SUPPORTING INFORMATION

Plasmonic Sensing with 3D Printed Optics

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■ EXPERIMENTAL METHODS

Materials and Reagents. Gold (III) chloride trihydrate, dopamine hydrochloride, 3-mercaptopropanol (MPO), and cholera toxin from *Vibrio cholerae* (CT) were from Sigma Aldrich (St. Louis, MO). 1-oleoyl-2-palmitoyl-*sn*-glycero-3-phosphocholine (POPC) was from Avanti Polar Lipids (Alabaster, AL). Monosialoganglioside receptor GM_1 was from Matreya (Pleasant Gap, PA). Clear photoactive resin (GPCL02) was from Formlabs, Inc. (Somerville, MA). BK-7 (n = 1.517) and SF2 (n = 1.648) equilateral prisms were from Surplus Shed (Fleetwood, PA). Chromium and gold used for electron-beam evaporation were acquired as pellets of 99.99% purity from Kurt J. Lesker (Jefferson Hills, PA). 1×PBS was composed of 10 mM Na_2HPO_4, 1.8 mM KH_2PO_4, 137 mM NaCl, 2.7 mM KCl, and titrated to pH 7.4. Nanopure water (≥18 MΩ•cm), purified through a Barnstead E-Pure filtration system (Thermo Scientific, Rockford, IL), was used for all reagent preparations.

Instrumentation. Surface plasmon resonance (SPR) spectroscopy and imaging were conducted at room temperature (*ca.* 23 °C) on a homebuilt SPR imaging setup, using nanopure water or 1×PBS as the running buffer set to a flow rate of 5 mL h^{-1} (*ca.* 83 μL min^{-1}) unless otherwise noted. For real-time binding measurements, the incident angle was set to the position where the starting SPR reflectivity curve measured 30 %R, as the slope is highest at this location and changes in image contrast are greatest. Absorbance spectra were collected using a USB 2000+ UV-Vis spectrometer with illumination from a HL-2000 Tungsten-Halogen light source guided through 200 μm optical fibers (Ocean Optics, Dunedin, FL). FT-IR analysis was performed on a Nicolet 6700 spectrometer (Thermo Scientific, Rockville, IL), and ellipsometry was performed on a UVISEL M200 (Horiba Jobin Yvon, France). Scanning electron microscopy (SEM) was conducted on an FEI NNS450 SEM (Hillsboro, OR) in CFAMM at UC Riverside. Atomic force microscopy was conducted on a Veeco Dimension 5000 (Santa Barbara, CA) under tapping mode at a scan rate of 1 Hz.

Stereolithography. Prisms were designed in SketchUp (Trimble, Inc., Sunnyvale, CA), and uploaded to a commercial stereolithography printer, a Formlabs Form 2 (Somerville, MA), through manufacturer provided software. The Form 2 includes a 250 mW UV laser with 140 μm spot size, and layer thickness was set to the highest resolution (25 μm). When the automated

process was complete, the cured prisms were washed in an isopropanol bath, dried under compressed air, and subjected to a 1 h post-cure in a CL-1000 UV crosslinker (UVP Inc., Upland, CA). Final polishing was performed through a combination of wet sanding and buffer wheel/polishing compound treatment (Central Machinery, USA). Altogether, manual treatment of each printed prism (sanding + polishing wheel) takes <10 min.

Gold Nanofilm Preparation. SPR active prisms were fabricated from BK-7, SF2, or 3D printed equilateral prisms (25 × 25 × 25 mm). The prisms were first cleaned through copious rinsing with isopropanol and dried under compressed air. 2 nm of chromium (0.5 Å s^{-1}), followed by 50 nm of gold (1.0 Å s^{-1}) were then deposited on one face using electron-beam evaporation (Temescal, Berkeley, CA) at 5×10^{-6} Torr in a Class 1000 cleanroom facility (UCR Center for Nanoscale Science & Engineering). For supported lipid membrane analysis, the 3D printed prisms were subsequently immersed in a 5 mM MPO solution (10% v/v ethanol) for 4 h, followed by rinsing with nanopure water and drying under a nitrogen stream.

Polydopamine-Mediated Nanoparticle Growth. Dove prisms were first 3D printed using the above stereolithography protocol, with the short face measuring 22 × 20 mm, and the long face measuring 42 × 20 mm. Dopamine HCl was then suspended at 2 mg mL^{-1} in a Trizma-HCl buffer (10 mM, pH 8.5). Immediately thereafter, the dopamine solution was deposited on the surface of the prisms, which were incubated within humidity chambers at 4 °C for 18 h. Following thorough rinsing with nanopure water and drying under an N_2 stream, the prisms were fixed into the absorbance setup equipped with a low volume PDMS flow cell, and 0.3 mM gold chloride was incubated onto the surface within the flow cell environment.

