Supporting information

Enzymeless multi-sugar fuel cells with high power output based on 3D graphene-Co_3O_4 hybrid electrodes

Yun Chen, Kenath Priyanka Prasad, Xuewan Wang, Hongchang Pang, Ruyu Yan, Aung Than, Mary B. Chan-Park, Peng Chen*

*Division of Bioengineering, School of Chemical and Biomedical Engineering, Nanyang Technological University, 70 Nanyang Drive, 637457, Singapore. Fax: +65 67911761; Tel: +65 65141086 *E-mail: chenpeng@ntu.edu.sg*

1. Deposition of Co_3O_4 onto 3D graphene with different electrochemical deposition duration

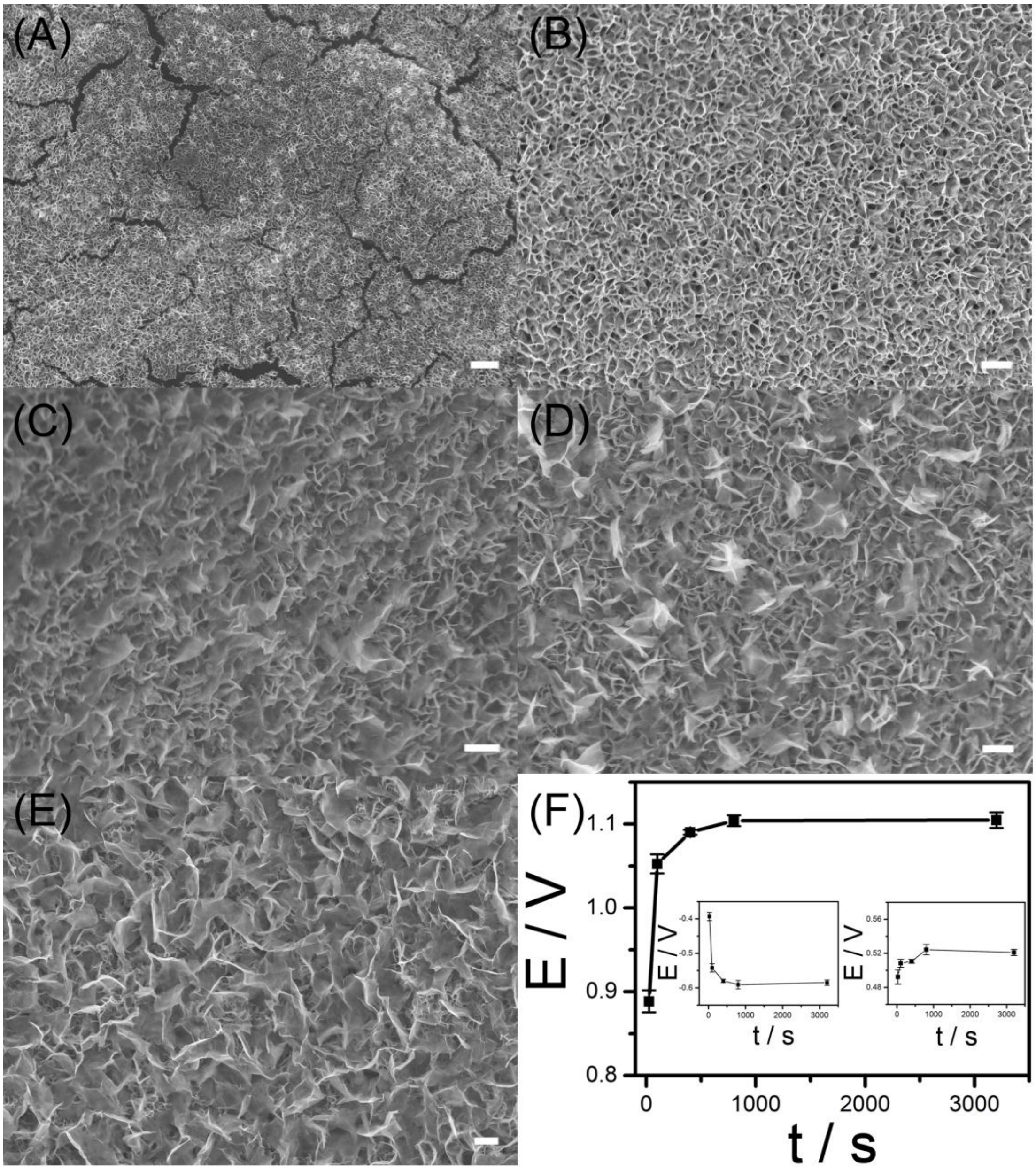

Fig. S1. (A – E) FESEM images of Co_3O_4 electrochemically deposited on 3D graphene with various deposition durations: 25 s (A), 100 s (B), 400 s (C), 800 s (D), 3200 s (E). Scale bars = 1 µm. (F) The open circuit voltage of a fuel cell with 3D graphene-Co_3O_4 anode and cathode (the different between anode and cathode). The time axis indicates the duration of electrochemical deposition of Co_3O_4 onto the electrode. The left inset shows the corresponding open circuit potential of 3D graphene-Co_3O_4 anode with varying Co_3O_4 coating measured in pH 5.0 buffer saturated with nitrogen and containing 200 mM glucose. The right inset shows the corresponding open circuit potential