A symmetric supercapacitor/biofuel cell hybrid device based on enzyme-modified nanoporous gold: an autonomous pulse generator

Xinxin Xiao, Peter Ó Conghaile, Dónal Leech, Roland Ludwig, EDMOND MAGNER

Supporting information

A symmetric supercapacitor/biofuel cell hybrid device using enzyme-modified nanoporous gold: an autonomous pulse generator

Xinxin Xiao[a], Peter Ó Conghaile[b], Dónal Leech[b], Roland Ludwig[c] and Edmond Magner[a,*]

[a]Department of Chemical and Environmental Sciences, Bernal Institute, University of Limerick, Limerick, Ireland

[b]School of Chemistry & Ryan Institute, National University of Ireland Galway, Galway, Ireland

[c]Department of Food Science and Technology BOKU-University of Natural Resources and Life Sciences, Muthgasse 18, 1190 Vienna, Austria

[*]Corresponding author: Edmond Magner, E-mail address: edmond.magner@ul.ie; Fax: +353 61 213529; Tel: +353 61 202629

Relevant equations

➢ The specific capacitance, C (unit: μF cm^{-2}), can be obtained from CV response using equation:

$$C_{CV} = \frac{(j_a - j_c)}{(2 \times v)} \quad (1)$$

where j_a and j_c are the anodic and cathodic current densities (μA cm^{-2}), respecitively, obtained in the potential range where no faradaic processes were occurring, v is the scan rate in V s^{-1}.

➢ According to the galvanostatic discharge curves, the specific capacitance can be obtained from equation (2):

$$C_g = \frac{j_{pulse}}{\left[-\left(\frac{\Delta V}{\Delta t}\right)\right]} \quad (2)$$

where j_{pulse} is the applied current density (in μA cm^{-2}), ΔV/Δt is the slope of the discharge curve after the voltage drop (in V s^{-1}).

➢ For an assembled supercapacitor, the overall capacitance, C, is determined by the positive and negative electrodes based on the equation:

$$\frac{1}{C} = \frac{1}{C_1} + \frac{1}{C_2} \quad (3)$$

where C_1 and C_2 are the individual capacitance of the positive and negative electrode seperately.

➢ The equivalent series resistance (ESR) in Ω, can be calculated according to Ohm's law:

$$\mathrm{ESR} = \frac{\Delta \mathrm{V}_{ohmic}}{i_{pulse}} \quad (4)$$

where i_{pulse} is applied current (in A) and ΔV_{ohmic} is the voltage drop in V.

➢ The maximum power density for each galvanostatic discharge, P_{max}, in μW cm^{-2} can be determined by the equation:

$$\mathrm{P}_{max} = j_{pulse} \times V_{max} \quad (5)$$

where V_{max} is the instant potential at the end of voltage drop and the beginning of each discharge.

➢ To describe the relationship between V_{max} and ESR, ΔV_{ohmic}, one can conclude that:

$$\mathrm{V}_{cutoff} = \mathrm{V}_{max} + \Delta \mathrm{V}_{ohmic} \quad (6)$$

$$\mathrm{V}_{cutoff} = \mathrm{V}_{max} + \mathrm{ESR} \times \mathrm{i}_{pulse} \quad (7)$$

where V_{cutoff} is the maximum voltage the hybrid device can reach for each reset.

The relationship between j_{pulse} and P_{max} can be expressed by combining Eq. (5) and (7):

$$\mathrm{P}_{max} = j_{pulse} \times (V_{\mathrm{cutoff}} - ESR \times j_{pulse} \times A) \quad (8)$$

where A is the geometric surface area of the electrode in cm^2.

Table S1. Electrochemical capacitances of various modified electrodes (obtained from Fig. 1A).

Electrode	Capacitance[a] ($\mu F\ cm^{-2}$)	Factor
Bare Au	27	1
Bare NPG	258	9.6
NPG/PEDOT	821	30.4
NPG/$Os(bpy)_2$PVI/FAD-GDH	480	17.8
NPG/PEDOT/$Os(bpy)_2$PVI/FAD-GDH	1148	42.5

[a]: calculated by Eq. S1.

