

Electronic Supplementary Information for *chemical communications*

**polydopamine nanocoating on individual cells for enhanced
extracellular electron transfer**

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Experimental section

Materials: Yeast extract, Peptone and Tris(hydroxymethyl)aminomethane (Tris-HCl) were purchased from Sangon Biotechnology Co. Ltd. (Shanghai, China). Dopamine hydrochloride was obtained from Aladdin Company (Shanghai, China). BacLight LIVE/DEAD L7012 stain Kit was obtained from Life Technologies (Singapore). All the other chemicals were used as received without further purification. All materials and solutions were sterilized before use.

Culturing *S. xiamenensis*: An isolated wild strain *Shewanella xiamenensis* (*S. xiamenensis*) BC01 was identified by 16S rRNA sequences and can be EET-based to catalyze Cr(VI) reduction in our previous reported.^{1,2} A single clone of *S. xiamenensis* was routinely cultivated in 20 mL of LB medium (5 g/L yeast extract, 10 g/L peptone and 10 g/L NaCl) overnight at 37 °C. Then, the secondary propagation of *S. xiamenensis* was inoculated into fresh LB medium followed by incubating at 37 °C with shaking (200 rpm) for 18 h. The bacterial cells were harvested by centrifugation at 6000 rpm in 4 °C for 10 minutes.

Coating PDA around *S. xiamenensis*: The as-obtained *S. xiamenensis* cells were washed with 0.85% aqueous NaCl solution and Tris-HCl buffer (10 mM, PH 8.0), and then *S. xiamenensis* cells were re-suspended in 10 mL Tris-HCl buffer solution was supplemented with dopamine hydrochloride with the final concentration of 3 mg/mL. The mixture was placed on a shaking stage for 3 h for the formation of PDA coatings. PDA coated *S. xiamenensis* cells were washed with sterile M9 buffer solution for three times to remove the excess PDA precursors and restored in 5 mL sterile M9 buffer solution for further usage.

Bioelectrodes preparation: The bio-electrodes were fabricated through a simple drop-coating process: A piece of carbon felt electrode (1 cm × 1cm, project area 2 cm²) was purified with concentrated HCl, acetone and ultrapure water. After coated, the bacteria cells were concentrated by centrifugation at 6000 rpm for 10 min. The cells ink were dropped on carbon felt electrode, immersed in naphthol solution for a while and allowed to dry at 4 °C. Control experiments were performed with native *S. xiamenensis* electrode was prepared in the same way as *S. xiamenensis*-PDA.

Structural Characterization: Cells suspension were fixed for 4 h in the 2.5% glutaraldehyde, and then wash three time with M9 buffer solution, dehydrated with increasing concentration of ethanol (25%, 50%, 75%, 95 % and 100% twice) in steps of 20 min duration. The suspension was dropped on the silicon wafer and air dried for 24 h. SEM images were recorded on field-emission scanning electron microscopy (FE-SEM, HITACHI, S4800) SEM with accelerating voltage of 10 kV. TEM samples were prepared by dropping suspensions onto a carbon-coated copper grid for analysis by transmission electron microscopy (HITACHI, HT-7800) working on 80 kV. Fourier transform infrared spectroscopy (FTIR) analyses were carried out by FTIR

spectrometer (Nicolet 330). Before tablet, suspensions were dried by freeze drying and then mixed the sample with KBr (1:100).

Viability test: Cell viability was monitored via SYTO 9/PI staining with the LIVE/DEAD *BacLight* Bacterial Viability Kit (Molecular Probes, Eugene). The staining procedure was conducted according to the manufacturer's instruction. The stained cells were imaged through inverted laser confocal microscopy (Lecai TCS SP5) with oil immersion lens. Bacteria counting was performed as followed, after coating for 3 h, *S. xiamenensis* and *S. xiamenensis*-PDA were re-suspended in 10 mL M9 buffer solution for 0, 1, 3 and 5 days, respectively. Afterward, the bacterial suspension was serially diluted in tenfold steps with M9 buffer solution and the bacterial suspension (100 μ L) was dropped onto the surface of LB agar culture plate for further incubation. After observable colonies formed, circular colonies were counted to determine the CFU per milliliter as a measure of cell number and viability.

