

Supporting Information for

Binder-free Nitrogen-doped Graphene Catalyst Air-cathode for Microbial Fuel Cells

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Experimental Section

Nitrogen-doped graphene synthesis and characterization. The growth of NG was conducted by using a CVD process (Figure S1). Briefly, a nickel mesh (40×40 , Φ 0.13 mm, Alfa Aesar) was placed in a tube furnace. The furnace was heated up to 1000 °C with a rate of 10 °C/min under a highly pure Ar and H₂ flow, in order to anneal the nickel mesh. Initially, the flow rates were 300 mL/min for Ar and 20 mL/min for H₂, and after 30 min, were changed to 1000 mL/min for Ar and 50 mL/min for H₂ at the same time. At 1000 °C, the acetonitrile was fed into the CVD reactor as a NG precursor with the feeding time of 5 min, but using different feeding rates from 10 μ L/min to 50 μ L/min. At the optimal feeding rate, the feeding time was changed, varying from 5 min to 20 min. The NG was characterized by scanning electron microscope (SEM, TESCAN MIRA 3LMH), Raman spectroscopy (LabRAM HR Evolution), and X-ray photoelectron spectroscopy (XPS, ESCALAB 250 Xi).

Air-cathode fabrication. The air-cathode contained three layers, including a diffusion layer, a catalyst layer and a supporting layer. The diffusion layer was fabricated with carbon black (25 mg/cm², Clean Fuel Cell Energy, CB-XC72) and polytetrafluoroethylene (PTFE, 37.5 mg/cm², Sigma–Aldrich, 60 wt.% dispersed in water) using a batch press process, as previously described. The catalyst layer was the nickel mesh covered with N-doped graphene, and the supporting layer was 50×50 stainless steel mesh. The catalyst layer was sandwiched between a supporting layer and a diffusion layer. These layers were pressed together without any binder in the MFC reactors. Pt air-cathodes were fabricated by a common method using 5 mg/cm² 10%

Pt/C catalyst, 5 wt% Nafion binder, and 30% wet-proofing carbon cloth with four PTFE diffusion layer as a benchmark.

Electrochemical Analysis and MFC Experiment. The electrochemical reactor consisted of two 2-cm cubic-shaped chambers separated by an anion exchange membrane in the middle. A high purity platinum mesh (99.99%, 1 cm²) was placed in one chamber as a counter electrode, and a saturated calomel electrode (SCE) was placed in the other chamber as a reference electrode (3 M KCl, 0.241 V versus a standard hydrogen electrode) close to an air-cathode, the working electrode. Electrochemical tests were conducted in 50 mM phosphate buffer solution (PBS). Linear sweep voltammetry (LSV) was carried out from 0 V to −0.4 V vs SCE with a scan rate of 1 mV/s. In the chronoamperometry tests, each potential (0 V, −0.1 V, −0.2 V, −0.3 V and −0.4 V versus SCE) was applied for ~1 h.

These cathodes were also tested in MFC reactors, cubic-shaped single-chambers (4 cm long and 3 cm in diameter). The anode was a graphite fiber brush (2.5 cm in both diameter and length) with two twisted titanium wires as a core. The medium was 50 mM PBS with 1 g/L sodium acetate, 5 mL/L vitamins and 12.5 mL/L minerals. All the MFCs were operated at 30 °C. The polarization tests were conducted by applying different resistors from 1000 Ω to 20 Ω , with each resistor used for a complete cycle.