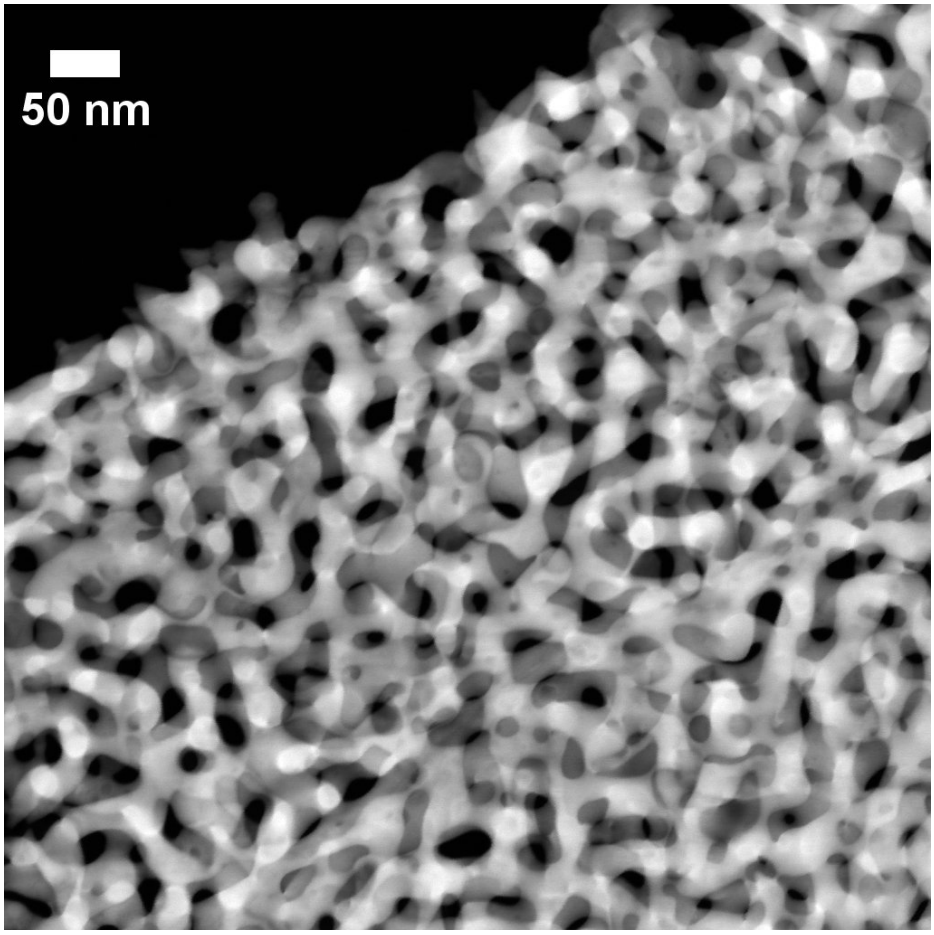

Fig. S1. STEM dark-field micrograph of bare NPG at 300 kX.

