Electronic Supplementary Material (ESI) for Sustainable Energy & Fuels.

Supporting Information

Hollow Structure Engineering of FeCo Alloy Nanoparticles Electrospun in Nitrogen-doped Carbon Enable High Performing Flexible All-Solid-State Zinc-Air Battery

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Experimental Section

Electrochemical measurement: The electrocatalytic activities of the samples were investigated using a standard three-electrode set-up electrochemical station (Autolab PGSTAT302N). Ag/AgCl (in 3M KCl) was employed as the reference electrode, Pt and graphite rod were served as the counter electrode for OER and ORR, respectively. 5 mm catalyst-coated glassy carbon rotating disc electrode (RDE) was used as the working electrode. All potentials were referenced to a reversible hydrogen electrode (RHE), calculated by the formula $E_{RHE} = E_{Ag/AgCl\ (3M\ KCl)} + 0.209\ V + 0.059\ V \times pH$. The catalyst ink was prepared by dispersing 2.4 mg sample and 0.6 mg carbon black into 0.8 mL solution containing H_2O: IPA: Nafion (ratio of 2.5: 1: 0.094). The catalyst was drop-cast on the cleaned RDE tip at a mass loading of 0.2 mg cm^{-2} and dried at room temperature. ORR property was tested in the oxygen saturated 0.1 M potassium hydroxide solution, and OER study was performed in the nitrogen saturated 1 M potassium hydroxide electrolyte. Before testing, the electrolyte was purged by continuous oxygen or nitrogen gas flow for 30 mins.

The ORR linear sweeping voltammetry (LSV) curves were recorded at 5 mV s^{-1} at various rotating speeds. The number (n) of electron transfer and kinetic current density (j_k) during the ORR process were calculated based on the Koutecky-Levich equation.

$$\frac{1}{J} = \frac{1}{J_L} + \frac{1}{J_K} = \frac{1}{B\omega^{\frac{1}{2}}} + \frac{1}{J_K} \quad (1)$$

$$B = 0.62nFC_0D_0^{\frac{2}{3}}V^{-\frac{1}{6}} \quad (2)$$

where J is the measured current density, J_L and J_K are the limiting and kinetics current densities. F is the Faraday constant (96485 C mol^{-1}), C_0 is the bulk concentration of O_2 (1.21×10^{-6} mol cm^{-3}), D_0 is the diffusion coefficient of O_2 in the electrolyte (1.88×10^{-5} cm^2 s^{-1}), and V is the kinematic viscosity of electrolyte (0.01 cm^2 s^{-1}). For OER, the LSV curves were recorded at the same scan rate (with 95% iR correction) and 1600 rpm rotating speed.

Assembly of the rechargeable Zn-air battery:

Aqueous Zn-air battery: To explore the practical use of FeCo alloy/N-CNFs in energy storage devices, a homemade cell consisting of the Zn plate anode, air cathode and electrolyte (6 M KOH and 0.1 M zinc acetate) is designed for the aqueous Zn-air battery tests. The cathode is prepared as follows: 7.5 mg of catalyst, 1.875 mg carbon and 20.3 µl Nafion were dispersed in 3 ml ethanol solution by ultrasonic treatment to form a homogeneous solution. After that, the mixed solution was drop cast onto a carbon paper dried at room temperature (a mass loading of 1.5 ± 0.1 mg cm^{-2}). A Ti mesh and hydrophobic PTFE film were placed next to the air cathode as the current collector and waterproof backing layer, respectively. Autolab PGSTAT302N electrochemical station was used to obtain the discharge-charge polarization (scan rate: 5 mA s^{-1}) and electrochemical impedance spectroscopy (EIS) curves. The galvanostatic cycling test was carried out by using NEWARE BTS-5V10A instrument using 10-min discharge followed by 10-min charge at 10 mA cm^{-2}.

