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Graphene oxide nanoribbons greatly enhance extracellular electron transfer in bio-electrochemical systems

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1. Preparation of graphene oxide nanoribbons (GONRs)

The multiwalled carbon nanotubes (MWCNTs) purchased from Nanoport Co. (Shenzhen, China) have an average diameter of 10-30 nm and a length of 5~15 μm . The principles and the method to prepare GONRs by lengthwise cutting and unravelling of MWCNTs were described by Kosynkin et al.¹ In brief, the MWCNTs (150 mg) were suspended in H_2SO_4 (150 ml) for 12 h and then added with KMnO_4 (750 mg). The suspension was stirred for 1 h at 20°C. The reaction was then heated in a water bath at 55°C for 30 min, and 65°C for 4 h. The reaction was completely when the mixture became yellow/brown, and then the temperature increased to 70°C in 10 min. To stop the reaction, the suspension was removed from the water bath, cooled to room temperatures and carefully poured onto 400 ml of ice containing 5 ml of 30% H_2O_2 . The mixture was filtrated through a PTFE membrane, the solid was cleaned by deionized water and then ether. The final product was dried at 60°C and the GONRs were prepared.

2. Preparation of the GONRs-modified carbon paper

The GONRs were solubilized by mixing 10 mg of GONRs with 50 mg of cetyltrimethyl ammonium bromide (CTAB) in 25 ml of tetrahydrofuran (THF). To obtain a stable GONRs suspension, the mixture was sonicated for 30 min. The black suspension was

centrifuged at 12,000 rpm for 10 min. The clear supernatant liquid containing unbound CTAB was discarded. The residue was re-suspended in 25 ml THF by sonication. Modification of carbon paper with GONRs was conducted through the electrophoretic deposition. Two pieces of carbon paper with the same areas (Toray Co., Japan) were used as electrodes, which were kept 5 mm apart in an electrophoretic cell containing GONRs suspension in THF. A dc voltage of 30 V was applied for 10 min and a film of GONRs was formed in the anode. The modified carbon paper was then rinsed with deionized water and dried at room temperatures. To connect the carbon electrode to the copper wire, silver conductive adhesive was used. After thermofixation in 120°C for 4 h, the connected portion was protected by epoxy.

3. Characterization

Transmission electron microscopy (TEM) images of the MWCNTs and the GONRs were obtained with a JEOL-2010 high-resolution TEM. Scanning electron microscopy (SEM) imaging was performed on a Sirion 200 SEM. X-ray photoelectron spectroscopy (XPS) analysis was performed with an ESCALAB 250 instrument with a monochromatic Mg K α X-ray source. A commercial atomic force microscope (AFM) (Nanoscope IIIa; Digital Instruments Inc., US), equipped with a J scanner was used to measure the morphology of the samples. A Si₃N₄ tip (Nanoprobes, Digital Instruments Inc.) was used in the contact mode.

4. Operation of electrochemical cells (ECs) and microbial fuel cells (MFCs)

Shewanella oneidensis MR-1 was firstly cultivated in Luria-Bertani medium, then transferred into the EC or MFC systems containing minimal salts medium as reported by Marsili et al.²

For ECs tests, ECs (50 ml volume) made of glass were used. A piece of carbon paper electrode (6 cm²), platinum wire and Ag/AgCl (KCl sat.) electrode were used as the working, counter and reference electrodes, respectively. A constant potential of 0.324 V vs. SHE was applied to the working electrode with a CHI 1030A potentiostat. Sodium lactate (~14 mM) was injected as the electron donor 10 h later after the inoculation.

For MFCs tests, two-bottle configuration MFCs were constructed with glass bottles separated by a cation exchange membrane (CMI7000, Membranes International Inc., US). Each bottle had a volume of 120 ml. Pieces of carbon paper (9 cm² for each piece) were used both as anodes and cathodes. Either pure culture (*S. oneidensis* MR-1) or pre-acclimated mixed cultures from another MFC was inoculated. The anode chamber was fed with 100 ml of medium containing 0.1 g L⁻¹ of acetate in 50 mM phosphate buffer solution (mixed-culture-inoculated MFCs) or ~14 mM sodium lactate in minimal salts medium (*Shewanella*-inoculated MFCs) with 10 ml of microbes, while the cathode chamber contained 110 ml of 0.1 M K₃Fe(CN)₆ as the electron receptor. The output

voltage was collected using Agilent 34970A Data Acquisition/Switch Unit (with an external resistance of 100 Ω for the *S. oneidensis* MR-1-inoculated MFCs and 1000 Ω for the mixed culture-inoculated MFCs). Polarization curves were obtained by measuring the stable voltage generated at various external resistances and then used to evaluate the maximum power density.³ After each fed-batch cycle, the MFCs were drained, and refilled with substrate solution, and sparged with nitrogen for 30 min. The mixed culture-inoculated MFCs were run for at least two complete operation cycles, each of which took ~2 days.