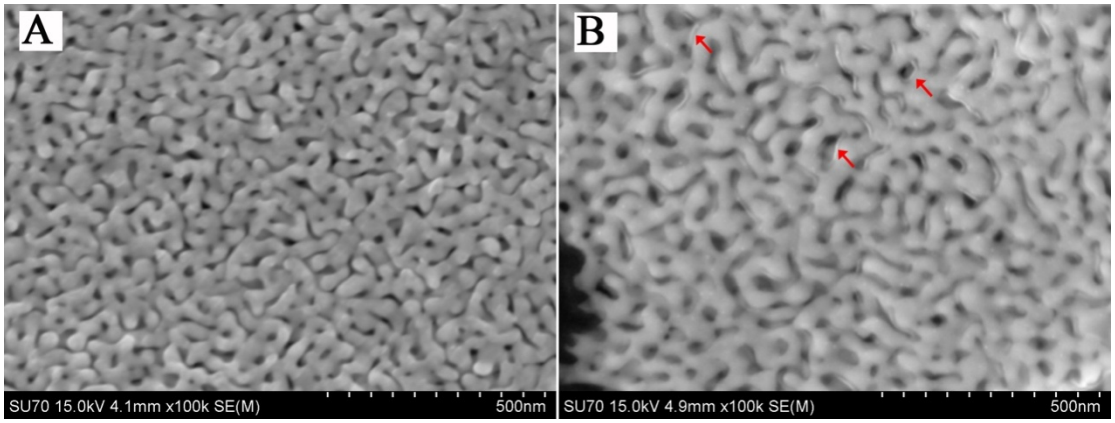

Fig. S2. SEM images of the bare NPG (A) and NPG/PEDOT/Os(bpy)$_2$PVI/FAD-GDH (300 s deposition) (B).

