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Visible-light-enhanced power generation in microbial fuel cells coupling with 3D nitrogen-doped graphene

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Section A Experiments

1 Materials and chemicals

Graphite (ks-10, 99.95%) and copper chloride were purchased from Sigma-Aldrich. Thiourea, dicyandiamide ($C_2H_4N_4$) and NaAc were purchased from Nanjing Reagent Company, China. All reagents were of analytical grade and were used without further purification. Carbon paper (CP) was bought from HeSen Electrical Co. (Shanghai, China). Ultra-pure water (18.2 MΩ resistivity, Milli-Q, Millipore) was used for all the experiments.

2 Apparatus

The morphology of the samples was observed by a Hitachi S4800 field-emission scanning electron microscopy (FESEM) and a JEOL JEM 200CX transmission electron microscopy (TEM, 200kV). XRD was performed on a diffractometer (XRD-6000, Shimadzu, Japan) with Cu Kα radiation (λ = 1.5405 Å). Raman spectra was obtained with a confocal Raman Spectrometer (Renishaw invia Raman microscope) with an excitation wavelength of 633 nm. The X-ray photoelectron spectra (XPS) analysis were carried out on an electron energy spectrometer (K-alpha, Thermo Scientific, USA) using Al Kα (1486.6 eV) as the X-ray excitation source. The electrochemical impedance spectroscopy (EIS) of the inoculated bio-anodes was recorded on an Autolab PGSTAT12 (Metrohm/Eco Chemie, BV, The Netherlands) in suspensions of bacterial cells at open-circuit potential. The frequency range was between 10^{-2} and 10^{5} Hz. Other electrochemical measurements were performed using an electrochemical workstation (CHI660D, Chenhua, China). A PALS Zeta Potential Analyzer Ver. 3.43 (Brookhaven Instruments Corp.) was employed for Zeta potential analysis. In the measurement of VLD-MFC, a 500 W xenon lamp coupled with an AM 1.5 global filter was utilized as the irradiation source. The UV-visible (UV-vis) absorption spectra was tested on a UV-3600 UV-visible spectrophotometer (Shimadzu, Japan).

3 Synthesis of 3D NG-SSs

GO was prepared from natural graphite powder according to a modified Hummer's method.[1, 2] NG-SS was synthesized by a combined solvothermal assembly and freeze-drying process. In a typical procedure, 6 mL GO (3 mg mL^{-1}, ethylene glycol as solvent) dispersion containing 0.0303 g $C_2H_4N_4$ was first treated by sonication for 10 min in an ice bath, NaAc (0.0340 g) was then added to the solution, followed by vigorous stirring for 15 min to obtain stable mixed suspension (Fig. S1A). Two milliliters of the suspension were transferred to a vial, and then the vial was sealed in a Teflon-lined stainless steel autoclave and maintained at 200 °C for 6 h. After cooling down to room temperature, the as-prepared hybrid architecture was dialyzed with ultrapure water for 72 h, the ultrapure water was changed for every 12 h (Fig. S1B). Finally, the resulting sample was freeze-dried to obtain a monolithic NG-SS (denoted as 3D NG-SS) (Fig. S1C). For comparison, samples containing different nitrogen contents were prepared with different contents of $C_2H_4N_4$ at 0.0 g, 0.0200 g, 0.0610 g, respectively, denoted as 3D G-SS, 3D NG-SS-1 and 3D NG-SS-2.

