Supplementary information

A quasi-solid-state and self-powered biosupercapacitor based on flexible nanoporous gold electrodes

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1. EXPERIMENTAL SECTION

1.1. Materials

D-(+)-glucose (99.5%), GOx from *Aspergillus niger* (EC 1.1.3.4, type II, ⩾15,000 U g-1), phosphoric acid (⩾85%), potassium hydroxide pellets (KOH), PVA (MW 146000-186,000, ≥99% hydrolysed), poly(ethylene glycol)diglycidyl ether (PEGDGE), sodium phosphate (monobasic dehydrate ≥99% and dibasic ≥99%), sodium fluoride (NaF, 99.99%) and sulfuric acid (H_2SO_4, 95-98%) were purchased from Sigma-Aldrich Ireland, Ltd. *Myrothecium verrucaria* BOx (EC 1.3.3.5, 2.63 U mg^{-1}) was obtained as a gift from Amano Enzyme Inc., Japan. Os(dmbpy)$_2$PVI and Os(bpy)$_2$PVI were synthesised according to an established procedure [1, 2]. Deionised water (18.2 MΩ cm, Elga Purelab Ultra, UK) was used to prepare all the solutions.

1.2. Electrochemical dealloying

100 nm Ag_{70}/Au_{30} (atomic %) alloy was magnetic sputtered onto 100 μm thin polyethylene terephthalate (PET) in an ultra-high vacuum chamber following a previous report[3]. Typically, PET substrates were firstly cleaned using Ar plasma treatment, followed by the coating of a Ti adhesive layer (10 nm), Au protective layer (*ca*. 35 nm) and alloy layer. The as-sputtered sheet with a diameter of 85 mm was cut using scissors

into rectangular pieces and painted with dielectric paste (Gwent Group, UK) to define an electrode area of 1 cm^2.

An electrochemical dealloying procedure was employed to prepare NPG[4]. Briefly, the alloy was allowed to be anodized at +1.5 V vs. SCE in 0.5 M NaF at room temperature (20±2 °C) for 10 min and subsequently cleaned by scanning the potential from -0.2 to 1.65 V in 1 M H_2SO_4 at 100 mV s^{-1} for 15 cycles. The reduction peak of 15th cycle of cyclic voltammogram (CV) was used to calculated the electrochemically addressable surface area (A_{real}) of NPG assuming a unit of 390 µC cm^{-2} for the reduction of a single layer of gold oxide [5]. The roughness factor (R_f) is defined as the ratio of A_{real} to the geometric area (A_{geo}). The average pore size and crack width of NPG by analysing at least 30 measurement points of scanning electron microscopic (SEM) images obtained a Hitachi SU-70 SEM at 15 kV.

1.3. Enzyme immobilisation

A 21.2 µL of 6 mg mL^{-1} aqueous solution of redox polymer, Os(dmbpy)$_2$PVI or Os(bpy)$_2$PVI, was mixed homogeneously with 5.2 µL of 15 mg mL^{-1} aqueous solution of PEGDGE and, either 12.8 µL of 10 mg mL^{-1} solution of GOx or BOx. The as-prepared solution was drop-casted onto a NPG electrode to cover its surface carefully. The electrodes were allowed to be placed in a vacuum desiccator connected to a vacuum pump for 20 min, which were then transferred into a 4°C fridge, allowed to dry overnight in the dark. To elucidate the role of the enzymes on the potential recovery, NPG electrodes modified only with redox polymer and cross-linker were also prepared following the same protocol.

1.4. Solid-state electrolyte preparation and characterisation

3 g PVA powder was added into a beaker containing 30 mL of 0.1 M phosphoric acid and was completely dissolved for about 30 min stirring in a 90 °C water-bath. The hot solution was then poured into a polystyrene petri dish with a diameter of 90 mm. An even and transparent film was formed after 24 h dry in a 30 °C oven. The obtained film was immersed in a 0.1 M KOH solution for 2 h to neutralise its pH. Prior to using, the film

was further soaked in 0.1 M pH 7.0 PBS containing 100 mM glucose for 24 h to load proper amount of substrate for enzymes. The thickness of the dry PVA film was 270 μm determined by SEM.

Fourier transform infrared (FTIR) analysis was performed to examine the structure of PVA films using a Perkin Elmer Spectrum 100 interferometer. Water content of PVA hydrogel was obtained by thermogravimetric analysis (TGA, TGA 4000, Perkin Elmer) in a temperature range from 30 to 300 ^{o}C with a heating rate of 10 ^{o}C min^{-1} under a N_2 stream with a flow rate of 20 mL min^{-1}. Electrochemical impedance spectroscopy (EIS, from 10 to 200 kHz) of Toray carbon paper (Fuel Cell Etc., USA) sandwiched PVA hydrogel was conducted to measure the ionic conductivity (σ, S cm^{-1}) of the PVA hydrogel, which can be obtained by the following equation:

$$\sigma = \frac{l}{R_b \times A} \ (S1)$$

where l (cm) is the PVA film thickness, R (Ω) is the bulk resistance obtained from the Nyquist plot, A (cm^{-2}) is the contact area of the PVA film with Toray paper electrodes.

