

## Supporting information

### **GO/PEDOT modified biocathode promoting CO<sub>2</sub> reduction to CH<sub>4</sub> in microbial electrosynthesis**

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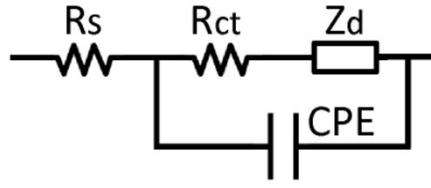
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## Preparation of graphene oxide

Graphene oxide (GO) solution was prepared by a modified hummer method with a little bit change [1]. Briefly, 1 g graphite powder was added to the mixture of 20 ml nitric acid and 46 ml sulfuric acid in the ice bath, stirring until it is evenly dispersed. Then 6 g potassium permanganate was slowly added to the mixture with stir. The mixture was transferred to a constant temperature shaker for 3 h, which was operated in 35°C and 120 rpm. After the exfoliation, the mixture was firstly added with 80ml H<sub>2</sub>O, and then stirred for 12h, followed by added 400 ml H<sub>2</sub>O and 6 ml H<sub>2</sub>O<sub>2</sub>. Simultaneously, the color of the mixture was turned to gold. After all those operating, the GO solution was washed until nearly neutral with centrifugation, and adjusted to 5 mg/ml for spare.

## Contents of anaerobic medium solution

The contents of anaerobic medium solution was 0.136 g/l  $\text{KH}_2\text{PO}_4$ ; 2.5 g/l  $\text{NaHCO}_3$ ; 0.54 g/l  $\text{NH}_4\text{Cl}$ ; 0.2 g/l  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ ; 0.111 g/l  $\text{CaCl}_2$  with 5 ml/l vitamin solution (10 mg/l  $\text{C}_8\text{H}_{12}\text{ClNO}_3$ , 5 mg/l  $\text{C}_{12}\text{H}_{18}\text{Cl}_2\text{N}_4\text{OS}$ , 5 mg/l  $\text{C}_{17}\text{H}_{20}\text{N}_4\text{O}_6$ , 5 mg/l  $\text{C}_6\text{H}_5\text{NO}_2$ , 5 mg/l  $\text{C}_{18}\text{H}_{32}\text{CaN}_2\text{O}_{10}$ , 5 mg/l  $\text{C}_7\text{H}_7\text{NO}_2$ , 5 mg/l  $\text{C}_8\text{H}_{14}\text{O}_2\text{S}_2$ , 2 mg/l  $\text{C}_{10}\text{H}_{16}\text{N}_2\text{O}_3\text{S}$ , 2 mg/l  $\text{C}_{19}\text{H}_{19}\text{N}_7\text{O}_6$ , and 0.1 mg/l  $\text{C}_{63}\text{H}_{88}\text{CoN}_{14}\text{O}_{14}\text{P}$ ) and 5 ml/l mineral solution (3 g/l  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ , 1 g  $\text{NaCl}$ , 0.1 g/l  $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ , 0.1 g  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ , 0.1 g/l  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ , 0.1 g/l  $\text{CaCl}_2$ , 0.1 g/l  $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ , 10 mg/l  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ , 10 mg/l  $\text{AlK}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ , 10 mg/l  $\text{H}_3\text{BO}_3$ , and 10 mg/l  $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ )



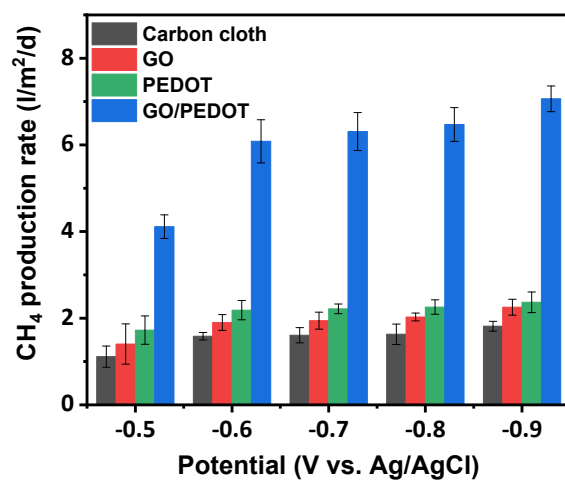
**Fig. S1.** The equivalent circuit for fitting the Nyquist plot.

