## **Supporting Information**

## Layer-by-Layer assemble of Au and CdS nanoparticles on the surface of bacterial cell for photo-assisted bioanode in microbial

## fuel cells

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Fig. S1 Transmission electron microscopy images of Au NPs (A) and CdS NPs (B). The inset is the enlarged view of the images. Scanning electron microscopy images of Au NPs (C) and CdS NPs (D). ζ-potential (E), X-ray diffraction analysis (F) and UV-Visible spectroscopy analysis (G) of Au NPs (I) and CdS NPs (II). The hydrodynamic diameter of Au NPs (H) and CdS NPs (I). The size of Au NPs were about 10-15 nm while the size of CdS NPs were about 3-5 nm. Regular and uniform spherical shapes are observed for the Au NPs. The  $\zeta$ -potential of Au NPs and CdS NPs were 41.3 ± 0.9 mV and  $-38.9 \pm 1.6$  mV respectively. In the XRD pattern, the peaks at  $2\theta$  = 38.2°,44.4°, 64.6° and 77.6° (curve I) correspond to (111), (200), (220) and (311) planes of Au NPs, while the peaks at  $2\theta = 26.4^{\circ}$ ,  $43.9^{\circ}$ ,  $51.9^{\circ}$ , can be assigned to (111), (220) and (311) planes of CdS NPs.<sup>1, 2</sup> As shown in Fig. S1G, there were obvious absorption peak at 525 nm (I) and 420 nm (II) in curve, corresponding to the absorption peaks of Au and CdS respectively.<sup>1,2</sup> Dynamic Light Scattering (DLS) revealed the hydrodynamic diameter of Au NPs were  $18.36 \pm 0.18$  nm while the hydrodynamic diameter of CdS NPs were  $7.29 \pm 0.14$  nm. As mentioned above, the positively-charged Au NPs and negatively-charged CdS NPs were successfully prepared.



**Fig. S2** X-ray diffraction analysis of *E. coli* after each modification (A) and intensity ratio of peak at 38.2° to peak at 26.4° (B).



**Fig. S3** Cell-growth curves of native *E. coli* (I) and LbL self-assembled *E. coli* (II *E. coli*@Au<sub>1</sub>@CdS<sub>0</sub>, III *E. coli*@Au<sub>1</sub>@CdS<sub>1</sub>, and IV *E. coli*@Au<sub>3</sub>@CdS<sub>2</sub>). The inset is the enlarged view of the curves. Error bars represent standard error (s.e.) determined by three independent experiments.



**Fig. S4** The Nyquist curves (A) and current-time curves (B) of photo-bioanode with LbL self-assembled *E. coli* (I *E. coli*@Au<sub>2</sub>@CdS<sub>2</sub> and II *E. coli*@Au<sub>3</sub>@CdS<sub>2</sub>). The frequency ranged from  $10^5$  to  $10^{-3}$  Hz, and the inset is the enlarged view of the curves.



**Fig. S5** Current-time curve of electrode modified with Au NPs separately in the electrochemical cells (ECs) with the addition of 2-hydroxy-1, 4-naphthoquinone (HNQ) as mediator and the glucose as substrate.

Table S1 The statistical table of current density produced by photo-bioanodes in dat	k
condition and light illumination.	

Layer No.	plateau current density in each cycle   without light illumination   Layer   No. (mA cm <sup>-2</sup> )				average of three plateau currents densities in each cycle with light illumination (mA cm <sup>-2</sup> )				averaged current density increment (mA cm <sup>-2</sup> )	averaged current density increment / averaged plateau current density without light illumination	
	0	1	2	3	average	1	2	3	average		
0/0	0.23	0.21	0.16	0.15	0.19±0.04	0.27	0.24	0.20	0.24±0.04	0.05	26.32%
0/1	0.52	0.53	0.48	0.40	0.48±0.06	0.66	0.65	0.53	0.61±0.07	0.12	25.00%
1/1	0.40	0.40	0.36	0.37	0.38±0.02	0.52	0.53	0.47	0.51±0.03	0.13	34.21%
2/1	0.51	0.52	0.57	0.51	0.53±0.03	0.80	0.80	0.76	0.79±0.02	0.26	49.06%
2/2	0.41	0.37	0.37	0.46	0.4±0.04	0.54	0.49	0.57	0.53±0.04	0.13	32.50%
3/2	0.48	0.60	0.48	0.53	0.52±0.03	0.84	0.73	0.83	0.80±0.06	0.28	53.85%

