Supporting Information

Ultra-high sensitivity measurement of DNA sequences with conducting polymer-modified electrodes: mechanism, large-scale manufacture, and prospects for rapid polymerase chain reaction measurement (e-PCR)

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Contents

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1. **Calculation of bias potential for EIS measurement**

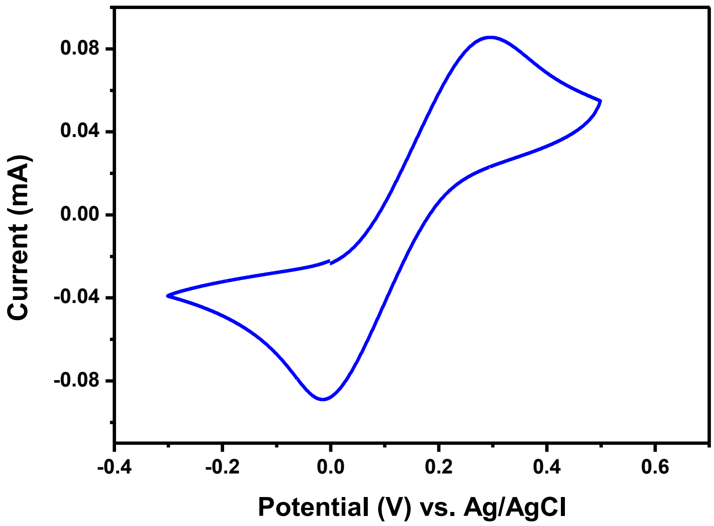

Figure S1. CV of poly(PyPhEG-*co*-PyPhON) modified SPCE.

The bias potential was calculated as the the potential of zero net current between the oxidation peak (0.29 V) and the reduction peak (-0.013V), which was 0.14 V.

2. **Calculation of the real surface area of SPCE**

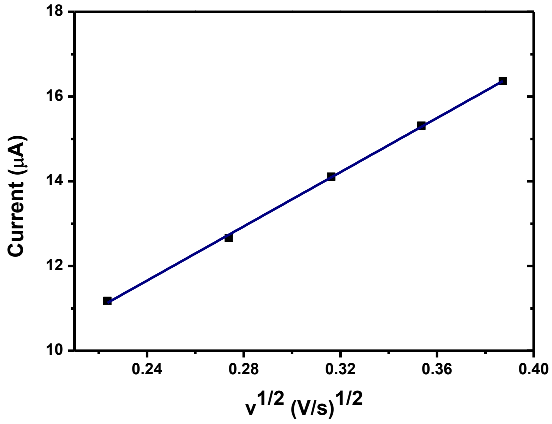

Figure S2. Peak current *vs.* square root at different scan rates for a bare SPCE electrode in 1 mM $Fe(CN)_6^{3-/4-}$ in 0.1 M KCl solution.

The surface area was estimated from cyclic voltammetry experiments, where the peak current is related to the surface area and the scan rate *via* the Eq. 1 [1]

$$i_p = 2.68 \times 10^5 n^{2/3} A D^{1/2} v^{1/2} c^0 \qquad \text{Eq. 1}$$

where *c*° is a mediator concentration, and *D* is the diffusion coefficient (6.9 ×10^{-6} cm^2/s). The peak current in CV, $i_p = kv^{1/2}$ and the slope of the linear fit of the peak current *vs.* square root $\mathrm{k} =$

$2.68 \times 10^5 n^{2/3} A D^{1/2} c^0$. The slope k for the bare SPCE is $3.04 \times 10^{-5} A\, s^{1/2} / V^{1/2}$. The calculated surface area of the SPCE is 0.0425 cm^2, with a roughness factor of 1.35 (2 mm diameter of SPCE).

3. **Calculation of the thickness of deposited poly(PyPhEG-*co*-PyPhON) film**

The thickness of the polymer film was estimated based on a conversion factor published by Lassalle et al. [2], where 1 mC/cm^2 gave the PPy film thickness of 4.76 nm. The charge passed in this study was 0.16±0.04 mC, which gave an estimated thickness of 20±5 nm.

