

Supplementary Information for

Design of Broadband SERS Substrates by Laser-Induced Aggregation of Gold Nanoparticles

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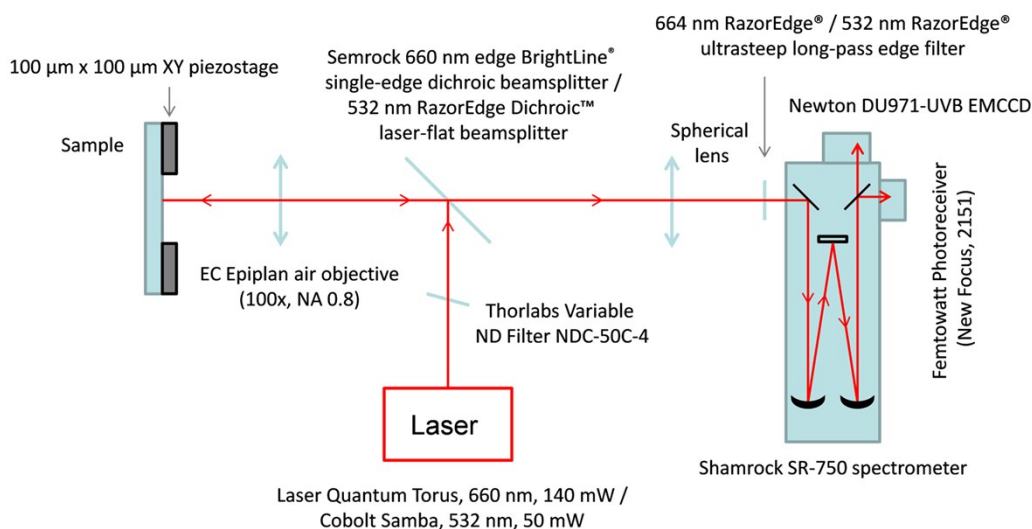
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The scheme of optical setup

Raman configuration



UV-Vis configuration

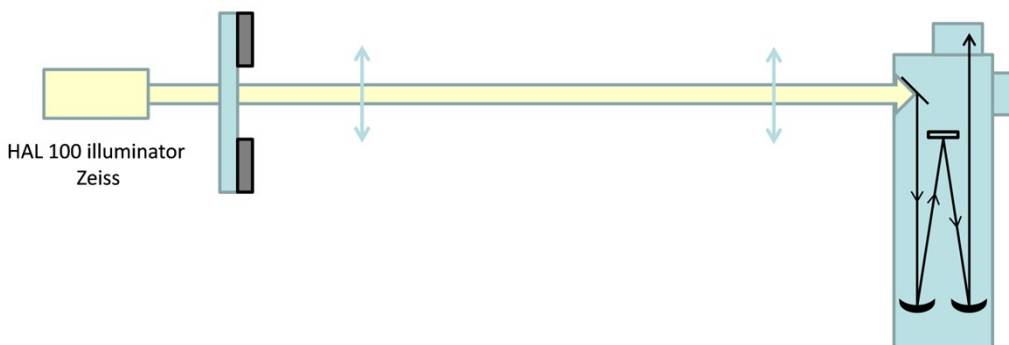


Figure S1. The scheme of Raman and UV-Vis configurations used in the experiment. The detailed description of the setup is provided below.

UV-Vis characterization of the immobilized Au NPs was performed on an inverted optical microscope (Axiovert 200, Zeiss) in transmitted light illumination (HAL 100 illuminator, Zeiss) coupling a microscope with a 750 mm long spectrometer (Shamrock SR-750, Andor Technology plc). First, a sample was mounted on the XY sample holder in order to obtain the confocal laser scanning images. 532 nm (Cobolt Samba, 50 mW, bandwidth 1MHz) or 660 nm (Laser Quantum Torus, 140 mW, bandwidth 1MHz) CW laser was used as the source of monochromatic light. A laser beam was reflected by a beamsplitter, directed to the microscope and then focused on the sample by 100x air objective (NA 0.8, EC Epiplan, Zeiss) resulting in a diameter of laser spot on the sample of around 0.5 μm . The reflected light was collected by the same objective and then directed into the spectrometer with a mounted femtowatt photoreceiver (New Focus, 2151, Newport Corp.). The signal from a photoreceiver was transferred to

the controller of the atomic force microscope (Nanowizard II, JPK), which controls the XY piezostage (TAO module, JPK) and allows to scan a sample in the range of 100 μm by 100 μm , recording finally the confocal laser scanning images. The laser power on the sample was controlled by a variable metallic neutral density filter (NDC-50C-4M, Thorlabs) and kept at 0.01 mW. After that with a top illumination from a halogen source, the transmitted through the sample light was directed into a spectrometer, dispersed by a diffractive grating of 600 lines mm^{-1} , and finally analyzed using TE-cooled EMCCD (Newton DU971-UVB, Andor Technology plc). The position of the grating was controlled by Andor SOLIS software and changed automatically to cover a wavelength range of 450-900 nm. The XY sample holder allows move the sample with nm precision focusing on the locations of interest, i.e. on the patches (to measure the intensity of transmitted light I) or clean glass surface (to measure the reference intensity I_0).

