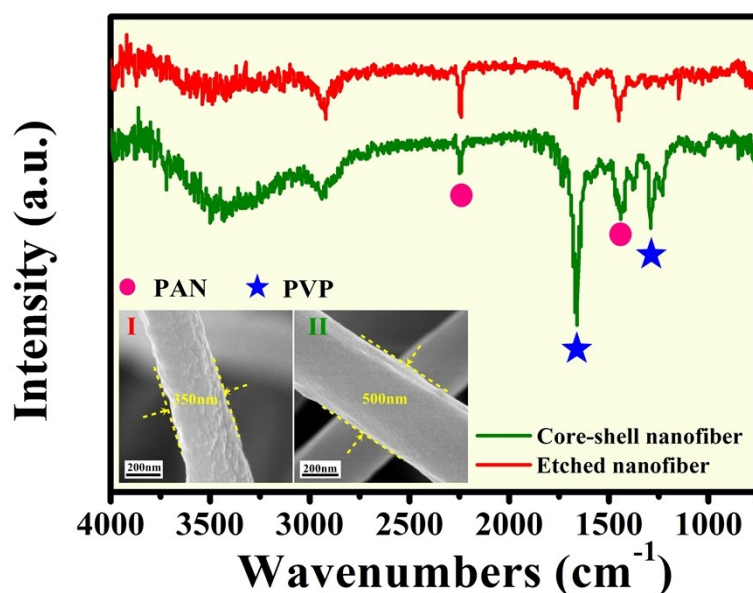


**Fig. S1** The scheme shows the resonance structure of PVP with metal cations.



**Fig. S2** FT-IR curves and SEM images (inset) of the core (PAN)/shell (PVP) nanofiber and PVP phase-etched nanofiber by distilled water: (I) etched nanofiber, (II) core-shell nanofiber

The core-shell structure of the polymer hybrid nanofibers can be confirmed by SEM and FT-IR analyses. As shown in SEM images (inset of Fig. S2), the polymer hybrid nanofibers show the remaining cores (around 350 nm in diameter) due to the remove of PVP shell after etching by distilled-water, and its surface changes from smooth to rough. In addition, FT-IR spectra of the core-shell polymer hybrid nanofibers exhibit characteristic peaks for PAN (2245 and 1438 cm<sup>-1</sup>) and PVP (1663 and 1288 cm<sup>-1</sup>), but the etched nanofibers display only the PAN peaks. These peaks are assigned according to previous paper [J. S. Lee, O. S. Kwon, S. J. Park, E. Y. Park, S. A. You, H. Yoon, and J. Jang, *ACS Nano*, 2011, **5**, 7992-8001.].

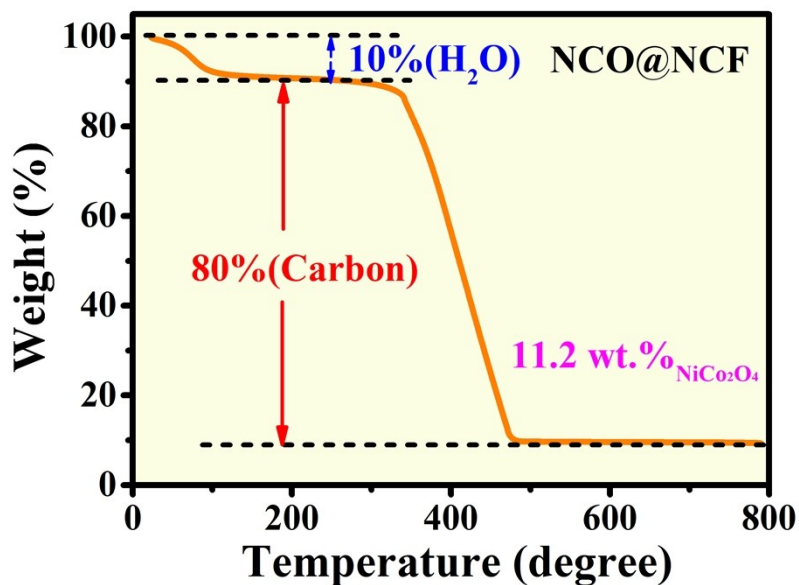


Fig. S3 TG curves of the self-supported NCO@NCF film subjected to temperatures ranging from room temperature to 800 °C under an air atmosphere

