Electronic Supplementary Information For

Novel pH-responsive nanoplasmonic sensor: Controlling polymer structural change to modulate localized surface plasmon resonance response

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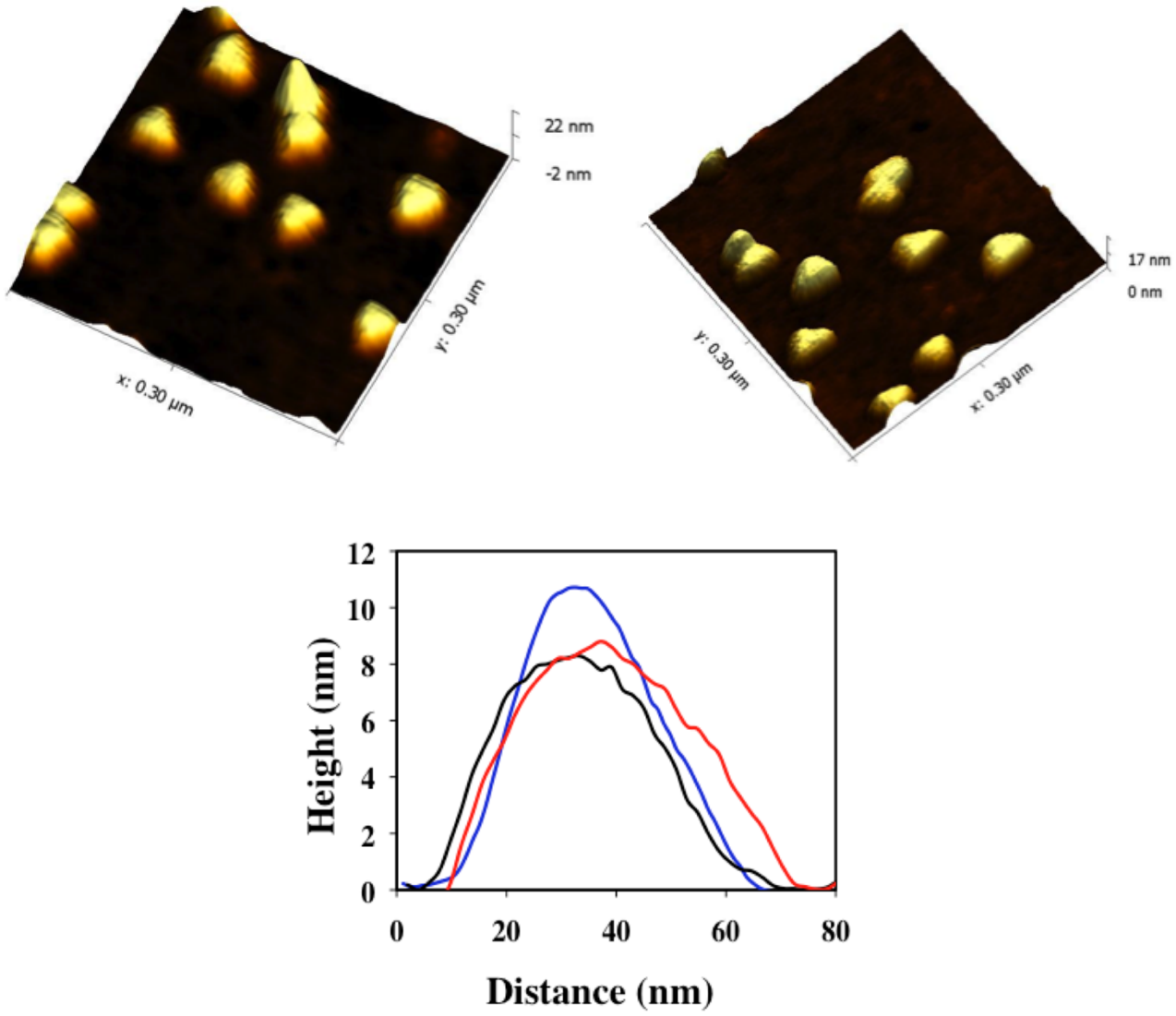
Experimental Procedure:

Spectroscopy Measurements. Absorption and extinction spectra in the range of 300-1000 nm were collected with a Varian Cary 50 Scan UV-visible spectrophotometer using 1 cm quartz cuvette. All the absorbance spectrums were collected using the 0.3 mL of nanoprism reaction mixture diluted to 2.0 mL of acetonitrile. All extinction spectra were collected by positioning the sensing platforms in the cuvette holder using a cuvette for support. Scanning electron microscopy (SEM) micrographs were obtained using a Hitachi S-4700 FESEM at 20 kV operating voltage. The average edge lengths of the nanoprisms were determined from the SEM images using Image J software. Atomic force microscopy (AFM) images were acquired using Bioscope AFM instrument. The instrument was operated in tapping mode using beam shaped super sharp silicon cantilevers (nanoscope) having an average force constant of 42 N/m. The operation frequency of the cantilevers for all measurements was 330 KHz.

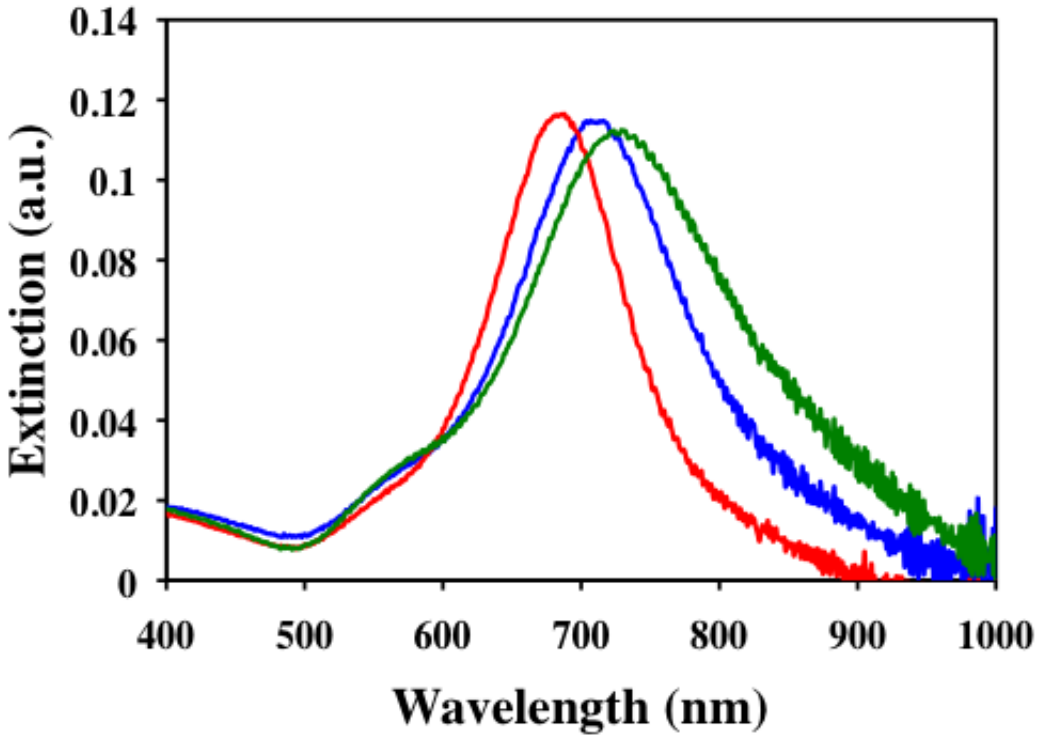
Synthesis of Gold Nanoprisms. Gold nanoprisms were synthesized according to our previously published procedure.[1] PMHS and TOA were used as a reducing agent and TOA as a stabilizing ligand, respectively. In a typical synthesis, 0.02 mmol of Et_3PAuCl was dissolved in 20 mL acetonitrile and the solution was stirred for 30 min at room temperature. Then 0.06 mL of TOA was injected followed by another 30 min of stirring. Next, 0.3 mL of PMHS was added and the reaction mixture was stirred at room temperature for 30 min followed by heating to 40 ^{0}C. After 220 min at 40 ^{0}C, the solution became dark blue and displayed stable absorption maxima at 700 nm. The solution was then removed from heat, centrifuged, and used for pH-based nanoplasmonic sensor fabrication. The SEM analysis provided the average edge length of the nanoprisms as ~28 nm (SI Figure 2). The AFM analysis showed the average height of the nanoprisms as ~8.3 nm.

