Electronic Supplementary Information

Localized surface plasmon resonance (LSPR) sensitivity of Au nanodot patterns to probe solvation effects in polyelectrolyte brushes

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S1. Fabrication method of Au nanodot array

The Au dot pattern were prepared using colloid lithography.[s1] First, Au layers of 20, 40 nm and 60 nm thickness were deposited on each glass substrate using a thermal evaporator (Edwards). A thin (2 nm) chromium under-layer was pre-deposited to enhance adhesion between the metal film and substrate. Then, polystyrene homopolymer solution (0.5 wt %, Mw 9,100, thickness: 20 nm) was spin coated on the Au film. Colloidal PS spheres of 220 nm diameter were synthesized by emulsifier-free emulsion polymerization with polydispersity of 0.5%.[s2] It was dispersed in water and then further diluted in a solution of surfactant Triton X-100/methanol (1:400 by volume). A monolayer of hexagonally close packed PS spheres was prepared by spin casting (3000 rpm). This well-ordered colloidal particle array was subsequently exposed to Reactive Ion Etching (RIE) conditions for 75 sec using a mixture of O_2 (30 sccm) and CF_4 (20 sccm) at a pressure of 60 mTorr and a power density of 80 W. Then, the RIE modified particle array was used as a mask for Ar ion milling.

The DC bias for the ion milling was 500 V, and the Ar pressure was kept below 4×10^{-4} Torr. Finally, by removing the colloidal mask using oxygen plasma and ultrasonic sonication, patterned Au dots (D≈100 nm) were fabricated. The morphologies of the colloidal mask and metal dot array were observed by scanning electron microscope (SEM, Philips–XL 20SFEG).

S2. Sensitivity of bare nanodot patterns

A sandwich structure was fabricated in order to measure LSPR characteristics of metal pattern. This glass-metal nanopattern-glass sandwich was immersed in different solvents for sensitivity test. UV-Vis optical spectra measurements were performed on a Cary 4000 spectrophotometer (wavelength:

400 nm - 900 nm). Fig. S1 shows the extinction spectra in air (n =1), water (n=1.33), 1:1(v/v) ethanol/toluene mixture (n=1.429) and toluene (n=1.495) for samples T1(A), T2(B) and T3(C) respectively. Optical data were averaged over ~10^{10} individual disks. There is a continuous red-shift for thicknesses as the refractive index of the surrounding medium increased from 1 to 1.5, along with an increase in the extinction intensity.

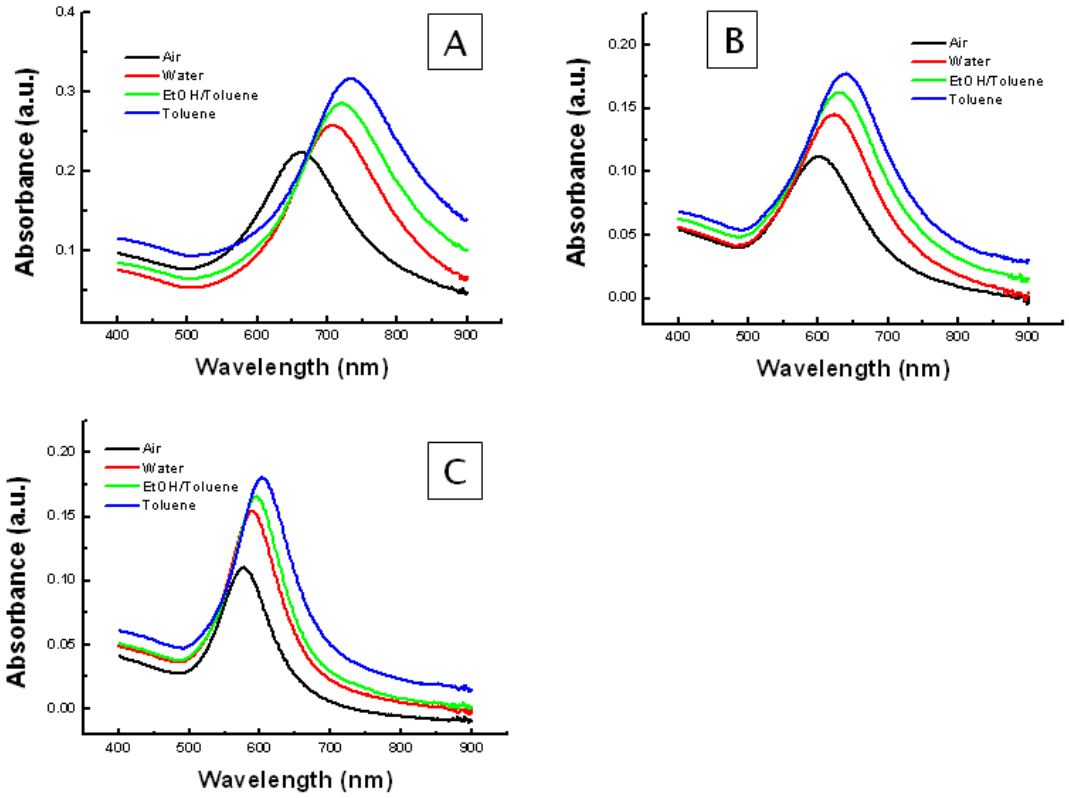

Fig. S1. LSPR sensitivity in response to the dielectric environment. The LSPR spectra of Au nanodot array of T1 (A) T2 (B), and T3 (C) upon a change in dielectric medium from 1 to 1.5.

S3. Synthesis of PMETAC polymer brush

In order to grow PMETAC on Au thin films and patterns, bare Au samples were initiated by ω-Mercapto-undecylbromoisobutyrate (thiol initiator) which was synthesized following a literature procedure.[s3] The polymerization solution was prepared as follows: METAC monomer (41.54 g, 100 mmol), 2,2'-dipyridyl (1.562 g, 5 mmol) and $Cu^{I}Cl$ (0.396 g, 2 mmol) were dissolved in methanol (32 ml) and water (8 ml). $Cu^{II}Cl_2$ (0.0268 g, 1 mmol) was added to the solution after degassing and the mixture further degassed for 20 min. The polymerization solution was then syringed in to each Schlenk tube, adding enough solution to submerge each sample completely in N_2 environment. After various polymerization times, the samples were removed, washed with methanol, and dried under

stream of N_2. Polymer film thicknesses were measured on reference Au substrates (planar, non-patterned) using spectroscopic ellipsometry (alpha-SE, Woollam) thickness on Au thin film was checked by spectroscopic ellipsometers and surface modified Au patterns was characterized by UV-vis spectrometer.

Reference

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S2 G. R. Yi, J. H. Moon and S.-M.Yang, *Chem. Mater*., 2001, **13**, 2613.
S3 D. M. Jones, A. A. Brown and W. T. S. Huck, *Langmuir*, 2002, **18**, 1265.