Supporting information for

Deep oxidation of glucose driven by 4-acetamido-TEMPO for glucose fuel cell under room temperature

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Experimental

Chemicals and solutions

All chemicals were used as received without further purification unless otherwise stated. TEMPO, 4-methoxy-TEMPO (CH_3O-TEMPO), 4-hydroxyl-TEMPO (HO-TEMPO), 4-carboxy-TEMPO (HOOC-TEMPO), 4-oxo-TEMPO (O=TEMPO), 4-acetamido-TEMPO (ACT), 10 wt% Pt/C, Nafion 117 solution (5% in a mixture of lower aliphatic alcohols and water), Nafion 117 proton exchange membrane, and Toray carbon cloth were purchased from Sigma-Aldrich. Phosphoric acid, boracic acid, acetic acid, sodium hydroxide (NaOH), acetylene black, and polytetrafluoroethylene (PTFE) solution (60 wt% in water) were purchased from Aladdin Ind., Corp. Carbon black (EC-300J) was purchased from AkzoNobel. Before using, it was heated at 1600 ºC for 2 h under Ar atmosphere. Milli-Q ultrapure water (18.2 MΩ cm) was used throughout the experiments. Britton-Robinson (B-R) buffer containing 0.04 M phosphate, 0.04 M borate, and 0.04 M acetate was used for all pH profiles due to its broad buffering range. The pH of all buffers was adjusted using 0.2 M NaOH.

Preparation of air-breathing Pt cathode

Air-breathing Pt cathode consisting of Pt/C catalyst layer, carbon base layer, and PTFE diffusion layers was fabricated according to Cheng's work with some modifications.[1,2] Typically, 40 mg of acetylene black was mixed with 600 μL of 40 wt% PFTE solution. The mixture was coated onto the one side of a Toray carbon cloth (25 cm^2). After the coating was air-dried, the carbon cloth was placed on a ceramic plate in a pre-heated furnace at 370 ºC for 30 min to form a carbon base layer. After cooling down to room temperature, 200 μL of 60 wt% PFTE solution was coated onto the previously coated side of the carbon cloth and allowed the coating layer to air-dry. The dried carbon cloth was placed on a ceramic plate in a pre-heated furnace at 370 ºC for 20 min. These steps were repeated for four times to form PTFE diffusion layers. For the construction of Pt/C catalyst layer, 125 mg of 10 wt% Pt/C was dispersed in a mixture of Nafion 117 solution (875 μL), deionized water (125 μL), and iso-propanol (625 μL). The mixture was then coated onto the side opposite the PTFE diffusion layers and dried at room temperature.

Electrochemical methods

Electrochemical experiments were performed on an electrochemical workstation (CHI 660E) with a standard three-electrode system. Cyclic voltammetry (CV) and Chronoamperometric (CA) measurements were performed using an Ag/AgCl (in 3 M KCl) reference electrode, a Pt foil (1 cm^2) counter electrode, and a glassy carbon (3 mm in diameter) working electrode. Before using, the glassy carbon electrodes were polished, respectively, with alumina slurries (0.3 and 0.05 μm) on a polishing cloth and ultrasonicated successively in deionized water, 1 M H_2SO_4, and absolute ethyl alcohol for 3 min, separately, and then dried under Ar-flow. The potential for CA experiments was held at 0.8 V (*vs*. Ag/AgCl) at room temperature. Bulk electrolysis experiments were performed using an Ag/AgCl (in 3 M KCl) reference electrode, a Pt foil (1 cm^2) counter electrode, and a Toray carbon cloth (1 cm^2) working electrode. The potential for electrolysis experiments was held at 0.8 V (*vs*. Ag/AgCl) at room temperature for 72 h.

Product analysis

Oxidation products were quantified by Fourier transform infrared spectroscopy (FTIR, Perkin Elmer, Spectrum 100 FT-IR) and mass spectrometry (MS, Thermo Fisher Scientific LTQ FT Utra (ESI) mass spectrometer). Transmission electron microscopy (TEM) was operated on a JEOL JEM-2100 microscope at an acceleration voltage of 200 kV.