An equivalent circuit was used to fit the Nyquist plot (see Fig. S3), in which the  $R_s$  stood for the total ohmic resistance consisted of the resistance of solution and electrical connection, and the  $R_{ct}$  stood for the charge transfer resistance between the electrode and solution [2, 3].

## Phylogenetic characterization of microorganisms on the biocathodes

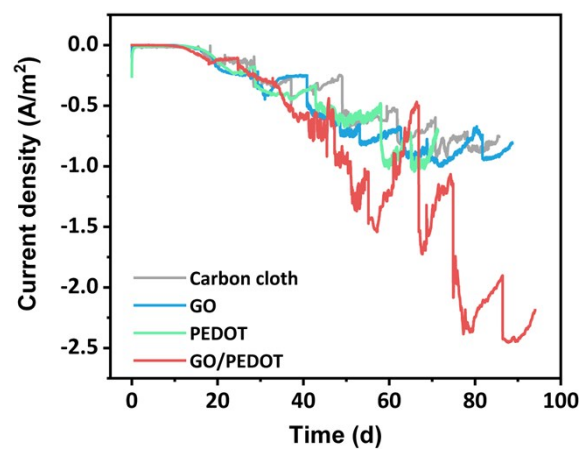
For molecular phylogenetic analysis of the microbial consortia associated with the biocathodes, 16S rRNA gene-amplicon libraries were constructed using DNA extracted from the biocathodes with different surface modifications as the PCR templates. V3–V4 regions of bacterial and archaeal 16S rRNA genes were amplified using universal primers: 338F (5'-ACTCCTACGGGAGGCAGCA-3') and 806R (5'-GGACTACHVGGGTWTCTAAT-3'); Arc349F (5'-GYGCASCAGKCGMGAAW-3') and Arc806R (5'-GGACTACVSGGGTATCTAAT-3'). A 30- $\mu$ l PCR reaction mixture contained Phusion High-Fidelity PCR Master Mix (2 $\times$ ) (New England Biolabs, Ipswich, MA, USA), 0.2  $\mu$ M of each barcoded primer and 10 ng of template DNA. PCR was performed under the following conditions: initial denaturation at 95°C for five minutes; 25 cycles at 95°C for 30 seconds, 50 °C for 30 seconds and 72°C for 40 seconds; and a final extension at 72°C for seven minutes. Sequence libraries were prepared using NEB Next Ultra DNA Library Prep Kit for Illumina (New England Biolabs, Ipswich, MA, USA) according to the manufactures instructions and then sequenced using an Illumina HiSeq 2500 (Illumina, San Diego, CA, USA) at Biomarker Technologies (Beijing, China). The raw Illumina reads were merged using FLASH [4]. The reads with ambiguous nucleotides, shorter than 280 bp or without a complete barcode and primer at one end were removed and excluded from further analysis by using Trimmomatic [5]. The chimeric reads were discarded using UCHIME [6]. The reads were clustered into operation taxonomic units (OTUs) at 97% sequence similarity using QIIME. Taxonomy was assigned to all OTUs using the RDP classifier within QIIME and the SILVA database. Sequences affiliated with non-targeted species (i.e. bacterial sequences in archaeal libraries, and vice versa) were excluded from further analyses. OTUs assigned to a phylum were further classified to lower taxonomic levels. The number of representative reads for each OTU was counted and the proportions of each group in a sample were calculated.

CH<sub>4</sub> producing performance



**Fig. S2.** CH<sub>4</sub> producing performance of biocathodes valued at the volumetric rate.

## Replication of biocathodes



**Fig. S3.** Current generation of the replicate biocathodes.

## Reference:

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