

**Electronic Supplementary Information (ESI)**  
**for**  
**Pristine carbon nanotube/iron phthalocyanine hybrids with a**  
**well-defined nanostructure show excellent efficiency and**  
**durability for oxygen reduction reaction**

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### **Experimental section**

#### **Catalysts synthesis**

The MWNT/FePc catalysts were prepared using FePc (Tokyo Chemical Industry Co., Ltd.) and MWNTs (average diameter: 20 nm, Nikkiso Co., Ltd.). Typically, 10 mg of FePc was deposited on 10 mg of MWNTs by shaking (200 rpm) at room temperature for 20 h, sonicating at room temperature for 6 h, and refluxing at 80 °C for 20 h in 40 ml THF

(Kishida Chemical Co., Ltd.) to obtain MWNT/FePc-SH, MWNT/FePc-SO and MWNT/FePc-RE, respectively. EtOH (Wako Pure Chemical Industries, Ltd.) was also used as a solvent in the shaking method. In addition, 5 mg, 10 mg, and 20 mg FePc were shaken together with 10 mg of MWNTs in 40 ml THF to prepare MWNT/FePc with a different FePc loading. For the preparation of oxMWNT/FePc, MWNTs were oxidized according to Ref. 34, and the obtained oxMWNTs (10 mg) was shaken with FePc (10 mg) in 40 ml THF for 20 h at room temperature. Pt/C catalyst (37 wt% Pt, TEC10V40E) and Pt/C gas diffusion electrode (Pt: 0.5 mg cm<sup>-2</sup>) were purchased from Tanaka Kikinzoku Kogyo and Electrochem. Inc, respectively.

### **Characterization**

The FePc loading in the catalysts was determined by thermogravimetric analysis (TGA, EXSTAR TG/DTA6300, Seiko Instruments, Inc.). The crystalline structure was examined using X-ray diffraction analysis (XRD, SmartLab, Rigaku Corp.). The microstructure was observed by scanning transmission electron microscope observation (STEM, SU9000, Hitachi High-Technologies Corp.). Raman spectra were measured using a confocal Raman system (533 nm, Raman-touch, Nanophoton Corp.). The electronic states of Fe, N, and C were determined by X-ray photoelectron spectroscopy (XPS, AXIS-ULTRA, Shimadzu Corp.).

## Electrochemical measurements

The ORR performance was evaluated by linear sweeping voltammetry (LSV) and cyclic voltammetry (CV) measured by a potentiostat (ALS760, BAS Inc.). The catalyst ink for each sample except Pt/C was prepared by dispersing 0.82 mg catalyst in the mixture of 6  $\mu\text{l}$  Nafion solution (5 wt%, Sigma-Aldrich Co. LLC.), 336  $\mu\text{l}$  2-propanol (Wako Pure Chemical Industries, Ltd.), and 84  $\mu\text{l}$  H<sub>2</sub>O by sonication. 20  $\mu\text{l}$  of the ink was cast on the glassy carbon electrode of a rotating ring-disk electrode (RRDE,  $\phi$  4 mm, Hokuto Denko Corp.). The catalyst loading was 0.3 mg cm<sup>-2</sup>. For Pt/C, the weight ratio of Pt/C to Nafion and the Pt loading were controlled to be 25 wt% and 14  $\mu\text{g}_{\text{Pt}}$  cm<sup>-2</sup>, respectively. An Ag/AgCl electrode in saturated KCl solution (Wako Pure Chemical Industries, Ltd.) and a Pt wire were applied as the reference and counter electrodes, respectively. 0.1 M KOH solution bubbled with N<sub>2</sub> or O<sub>2</sub> for 30 min was used as the electrolyte. In addition, methanol (0.1 M) was added to an N<sub>2</sub>-saturated 0.1 M KOH solution for the evaluation of methanol oxidation activity.

