



# Tailoring hierarchically porous graphene architecture by carbon nanotube to accelerate extracellular electron transfer of anodic biofilm in microbial fuel cells



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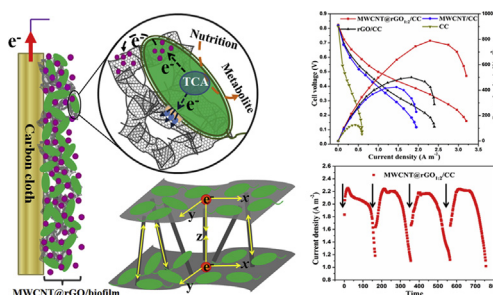
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## HIGHLIGHTS

- A hierarchically porous rGO skeleton architecture is tailored by inserting MWCNTs.
- MWCNT@rGO hybrid warrants rich bacterial growth and 3D electron transfer pathway.
- Biofilm accelerates the direct electrochemistry by raising flavin concentration.
- MWCNT@rGO/biofilm anode achieves a 6-fold higher power density over carbon cloth.

## GRAPHICAL ABSTRACT



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## ABSTRACT

To overcoming their respective shortcomings of graphene and carbon nanotube, a hierarchically porous multi-walled carbon nanotube@reduced graphene oxide (MWCNT@rGO) hybrid is fabricated through a versatile and scalable solvent method, in which the architecture is tailored by inserting MWCNTs as scaffolds into the rGO skeleton. An appropriate amount of inserted 1-D MWCNTs not only effectively prevent the aggregation of rGO sheets but also act as bridges to increase multidirectional connections between 2-D rGO sheets, resulting in a 3-D hierarchically porous structure with large surface area and excellent biocompatibility for rich bacterial biofilm and high electron transfer rate. The MWCNT@rGO<sub>1:2</sub>/biofilm anode delivers a maximum power density of 789 mW m<sup>-2</sup> in *Shewanella putrefaciens* CN32 microbial fuel cells, which is much higher than that of individual MWCNT and rGO, in particular, 6-fold higher than that of conventional carbon cloth. The great enhancement is ascribed to a synergistic effect of the integrated biofilm and hierarchically porous structure of MWCNT@rGO<sub>1:2</sub>/biofilm anode, in which the biofilm provides a large amount of bacterial cells to raise the concentration of local electron shuttles for accelerating the direct electrochemistry on the 3-D hierarchically porous structured anodes.

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## 1. Introduction

The deepening energy crisis and environmental pollution have triggered substantial research enthusiasm to develop new

sustainable green energy techniques. Microbial fuel cells (MFCs) is perceived as a promising renewable power source to harvest electricity from organic matter or/and organic wastes by microorganisms (biocatalysts), rendering great potential to produce electric power while cleaning environment [1–4]. However, the practical application of MFCs is greatly impeded by their lower power density than the conventional fuel cells, which is mainly due to the sluggish extracellular electron transfer (EET) from exoelectrogens to anodes and low bacterial loading. Electroactive biofilms grown on electrodes play a crucial role in bacterial EET [5]. To address this challenge, a tremendous amount of research have been carried out to develop various nanostructured anode materials with high surface area and electrical conductivity for enhanced bacterial adhesion/growth and interfacial electron transfer [5–19].

One-dimensional (1-D) carbon nanotube (CNT) and two-dimensional (2-D) graphene are the two superior nanostructured carbonaceous electrode materials by virtue of their good conductivity, outstanding electrochemical stability and excellent biocompatibility. CNT generally shows a good direct electrochemical property for many electrocatalytic reactions including bioelectrochemistry [20] but it's hard to provide 3-D architecture with enough interspace for bacterial growth. Alternatively, 2-D plane structured graphene can theoretically form 3-D inflated architecture through suitable crosslinking between each other. Chemical/thermal reduction of graphene oxide (GO) prepared from oxidizing graphite is one of the most convenient and cost-effective method for mass-production of graphene-based materials. However, GO nanosheets are easy to form irreversible agglomerates during reduction process due to their strong van der Waals interactions [21–25], thus leading to a heavy loss of intrinsic ultrahigh surface area and consequently fade the outstanding electrochemical performance of graphene [26]. Very recently, the introduction of 1-D CNT to 2-D graphene sheets has been proposed to inhibit the graphene re-stacking for improved utilization [27–30] while making complement to each other for overcoming their individual limitations. Chemical vapor deposition (CVD) [31–33], electrodeposition [34] and solvent methods [27–29,35–37] have been reported to fabricate 3-D CNT@graphene hybrid electrodes for energy conversion and storage such as supercapacitors [27,32], solar cells [28,34], lithium batteries [36,37] and fuel cells [33], electrocatalysis [35] but no microbial electrochemical systems. It is expected that 3-D hierarchically structured carbon materials could greatly boost MFC anode performance, considering their high surface area and rich porous network structure for improving microbial growth, electrolyte diffusion and electron transfer network, respectively [9,11–14,16].

