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A compartment-less nonenzymatic glucose–air fuel cell with nitrogen-doped mesoporous carbons and Au nanowires as catalysts

**Mi Chu, Yijia Zhang, Lu Yang, Yueming Tan*, Wenfang Deng, Ming Ma, Xiaoli Su,
Qingji Xie* and Shouzhao Yao**

Key Laboratory of Chemical Biology and Traditional Chinese Medicine Research (Ministry of Education of China), College of Chemistry and Chemical Engineering, Hunan Normal University, Changsha 410081, China

Email: tanyueming0813@126.com (Y. Tan); xielj@hunnu.edu.cn (Q. Xie)

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Experimental

Reagents. Oleylamine was purchased from Sigma-Aldrich, $\text{HAuCl}_4 \cdot 4\text{H}_2\text{O}$, aniline, oleic acid, $(\text{NH}_4)_2\text{S}_2\text{O}_8$, and *n*-butylamine were purchased from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China). Phosphate buffer solution (PBS) consisting of 0.10 M KH_2PO_4 - Na_2HPO_4 + 0.15 M KCl (pH 7.4) served as the supporting electrolyte. All other chemicals were of analytical grade or better quality. Ultrapure water (Millipore, $\geq 18 \text{ M}\Omega \text{ cm}$) was used throughout.

Instrumentation. Electrochemical experiments were conducted on a CHI760C electrochemical workstation (CH Instrument Co., USA). A conventional three-electrode system included a glassy carbon electrode (GCE, diameter 5 mm) or a rotating ring-disk electrode (RRDE, Pine Research Instrumentation) coated with catalysts, a Pt auxiliary electrode and a saturated calomel reference electrode (SCE). All potentials reported in this paper are referred to the SCE. The cell voltage (U_{cell}) and current (I_{cell}) of the glucose-air fuel cell at varying external resistance loads (R_{e}) were dynamically monitored with the electrochemical noise (ECN) module of an Autolab PGSTAT30 electrochemical workstation (Netherlands).^{S1} Transmission electron microscopy (TEM) and high resolution TEM (HRTEM) studies were performed on a TECNAI F-30 high-resolution transmission electron microscopy operating at 300 kV. Scanning electron microscopy (SEM) studies were performed on a Hitachi S4800 scanning electron microscope with a field emission electron gun. X-ray diffraction (XRD) studies were performed on a PANalytical X'pert Pro X-ray Diffractometer. X-ray photoelectron spectroscopy (XPS) was recorded on a PHI QUANTUM 2000 X-ray photoelectron spectroscopic instrument. Surface area and pore size were determined by a

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Surface Area and Porosity Analyzer (Micromeritics Instrument Corp. ASAP2020).

Synthesis of N-*m*-C: 250 mg of a 40 wt% aqueous dispersion of SiO₂ nanoparticles (Ludox HS40) were mixed with 30 mL of aqueous solution containing 0.1 M H₂SO₄ and 0.033 M aniline under continuous stirring for about 30 min. Then 60 mg of (NH₄)₂S₂O₈ and 50 mg FeCl₃ were added to the above solution, followed by continuous stirring for about 24 h. The precipitates were collected by centrifugation, washed with water, and finally dried at 60 °C for 12 h. Then, the resulting products were carbonized under flowing argon at 900 °C for 4 h. Finally, the resulting products were etched in excessive 20 wt% hydrofluoric acid to remove the silica template. The resulting products were collected by centrifugation, washed with water and finally dried at 60 °C for 12 h.

Synthesis of AuNWs. A mixture of 2 mL hexane, 0.2 g HAuCl₄·4H₂O, and 2 mL oleylamine was added to the mixture of 10 mL oleic acid and 8 mL oleylamine at 80 °C under vigorous magnetic stirring. Magnetic stirring was stopped after 5 min, and the solution was kept steady at this temperature for 4 h. The AuNWs were precipitated out by adding ethanol and then centrifugation. The solid product was dispersed in *n*-butylamine and kept under stirring for 3 days and then collected by centrifugation.^{S2} The precipitate was re-dispersed in methanol by sonicating for 15 min and then separated by centrifugation. This procedure was repeated three times. The final samples were dispersed in ethanol for further characterization and electrochemical studies.

Electrochemical studies. The GCE was polished with 1 and 0.05 μm alumina slurry sequentially and then washed ultrasonically in water and ethanol for 15 min, respectively. Then, the GCE was subjected to potential cycling (-0.2 to 1.0 V, 10 mV/s) in 0.10 M aqueous

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HClO₄ until reproducible cyclic voltammograms were obtained.