5. Electrochemical analysis

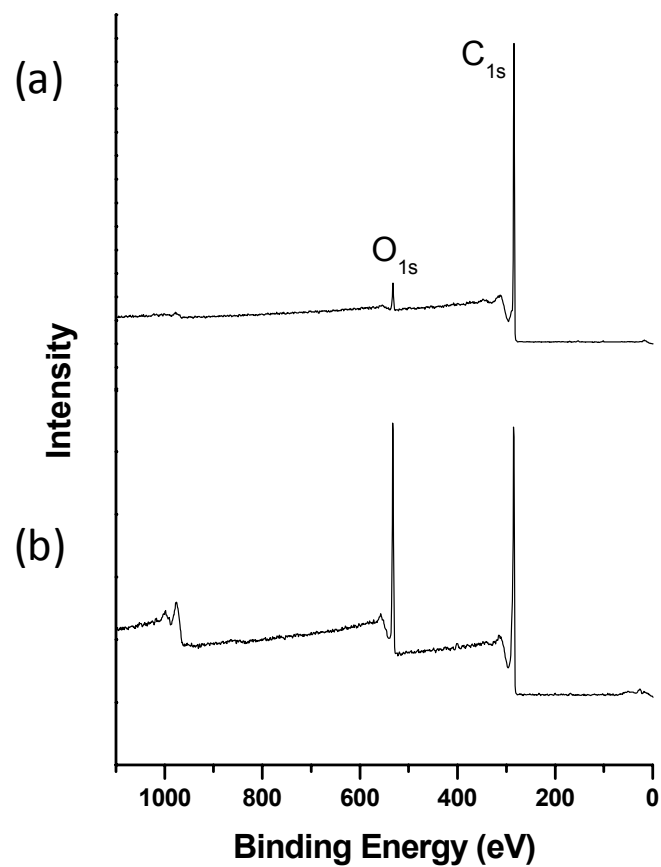
Electrochemical measurements were conducted with a CHI 660C potentiostat. The electrochemical active surface area of different anode materials was estimated by cyclic voltammetry (CV) using a ferrocyanide solution. The ferrocyanide solution (5 mM, 0.2 M Na₂SO₄ as the supporting electrolyte) was placed in an electrochemical cell, which contained a piece of raw carbon paper or GONRs-modified carbon paper (working electrode, 1 cm²), a platinum wire (counter electrode) and an Ag/AgCl reference electrode. CV tests were carried out at a scan rate of 50 mV s⁻¹ and over a potential range of 0 to 1.0 V (vs. SHE). The electrochemical active surface area was calculated using the following equation:⁴

$$t_p = 0.4463 \times 10^{-8} \left(\frac{F^2}{RT} \right)^{1/2} n^{3/2} A D_o^{1/2} C_o^* \nu^{1/2} \quad (1)$$

where $n = 1$ is the number of electrons transferred, $F = 96485$ C mol⁻¹ is Faraday's constant, $R = 8.314$ J mol⁻¹ K⁻¹ is the gas constant, $T = 298$ K is the temperature, and C_o^* (mol L⁻¹) is the initial riboflavin concentration, and $\nu = 0.05$ V s⁻¹ is the scan rate. The diffusion coefficient ($D_o^{1/2}$) of ferrocyanide was calculated as 3.67×10^{-6} cm² s⁻¹ using equation 1 with an Au disk electrode as the working electrode ($A = 0.0314$ cm²).

In the ECs tests, CV analysis was performed before and after sodium lactate injection at a scan rate of 10 mV s⁻¹ and over a range of -0.33 to 0.23 V (vs. SHE).

Before the *Shewanella* MFC tests, electrochemical impedance spectroscopy (EIS) was conducted in an electrochemical cell containing 0.1 M KCl with 10 mM [Fe(CN)₆]^{3-/4-} or minimal salt medium with 14 mM sodium lactate. For [Fe(CN)₆]^{3-/4-} tests, carbon paper with 1 cm² (geometric area) was used as the working electrode and it would not be used in further experiments. Other experimental conditions were the same as the CV tests as mentioned above. When the *Shewanella*-inoculated MFC tests were completed, the anode electrodes were carefully transferred to the electrochemical cell containing fresh medium with sodium lactate, then EIS tests were conducted again. The EIS parameters were as follows: initial potential was set as an open circuit potential, high frequency = 100000 Hz, low frequency = 0.01 Hz, amplitude = 5 mV.



(c)

XPS Atomic Concentrations (%)

	Raw carbon paper	GONRs modified carbon paper
C	93.65	72.98
O	5.65	26.19
N	0.7	0.83

Figure S1. (a) XPS survey for the raw carbon paper and (b) the GONRs-modified carbon paper, and (c) their compositions determined by XPS.

