

## Supporting Information

### Regioselective surface functionalization of lithographically designed gold nanorods by plasmon-mediated reduction of aryl diazonium salts

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#### Materials and Methods

Reagent grade solvents were supplied by VWR, Sigma Aldrich and Alfa Aesar. 2-(4-Aminophenyl)ethanol (98%) and tert-butyl nitrite (90%) were purchased from Sigma-Aldrich and used without further purification. The diazonium salt was prepared by standard diazotation of the corresponding amine with tert-butyl nitrite in acetonitrile for 4-(2-hydroxyethyl)-benzene diazonium tetrafluoroborate salt. The 4-(2-hydroxyethyl)-benzene diazonium tetrafluoroborate salt, noted HEBDT ( $+N_2-C_6H_4-CH_2-CH_2-OH$ ) was synthesized following this protocol: A stirred solution of 2-(4-aminophenyl)ethanol (0.69 g) and  $HBF_4$  (1.8 mL) in acetonitrile (3 mL) at  $-10^\circ C$  was added dropwise to a solution of tertbutylnitrite (0.63 g) in acetonitrile (3 mL) at  $-10^\circ C$ . The resulting mixture was kept overnight at  $-10^\circ C$ . The precipitate was washed three times with 50 mL of diethyl ether, then with 50 mL of acetone and finally evaporated under vacuum. The HEBDT salt was stored at  $-10^\circ C$ .  $^1H$  NMR (Bruker Avance III, 300 MHz,  $CDCl_3$ ),  $\delta$  ppm: 8.6-8.5 (m, 2H, aromatic protons  $\beta$  to the diazonium function), 7.8 (m, 2H, aromatic protons  $\beta$  to the benzylic carbon), 3.71 (t,  $J=6.3$ Hz, 2H,  $-CH_2-OH$ ), 2.97 (t,  $J=6.2$ Hz, 2H,  $-Ar-CH_2-$ ).

#### Elaboration of lithographic gold nanorod arrays by Electron Beam Lithography

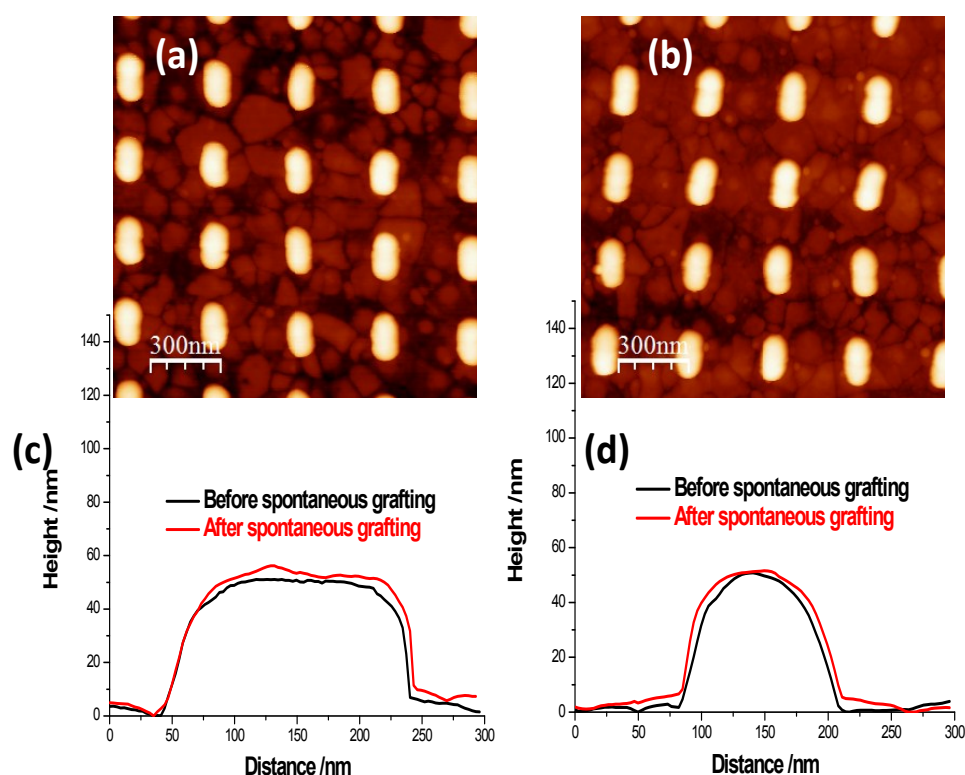
Electron Beam Lithography (EBL) was used for the fabrication of the gold nanorod arrays. We used glass slides coated with a 160 nm indium-tin oxide (ITO) layer (Luminescence Technology Corp). First, high resolution resist, poly(methyl methacrylate) (PMMA, 350 000 Mw, Sigma Aldrich) dissolved in anisole at the concentration of 65 g/L, was spin-coated on the substrates. The PMMA layer was  $90 \pm 5$  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 solution for 40 seconds. Finally,  $47 \pm 3$  nm of gold was deposited by thermal evaporation. A lift-off of the remaining PMMA layer was performed in acetone overnight. Gold nanorod (AuNRs) arrays with a long axis of  $165 \pm 5$  nm and a short axis of  $100 \pm 5$  nm were obtained (arrays of  $100 \mu m \times 100 \mu m$ ). The gap (edge to edge) between AuNRs was set to 300 nm avoiding any significant near-field or far-field coupling.