5 mg N-*m*-C catalyst was dispersed in 5 ml ethanol, and then ultrasonicated to form a uniform black ink. 40 μL N-*m*-C-contained ethanol solutions were cast-coated on GCE or RRDE and air-dried, and thus the catalyst loadings were 204 μg cm⁻². 15 μL of Nafion solution (0.1 wt%) was placed on the surface of the above N-*m*-C modified GCE or RRDE and air-dried before electrochemical experiments. For the RRDE measurements, the disk electrode was scanned cathodically at a rate of 5 mV s⁻¹ and the ring potential was kept at 0.7 V vs SCE. 0.1 M PBS (pH 7.4) saturated with oxygen by bubbling O₂ for 30 min served as the supporting electrolyte. A flow of O₂ was maintained over the electrolyte solution for continued O₂ saturation during electrochemical scan. The percentage of H₂O₂ and the electron transfer number (*n*) were determined by the followed equations:^{S3}

$$\text{H}_2\text{O}_2\% = 200 \times \frac{i_r / N}{i_d + i_r / N}$$

$$n = 4 \times \frac{I_d}{i_d + i_r / N}$$

where *I_d* is the disk current, *I_r* is the ring current and *N* is the current collection efficiency of the Pt ring. *N* was determined to be 0.38 from the reduction of K₃Fe[CN]₆, well consistent with the manufacturer's value (0.37).

AuNWs were dispersed in ethanol and adjusted to 1 mg mL⁻¹ based on the inductively coupled plasma-atomic emission spectroscopy (ICP-AES) measurements. 140 μL AuNWs-containing ethanol solutions were cast-coated on GCE and air-dried, and thus the Au loading was 710 μg cm⁻². 15 μL of Nafion solution (0.1 wt%) was placed on the surface of the above AuNWs modified GCE and air-dried before electrochemical experiments. Prior to

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electrochemical experiments, AuNWs modified GCE was subjected to continuous potential cycling (0 to 1.5 V, 50 mV s⁻¹) in 0.50 M aqueous H₂SO₄ until cyclic voltammograms became reproducible.

The compartment-less nonenzymatic glucose-air fuel cell was fabricated as follows. Anode is AuNWs modified GCE, and cathode is N-*m*-C modified GCE. The electrolyte is 0.1 M PBS (pH 7.4) containing 5 mM glucose and 0.15 M KCl. The performance of the glucose-air fuel cell was investigated by the ECN device.

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Table S1. Performance comparison among various nonenzymatic and enzymatic glucose-air fuel cells.

Anodic catalyst	Cathodic catalyst	Open-circuit potential (V)	Short-circuit current density (mA cm ⁻²)	Maximum power density (μW cm ⁻²)	References
AuNWs	N- <i>m</i> -C	0.520	0.490	64.3	This work
Pt-carbon nanotubes	Pt-carbon nanotubes	0.273	11	0.768	S4
Raney- Pt	Pt	0.016	0.698±0.010	4.4±0.2	S5
Pt-Au alloy nanoparticles	Laccase	0.4	0.1	16	S6
Pt-Ni	Pt-Al	~0.45	~0.023	1.32	S7
Activated platinum	Single-walled carbon nanotubes	0.192	0.18	3.4	S8
Glucose oxidase	Laccase	0.195	0.1098	28.4	S9
glucose dehydrogenase	Pt	0.55	0.13	32	S10
Glucose oxidase	Laccase	-	0.03	1.38	S11

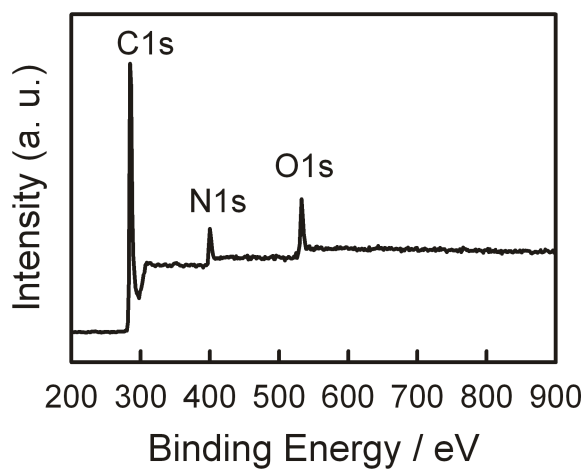


Fig. S1 XPS spectrum of N-*m*-C.