Design and evaluation of glucose/O_2 FCs

The glucose/O_2 FCs were assembled using a glassy carbon electrode (GCE, 3 mm in diameter) anode and an air-breathing Pt cathode separated by a Nafion 117 membrane. 0.04 M B-R buffer with different pH values containing 5 mM ACT and 50 mM glucose was used as anolyte. The volume of the solution used in the glucose/O_2 FCs was 10 mL. For the preparation of carbon black modified GCE, 10 μL of carbon black dispersion (5 mg mL^{-1} in ultrapure water) was casted on GCE and dried naturally at room temperature. The power output of GBFCs was calculated using linear sweep voltammetry (LSV), which was performed at a scan rate of 1.0 mV s^{-1} at room temperature. The assembled glucose/O_2 FCs were operated in quiescent condition with pure O_2 flowing in the cathode chamber.

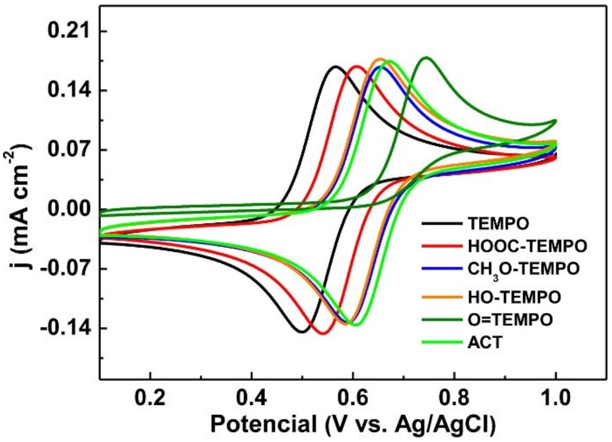

Fig. S1 CVs of 1 mM TEMPO, HOOC-TEMPO, CH_3O-TEMPO, HO-TEMPO, O=TEMPO, and ACT in the absence of glucose in 0.04 M B-R buffer solution (pH 7.0), scan rate 50 mV s^{-1}.

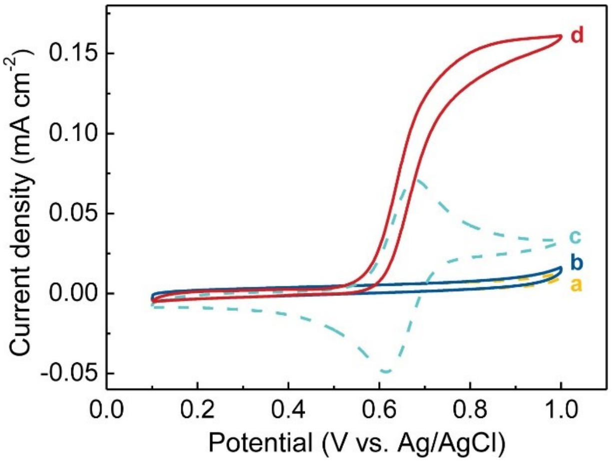

Fig. S2 Catalytic CVs of GCE in 0.04 M B-R buffer (pH 7.0) in the absence (a, b) and presence (c, d) of 1 mM ACT with (b, d) and without (a, c) 50 mM glucose at a scan rate of 10 mV s^{-1}.

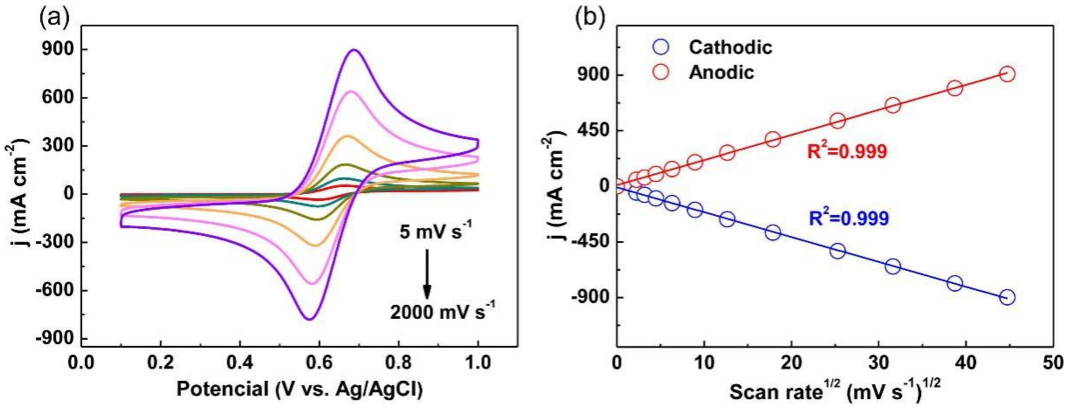

Fig. S3 (a) CVs of 1 mM ACT in the absence of glucose in 0.04 M B-R buffer solution (pH 7.0) at different scan rates. (b) Peak currents *vs*. square root of scan rates.

