**Supplementary Information**

**Nitrogen doping to atomically match reaction sites in microbial fuel cells**

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Supplementary Figure 1. FESEM micrographs of PANI nanowires without any treatment (a), N-CNWs/CC-700 (b), N-CNWs/CC-800 (c) and N-CNWs/CC-1000 (d). (e) Raman spectra of different N-CNWs/CC.

Supplementary Figure 2. XPS survey spectra of PANI and different N-CNWs.
Supplementary Figure 3. XPS N1s spectrum of PANI nanowire and N-CNWs (a: PANI nanowire, b: N-CNWs/CC-600, c: N-CNWs/CC-700, d: N-CNWs/CC-800, e: N-CNWs/CC-900, f: N-CNWs/CC-1000).
Supplementary Figure 4. (a) CVs of N-CNWs electrodes in 50 mM potassium ferricyanide solution. (b) CVs of N-CNWs/CC-900 in 2 μM FMN solution change with time. CVs (c) and DPV (d: the insert is peak current density histogram of different N-CNWs) of FMN spontaneously adsorbing onto N-CNWs electrodes from a 2 μM FMN solution in 0.1M phosphate buffer (PBS) at PH=7.4 over 50h. Error bars represent one standard deviation.
**Supplementary Figure 5.** The peak current and the ratio of Quaternary N over oxidized N of differently N-CNWs/CC electrodes. Error bars represent one standard deviation.

**Supplementary Figure 6.** Total XPS spectra (the insert is P2p spectra) of N-CNWs/CC-900 before and after absorbed FMN.
**Supplementary Figure 7.** Peak current density against time of carbon cloth, N-CNWs/CC-600 and N-CNWs/CC-700 in 2 μM FMN solution with 0.1M phosphate buffer (PBS) at PH=7.4. Error bars represent one standard deviation.

**Supplementary Figure 8.** FESEM micrographs of *S. putrefaciens* cells adhered on the surface of FMN-immobilized electrode.
Supplementary Figure 9. CV curves at different scan rate of FMN-immobilized electrode measured in an anaerobic of *S. putrefaciens* CN32 suspension with 18 mmol L\(^{-1}\) lactate medium.

Supplementary Figure 10. Peak current density and CV curves at different scan rate of the plain carbon electrode measured in an anaerobic of *S. putrefaciens* CN32 suspension with 18 mmol L\(^{-1}\) lactate medium.
**Supplementary Figure 11.** Optimized structures of FMN adsorbed on carbon surface, N-CNWs/CC-900, N-CNWs/CC-800 and N-CNWs/CC-700.

**Supplementary Figure 12.** (a): The molecular structure and the two-electron redox reaction equations of RF. CVs (b), peak current histogram image (c) and Nyquist plots (d) of RF spontaneously adsorbing onto N-CNWs/CC electrodes from a 2 μM RF solution in 0.1M phosphate buffer (PBS) at pH=7.4 over 50h. Error bars represent one standard deviation.
| N-CNWs/CC-700 | N-CNWs/CC-800 | N-CNWs/CC-900 | N-CNWs/CC-1000 |
|---------------|---------------|---------------|----------------|
| BET surface area (m²/g) | 143.9 | 148.1 | 167.3 | 170.6 |
| Pore Size (nm) | 3.071 | 3.661 | 2.863 | 2.762 |
| Water contact angle (°) | 101.8 | 102.5 | 103.6 | 106.9 |
| Electron conductivity (Ω) | 13.83 | 8.376 | 6.995 | 13.07 |
| Electroactive surface area (cm²/g) | 371.9 | 426.1 | 601.3 | 557.58 |

**Supplementary Table 1** Summary of BET surface area, pore size, water contact angle, and electron conductivity of the nanowires after carbonized at different temperatures.

