Electronic Supplementary Material (ESI) for Nanoscale.

†ELECTRONIC SUPPLEMENTARY INFORMATION (ESI)

Calcinated Gold Nanoparticle Arrays for On-Chip, Multiplexed and Matrix-Free Mass Spectrometric Analysis of Peptides and Small Molecules

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SUPPLEMENTARY FIGURES

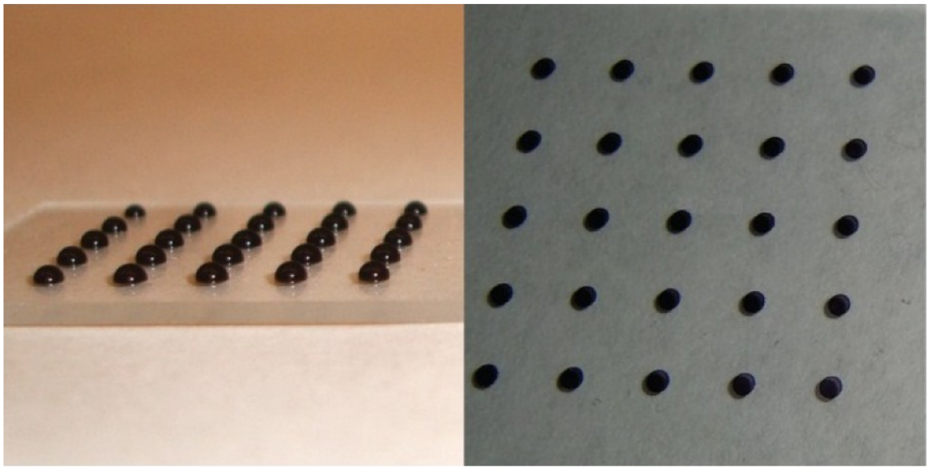

Figure S1. Solution confinement of colloidal gold nanoparticle solutions on photocatalytically patterned glass microscope slides, exhibiting hydrophilic spots with hydrophobic surroundings. (Left) Microarray spots immediately after deposition. (Right) Microarray spots after colloidal suspensions are dried.