The ionic conductivity of 0.1 M pH 7.0 PBS was measured at 25 ^{o}C using a Jenway 4510 conductivity meter (cell constant = 1.01 cm^{-1}).

1.5. Assembly of the all-solid-state biosupercapacitor

The device was assembled by sandwiching the PVA hydrogel as a solid electrolyte between a NPG/Os(dmbpy)$_2$PVI/GOx bioanode and a NPG/Os(bpy)$_2$PVI/BOx biocathode. Dialysis cellulose membranes (Spectra/Por® 1, 6-8 kD Molecular weight cut-off, Spectrum Medical Devices, CA) were used to encapsulate the assembled cells.

1.6. Electrochemical measurements

Electrochemical characterisation was performed using a CHI802 potentiostat (CH Instruments, Austin, Texas) with a three-electrode system comprising NPG based working electrodes, a saturated calomel electrode (SCE) as the reference electrode and a platinum mesh counter electrode. All experiments were carried out at room temperature (20±2 °C) unless stated otherwise.

The assembled EBFCs using aqueous or solid-state electrolyte were tested in a two-electrode system by using a NPG/Os(dmbpy)$_2$PVI/GOx bioanode as the working electrode and a NPG/Os(bpy)$_2$PVI/BOx biocathode as the combined counter/reference electrode. The current in the potential range between the open circuit voltage (OCV) of the EBFC and 0 V at 1 mV s^{-1} was measured, according to which power density profile can be calculated.

Testing of the self-charge/discharge properties of the biosupercapacitor was performed with an Autolab PGSTAT302N potentiostat (Eco Chimie, Netherlands). The NPG/Os(bpy)$_2$PVI/BOx biocathode and NPG/Os(dmbpy)$_2$PVI/GOx bioanode were used as working and combined counter/reference electrodes, respectively. The testing sequence was composed of (i) stand at open-circuit with open-circuit-potential (OCP) recorded and (ii) galvanostatic discharge at certain current densities ranging from 5 to 500 μA cm^{-2}. Discharge was triggered when any of the following conditions was satisfied: i) standing time reached to 20 min; ii) OCP reached to the set cut-off potential (*e.g.* 0.3 V), which was lower than the OCV of the biofuel cell.

2. Supplementary figures

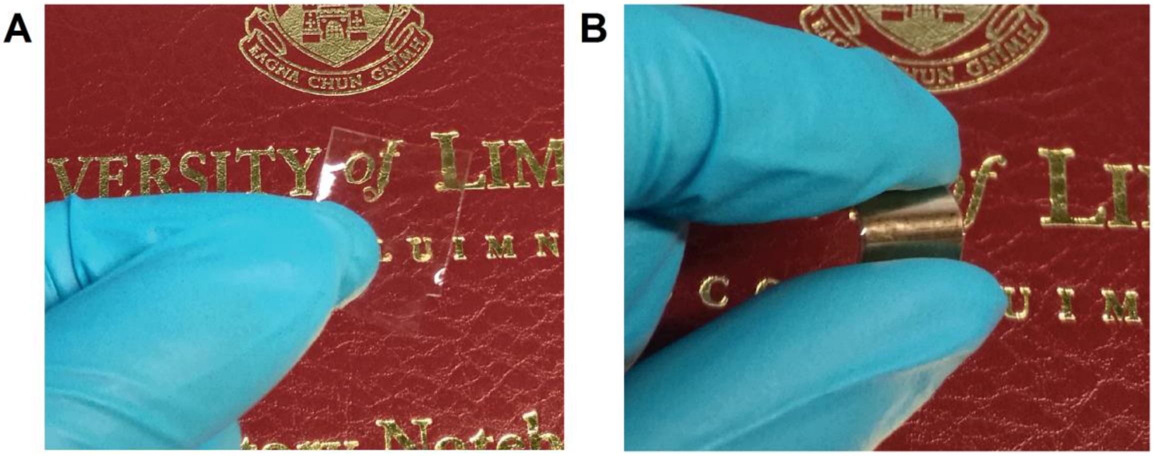

Fig. S1. Photograph of the PVA hydrogel (A) and assembled flexible device (B).