The Raman measurements were performed in the reflection geometry on the same setup with minor modifications. Two CW lasers with the excitation wavelengths of 532 nm (Cobolt Samba) and 660 nm (Laser Quantum Torus) were used. A laser beam was reflected by suitable 45 degrees oriented beamsplitter, directed to the inverted microscope and then focused on the mounted sample by the same 100x air objective (NA 0.8, EC Epiplan). The reflected light is collected and directed onto the beamsplitter by the same optical path. The light is then focused by a spherical lens on the entrance of spectrometer through the edge filter and registered by CCD. As previously described, 100 μm by 100 μm confocal laser scanning images were recorded first using the XY piezostage (TAO module) and then the averaged Raman spectra on the patterns were measured, acquiring the signal from 20x20 μm^2 area scanning the sample. A laser power on the sample was controlled by a metallic neutral density filter and kept at 0.1 mW to avoid the heating of the samples.

SAXS measurements

The beamline was operated at 16 keV. The size of beam was cut to 120 x 120 μm . The sample was mounted perpendicularly to the beam on controllable XY translation stage and scanned with 40 μm step width in both horizontal and vertical direction resulting in a map of 5 by 15 pixels (200 μm by 600 μm). The data were collected using a 2D Pixel detector Pilatus3 1M (Dectris, Villigen, Switzerland). The sample-to-detector distance was set to 1.3 m, which provided a modulus of the scattering vector q ($q = 4\pi \sin \vartheta / \lambda$, with 2ϑ being the scattering angle and λ equal to 1.54 \AA the X-ray wavelength) ranging from 0.08 to 7 nm^{-1} . Acquisition time was 300 s per every pixel. Data have been corrected by the measured transmission and have been azimuthal integrated with the program Fit2D [S1]. The background from the glass has been removed for an equivalent scan for each position. The scattered intensity is finally reported as a function of the scattering vector.

The fitting has been performed using generalization of the Guinier-Porod model [S2]:

$$I(q) = \frac{G}{q^s} \exp\left(\frac{-q^2 R_g^2}{3-s}\right) \text{ for } q \leq q_1$$

$$I(q) = \frac{D}{q^d} \text{ for } q \geq q_1$$

where q is the scattering vector, $I(q)$ is the scattered intensity, R_g is the radius of gyration, d is the Porod exponent, and G and D are the Guinier and Porod scale factors, respectively.

Note that s parameter describes models for nonspherical objects, and $s = 0$ for spheres, $s = 1$ for rods, and $s = 2$ for platelets; while the scattering inhomogeneities can be defined through the Porod exponent d , $d = 4$ points to particles with smooth surfaces while $d = 3$ points to very rough surfaces; the radius of gyration for a cylindrical of rod length L and radius R in the asymptotical cross sectional regime is given by [S3]:

$$R_g^2 = \frac{R^2}{2}$$

*Table S1. The derived fit parameters (Figure S2).
The constraints $d > s$ and $s < 3$ are satisfied.*

	0.6mW	4.0mW
I_0	5.51 ± 0.51	9.13 ± 0.68
R_g, nm	2.5 ± 0.1	2.6 ± 0.1
s	1.30 ± 0.05	1.20 ± 0.04
d	4 ± 0.21	4 ± 0.14

