

SUPPORTING INFORMATION FOR “Bottom-up Fabrication of Nanohole Arrays loaded with Gold Nanoparticles: Extraordinary Plasmonic Sensors”

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Materials & Methods:

All reagents were used as received except N-isopropylacrylamide which was recrystallized from hexane. N-isopropylacrylamide (NIPAM), 3-aminopropyltriethoxysilane (APTES), $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$, trisodium citrate dihydrate were purchased from Sigma Aldrich. $\text{HONH}_2 \cdot \text{HCl}$ was supplied by Acros Organics. Ethanol, $\text{N,N}'$ -methylene bisacrylamide (BIS) and H_2SO_4 were obtained from Carl Roth. NaCl and H_2O_2 were received from Merck. Potassiumperoxodisulfate (KPS) was supplied by Fluka. Albumine bovine Fraction V (BSA) was purchased from Serva. Water was deionized to a resistance of at least $18.2 \text{ M}\Omega$ (Ultra pure water system (TKA, Germany)) and then filtered through a $0.2 \mu\text{m}$ filter. The glass substrates used in the experiments were $24 \times 24 \text{ mm}$ glass cover slips obtained from Carl Roth (Germany). Samples were imaged with a Zeiss Ultra 55 "Gemini" scanning electron microscopy (SEM). Transmission spectra were recorded with a Cary 5000 UV-VIS-NIR Spectrometer (Varian, USA) with a 5 mm aperture in dual beam mode. Transmission spectra of the samples in liquid were carried out using precision cells with 2 mm light path type 100.099-OS from Hellma Analytics. The surface topography of the samples was studied by AFM in tapping mode using a JPK Nanowizard 2 with Nanoworld NCHR cantilevers (spring constant 42 N/m , resonant frequency 320 KHz).

Synthesis of polyNIPAM microspheres:

Poly(NIPAM) microspheres were prepared by aqueous free-radical polymerization.^[1] Briefly, 2.65 g of NIPAM and 0.1 g of BIS were dissolved in 124 mL of deionized water. The solution was heated to $\sim 70^\circ\text{C}$ under an inert atmosphere and stirred with a magnetic stir bar for $\sim 30 \text{ min}$. After injection of a KPS solution (0.04 g in 4 mL deionized water) the reaction was stirred for additional 6 h at $\sim 70^\circ\text{C}$ under an Ar environment. The resulting microspheres were purified by centrifugation, decantation, and then washed with deionized water (at least three times).

Synthesis of gold nanoparticles:

Gold colloids were synthesized by reduction of HAuCl_4 in deionized water with sodium citrate.^[2] For this purpose 78.9 mg HAuCl_4 was dissolved in 200 mL deionized water ($\sim 18.2 \text{ M}\Omega \text{ cm}$). The solution was heated to boil and vigorously stirred upon addition of a citrate solution made up from 228.2 mg trisodium citrate dihydrate in 20 mL deionized water ($\sim 18.2 \text{ M}\Omega \text{ cm}$). After heating the reaction solution for additional 30 min the heating mantle was removed and the solution was left stirring for 1 h to cool down. The solution was stored at 6°C until use.

Fabrication of hole arrays loaded with gold nanoparticles:

Glass cover slips were cleaned in piranha solution (3:1 mixture of H₂SO₄ (95-98%) and H₂O₂ (30%)) for 24 h followed by extensive rinsing with deionized water (~18.2 MΩ cm). Prior to use the glass cover slips were blown dry in a stream of nitrogen. For the deposition of PolyNIPAM microsphere arrays 100 μL of a 10 vol% ethanol:water mixture was placed onto a cleaned glass substrate and mixed with 14 μL of a diluted PolyNIPAM solution (1:7 with deionized water). A pressure modulated stream of nitrogen was directed to the substrate surface in order to support the formation of highly ordered polyNIPAM arrays at the air/liquid interface that were subsequently deposited onto the glass surface by spin-coating at 500 rpm for 5 min followed by 2000 rpm for 20 s (Laurell WS-400A-6NPP Lite spin coater). Afterwards the samples were silanized with APTES by vapor phase deposition including thermal treatment at 80 °C for 1 h. Then the functionalized glass cover slips were immersed in a gold nanoparticle solution at 40°C for 30 min and subsequently rinsed with deionized water (~18.2 MΩ cm). Then samples decorated with gold nanoparticles were immersed in an aqueous solution of 0.4 mM hydroxylamine hydrochloride and 0.5 % (w/v) H_{AuCl₄•3H₂O}. The electroless deposition of gold was carried on a vibrating table to ensure the formation of a homogenous gold film. After 20 min the samples were rinsed with deionized water (~18.2 MΩ cm) and blown dry with N₂. To increase the gold nanoparticle density on/in the PolyNIPAM microspheres the samples were immersed once more in a colloidal gold solution and incubated at room temperature for 24 h followed by rinsing with deionized water (~18.2 MΩ cm) and drying in a stream of N₂. Then, 100 μl Ethanol were added to the sample surface and inflamed with a pocket lighter. The burning ethanol has a temperature exceeding the LCST of the polyNIPAM and thereby induces a collapse of the stimuli-responsive hydrogel. Finally the samples were thermally annealed in a preheated oven at 500°C for 15 min in a suitable container.

If necessary the thermally annealed samples were immersed in an aqueous solution of KI and I₂ (KI 0.7108 mg/mL; I₂ 0.3482 mg/mL) for 30 min, rinsed with deionized water (~18.2 MΩ cm) and blown dry with N₂.

Separation of hole arrays loaded with gold nanoparticles into its components:

Samples were incubated in a 0.1 M aqueous solution of NaOH for 1h in order to break the covalent bond between the gold film and the glass surface. Afterwards the structures were scratched with a diamond pen and immersed in deionized water (~18.2 MΩ cm). Thus the gold films were detached from the glass surface utilizing capillary forces. The floating 'perforated' gold film floated on the water surface and could be picked up with a clean glass slide. The AuNPs remained on the sample surface during this process. Finally the all structures were dried at room temperature.

Deposition of BSA layers:

Fabricated plasmonic sensors were immersed in an aqueous solution of bovine serum albumine (BSA) with varying molar concentrations for 1 h and directly dried in a stream of N₂. The thicknesses of the resulting BSA layers were determined with AFM.

Fitting routine:

In order to extract the positions of the employed transmission peaks, we have used a Matlab script which first determined the absolute maxima. These maxima were taken as starting point. Then, we chose 40 data points, which surrounded these absolute maxima, and fitted these points with the polyfit Matlab function with a degree of $n = 2$.

