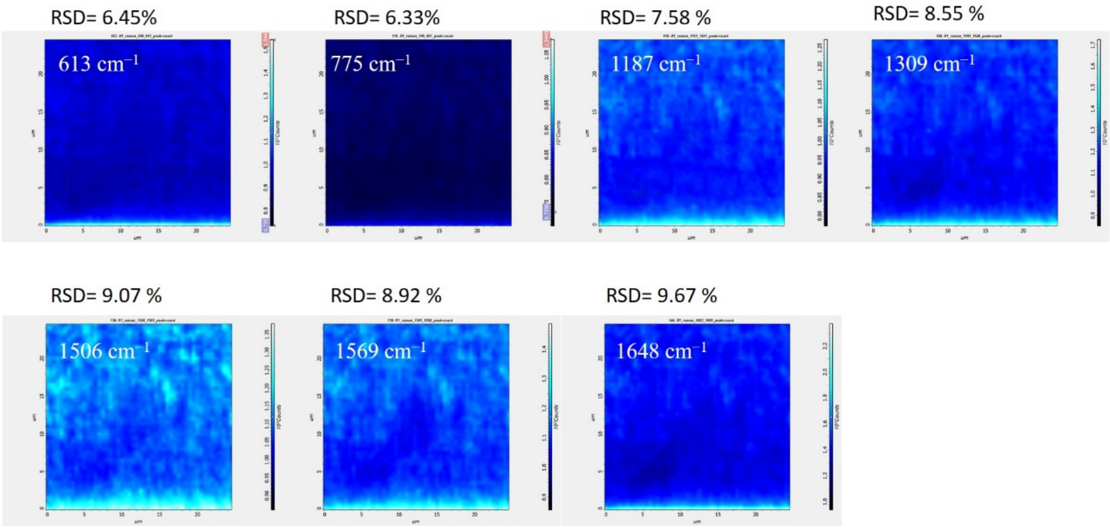

Figure S5. Raman intensity spatial distribution of the R6G 613 cm^{-1}, R6G 775 cm^{-1}, R6G 1187 cm^{-1}, R6G 1309 cm^{-1}, R6G 1506 cm-1, R6G 1569 cm^{-1} and R6G 1648 cm^{-1} band over the mapping area obtained from the R6G-decorated 3D-Ag-HNA substrate at the excitation wavelength of 473 nm.