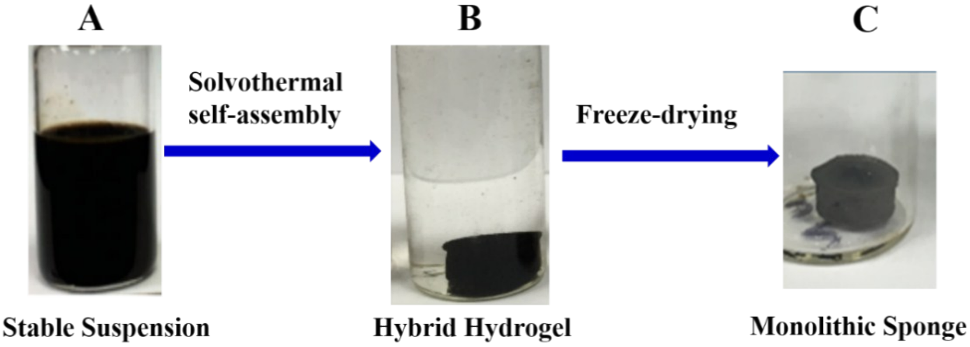

Fig. S1 Fabrication process for the 3D N-doped graphene self-standing sponge. (A) Stable suspension of Go, $C_2H_4N_4$ and NaAc in a vial. (B) N-doped graphene hybrid hydrogel prepared by hydrothermal self-assembly. (C) Monolithic 3D NG-SS obtained after freeze-drying.

4 Synthesis of p-type semiconductor CuS

In a typical procedure, 0.1613 g copper chloride and 0.1827 g thiourea were dissolved in 20 mL ethylene glycol solvent under vigorous stirring, respectively. Subsequently, thiourea solution was gradually dropped into copper chloride solution and the solution was stirred for 1 h. Then the mixture was transferred to a Teflon-lined stainless steel autoclave and maintained at 170 °C for 24 h. The as-synthesized product was collected by centrifugation and washed with ethanol for several times. Finally, the sample was freeze-dried for 7 h.

5 Electrode preparation

The geometric surface area of the 3D electrodes was precisely measured by the vernier caliper. For 3D NG-SSs and G-SS electrode preparation, two monolithic sponges were glued to both sides of a stainless-steel mesh (60 × 60 mesh, type SUS304, Xinsilu Metal Product Co. Ltd., Shanghai, China) which was used as the substrate electrode. The glue was conductive carbon paint (Structure Probe, Inc., SPI Supplies, USA). The stainless-steel mesh (15 mm × 20 mm) was placed in acetone for 3 h before the experiment. To keep the shape of graphite rod electrodes similar with that of the prepared 3D electrodes, commercial available graphite rods (10 mm diameter, 10 cm height) were cut into slices (10 mm diameter, 3 mm height), and they were directly glued to both sides of a stainless-steel mesh. Prior to be glued, the slices were sterilized in boiling 0.1 M H_2SO_4 for 30 min and washed several times with ultrapure water, followed by placing in absolute ethanol overnight.

The fabrication of the photocathode was very simple. 6 mg of the as-prepared CuS powder was scattered in 1 mL of the ultrapure water ultrasonically, and then 300 μL of this uniformly distributed suspension was dropped on a carbon paper electrode with a premodified area of 3.14 cm^2. After being dried, the electrode was treated at 170 °C for 30 min in air and then naturally cooled to the room temperature. Accordingly, the loading content of CuS (mg cm^{-2}) on photocathode was normalized to the area of carbon paper (2 × 2 cm). To optimized the CuS content, different concentrations of CuS suspension was coated on carbon paper.

6 MFC construction and operation

H-shaped dual-chamber MFCs were constructed by connecting two glass bottles with a 30 mm diameter tube. The *Shewanella oneidensis* MR-1 cells harvested at late stationary phase were inoculated into the MFC anode chamber containing 100 mL of M9 buffer solution with 5% Luria–Bertani (LB) broth and 30 mM lactate as the electron donor. The anode chambers were maintained under anaerobic conditions. The catholyte was 50 mM $K_3[Fe(CN)_6]$ in 100 mM phosphate buffer (PBS, pH 7.4) solution, and the traditional commercial carbon paper (2 × 2 cm) was used as the regular cathode. To investigate the influence of different nitrogen-doping contents of 3D NG-SSs on the performance of MFC, the four 3D electrodes (3D G-SS, 3D NG-SS, 3D NG-SS-1, 3D NG-SS-2) were immersed in the same anode chamber simultaneously. In VLD-MFC measurement, the cathode was replaced by the prepared photocathode. The anode and the cathode chambers were separated by a proton-exchange membrane (Nafion 211, DuPont), and connected to an external resistance of 1000 Ω with titanium wire. The voltage was recorded with a multimeter. Linear sweep voltammetry was used to obtain the polarization curves in one typical cycle at a scan rate of 1 mV s^{-1}. The current density and power density in electrochemical measurements were normalized to the geometric surface area of anode with no special instruction. To evaluate the solo photocathode performance, the response of current to potential was measured by using a three-electrode cell with the photocathode as the working electrode, a Pt wire counter electrode and a saturated calomel reference electrode. The *Shewanella oneidensis* MR-1 cells were cultivated aerobically at 30 °C in 5 mL of LB broth for 12 h, and then the strain was further cultured at 30 °C and agitated at a rate of 150 rpm for 24 h. The cells were harvested at late stationary phase by centrifugation (6000 rpm, 5 min), washed three times with PBS, and then suspended in the MFC anode chamber. M9 buffer solution was composed of 22 mM KH_2PO_4, 42 mM Na_2HPO_4, 5.5 mM NaCl, and 1.0 mM $MgSO_4$. All media were sterilized before use.