MFC Setup and Operation: H-type dual-chamber MFCs with a working volume of 100 mL separated by a proton exchange membrane (PEM, Nafion 117, Dupont) with carbon felt (2 cm \times 2 cm) as cathode. The prepared electrode was used as the MFC anode. Fresh M9 buffer solution ($\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$, 42 mM; KH_2PO_4 , 22 mM; NaCl, 85.5 mM; MgSO_4 , 1 mM and CaCl_2 , 0.1 mM) with 5% LB broth and 18 mM Sodium lactate were added into the anodic chamber of MFCs and purged with pure nitrogen gas to remove the dissolved oxygen. The catholyte was 100 mM phosphate buffer solution with 50 mM $\text{K}_3\text{Fe}(\text{CN})_6$. All the MFCs with 1 K Ω external resistance were operated at 30 $^\circ\text{C}$. At the steady state of MFC, the polarization curves were obtained by switching external resistor (10000 Ω - 50 Ω). Current was calculated using $I = V (\text{output voltage}) / R (\text{external resistance})$. Power was obtained by the following equation: $P = V \times I$. Current density (A/m²) were normalized to the anode projected area.

Electrochemical Characterization: The electrochemical behaviors of the bioelectrodes were investigated with a three-electrode cell based on CHI 600D electrochemical system. The bioelectrode was used as the working electrode, platinum wire and Ag/AgCl were used as counter and reference electrodes, respectively. M9 buffer (100 mM, pH 7.0) was used as electrolyte. All experiments were conducted under an anaerobic atmosphere. The parameters at both turnover and non-turnover conditions were as follows: for CV: $E_i = -0.6$ V; $E_f = 0.1$ V; and scan rate, 10 mV/s; for DPV: $E_i = -0.6$ V; $E_f = 0.1$ V; potential increment, 5 mV; amplitude, 50 mV; pulse width, 200 ms; and pulse period, 400 ms; for EIS: frequency, 100 kHz-0.1Hz; and amplitude, 5 mV; for *i-t* chronoamperometry: $E = 0.35$ V.

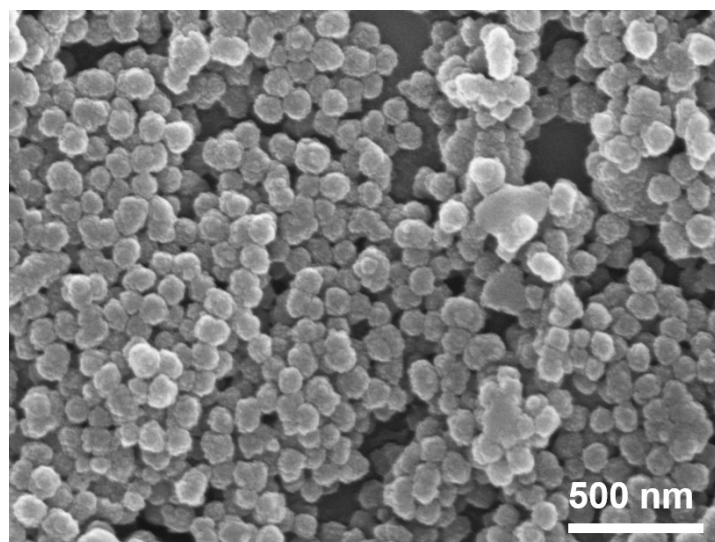


Fig. S1 SEM image of pure PDA.

