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## **Supporting Information**

# Bio-photoelectrochemical cell with MoS<sub>3</sub>-modifed silicon nanowire photocathode for hydrogen and electricity production

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Figure S1. Schematic diagram of the BPEC setup

#### Enrichment of the electrochemically active bacteria in the bioanode

After about one-month accumulation, stable electricity production was achieved in the bio-electrochemical system (carbon felt was used as the cathode, and the cathode compartment was continuously sparged with air in experiments where oxygen was used as the electron acceptor). Figure S6 shows a stable voltage output for about 500 hours. The maximum power density obtained was about 2 W m<sup>-3</sup> (normalized to the bioanode chamber volume). After the output voltage reached above 300 mV and became stabilized (with an external resistance of 500  $\Omega$ ), the bioanode was used to couple with the photocathode to construct the BPEC for hydrogen production.



*Figure S2.* Variation of cell voltage during the long-term operation (A); and

Polarization curves of the bio-electrochemical system (B)

### SEM images of the bioanode

SEM imaging was used to show the presence of the electrochemically active bacteria in the bioanode of the BPEC. The detailed procedures about the SEM analysis could be found in our previous study (Zang et al., Environ. Sci. Technol. 2010, 44, 2715-2720). After the output voltage of the bio-electrochemical system reached above 300 mV (with an external resistance of 500  $\Omega$ ) and became stabilized, the electrode was sampled and used for SEM analysis. The images show that the microorganisms colonized on the electrode surface and displayed mainly in rods, implying the success enrichment of the electrochemically active bacteria on the bioanode.



Figure S3. SEM image of the anode-attached microorganisms



*Figure S4.* XPS spectra of the MoS<sub>3</sub>/SiNW electrode

## Cyclic voltammetry (CV) of MoS<sub>3</sub>-modified SiNW

The tests on the chemical stability of the electrode with CV was conducted. And the results showed that no feature peaks other than photoreduction of water were found in the CV curves, implying the chemical stability of the catalyst.



Figure S5. CV of the MoS<sub>3</sub>-SiNW electrode in dark and light

#### Polarization curves of the anode and the photocathode in the BPEC

The polarization curves of the photocathode in the BPEC were measured in a three electrode system, where the photocathode served as the working electrode, the Pt electrode as the counter electrode and a Ag/AgCl electrode as the reference electrode. The polarization curves of the anode in the BPEC were also measured in a three electrode system, where the anode served as the working electrode, pt electrode s the counter electrode and a Ag/AgCl electrode as the reference.



*Figure S6.* Polarization curves of the anode (A) and the photocathode (B) in the BPEC in dark and light



*Figure S7*. Voltage of the PEC with the SINW photocathode and the abiotic-anode (across 52.4  $\Omega$  resistor) during the light and dark cycles