7 SEM characterization of *Shewanella oneidensis* MR-1 cells

The bioanodes were removed from anode chamber of the MFC and immediately fixed in 2.5% glutaraldehyde solution for 2 h, washed three times with PBS, and dehydrated in a graded series of aqueous ethanol solutions (25, 50, 75, 95, and 100%) for 10 min each. The samples were then dried to remove residual moisture and coated with Au prior to SEM observation.

Section B Results and Discussion

1 Characterizations of 3D monolithic sponges

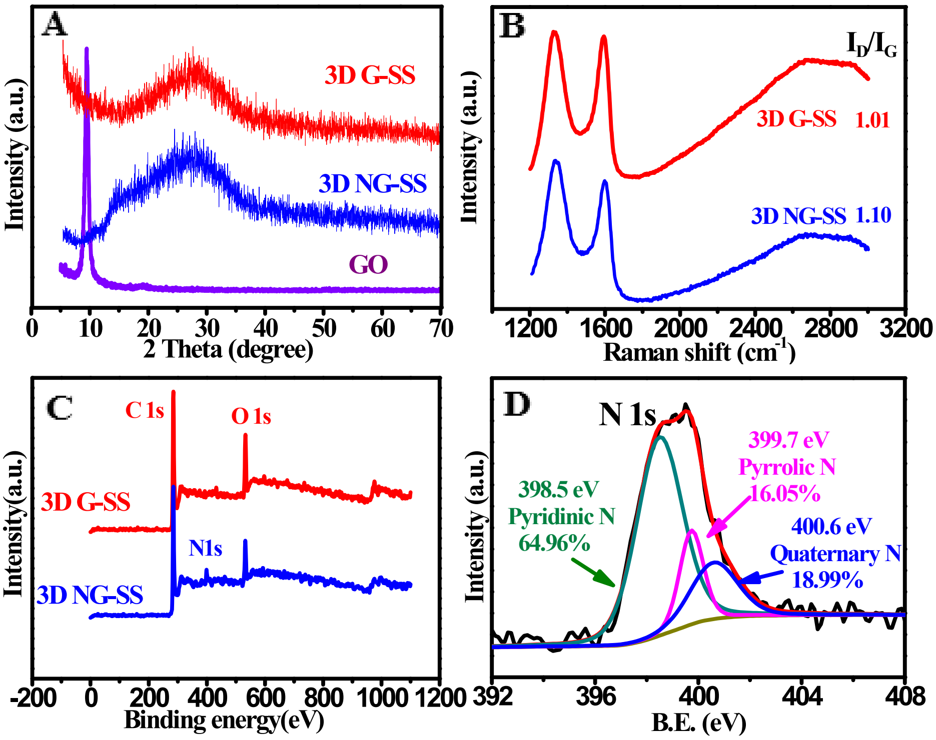

Fig. S2 (A) XRD patterns of the 3D G-SS, 3D NG-SS and GO. (B) Raman spectra and (C) X-ray photoelectron survey spectra of the 3D G-SS and 3D NG-SS. (D) High-resolution N 1s spectra of the 3D NG-SS with 5.04 at% nitrogen-doping content.

