Supporting Information

1. Supporting information of experimental method

1.1 Preparation of air cathodes

In a diffusion layer, 212 mg carbon black and 705.5 mg polytetrafluoroethylene were mixed uniformly, rolled onto a current collector under 5 MPa for 10 min then sintered at 340 °C for 20 min to fabricate the diffusion layer. For the catalyst layer, 20 mg catalyst was mixed with 80 mg activated carbon and 40 μL PTFE to form a homogeneous paste, which was then rolled onto a stainless steel mesh identical to the current collector. Then, the catalyst layer and diffusion layer were pressed (4.5 MPa, 20 min) together and heated (80 °C, 10 min) to fabricate an air cathode.

1.2 Material characteristics

X-ray diffraction (XRD; D8 Advance, Bruker, Germany) experiments were conducted at 40 kV and 40 mA with Cu Kα radiation (λ = 0.15418 nm) to characterize the structure of catalysts. The catalysts were scanned at 4° min−1 from 15° to 90° at 0.01° intervals.

The surface morphologies of catalysts (pre-treated with Pt to increase their conductivity) were studied using scanning electron microscopy (SEM, MERLIN VP Compact) with an accelerating voltage of 20 kV, transmission electron microscopy (TEM, JEOL JEM-2100F) and high-resolution TEM (HRTEM, JEOL JEM-2100F) with an accelerating voltage of 200 kV.

X-ray photoelectron spectroscopy (XPS) was performed using an electron spectrometer (Thermo Fisher, ESCALAB 250Xi) equipped with an Al Kα (*hν* = 1486.6 eV) radiation source. The spectra were calibrated internally using the binding energy (BE) of carbon C1s at 284.8 eV.

Raman spectra were recorded on a Jobin Yvon (Laboratory RAM HR1800) confocal micro-Raman spectrometer with backscattered geometry through a 10× (NA = 0.25) microscope objective. An Ar^+ laser (514.5 nm) was used as the excitation source.

1.3 MFC tests

MFC experiments were carried out in a single-chamber cubic-shaped reactor consisting of a 4 cm Lexan block containing a single cylindrical chamber (d ~ 3 cm). The gap between cathode and anode was approximately 1 cm to avoid direct contact. The diffusion layer of the air cathode faced the air to obtain sufficient O_2 for ORR. The MFCs were inoculated with the effluent of well-running MFCs. A solution composed of 1 g L^{-1} of NaAc,

4.57 g L^{-1} of Na_2HPO_4, 2.45 g L^{-1} of $NaH_2PO_4 \cdot H_2O$, 0.31 g L^{-1} of NH_4Cl, 0.13 g L^{-1} of KCl, a mineral and a vitamin solution was used as synthetic wastewater, thus the electrolyte.

1.4 Electrochemical tests

In electrochemical tests, the electrolyte (50 mM PBS) consisted of 4.57 g/L of Na_2HPO_4, 2.45 g/L of $NaH_2PO_4 \cdot H_2O$, 0.31 g/L of NH_4Cl, 0.13 g/L of KCl. CA tests were conducted to assess the catalytic performance of the air cathodes using an Autolab PGSTAT-204 potentiostat with a 1 h trial for each potential (0.2, 0.1, 0, –0.1, –0.2, –0.3 and –0.4 V vs. SCE).

Catalytic activities for the ORR of the graphene-based materials were measured using a rotating disk electrode (RDE), a rotating ring-disk electrode (RRDE) setup (MSR rotator, PINE Instruments, USA) and an Autolab PGSTAT-128N potentiostat equipped with the Nova 1.10 software. To prepare the catalyst-coated working electrodes, catalysts (5 mg), 95 μL absolute ethyl alcohol and 5 μL Nafion solution (5%) were mixed together using 30 min of sonication to form a homogeneous catalytic ink. Then, 10 μL catalyst ink was dripped onto the central surface of a glassy-carbon electrode and dried naturally. RDE and RRDE tests were conducted in O_2-saturated 50 mM PBS electrolytes at 1600 rpm with a sweep rate of 10 mV/s at room temperature. For RRDE tests, the electron transfer number (n) and hydrogen peroxide (% H_2O_2) were calculated as below:

$$n = 4 \times \frac{I_d}{I_d + I_r / N} \qquad (2\text{-}1)$$

$$\%H_2O_2 = 200 \times \frac{I_r / N}{I_d + I_r / N} \qquad (2\text{-}2)$$

where I_d and I_r represent the disk and ring current, respectively, and N=0.412 is the experimentally determined collection efficiency.

