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Multi-functionalization of lithographically designed gold nanodisks by plasmon-mediated reduction of aryl diazonium salts

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Abstract: Plasmon-driven surface functionalization of nanoparticles is receiving growing attention as it allows generating locally tailored chemical reactivity on the nanoparticle surface, which can be used to guide molecules, proteins or catalytic nanomaterials onto regions of maximum field enhancement. Although efficient strategies for single functionalization of surfaces, confined into nanoscale region, have been developed recently, their extension to the patterned multi-functionalization of surfaces still represents a major breakthrough in plasmon-mediated chemistry. We address this issue in the present paper by monitoring the incident light polarization on gold nanodisks, under plasmon excitation, to trigger regiospecific surface double-functionalization, using diazonium salts as surface functionalization agents. This plasmon-based multi-functionalization approach offers promising perspectives for nanoscale regio-selective surface chemistry.

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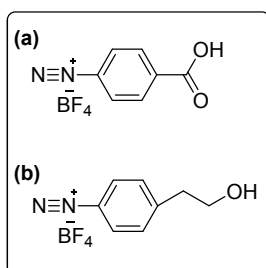
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Chemicals

Reagent grade solvents were supplied by VWR, Sigma Aldrich and Alfa Aesar. 4-aminobenzoic acid (99%), 2-(4-Aminophenyl)ethanol (98%) and tert-butyl nitrite (90%) were purchased from Sigma-Aldrich and used without further purification.

Chemical synthesis of diazonium salts



The diazonium salts were prepared by standard diazotation of the corresponding amines with NaNO_2 in acidic medium for 4-carboxyphenyldiazonium tetrafluoroborate salt **(a)** and with tert-butyl nitrite in acetonitrile for 4-(2-hydroxyethyl)-benzene diazonium tetrafluoroborate salt **(b)**. White solid for **(a)**; ^1H NMR (DMSO-d_6 , Bruker 400 Mhz) δ ppm: 8.76, 8.78 (d, 2H), 8.44, 8.41 (d, 2H). and for **(b)**: ^1H NMR (400 MHz, DMSO-d_6): δ (ppm) 8.41 (d, 2H,) et 8.77 (d, 2H).

Samples fabrication

Electron Beam Lithography (EBL) was used for the fabrication of the gold nanoparticle arrays. We used glass slides coated with a 160 nm indium–tin oxide (ITO) layer (Luminescence Technology Corp). First, high resolution resist, poly(methyl methacrylate) (PMMA, 350 000 Mw, Sigma Aldrich) dissolved in anisole at the concentration of 65 g/L, was spin-coated on the substrates. The PMMA layer was 145 ± 5 nm (thickness verified with a profilometer KLA-Tencor AS-IQ). The PMMA was then exposed to an electron beam using a scanning electron microscope (FESEM, Pioneer, Raith), and its further development was completed by immersing substrates in a standard 1:3 methyl isobutyl ketone/isopropanol (MIBK/IPA) solution for 40 seconds. Finally, 50 ± 5 nm of gold was deposited by thermal evaporation. A lift-off of the remaining PMMA layer was performed in acetone overnight. Gold nanodisks (GNDs) arrays with a diameter of 100 ± 5 nm are displayed (arrays of $10\mu\text{m} \times 10\mu\text{m}$). The gap (edge to edge) between GNDs was set to 200 nm avoiding any significant near-field or far-field coupling. Figure S1 displays the SEM image of a typical gold nanodisk array obtained by EBL. In order to simplify the further characterization, patterns were surrounded by markers (Fig. S1a) ^[1].