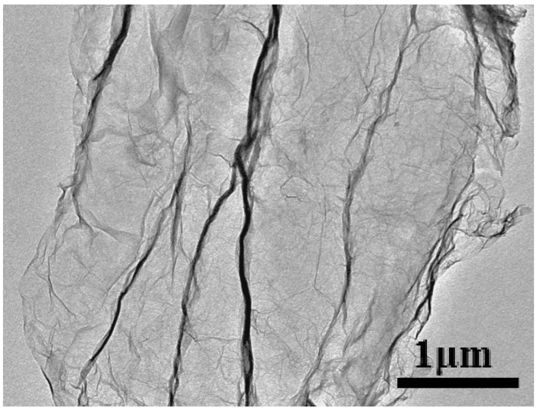

Fig. S3 TEM image of the 3D NG-SS.

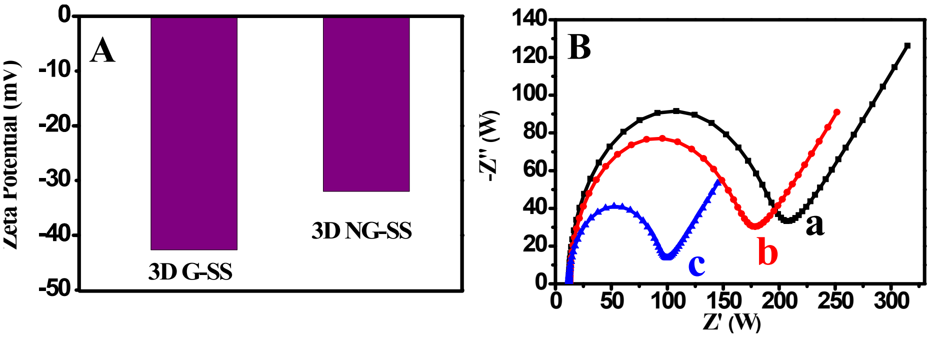

Fig. S4 (A) Zeta potential of the 3D G-SS and 3D NG-SS. (B) The Nyquist curves of different anodes: (a) 2D graphite rod plain anode, (b) 3D G-SS anode and (c) 3D NG-SS anode.

2 The effects of nitrogen-doping contents in 3D NG-SS anode on MFC

The effects of different nitrogen-doping contents on the performance of MFCs in 3D NG-SS-1 or 3D NG-SS-2 anode was also investigated. The structure characterizations of XRD and Raman were similar with that of 3D NG-SS, shown in Fig. S5. XPS spectra demonstrate that 4.23 at% and 8.61 at% nitrogen-doped were found in 3D NG-SS-1 and 3D NG-SS-2, respectively (Fig. S6A). The P_{max} of MFC (Fig. S7A) with 3D NG-SS-1 and 3D NG-SS-2 reached 1278 ± 14 mW m^{-2} and 1166 ± 8 mW m^{-2}, respectively. It demonstrates that overdose or insufficient nitrogen-doping would not guarantee the high output power of MFCs. The constant-load discharge curves in Fig. S7B also indicate the same conclusion. By comparing the high-resolution N 1s spectra of all 3D nitrogen-doped graphene anodes (Fig. S2D and Fig. S6B、C、D), it could be observed that the energy peak intensity of pyridinic N reach to the highest level when the nitrogen-doping content is 5.04 at%, and then it decreases with the increase of nitrogen-doping content, which indicates that pyridinic N plays an important role in improving EET.

