Supporting Information

Control of Bacterial Extracellular Electron Transfer by Solid-State Mediator of Polyaniline Nanowire Arrays

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1. Experimental setup

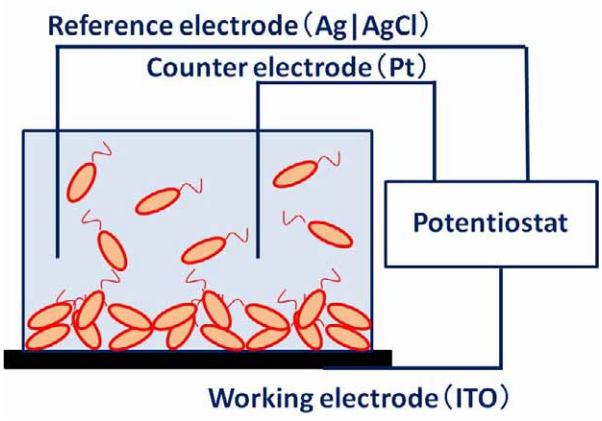

Fig. S1. The cartoon for the experimental setup used in this study. A single-chamber, three-electrode system was used to monitor the electrochemical behavior of microbes on various electrodes. PANI-NA/Au, smooth PANI/Au and bare Au were used as working electrode in this study, which was mounted on the bottom of the setup. An Ag|AgCl (sat. KCl) and platinum wire were used as the reference and counter electrodes, respectively.

2. Represented SEM images of bacterial cells on a smooth PANI/Au electrode after 30 h of electrochemical culture at 0.2 V, where cells were distributed randomly on the surface with little visible appendages.

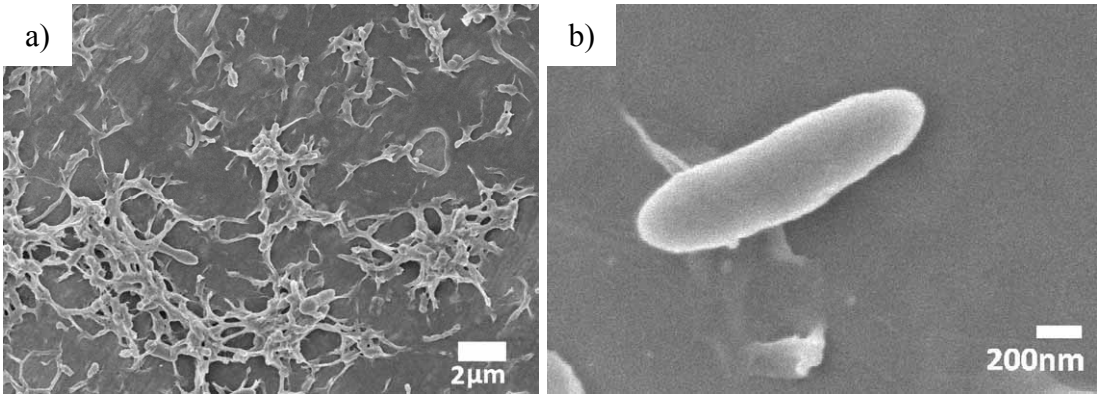

Fig. S2. (a) A large area SEM image of bacterial cells on a PANI-NA/Au electrode after 30 h of electrochemical culture at 0.2 V. (b) Enlarge SEM image of one intact microbe on smooth PANI/Au electrode after 30 h of electrochemical culture at 0.2V.