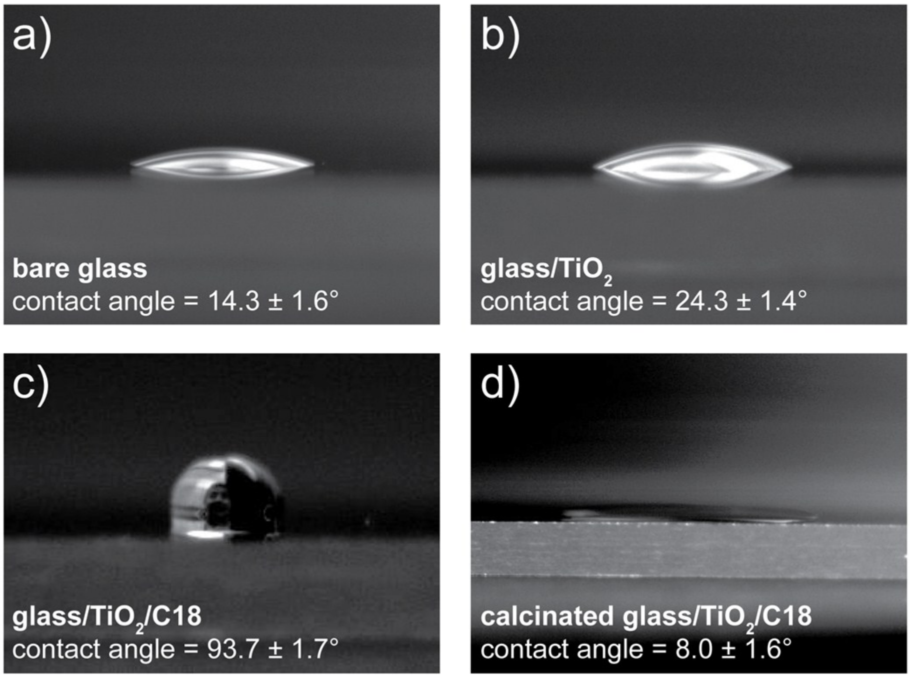

Figure S2. Contact angle measurements at various stages of material fabrication. $N = 5$ for all reported values. (a) Bare glass slide, cleaned with piranha solution. (b) Glass slide with TiO_2 coating. (c) Glass slide with TiO_2 coating, followed by C18 coating. (d) Calcinated glass slide with TiO_2 and C18 coatings. Decreased contact angle from bare glass is likely due to a thermal annealing effect of the glass surface from the high temperature used during calcination.