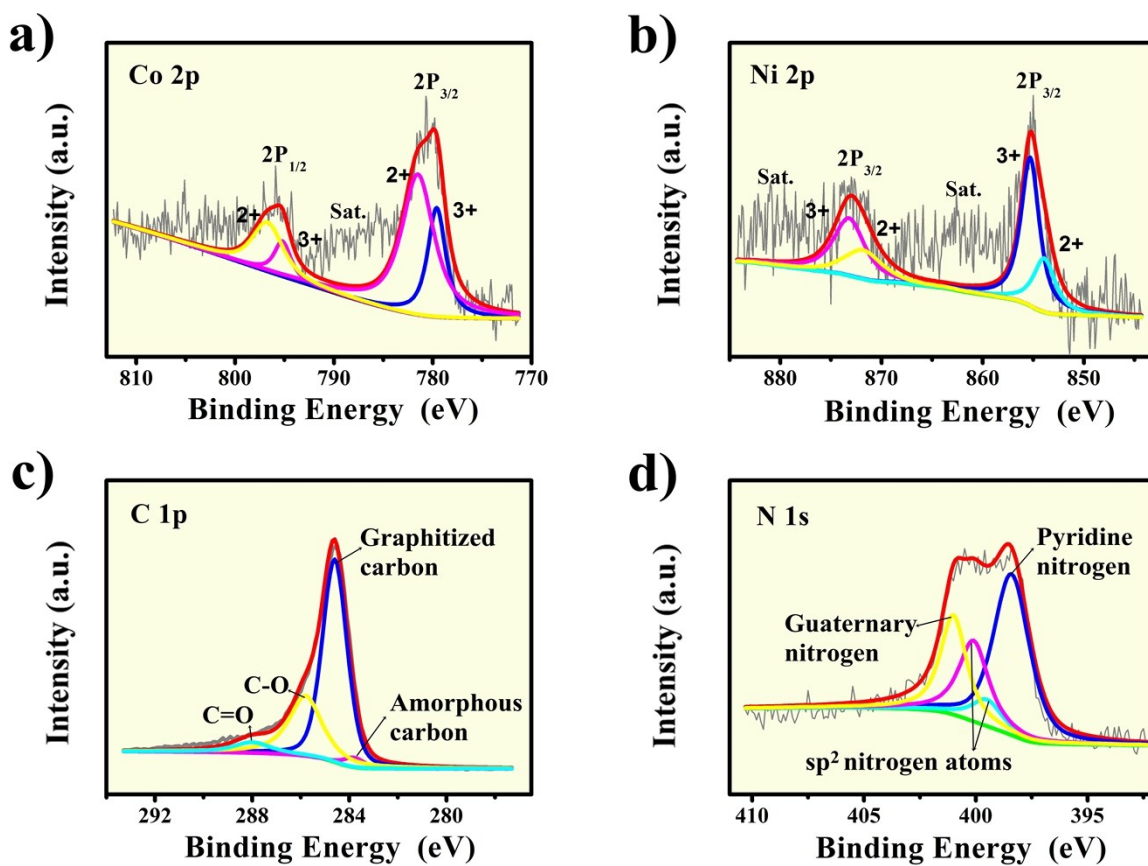
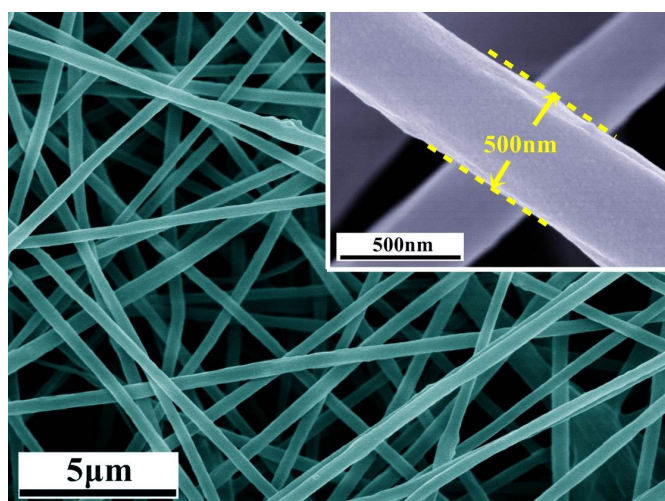
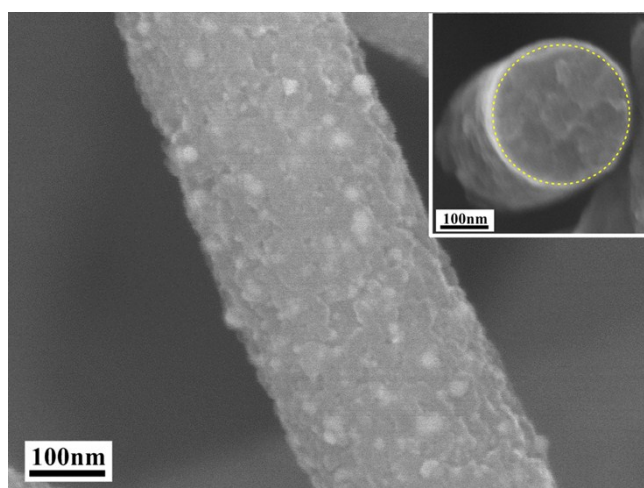