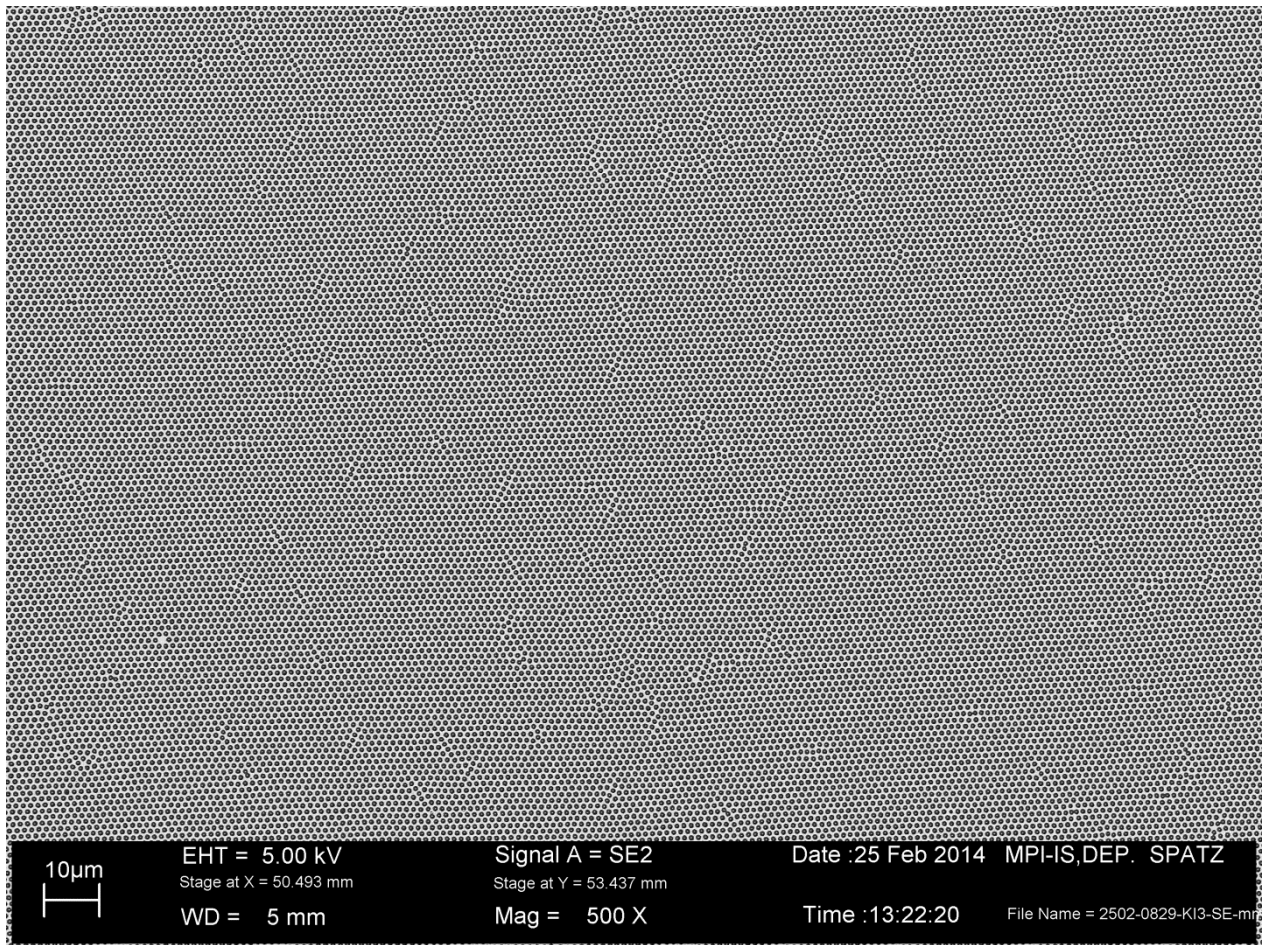


Figure S1. High resolution SEM overview image of a periodic hole array in a gold film loaded with gold nanoparticles.

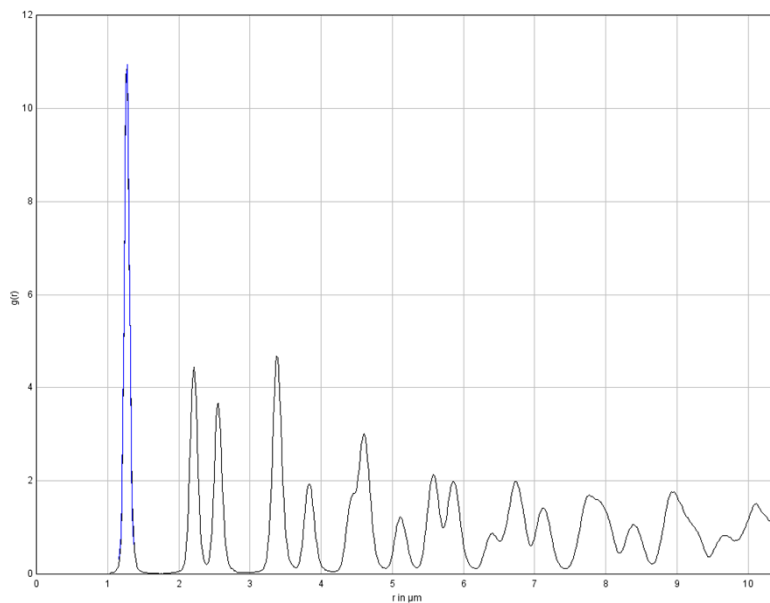


Figure S2. Radial distribution function $g(r)$ calculated from the SEM image shown in Figure S1.