Sandwich-like solid-state Zn-air battery: The air cathode was prepared by the same procedure as that for the catalyst ink for aqueous battery onto a carbon cloth (size: 1.5 × 0.5 cm^2) to obtain a mass loading of 3 ± 0.1 mg cm^{-2}. In a typical fabrication process, the air cathode, Ti mesh current collector, solid-state electrolyte and Zn foil were assembled in a sequence between two pieces of flexible acrylic covers (3M acrylic tape, 1 mm thick). An air inlet (1.5 × 0.4 cm^2) was made on the air cathode side, by cutting out some portion of the

cover. Another inserted piece of acrylic tape was cut to form a well (1.5 × 0.5 cm^2) to contain the solid electrolyte. The solid electrolyte was synthesized by the following process. 10 ml of electrolyte consisting of KOH (11.25 M) and ZnO (0.25 M) was mixed with 1 g of acrylic acid and 0.15 g N, N'-methylene-bisacrylamide, then the white precipitate was filtered out after 10-min stirring. Next, 100 µl of 0.3 M $K_2S_2O_8$ was added into the electrolyte solution, where 350 µl of the electrolyte solution was then poured straight away into the acrylic well once the solution started to polymerize. Cycling test was performed using a constant current of 0.75 mA and the batteries were tested in both the flat and folded states. All electrochemical measurements were conducted at room temperature.

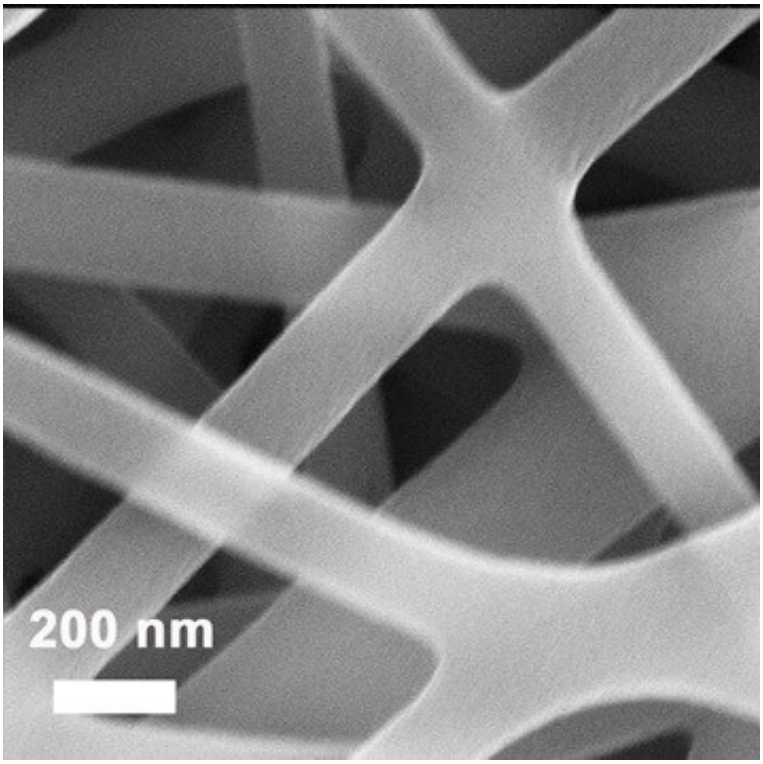

Fig. S1. SEM image of the N-CNFs.