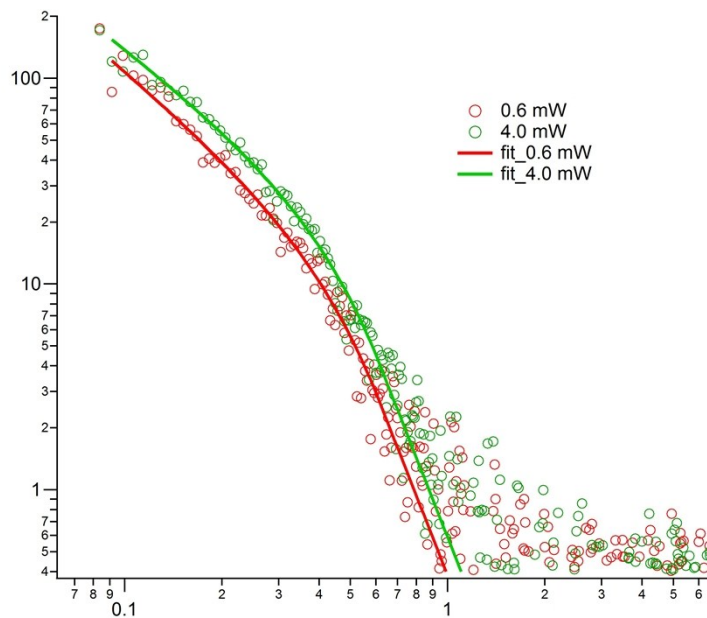


Figure S2. The SAXS spectra of the patterns produced at 0.6 mW and 4.0 mW DLW power and their fit using generalization of the Guinier-Porod model. The fit parameters are summarized in the Table S1.

S1. Hammersley P 1998 *Fit2D Reference Manual V3.1. Internal Report ESRF98HA01T. ESRF, Grenoble, France*

S2. Hammouda B 2010 *J. Appl. Crystallogr.* 43 716

S3. "Small Angle X-ray Scattering" edited by O. Glatter and O. Kratky, Academic press 1982

Raman spectra of the bare patterns

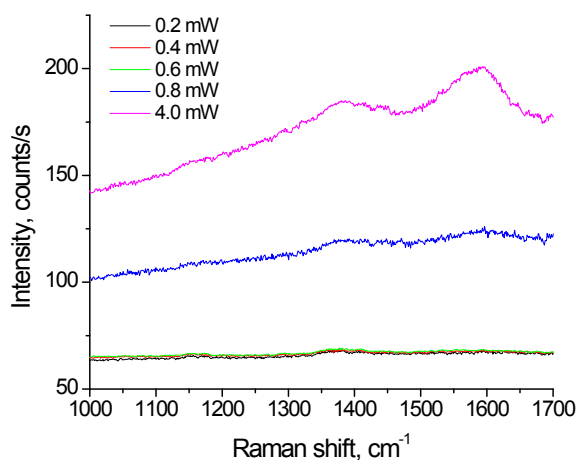


Figure S3. Raman spectra of the patterns produced at different DLW powers after plasma cleaning for 1 min at the power of 50 W and oxygen pressure of 10^{-2} mbar. The spectra are acquired at 532 nm excitation wavelength with the same laser power on a sample surface.

The broad peaks centered at 1350 cm^{-1} and 1600 cm^{-1} have been observed after plasma cleaning on the patterns which were fabricated at high DLW power (0.8 mW and 4.0 mW). This is an evidence of amorphous carbon [S4] that is formed in the pattern due to photodecomposition of organic molecules initially presented on both Au NP and glass surface.

S4. Ferrari AC and Robertson J 2001 Phys. Rev. B 64 075414

Absorption spectrum of BT-Azo dye

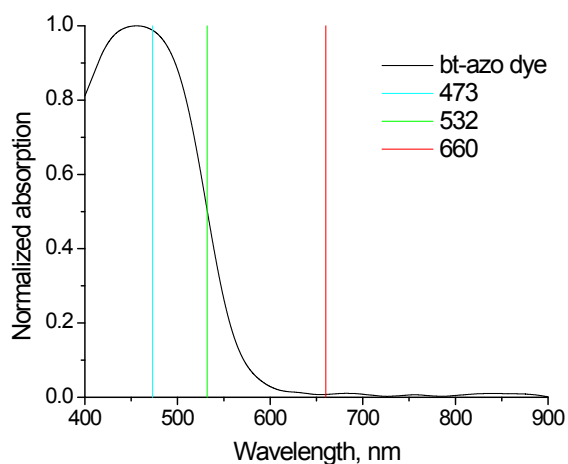


Figure S4. Normalized absorption spectrum of BT-Azo dye on glass substrate with highlighted vertical lines indicating the laser wavelengths used in Raman and SERRS experiments.