3. In situ electrical characterization of electrically property of filamentous material containing in biofilm.

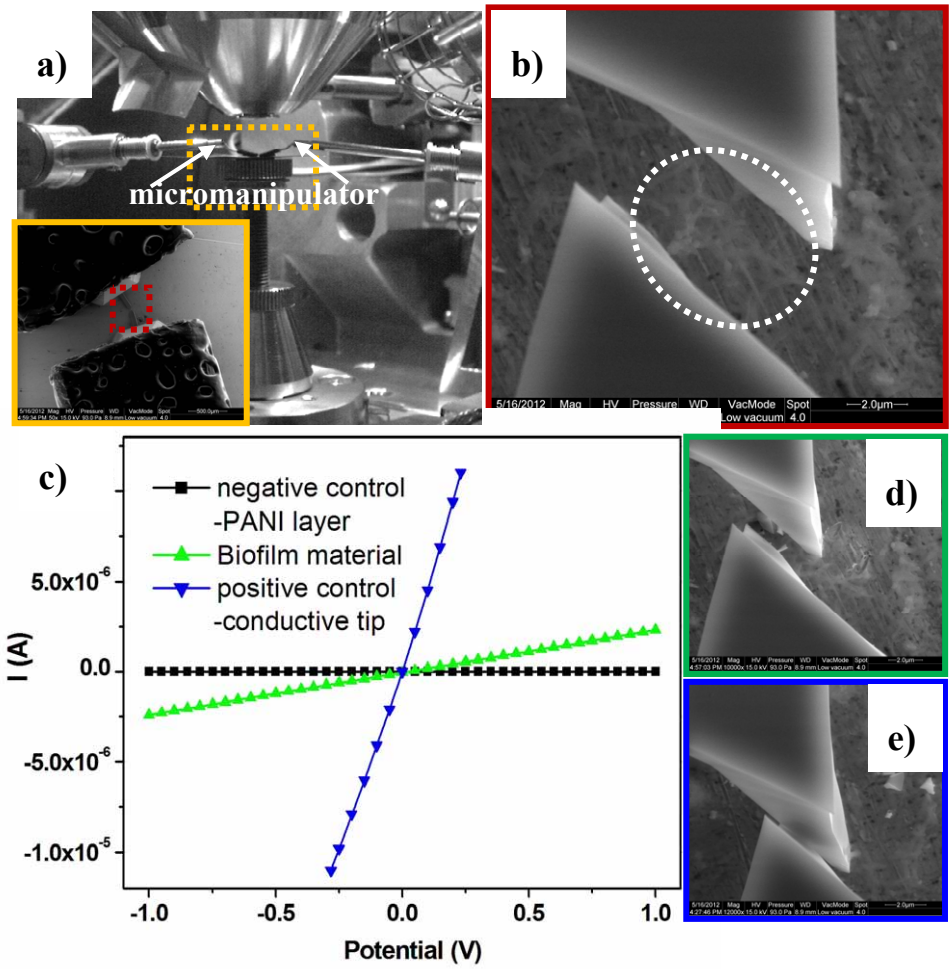

Fig. S3. (a) Optical picture of the experimental setup for the in situ characterization of electrical property of filamentous material containing in biofilm. Two conductive probes can be precisely

controlled by micromanipulators (as indicated with yellow dashed line) that mounted over the bacterial sample in the chamber of ESEM (Quanta 200 FEG). Inset show the corresponding SEM image where two conductive probes can be viewed. (b) SEM picture of the bacterial cells on a PANI-NA/Au electrode after 30 h of electrochemical culture at 0.2 V. The area circled by white dashed line are the area for several microbes that connected by filamentous materials. (c) Typical I-V curves obtained when the potential applied between two probes was swept from -1V to +1V under different conditions: green line show the I-V behavior when the probes were contacted with the bioflim containing filamentous materials (as shown in Fig.(d)); blue line show the I-V behavior when two probes was contacted with each other (as positive control, shown in Fig.(e)); black line show the I-V behavior when two probes contacted with the PANI film directly (as negative control)..

In this experiment, through combining ESEM (Quanta 200 FEG), micromanipulators and Keithley 4200 semiconductor characterization system, the in-situ electrical characterization was performed on the bacterial biofilm obtained on a PANI-NA/Au electrode after 30 h of electrochemical culture at 0.2 V. The temperature of sample stage was maintained at 25°C. The chamber pressure kept 93 Pa. Then ESEM imaging was performed at the HV of 20.0 KV.

I-V characters on several microbes that were connected with each other through filamentous materials were measured by using Keithley 4200 semiconductor characterization system. It is clear suggested that microbes connected by those filamentous materials are electrically conductive since the I-V curve show positive slope. Moreover, when two conducting probes was contacted with PANI layer directly (without microbe), no current flow was observed which further support that PANI layer is electrically non-conductive in our system.

4. The effect of the addition of riboflavin on the current generation at a constant potential of 0.2 V for cells of *S. loihica* PV-4 electrochemically cultured on a PANI-NA/Au electrode.