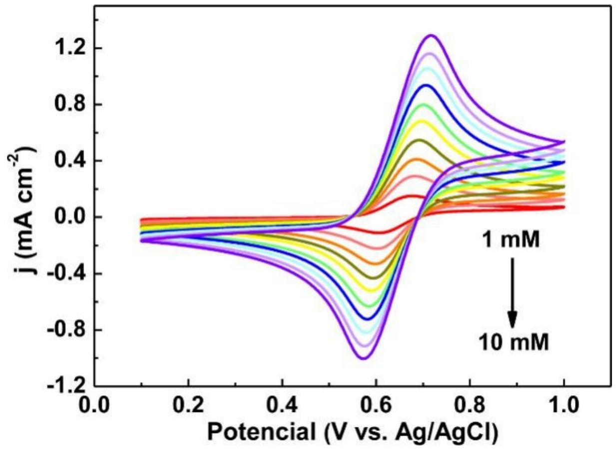

Fig. S4 CVs of different concentration of ACT in the absence of glucose in 0.04 M B-R buffer solution (pH 7.0) at a scan rate of 50 mV s^{-1}.

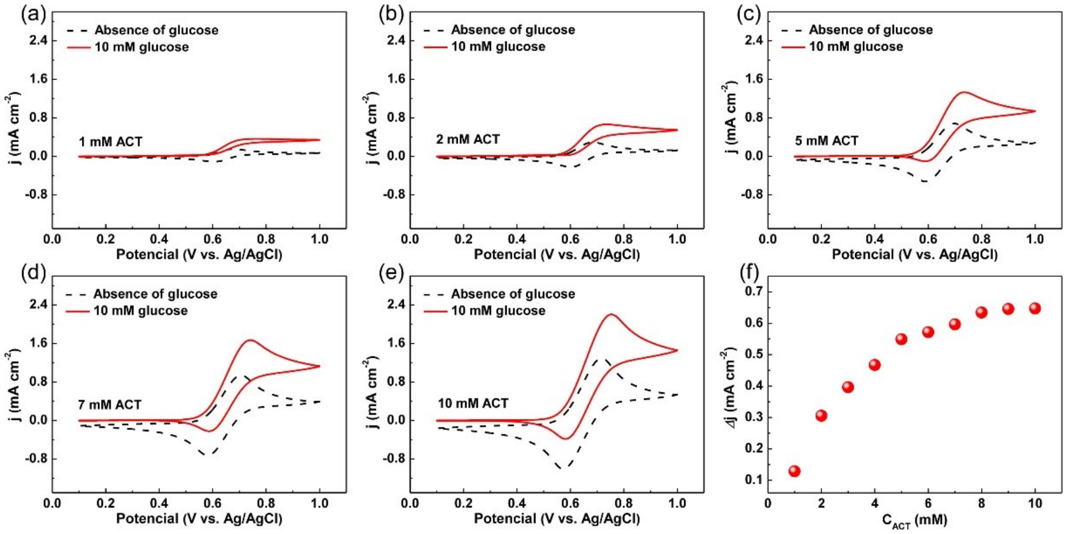

Fig. S5 (a-e) Catalytic CVs of ACT with different concentrations in the absence (dashed) and presence (solid) of 10 mM glucose. (f) Dependence of the catalytic currents (Δj) on concentration of ACT. Experiments were performed using a GCE in 0.04 M B-R buffer (pH 10.0) at a scan rate of 50 mV s^{-1}.

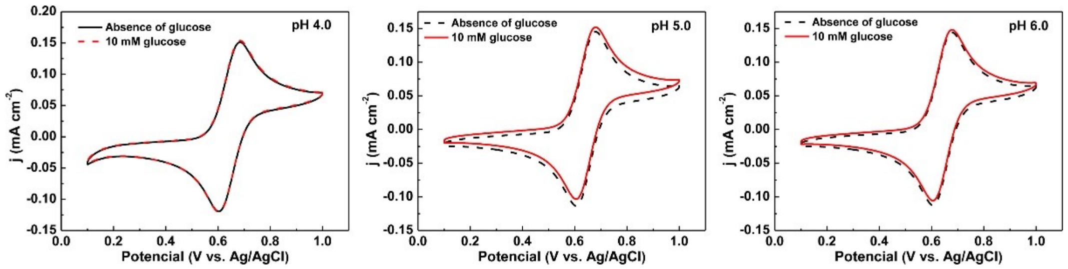

Fig. S6 CVs of 1 mM ACT in the absence and presence of 10 mM glucose in 0.04 M B-R buffer solution under different pH values, scan rate 50 mV s^{-1}.