The potential vs. Ag/AgCl was converted to the reversible hydrogen electrode (RHE) scale by:

$$E(\text{vs. RHE}) = E(\text{vs. Ag/AgCl}) + 0.197 + 0.059 V \times pH \quad (1)$$

The number of electrons (n) involved in the ORR was calculated according to the Koutecky-Levich's equation,

$$\frac{1}{j} = \frac{1}{j_k} + \frac{1}{j_d} = \frac{1}{nFAkC_{O_2}} + \frac{1}{0.62nFAD_{O_2}^{2/3}\nu^{-1/6}C_{O_2}\omega^{1/2}} \quad (2)$$

where  $j$ ,  $j_k$ , and  $j_d$  are the measured, kinetic, and diffusion-limiting current, respectively; F is Faraday constant (96485 C mol<sup>-1</sup>); A is the electrode area (0.1256 cm<sup>2</sup>); k is the rate constant for oxygen reduction (m s<sup>-1</sup>);  $D_{O_2}$  is the diffusion coefficient of O<sub>2</sub> in the electrolyte (1.93×10<sup>-5</sup> cm<sup>2</sup> s<sup>-1</sup>);  $\nu$  is the viscosity of electrolyte solution (1.009×10<sup>-5</sup> cm<sup>2</sup> s<sup>-1</sup>);  $C_{O_2}$  is the saturation concentration of O<sub>2</sub> in the electrolyte (1.26×10<sup>-6</sup> mol cm<sup>-3</sup>); and  $\omega$  is the angular rotating rate.<sup>1</sup> The H<sub>2</sub>O<sub>2</sub> yield can be determined by the following equation,

$$H_2O_2\% = \frac{2 \times J_r}{(N \times |J_d|) + J_r} \times 100 \quad (3)$$

where  $J_r$  and  $J_d$  are the ring and disk current, respectively; N is the RRDE collection efficiency, 0.4. For the durability test, CV measurements were conducted in the range of 0.2 V and -0.6 V vs. Ag/AgCl at 20 mV s<sup>-1</sup> for 1000 cycles. The RRDE was rotating at 1600 rpm during the measurement. In Fig. S5, only the profile of the negative scan was presented.

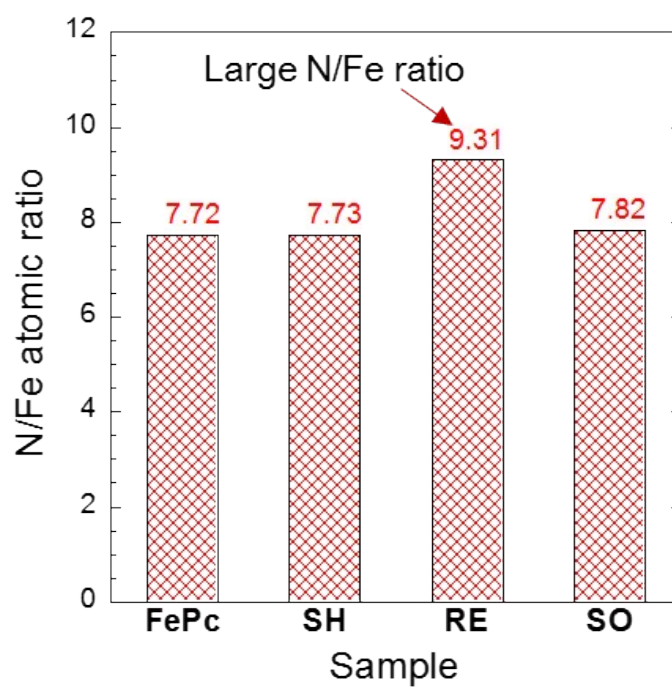
The cathode layer of zinc-air battery was prepared as follows. MWNT/FePc-SH was sonicated together with AS4 (catalyst:AS4 = 70:30 wt%; AS4: 5wt%, Tokuyama Corp.) in the mixture of 80 vol% 2-propanol and 20 vol% H<sub>2</sub>O. The obtained suspension was then dropped slowly into a square pool (1 cm×1 cm) and dried at 60 °C. The loading of MWNT/FePc-SH was controlled to be 1.0, 2.0, and 3.0 mg cm<sup>-2</sup>. The electrolyte was 6 M KOH solution. The cathode, Nylon mesh (100 mesh, AS ONE Corp.), gas diffusion layer (Tokuyama Corp.), stainless steel mesh (150 mesh, Nilako Corp.) and zinc plate (Nilako Corp.) were sandwiched by two Teflon plates as illustrated in Fig. 4a. Current-voltage characteristics of the cells were measured.