#### Instrumentation

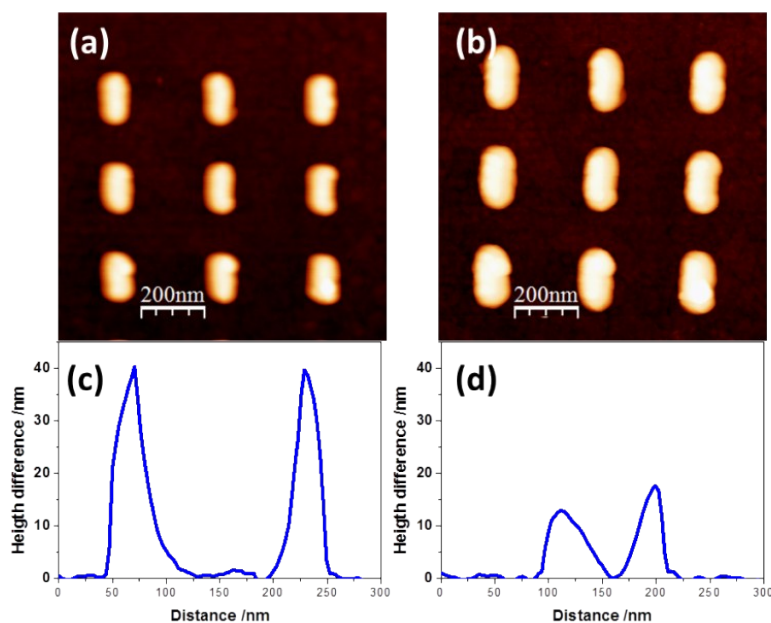
The LSP resonance of the samples was probed by far-field visible-NIR extinction micro-spectroscopy in the range of 500–900 nm, with irradiation by using a halogen lamp from the glass side at normal incidence. The spectrometer (LOT ORIEL model MS 260i) was coupled to an optical microscope

(OLYMPUS BX 51) equipped with a 50× objective (numerical aperture N.A. #0.75). The investigated area was a circle of approximately 80  $\mu\text{m}$  diameter, which was smaller than the structure array (100  $\times$  100 $\mu\text{m}$ ). Atomic force microscopy (AFM) measurements were performed using a tapping mode (on a SPM Nanoscope III, Veeco, Bruker) atomic force microscope. AFM images were processed and analyzed using the application WSxM. The irradiation experiments were carried out by using a laser with  $\lambda_{\text{inc}} = 785 \text{ nm}$ , focused on the sample, through a microscope equipped with a 100× objective (Olympus, NA #0.8). XPS spectra were recorded using a Thermo VG Scientific ESCALAB 250 system fitted with a microfocused, monochromatic Al K $\alpha$  X-ray source ( $h\nu = 1486.6 \text{ eV}$ ; spot size = 650  $\mu\text{m}$ ; power = 15 kV, 200 W). The pass energy was set at 150 and 40 eV for the survey and the narrow regions, respectively. Spectral calibration was determined by setting the main C1s component at 285 eV. The surface composition was determined using the integrated peak areas and the corresponding Scofield sensitivity factors corrected for the analyzer transmission function. The SERS spectra were performed using a Labram HR800 micro-spectrometer, 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  $\text{cm}^{-1}$ . The accumulation time for the SERS measurements was set to 20s with two repetitions.