It can be seen that the addition of the riboflavin resulted in only limited enhancement of the catalytic current on PANI-NA/Au electrode (Fig. S4a), indicating that electron transfer mediated by diffusive riboflavin was not efficient in this system. In order to exclude the possibility that there were already enough endogenously

released flavins in electrochemical cell after 20 h electrochemical culture, we performed the same experiment on ITO electrode at -0.2 V under which condition bacterial EET mediated by self-secreted flavins is active (*ChemSusChem, 2010, 3, 1253-1256; Biosens. Bioelectron,. 2010, 25, 2530*). As indicated in Fig.S4b, anodic EET current dramatically increases upon addition of riboflavin after about 25 h electrochemical culture. Figure S4c is the fluorescent spectra from the supernatant obtained after 25 h culture in electrochemical cell with a poised electrode at 0.2 V on PANI-NA/Au electrode, by which the accurate concentration of endogenously released flavin can be estimated as 1.6 μM. Taken together, it can be concluded that bacterial EET on PANI-NA/Au electrode mediated by self-secreted flavins was not efficient.

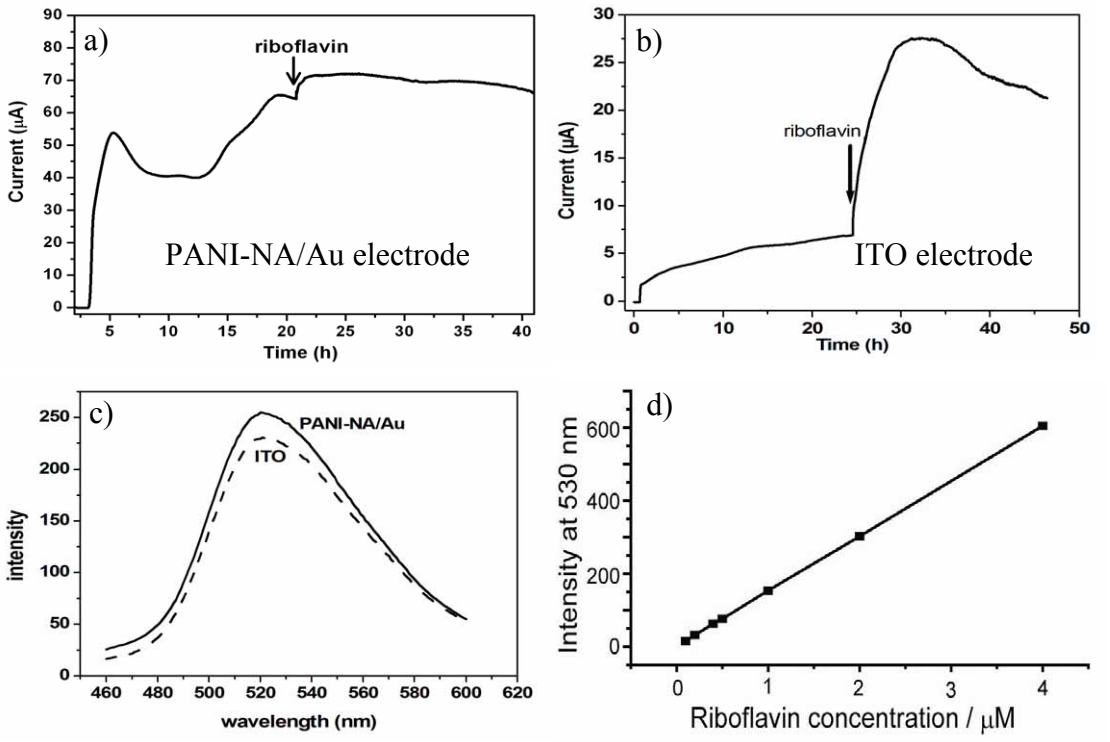

Fig. S4. a) Effects of the addition of 1 μm riboflavin on the current generation at constant potentials of 0.2 V for cells of S. loihica PV-4 electrochemically cultured on PANI-NA/Au electrodes. b) Effect of the exogenously added riboflavin on current generation when S. loihica PV-4 was electrochemically cultured at ITO electrode. Riboflavin was added at the point indicated by the arrow. c) Fluorescent spectra from the supernatant obtained after 25 h culture in electrochemical cell with a poised electrode at 0.2 V on PANI-NA/Au electrode (solid line) and with a poised potential of -0.2V on ITO electrode (dashed line). d) Relationship between fluorescent intensity at 530 nm and riboflavin concentration