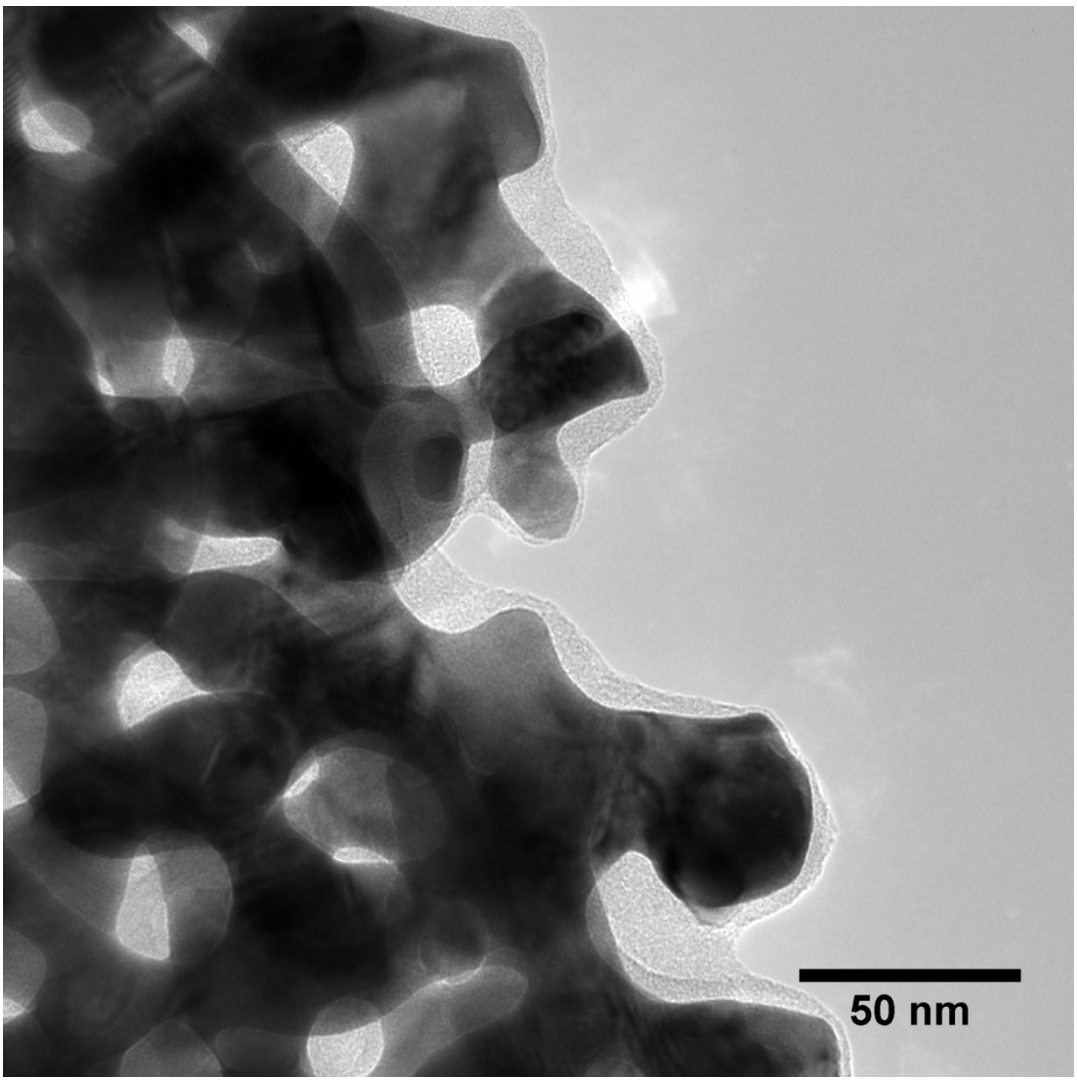

Fig. S3. TEM of NPG/PEDOT/Os(bpy)$_2$PVI/FAD-GDH (450 s deposition).

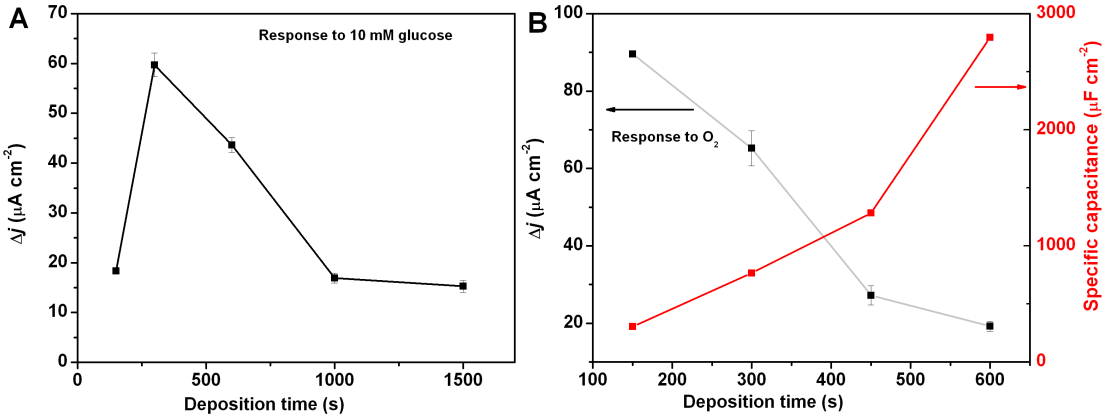

Fig. S4. Optimisation curves for the anode (A) and cathode (B).

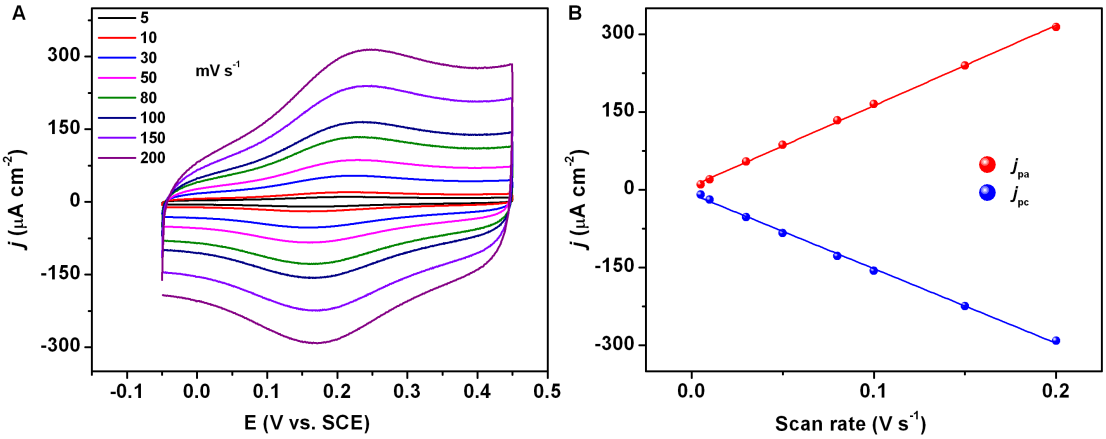

Fig. S5. (A) CVs of NPG/PEDOT/Os(bpy)$_2$PVI/FAD-GDH (300 s deposition) at various scan rates. (B) Calibration plots of the oxidation/reduction peak current vs. scan rate.