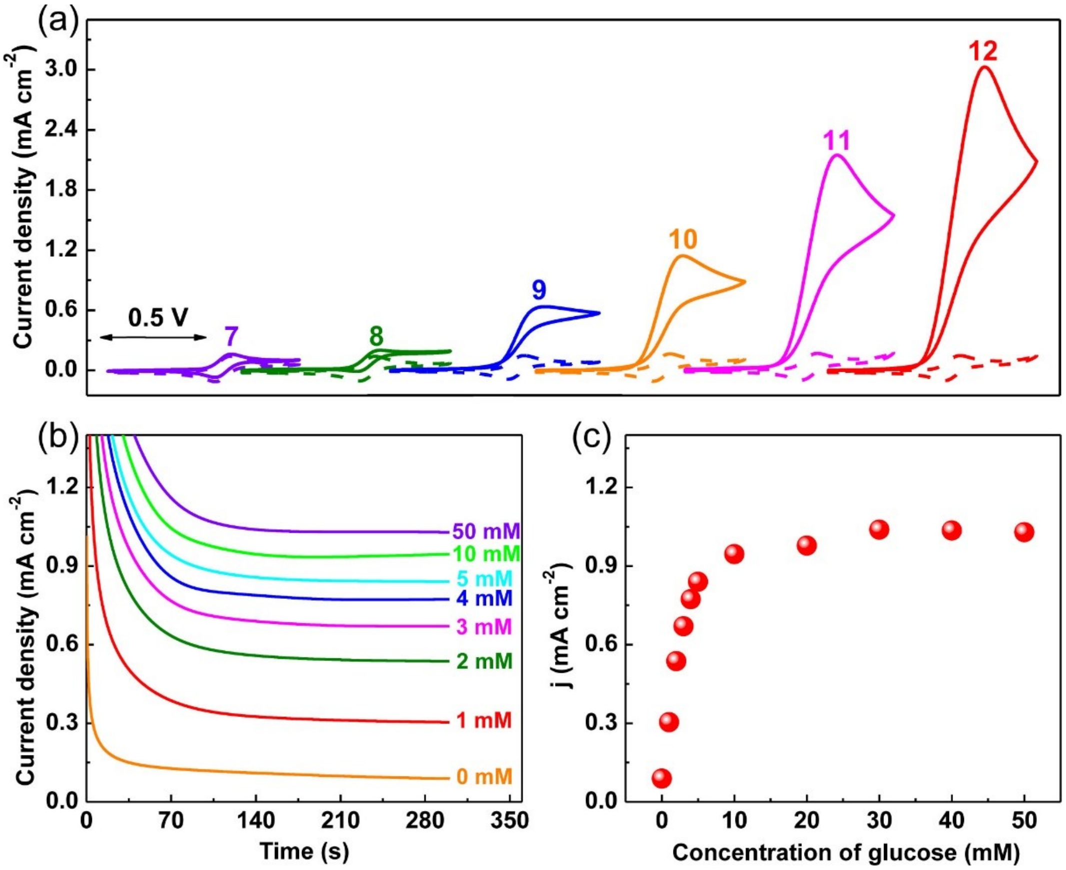

Fig. S7 Catalytic oxidation properties of glucose by ACT. (a) Catalytic CVs of 5 mM ACT in the absence (dashed) and presence (solid) of 10 mM glucose at various pH values. Experiments were performed using a GCE in 0.04 M B-R buffer at a scan rate of 50 mV s^{-1}. (b) CA curves of 5 mM ACT in the absence and presence of glucose with different concentrations. Experiments were performed using a GCE in 0.04 M B-R buffer (pH 12.0) with an applied potential 0.8 V vs. Ag/AgCl. (c) Dependence of the catalytic currents on concentrations of glucose.