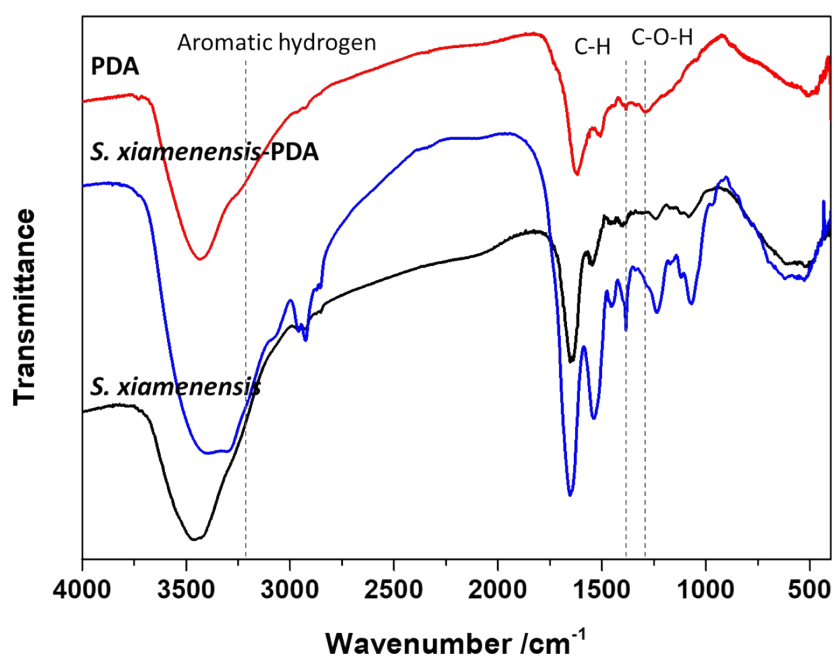
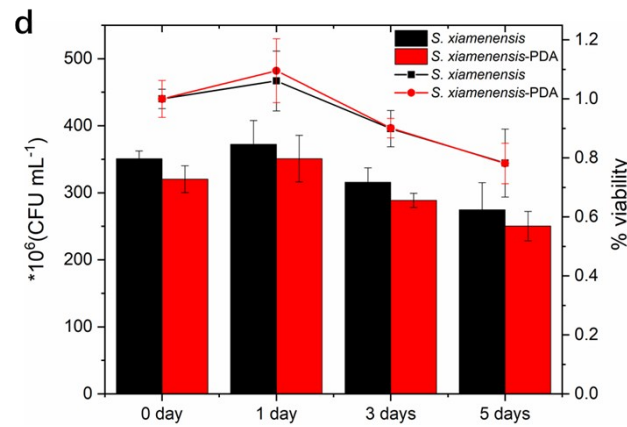
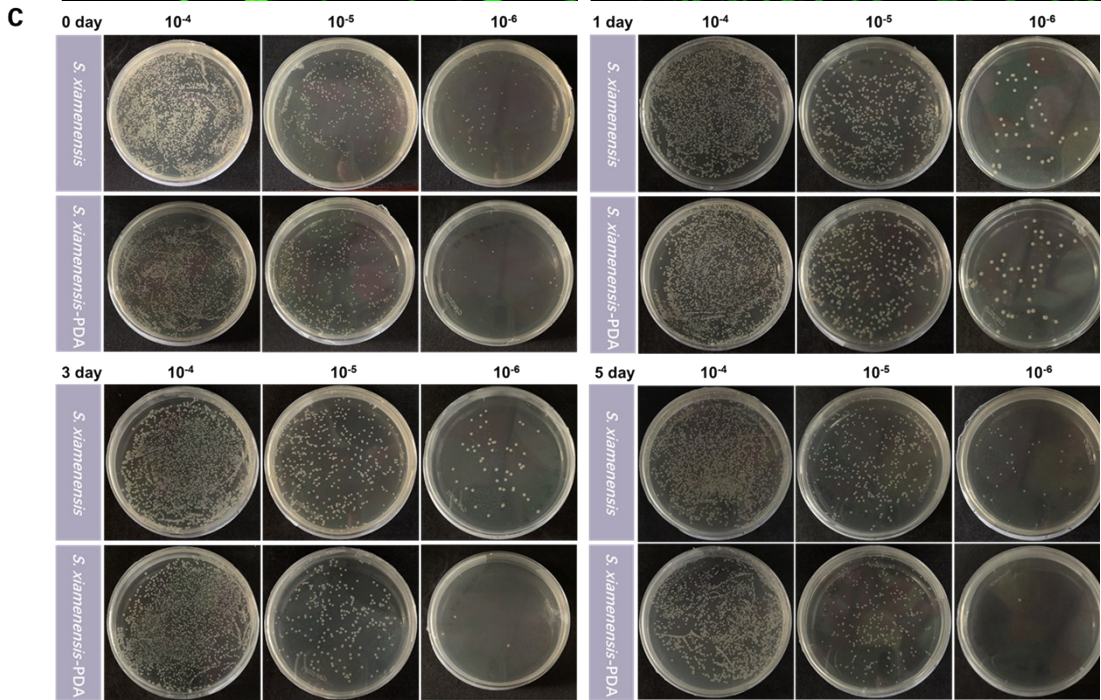
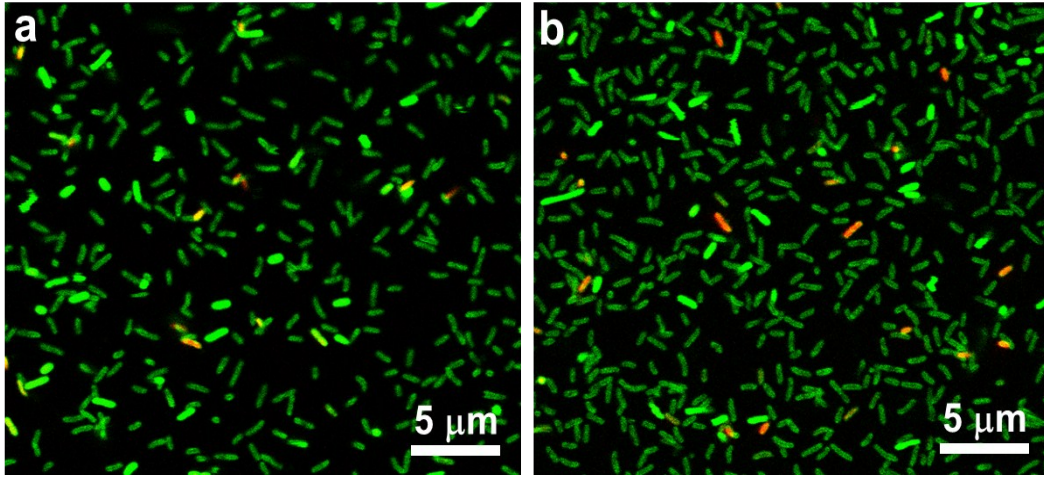