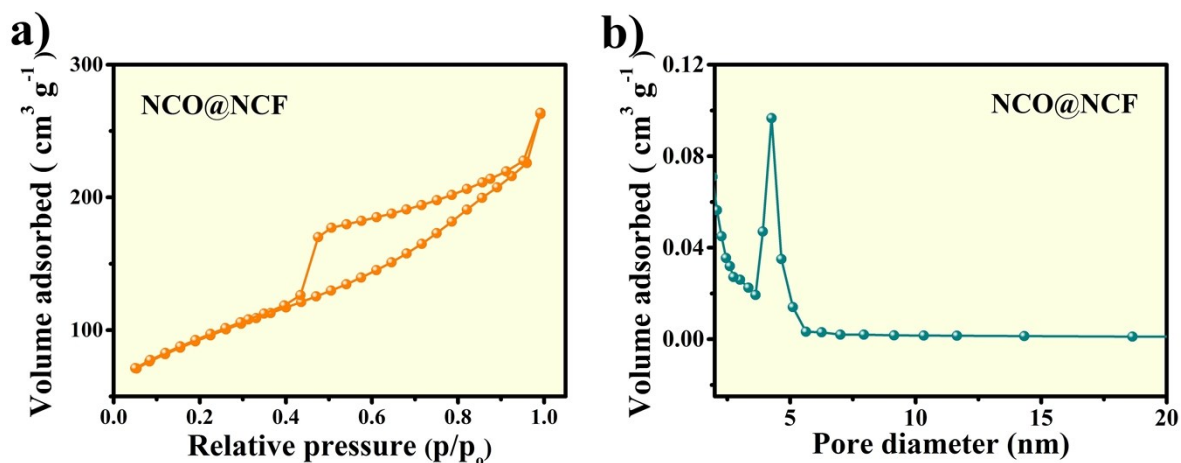
Fig. S4 XPS spectra of the self-supported NCO@NCF film