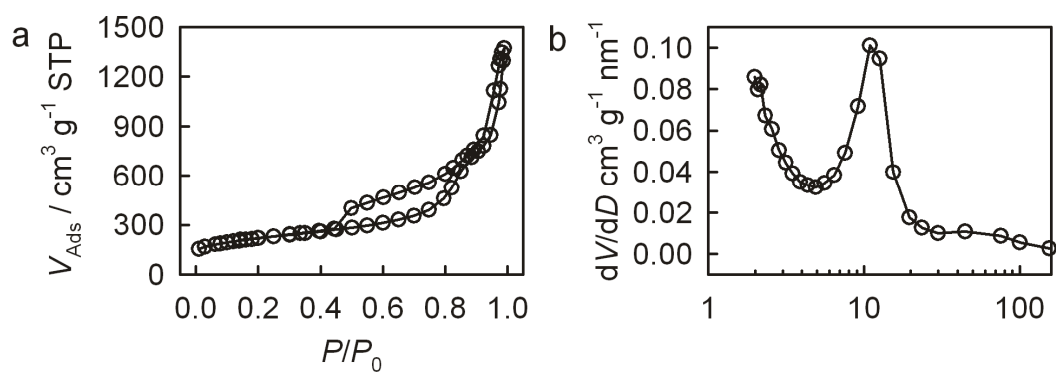


Fig. S2 Nitrogen adsorption/desorption isotherm (a) and pore size distribution curve (b) of N-*m*-C.

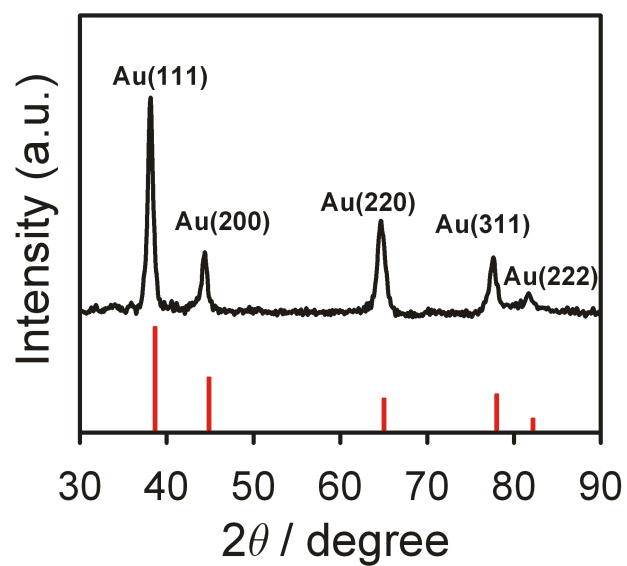


Fig. S3 XRD pattern of AuNWs.

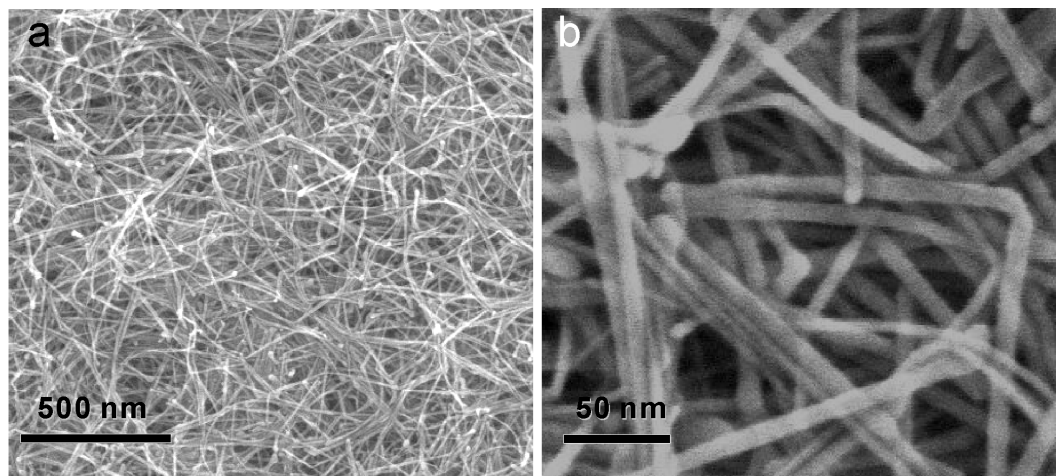


Fig. S4 SEM images of AuNWs.