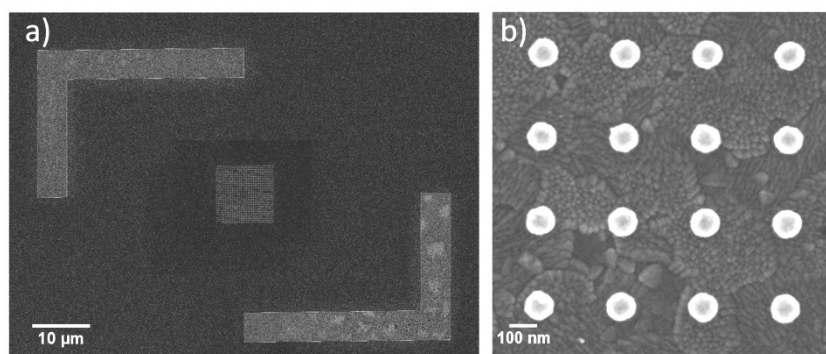


Figure S1. SEM micrographs of: (a) an GNDs array surrounded by markers; (b) an array of periodic GNDs with a diameter of 100 nm and a interparticle distance (center to center) of 300 nm.

Spontaneous surface functionalization

GNDs were functionalized using the synthesized diazonium salts (3 mM) by incubating the substrates in an aqueous solution for 1 hour at room temperature (RT). The substrates were then rinsed with milliQ water and

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ethanol in order to remove physically adsorbed molecules. It is noteworthy that the poly(aryl) layers covalently linked to the gold surface should not be removed by this procedure.

Plasmon-induced surface functionalization

The lithographic structures were immersed into an aqueous diazonium salts solutions (3 mL of 3 mM), and exposed to a He–Ne laser (632.8 nm) with a power of 0.8 mW at various exposure times. The laser was focused on the sample using a microscope objective of 10 fold magnification (0.25 N.A.). After irradiation, the substrates were thoroughly rinsed with milliQ water and ethanol.

Optical characterizations

Raman and extinction measurements were performed using a Labram HR800 micro-spectrometer. Extinction spectra were recorded after removing the edge filters with a non-polarized white lamp, and the transmitted light was collected with a 10× magnification objective (N. A. 0.25). Raman spectra of the synthesized diazonium salts and the SERS spectra of the functionalized GNDs were obtained in backscattering configuration using an excitation line of 633 nm with a power of 0.6 mW. The scattered light was collected with a long working distance objective of 100 fold magnification (0.9 N.A.). The spectral resolution was less than 3 cm⁻¹. The accumulation time for the SERS measurements was set to 20s with two repetitions. Both extinction and SERS spectra were recorded on GNDs in aqueous solution.

Microscopic characterizations

Atomic force microscopy (AFM) measurements were performed in tapping mode with a SPM Nanoscope III, Veeco, Bruker. AFM images were processed and analyzed using the application WSxM.42 [3]. SEM images were performed on a field emission scanning electron microscope (FE-SEM; Zeiss, Supra).

Computational methods

Discrete dipole approximation method (DDA) method was performed in order to model the experimental far field extinction spectra and the near field response of the GNDs^[2]. This is one particular discretization method for solving Maxwell's equations in the presence of a particle in which the continuum particle is replaced by an array of polarizable N-point dipoles located on cubic lattice sites. Computations were performed using the DDSCAT 7.0 software, which calculates efficiency factors, $Q_{\text{ext}} = C_{\text{ext}}/\pi a_{\text{eff}}^2$ (C_{ext} is the extinction cross section and a is the effective radius of the particle). The interaction between the GNDs and the substrate was taken into account, enabling reliable comparisons between the experimental and calculated spectra.

Table S1. Band assignments for Raman and SERS spectra of the diazonium salts and the poly(aryl) layers grafted on the gold nanoarrays (cm⁻¹).

Free diazonium salts		Grafted poly(aryl) layers		Assignments
COOH-	HO-(CH ₂) ₂ -	COOH-	HO-(CH ₂) ₂ -	
1074	1082	1074	1074	CH in-plane bending for para- and mono-substituted benzenes
1591	1583	1586	1587	C=C stretching
2304	2277	-	-	N≡N stretching