Fig. S2 FTIR of *S. xiamenensis*, *S. xiamenensis*-PDA and pure PDA.



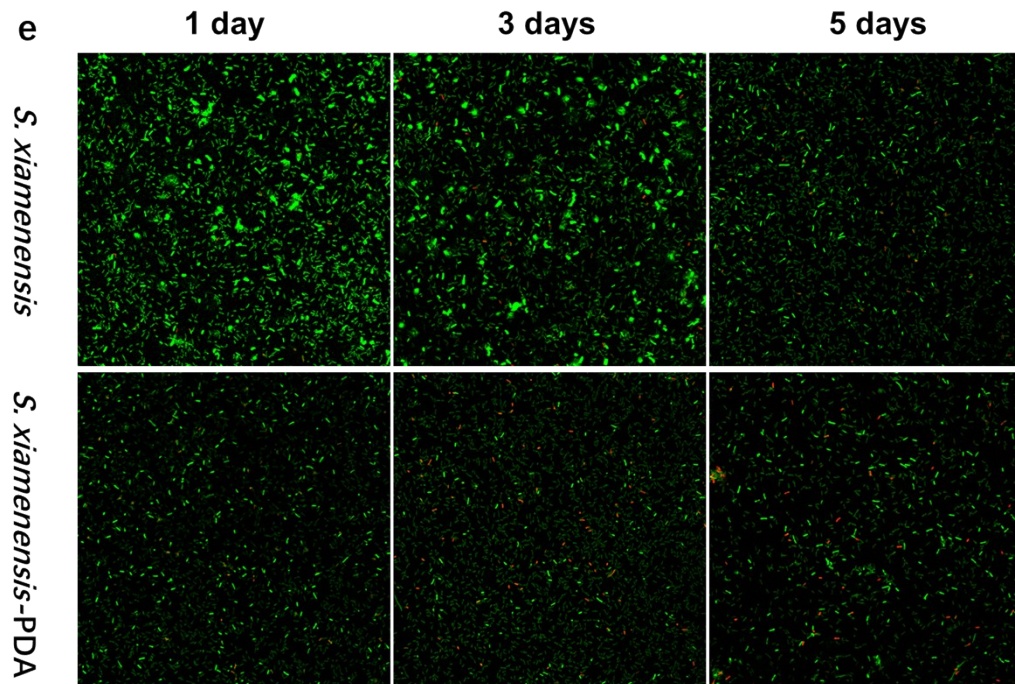


Fig. S3 High-resolution CLSM image of *S. xiamenensis* (a) and *S. xiamenensis*-PDA (b) after staining with Live/Dead BacLight kit. Cell viability evaluation of *S. xiamenensis* and *S. xiamenensis*-PDA were remained in M9 buffer solution for 0 day, 1 day, 3 days and 5 days, photographs (c) and statistical diagram (d) (with error bars) of bacterial colonies counted from the dilutions of the bacterial suspension. (e) CLSM images of of *S. xiamenensis* and *S. xiamenensis*-PDA were remained in M9 buffer solution for 1 day, 3 days and 5 days.