Electrode Substrates	Photoanode Materials	Exoelectrogen Type	Maximum Power Density (mW m <sup>-2</sup> )	Ref.
FTO	Fe <sub>2</sub> O <sub>3</sub>	Shewanella oneidensis	185 (light)	3
Crabon Felt	TiO <sub>2</sub> /TNT	sludge	1284 (light)	4
/	Nb <sub>2</sub> O <sub>5</sub>	Escherichia coli	1196 (light)	5
FTO	Ag-TiO <sub>2</sub>	sludge	1850 (light)	6
Graphite Felt	TiO <sub>2</sub> /Fe <sub>2</sub> O <sub>3</sub>	sludge	638.3 (light)	7
Carbon Felt	/	carbon dots-coated Shewanella oneidensis	1697.9 (light)	8
Carbon Cloth	/	carbon dots-fed Shewanella oneidensis	491 (dark)	9
Carbon Felt	/	PDA modified S.xiamenensi	452.8 (dark)	10
Carbon Cloth	/	Polypyrrole-coated Shewanella oneidensis	1479 (dark)	11
Carbon Felt	/	LbL self- assembled <i>Escherichia coli</i>	1704.3 (dark) 2300.4 (light)	This work

**Table S2** Comparison of the performance of previous photo-assisted MFCsemploying biofilm-attached photoanodes and previous MFCs using functionalizedbacterial cells.

## References

- 1. R.-B. Song, S. Zhou, D. Guo, P. Li, L.-P. Jiang, J.-R. Zhang, X. Wu and J.-J. Zhu, *ACS Sustainable Chem. Eng.*, 2019, **8**, 1311-1318.
- 2. A. Aboulaich, D. Billaud, M. Abyan, L. Balan, J. J. Gaumet, G. Medjadhi, J. Ghanbaja and R. Schneider, *ACS Appl. Mater. Interfaces*, 2012, **4**, 2561-2569.
- G. Zhu, Y. Yang, J. Liu, F. Liu, A. Lu and W. He, *Biosens. Bioelectron.*, 2017, 94, 227-234.
- 4. H.-W. Kim, K.-S. Lee, A. Razzaq, S. H. Lee, C. A. Grimes and S.-I. In, *Energy Technol.*, 2018, **6**, 257-262.
- M. Li, X. He, Y. Zeng, M. Chen, Z. Zhang, H. Yang, P. Fang, X. Lu and Y. Tong, *Chem. Sci.*, 2015, 6, 6799-6805.
- 6. G. Lui, G. Jiang, M. Fowler, A. Yu and Z. Chen, *J. Power Sources*, 2019, **425**, 69-75.
- 7. G. Ren, Y. Sun, A. Lu, Y. Li and H. Ding, J. Power Sources, 2018, 408, 46-50.
- D. Guo, H.-F. Wei, R.-B. Song, J. Fu, X. Lu, R. Jelinek, Q. Min, J.-R. Zhang, Q. Zhang and J.-J. Zhu, *Nano Energy*, 2019, 63. 103875.
- C. Yang, H. Aslan, P. Zhang, S. Zhu, Y. Xiao, L. Chen, N. Khan, T. Boesen, Y. Wang, Y. Liu, L. Wang, Y. Sun, Y. Feng, F. Besenbacher, F. Zhao and M. Yu, *Nat. Commun.*, 2020, 11, 1379.
- 10. S.-R. Liu, L.-F. Cai, L.-Y. Wang, X.-F. Yi, Y.-J. Peng, N. He, X. Wu and Y.-P. Wang, *Chem. Commun.*, 2019, **55**, 10535-10538.
- R.-B. Song, Y. Wu, Z.-Q. Lin, J. Xie, C. H. Tan, J. S. C. Loo, B. Cao, J.-R. Zhang, J.-J. Zhu and Q. Zhang, *Angew. Chem. Int. Ed.*, 2017, 56, 10516-10520.