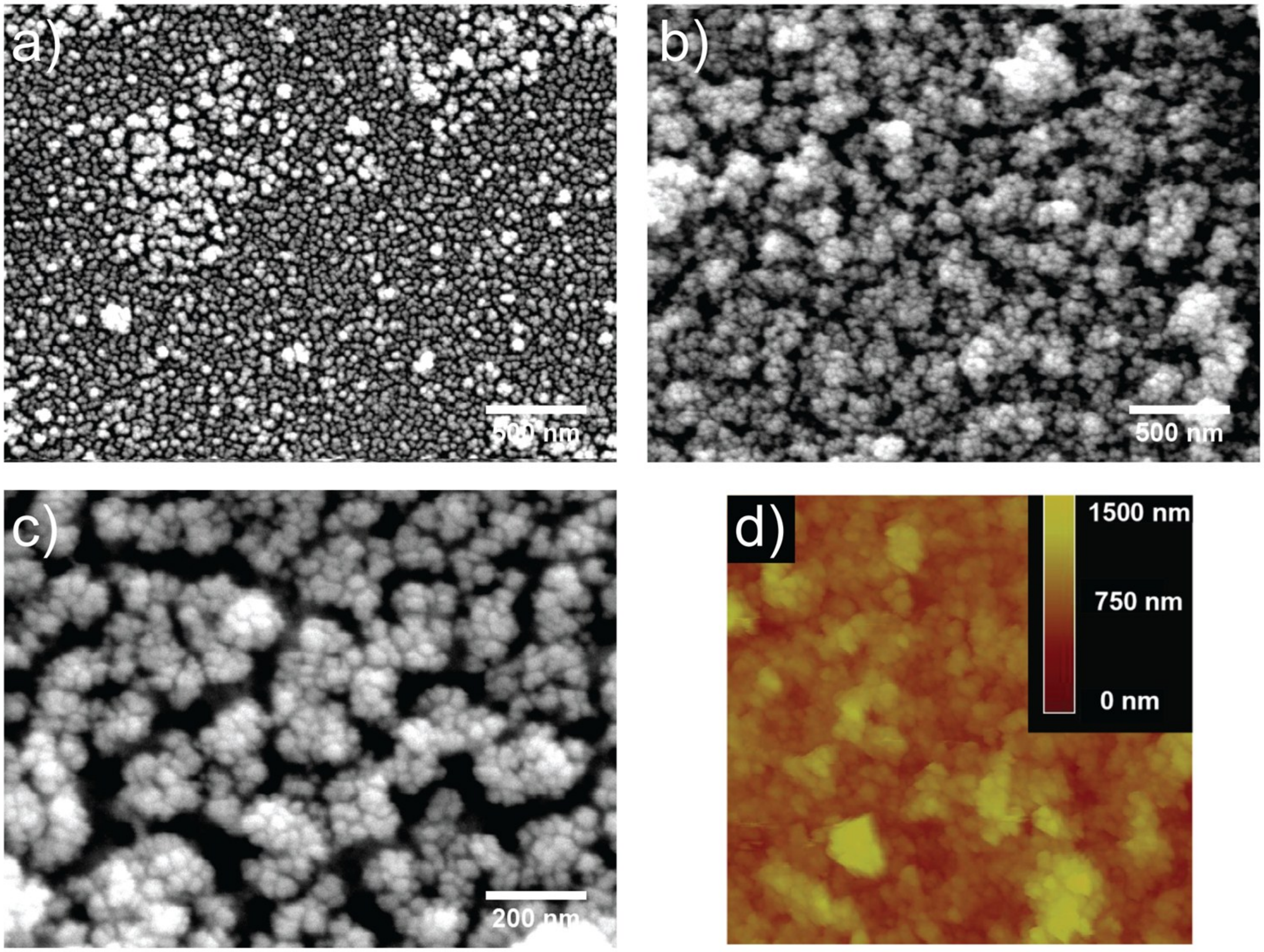

Figure S3. SEM (a-c) and AFM (d) images of calcinated gold nanoparticles. (a) 100,000× magnification, scale bar represents 500 nm. (b) 100,000× magnification, scale bar represents 500 nm. (c) 250,000× magnification, scale bar represents 200 nm. (d) AFM image to visualize z-axis roughness and porosity.

