Electronic Supplementary Material (ESI) for Sustainable Energy & Fuels.

In-situ formed graphene nanosheets enhance bidirectional electron transfer in bioelectrochemical systems

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MES Setups and operation

Typical H-type cells were used in this study. The final volume of each chamber was 360 mL, and cation exchange membranes (UltrexCMI-7000, Membranes International Inc., Ringwood, NJ, USA, 9.6 cm^2) were used as separators. GP and EGP-200 were used as cathodes (8 cm^2) with carbon clothes (TMIL Ltd., Ibaraki, Japan, 20 cm^2) as the anodes. An Ag/AgCl reference electrode were inserted into the cathode chamber. The cathode potential was poised at −950 mV vs. Ag/AgCl by a potentiostat (VMP3, Bio-Logic, Seyssinet-Pariset, France) and CO_2 was used as the solo carbon source. The cathode chamber was filled with 100 mL liquid of the inoculum, 150 mL of medium (0.136 g KH_2PO_4, 2.5 g $NaHCO_3$, 0.111 g $CaCl_2$, 0.2 g $MgCl_2$•$6H_2O$ and 0.54 g NH4Cl per liter, pH 7.2), 5 mL of a mineral solution (3 g $MgSO_4$•$7H_2O$, 1 g NaCl, 0.1 g $MnSO_4$•H_2O, 0.1 g $FeSO_4$•$7H_2O$, 0.1 g $CoCl_2$•$6H_2O$, 0.1 g $CaCl_2$, 0.1 g $ZnSO_4$•$7H_2O$, 10 mg $CuSO_4$•$5H_2O$, 10 mg $AlK(SO_4)_2$•$12H_2O$, 10 mg H_3BO_3, and 10 mg Na_2MoO_4•$2H_2O$ per liter) and 5 mL of a vitamin solution (10 mg $C_8H_{12}ClNO_3$, 5 mg $C_{12}H_{18}Cl_2N_4OS$, 5 mg $C_{17}H_{20}N_4O_6$, 5 mg $C_6H_5NO_2$, 5 mg $C_{18}H_{32}CaN_2O_{10}$, 5 mg $C_7H_7NO_2$, 5 mg $C_8H_{14}O_2S_2$, 2 mg $C_{10}H_{16}N_2O_3S$, 2 mg $C_{19}H_{19}N_7O_6$, and 0.1 mg $C_{63}H_{88}CoN_{14}O_{14}P$ per liter). The anode chamber was filled with 250 mL of medium without inoculation.

Gas analyses of biocathodes

Gas chromatography (GC) (Trace 1300; Thermo Scientific) equipped with a micropacked column (ShinCarbon ST Columns, 2 m, ID 1.0 mm, OD 1/16", Mesh 100/120) was used to analyze gas samples. N_2 was used as the carrier gas. CH_4 was detected by thermal conductivity detection (TCD). The inlet temperature was 120℃, the column flow was 4.0 ml/min and the oven temperature was 110℃. The split ratio was 29.

Faradaic efficiency

Faradaic efficiency (or current capture efficiency) was calculated by the equation as follows:

$$\eta = \frac{8nF}{\int_{t=0}^{t} Idt} \times 100\%$$

where n is the mole of CH_4 (mol), F = 96,485 (C mol^{-1}; the Faraday constant)

