Electronic Supplementary Information (ESI):

Use of Low Cost and Easily Regenerated Prussian Blue Cathodes for Efficient Electrical Energy Recovery in a Microbial Battery

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Materials and Methods

PB electrode preparation. Iron ferricyanide ($Fe[Fe(CN)_6]$) nanoparticles were synthesized by a simple and scalable solution-based chemical reaction. Specifically, 0.5 M potassium ferricyanide ($K_3[Fe(CN)_6]$) and 0.5 M ferric chloride ($FeCl_3$) were mixed in hydrochloride acid solution with pH 2. After 24 hours, the green precipitate was collected by centrifugation, washed three times with deionized water, and dried in a vacuum oven. A slurry was created by mixing dried green powder (85% wt), conductive carbon black (Super-P, TIMCAL, 8% wt) and PVDF (Sigma-Aldrich, 7% wt) in NMP (Sigma-Aldrich) were mixed and stirring overnight. The slurry was coated onto a piece of carbon cloth current collector (3 cm × 3 cm, Fuel Cell Earth, LLC). The coated carbon cloth electrodes were dried in a vacuum for 2 days, resulting in a total mass loading of ~60 mg. The electrodes were then reduced electrochemically in a phosphate buffer solution (PBS, pH 7) to 0 V vs. Ag/AgCl with 0.5 mA current. The resulting PB electrodes were exposed to air overnight before use.

MB construction and operation. Two single-chambered, membrane-free MB reactors were fabricated: one was a plate-shaped plexiglass chamber of 3 cm × 3 cm × 0.3 cm [S1]; the other was simply a 100-mL glass bottle. The anode was a carbon cloth (3 cm × 3 cm, Fuel Cell Earth) microbial anode that was pre-cultured and producing current in a classic H-shaped MFC for more than 3 months [S2]. The original inoculum was domestic wastewater from the Palo Alto Regional Water Quality Control Plant. The cathode was the PB electrode. A plastic mesh was placed between the anode and cathode to prevent contact. The electrolyte was a phosphate buffer solution (PBS) containing ~1 g/L glucose [S2]. The MB was operated with a fixed current output, controlled by a Bio-Logic VMP3 potentiostat-galvanostat. For the plate-shaped MB used to investigate the charge efficiency and energy efficiency of the MB, the operation was stopped when the cell voltage dropped to 0 V. At this point, the electrolyte before and after the operation cycle

was analyzed. The bottle-shaped MB was applied to study operational parameters and the cycling performance of PB electrodes, where a double junction Ag|AgCl|KCl reference electrode (RE) was placed in the MB. The operation was stopped at designated cut-off potentials for the PB electrode.

Characterization. A BioLogic VMP3 potentiostat-galvanostat was used for all electrochemical characterizations. A double junction Ag|AgCl|KCl reference electrode (RE) and a Pt counter electrode (CE) were used as needed. X-ray diffraction measurements (XRDs) were carried out with a PANalytical X'Pert (Ni-filtered Cu Kα radiation). Scanning electron microscope (SEM) images were obtained with a FEI Nova NanoSEM. For the SEM, the anode sample was pretreated with a fixing and critical point drying process [S2]. The chemical oxygen demand (COD) of the electrolyte was determined using a HACH COD analysis kit (HACH, Co., USA).

References

S1. X. Xie, M. Ye, P.-C. Hsu, N. Liu, C. S. Criddle and Y. Cui, *Proceedings of the National Academy of Sciences of the United States of America*, 2013, 110, 15925-15930.

S2. X. Xie, L. Hu, M. Pasta, G. F. Wells, D. Kong, C. S. Criddle and Y. Cui, *Nano Letters*, 2011, 11, 291-296.

Supplementary Figures

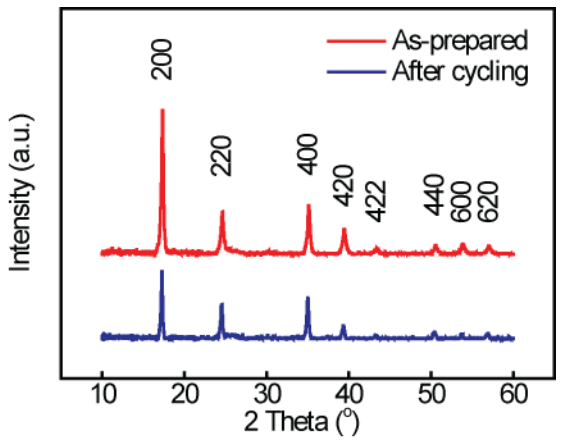

Fig. S1. X-ray diffraction (XRD) patterns of the PB electrodes as-prepared and after 20 cycles of reduction-and-regeneration operation in a MB.

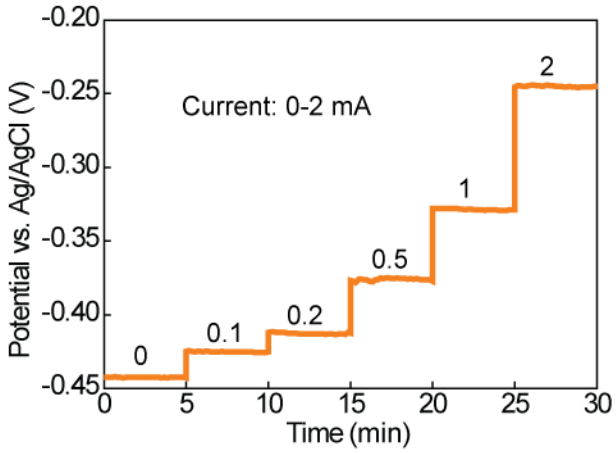

Fig. S2. Potential of the pre-cultured carbon cloth microbial anode (3 cm × 3 cm) at different current outputs. The current output values are labeled above the potential curve.

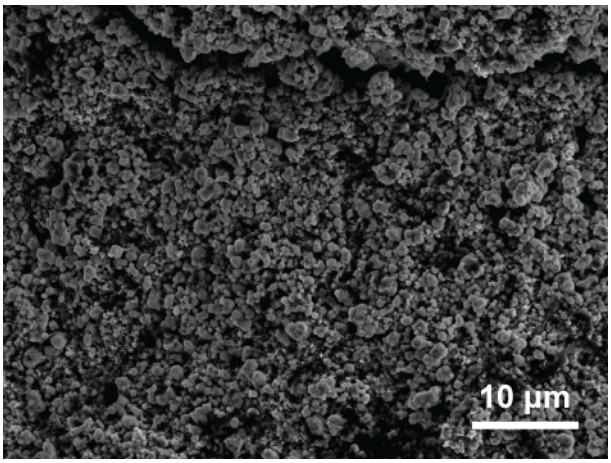

Fig. S3. Scanning electron microscope (SEM) image of the PB electrodes after 20 cycles of reduction-and-regeneration operation in an MB.