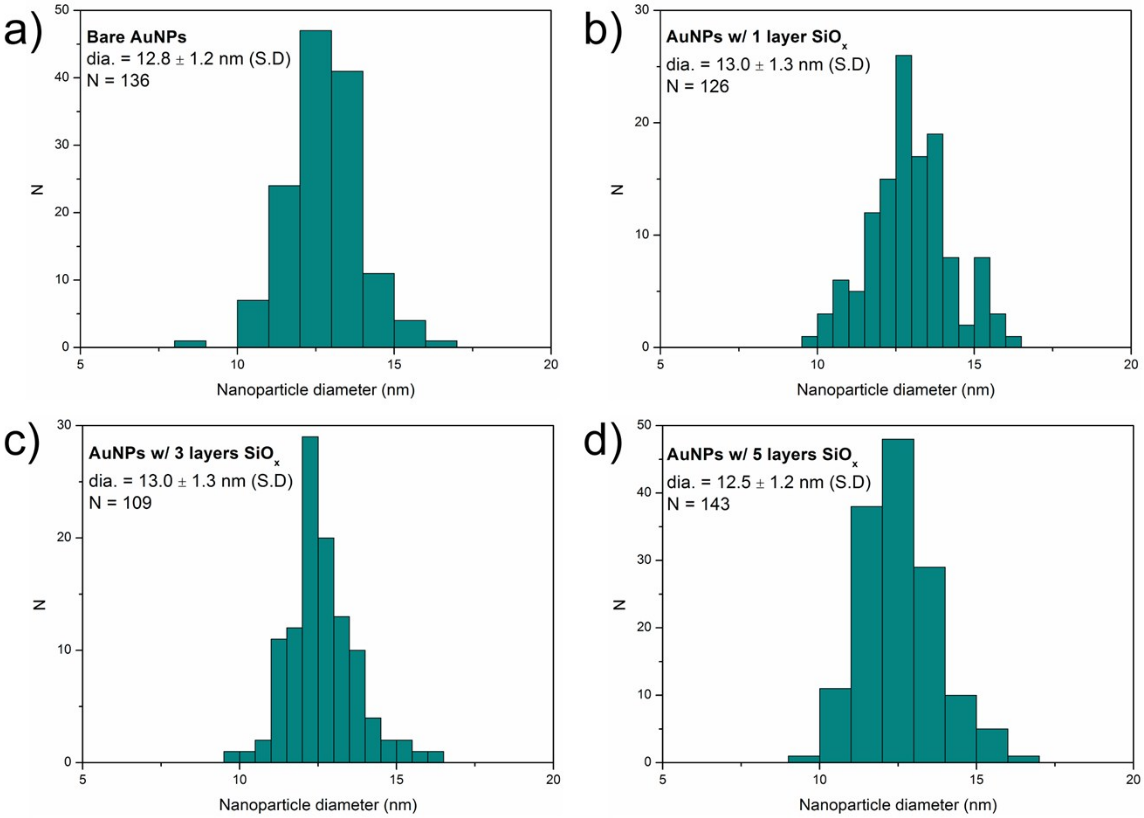

Figure S4. Frequency distributions of diameters for individual nanoparticles in Figure 2 of the main text. Diameters are unaffected by calcination process with silicate coating. (a) Bare AuNs, no treatment. (b) AuNPs with 1 layers of silicate and calcinated. (c) AuNPs with 3 layers of silicate and calcinated. (d) AuNPs with 5 layers of silicate and calcinated.

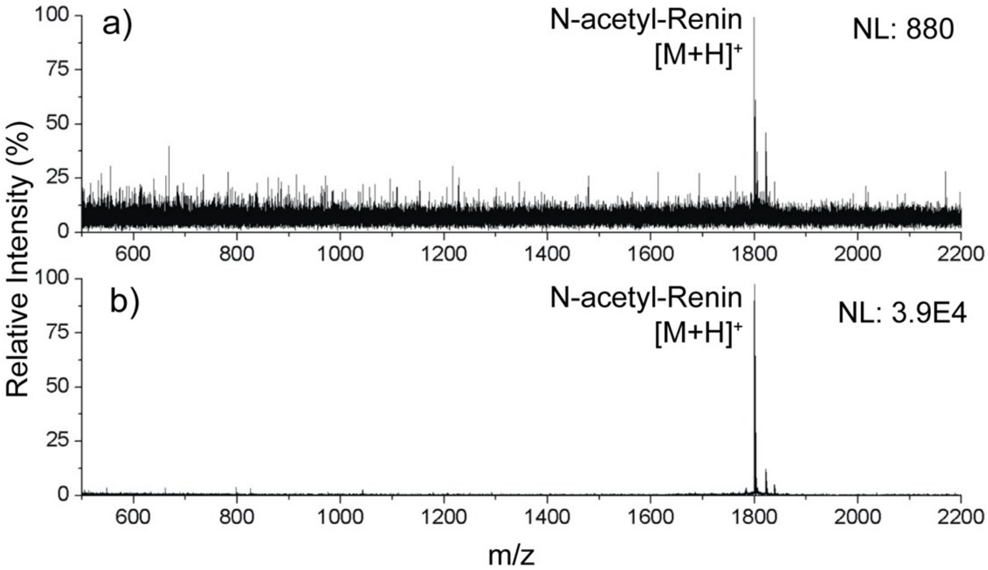

Figure S5. Deposited AuNP-(PAH-silicate)$_1$ calcination effects on ionization of N-acetyl tetradecapeptide renin substrate. S/N ratios are reported for the N-acetyl-Renin peak. (a) Before calcination (S/N = 5.5). (b) After calcination (S/N = 60).