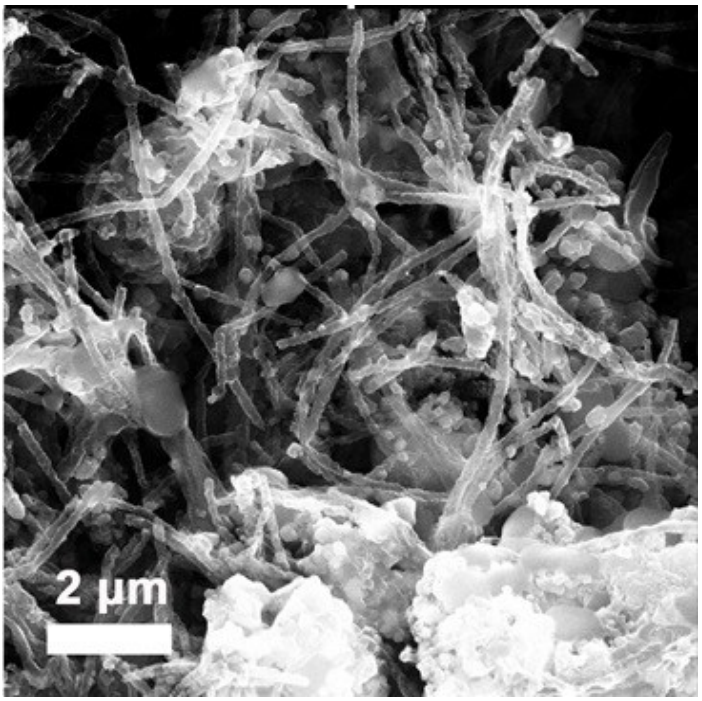

Fig. S2. SEM image of Fe NP/N-CNFs.