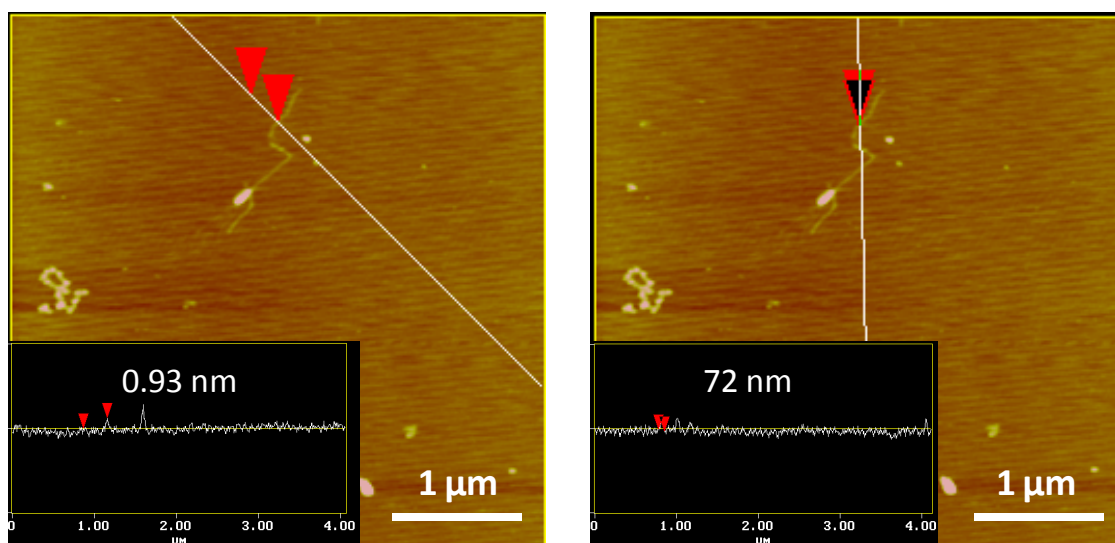


Figure S2. AFM images of a single GONR, the inset images show the height and the width data.

