Supporting information for

Ultrasonic Detection of Enzymatic Activity with Nanowire Electrodes

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Methods

MATERIALS

Prostate specific antigen from human semen (buffered aqueous solution, P3338) was obtained from Sigma-Aldrich Chemicals Inc. Human serum from human AB plasma, sterile-filtered (H4522) was obtained from Sigma-Aldrich and Cambrex Corporation (14-402E). Cystamine dihydrochloride (C121509) was obtained from Sigma-Aldrich.

FABRICATION OF NANOWIRE ELECTRODES

Three-dimensional nanoscale electrodes were prepared using slight modifications to a previously reported method.¹⁴⁻¹⁶ A small piece of gold-plated membrane was placed, with the most reflective side facing up, on a piece of adhesive copper. Another strip of copper was placed below the gold membrane. The thin layer of surface gold was removed using cotton tipped applicators moistened in ethanol. This procedure led to an increased yield of functional nanoelectrodes. The exposed polycarbonate membrane was then O₂ etched using a SAMCO RIE-1C plasma etcher for 3 min at a power of 11 W under a pressure of 100 mTorr and a flow rate of 2.5 L/min. These conditions

consistently produced exposed wires of 100 - 200 nm. The assemblies were then heat treated in the oven at 155°C for 30 min to improve sealing of the polycarbonate around the wires. The templates were then sandwiched between two pieces of 3M Scotch brand No. 898 tape, with a 0.07 cm² opening in the upper layer exposing the electrodes to solution.

SYNTHESIS OF PEPTIDES

Peptides were prepared on solid support functionalized with a Rink amide linker using standard Fmoc synthetic methods, and cleaved from the resin. This procedure produced highly pure materials, with purities of ~ 95% as judged by HPLC. The peptide sequence for PSA detection was: CEEEHSSLKQKKKK

MONOLAYER DEPOSITION ON NANOWIRE ELECTRODES

The peptide sequence used for PSA detection was dissolved in 25 mM sodium phosphate / 25 mM NaCl (pH = 7) and deposited on nanoscale electrodes over one hour in a humidity chamber at room temperature. After monolayer immobilization, electrodes were then rinsed in 25 mM sodium phosphate / 25 mM NaCl (pH = 7) and used immediately.

ELECTROCHEMICAL MEASUREMENTS

Chronocoulometry (CC) was performed using a Bioanalytical Systems (BAS) Epsilon potentiostat/galvanostat controlled with BAS Epsilon EC software. All measurements were conducted with a three-electrode configuration at room temperature with nanoelectrodes as working electrodes, a platinum wire as the counter electrode and reported vs. Ag/AgCl equipped with a Luggin capillary. CC measurements for PSA detection were performed in solutions of 100 μ M Ru(NH)₆³⁺ with 1 mM Fe(CN)₆³⁻ in 25

mM sodium phosphate / 25 mM NaCl (pH = 7) using a potential step of – 450 mV for 5 s. All electrochemical measurements were performed using > 4 different electrodes and integrated charge with standard deviations are reported.

Figure S1. Quantitation of signal changes observed for PSA in serum (blue = 1 μ M, green = 100 pM) at peptide-modified and cystamine-modified nanowire electrodes. Data shown represent averages of six independent trials, and errors are standard deviation values.