4. **EIS of bare SPCE in the redox couple solution**

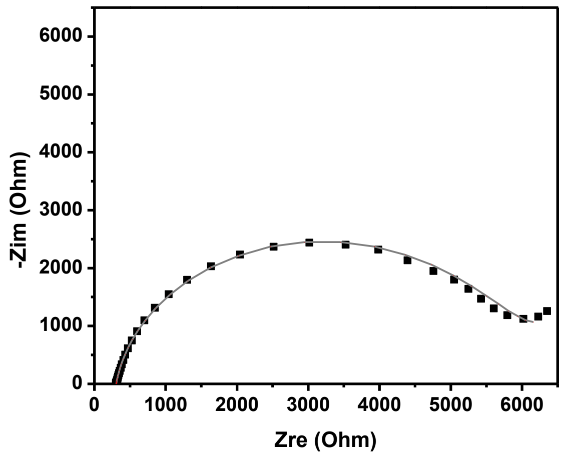

Figure S3 Nyquist diagrams of bare SPCE in 10 mM $K_3[Fe(CN)_6]/K_4[Fe(CN)_6]$. Line is the fit, point is the experimental data.

5. **EIS data of poly(PyPhEG-*co*-PyPhON) films with different polymerisation time.**

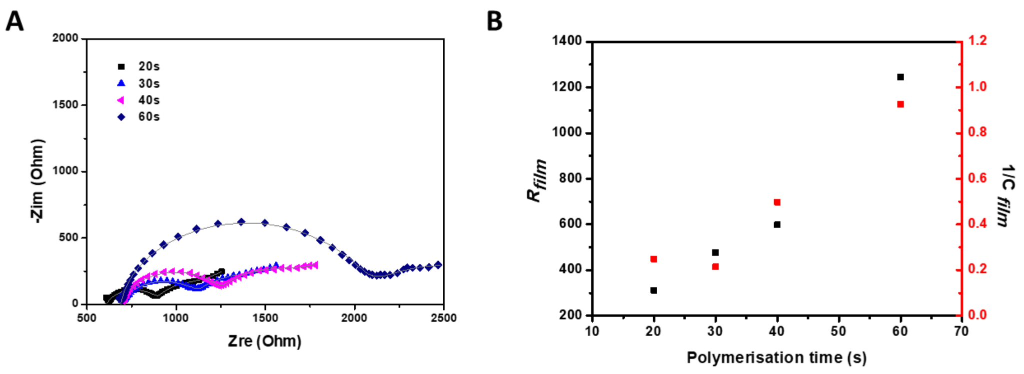

Figure S4 (A) Nyquist diagrams of poly(PyPhEG-*co*-PyPhON) films prepared at different times. (B) R_{film} *vs.* different polymerisation rime and $1/C_{film}$ *vs.* different polymerisation time.

Table S1 Fitted EIS data for poly(PyPhEG-*co*-PyPhON) films with different polymerisation time.

Polymerisation time	**20s**	**30s**	**40s**	**60s**
R_s (Ohm)	609	690	693	690
R_{film} (Ohm)	311	477	598	1245

$C_{interface}$ (F x10^{-5})	6.21	6.52	5.4	-
$R_{interface}$ (Ohm)	198	269	375	-
C_{film} (Fx10^{-6})	4.03	4.68	2.01	1.075

6. **EIS data after detection of bacterial lysate**

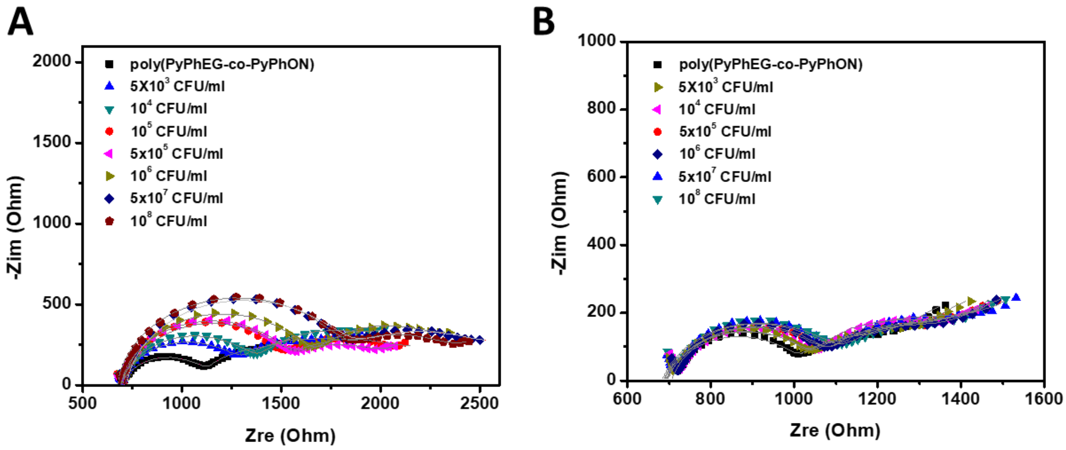

Figure S5 Impedance response to increasing concentration of bacterial lysate. A): *E. coli*; B): *Salmonella*. Lines are the fit, points are the experimental data.