| Sample | Conten t of nitrogen atoms | Pyridine N 398.5±0.3e V | Pyridine or Pyrrole N 400.5±0.3e V | Quaternary N 401.2±0.3e V | Oxidized N 402.9±0.3e V | Ratio of Quaternary N and Oxidized N | O1s peak connect with nitrogen 533.3±0.3e V |
|--------|---------------------------|--------------------------|---------------------------------|--------------------------|--------------------------|---------------------------------------|----------------------------------|
| N-CNWs-600 | 10.94% | 4.25% | 5.02% | 0.37% | 1.3% | 0.28 | 1.8% |
| N-CNWs-700 | 10.345% | 4.03% | 4.85% | 0.445% | 1.02% | 0.437 | 1.5% |
| N-CNWs-800 | 8.19% | 2.94% | 3.36% | 1.01% | 0.88% | 1.15 | 2.09% |
| N-CNWs-900 | 7.8% | 2.55% | 2.52% | 1.9% | 0.53% | 3.55 | 2.1% |
| N-CNWs-1000 | 0.624% | 0.18% | 0.17% | 0.2% | 0.074% | 2.74 | 1.5% |

**Supplementary Table 2** Distribution of N species obtained from the deconvolution of the N1s peak of N-CNWs.
**Supplementary Table 3** Summary of reported bioelectrode materials for MFCs applications with *S. putrefaciens* or *S. oneidensis* as biocatalyst.

| Electrode | Inoculum | Substrate | Device type | Performance | Ref.  |
|-----------|----------|-----------|-------------|-------------|-------|
| FMN-immobilized atomic matched nitrogen doped anode | *S. putrefaciens CN32* | Lactate medium | Dual-chamber MFC | 2102.88 mW m$^{-2}$ | This work |
| graphene-containing foam | *S. putrefaciens* | Lactate medium | Dual-chamber MFC | 786 mW m$^{-2}$ | 1 |
| Carbon nanotubes and polyaniline (PANI) on microporous graphite felt | *S. putrefaciens* | Acetate medium | Dual-chamber MFC | 308 mW m$^{-2}$ | 2 |
| PANI networks onto graphene nanoribbons coated carbon paper | *S. oneidensis* | Lactate medium | Dual-chamber MFC | 856 mW m$^{-2}$ | 3 |
| PANI networks onto graphene nanoribbons coated carbon paper | *S. oneidensis* | Lactate medium | Dual-chamber MFC | 856 mW m$^{-2}$ | 3 |
| Graphene aerogel | *S. putrefaciens CN32* | Lysogeny broth (LB) | Dual-chamber MFC | 679.7 mW m$^{-2}$ | 4 |
| Graphene aerogel | *S. putrefaciens CN32* | Lysogeny broth (LB) | Dual-chamber MFC | 679.7 mW m$^{-2}$ | 4 |
| TiO$_2$ nanocrystal/rGO | *S. putrefaciens CN32* | LB medium | Dual-chamber MFC | 540 mW m$^{-2}$ | 6 |
| Graphene/amineous TiO$_2$ | *S. oneidensis* | Lactate medium | Dual-chamber MFC | 1060 mW m$^{-2}$ | 7 |
| N-doping graphene aerogel (N-GA) | *S. oneidensis MR-1* | Trypticase soy broth | Dual-chamber MFC | 1990.8±106.1 mW m$^{-2}$ | 8 |
| Macroporous graphitic carbon foam polydopamine (PDA) | *S. putrefaciens* | Lactate medium | Dual-chamber MFC | 1735 mW m$^{-2}$ | 9 |
| Mo2C-functionalized carbon felt | *S. putrefaciens CN32* | Lactate medium | Dual-chamber MFC | 1025 mW m$^{-2}$ | 10 |
| Polyaniline hybridized large mesoporous carbon (PANI-LMC) | *S. putrefaciens CN32* | Lactate medium | Dual-chamber MFC | 1280 mW m$^{-2}$ | 11 |

**Supplementary Table 4** Adsorption energy of FMN adsorbed on different electrode interface.

| Structure | Carbon surface | N-CNWs-900 | N-CNWs-800 | N-CNWs-700 |
|-----------|----------------|------------|------------|------------|
| $E_{haxel}$ (eV) | -553.713 | -537.158 | -541.884 | -531.586 |
| $E_{FMN}$ (eV) | -332.711 | -332.711 | -332.711 | -332.711 |
| $E_{total}$ (eV) | -886.431 | -870.129 | -874.683 | -864.356 |
| $E_{ads}$ (eV) | -0.007 | -0.260 | -0.088 | -0.059 |
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