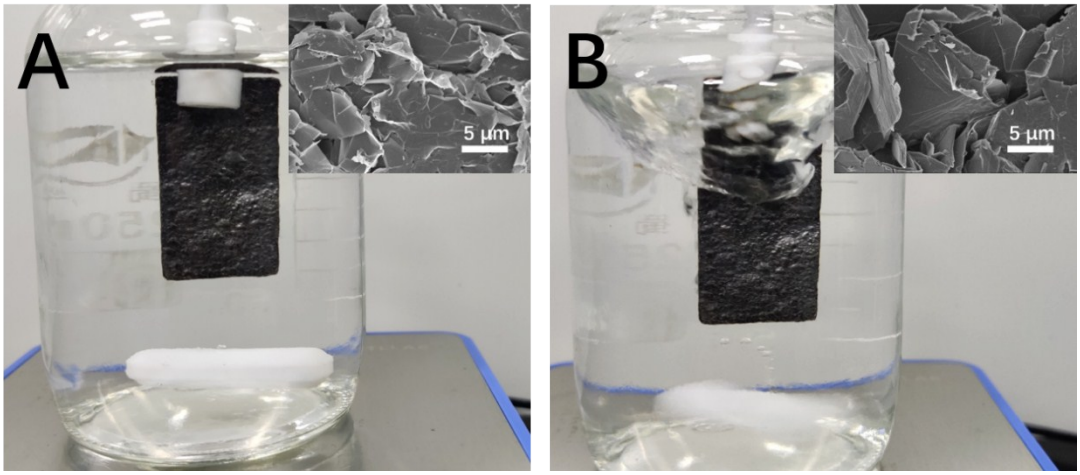

Fig. S1 Strong attachment of graphene nanosheets atop the graphite base. (A) an exfoliated graphite paper (EGP) immersed in deionized water without stirring (inset showed the SEM image of EGP before stirring). (B) the EGP immersed in deionized water with strong stirring (inset showed the SEM image of EGP after stirring).

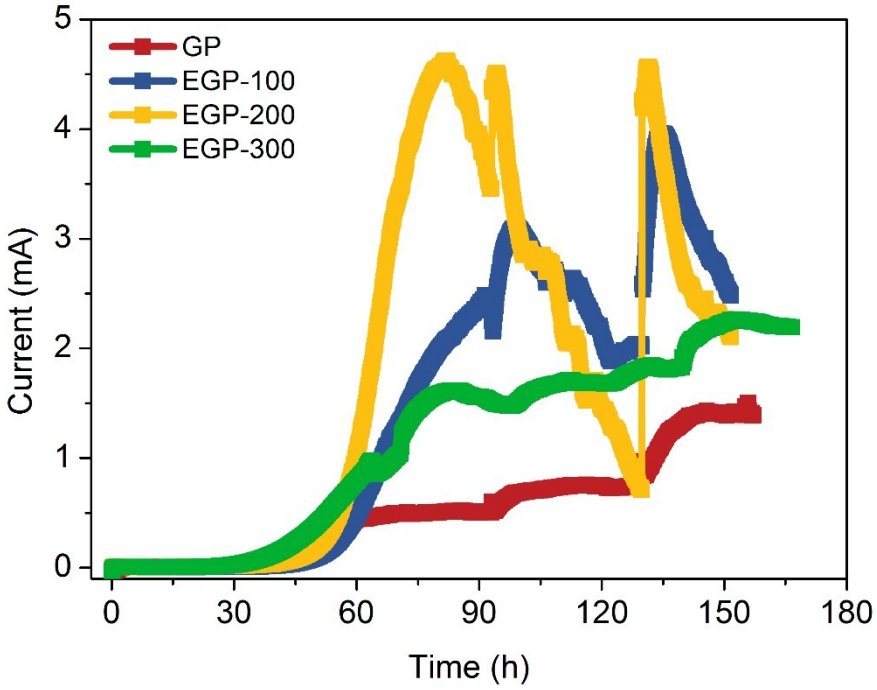

Fig. S2 Startup curves of GP, EGP-100, EGP-200, and EGP-300 with 20 mM acetate as electron donor. The anode potential was set at 50 mV vs. Ag/AgCl