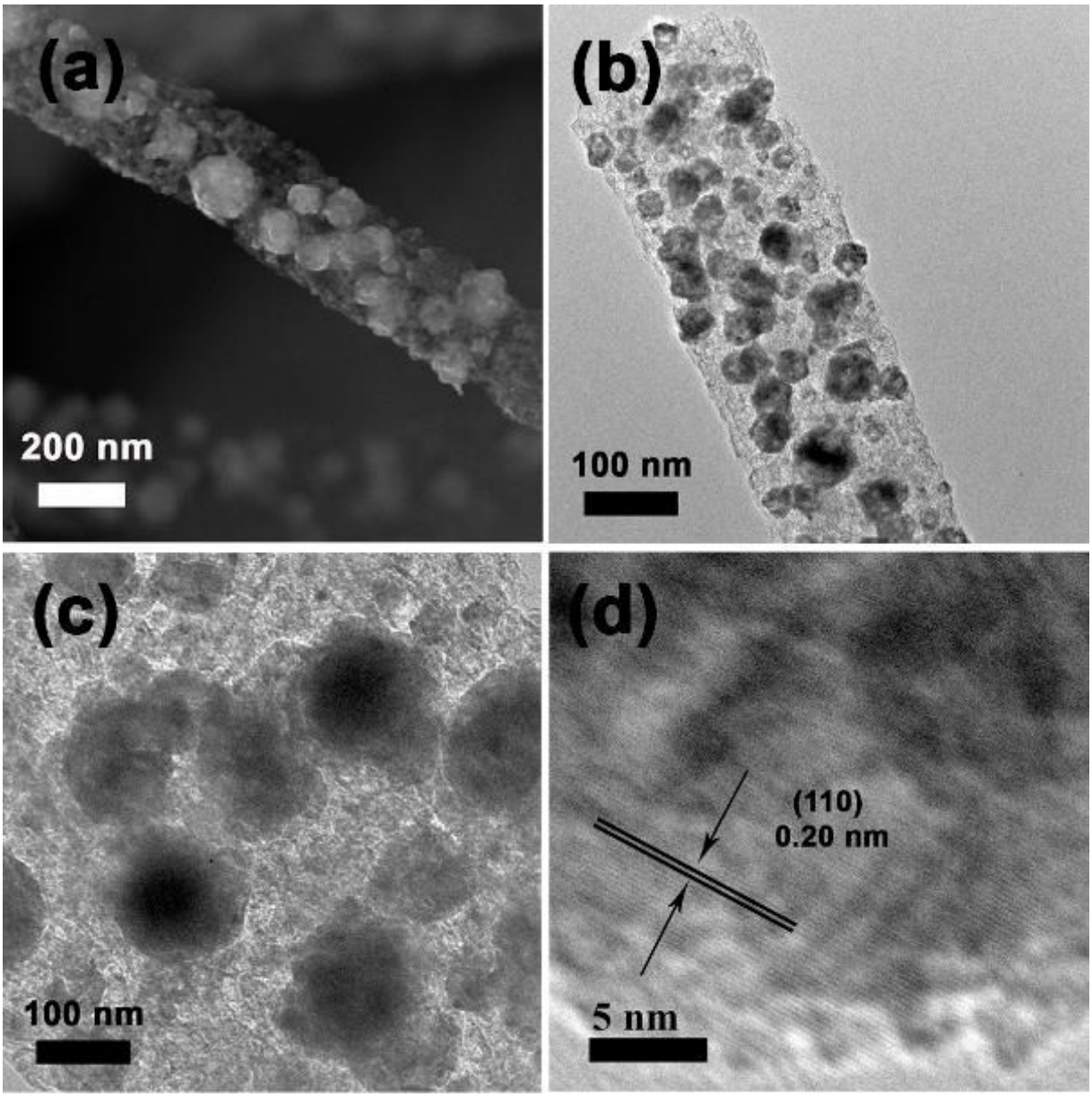

Fig. S3. SEM image (a), TEM images (b, c), and HRTEM image (d) of *s*-FeCo alloy /N-CNFs.

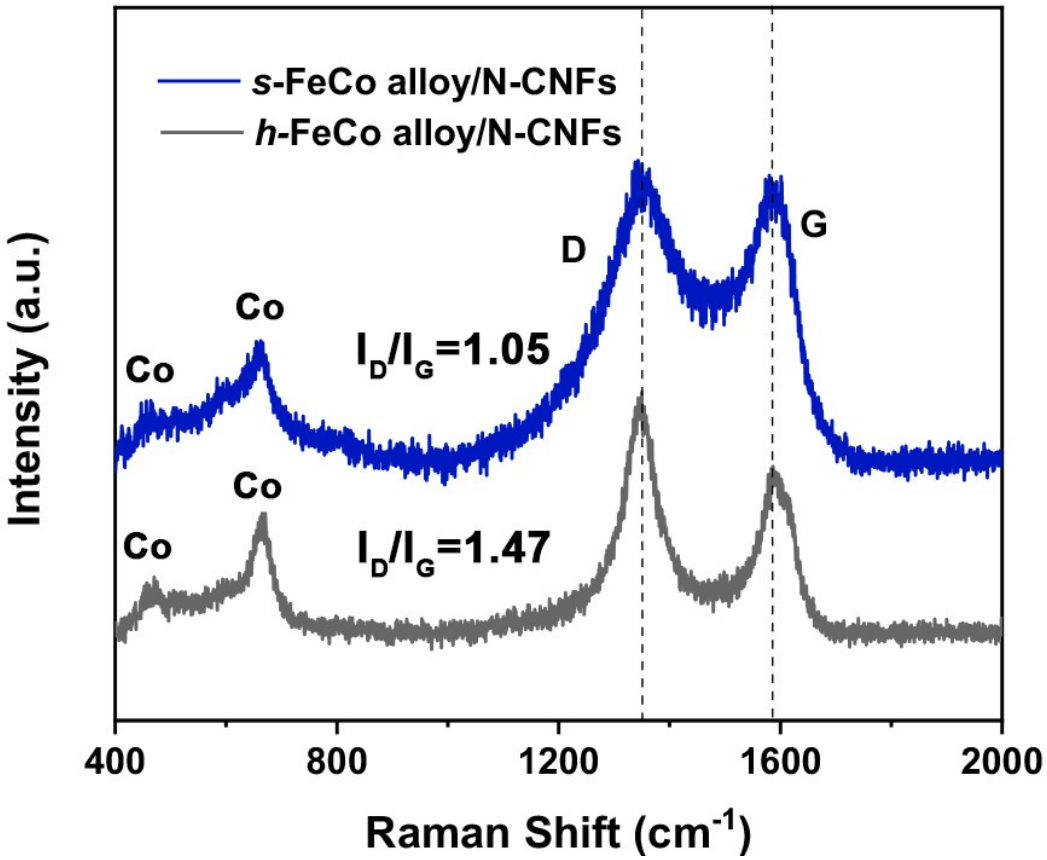

Fig. S4. Raman spectra of *h*-FeCo alloy/N-CNFs and *s*-FeCo/N-CNFs synthesized in the present study.