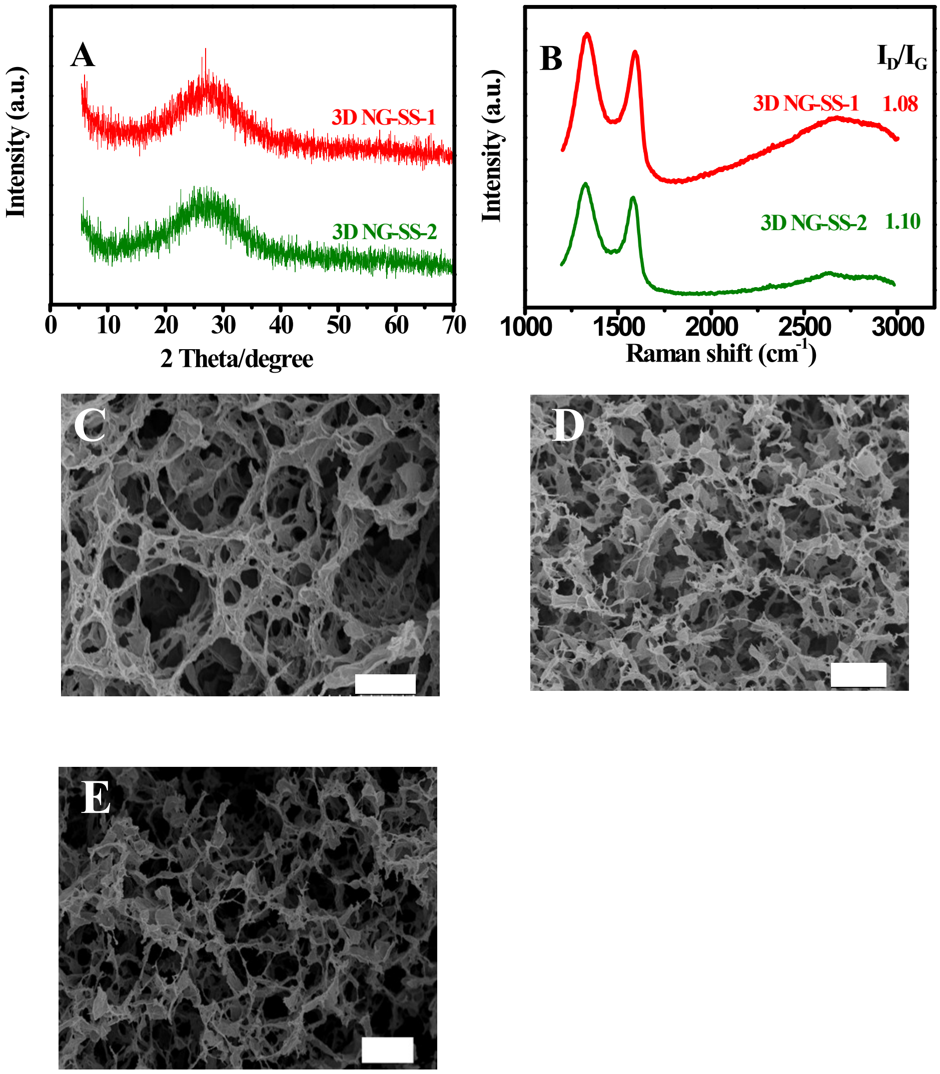

Fig. S5 (A) XRD patterns of the 3D NG-SS-1 and the 3D NG-SS-2. (B) Raman spectra of the 3D NG-SS-1 and the 3D NG-SS-2. (C) SEM images of 3D G-SS. Scale bar: 5 µm. (D) SEM images of 3D NG-SS-1. Scale bar: 15 µm. (E) SEM images of 3D NG-SS-2. Scale bar: 15 µm

