Supporting Information

Ultrasensitive protein detection using aptamer-functionalized single polyaniline nanowire

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Experimental details

Chemicals and materials. Aniline (≥ 99.5%), 1-ethyl-3-(3-dimethylaminopropyl) carbodiimide (EDC), N-hydroxysuccinimide (NHS), and bovine serum albumin (BSA) were purchased from Sigma-Aldrich. Immunoglobulin E (IgE, MW 200,000) from human myeloma plasma was purchased from Athens Research & Technology Inc., and rabbit Immunoglobulin G (IgG) was purchased from Invitrogen. The anti-IgE

aptamer (5'-GGGGCACGTTTATCCGTCCCTCCTAGTGGCGTGCCCC-3') was purchased from Integrated DNA Technologies, Inc., and for the fluorescence characterization, the 3' end of the aptamer was labeled with the fluorophore 6-carboxyfluorescein (6-FAM). All other chemicals were of analytical grade, and Milli-Q water from a Millipore Q water purification system was used throughout.

Synthesis of single PANI nanowire. The single PANI nanowires were electrodeposited in 100 nm wide polymethylmethacrylate (PMMA) nanochannels patterned between two Au microelectrodes. The Au microelectrodes and PMMA nanochannels were microfabricated lithographically using an electron-beam evaporator (VE-180, Thermionics) and an electron-beam lithography machine (e-line, Raith), similar to our previous report[19, 26, 34]. The growth of single PANI nanowire was performed using a probe station and a semiconductor device analyzer (B1500A, Agilent). A drop (0.3μL) of solution containing 0.1 M HCl and 0.01 M aniline (99.5%, Sigma-Aldrich) was placed on the nanochannel between two Au microelectrodes by a micropipette, and a constant current of 500 nA was applied between the two Au microelectrodes. The corresponding voltage was monitored during the growing process, and once the nanowire growth along the nanochannel was completed, the voltage will decrease rapidly, indicating that the two Au microelectrodes was connected by the synthesized PANI nanowire[27]. After synthesis, the PMMA layer was removed by soaking in acetone for 5 minutes to expose the whole PANI nanowire, and the Au electrodes with PANI nanowires were then rinsed with water and stored in

air for later use.

Immobilization of aptamer onto PANI nanowire. The aptamer was covalently attached to the PANI nanowire with the assist of EDC and NHS. Generally, about 10μL phosphate buffer saline (PBS, 10 mM, pH 7.4) containing 0.1 M EDC, 0.1 M NHS and 0.01mM aptamer was dropped to cover the whole PANI nanowire for 3 hours at room temperature, and the phosphate group at the 5' end of aptamer with react with the amine groups on the surface of the PANI nanowire under the help of EDC/NHS. After aptamer immobilization, the PANI nanowire was thoroughly rinsed with PBS to get rid of the physically adsorbed aptamer. In order to prevent the possible nonspecific adsorption of other biomolecules to the PANI nanowire during sensing, the PANI nanowire was soaked in PBS containing 2 mg/mL BSA for 30 minutes to block the free sites on its surface.

Detection of IgE. The detection of IgE with the aptamer functionalized single PANI nanowire was based on measuring the conductance change of the single PANI nanowire upon specific binding of IgE to the aptamer with a semiconductor device analyzer, and the measuring system was covered with a metal box to shield outside interference. The measurement was carried out by applying a constant current of 50 nA through the PANI nanowire with a sampling ratio of 2 Hz. When a stable baseline of the conductance was obtained after the addition of 0.5μL PBS (10 mM, pH 7.4) that submerges the PANI nanowire, the same volume of PBS containing IgE or other

proteins was added in sequence, and the corresponding conductance changes of the PANI nanowire were recorded. The conductance change ratio $(G-G_0)/G_0$ was taken as response, where G_0 is the conductance of the PANI nanowire in pure PBS, and G is the conductance of the PANI nanowire after exposure to IgE.