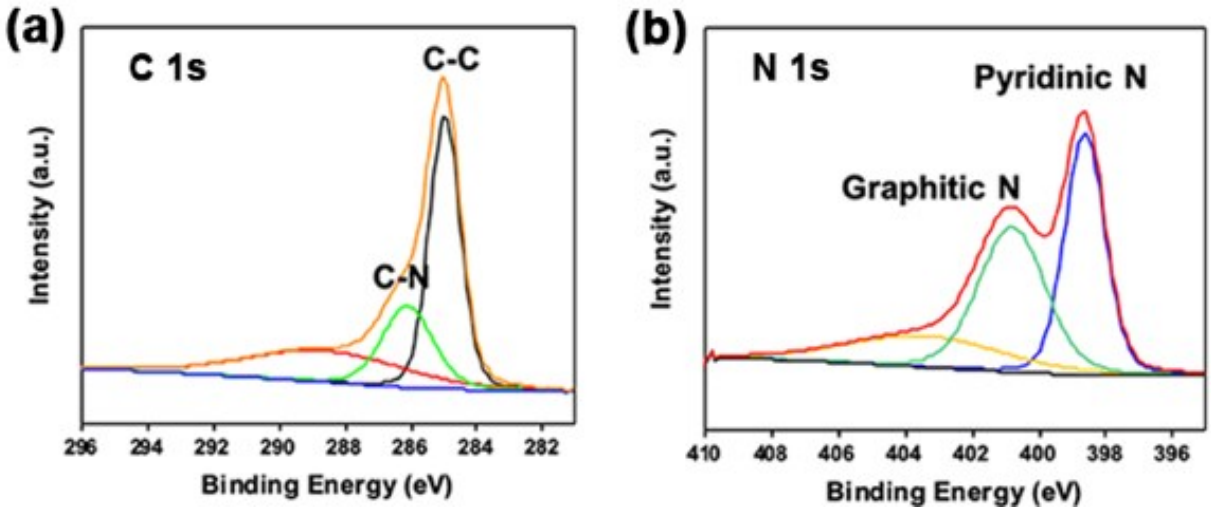

Fig. S5. High-resolution XPS spectra of *h*-FeCo alloy/N-CNFs (a) C 1s. (b) N 1s.