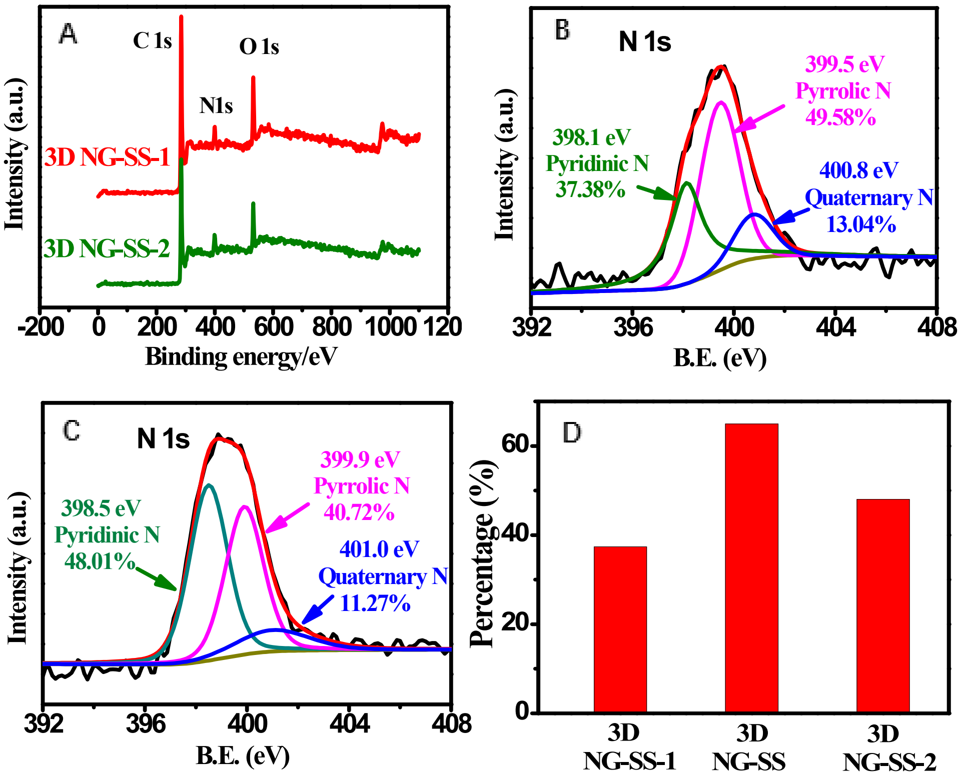

Fig. S6 (A) X-ray photoelectron survey spectra (XPS) of the 3D NG-SS-1 and the 3D NG-SS-2. (B) High-resolution N 1s spectra of the 3D NG-SS-1 with 4.23% nitrogen-doping contents. (C) High-resolution N 1s spectra of the 3D NG-SS-2 with 8.61% nitrogen-doping contents. (D) The percentage of pyridinic N in 3D NG-SS、3D NG-SS-1、3D NG-SS-2.

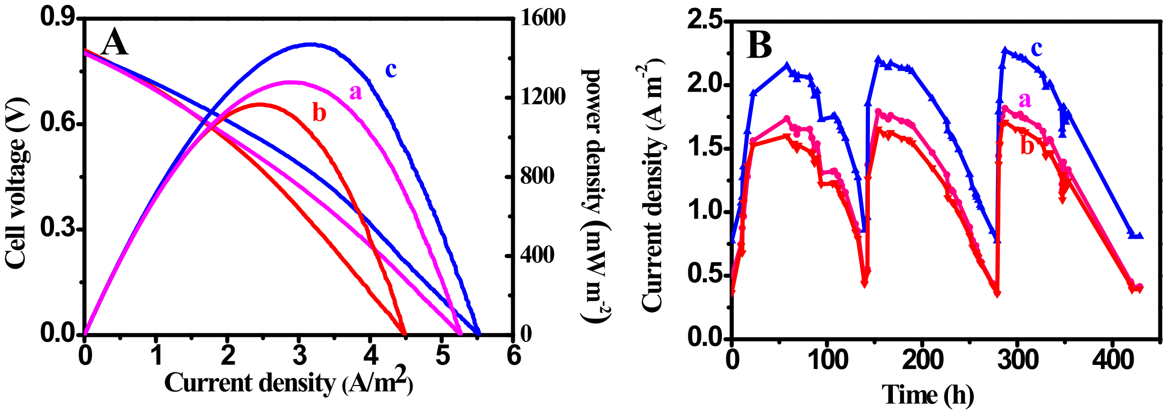

Fig. S7 (A) Polarization curves and (B) Constant-load discharge curves of MFCs with (a) 3D NG-SS-1 anode, (b) 3D NG-SS-2 anode and (c) 3D NG-SS anode.

