SUPPORTING INFORMATION

Mesoscopically bi-continuous Ag-Au hybrid nanosponges with tunable plasmon resonances as bottom-up substrates for surface-enhanced Raman spectroscopy (SERS)

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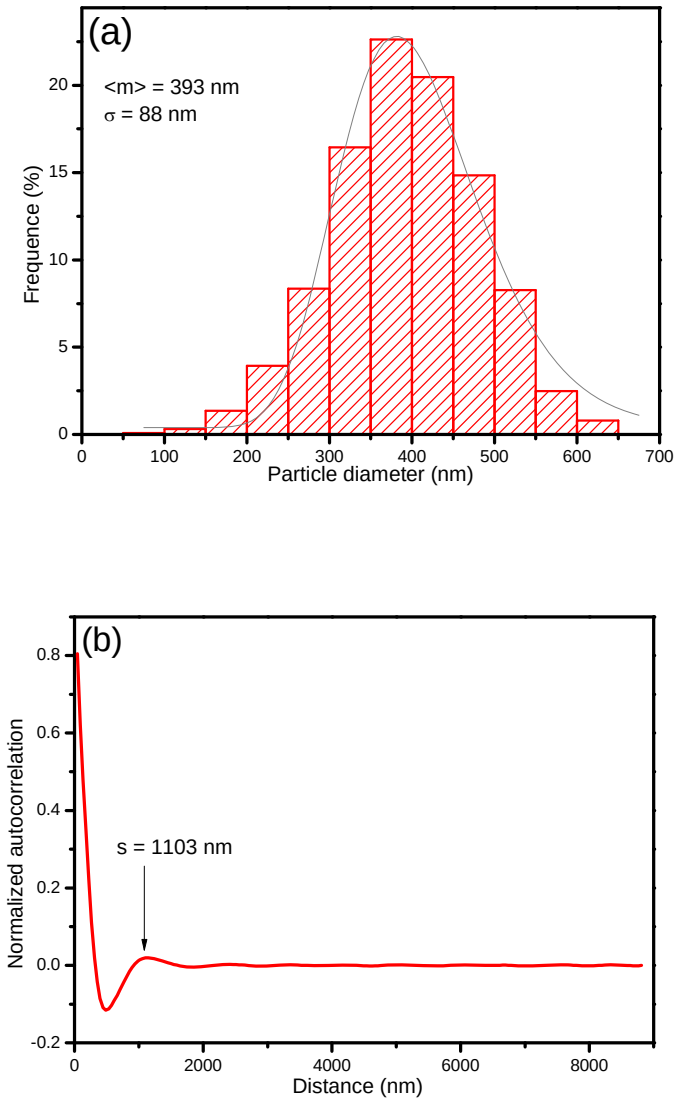

Figure S1. Histogram of the radially averaged autocorrelation measured ligament size of the Au NSs. Fitting curves (lognormal function) are superimposed on the histogram. The values <m> and σ indicate the mean particle diameter and its standard deviation, and "s" denotes the characteristic particle spacing (all in nm).

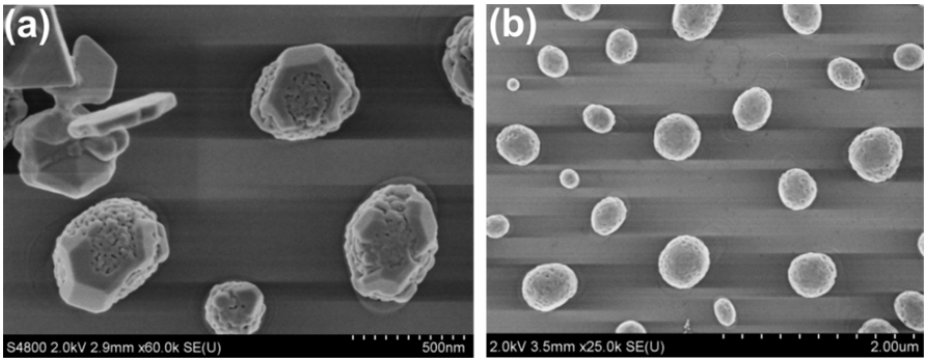

Figure S2. SEM images: (a) Ag deposited clearly outside of the porous structure after the traditional electroless deposition process in a mixed solution of the ascorbic acid and silver nitrate, and (b) Ag deposited only inside and on the porous structure after the cyclic electroless deposition process.

The volume porosity of the as-prepared Au NSs is assumed as 66%. The relative volume of Ag to Au in the hybrid NSs can be calculated based on the values of the Ag concentration in the hybrid NSs determined by the EDS analysis (Figure 2). Then the volume porosities for the hybrid NSs can be determined as the ratios between the free volume and the total particle volume. The obtained results are shown in Figure S3. The sum of free volume and the volume of both Ag and Au components is the total particle volume.