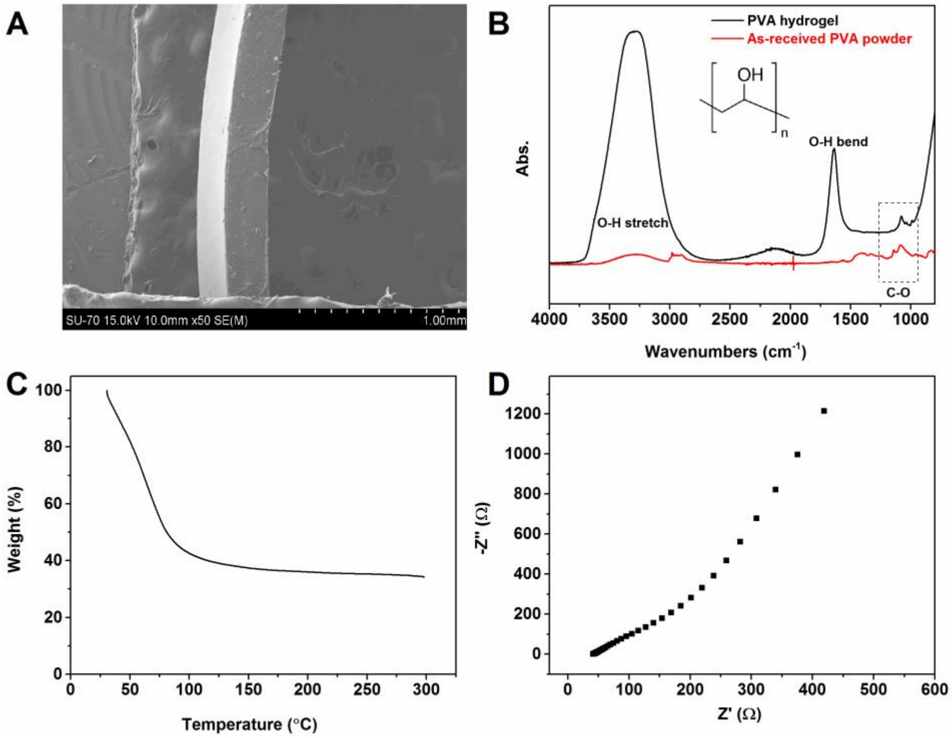

Fig. S2. (A) Cross-section viewed SEM image of a PVA film; (B) FTIR spectra of the PVA hydrogel and as-received PVA powder; inset of (B) indicates the structure of PVA. (C) The TGA curve of the PVA hydrogel; (D) Nyquist plot of the prepared solid-state electrolyte.

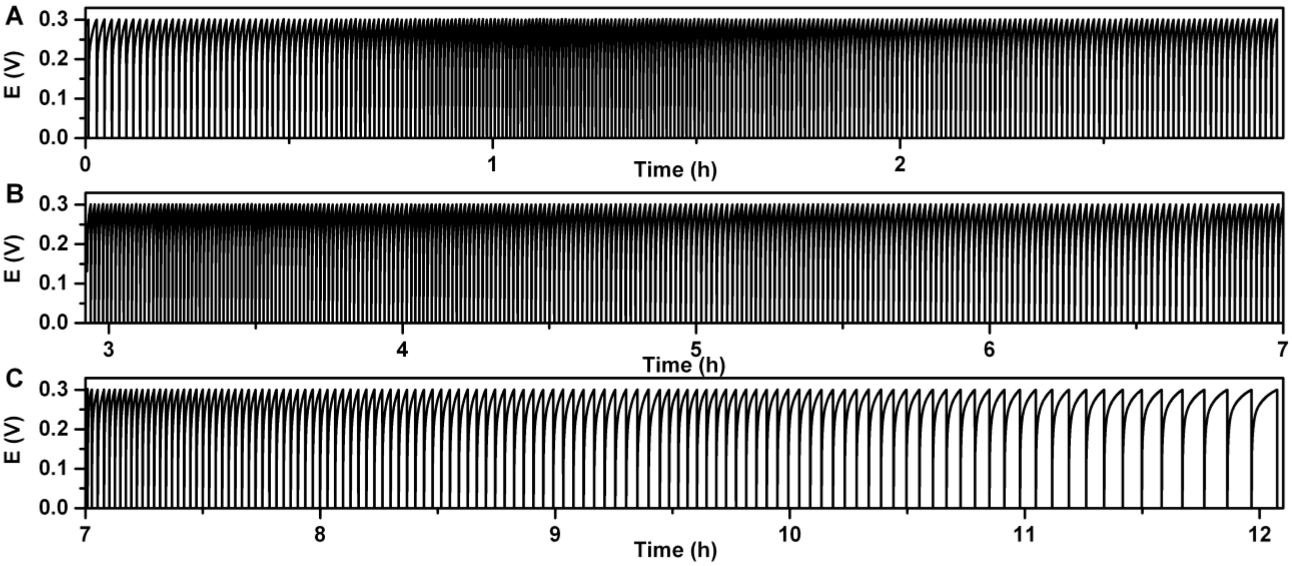

Fig. S3. Potential profile of the all-solid-state device for 620 cycles: (A): 1-250th; (B): 251-500th, (C): 501-620th cycle; Experimental protocol: reset at open-circuit for 20 min and cutoff at 0.3 V, followed by discharging at 0.1 mA cm^{-2} and cutoff at 0 V.

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