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## Electronic Supplementary Information

### Mediator-free Carbon Nanotube Yarn Biofuel Cell

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### Materials and method

#### *Materials*

Multi-walled carbon nanotube sheets, drawn from the sidewalls of MWCNT forests [S1] grown on a Si wafer were used as host material. The anodic enzyme was glucose oxidase (GOx) from *Aspergillus niger* (180 U mg<sup>-1</sup>) purchased from Amano Enzyme Inc. (Nagoya, Japan) and its kinetics were shown in the additional reference [S2]. The cathodic enzyme was bilirubin oxidase (BOD) from *Myrothecium verrucaria* (1.2 U mg<sup>-1</sup>) purchased from Amano Enzyme Inc. (Nagoya, Japan) and its kinetics were shown in the additional reference [S3]. GOx's activity was maximized at pH 6 and around the temperature of 35 °C. BOD's activity was maximized at pH 7 and around the temperature of 40 °C (These activities of both

enzymes were provided by Amano Enzyme Inc.). (PEDOT) coating on the MWCNT sheet, iron(III) p-toluenesulfonate hexahydrate (Fe(III)PTS,  $M_w$  677.52), pyridine (anhydrous, 99.8%), 1-butanol (for molecular biology,  $\geq 99\%$ ), and 3,4 ethylenedioxythiophene (EDOT) monomer (97%) were purchased from Sigma-Aldrich. All other chemicals used in this study were of analytical reagent grade.

### ***Fabrication of enzyme electrodes***

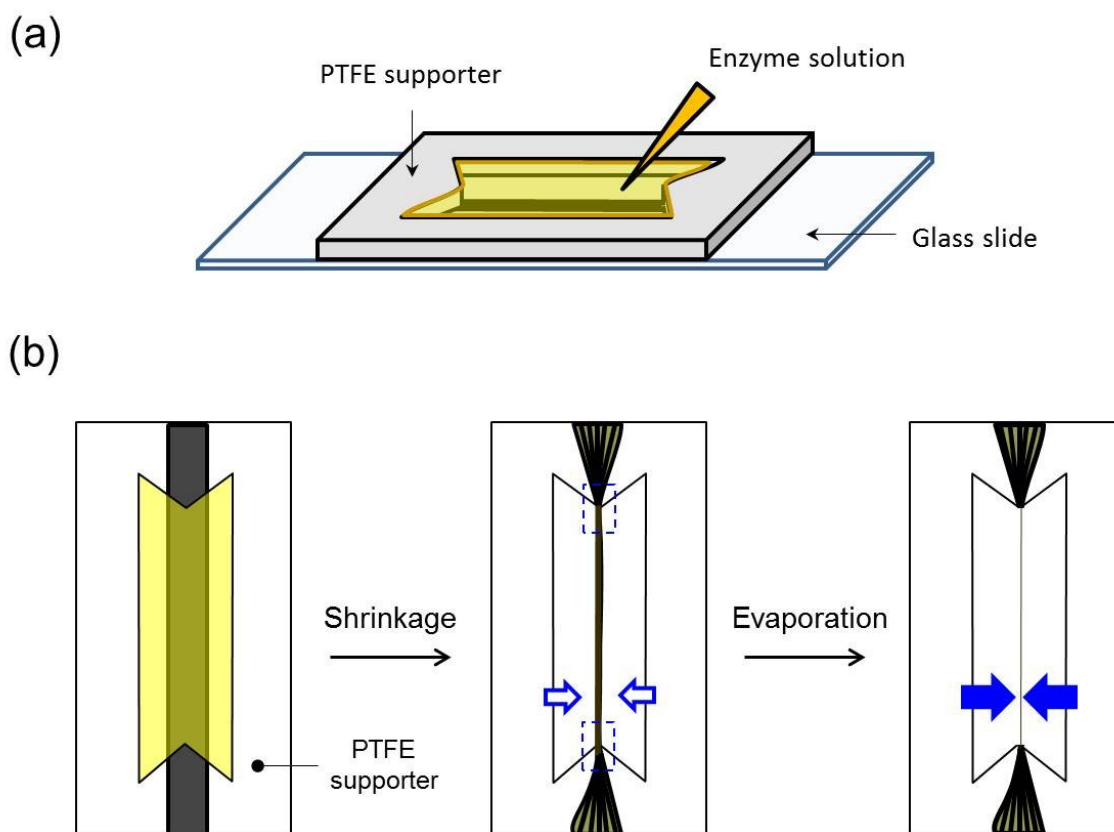
Three-layer MWCNT sheets drawn from the sidewalls of MWCNT forest [S1] were placed on a PTFE supporter (50 × 25 mm), and 2 wt% of PEDOT was coated on the sheet by vapor phase polymerization, as reported [S4]. GOx and BOD were dissolved in distilled water for the anode and cathode (187.5 mg mL<sup>-1</sup>). Each PEDOT-coated MWCNT sheet on the supporter was immersed in the enzyme solution for overnight, and then taken out and dried for a few hours at room temperature. Finally, the shrunken MWCNT anodic and cathodic electrodes were fabricated separately.