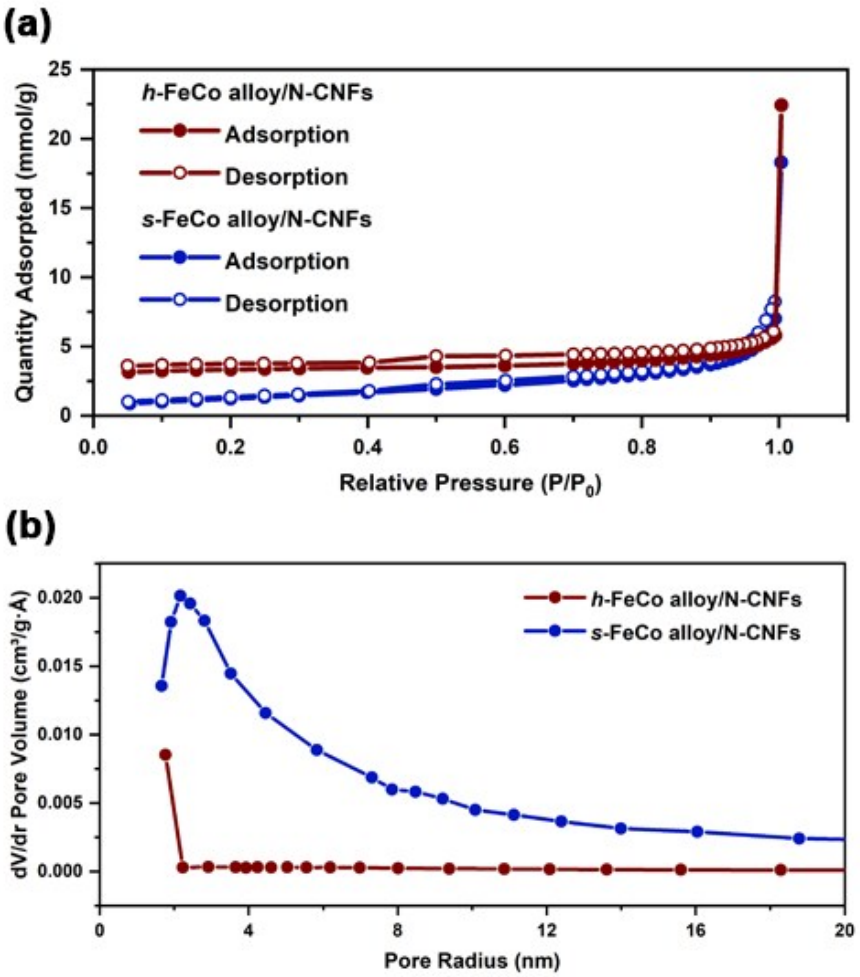

Fig. S6. (a) Nitrogen sorption isothermal plots. (b) Corresponding pore size distribution curves.

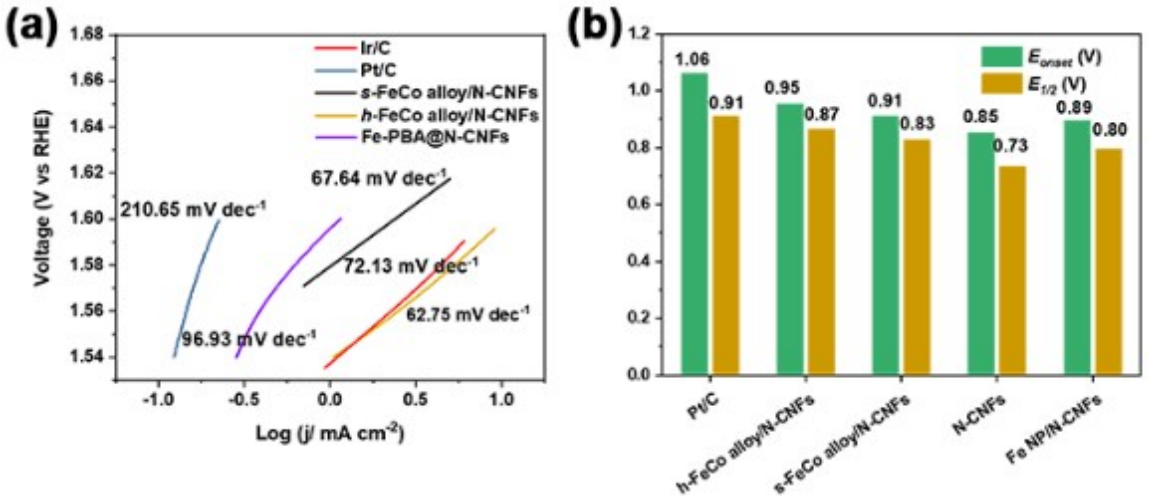

Fig. S7. (a) Tafel plots for each of the electrocatalysts derived from OER polarization curves (b) E_{onset} and $E_{1/2}$ for each electrocatalysts