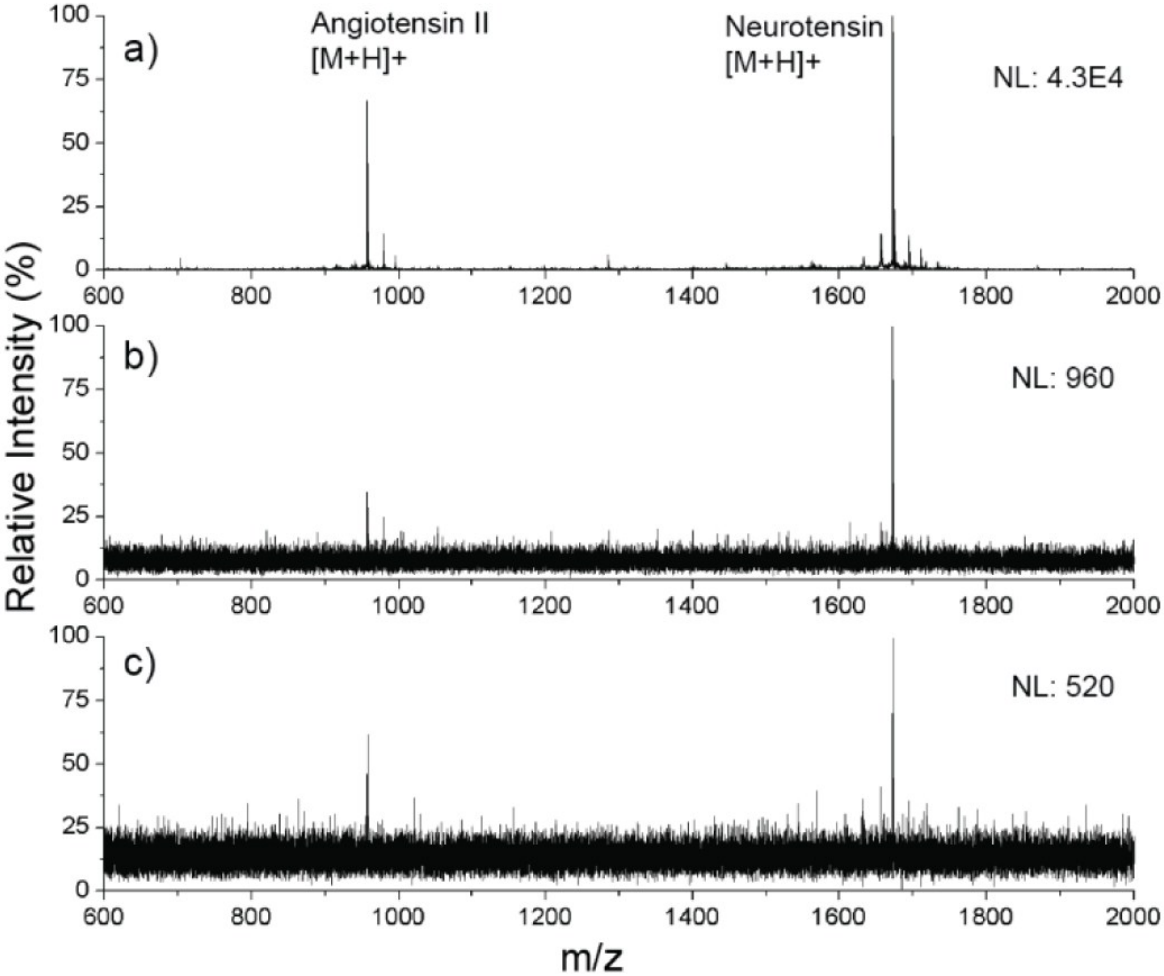

Figure S6. Laser fluence threshold study for ionization of 20 pmol [Sar^1, Thr^8]-angiotensin II and neurotensin. (a) Laser fluence = 1900 a.u. (b) Laser fluence = 1600 a.u. (c) Laser fluence = 1450 a.u.