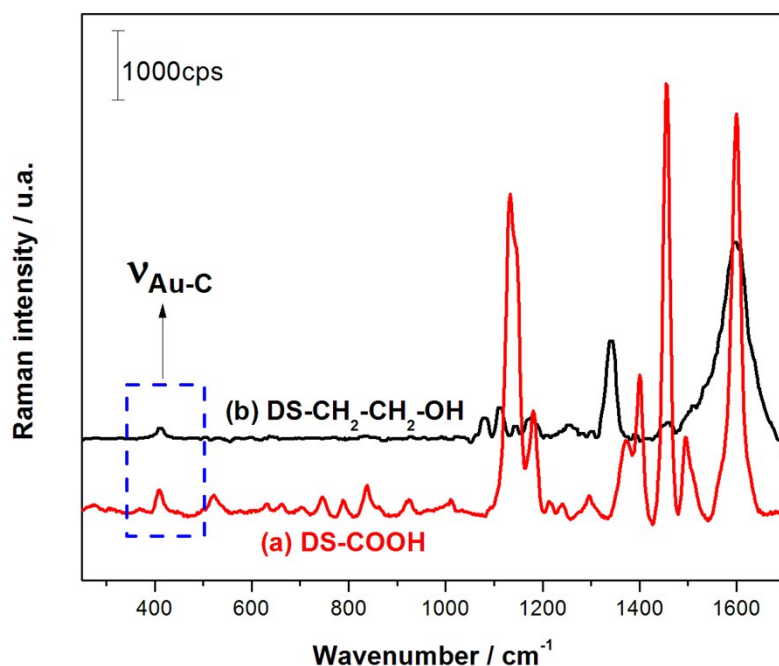


Figure S2. SERS spectra recorded after the plasmon-induced grafting of (a) carboxy-aryl layers and (b) hydroxyethyl-aryl layers. Laser excitation takes place at 633 nm.

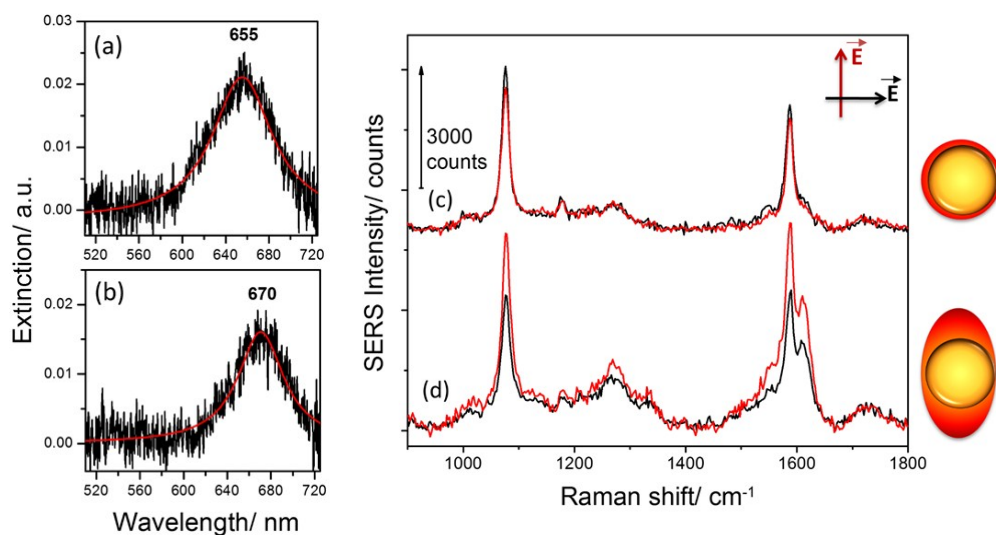


Figure S3. (Left): Extinction spectra after a first plasmon-induced surface functionalization by carboxy-aryl layers: (a) Extinction spectrum of a GNDs array in water after a spontaneous grafting. No significant wavelength shift is observed, compared the spectrum before any grafting; (b) Extinction spectrum of a GNDs array in water after a plasmon-induced surface functionalization (optical exposure performed under normal incidence, at $\lambda_{inc} = 633$ nm, focused on the GNDs array through a microscope objective: $\times 10$ numerical aperture N.A. #0.8 #0.25). A red-shift of 15 nm of the plasmon band is observed, compared to the spectrum before any grafting. (Right): (c) SERS spectra after a spontaneous grafting; (d) SERS spectra after a first plasmon-induced surface functionalization by carboxy-aryl layers. The colors of the spectra indicate the laser polarization direction. Laser excitation takes place at 633 nm.