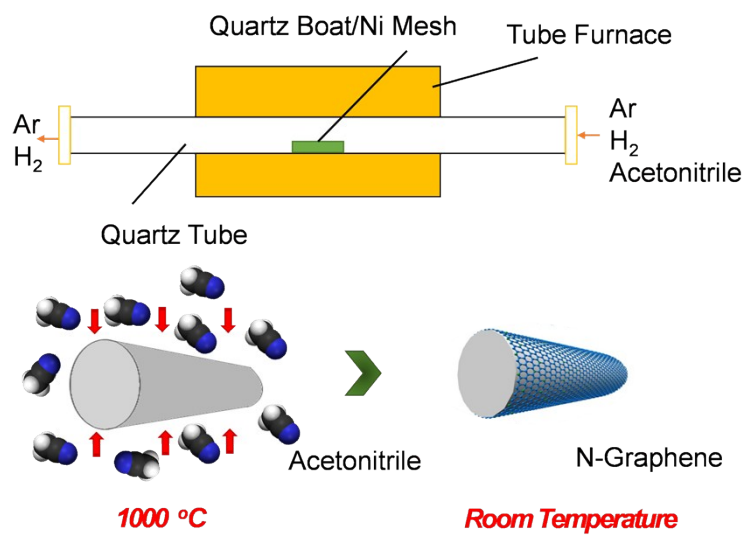


Figure S1 Schematic of a CVD process for growing N-doped graphene on a nickel mesh.

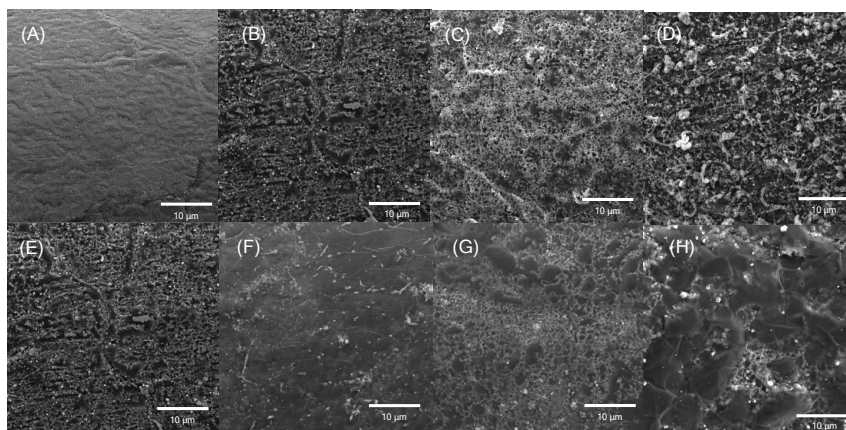


Figure S2. High-magnification SEM images of NG/Ni mesh synthesized at different precursor feeding rates (A-D) and time spans (E-H). From A to D, the feeding rate increased gradually, 10 $\mu\text{L}/\text{min}$, 20 $\mu\text{L}/\text{min}$, 40 $\mu\text{L}/\text{min}$, 50 $\mu\text{L}/\text{min}$ respectively, and the feeding time was fixed as 5 min. From E to H, the feeding time increased gradually, 5 min, 10 min, 15min, 20 min respectively, and the feeding rate was fixed as 20 $\mu\text{L}/\text{min}$.

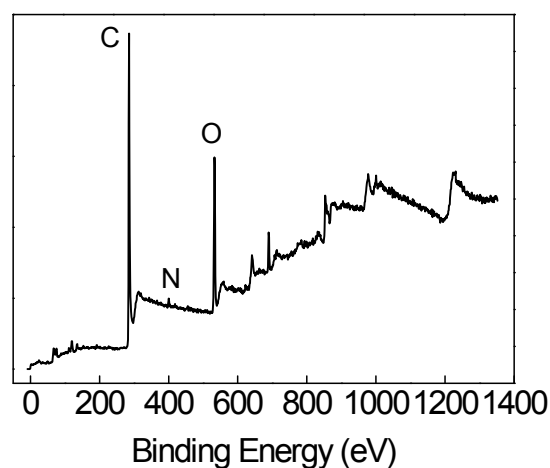


Figure S3. XPS survey scan of NG synthesized with 20 $\mu\text{L}/\text{min}$ feeding rate.