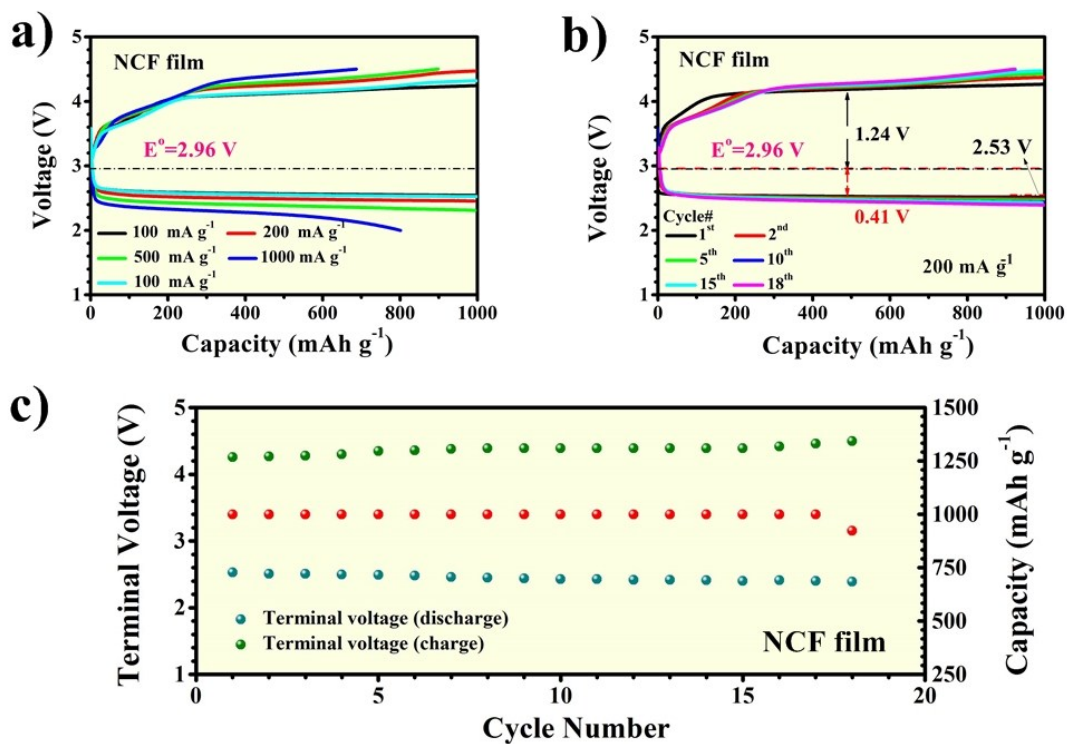
**Fig. S5** SEM images of the polymer hybrid film precursor



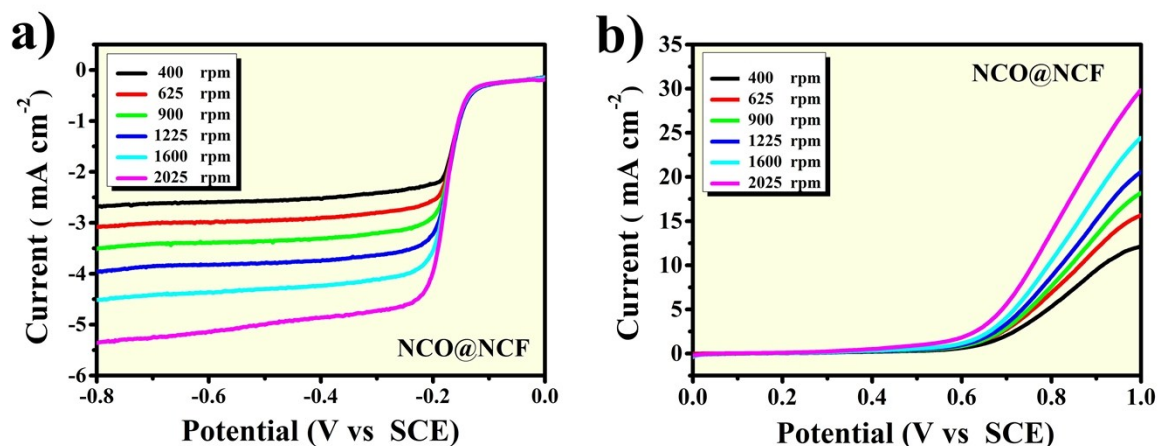
**Fig. S6** SEM and cross-section SEM (inset) images of the NCO@NPC film.



**Fig. S7** (a)  $N_2$  adsorption-desorption isotherm and (b) pore-size distribution of the self-supported NCO@NCF film



**Fig. S8** (a) Galvanostatic discharge-charge curves of the self-supported NCF film cathode at different current densities, (b) the discharge-charge profiles, and (c) cyclic stability and the variation of the terminal charge and discharge voltages of the self-supported NCF film cathode.