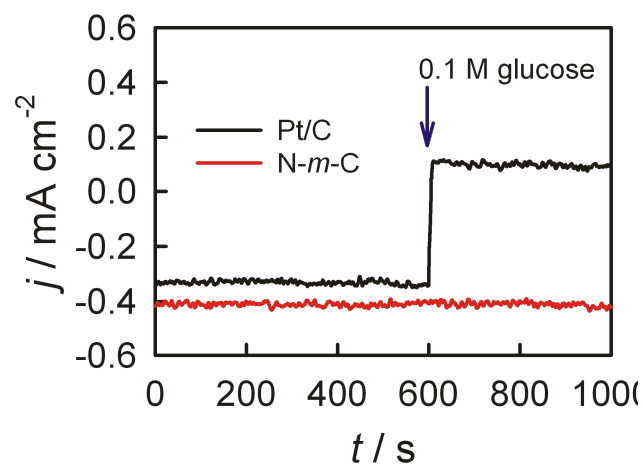


Fig. S5 Chronoamperometric responses to injection of 0.1 M glucose into stirred air-saturated 0.1 M PBS (pH 7.4) at Pt/C and N-*m*-C catalysts modified electrodes. Applied potential: 0 V.

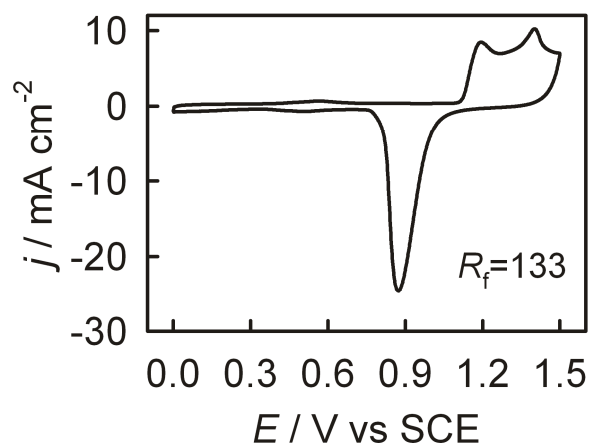


Fig. S6 Cyclic voltammograms of AuNWs modified GCE in 0.5 M H_2SO_4 aqueous solution.

Au loadings: $710 \mu\text{g cm}^{-2}$.

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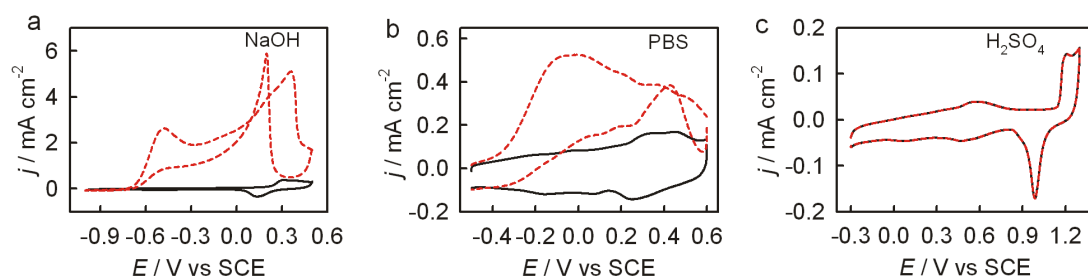


Fig. S7. (a) Cyclic voltammograms of the Au network film electrode in 1 M NaOH aqueous solution (a), 0.1 M phosphate buffer solution (b), and 1 M H₂SO₄ aqueous solution (c) containing 0 (blank curve) and 5 mM (red curve) glucose at 10 mV s⁻¹.

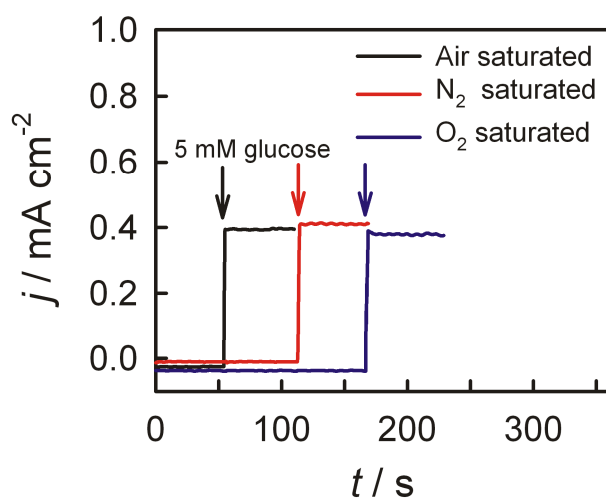


Fig. S8 Chronoamperometric responses at 0 V to injections of 5 mM glucose into air, N₂, and O₂-saturated PBS (pH 7.4, containing 0.15 M Cl⁻) at the network film electrode.