of 3D graphene-Co_3O_4 cathode with varying Co_3O_4 coating measured in pH 5.0 buffer saturated with oxygen. Each data point is the average obtained from three independent measurements and the error bar indicates the standard deviation.

2. XRD characterization of 3D graphene-CoOOH and 3D graphene-$Co(OH)_2$

With Cobalt(III) acetylacetonate solution containing 0.1 M $NaNO_3$ as the electrolyte, Cobalt(III) was electrochemically deposited onto 3D graphene by applying a constant potential of -1.0 V (vs. Ag/AgCl reference electrode) for 800s. After thorough rinsing with DI-water, the hybrid was annealed at 400 °C for 4 h to obtain 3D graphene-CoOOH. The XRD pattern shown in Fig. S2A displays three diffraction peaks at 2θ = 28.3°, 36.7°, and 44.8° resulting from the (110), (120), and (130) reflections of CoOOH, respectively (JCPDS 26-0480). 3D graphene-$Co(OH)_2$ was synthesized as described in the main text. Its XRD pattern (Fig. S2B) exihibits four diffraction peaks at 2θ = 18.8°, 37.6°, 51.0° and 61.3° ascribed to the (001), (101), (102) and (111) reflections of $Co(OH)_2$, respectively (JCPDS 30-0443).

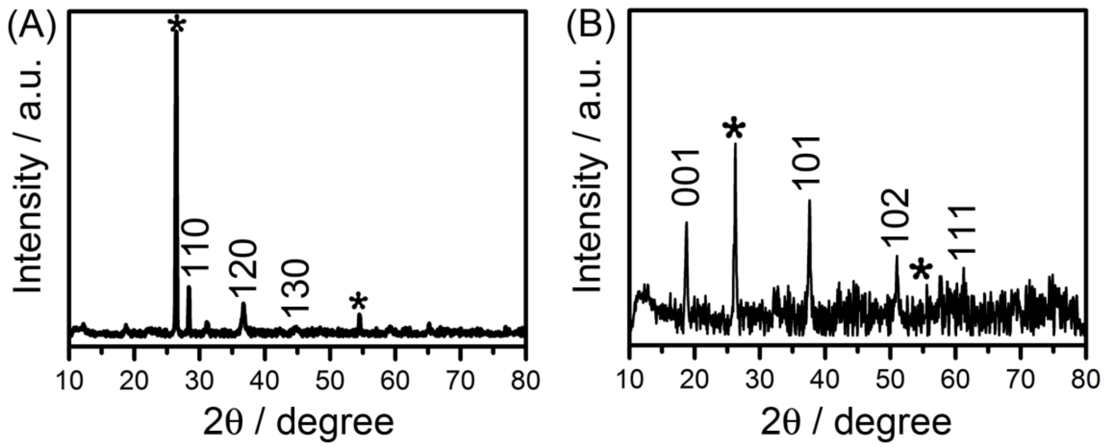

Fig. S2. XRD patterns of 3D graphene-CoOOH (A) and 3D graphene-$Co(OH)_2$ (B). * marks the signal from 3D graphene.