### ***Electrochemical measurements***

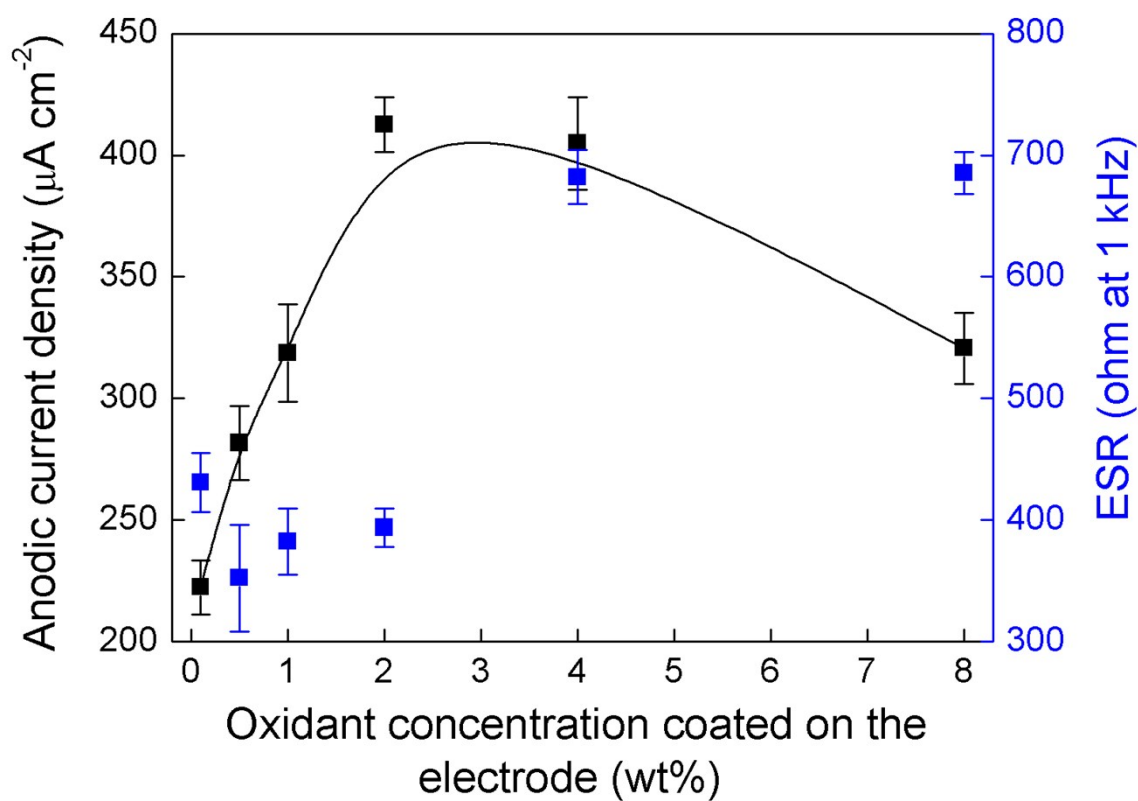
A three-electrode system was used for cyclic voltammetry using a scan rate of 5 mV s<sup>-1</sup>. Anodic and cathodic yarn working electrodes were used, with a silver chloride reference electrode, and a platinum mesh counter electrode. The measurement was done at 37 °C in 50 mL PBS (20 mM phosphate, 0.14 mol L<sup>-1</sup> NaCl) (pH: ~7.4). The power density of the BFC system was measured by linear sweep voltammetry with a scan rate of 5 mV s<sup>-1</sup> over a range of 0 to 0.85 V.