### Computational calculation

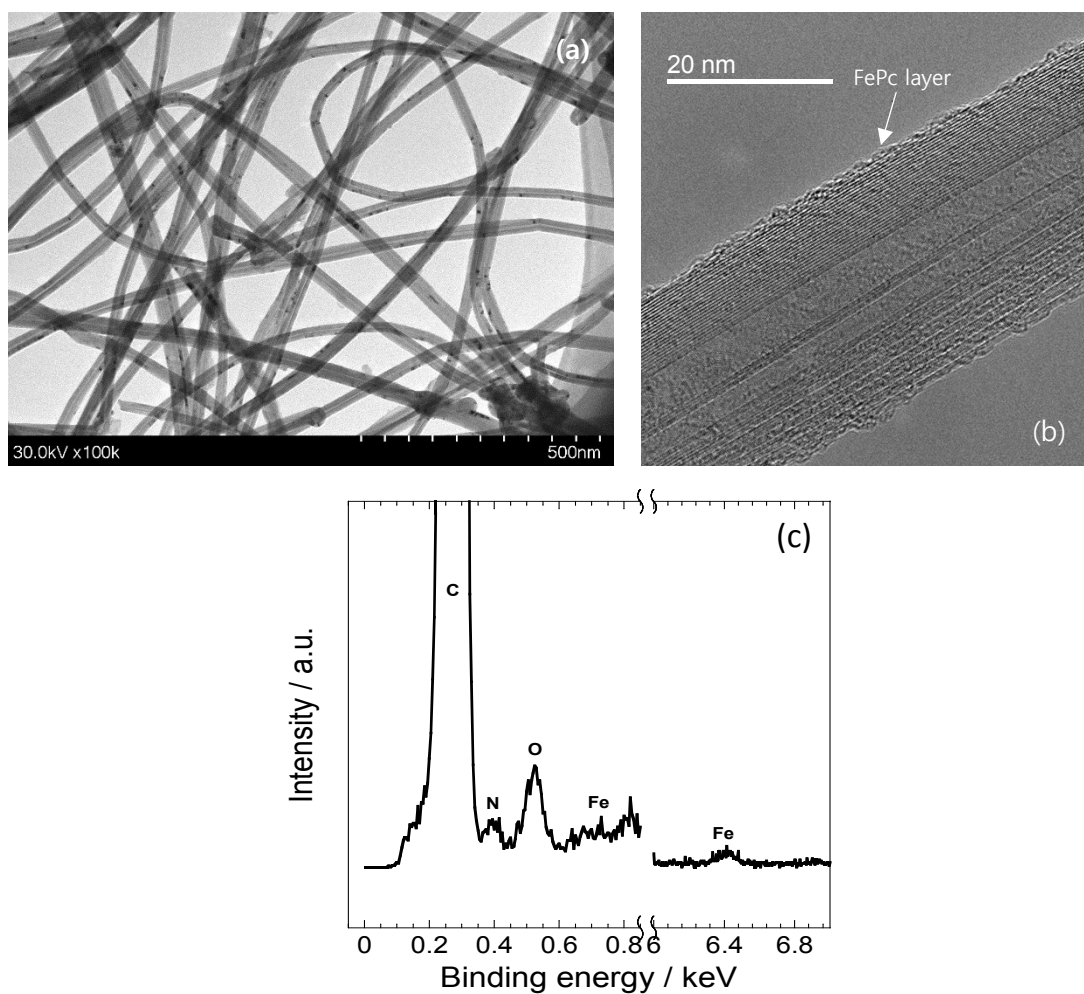
The density function theory (DFT) calculation was carried out using a software, Jaguar as included in Maestro (version: 2015/2). A piece of bent graphene plane (chirality: (150, 150)) terminated with proton on the edge was used to simulate a part of the MWNT's outer surface ( $\phi=20$  nm). The geometric optimizations for the MWNT-FePc system and FePc were performed with the LACV3P\*\* basis. The Mulliken population was investigated to evaluate the electronic states centered Fe ion. The adsorption energy of OH ( $E_{OH,abs}$ ) was accessed by,