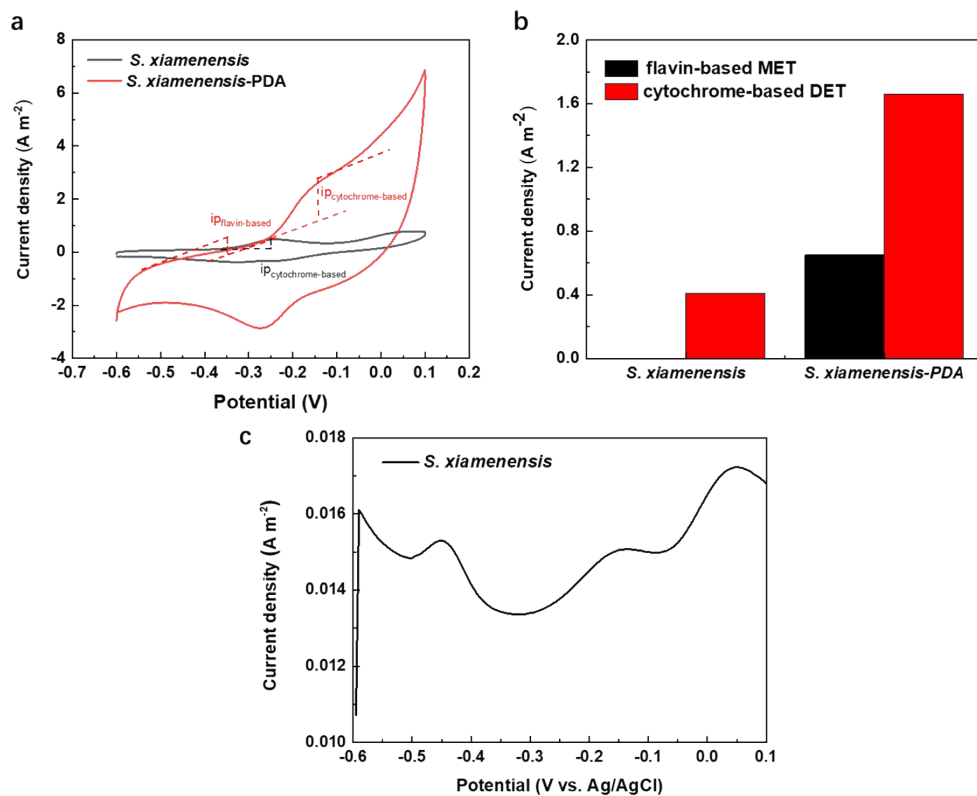


Fig. S4 (a) CV without turnover current of *S. xiamenensis* and *S. xiamenensis*-PDA electrodes. (b) The statistics of PDA to DET and MET current density. (c) DPV of *S. xiamenensis* measure with a glassy carbon electrode.

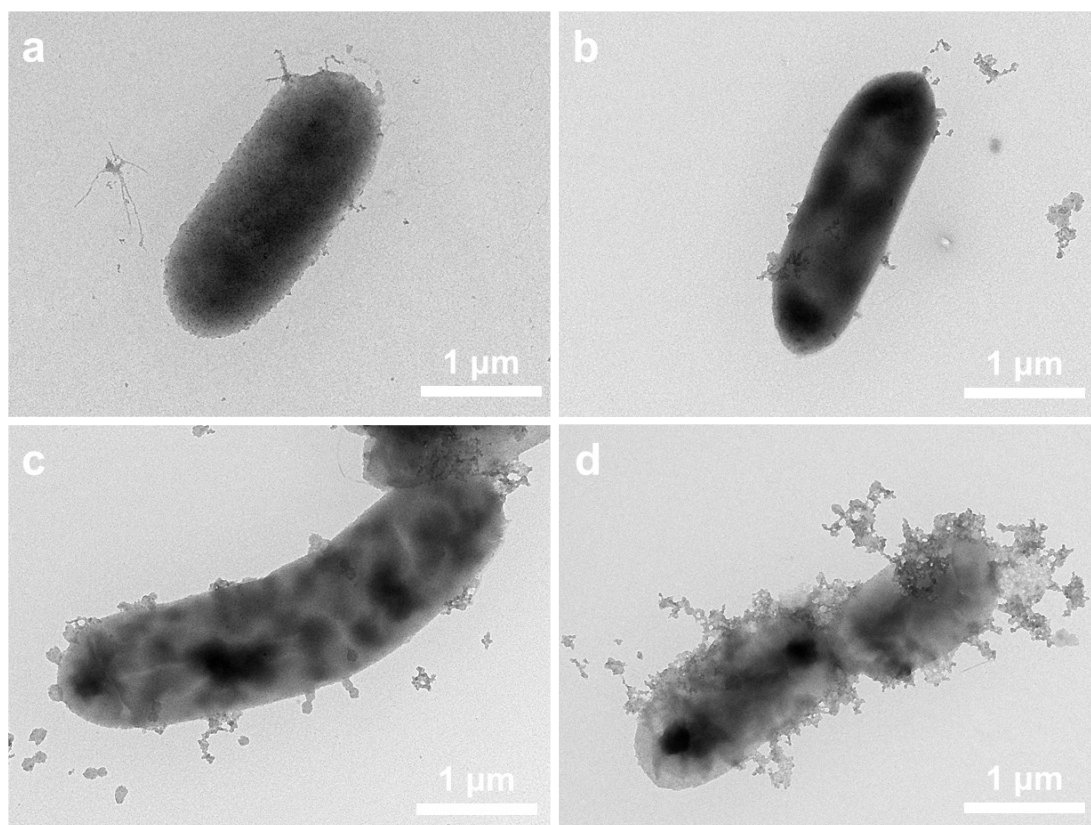


Fig. S5 TEM of *S. xiamenensis*-PDA prepared at different dopamine concentrations: (a) 1 mg/mL; (b) 2 mg/mL; (c) 3 mg/mL; (d) 4 mg/mL.