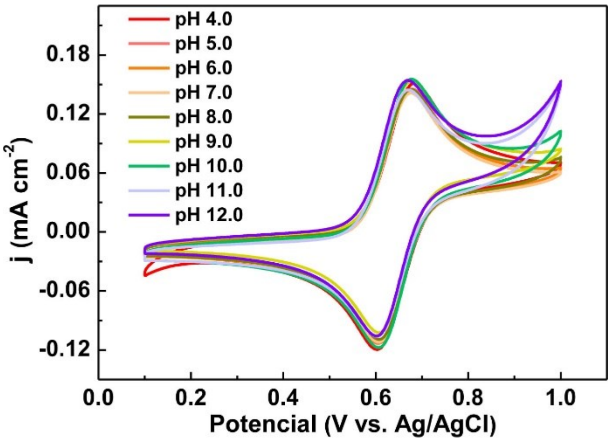

Fig. S8 CVs of 1 mM ACT in the absence of glucose in 0.04 M B-R buffer solution under different pH values at a scan rate of 50 mV s^{-1}.

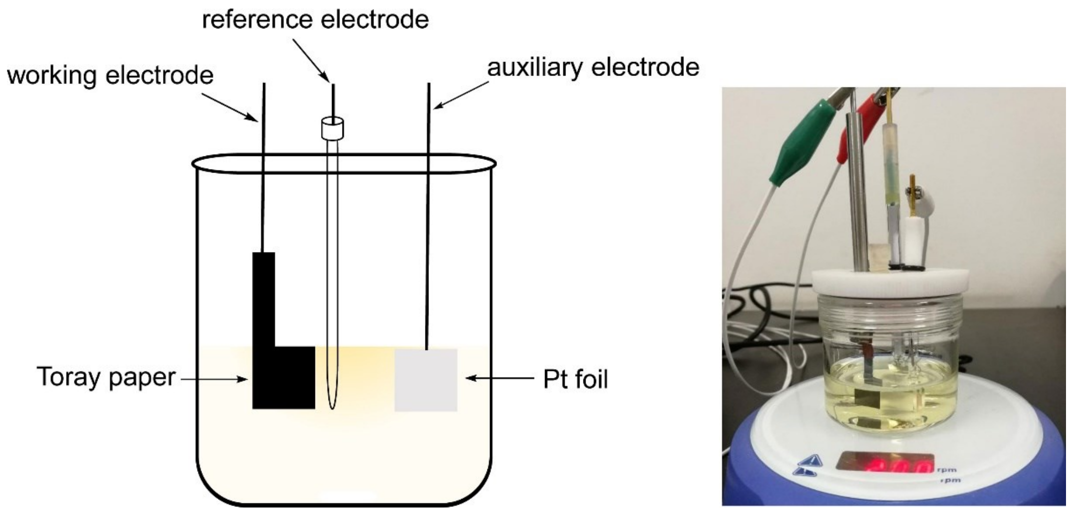

Fig. S9 Diagram (left) and digital photograph (right) of experimental setup for the 72 h bulk electrolysis of 50 mM glucose with 5 mM ACT in 0.04 M B-R buffer (pH 7.0, 9.0, and 12.0) at 0.8 V *vs*. Ag/AgCl and room temperature.