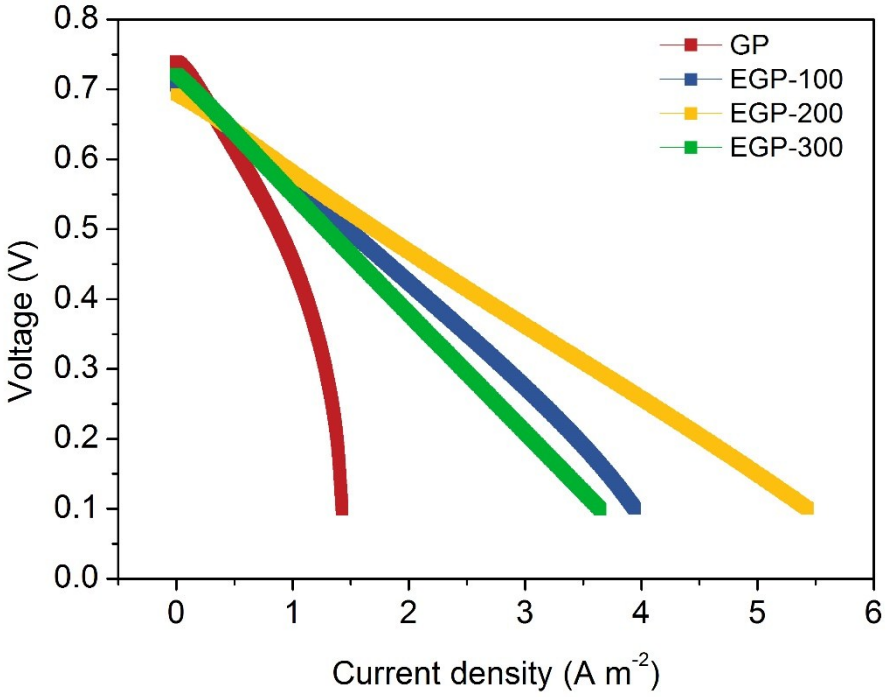

Fig. S3 Polarization curves of MFCs equipped with GP, EGP-100, EGP-200, and EGP-300 as anodes.

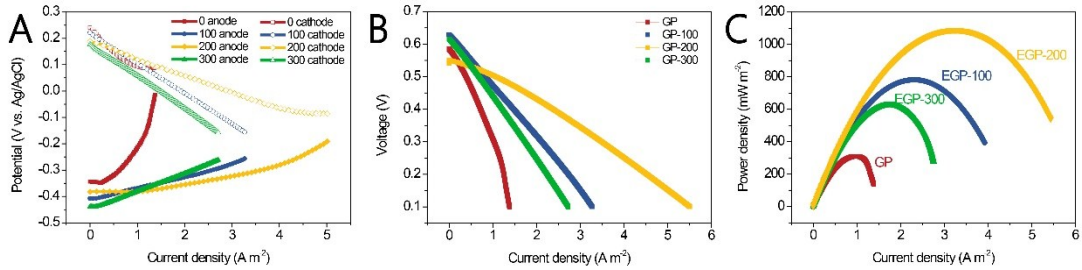

Fig. S4 Repeated data of electrode potentials (A), MFC polarization curve (B) and power density (C).

Table S1 Impedance parameters derived using equivalent circuit model for GP, EGP-100, EGP-200, and EGP-300 anodes

Electrodes	**R_s (Ω)**	**Q ($\mu F\ s^{n-1}$)**	**n**	**R_{ct} (Ω)**	**R_d (Ω)**
GP	5.1 ± 0.5	40	0.71	32.8 ± 1.3	160 ± 58
EGP-100	5.5 ± 0.7	86	0.74	5.5 ± 0.2	53 ± 12
EGP-200	6 ± 0.7	113	0.70	4.3 ± 0.3	43 ± 12
EGP-300	6.5 ± 0.5	70	0.66	20.1 ± 0.8	80 ± 11