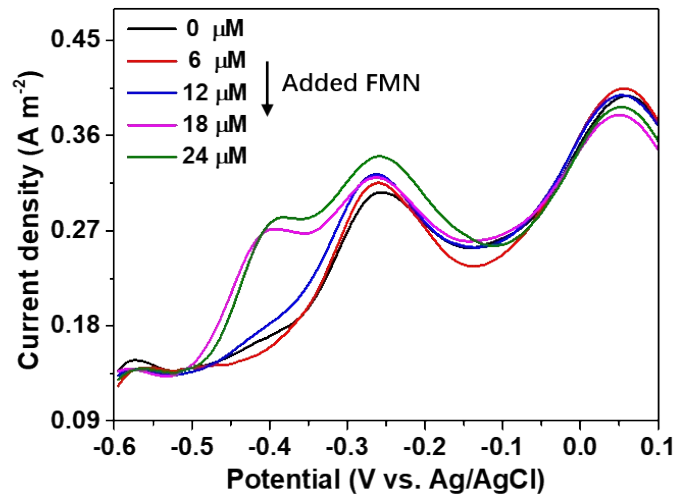


Fig. S6 Effect of adding flavin mononucleotide (FMN, final concentrations noted) with *S. xiamenensis* on the DPV profiles.

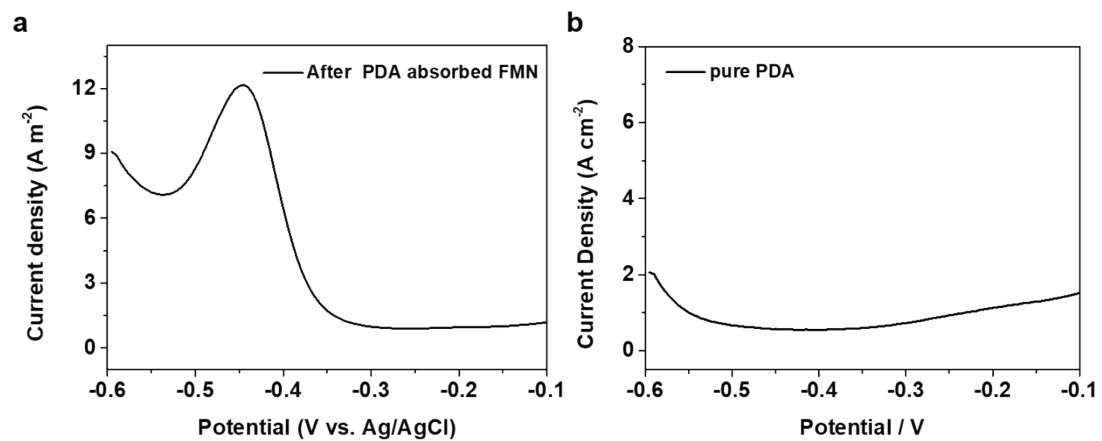


Fig. S7 (a) DPV curve of precipitate after the reaction of PDA with FMN and (b) DPV curve of pure PDA.