## ***Characterization***

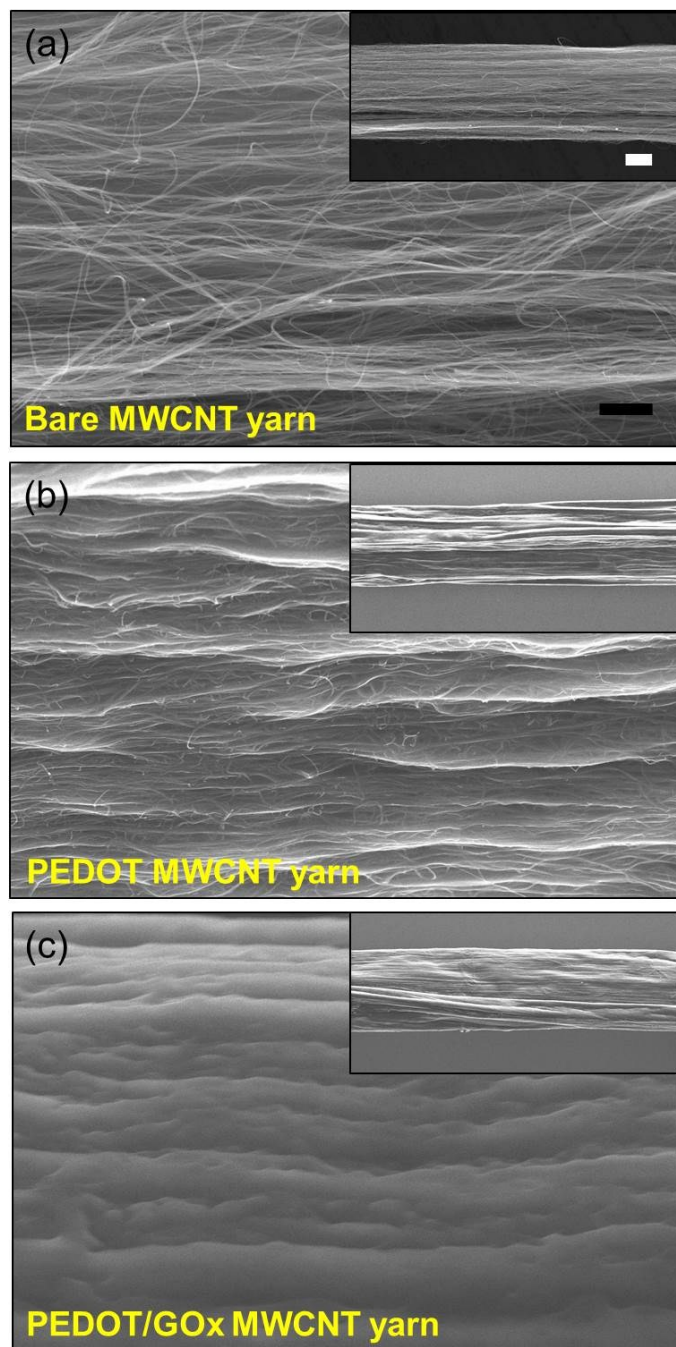
Surface morphology and cross-sectional images of the yarn electrode were obtained using scanning electron microscopy (SEM, Hitachi S4700, Tokyo, Japan). Cyclic voltammetry measurements were obtained using electrochemical analyzers (CHI 627B from CH Instruments, Austin, TX, USA). Electrochemical impedance measurements were measured using a Gamry Reference 600 potentiostat (Gamry Instruments, Warminster, PA, USA).