3 Characterization of CuS

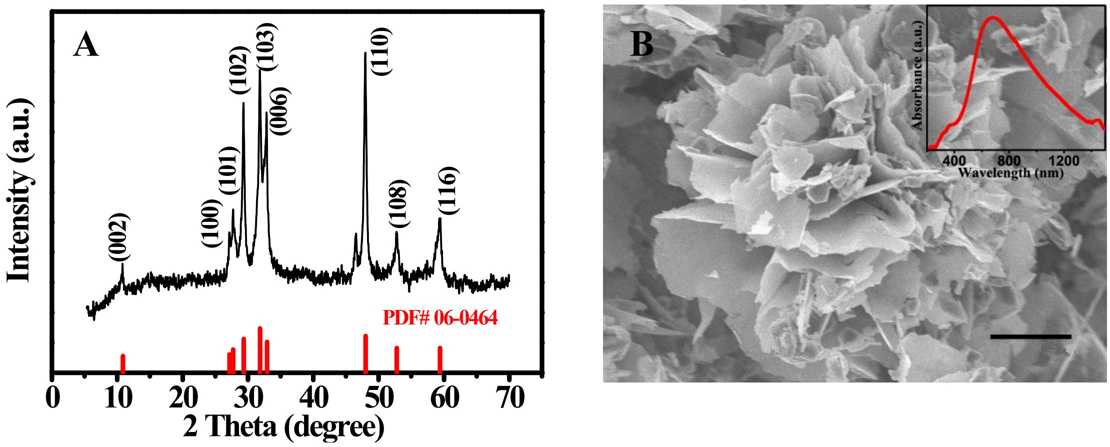

Fig. S8 (A) XRD patterns and (B) SEM image of the as-prepared semiconductor CuS. Scale bar: 2 μm. Inset of part B is the UV-vis absorption spectrum of CuS.

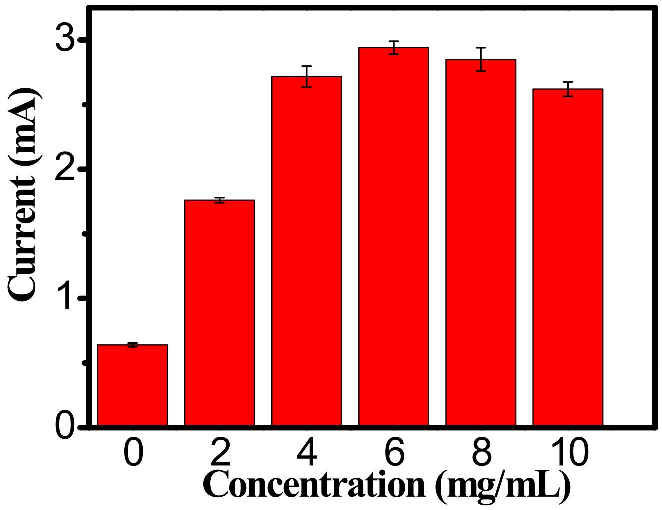

Fig. S9 The reduction current of different loading contents of CuS coated photocathode in $K_3[Fe(CN)_6]$ electrolyte at 0.1V vs. SCE. Scan rate: 10 mV s^{-1}.

Table S1. Performance of the recently reported MFCs

anode	cathode	bacteria	power density(mW/m^2)	Reference
3D NG-SS	Carbon paper	S. oneidensis MR-1	1471	This work
3D NG-SS	CuS photocathode	S. oneidensis MR-1	2607	This work
3D MWCNT@rGo	Carbon fiber brush	S. putrefaciens CN32	789	[3]
3D N-enriched graphitic carbon	Carbon cloth	S. oneidensis MR-1	750	[4]
PPy nanotubular coated-carbon textile	Carbon textile	Activated anaerobic sludge	727	[5]
3D open-celled carbon scaffold	Carbon paper	E. coli	30.7	[6]
Graphene-containing foam	Carbon paper	S. putrefaciens.	786	[7]
CNT-sponge	Pt-coated CNT-sponge	Domestic wastewater	1240	[8]
Monolithic 3D-graphene	Pt/C coated carbon paper	E. coli	897	[9]
Nitrogen-doped graphene nanosheet	Carbon cloth	E. coli	1008	[10]
3D nitrogen-doped graphene aerogel	Carbon cloth	S. oneidensis	1990	[11]

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