$$E_{OH,abs} = E_{MWNT-FePc} + E_{OH} - E_{MWNT-FePc-OH} \quad (4)$$

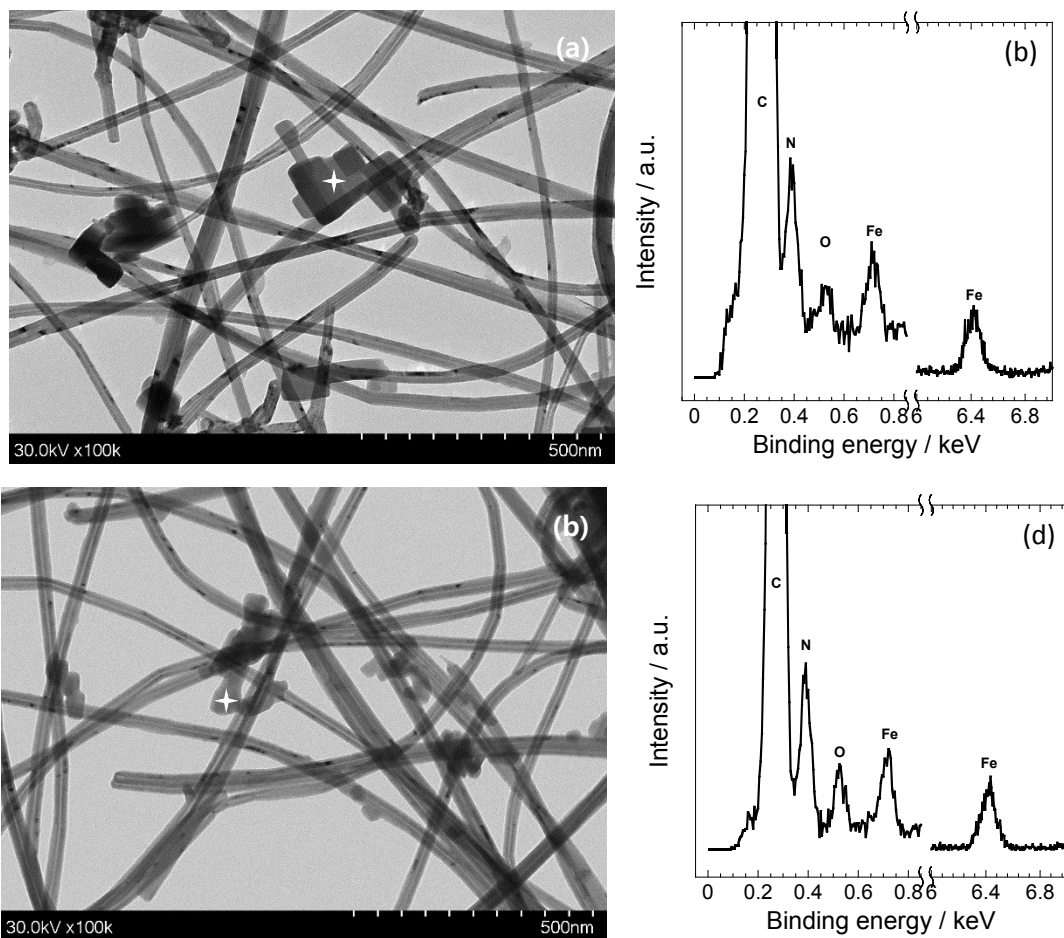
where  $E_{MWNT-FePc}$ ,  $E_{OH}$ , and  $E_{MWNT-FePc-M}$  represent the energies of the MWNT-FePc, OH radical, and MWNT-FePc-OH, respectively.