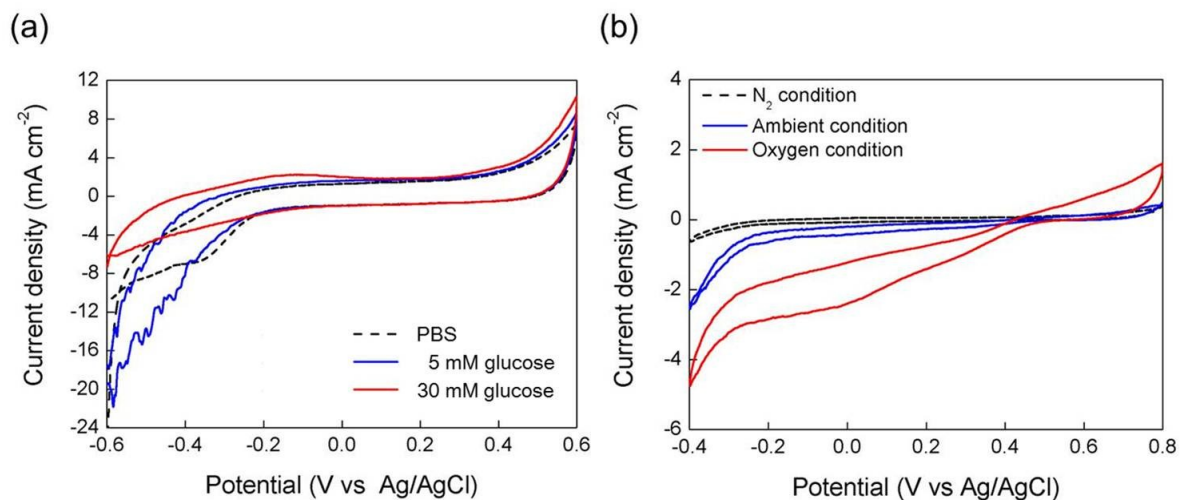
**Fig. S1** Schematic representation of the enzyme-loaded PEDOT/MWCNT self-assembled yarn electrodes. (a) Schematic diagram of immobilizing enzyme on the PEDOT/MWCNT sheet (side view). (b) Schematic diagrams of the sequential PEDOT/MWCNT shapes produced by evaporative shrinkage.



**Fig. S2** Optimization of PEDOT coating by changing the PEDOT oxidant weight percentage coated on the MWCNT electrode at 0.1 wt% to 8 wt%. The anodic current density was measured at 0 V, and the internal resistance of the anode electrode was compared by equivalent series resistance (ESR), measured at 1 kHz.

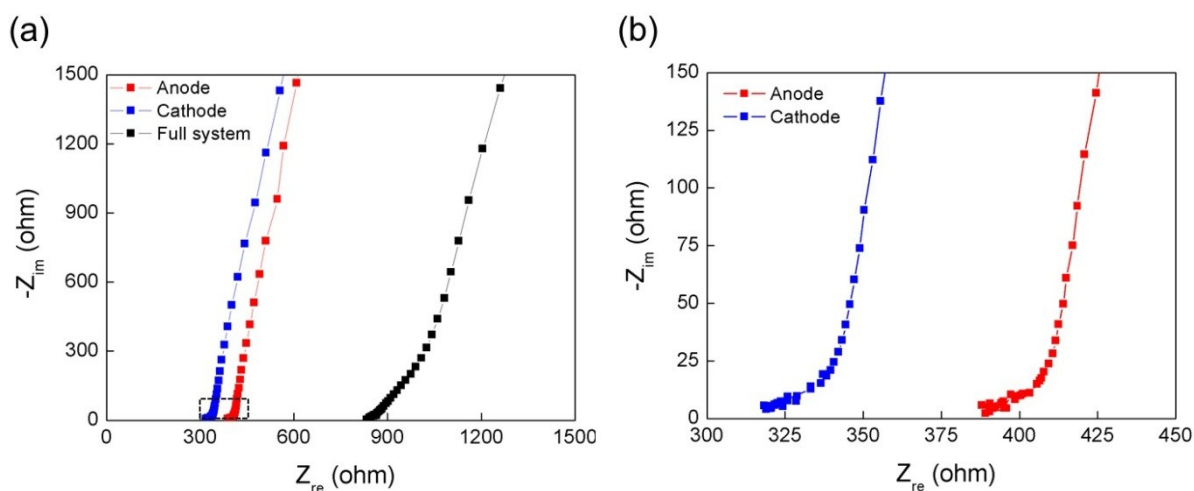


**Fig. S3** SEM images for (a) bare MWCNT yarn; (b) PEDOT/MWCNT yarn; and (c) GOx-entrapped PEDOT/ MWCNT yarn. Scale bars = 10  $\mu\text{m}$  in (a) and 1  $\mu\text{m}$  in the insets.