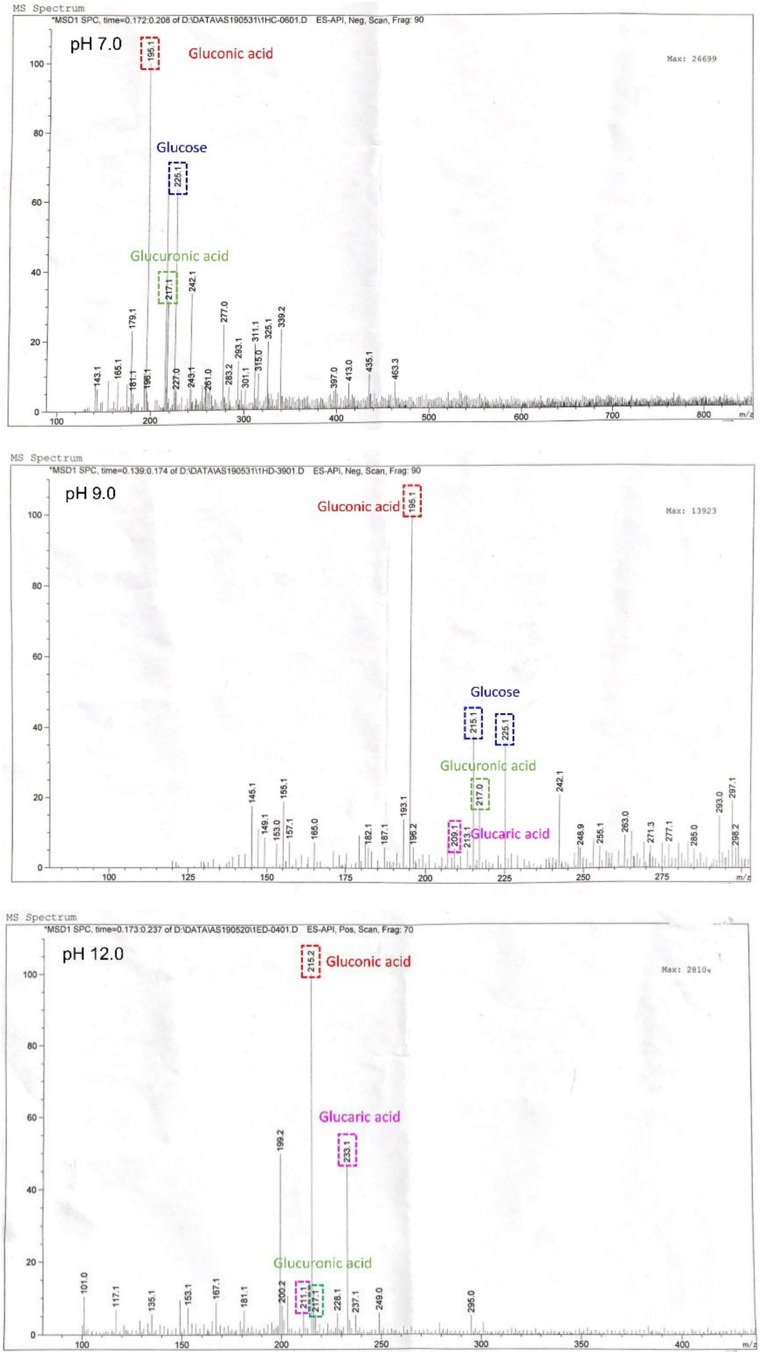

Fig. S10 Mass spectrometry results for electrolysis product solution at different pH. (ESI) *m/z* (%): 195.1 [M1-H]$^-$ (M1=196.1, gluconic acid), 214.2 [M1+NH$_4$]$^+$ (M1=196.1, gluconic acid), 217.1 [M2+Na]$^+$ (M2=194.1, glucuronic acid), 225.1 [M3+COOH]$^-$, (M3=180, glucose), 215.1 [M3+Cl]$^-$, (M3=180, glucose), 225.1 [M3+COOH]$^-$ (M3=180, glucose), 209.1 [M4-H]$^-$ (M4=210.1, glucaric acid), 211.1 [M4+H]$^-$ (M3=210.1, glucaric acid), 233.1 [M4+Na]$^+$, (M3=210.1, glucaric acid).

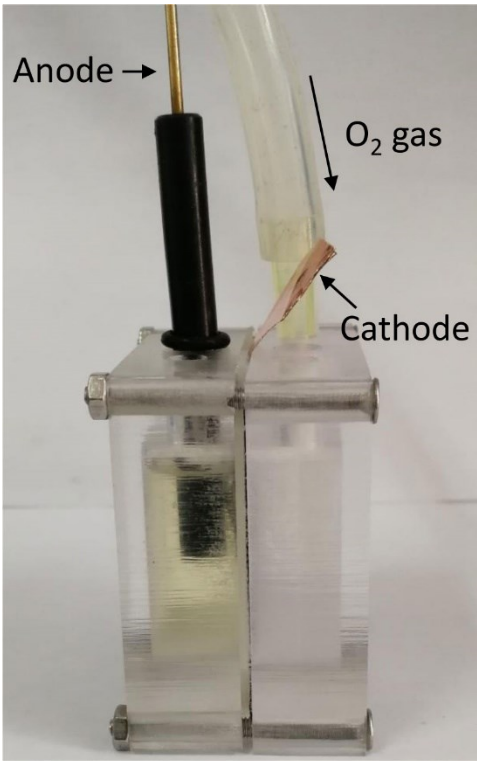

Fig. S11 Digital photograph of the constructed glucose/O_2 fuel cell.