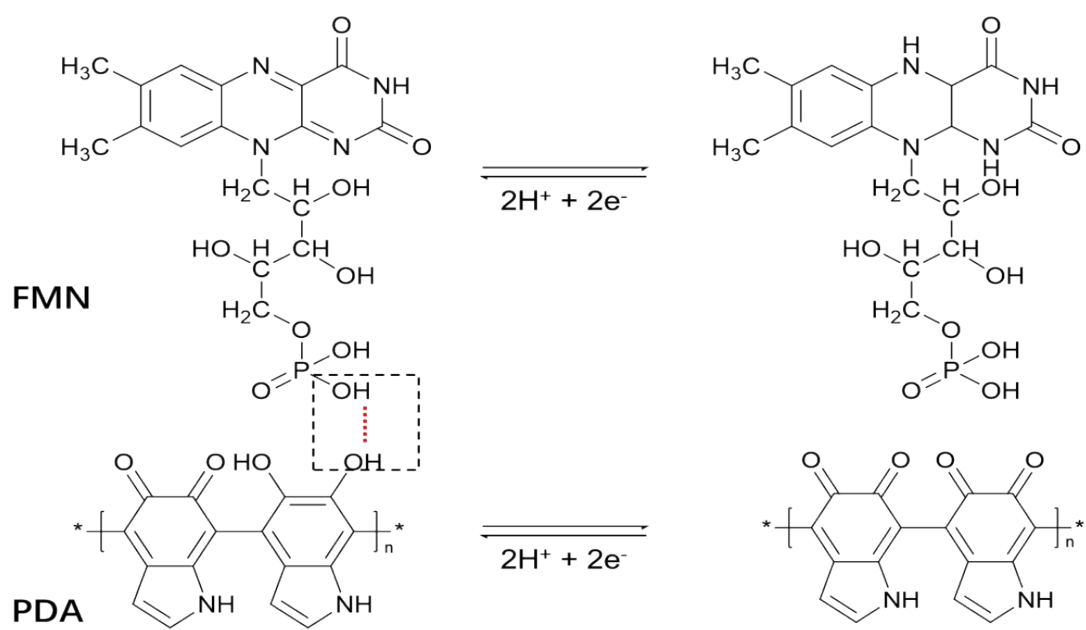


Fig. S8 The two-electron redox reaction equation of FMN, PDA and adsorption mechanism.

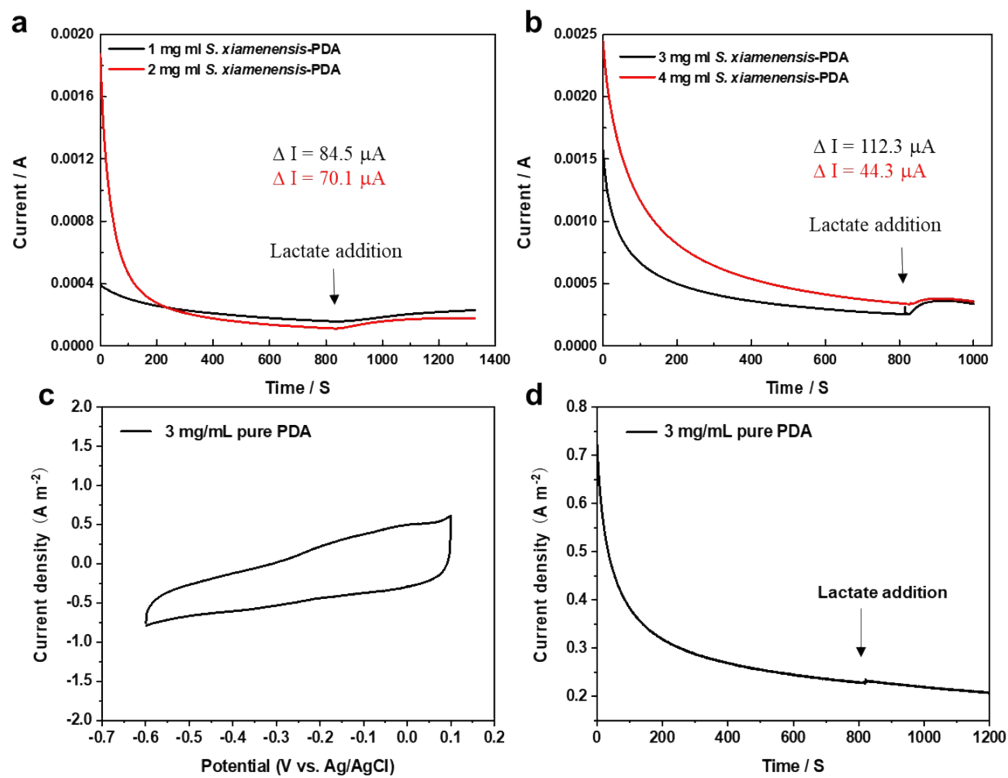


Fig. S9 (a) and (b) Potentiostatic lactate oxidation of *S. xiamenensis*-PDA prepared at different dopamine concentrations. (c) CV of 3 mg/mL pure PDA. (d) Potentiostatic lactate oxidation of 3 mg/mL pure PDA held at a potential of +0.35 V versus Ag/AgCl.