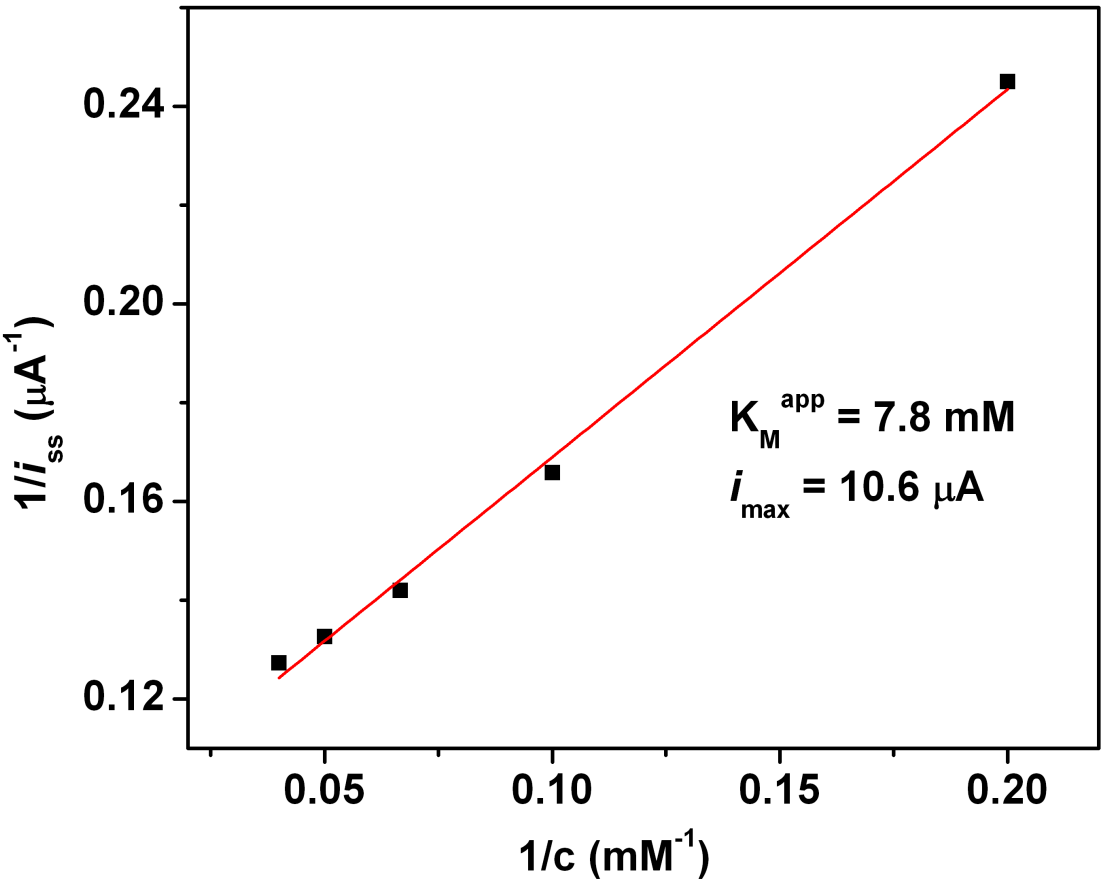

Fig. S6. Lineweaver–Burk plot for the NPG based FAD-GDH bioelectrode.