3. The open circuit potentials of 3D graphene-CoOOH hybrid and 3D graphene-$Co(OH)_2$ hybrid to glucose and O_2

As shown in Fig. S3, the graphene-CoOOH electrode (containing only Co^{III}) gave a significant open circuit potential (E_a^{ocp} = -0.587 ± 0.049 V, n = 3) in the presence of glucose and a small E_c^{ocp} (0.047 ± 0.017 V, n=3) in the presence of oxygen. Conversely, the graphene-$Co(OH)_2$ electrode (containing only Co^{II}) gave a negligible E_a^{ocp} (0.018 ± 0.002 V, n=3) in the presence of glucose and a large E_c^{ocp} (0.543 ± 0.020 V, n=3) in the presence of oxygen. These experiments confirm the oxidation ability of Co^{III} and reduction ability of Co^{II}.

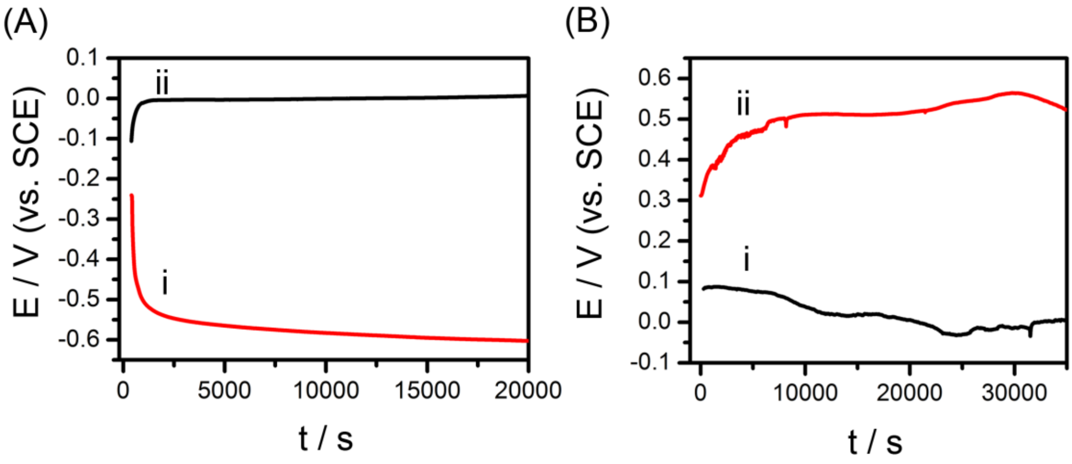

Fig. S3. The open circuit potential of a 3D graphene-CoOOH hybrid (A) and a 3D graphene-$Co(OH)_2$ hybrid (B) in pH 5.0 electrolyte solution which contained either 200 mM glucose and saturated nitrogen (i) or saturated oxygen (ii).