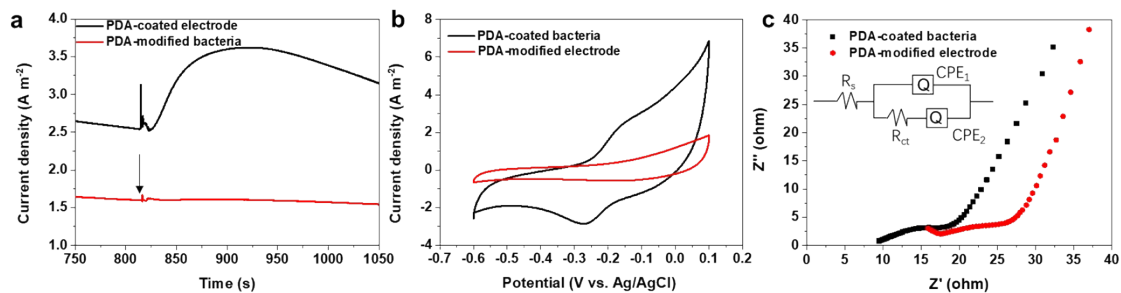


Fig. S10 (a) Potentiostatic lactate oxidation of PDA-coated bacteria and PDA-modified electrode held at a potential of + 0.35 V versus Ag/AgCl. (b) CV of PDA-coated bacteria and PDA-modified electrode. (c) EIS of PDA-coated bacteria and PDA-modified electrode.

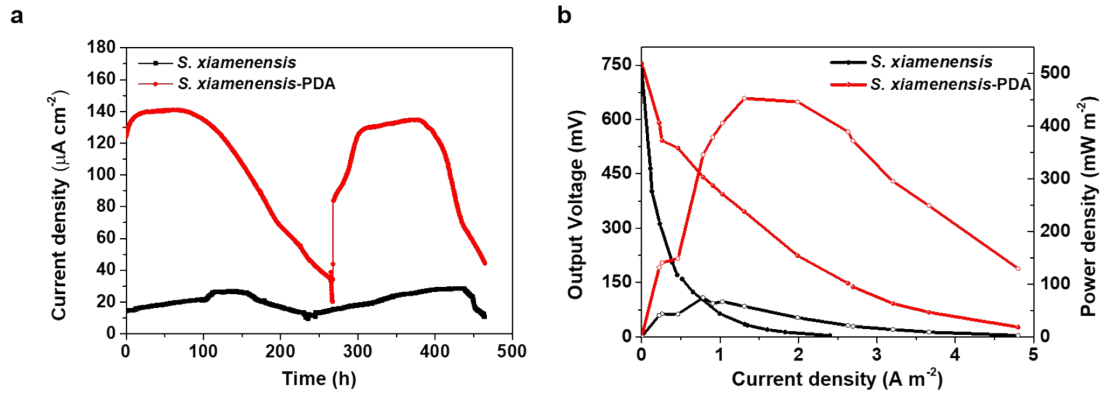


Fig. S11 MFCs performance of different anodes. (a) Time courses of the current generation in MFCs with an external resistor of $1 \text{ K}\Omega$ and (b) Polarization and power-density curves of MFCs.

Table S1. Comparison the contribution of redox mediators to enhance power generation.

Introduction methods	Redox mediator ^a	Electrode	Microorganism	Maximum power density (mW m ⁻²)	Impact of RM ^b	Ref
Soluble form	MB	Graphite rod	Mixed	-	V: 1.5 x	[S3]
Soluble form	Resazurin	Carbon cloth	Mixed	68	PD: 1.4 x	[S4]
Soluble form	AQDS HA	Carbon cloth	<i>Shewanella putrefaciens</i>	8.5 4.3	PD: 5.5 x 2.8 x	[S5]
Soluble form	Pyocyanin	Graphite plate	<i>Pseudomonas aeruginosa</i>	4.0	PD: 5.6 x	[S6]
Soluble form	HCF	gold-coated glass slide	<i>Pseudomonas aeruginosa</i>	-	V: 5.8 x	[S7]
Modified electrodes	PDA-activated carbon	Stainless steel mesh	Mixed	803	PD: 1.3 x	[S8]
Modified electrodes	NQ-LPEI	Carbon felt	<i>Shewanella oneisensis</i> MR-1	530	PD: 2.7 x	[S9]
Modified electrodes	RF-peptide nanotubes	Carbon cloth	<i>Shewanella oneisensis</i> MR-1	767	PD: 2.9 x	[S10]
Modified electrodes	AQDS	Graphite disks	Mixed	98	PD: 4.9 x	[S11]
Modified electrodes	NR	Carbon felt	<i>Saccharomyces cerevisiae</i>	6.1	PD: 1.9 x	[S12]
Modified electrodes	AQDS/Mn/P Py	Graphite felt	Mixed	84.6	PD: 2.9 x	[S13]
Coated bacteria	PDA	Carbon felt	<i>Shewanella xiamenensis</i>	452.8	PD: 6.1 x	This work

^a MB: methylene; AQDS: anthraquinone-2,6-disulfonate; HA: humic acids; HCF: hexacyanoferrate; NQ-LPEI: Naphthoquinone functionalized linear poly(ethylenimine); RF: riboflavin; NR: neutral red; PPy: polypyrrole.

^b V: voltage; PD: power density; “x” refer the x-fold increase respect to the control lacking RM.

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