In order to regenerate the aptasensor, the aptamer functionalized PANI nanowire after sensing was soaked in 0.1 M HCl for 15 minutes to dissociate the aptamer-IgE conjugation and release the IgE. The aptamer functionalized PANI nanowire was then washed with water and soaked in PBS for about 10 minutes to recover the aptamer for the next sensing experiment (after re-applying BSA to block the free sites).

Figure S1

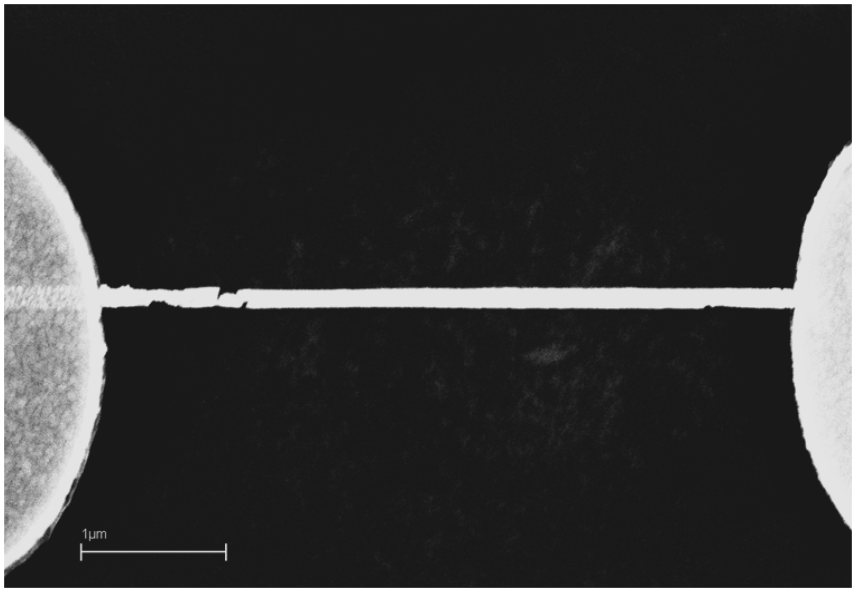

Figure S1. SEM image of a synthesized single PANI nanowire. The scale bar represents 1μm.

Figure S2

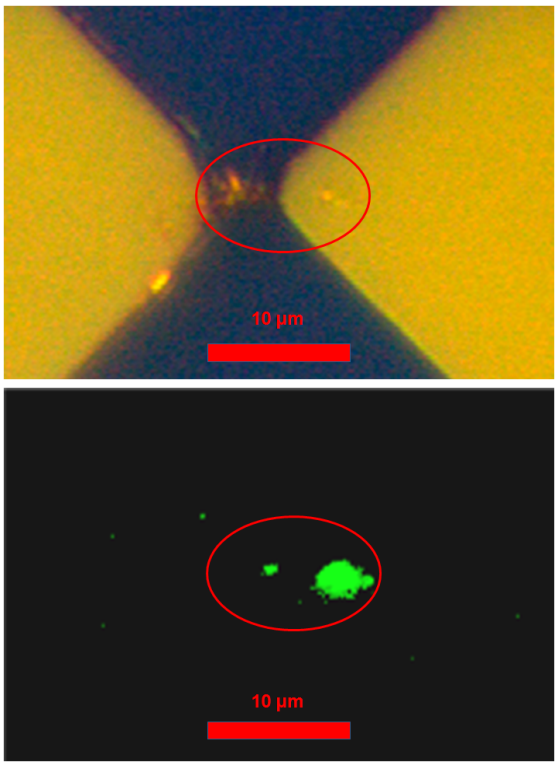

Figure S2. The optical (top) and fluorescent (bottom) microscope images of a PANI nanowire functionalized with 6-FAM labeled aptamer. Due to the optical limit of the microscope, perfect nanowires with fluorescence were too small to visualize clearly. Here, a PANI nanowire with a big spot of PANI formed next to it due to partial poor insulation was selected for better visibility. It is clear that the green fluorescence can only be observed from areas covered with PANI, indicating that the fluorescently tagged aptamers were indeed selectively immobilized on the PANI surface.