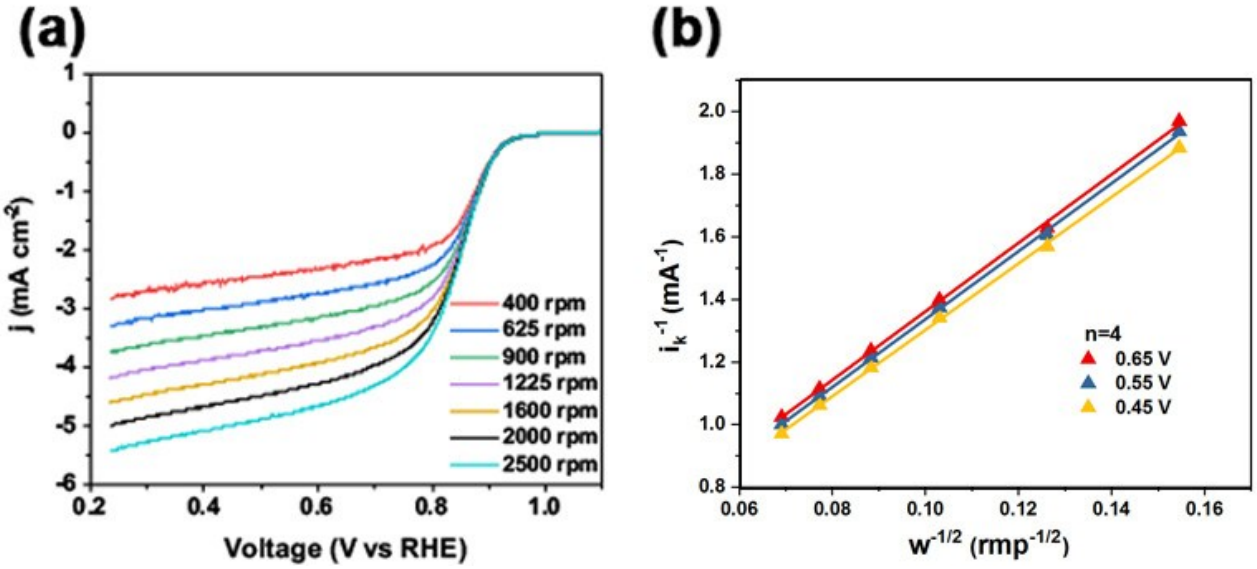

Fig. S8. (a) LSV curves of *h*-FeCo alloy/N-CNFs at different rotating speed.

(b) the corresponding Koutecky-Levich plots.

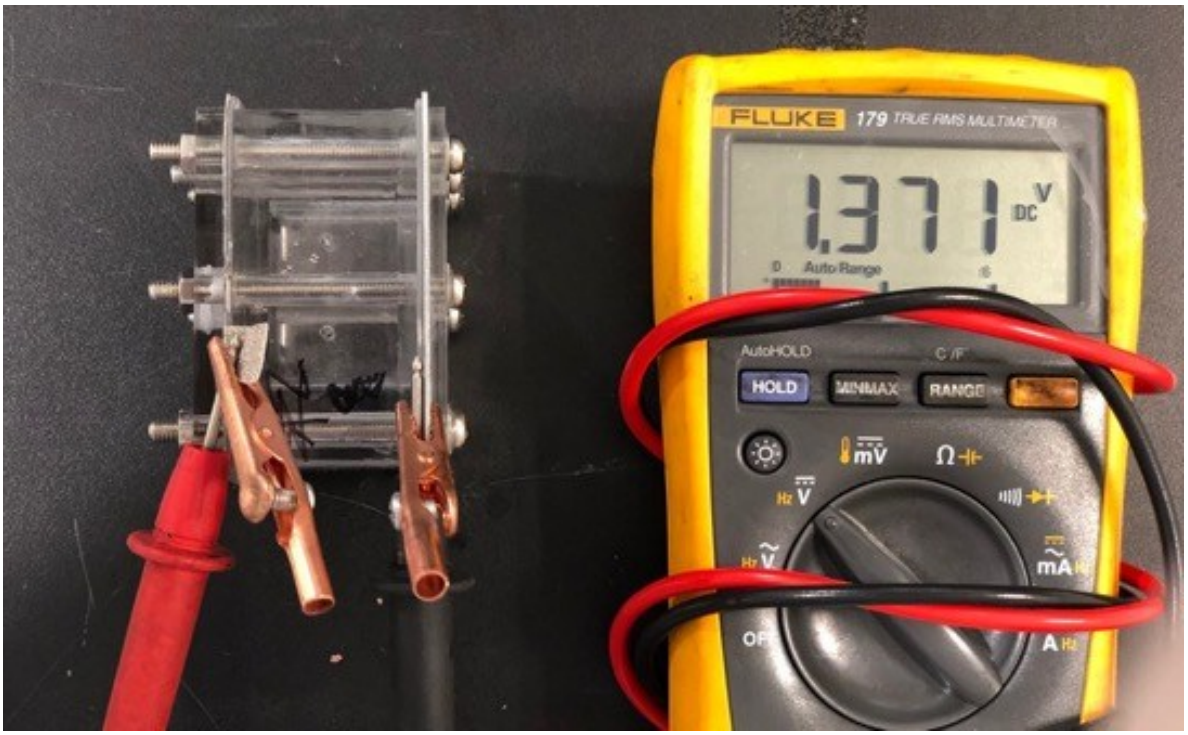

Fig. S9. Digital image of the aqueous Zn-air battery using *h*-FeCo alloy/N-CNFs air cathode.