Herein, a hierarchically porous multi-walled carbon nanotube-reduced graphene oxide (MWCNT@rGO) hybrid was fabricated in a facile and scalable solvent method to tailor a 3-D rGO skeleton/MWCNT pregnant architecture by inserting MWCNT into rGO stacks and further used as anode materials in *Shewanella putrefaciens* CN32 MFCs for the first time. The hierarchical morphologies and nanostructure of the hybrids and their bioelectrochemical performances were optimized by varying the input ratio of MWCNT to GO. A strong synergistic effect from these two nanostructured carbons in the hierarchically porous structure to greatly enhance EET is proposed, and the enhancement mechanism by the strengthened direct electrochemistry of anodic biofilm is confirmed by experimental results.

## 2. Experimental section

### 2.1. Preparation and characterization of MWCNT@rGO hybrids

The fabrication process of a hierarchically porous MWCNT@rGO

hybrid is shown in Fig. 1, in which GO was synthesized from purchased natural graphite (Aladdin Inc., Shanghai, China) via a modified Hummers method [38], followed by dispersing the obtained GO ( $2 \text{ mg mL}^{-1}$ ) and pristine MWCNT ( $2 \text{ mg mL}^{-1}$ , Aladdin Inc., Shanghai, China) in ethanol/water solution (1:1, v/v), respectively under sonication for 1 h and then mixing the as-prepared two dispersion solutions for another 1 h sonication to form a uniform MWCNT@GO dispersion. The resulted mixture was transferred into a Teflon-lined autoclave and maintained at  $180 \text{ }^\circ\text{C}$  for 12 h to form an MWCNT@rGO hydrogel. Finally, a fluffy aerogel was obtained from the hydrogel through a freeze-drying process. The morphologies and nanostructure of MWCNT@rGO hybrid aerogels were systematically investigated by varying the input ratio of MWCNT to GO as 2:1, 1:1, 1:2, 1:4 and 1:8, and the corresponding products were denoted as MWCNT@rGO<sub>2:1</sub>, MWCNT@rGO<sub>1:1</sub>, MWCNT@rGO<sub>1:2</sub>, MWCNT@rGO<sub>1:4</sub> and MWCNT@rGO<sub>1:8</sub>, respectively.

Powder X-ray diffraction (XRD) pattern was recorded on a XRD-7000 (Shimadzu, Japan) at 40 kV and 30 mA with Cu K $\alpha$  radiation ( $\lambda = 0.15406 \text{ nm}$ ) in the  $2\theta$  range from 5 to  $80^\circ$  with  $2^\circ/\text{min}$ . The morphology and microstructure were investigated by scanning electron microscopy (SEM, JEOL JSM-6510LV, Japan) and transmission electron microscopy (TEM, JEOL JEM-2100F, Japan). The Brunauer-Emmett-Teller (BET) specific surface area and porosity were evaluated by nitrogen sorption isotherm measured at 77 K using an automatic adsorption instrument NOVA 1200e (Quantachrome, Boynton Beach, Florida). The fluorescent emission spectrum analysis was executed at a RF-5301pc (Shimadzu, Japan) with the excitation wavelength of 440 nm.

### 2.2. MFC setup and operation

The bacterial culture, the setup and operation of the H-type dual-chamber MFCs used by us have been reported in our previous works [17,39]. In particular, the powdered materials were mixed with poly(tetrafluoroethylene) solution (1 wt%) to prepare a paste, then coated on both surfaces of carbon cloth (CC,  $1 \text{ cm} \times 1 \text{ cm}$ ) with a loading of about  $5 \text{ mg/cm}^2$  followed by drying at  $100 \text{ }^\circ\text{C}$  for 3 h. The as-prepared electrode was used as the anode and a carbon fiber brush was used as the cathode. Lactate with a final concentration of 18 mM was added into anolyte (M9 buffer,  $\text{Na}_2\text{HPO}_4$ ,  $6 \text{ g L}^{-1}$ ;  $\text{KH}_2\text{PO}_4$ ,  $3 \text{ g L}^{-1}$ ;  $\text{NH}_4\text{Cl}$ ,  $1 \text{ g L}^{-1}$ ;  $\text{NaCl}$ ,  $0.5 \text{ g L}^{-1}$ ;  $\text{MgSO}_4$ ,  $1 \text{ mM}$ ; and  $\text{CaCl}_2$ ,  $0.1 \text{ mM}$ ) as the sole electron donor and potassium ferricyanide was dissolved in catholyte (0.01 M phosphate buffer) as the terminal electron acceptor. The MFC was operated at room temperature with an external loading resistance ( $R$ ) of 1.5 k $\Omega$ , and the output voltage was recorded by a digital multimeter. At the steady-state of MFC, the polarization and power density curves were obtained by measuring the stable voltage generated at various external resistances (1–50 k $\Omega$ ). The surface morphology of the discharged anode was investigated in our previous work.

### 2.3. Electrochemical characterization

Cyclic voltammogram (CV), square wave voltammogram (SWV) and electrochemical impedance spectroscopy (EIS) experiments were performed on a CHI 660E electrochemical working station (CHI Instrument, Shanghai, China) in a three-electrode electrochemical cell (EC) consisted of a working electrode, a saturated calomel electrode (SCE) as reference electrode, and a titanium plate as counter electrode. Except otherwise stated, all potentials reported in this work were presented as SCE. SWV was scanned from  $-0.8$  to  $0 \text{ V}$  with a potential step of 4 mV, a frequency of 1 Hz, and an amplitude of 25 mV. EIS was performed over a frequency

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