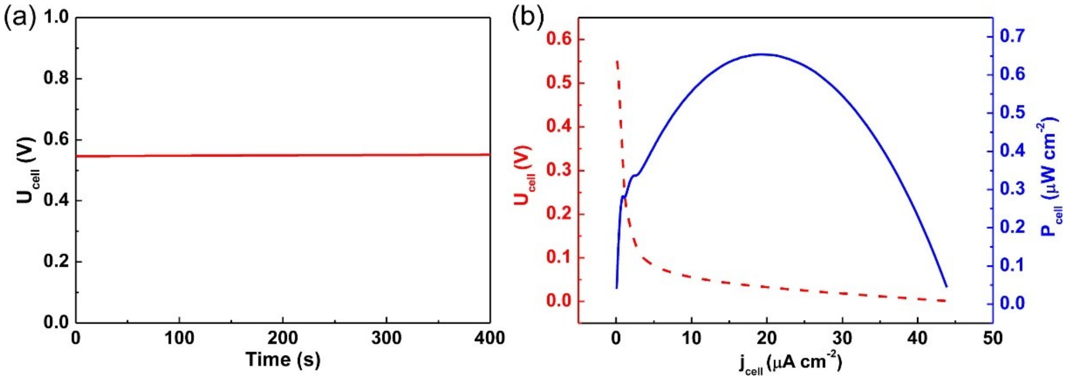

Fig. S12 (a) OCP of the GFC in the absence of ACT. (b) Dependence of the U_{cell} and P_{cell} on the j_{cell} in the absence of ACT.

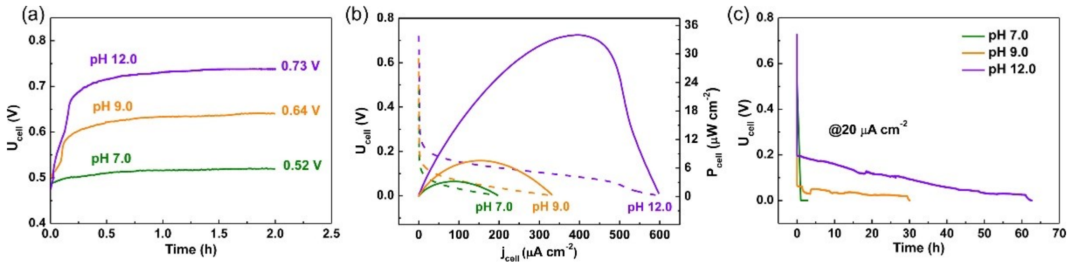

Fig. S13 (a) OCP, (b) dependence of the U_{cell} and P_{cell} on the j_{cell}, and (c) galvanostatic discharge curves of GFCs at different pH values.

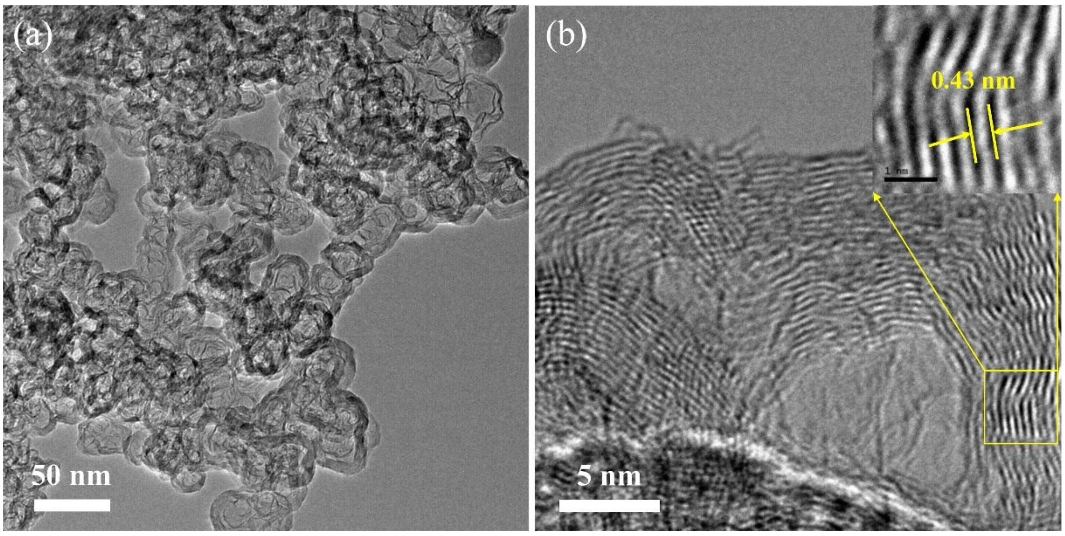

Fig. S14 (a) TEM and (b) HRTEM images of the conducting carbon black.