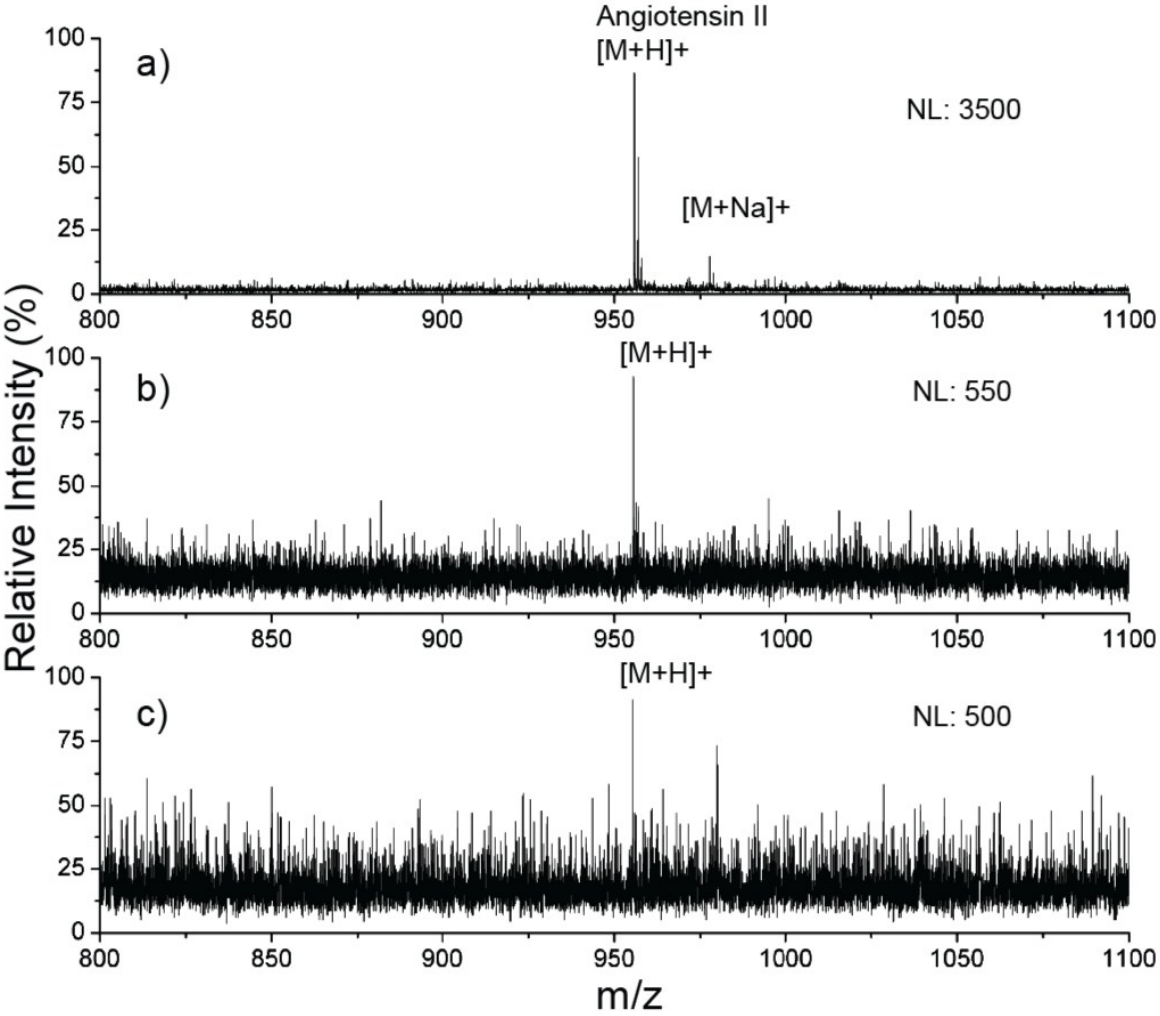

Figure S7. Detection of [Sar^1, Thr^8]-angiotensin II in the low femtomole range. (a) 200 fmol. (b) 20 fmol. (c) 2 fmol.

