Supporting information

Dynamic plasmonic platform to investigate the correlation between far-field optical response and SERS signal of analytes

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1. Functionalization of gold nanostructures by PNIPAM brushes 

\textbf{Figure SI1:} Multi-step strategy for the functionalization of gold surfaces by PNIPAM: (i) spontaneous grafting of aryl film derived from 4-hydroxyethylbenzene diazonium tetrafluoroborate salt (HEBDT); (ii) esterification with 2–bromoisobutyryl bromide and (iii) ATRP of N-Isopropylacrylamide on the initiator-modified gold substrates. 

\textbf{1.1. Synthesis of diazonium salt (HEBDT):} 

The 4-Hydroxyethylbenzene Diazonium Tetrafluoroborate Salt (+N\textsubscript{2–}C\textsubscript{6}H\textsubscript{4–}CH\textsubscript{2–}CH\textsubscript{2}–OH) was synthesized through the following protocol: a stirred solution of 2-(4-aminophenyl)ethanol (0.69 g) and HBF\textsubscript{4} (1.8 mL) in acetonitrile (3 mL) at −10 °C was added dropwise to a solution of tert-butylnitrite (0.63 g) in acetonitrile (3 mL) at −10 °C. The resulting mixture was kept overnight at −10 °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 4-(2-hydroxyethyl)benzene diazonium tetrafluoroborate salt was stored at −10 °C.

1.2. *Initiator-modified gold surfaces:*

The atom transfer radical polymerization initiator was grafted in 2 steps. *(i)* spontaneous grafting of 4–hydroxyethylbenzene diazonium tetrafluoroborate salt (3 mM) was achieved on cleaned gold nanostructures array by incubation for 6h at room temperature; *(ii)* then, the terminal hydroxyl groups were treated with 2-bromoisoobutyryl bromide (0.1 M, toluene) in the presence of TEA (0.12 M) for 5 min to produce bromo-terminated ester groups.

1.3. *Atomic Transfer Radical Polymerization (ATRP) of NIPAM:*

Solutions were prepared and kept at room temperature during degassing by passing a continuous stream of argon through the solution while being stirred. The polymerization solution was prepared by adding a solution of an organometallic catalyst to a solution of NIPAM monomer. The extremely oxygen sensitive organometallic catalyst was prepared by adding a 5 mL solution of PMDETA in methanol (200 µL, 1 mmol) to 30 mg of CuBr (0.2 mmol). A 3 mL portion of the resulting green solution (which could possibly turn blue due to presence of CuBr$_2$ and provide unsuccessful ATRP) was added to a solution of NIPAM monomer (2 g, 18 mmol) in 11 mL of deionized water under a continuous stream of argon. The polymerization solution was allowed to stir during degassing for 15 min and then transferred into a flask containing the initiator-modified gold surface. The resulting solution was allowed to stir at room temperature under argon for 20 min. Substrates were then removed from the flask and rinsed thoroughly with ethanol and water and subsequently dried under a flush of argon.
2. Characterization of the samples

2.1. AFM images

**Figure S12.** AFM images recorded in air at room temperature of gold nanosquare array (width ~ 130 nm, length ~ 140 nm and height ~ 30 nm) before (a) and after (b) PNIPAM grafting.

**Figure S13.** AFM images of gold nanocylinders array (diameter ~ 160 nm and a height ~ 45 nm); (a) before functionalization, recorded in air; (b) after PNIPAM grafting, recorded in air; (c) after PNIPAM grafting recorded in water at room temperature.
**Figure SI4.** AFM images of gold nanocylinder array (diameter ~ 130 nm and a height ~ 45 nm) before (a) and after (b) PNIPAM coating.

**Synthesis of an alkyne derivative of azobenzene:**

From 4-phenylphenol (C₆H₅C₆H₄OH, Sigma-Aldrich), a one-step synthesis leads to the alkyne derivative (Fig. SI5a). Briefly, a solution of 4-phenylphenol (500 mg) and K₂CO₃ (1.75 g) in anhydrous acetonitrile (30 mL) was stirred at room temperature for 30 min under nitrogen. Propargyl bromide (80 % w/w in toluene, 1.5 g) was added and the mixture was stirred at room temperature for 2 days. The solvent was removed by evaporation under vacuum and the crude product was dissolved in ethyl acetate. Water was added in order to dissolve K₂CO₃ residual. Then, the aqueous phase was extracted. The organic phase containing the product in ethyl acetate was dehydrated by adding MgSO₄. After filtration, the solution was evaporated under vacuum in order to eliminate the solvent and to obtain the product as a powder. The ¹H NMR data (Bruker Avance III, 300 MHz, CDCl₃) confirmed the synthesis of the final alkyne derivative product (result not showed).

**Functionalization of PNIPAM-coated gold nanocylinders by azobenzene**

The attachment of azobenzene at the very end of PNIPAM chains via click chemistry includes step (i) and step (ii) in Fig. SI5b: (i) substitution of the bromo-end groups (of PNIPAM brushes) to azide functions was carried out by reacting Au@PNIPAM substrate in NaN₃ solution (0.05 M, DMF) for 24 h at room temperature in order to obtain click active substrates; (ii): the azide-terminated substrates were immersed in a mixture containing β-cyclodextrin (1.25 mM), AB alkyne (0.05 M), Cu(II) sulfate pentahydrate (2.5 mM) and L-ascorbic acid sodium salt (7.5 mM) dissolved in water at room temperature following a typical click-chemistry procedure (azide-
alkyne cycloaddition). The obtained mixture was degassed by argon bubbling while being stirred during 24h.

**Figure S15.** Illustration of the synthesis of the alkyne derivative of azobenzene (a) and the attachment of azobenzene derivative on Au@PNIPAM (b).

**Figure S16.** Reversible intensity variation as a function of temperature for the Raman band of AB at 1142 cm\(^{-1}\) recorded on gold nanocylinders coated by PNIPAM and AB end groups.
3. Finite Difference Time Domain simulations:

The theoretical simulations are performed using the Finite Difference Time Domain method (FDTD) [1-2]. The modeled structure consists of a periodic array of gold nanosquares surrounded by water and deposited onto a glass substrate. Since the structure is bi-periodic in the (XY) plane and have a finite size in the z direction, we use a 3D-FDTD homemade code that combines Floquet Bloch’s periodic boundary conditions in both x and y directions to reproduce the elementary pattern of the structure, and Perfectly Matched Layer (PML) as absorbing conditions to model the finite space in the third one direction. We consider the refractive indices of glass and water equal to 1.5 and 1.3, respectively, while the Drude Critical Point model describes the dielectric function (dispersion) of gold [3], where a fitting with the experimental values of Johnson and Christy [4] optimizes model’s parameters. The structure is illuminated, at normal incidence, along the z-axis from the glass (see Fig. S17).

![Figure S17. The FDTD calculation window.](image)

For the far field calculations of extinction, we use a plane wave with a Gaussian time profile as electromagnetic excitation and we collect transmitted field signal in time with a detector placed far from the structure. Then, we use Fourier transformation to obtain the full spectrum in the frequency domain.

For the electric field intensity calculations in near field, we use a monochromatic wave at the desired wavelength of excitation and the electric field components are saved by placing a detector near the structure.
4. SERS spectrum of aryl-grafted substrate

![SERS spectrum of aryl-grafted substrate](image)

**Figure SI8.** SERS spectrum of aryl-grafted substrate.

**References**

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