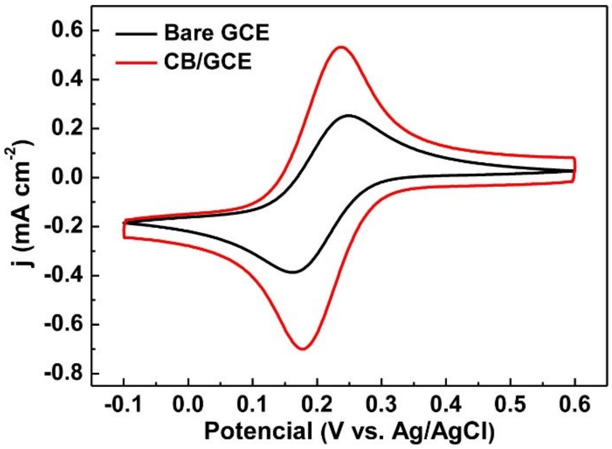

Fig. S15 CV curves of bare GCE and carbon black modified GCE (CB/GCE) with 5 mM $[Fe(CN)_6]^{3-/4-}$ in 0.1 M KCl solution at a scan rate of 50 mV s^{-1}. Both electrodes exhibit a well-defined redox peak. Note that CB/GCE shows higher faradaic current and lower peak-to-peak separation (ΔE_p) value than those of bare GCE, indicating higher electroactive area and faster electron transfer kinetics of CB/GCE than bare GCE.

Table S1 Comparison of electrocatalysis performance of glucose by TEMPO derivatives in 0.04 M B-R buffer (pH 7.0). Data come from Fig. 1 in the manuscript. Catalytic current was calculated at 1.0 V (vs. Ag/AgCl).

Catalysts	E'^0 (V)	I_{cat} (mA cm^{-2})	Reversibility
TEMPO	0.54	0.045	Reversible
CH_3O-TEMPO	0.63	0.075	Reversible
HO-TEMPO	0.63	0.083	Reversible
O=TEMPO	-	0.015	Irreversible
HOOC-TEMPO	0.59	0.045	Reversible
ACT	0.64	0.127	Reversible

Table S2 Cell performance using bare GCE anode and air-breathing Pt cathode under different operating conditions.

pH value	OCP (V)	P (μW cm^{-2})	j (μA cm^{-2})
7.0	0.52	3.2	197.7
9.0	0.64	7.6	332.5
12.0	0.73	34.3	603.7

Table S3 Performance comparison of the biofuel cells based on enzymatic and organic catalysts.

Anodic catalyst	Cathodic catalyst	Open circuit potential (V)	Maximum current density (μA cm^{-2})	Maximum power density (μW cm^{-2})	Ref.
ACT	**Pt/C**	**0.73**	**973.3**	**100**	**this work**
GOx	BOD	0.43	-	28	3
GOx	Pt/Au	0.34	1250	54.5	4
GOx	Lac	0.6	50	6	5
GOx	Lac	0.53	-	8.15	6
G6PDH	Hexokinase	0.62	270.8	28.28	7
GOx	Lac	0.5	160	21	8
GOx/Cat	Lac	0.41	169.7	40.7	9
GOx	Pt/C	0.48	710	50.7	10
GOx	PPO	0.32	-	40.8	11
GOx	Lac	0.6	-	103	12
GOx	Pt/C	0.94	ca. 310	120	13
Cellulase/GDH	Lac	0.75	ca. 700	128	14
GOx	BOD	0.49	100	13	15
ADH/AlDH	BOD	ca. 0.5	ca. 130	33.4 ± 4.5	16

Abbreviation:

ACT: 4-acetamido-2,2,6,6-tetramethyl-1-piperidine N-oxyl

PPO: polyphenol oxidase

GDH: glucose dehydrogenase

MPP: maltodextrin phosphorylase

ADH: alcohol dehydrogenase

GOx: glucose oxidase

Cat: catalase

Lac: laccase

BOD: bilirubin oxidase

AlDH: aldehyde dehydrogenase

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