Functionalization of Glass Cover Slips with MPTES and Construction of Sensing Platforms. The glass coverslips (substrate) were functionalised with MPTES using our published procedures.[1] Briefly, cover slips were immersed in a 20% (v/v) aqueous RBS 35 detergent solution at 90 ^{0}C for 30 minutes and then sonicated for 5 min, followed by rinsing with a copious amount of water and then immersing in a solution of hydrochloric acid and methanol (1:1 v/v) for 30 minutes. After rinsing with nanopure water multiple times, cover slips were dried in a vacuum oven at 60 ^{0}C overnight. The cover slips were then placed in a solution of 10% MPTES in ethanol for 30 min, followed by 5 min of sonication and rinsing with anhydrous

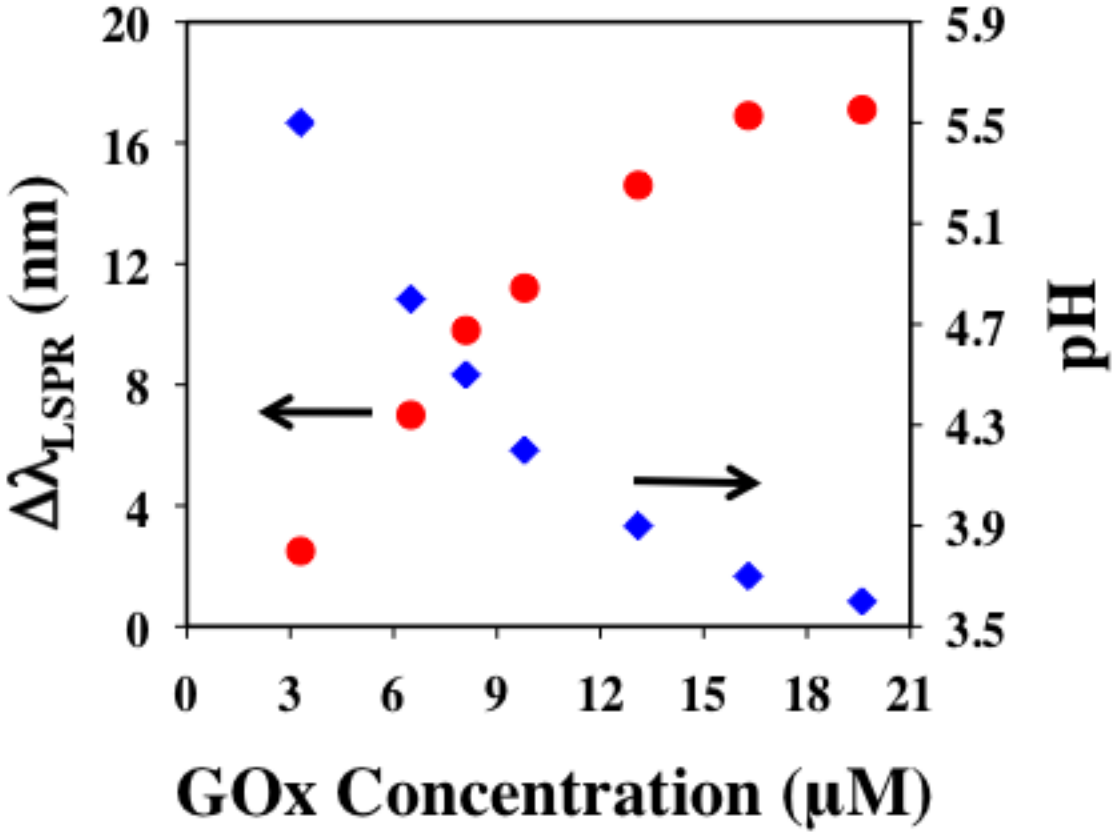
ethanol. The ethanol rinse and sonication steps were repeated at least 5 times. The cover slips were then placed in a vacuum oven for 3 hours at 120 ^{0}C. The MPTES-functionalized cover slips (supporting substrates) were then immersed in freshly prepared nanoprism solution for 30 min. The nanoprisms containing supporting substrates were then removed and rinsed with ethanol and dried under nitrogen flow and stored under nitrogen at 4 ^{0}C.