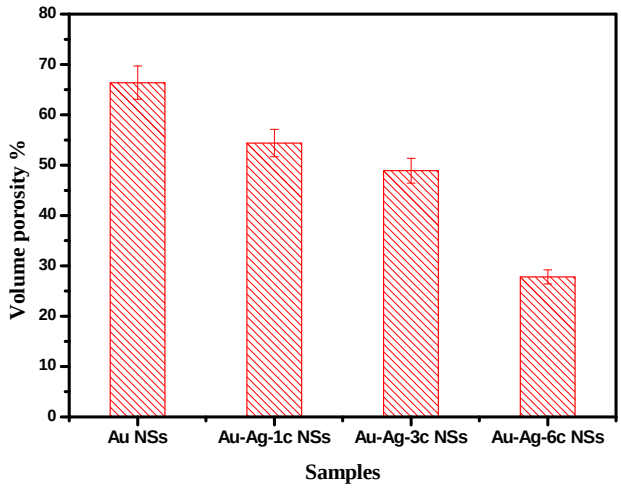

Figure S3. The calculated volume porosity of Au NSs before and after Ag deposition: Au NSs, Au-Ag-1c hybrid NSs, Au-Ag-3c hybrid NSs, and Au-Ag-6c hybrid NSs.

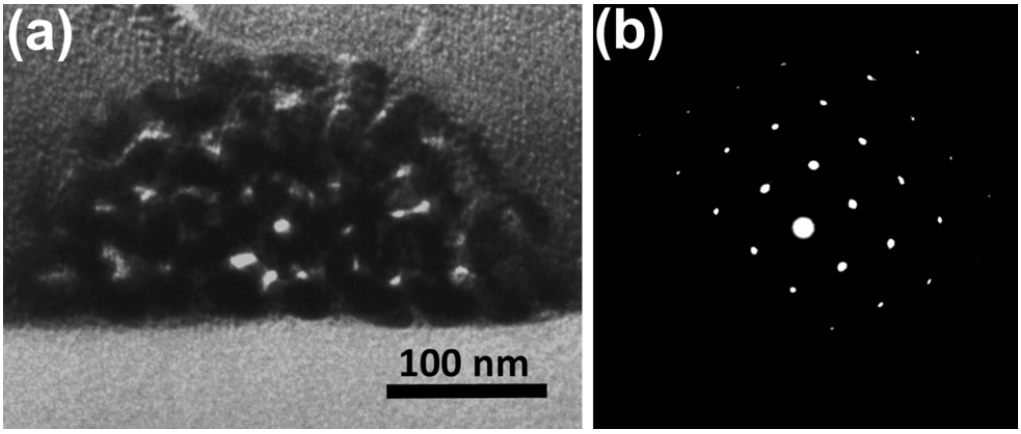

Figure S4. (a) TEM image of an Au NS, and (b) the corresponding SAED image.

Models of nanosponges (NS) for the Finite-difference time-domain (FDTD) simulations

The volume porosity of the as-prepared Au-NSs is assumed as 66%. The diameter of the spherical Au NSs in simulation is 393 nm. The model of the NSs was constructed using a large sphere etched by N randomly distributed spherical air pores with diameter of 20 nm. The distribution volume of the air pores is the same trough the large sphere. Volume overlap of the air pores was assumed as 20% in total. It is very difficult to build a model of the Au-Ag NSs, and accordingly Au and Ag NSs with different porosity were simulated and the results were discussed. The volume porosities of the NSs can be varied by changing the number of air pores, N.

Based on the quantitative values of the Au/Ag atomic ratio introduced in Figure 3, the volume porosities of the Au-Ag-1c, Au-Ag-3c, and Au-Ag-6c hybrid NSs can be calculated as 54%, 49%, and 28%. Au NSs with different porosities of 66%, 54%, 49%, and 28% were simulated. The number of the air pores in the sphere, N, can be calculated as 6250, 5120, 4602 and 2617, respectively.

Similarly, 3 models of Ag NSs with different porosities and the same spherical diameter of 393 nm were constructed. The Ag amounts in the models of NSs are the same as in the Au-Ag-1c, Au-Ag-3c, and Au-Ag-6c hybrid NSs (calculated based on the estimation from EDS analysis in Figure 2), respectively. The corresponding porosities are calculated as 88%, 84% and 60%, respectively. The number of the air pores in the sphere, N, can be calculated as 8264, 7924 and 5626, respectively.