5. EET behavior on PANI-NA/Au and bare Au electrode at different constant potentials.

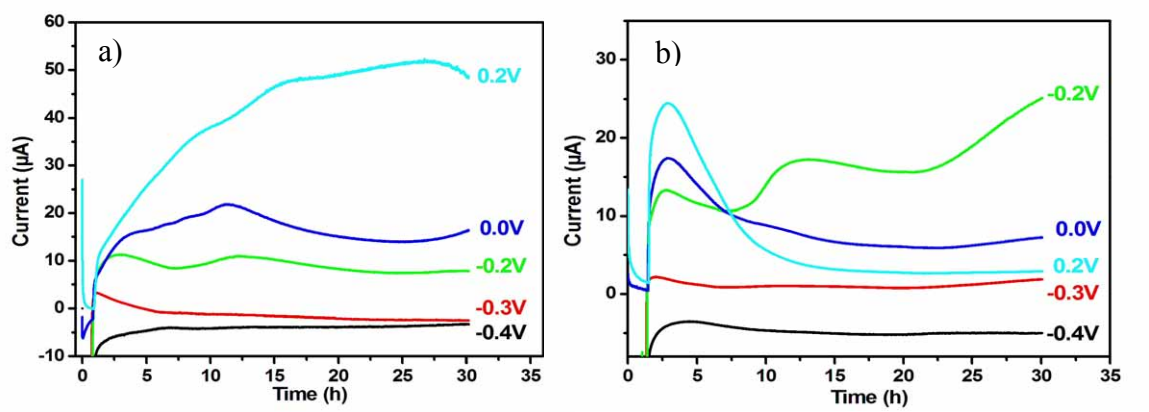

Fig. S5. Current vs. time curves at constant potentials of -0.4 V (dark), -0.3 V (red), -0.2 V (green), 0.0 V (blue) and 0.2 V (turquoise) for cells of S. loihica PV-4 electrochemically cultured on (a) a PANI-NA/Au electrode and (b) bare Au electrode.

On PANI-NA/Au electrode, an anodic current was first detected at an applied potential of -0.2 V. Notably, at -0.2 V, catalytic current generation on PANI-NA/Au remained fairly constant with time, but was only approximately 10 μA (Fig. S5a, green line). Similar current generation behavior was observed at a poised potential of 0 V, although the current reached a comparatively higher value of 19 μA (Fig. S5a, blue line). When an applied potential of 0.2 V were applied, the anodic current continued to increase with time and reached maximum values of 51 μA (Fig. S5a, turquoise line). However, on bare Au, the EET activity exhibits extremely different behavior. As shown in Fig. S5b, the EET current gradually increased at a potential of -0.2 V, with the highest value of 25 μA after 30 h of operation; but the EET current decreased with time and was stably maintained at less than 10 μA at more positive potential regions (0 and 0.2 V). Furthermore, long time experiments were performed under same condition and the representative current vs. time curves were shown in Fig. S9.

6. Experimental evidence (UV-vis spectra and digital image) to show that the as-prepared PANI-NA film was not conductive when it was immersed into DML solution used for electrochemical measurement.

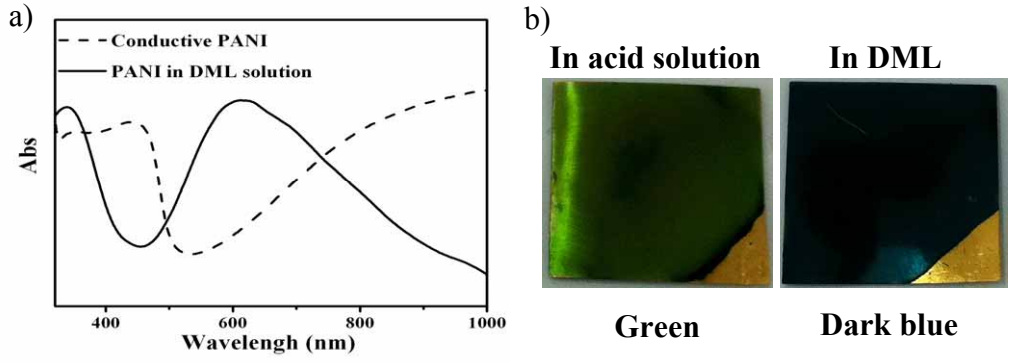

Fig. S6. a) UV-vis spectra for PANI dispersed in DML solution (solid line) and m-cresol solvent (dashed line). b): Digital image of an as-prepared PANI-NA/Au electrode after immersion in DML medium (right) and acid solution (left), appearing dark blue and green in color, respectively.