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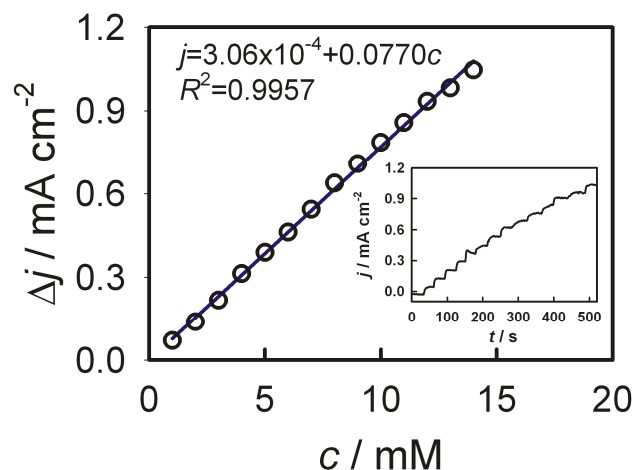


Fig. S9 Calibration curve and time-dependent current response (inset) for Au network film electrode at 0 V to successive injections of 1 mM glucose (final concentration) into stirred PBS (pH 7.4, containing 0.15 M Cl⁻) under air atmosphere. The sensitivity at the network film electrode toward glucose oxidation is 77.0 $\mu\text{A cm}^{-2} \text{ mM}^{-1}$, which is higher than those at nanoporous noble metal film electrodes reported by Park et al. (9.6 $\mu\text{A cm}^{-2} \text{ mM}^{-1}$)^{S12}, Xie et al. (47.2 $\mu\text{A cm}^{-2} \text{ mM}^{-1}$)^{S13}, Wang et al. (10.8 $\mu\text{A cm}^{-2} \text{ mM}^{-1}$)^{S14}, Zhao et al. (13.7 $\mu\text{A cm}^{-2} \text{ mM}^{-1}$)^{S15}, and Su et al. (7.266 $\mu\text{A cm}^{-2} \text{ mM}^{-1}$)^{S16}.

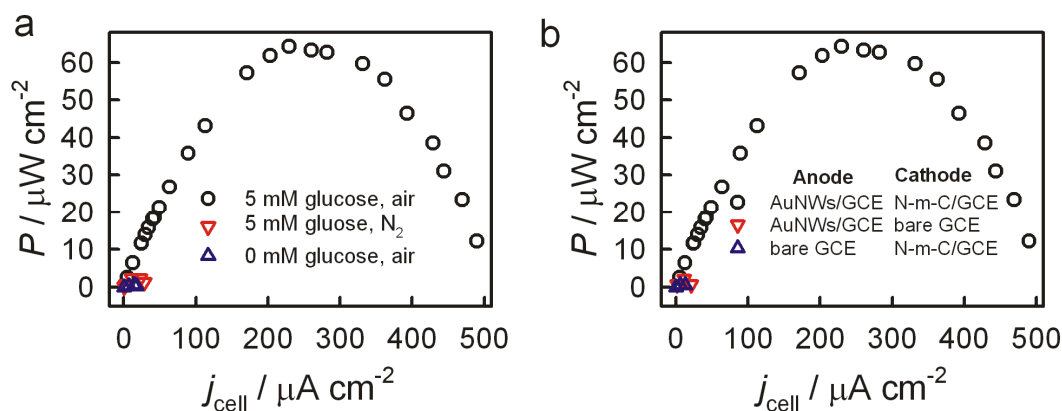


Fig. S10 (a) Power density vs current density measured in solutions of PBS exposed to air, 5 mM glucose in PBS exposed to air, or 5 mM glucose in N₂-purged PBS. (b) Power density vs current density measured in PBS containing 5 mM glucose under air atmosphere with AuNWs/GCE as anode and N-*m*-C/GCE as cathode, AuNWs/GCE as anode and bare GCE as

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cathode, or bare GCE as anode and N-m-C/GCE as cathode.

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