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Supporting Information

A sensitive electrochemiluminescence immunosensor for celiac disease diagnosis based on nanoelectrode ensembles

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Assembly of the nanoelectrode ensemble

A schematic drawing of a NEEs is shown in Figure S1. The assembly of the NEE starts by carefully cutting small pieces (typically, $5 \text{ mm} \times 6 \text{ mm}$) of the golden PC membrane, obtained by electroless deposition, with gold within the pores and on both outer faces of the membrane. Each of the pieces is attached to a 6 mm × 15 mm piece of adhesive aluminum foil tape (c in scheme 1). The membrane is placed on the Al foil so that the Au film covering the rough face of the membrane is down (i.e., against the adhesive). A strip ($6 \text{ mm} \times 40 \text{ mm}$) of copper foil with a conductive adhesive is affixed to the lower Au-coated surface of the membrane, between the Au on the rough face of the membrane and the Al foil. The copper foil is positioned so that it covers only about 1 mm of the membrane. Since the conductive glue on the Cu tape contains metal particles which can punch the PC membrane, care must be taken to avoid contact between the Cu tape and the part of the golden PC membrane which will be finally exposed to the electrolyte solution (black area in Fig. 1).



Figure S1. Schematic drawing of an Au-NEE: a) track etched golden polycarbonate membrane: the Au nanoelectrodes (yellow) are connected together by a back Au layer left after the electroless deposition; b) copper adhesive tape with conductive glue to connect to instrumentation; c) aluminum adhesive foil with non-conductive glue, to improve the mechanical strength of the NEE; d) insulating tape which covers all the assembly apart a hole of 3 mm diameter, which defines the geometric area of the NEE exposed to the electrolyte solution. Note: the components shown are not to scale.

The copper strip acts as current collector and working electrode lead for the NEE. The upper Au surface layer from the portion of membrane not covered by the Cu or Al tape is removed by applying and then removing a strip of adhesive tape (3M Scotch® MagicTM Tape). This allows the removal of the Au outer layer to expose the disk ends of the Au nanowires produced inside the pores. These nanodisks will become the active electrode elements. At this point, the NEE assembly is heat-treated at 150°C for 15 min, that is a temperature slightly higher than the glass transition temperature of PC. This procedure produces a water tight seal between the Au nanowires and the pore walls. Finally, strips of light weight plastic shrink wrap film (Topflite Monokote TM) are applied to the lower and upper surfaces of the assembly to insulate the Al and Cu foil tapes. A hole (diameter of 3 mm) is punched into the upper piece of tape prior to the placement on the assembly. This hole defines the geometric area (A_{geom}) of the NEE exposed to the electrolyte solution. All the nanoelectrodes in the NEE are connected to each other, so that they all experience the same applied potential.

Differential pulse voltammetry



Figure S2. Differential pulse voltammograms (DPVs) recorded at bare NEE in PBS containing 0, 1, 5, 10, 50, 100 mM (a-f) TPrA or (g) 100 μ M Ru(bpy)₃²⁺.

EDX microanalysis



Figure S3. EDX microanalysis spectrum of the surface of a NEEs.

Calibration plot at low concentrations of anti-tTG



Figure S4. Calibration plot showing the ECL emission as a function of anti-tTG concentration in the 1-100 ng mL⁻¹ range.