7. Whole-cell CVs of PANI-NA/Au electrodes in DML medium with and without bacterial cells.

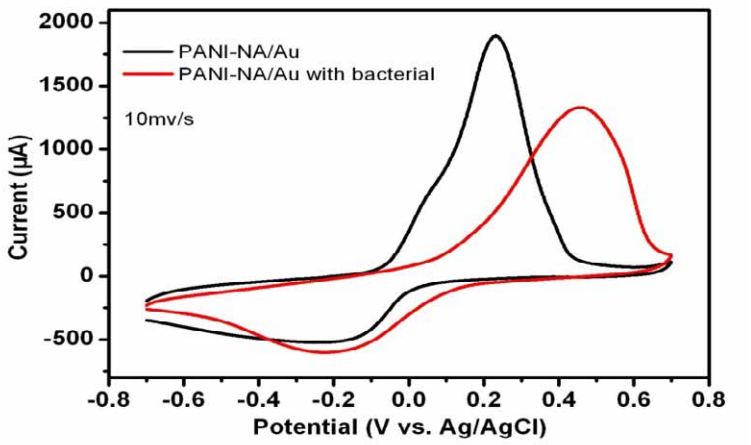

Fig. S7. Whole-cell CVs of PANI-NA/Au electrode in DML medium obtained in the absence (black line) and presence (red line) of bacterial cells with a scan rate of 10 mV s-1. Dark line: Well-defined redox peaks were observed when the PANI-NA/Au electrode was immersed into DML medium lacking microbes. The peaks were assignable to the oxidation and reduction of PANI under the electrochemical operation conditions used in this study. CV curves obtained after microbial electrochemical culture at +0.2 V for 30 h (red line) give essential similar pattern. The positive shift of the anodic peak in the presence of microbes might due to continuous electron injection from cells to PANI-NA that affects the dynamics of the redox processes involved in EET.

8. Whole-cell CVs of microbes on a PANI-NA/Au electrode after 30h electrochemical culture at various applied potentials ranging from -0.3, -0.2, 0.0 to 0.2 V.

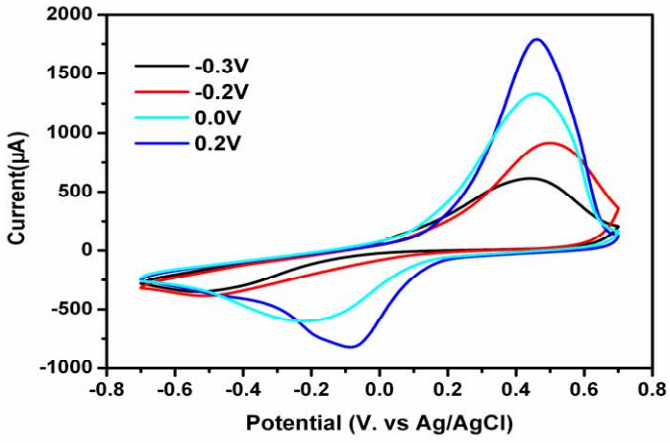

Fig. S8. Whole-cell CVs of microbes on a PANI-NA/Au electrode after 30 h electrochemical culture for 30 h at various applied potentials of -0.3 V (black), -0.2 V (red), 0.0 V (turquoise) and 0.2V (blue).

For PANI-NA/Au electrodes, no detectable redox peaks assignable to OMCs were observed after 30 h of electrochemical culture of microbes for any of the examined potentials. The CVs obtained at various applied potentials showed essentially the same behavior, as only one redox peak assignable to the redox activity of PANI was observed.