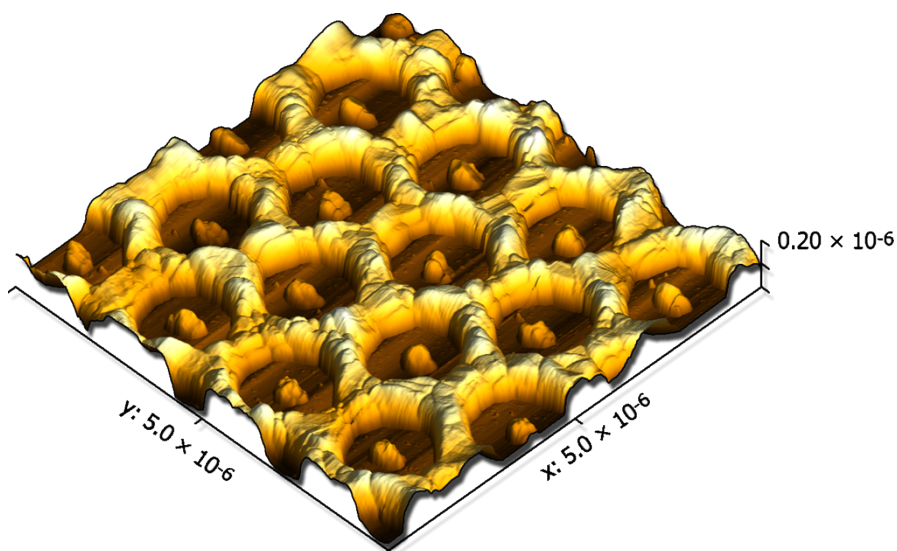


Figure S3. Topographical AFM image of a periodic hole array in a gold film loaded with gold nanoparticles.

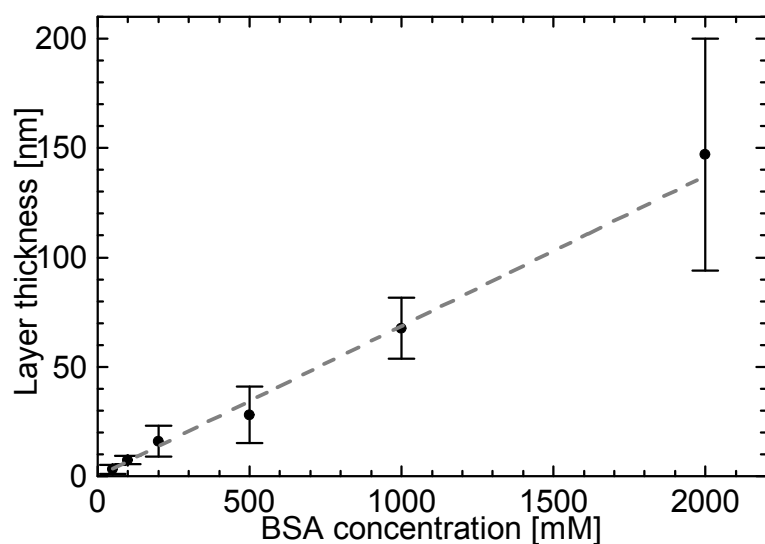


Figure S4: Thickness of bovine serum albumin (BSA) layer deposited on the sensor surface as a function of the concentration of the BSA solution in which the samples have been incubated.

References

- [1] R. H. Pelton, P. Chibante, *Colloids and Surfaces* **1986**, 20, 247.
- [2] J. Turkevich, P. C. Stevenson, J. Hillier, *J. Phys. Chem.* **1953**, 57, 670.