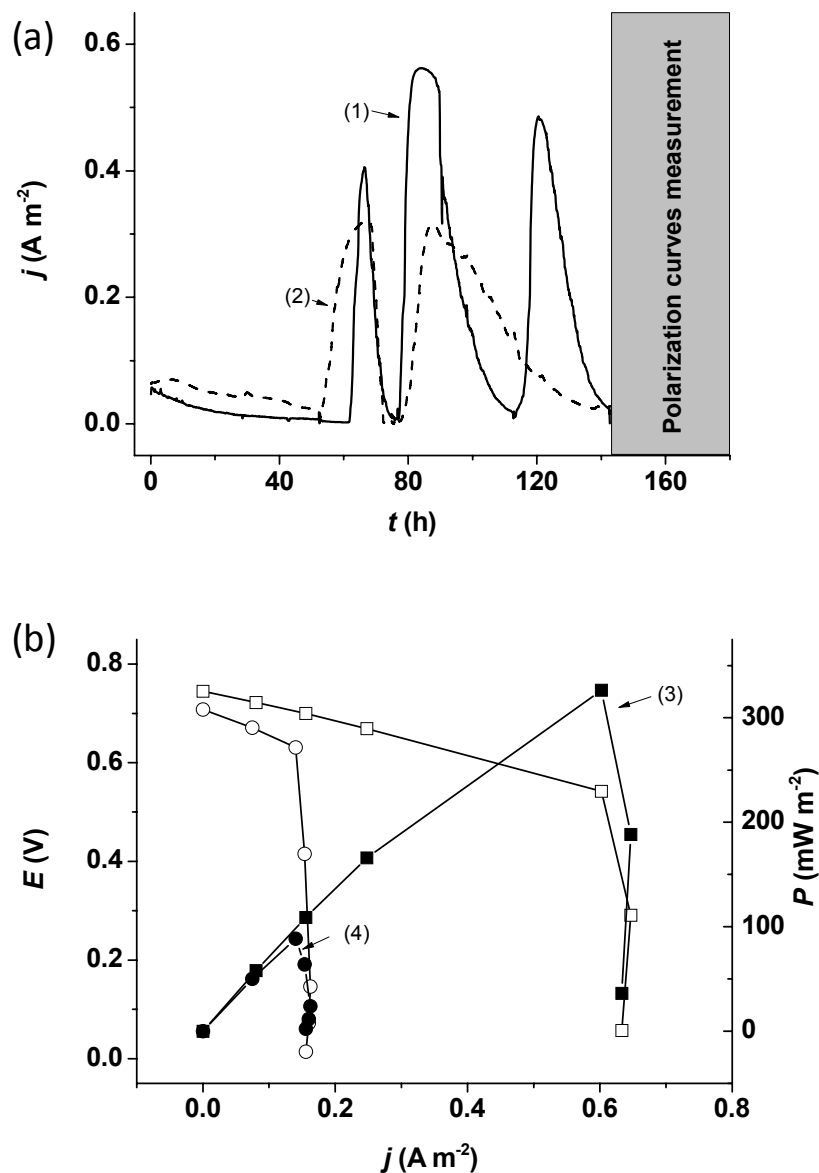


Figure S3. Current generation by the mixed culture-inoculated MFCs (a) with the following anodes: (1) GONRs, (2) raw carbon paper. Polarization (open symbols) and power density (closed symbols) curves for MFCs (b) with GONRs (3) and control (4) anodes. Current and power densities were calculated based on the geometric surface areas.

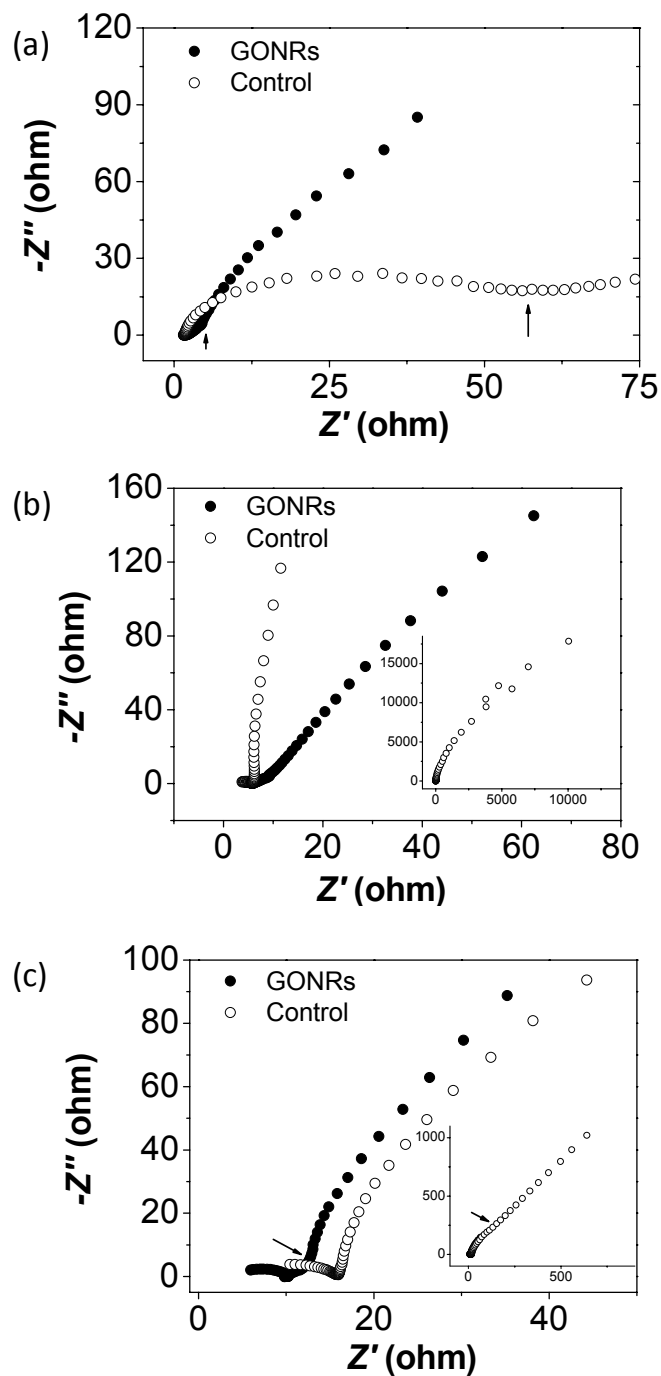


Figure S4. EIS Nyquist plots of GONRs electrode and control electrode in (a) 0.1 M KCl with 10 mM $[\text{Fe}(\text{CN})_6]^{3-/4-}$, (b) minimal salts medium with 14 mM sodium lactate in the absence of bacteria and (c) minimal salts medium with 14 mM sodium lactate when *Shewanella* biofilm was formed after MFCs tests. The arrows indicate the point that the system becomes a diffusion control from a kinetic control.

Table S1 Current density and power density of the MFCs inoculated with pure/mixed cultures

Microbe	Anode material	Maximum current density / A m ⁻²	Maximum power density / mW m ⁻²
<i>S. oneidensis</i> MR-1 ^[a]	GONRs network	0.30	34.2
	control	0.075	6.8
mixed cultures ^[b]	GONRs network	0.523 ^[c]	326
	control	0.315 ^[c]	88

[a] External resistance: 100 Ω

[b] External resistance: 1000 Ω

[c] Average of two cycles

References

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