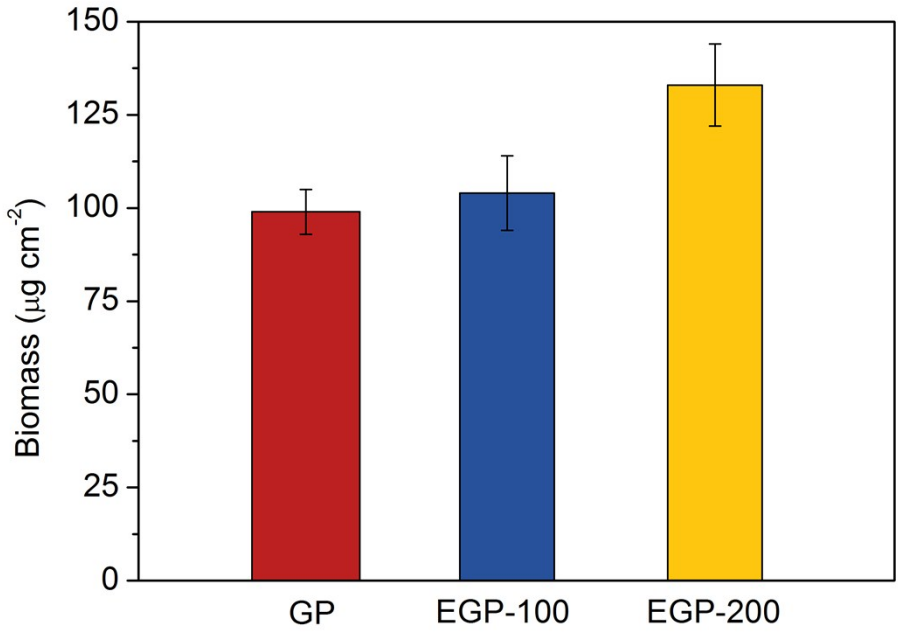

Fig. S5 Biomass of GP, EGP-100 and EGP-200 biocathodes.

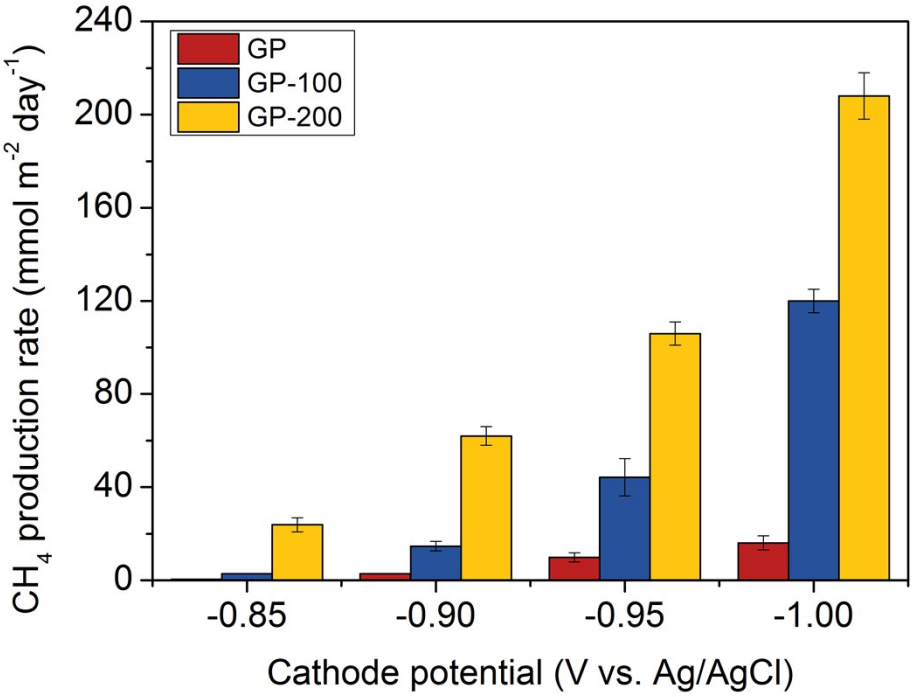

Fig. S6 CH_4 production rate of GP, EGP-100 and EGP-200 biocathodes at different cathode potentials. The GP, EGP-100 and EGP-200 biocathodes were initially operated at −950 mV vs. Ag/AgCl, and the biofilms reached their steady state before CH_4 production rate were analyzed at different potentials.