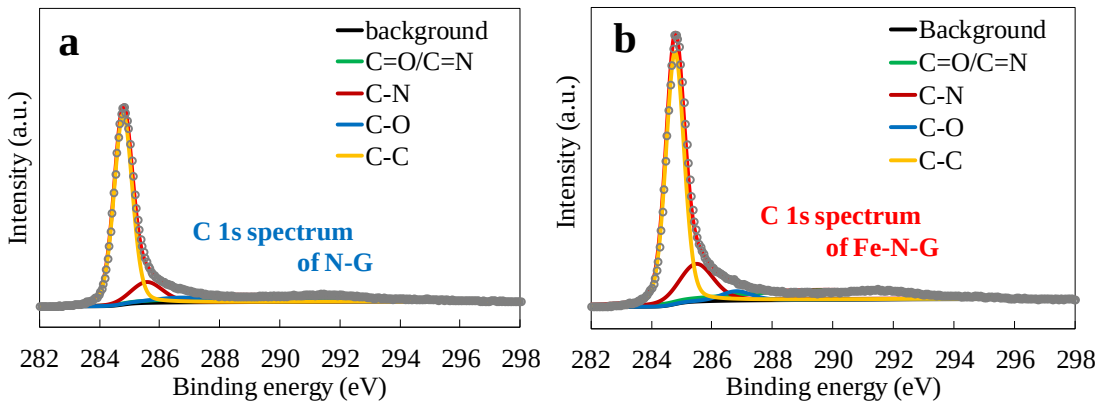

Figure S1. C 1s spectrum of N-G and Fe-N-G samples based on XPS results.

Table S1. Element concentration of N-G and Fe-N-G based on XPS results.

Samples	Element concentration (at. %)			
	C	O	N	Fe
Fe-N-G	90.37	5.63	1.57	2.42
N-G	97.45	1.42	1.13	-

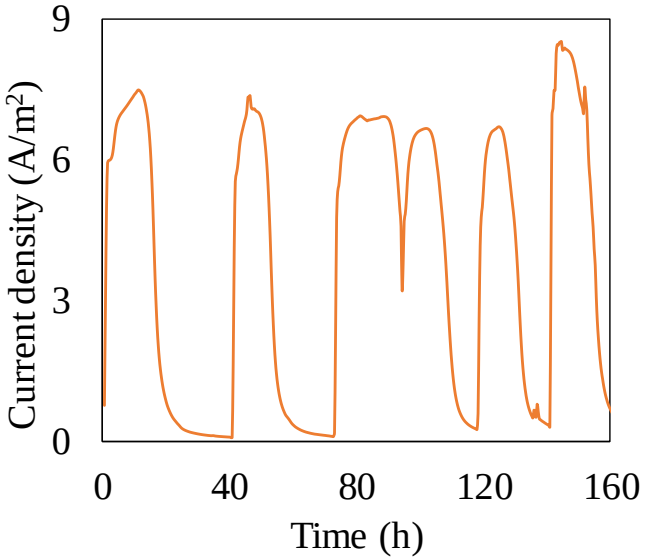

Figure S2. Current density changes of the MFC using Fe-N-G catalysts.