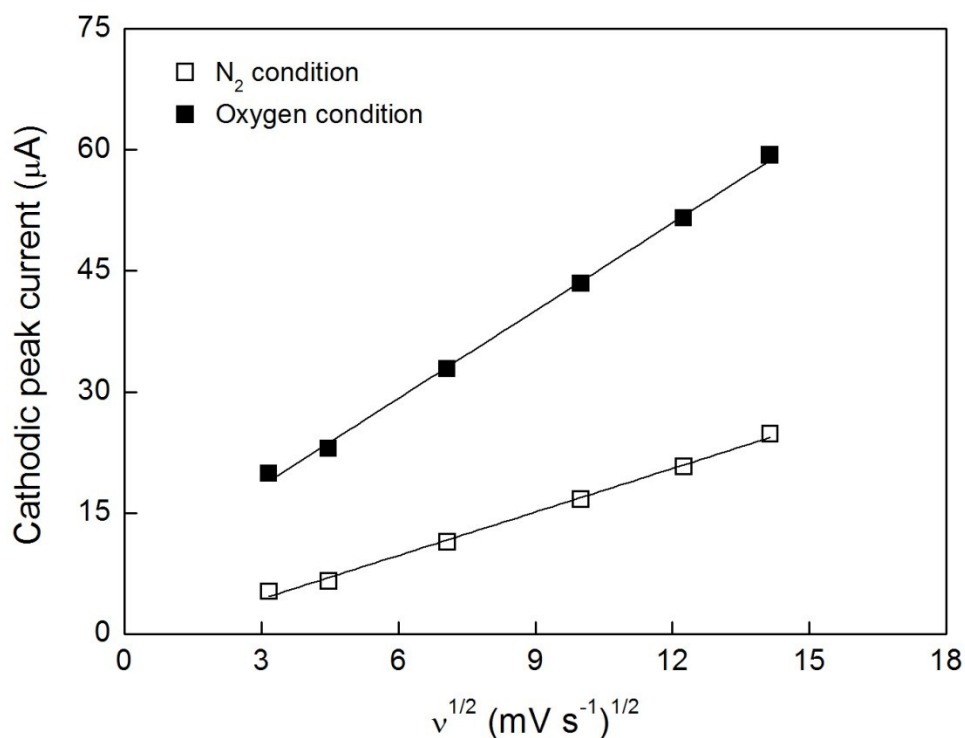
**Fig. S4** Cyclic voltammetry of anode and cathode yarn electrodes over a wide potential range.

(a) Cyclic voltammetry curve of anode in the buffer solution not containing glucose (black dotted line), in the solution containing 5 mM glucose (blue solid line), in a solution containing 30 mM glucose (red solid line). (b) Cyclic voltammetry curve of cathode in N<sub>2</sub>-saturated condition (black dotted line), and in ambient condition (blue solid line), and oxygen-saturated condition (red solid line).



**Fig. S5.** Electrical resistances data for the BFC system. (a) Internal charge transfer resistance measurement by Nyquist plots (realized impedance change,  $Z_{re}$ , vs. imaginary impedance change,  $|Z_{im}|$ ), corresponding to the impedance spectra for cathode electrode over a range of 0.001 to 100,000 Hz (three-electrode mode). (b) Enlarged graph of the plot in the black dashed box in (a).





**Fig. S6.** Dependencies of the cathodic peak currents on the square root of scan rates ( $v^{1/2}$ ) obtained from CVs under N<sub>2</sub>-saturated condition (empty square) and oxygen saturated condition (full square).

### Supplementary References

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- S2. Q. H. Gibson, B. E. Swoboda, V. Massey, *J. Biol. Chem.* 1964, **239**, 3927–3934
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- S4. J. A. Lee, M. K. Shin, S. H. Kim, S. J. Kim, G. M. Spinks, G. G. Wallace, R. Ovalle-Robles, M. D. Lima, M. E. Kozlov, R. H. Baughman, *ACS Nano* 2012, **6**, 327–334.