**Fig. S9** LSV curves of the NCO@NCF sample at different rotor speeds in 1 M KOH solution: (a) ORR; (b) OER

The catalyst electrode (working electrode) was prepared as follows. Firstly, 5 mg of NCO@NPC was mixed with 1 mL ethanol and 50  $\mu\text{L}$  of Nafion solution (5 wt %). After sonicating for 30 min, the mixture formed an inky slurry, and then 25  $\mu\text{L}$  of the obtained slurry was dropped on the glassy carbon electrode surface (4 mm diameter). Finally, a thin layer 0.1256 cm<sup>2</sup> was obtained after drying. Linear sweep voltammetry (LSV) measurement was conducted on a CHI660C electrochemical workstation. The LSV experiment was carried out a conventional three-electrode cell in 0.1 mol L<sup>-1</sup> KOH saturated with O<sub>2</sub> with a scan rate of 5 mV s<sup>-1</sup>, in which the platinum foil electrode and saturated calomel electrode (SCE) were used as the counter electrode and reference electrode, respectively.

**Table S1.** Electrochemical performance of the binder-free self-supported NCO@NCF electrode in this study as compared with some other non-precious metal/metal oxide-based electrodes reported in previous literatures

Reference	Type of material	Current density	Limited capacity (mAh g <sup>-1</sup> )	Cycle number
This work	NCO@NCF	200 mA g <sup>-1</sup>	1000	92
S1	Co <sub>3</sub> O <sub>4</sub> nanofibers/graphene	200 mA g <sup>-1</sup>	1000	80
S2	Co@C	200 mA g <sup>-1</sup>	600	80
S3	CaMnO <sub>3</sub>	50 mA g <sup>-1</sup>	500	80
S4	LaNiO <sub>3</sub> nanocubes	0.08 mA cm <sup>-2</sup>	1000	76
S5	Co <sub>3</sub> O <sub>4</sub>	0.1 mA cm <sup>-2</sup>	1000	60
S6	CoO-Ni	100 mA g <sup>-1</sup>	500	50
S7	NiCo <sub>2</sub> O <sub>4</sub> nanosheets	200 mA g <sup>-1</sup>	1000	30
S8	ZnCo <sub>2</sub> O <sub>4</sub> nanoflakes	0.1 mA cm <sup>-2</sup>	500	30
S9	CoFe <sub>2</sub> O <sub>4</sub> -rGO	50 mA g <sup>-1</sup>	1000	30
S10	Carbon embedded $\alpha$ -MnO <sub>2</sub> @Graphene nanosheets	100 mA g <sup>-1</sup>	1000	47

#### References:

- [S1] W. H. Ryu, T. H. Yoon, S. H. Song, S. Jeon, Y. J. Park and I. D. Kim, *Nano letters*, 2013, **13**, 4190-4197.
- [S2] Z. Zhang, L. W. Su, M. Yang, M. Hu, J. Bao, J. P. Wei and Z. Zhou, *Chem. Commun.*, 2014, **50**, 776-778.
- [S3] X. P. Han, Y. X. Hu, J. G. Yang, F. Y. Cheng and J. Chen, *Chem. Commun.*, 2014, **50**, 1497-1499.
- [S4] J. Zhang, Y. B. Zhao, X. Zhao, Z. L. Liu and W. Chen, *Sci. Rep.*, 2014, **4**, 6005.
- [S5] Z. S. Wu, W. C. Ren, L. Wen, L. Gao, J. P. Zhao, Z. P. Chen, G. M. Zhou, F. Li and H. M. Cheng, *ACS Nano*, 2010, **4**, 3187-3194.
- [S6] B. S. Wu, Z. H. Zhang, W. Zhou, M. R. Wang, X. F. Li and H. M. Zhang, *ACS Appl. Mater. Interfaces*, 2015, **7**, 23182-23189.
- [S7] B. Sun, X. D. Huang, S. Q. Chen, Y. F. Zhao, J. Q. Zhang, P. Munroe and G. X. Wang, *J. Mater. Chem. A*, 2014, **2**, 12053-12059.
- [S8] T. F. Hung, S. G. Mohamed, C. C. Shen, Y. Q. Tsai, W. S. Chang and R. S. Liu, *Nanoscale*, 2013, **5**, 12115-12119.
- [S9] Y. Cao, S. R. Cai, S. C. Fan, W. Q. Hu, M. S. Zheng and Q. F. Dong, *Faraday Discuss.*, 2014, **172**, 215-221.
- [S10] Y. Cao, M. S. Zheng, S. R. Cai, X. D. Lin, C. Yang, W. Q. Hu and Q. F. Dong, *J. Mater. Chem. A*, 2014, **2**, 18736-18741.