## AFM analysis

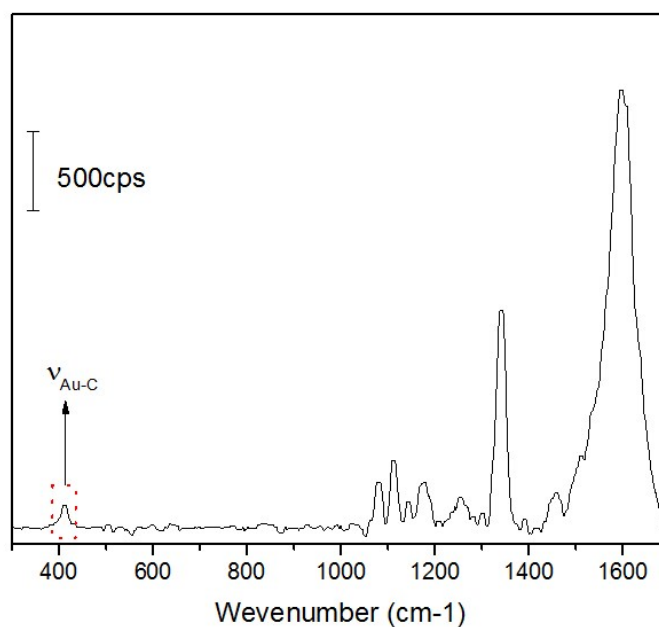


**Figure S1:** AFM images of the nanorod array before (a) and after (b) spontaneous grafting of poly(aryl) layer for 6 hours of incubation time. AFM lateral cross section profiles along the long axis of the rod (c) and short axis (d), before (black curves) and after (red curves) spontaneous grafting of poly(aryl) layer.



**Figure S2.** (a)(b) AFM images of the nanorod array before (a) and after (b) plasmon-induced grafting using a laser at  $\lambda_{inc} = 785$  nm, polarized along the long axis of the nanorods. (c) and (d) represent the differential lateral cross section along the long axis (c) revealing two lobes on each ends of the nanoparticle, and along the short axis (d) confirming that the grafting along the short axis direction is low.

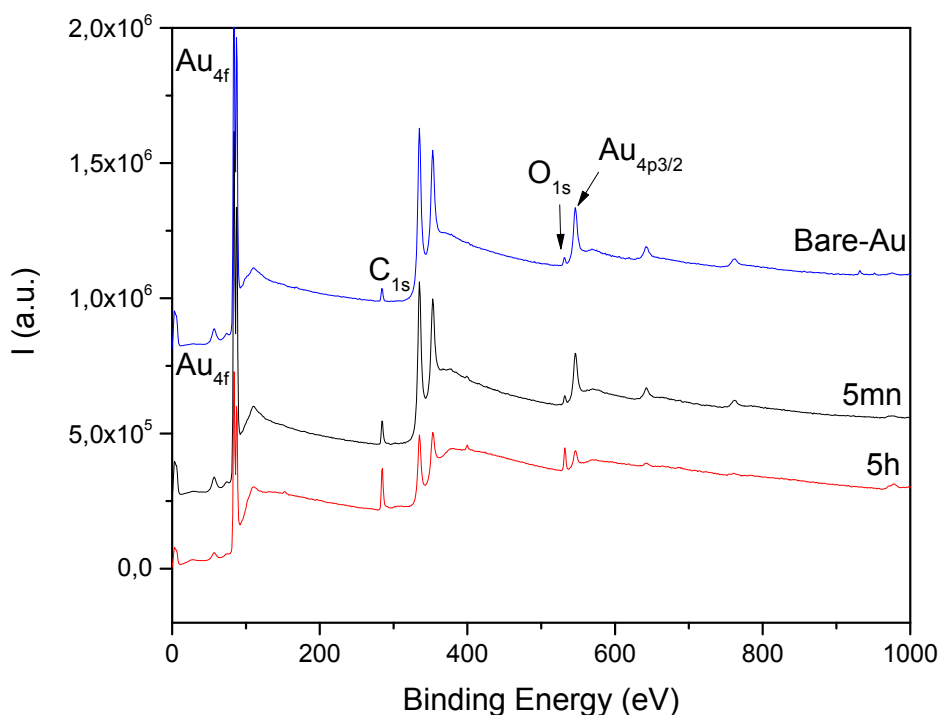
### SERS analysis



**Figure S3.** SERS spectrum of the poly(aryl) layers derived from hydroxyethyl-terminated diazonium salts on the gold substrate after plasmon-induced grafting. The grafting was performed in aqueous solution ( $c = 3$  mM) of the diazonium salt, during 180 s under plasmon excitation.