SERS investigation

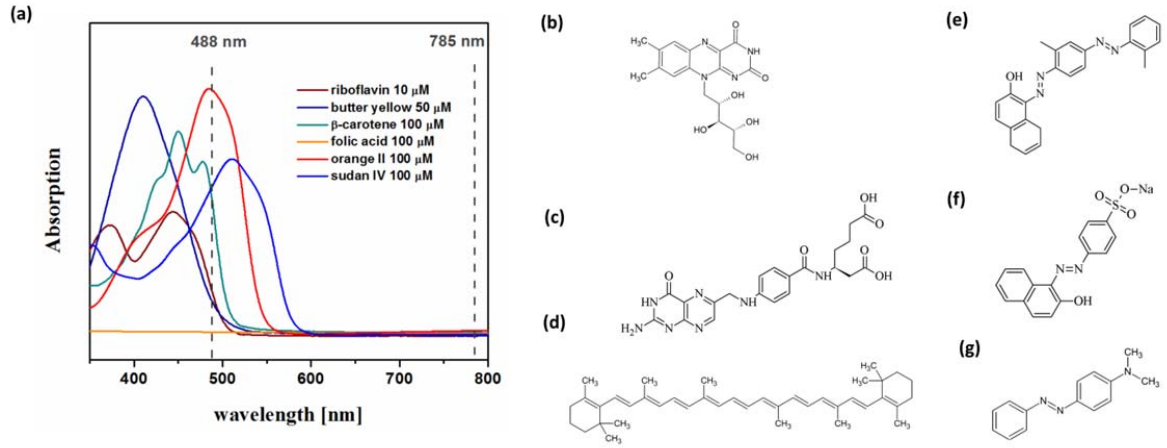

Figure S5. Absorption spectra of the analytes used for the SERS measurements (a) and the chemical structures of riboflavin (b), folic acid (c), β-carotene (d), sudan IV (e), orange II sodium salt (f) and BY (g).

Enhancement Factor calculation

The Raman signal of the analyte was measured first on the SERS active substrate and then on flat substrates. The same measurement conditions were used for all the measurements. That is, for all presented measurements the light was focused via a 100x objective (NA 0.8) onto the sample and the Raman scattered light was collected with the same microscope objective. Scans consisting of 100 point measurements were recorded with an integration time of 0.5 s per point. The power at the surface of the sample was adjusted to 20 µW. Prior to the measurement, the substrates were incubated in the analyte solution for 30 min and dried using N_2. In order to have comparable binding conditions for the measurements two different types of non-nanostructured substrates ware used: flat Au substrate and flat Ag substrate.

The average SERS EF was calculated based on the formula:

$EF = I_{SERS}N_0/I_0N_{SERS} + CEF$

where I_{SERS} and N_{SERS} are Raman intensity and number of molecules under SERS conditions, I_0 and N_0 are Raman intensity and number of molecules for the measurements of the flat Au or Ag conditions and CEF is the chemical contribution to the enhancement factor.

By using the experimental conditions described above $N_0 = N_{SERS}$. Additionally, the chemical

contribution to the enhancement factor is expected to be in the order of 10^2.[1] Considering this, enhancement factors of 3.4×10^4, 2×10^5, $2\cdot10^5$ and 6.4×10^5 were obtained for samples of Au NSs, Au-Ag-1c, Au-Ag-3c and Au-Ag-6c respectively.

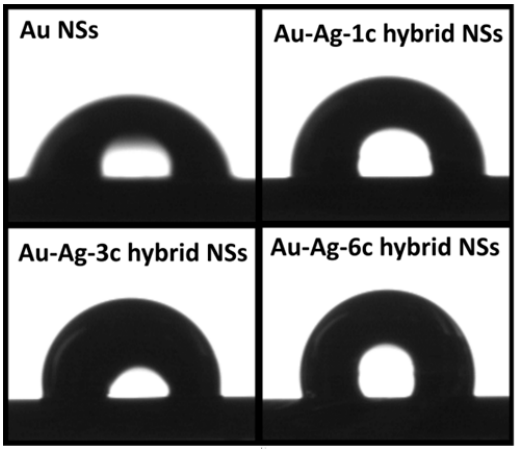

Figure S6. Distilled water droplets on the surface of Au NSs, Au-Ag-1c hybrid NSs, Au-Ag-3c hybrid NSs and Au-Ag-6c hybrid NSs.

[1] Campion, A.; Ivanecky, J. E.; Child, C. M.; Foster, M., On the Mechanism of Chemical Enhancement in Surface-Enhanced Raman Scattering. J. Am. Chem. Soc. 1995, 117, 11807-11808.1.