**Fig. S1.** Molar ratio of N/Fe of FePc, MWNT/FePc-SH, MWNT/FePc-RE, and MWNT/FePc-SO estimated from XPS spectra.

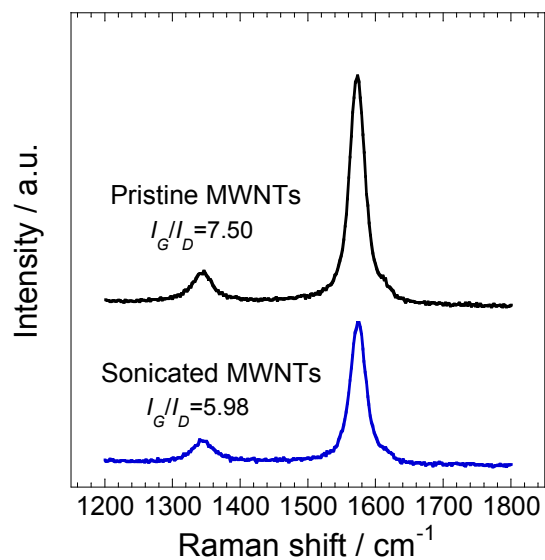


**Fig. S2.** (a) STEM and (b) TEM images of MWNT/FePc-SH; (c) EDX spectra of the total vision field of MWNT/FePc-SH in (a). The STEM image and EDS profile were obtained under a low accelerating voltage of 30 kV and the TEM image with high resolution was obtained under a high accelerating voltage of 120 kV.

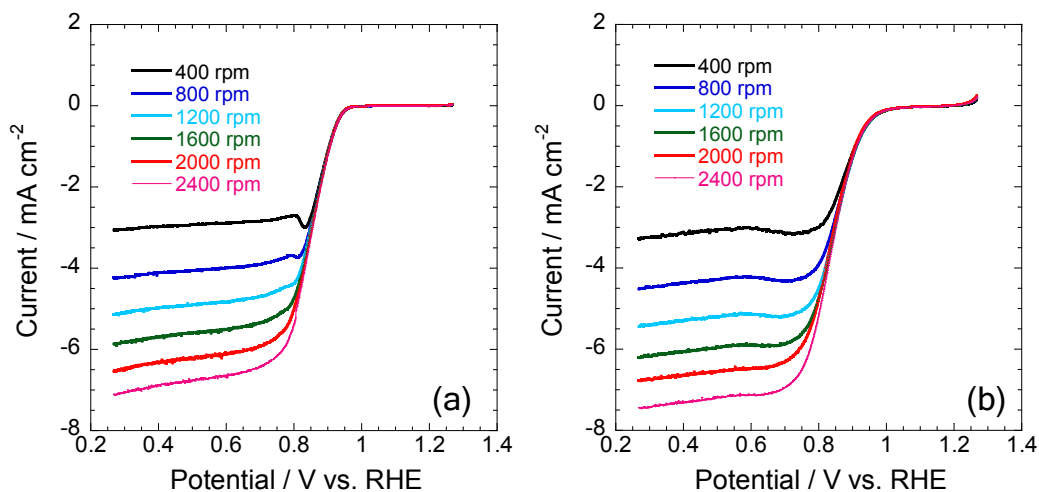


**Fig. S3.** STEM images of (a) MWNT/FePc-RE and (c) MWNT/FePc-SO; EDX spectra of (b) the asterisk-marked spot in (a) and (d) the asterisk-marked spot in (c). The STEM image and EDS profile were obtained under a low accelerating voltage of 30 kV.