9. Long time performance of the PANI-NA/Au electrode in boosting bacterial EET. It can be seen that the current reached a steady state around 25 hours and then maintained constant for a long time. It was proposed that the full coverage of biofilm on PANI-NA/Au electrode was mostly finished within the initial 25 hours. In the later period, the bioflim gets thicker but exhibits little effect on current generation. We previously reported that for genus *Shewanella*, the microbes directly attached to the electrode make the main contribution to the current generation based on the fact that the current generation behavior has essentially little relationship with the microbe's population under the operation condition (*Angew. Chem. Int. Ed., 2009, 48, 508*). Therefore, microbe directly attached on the PANI-NA/Au electrode play a key role for current generation. This result also suggests that the physical interaction between

microbe and PANI-NA/Au electrode can greatly affect the current generation behavior.

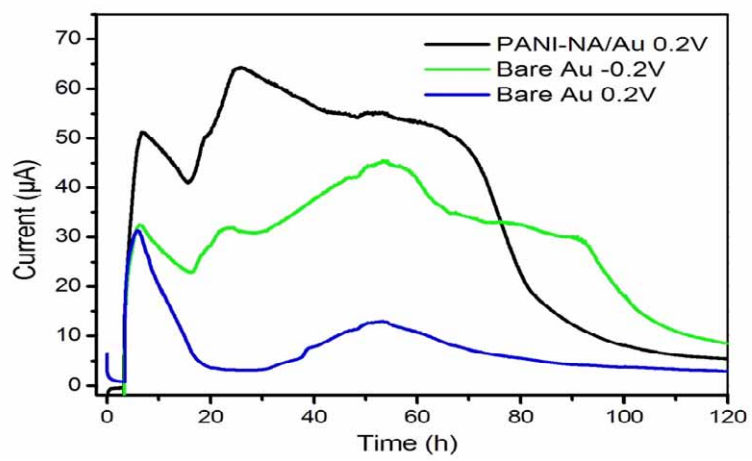

Fig. S9. Long time EET performance on various electrodes at constant potentials: Current vs. time curves at constant potentials of 0.2 V for PANI-NA/Au electrode (dark), 0.2 V for bare Au electrode (blue) and -0.2 V for bare Au electrode (green) for cells of *S. loihica* PV-4 electrochemically cultured over 5 days. The decrease of current at around 80 hours can be attributed to the shortage of lactate in the system.

10. Representive SEM images of bacterial cells on the PANI-NA/Au electrode after 5 days of electrochemical culture at 0.2 V, where thick biofilm was formed around the entire electrode surface.

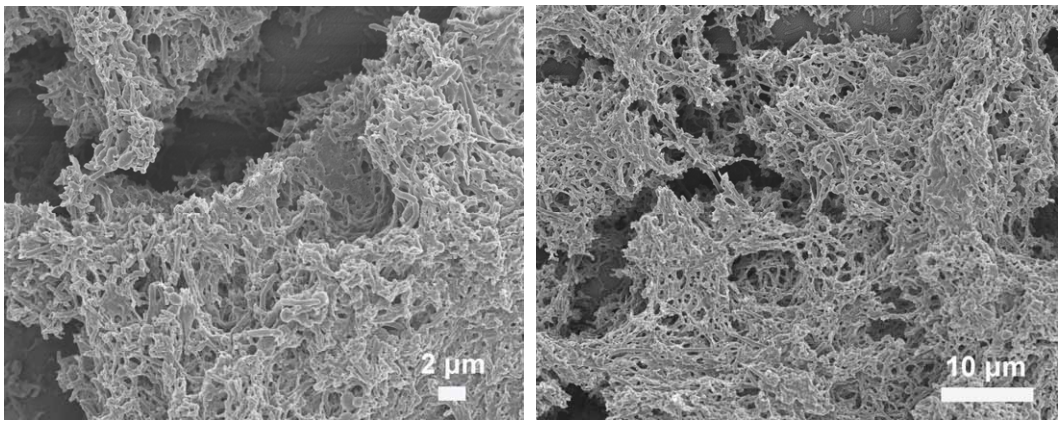

Fig. S10. Representative SEM imgaes of the bioflim on the PANI-NA/Au electrode after 5 days of electrochemical culture at 0.2 V, suggesting the thick bioflim was formed