Table S2 Fitted EIS data after detection of *E. coli* lysate

E. coli **(CFU/ml)**	**buffer**	**5x10^3**	**1x10^4**	**1x10^5**	**5x10^5**	**1x10^6**	**5x10^7**	**1x10^8**
R_s (Ohm)	690	689	691	715	692	701	674	722
R_{film} (Ohm)	477.3	668	742	862	912	1009	1206	1163
$C_{interface}$ (F x10^{-5})	6.52	4.73	4.84	6.16	4.21	5.05	4.05	7.33
$R_{interface}$ (Ohm)	269.4	374	562	532	350.5	444.2	437.4	656
C_{film} (Fx10^{-6})	4.68	2.43	2.13	1.07	1.08	1.28	0.91	0.93

Table S3 Fitted EIS data after detection of *Salmonella* lysate

Salmonella **(CFU/ml)**	**buffer**	**5x10^3**	**1x10^4**	**5x10^5**	**1x10^6**	**5x10^7**	**1x10^8**
R_s (Ohm)	694	702	700	702	705.8	705	699
R_{film} (Ohm)	343.3	378.2	388.7	412.8	407.3	442.8	458.4
$C_{interface}$ (F x10^{-5})	4.75	4.60	4.85	4.55	4.31	4.77	5.12
$R_{interface}$ (Ohm)	162.9	186.2	249.2	214.6	210.5	251.9	206
C_{film} (Fx10^{-6})	2.67	2.49	3.27	2.73	2.21	2.93	3.02

7. **Additional files**

a. *VBA code for calculation of resistance of a random resistor network on a cubic lattice*

This pdf file gives the code used. It iteratively solves the Kirchoff current law at the nodes of the network. Conductance between nodes is expressed as the arithmetic mean of values set at the nodes. It implements fixed boundary conditions for the electric potential on two opposing faces, through which the external current is set to pass in response to the imposed potential difference, and hence determines the conductance between these faces. Cyclic boundary conditions for the electric potential are applied at the other opposing faces.

The distribution of resistances in the cube can be arbitrarily chosen. Here, a spreadsheet function is used to draw the resistances randomly from a log-normal distribution. The functions Rnd() and Randomise provide a random number seed to choose the cumulative probability value at random but with very low and very high values avoided: it was empirically discovered that this was necessary to avoid an error in getting the inverse distribution:

seed = Rnd() * 0.9999999 + 0.00000001

The LOGINV spreadsheet function is then used to get the resistor value drawn from the distribution

final_conductance = 1 / Application.WorksheetFunction.LogInv(seed, logmean, logsd)

The resistance response of the cube against relative concentration is calculated according to the assumed linear response law for each resistor in the network $\Delta R/R_0 = sC$ where s denotes the sensitivity drawn from a log-normal distribution.

The authors have used their best endeavours to ensure that the program is free of bugs, is accurate and works as intended, but no guarantee is given and we disclaim any responsibility for its use.

b. *Excel spreadsheet giving example results.* The sheet labelled 'comment' gives a description. The sheet labelled 'calculation' runs the calculation if the code is inserted. The other sheets give results for a particular set of realisations, using a smaller log standard deviation (σ= 4.5) for the underlying resistor distribution than that exemplified in the main text. As a result, the computed distribution of resistance for the cube is significantly narrowed and the effect of the imposed response is of a narrow distribution that is simply shifted along the resistance axis.

Reference

1. Jarzabek, G. y.; Borkowska, Z., On the real surface area of smooth solid electrodes. *Electrochim. Acta.* **1997,** *42* (19), 2915-2918.

2. Lassalle, N.; Mailley, P.; Vieil, E.; Livache, T.; Roget, A.; Correia, J.; Abrantes, L. J. J. o. E. C., Electronically conductive polymer grafted with oligonucleotides as electrosensors of DNA: Preliminary study of real time monitoring by in situ techniques. *J. Electroanal. Chem.* **2001,** *509* (1), 48-57.