4. The continuous performance of the fuel cell

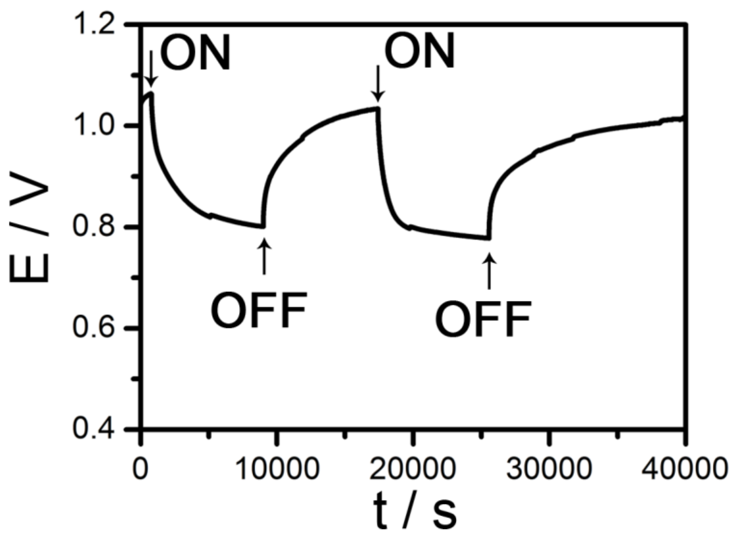

Fig. S4. The continuous voltage output of a fuel cell with a 100 kohm load and 200 mM glucose. "ON" and "OFF" indicate when the circuit is turned on or turned off, respectively.

5. The cytotoxicity assay of 3D Graphene-Co_3O_4 to PC12 cells

PC12 cells (American Type Culture Collection, USA) were cultured in Dulbecco's modified Eagle's medium (Gibco, USA) supplemented with 10% (v/v) fetal bovine serum (Gibco) and 1% penicillin–streptomycin at 37 °C under a humidified atmosphere containing 5% CO_2 and 95% air. The viability of the cells were determined using a MTT (3-(4,5-dimethylthiazol-2-yl)-2,5-diphenyl tetrasodium bromide)-based cell growth determination kit (Sigma-Aldrich, USA). Briefly, after washing with phosphate buffer saline (PBS), the cells were incubated in the culture medium containing MTT reagent solution (5 mg/ml MTT in RPMI-1640 without phenol red) (10% v/v) for 4 h at 37 °C. MTT solvent (0.1 N HCl in anhydrous isopropanol) was then added to the culturing well (50% v/v), followed by measuring the absorbance of MTT formazan crystals at 570 nm using a Victor3 plate reader (PerkinElmer Inc., USA). With a bare 3D graphene electrode or a 3D graphene-Co_3O_4 hybrid electrode immersed in the culture medium for 2 days, the proliferation and viability of the cells were determined by optical observation and MTT assay in comparison with the control cells. As shown in Fig. S4, 3D graphene-Co_3O_4 hybrid electrode did not cause obvious cytotoxicity to PC12 cells.

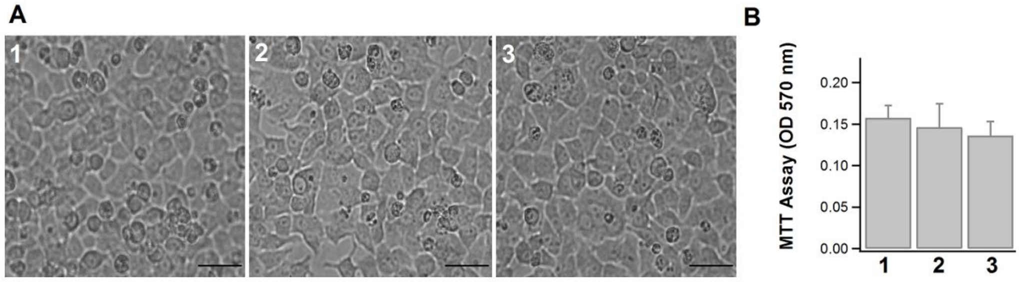

Fig. S5. (A) Optical images of PC12 cells cultured without (1), or with a bare 3D graphene electrode (2) or a 3D graphene-Co_3O_4 hybrid electrode (3). Scale bars = 20 µm. (B) MTT assay of cell viability. Optical density (OD) at 570 nm was measured as the indicator of cell viability. The error bars are standard deviations (n = 4 samples).