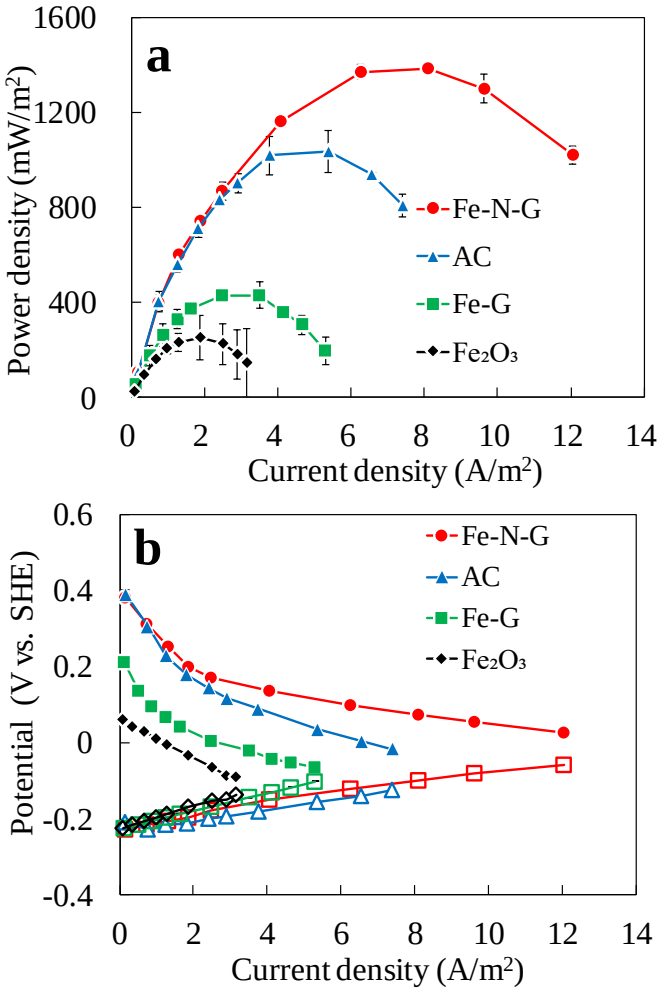

Figure S3. Power density of Fe-N-G, Fe-G, AC and Fe_2O_3 catalysts.

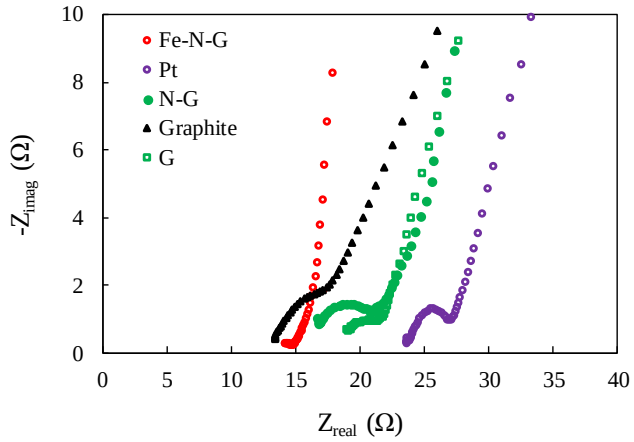

Figure S4. EIS results of graphene-based catalysts, graphite and Pt.

Table S2. Comparison of the Fe-N-G catalysts with graphite or graphene-based catalysts reported in the last five years

Catalyst	MCD (A/m^2)	MPD (mW/m^2)	Anode Substrate	Electrolyte	Cathode size (cm^2)	Catalyst loading (mg/cm^2)	Reference
Fe-N-G	12.1	1380	1 g/L NaAc	50 mM PBS	7.0	2.9	This work
PNCN	~4.5	1160	1 g/L NaAc	50 mM PBS	2.0	5	*Bioelectrochemistry*
NCN							(Wen et al., 2014)
	~3.0	660					
Graphene	~1.2	160	5 mL anaerobic	50mM PBS	1.0	--	*J. Hazard. Mater.*
biocathode	~0.4	40	activated sludge	containing			(Song et al., 2016)
Graphite felt	~0.32	30	and 95 mL	40 mg/L			
			glucose culture	Cr(VI)			
			medium				
V_2O_5/rGO	~3.8	530	1 g/L NaAc	Mixture of	15	0.5	*Electrochim. Acta*
				50mM PBS			(Noori et al., 2017)
	~2.5	380		and fish			
				market			
				wastewater			
GP-HG	~1.4	220	--	100 mM	7.0	0.125	*Prog. Nat. Sci.*
GP-TiO_2				PBS			(Mashkour et al.,
GP							2017)
	~0.8	85					
	~0.3	32					
PNIPAM GO	~3.7	450	300×10^{-6} M	100 mM	--	--	*Macromol. Rapid*
	~2.5	250	HNQ and 1 M	PBS			*Comm.* (kumar et al.,
			glucose solution				2014)
NG	~7.0	1470	1g/L NaAc	50 mM PBS	7.0	2.9	*J. Mater. Chem. A*
							(Wang et al., 2016)
FePc/GO_LiCl	~1.2	295	--	50 mM PBS	4.0	0.5	*J. Power Sources*
							(Costa de Oliveira et
							al., 2017)
GBC	~0.2	65	Glucose	50 mM PBS	30	--	*Int. J. Hydrogen*
							Energ. (Chen et al.,
							2017)
Fe_3O_4-RGO	~1.5	283	--	phenol and	--	--	*Adv. Mater. Res.* (Qi et
				glucose			al., 2014)
MN/NrGO	~1.0	135	anaerobic sludge	Synthetic	14	0.5	*RSC Adv.* (Gautam et
				Waste and 50			al., 2016)
				mM PBS			

MPD: the maximum power density of MFCs; MCD: the maximum current density of MFCs; NaAc: sodium acetate.

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