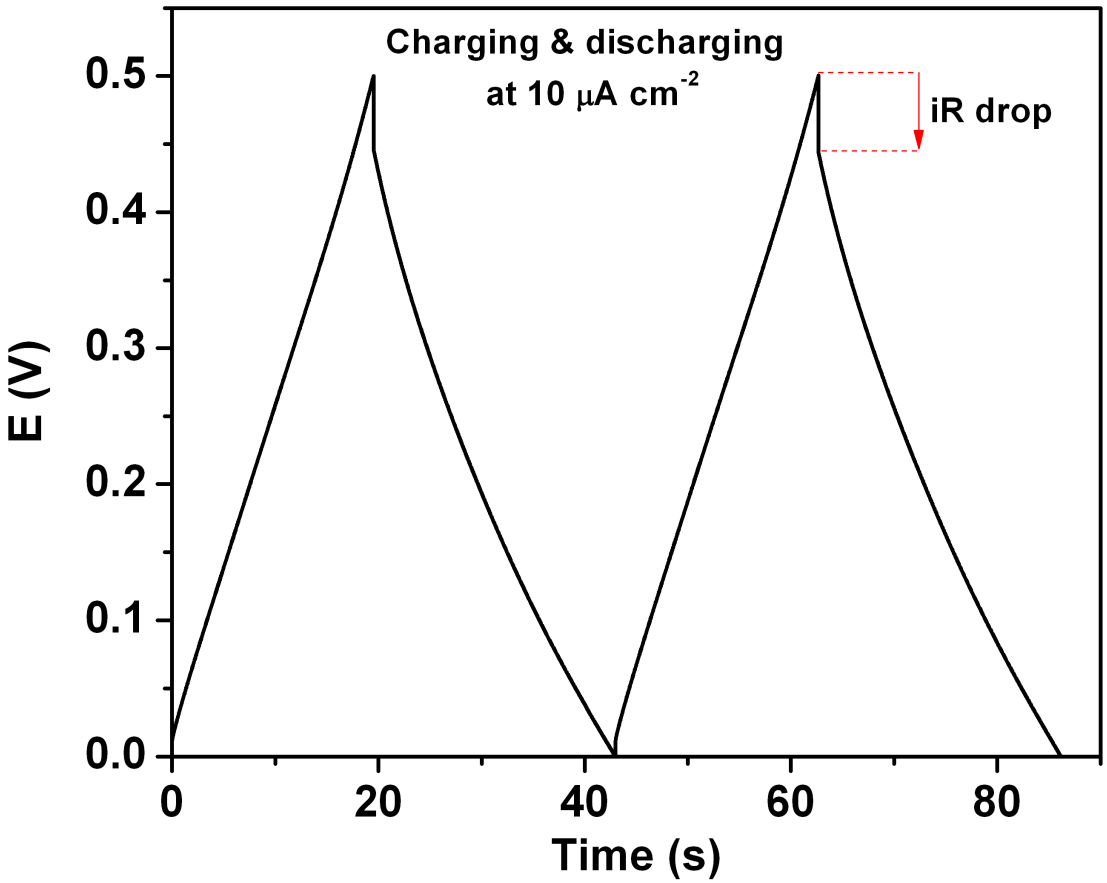

Fig. S7. Galvanostatic charge/discharge at 10 μA cm^{-2} of the symmetric supercapacitor consisting of NPG/PEDOT/Os(bpy)2PVI/FAD-GDH and NPG/PEDOT/Os(bpy)2PVI/FAD-GDH in a blank PBS solution.

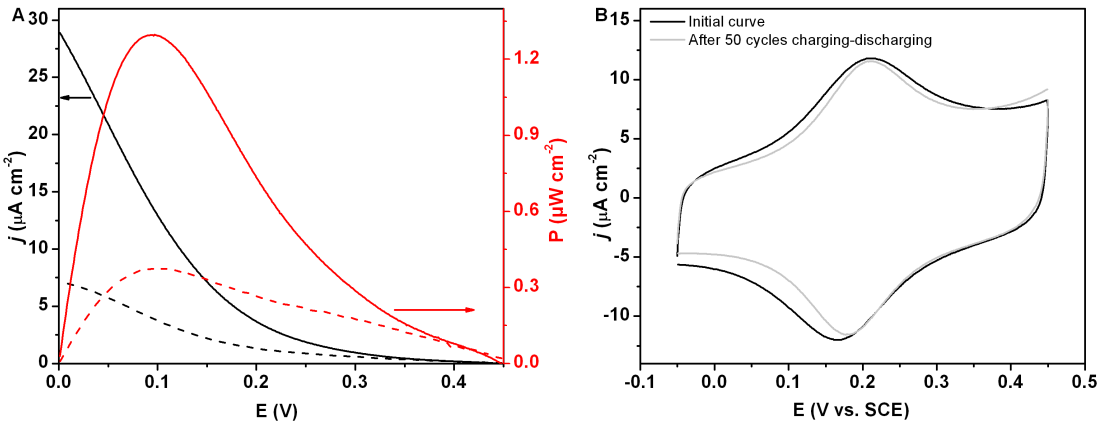

Fig. S8. (A) Polarisation and power curves for the BFC (initial curves: solid line; after long-term operation: dashed line). (B) CVs of the bioanode in PBS before and after long-term testing.