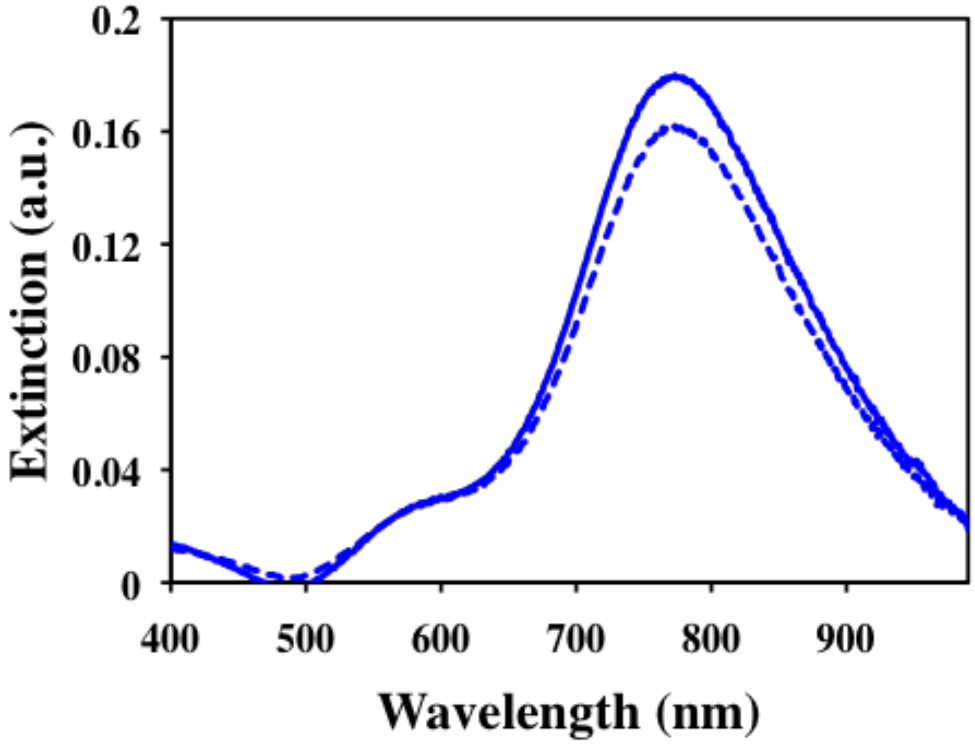
ESI-Fig. 1 (A) AFM image of gold nanoprisms onto silanized glass coverslip after incubating in PAA solution. (B) The same coverslips treated with pH 3.5 solution and washing with water. (C) The height profile at different state: nanoprisms before PAA incubation (black line), after PAA treatment (blue line), and after treating with pH 3.5 solution and washing with water (red line).



ESI-Fig. 2 UV-visible extinction spectra of substrate-attached nanoprisms in air after tape cleaning (red, λ_{LSPR} = 694 nm) after MUA functionalization (blue, λ_{LSPR} = 717 nm), and after attachment of PAA by EDC/NHS coupling (green, λ_{LSPR} = 732 nm).



ESI-Fig. 4. The changes of solution pH and LSPR peak shift as a function of the GOx concentration. The sensing platform was immersed in a 5 mM glucose solution.



ESI-Fig. 4. Extinction spectra of pH-based nanoplasmonic sensor in pH 4.0 solution before (solid, λ_{LSPR} = 784 nm) and after addition of GOx (dotted, λ_{LSPR} = 784.5 nm).

References:

[1] G. K. Joshi, P. J. McClory, B. B. Muhoberac, A. Kumbhar, K. A. Smith, R. Sardar, *J. Phys. Chem. C* **2012**, *116*, 20990.