■ SUPPLEMENTARY FIGURES

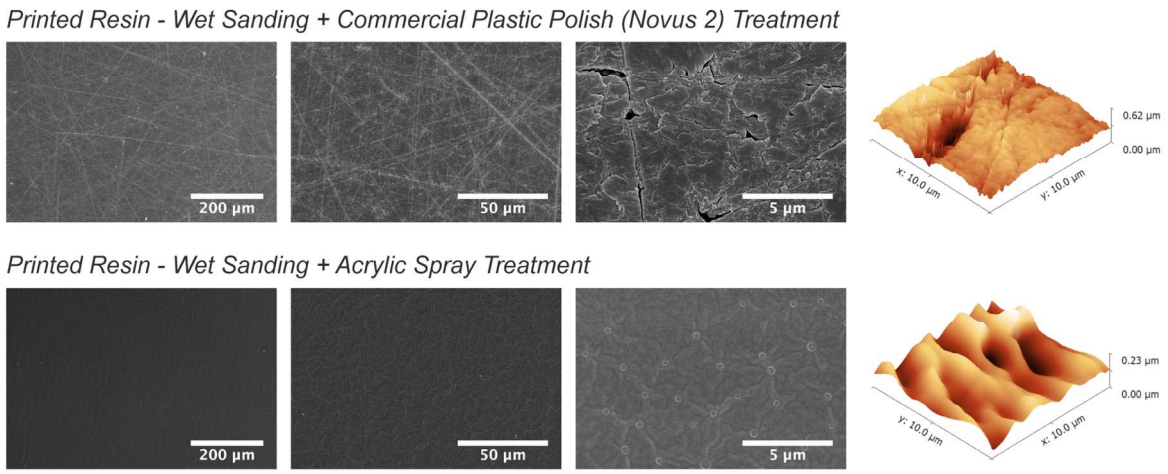

Figure S1. Alternative prism treatments. Scanning electron and atomic force micrographs of 3d printed prisms under various surface treatments, including a commercial plastic polish and an acrylic spray.

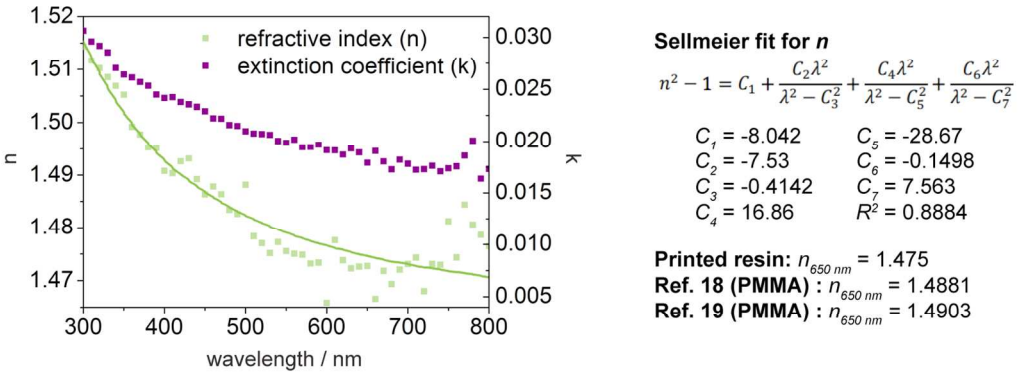

Figure S2. Ellipsometry measurements and Sellmeier fitting. Ellipsometry data for the refractive index (n) and extinction coefficient (k) are provided in the plot on the left, with fitting data for n provided on the right. The refractive index at 650 nm (common operating wavelength for SPR) matches closely with that obtained by other researchers for PMMA.

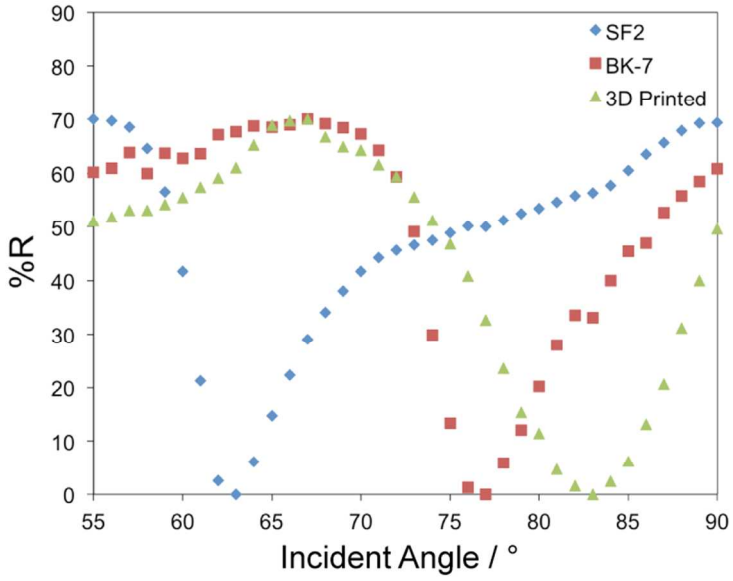

Figure S3. Surface plasmon resonance reflectivity curves with varying prism materials. Chosen substrates include SF2 and BK7 glasses (typically used within commercial SPR instruments), along with 3D printed substrate.

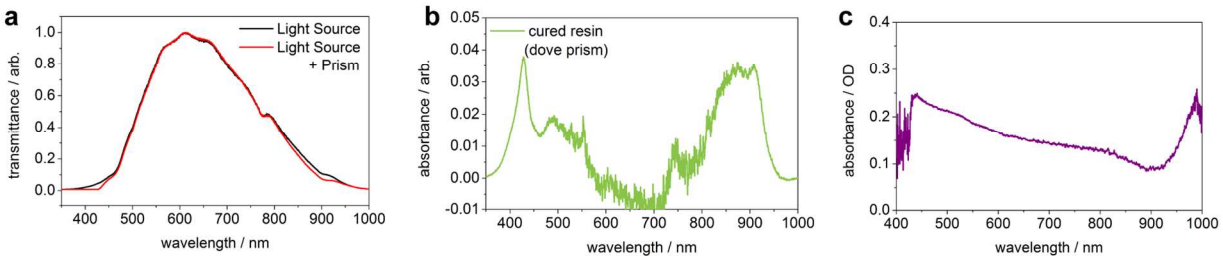

Figure S4. Spectroscopic measurements of materials used in the LSPR studies. a) Transmission spectra of the light source alone, and light source with prism (normalized for better visualization of prism absorbance wavelengths). b) Absorbance spectrum of dove prism. c) Absorbance spectrum of polydopamine on the dove prism (grown for 18 h), with absorbance of the prism itself background subtracted.