AFM characterization of the bare patterns and analyte areal density evaluation

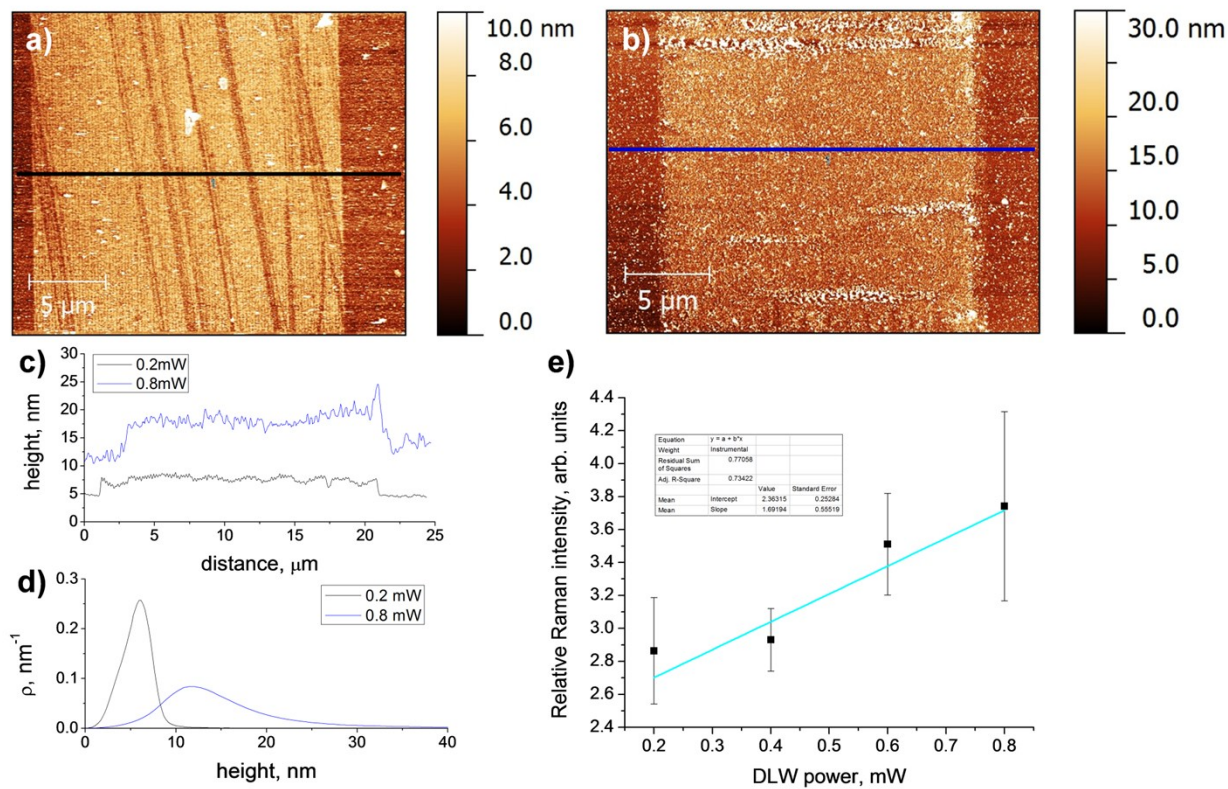


Figure S5. (a, b) AFM images of the patterns produced at 0.2 mW and 0.8 mW DLW power correspondingly. (c) Height cross-sections along black and blue lines displayed in (a) and (b) demonstrating an increase of the pattern height with increased DLW power as a result of higher number of immobilized AuNPs. (d) Surface roughness distribution calculated for entire AFM scans justifying the two time increase of height for the pattern produced at higher DLW power. (e) Relative Raman signal of BT-Azo dye 1420 cm^{-1} mode acquired at 473 nm excitation wavelength as a function of DLW power calculated as a ratio of the corresponding intensity to the signal acquired on the glass substrate outside the pattern demonstrating a slight increase of relative signal as a result of higher concentration of BT-Azo dye adsorbed on the pattern.

Absorption spectrum of hemin

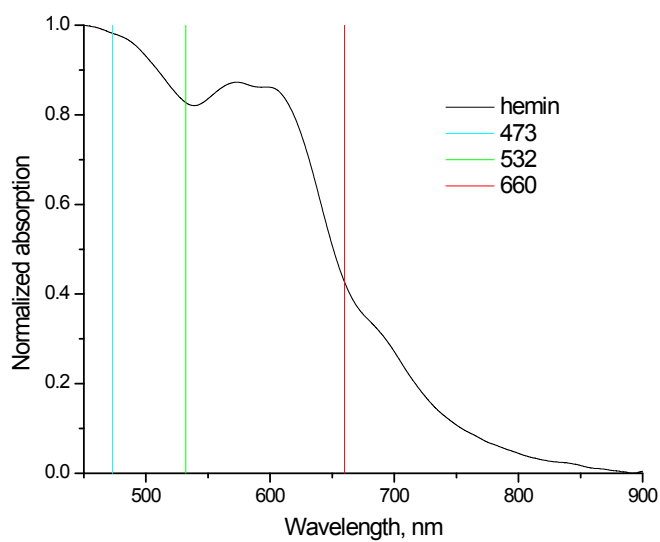


Figure S6. Normalized absorption spectrum of hemin on glass substrate with highlighted vertical lines indicating the laser wavelengths used in Raman and SERRS experiments.