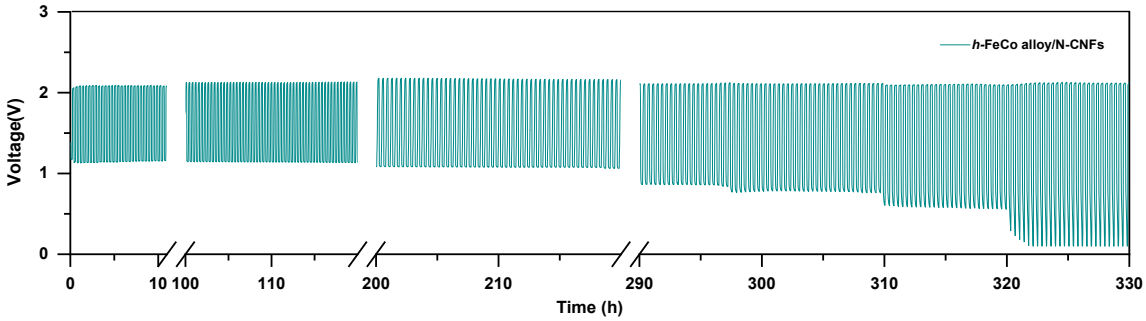

Fig. S10. Cycling test of the aqueous rechargeable Zn–air battery using the h-FeCo alloy/N-CNFs cathode.

Table S1. Comparison of the performance of Zn-air battery in other reported work.

Materials	Battery Voltage (V)	Cycling Time (h)
h-FeCo alloy/N-CNFs	1.371(aqueous)	238
h-FeCo alloy/N-CNFs	1.335 (solid)	19
Fe_2N@carbon[1]	1.43 (solid)	14.5
Co_2P[2]	1.34 (coin cell)	none
N-GCNT/FeCo [3]	1.25 (solid)	12
Co_3O_4 N-rGO[4]	1.31 (solid)	2
Fe@N-C[5]	~1.4 (aqueous)	~16.7
FeNi/HNC[6]	1.43 (aqueous)	16
Ni3FeN/NRGO[7]	aqueous	30
NCNF film[8]	1.256 (solid)	6

Reference

1 Z. Y. Chen, Y. N. Li, L. L. Lei, S. J. Bao, M. Q. Wang, H. Liu, Z. L. Zhao and M. W. Xu, *Catal. Sci. Technol.*, 2017, **7**, 5670–5676.

2 H. Li, Q. Li, P. Wen, T. B. Williams, S. Adhikari, C. Dun, C. Lu, D. Itanze, L. Jiang, D. L. Carroll, G. L. Donati, P. M. Lundin, Y. Qiu and S. M. Geyer, *Adv. Mater.*, 2018, **30**, 1–8.

3 C. Y. Su, H. Cheng, W. Li, Z. Q. Liu, N. Li, Z. F. Hou, F. Q. Bai, H. X. Zhang and T. Y. Ma, *Adv. Energy Mater.*, , DOI:10.1002/aenm.201602420.

4 *Br. J. Psychiatry*, 1965, **111**, 1009–1010.

5 J. Wang, H. Wu, D. Gao, S. Miao, G. Wang and X. Bao, *Nano Energy*, 2015,

13, 387–396.
6 H. Wu, M. Zeng, Z. Li, X. Zhu, C. Tian, C. Xia, L. He and S. Dai, *Sustain. Energy Fuels*, 2019, **3**, 136–141.
7 Y. C. Fan, S. Ida, A. Staykov, T. Akbay, H. Hagiwara, J. Matsuda, K. Kaneko and T. Ishihara*, Small*, 2017, **13**, 1–8.
8 Q. Liu, Y. Wang, L. Dai and J. Yao, *Adv. Mater.*, 2016, **28**, 3000–3006.