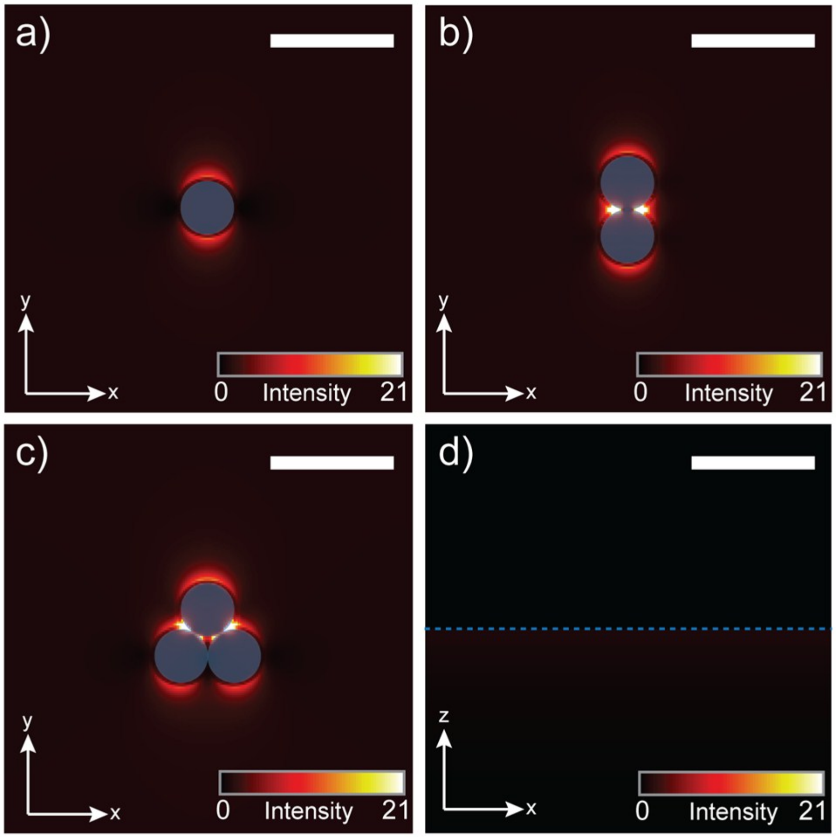

Figure S8. Numerical simulations of plasmonic fields induced by λ = 520 nm light source for different nanoscale geometries. Scale bars represent 30 nm and blue represents the gold surface. (a) Single gold nanoparticle. (b) Gold nanoparticle dimer. (c) Gold nanoparticle trimer. (d) Planar gold film.

SUPPLEMENTARY METHODS (from J. Duan, et al.[1])

Materials and Reagents (not included in the main text)

3-Mercaptopropionic acid (3-MPA) was from Sigma-Aldrich (St. Louis, MO). Chromium and gold were acquired as pellets of 99.99% purity from Kurt J. Lesker (Jefferson Hills, PA).

Gold Chip Fabrication

BK-7 glass substrates were cleaned using a boiling piranha solution (3:1 v/v H_2SO_4 and 30% H_2O_2) for 30 minutes, followed by rinsing with DI water and drying under compressed air. 2.0 nm of chromium (0.5 Å/s) followed by 46.0 nm of gold (1.0 Å/s) were then deposited using electron beam evaporation (Temescal, Berkeley, CA) at 5×10^{-6} Torr in a Class 1000 cleanroom facility (UCR Center for Nanoscale Science & Engineering).

Silicate Derivitization

Gold substrates were immersed in a 10 mM 3-MPA (ethanol) solution overnight, followed by extensive rinsing with ethanol and DI water the next day. PAH (1 mg/mL, pH 8.0) and sodium silicate (22 mg/mL, pH 9.5) were then alternately deposited on the surface using Nalgene pump spray bottles,[2] with DI water rinsing for one minute between each spray. This process was repeated until the designated number of layers was reached, followed by a final DI water rinse and drying under compressed air. Thereafter, the material was heated in a furnace to 450 °C for four hours at a rate of 17 °C/minute. Each slide was thoroughly rinsed with ethanol and DI water before use.

SUPPLEMENTARY REFERENCES

1. J. Duan, M. J. Linman and Q. Cheng, *Anal. Chem.*, 2010, **82**, 5088-5094.
2. M. J. Linman, S. P. Culver and Q. Cheng, *Langmuir*, 2009, **25**, 3075-3082.