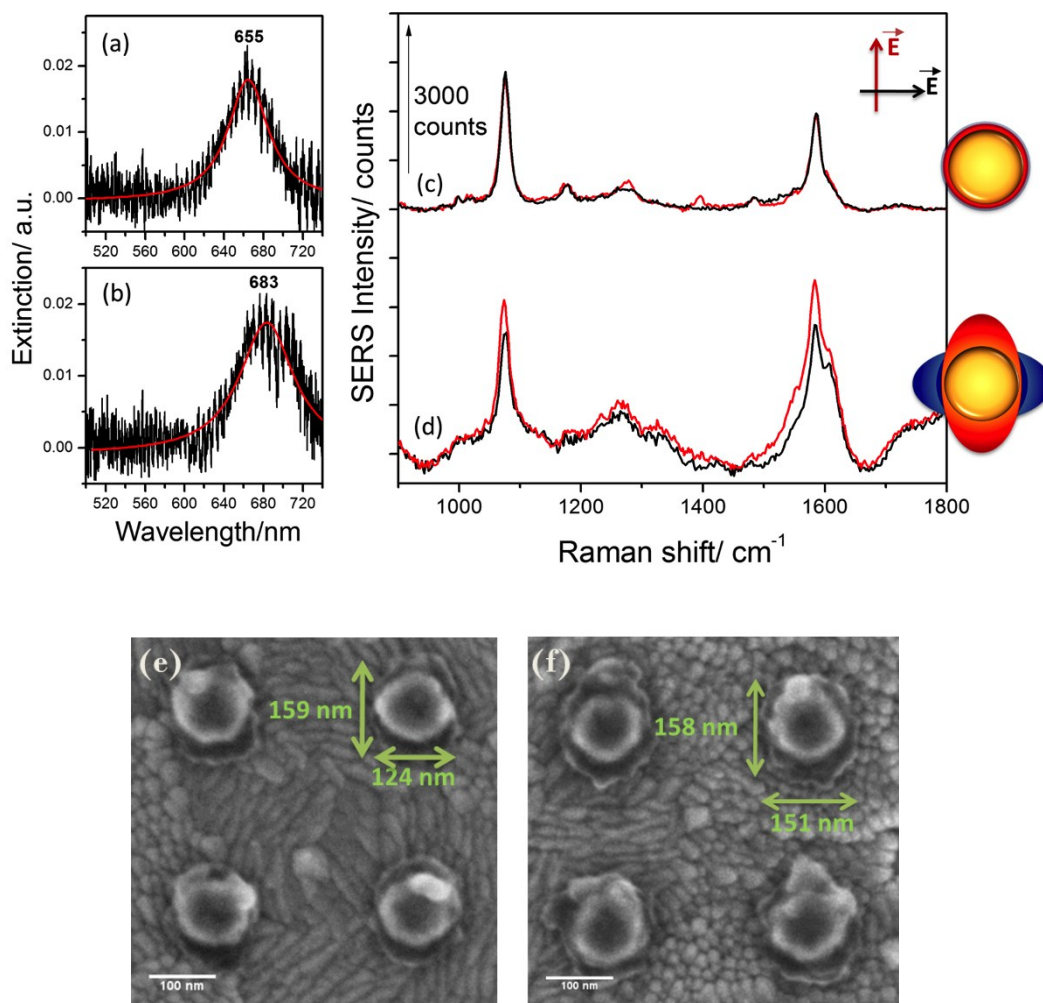


Figure S4. (Left) Optical measurements recorded after a second plasmon-induced surface-functionalization by hydroxyethyl-aryl layers. Extinction spectrum in water (a) before surface-functionalization. (b) after plasmon-induced surface double-functionalization. After the plasmon-induced grafting, a significant red-shift of 28 nm is observed. (Right) (c) SERS spectra after a spontaneous grafting; (d) SERS spectra after the second plasmon-induced surface functionalization by hydroxy-aryl layers. The colors of the spectra indicate the laser polarization direction. In the case of a spontaneous grafting (c), the SERS intensities vary less than 4% from one polarization to the other. In the case of the plasmon-induced grafting (d), SERS signals are detected for both polarizations, with a variation of ~ 21% from one polarization to the other, evidencing the presence of the hydroxy-aryl layers mainly along the X axis. (e): SEM image of a set of four gold disks after plasmon, after plasmon-induced grafting of carboxyphenyl layers along the Y direction, and (f) additional hydroxyethyl phenyl layers along the X axis. Irradiation conditions: $\lambda_{\text{inc}} = 633 \text{ nm}$, 180 seconds with a power of $P=0.8 \text{ mW } \mu\text{m}^{-2}$.

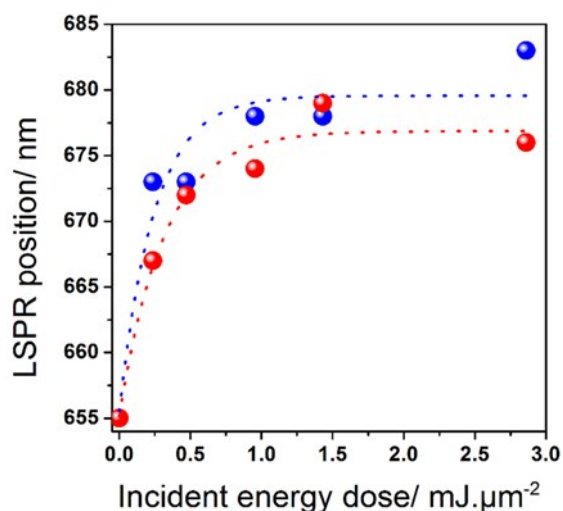


Figure S5: LSP wavelength *versus* the incident energy dose. The red spheres correspond to the measure of the LSP wavelength after the first surface functionalization by carboxy-aryl layers, and the blue spheres, to the measure of the LSP wavelength after the second surface functionalization by hydroxy-aryl layers.

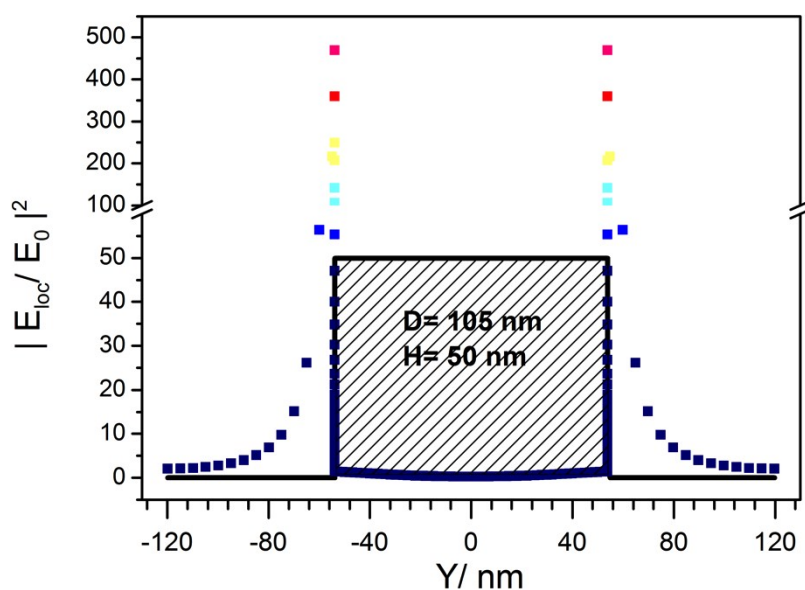


Figure S6: Dependence of the near-field intensity enhancement $|E_{loc}/E_0|^2$ with the distance from the center of a target corresponding to a GND (DDA method). The target corresponds to an array of circular disks (diameter 105 nm, height 50 nm) deposited on an ITO substrate. The grating constant is 300 nm. The near-field enhancement is maximum at the particle surface, and decreases rapidly with the distance from the surface.

References

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