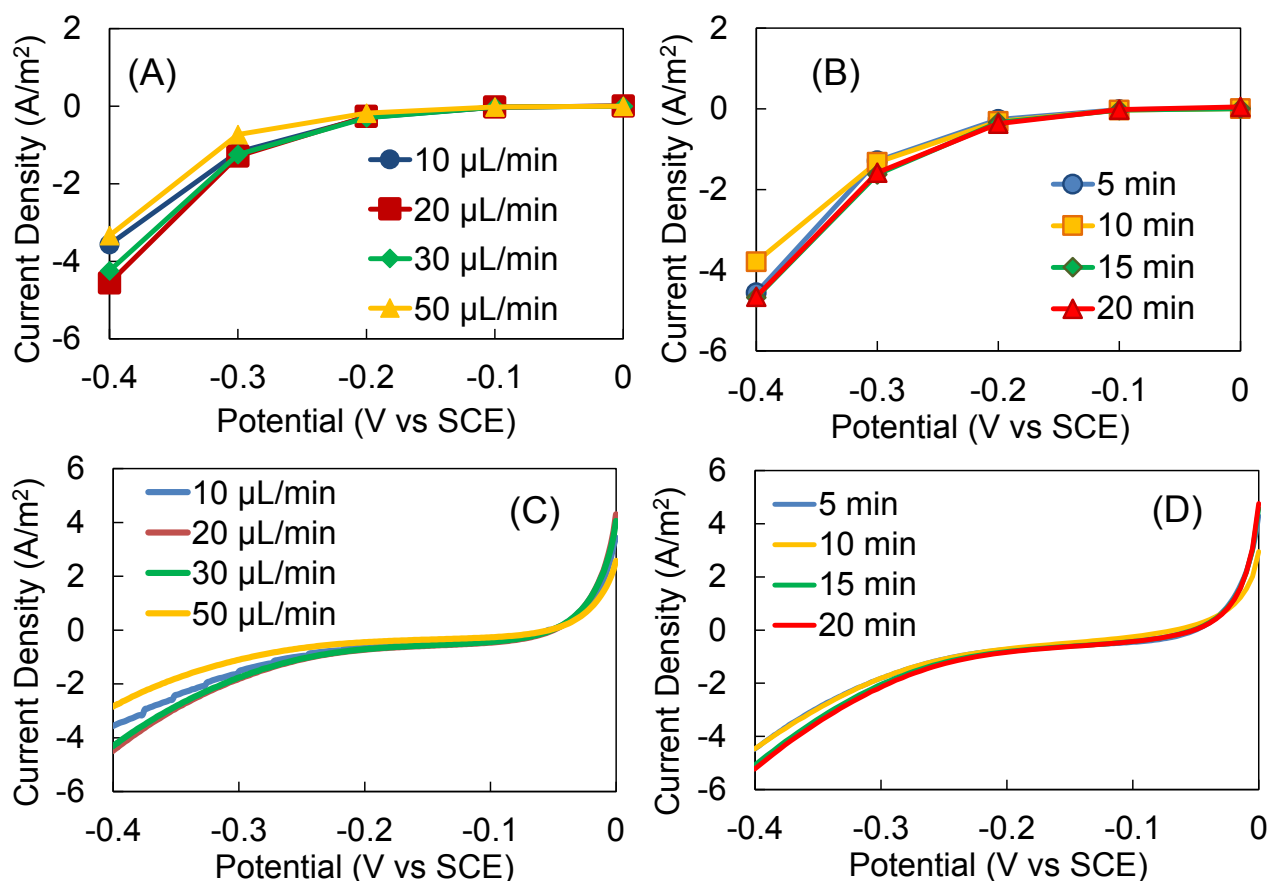


Figure S4. Current-potential curves of NG cathodes synthesized at different feeding rates (A) and feeding time (B), obtained using an abiotic electrochemical cell in chronoamperometry tests. Linear sweep voltammetry of NG cathodes synthesized at different feeding rates (C) and feeding time (D).