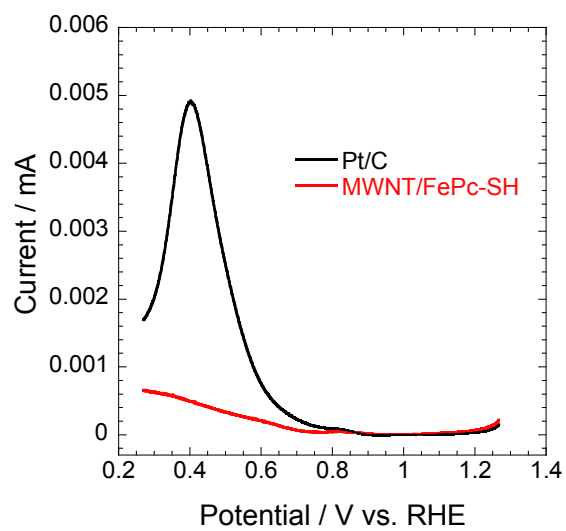




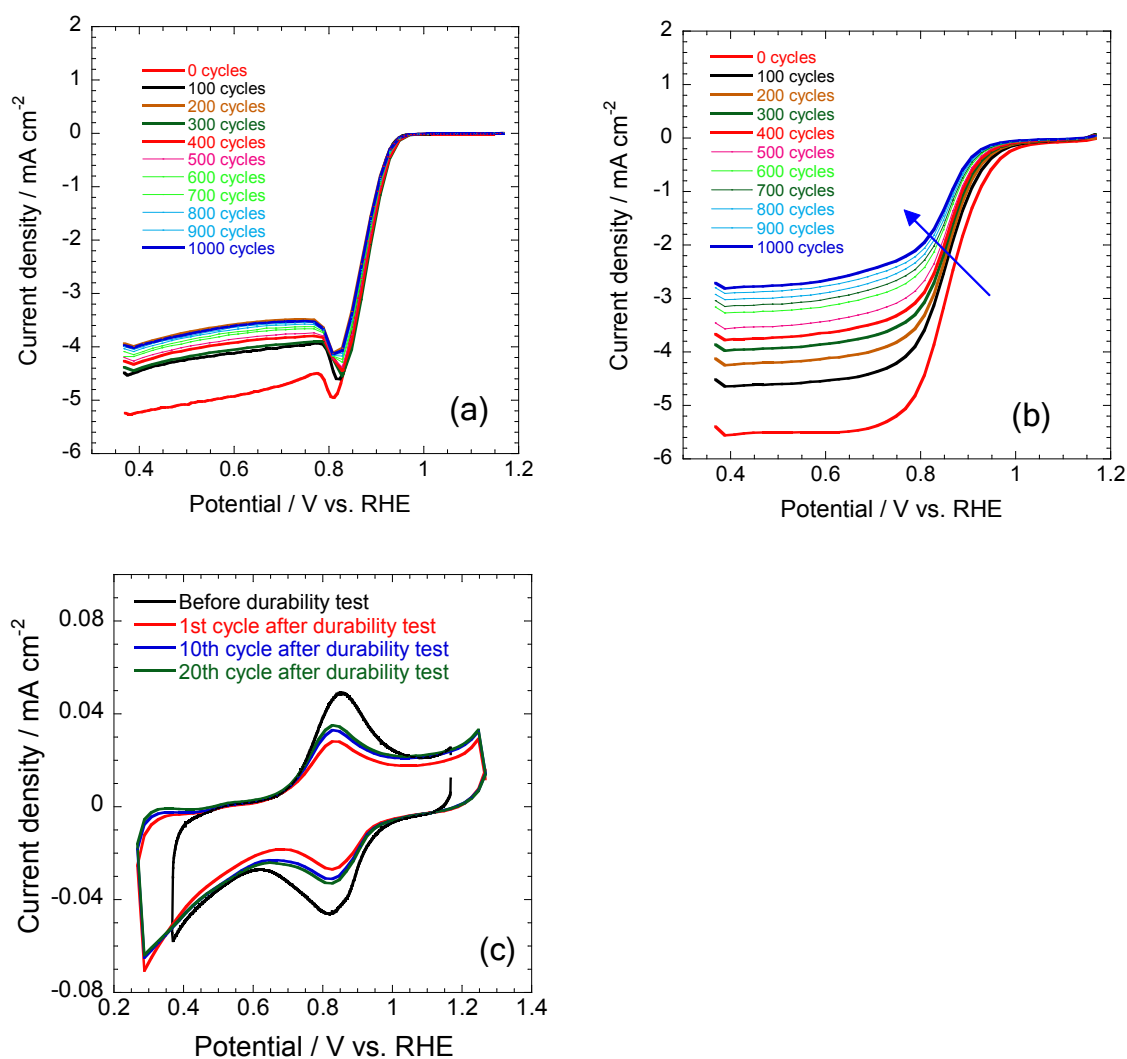
**Fig. S4.** Raman spectra of MWNTs before and after sonicated in THF for 2 h.