Table S2. Cell performance of the hybrid device upon various discharging current densities (j_{pulse}) (obtained from Fig. 5B).

Discharging j_{pulse} ($\mu A\ cm^{-2}$)	V_{max} (mV)	P_{max} [b] ($\mu W\ cm^{-2}$)
5	397.3	2.0
10	397.1	4.0
20	396.6	7.9
50	395.2	19.8
100	392.9	39.3
200	388.5	77.7
500	374.3	187.1
1000	352.1	352.1
2000	304.4	608.8

[b]: calculated by Eq. S5.

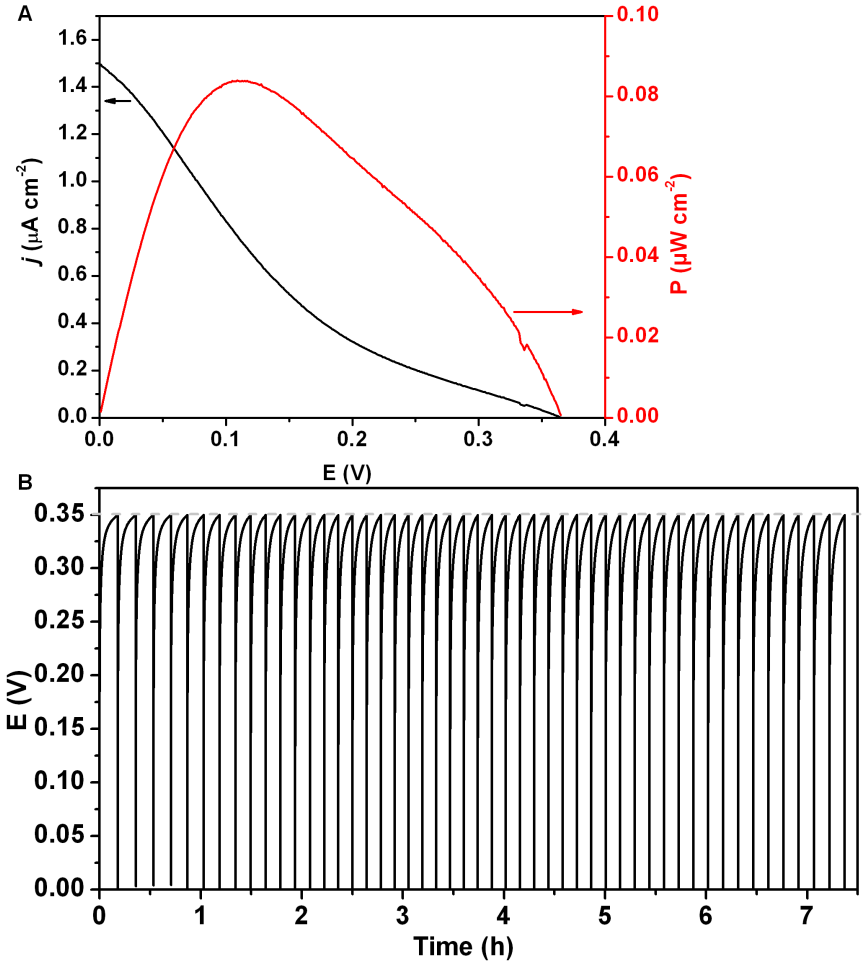

Fig. S9. (A) Polarisation and power curve for a planar Au based BFC. (B) Long-term testing of the biocapacitor for 50 cycles; Experimental setup: reset at OCV and cutoff at 0.35 V, followed by discharging at 0.2 mA cm^{-2} for 0.5 s and cutoff at 0 V.