## XPS analysis and thickness measurements

The spontaneous grafting of the diazonium-derived layer at the surface of planar gold substrates (cut in gold coated silicon wafers purchased from Sigma-Aldrich) was performed by simply incubating the substrates with the diazonium salt in water at room temperature. Strong modifications in surface chemical composition were observed by XPS after functionalization of the gold substrates (see spectra in Fig. S3). Indeed, the gold signal appears strongly attenuated while the carbon content increases, indicating the covering of gold by diazonium-derived layers, as evidenced by the evolution of the C/Au atomic ratio (see Table S1).



**Figure S4:** XPS survey spectra of bare Au (blue curve), Au coated by poly(aryl) layers after 5 minutes of incubation time (black curve) and after 5 hours of incubation time (red curve).

**Table S1:** C/Au atomic ratio determined by XPS and estimation of the organic layer thickness  $d$ . Details of the calculation are reported below.

<b>Sample</b>	<b>C/Au</b>	<b><math>d</math> (nm)</b>
Bare Au	0.5	-
Au-poly(aryl) after 5 min incubation	0.8	$1.1 \pm 0.2$
Au-poly(aryl) after 5 h incubation	3.1	$3.2 \pm 0.2$

The gold signal attenuation, observed all along the different chemical steps, is due to the covering of the electrode by the organic overlayer. This attenuation can be used to provide an estimation of the organic layer thickness. Indeed, the relative inhibition of the Au 4f<sub>7/2</sub> signal can be expressed as

$$I/I_0 = \exp(-d/\lambda \sin \theta)$$

where  $d$  is the layer thickness,  $\lambda$  the mean free path of the substrate-specific photoelectron in the organic layer,  $\theta$  the analysis takeoff angle relative to the surface, and  $I/I_0$  the ratio of the Au4f<sub>7/2</sub> peak intensities (modified surface/bare surface). In our experiments, the takeoff angle was 90° and the value of  $\lambda$  was deduced from the empirical formula derived by Seah and Dench:

$$\lambda_k = A_n/E_k^2 + B_n E_k^{1/2}$$

where  $E_k$  is the kinetic energy of photoelectrons. For an Al K<sub>α</sub> source:  $E_k = 1486.6 - E_B$ . If the substrate is coated with organic materials,  $A_n = 49$  and  $B_n = 0.11$ , here the unit of  $\lambda$  is mg.m<sup>-2</sup> and the unit of energy is the electronvolt. To convert  $\lambda$  into nanometer units, one has to divide  $\lambda$  in mg.m<sup>-2</sup> by the density of the overlayers, assumed here to be equal to 1.02 g/cm<sup>3</sup>. For Au4f<sub>7/2</sub>,  $\lambda_k$  is calculated to be 4.12 mg.m<sup>-2</sup> and the aryl adlayer thickness is found to be 3.5 nm.

## Computational methods

Discrete dipole approximation method (DDA) method was performed in order to model the near field response of the AuNRs<sup>[1,2]</sup>. 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,  $Q_{\text{ext}} = C_{\text{ext}}/\pi a_{\text{eff}}^2$  ( $C_{\text{ext}}$  is the extinction cross section and  $a$  is the effective radius of the particle). The interaction between the AuNRs and the substrate was taken into account, enabling reliable comparisons between the experimental and calculated spectra.

- [1] B. T. Draine and P. J. Flatau, User Guide for the Discrete Dipole Approximation Code DDSCAT7.0. <http://arxiv.org/pdf/0809.0337.pdf> (accessed November 11, 2013).
- [2] E. M. Purcell and C. R. Pennypacker, *Astrophys. J.*, 1973, **186**, 705-714.