**Fig. S5.** LSV profiles of (a) MWNT/FePc-SH and (b) Pt/C measured at  $10 \text{ mV s}^{-1}$  in  $\text{O}_2$ -saturated  $0.1 \text{ M KOH}$  with different rotation rates indicated.



**Fig. S6.** Ring current of MWNT/FePc-SH (black) and Pt/C (red) obtained from RDE rotated at 1600 rpm; scan rate:  $10 \text{ mV s}^{-1}$ ; electrolyte:  $\text{O}_2$ -saturated  $0.1 \text{ M KOH}$ .



**Fig. S7.** LSV curves for the ORR on (a) MWNT/FePc-SH and (b) Pt/C on an RRDE in O<sub>2</sub>-saturated 0.1 M KOH displaying initial and subsequent activities after every 100 cycles of potential sweeps during 0.2 and -0.6 V; (c) CV profiles of MWNT/FePc-SH before and after the durability test measured at 10 mV s<sup>-1</sup> in N<sub>2</sub>-saturated 0.1 M KOH; rotation rate: 1600 rpm; scan rate: 20 mV s<sup>-1</sup>.

**Table S1.** Element composition calculated based on the EDX spectra in Figs. S2b, d, and f.

Samples	Composition (at%)			
	C	N	O	Fe
MWNT/FePc-SH	87.54	7.04	4.51	0.91
Particle in MWNT/FePc-SO	83.29	13.80	1.20	1.71
Particle in MWNT/FePc-RE	81.58	9.36	7.74	1.32

**Table S2.** Onset potential and  $E_{1/2}$  of MWNT/FePc-SH, MWNT/FePc-RE, and MWNT/FePc-SO estimated from Fig. 1e.

Samples	Onset Potential (V vs. RHE)	$E_{1/2}$ / V (V vs. RHE)
MWNT/FePc-SH	0.971	0.864
MWNT/FePc-Re	0.959	0.844
MWNT/FePc-SO	0.956	0.835

**Table S3.** Onset potential and  $E_{1/2}$  of MWNT/FePc shaken in THF and EtOH estimated from Fig. S3d.

Solvent	Onset Potential (V vs. RHE)	$E_{1/2}$ / V (V vs. RHE)
THF	0.971	0.864
EtOH	0.970	0.844

**Table S4.** Onset potential and  $E_{1/2}$  of MWNT/FePc-SH-5, MWNT/FePc-SH, and MWNT/FePc-SH-20 estimated from Fig. S4e.

Catalysts	Initial ratio of MWNT/FePc	Onset Potential (V vs. RHE)	$E_{1/2}$ / V (V vs. RHE)
MWNT/FePc-SH-5	10 mg/5 mg	0.981	0.832
MWNT/FePc-SH	10 mg/10 mg	0.971	0.864
MWNT/FePc-SH-20	10 mg/20 mg	0.947	0.825

**Table S5.** Summary of ORR performance of unpyrolyzed FePc/nanocarbon composite catalysts reported in recent years.

Catalysts	Deposition method of FePc on carbon support	Loading ( $\text{mg cm}^{-2}$ )	Onset potential (V vs. RHE)	$E_{1/2}$ (V vs. RHE)	ORR potential* (V vs. RHE)	Reference
Pt/C	Commercial product	0.03	1.034	0.845	0.902	This work
FePc/MWNT	Shaking in THF at R. T.	0.30	0.971	0.864	0.808	
FePc-Py-SWNT	Refluxing of FePc and Py-SWNT	0.32	0.982	0.915	—	20
FePc/C	Sonicating Vulcan XC-72 and FePc in $\text{H}_2\text{SO}_4$ solution at R. T.	0.20	0.960	0.880	—	23
FePc/SWNT	Sonicating SWNT and FePc in $\text{CH}_3\text{Cl}$ at R. T.	0.29	0.948	0.868	0.808	24
FePc-Py-graphene	Heating in DMF at $60^\circ\text{C}$	0.08	0.951	0.820	0.735	25
FePc/graphene	Sonication in DMF at R. T.	0.11	0.960	0.880	0.900	26
FePc/SWNT	Two-step self organization of SWNT and FePc in 1-cyclo-hexyl-pyrrolidone and $\text{H}_2\text{O}$ at R. T.	0.05	0.868	0.918	0.708	31

**Table S6.** Onset potential and  $E_{1/2}$  of oxMWNT/FePc and MWNT/FePc-SH estimated from Fig. 3d.

Support	Onset Potential (V vs. RHE)	$E_{1/2}$ / V (V vs. RHE)
MWNT	0.971	0.864
oxMWNT	0.974	0.845

**Table S7.** DFT calculation results.

Sample	Mulliken charge around Fe (e)	O-O bond of adsorbed O <sub>2</sub> on Fe (Å)	O-O bond of OOH on Fe (Å)	Binding energy of OH on Fe (eV)
No catalyst	—	1.210	—	—
FePc	0.674	1.248	1.362	1.980
MWNT/FePc	0.789	1.243	1.440	1.881

**Table S8.** Comparison of the performance of zinc-air batteries.

Catalyst	Electrolyte	Performance	Reference
MWNT/FePc-SH	6 M KOH	Current density @ 1 V: 96 mA cm <sup>-2</sup> ; peak power density: 185 mW cm <sup>-2</sup> at 0.8 V	This work
Mn <sub>3</sub> O <sub>4</sub> /rGO-IL	6 M KOH	Current density @ 1 V: 70 mA cm <sup>-2</sup> ; peak power density: 120 mW cm <sup>-2</sup>	40
Mn <sub>3</sub> O <sub>4</sub> /CB	6 M KOH	Current density @ 1 V: 120 mA cm <sup>-2</sup> ; peak power density: ~190 mW cm <sup>-2</sup>	41
N-doped CNTs	6 M KOH	Current density @ 1 V: 50 mA cm <sup>-2</sup> ; peak power density: 69.5 mA cm <sup>-2</sup>	42
CoMn <sub>2</sub> O <sub>4</sub> /N-rGO	6 M KOH	Current density @ 1.1 V: 20 mA cm <sup>-2</sup> ;	43
La <sub>2</sub> NiO <sub>4</sub> /CB	6 M KOH	Current density @ 1.0 V: 50 mA cm <sup>-2</sup> ;	44
N-doped porous carbon fibers	6 M KOH	Current density @ 1 V: 150 mA cm <sup>-2</sup> ; peak power density: 194 mW cm <sup>-2</sup>	45

## Reference

1. N. Markovic, H. Gasteiger, B. Grgur, P. Ross, J. Electroanal. Chem., 1999, 467, 157-163.