**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\(^{-1}\)) and PVP (1663 and 1288 cm\(^{-1}\)), 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\textsubscript{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.
The catalyst electrode (working electrode) was prepared as follows. Firstly, 5 mg of NCO@NPC was mixed with 1 mL ethanol and 50 μL of Nafion solution (5 wt %). After sonicaing for 30 min, the mixture formed an inky slurry, and then 25 μL of the obtained slurry was dropped on the glassy carbon electrode surface (4 mm diameter). Finally, a thin layer 0.1256 cm² 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⁻¹ KOH saturated with O₂ with a scan rate of 5 mV s⁻¹, in which the platinum foil electrode and saturated calomel electrode (SCE) were used as the counter electrode and reference electrode, respectively.

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

<table>
<thead>
<tr>
<th>Reference</th>
<th>Type of material</th>
<th>Current density</th>
<th>Limited capacity (mAh g(^{-1}))</th>
<th>Cycle number</th>
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<tr>
<td>This work</td>
<td>NCO@NCF</td>
<td>200 mA g(^{-1})</td>
<td>1000</td>
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<td>Co(_3)O(_4) nanofibers/graphene</td>
<td>200 mA g(^{-1})</td>
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<td>80</td>
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<td>200 mA g(^{-1})</td>
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<td>80</td>
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<tr>
<td>S3</td>
<td>CaMnO(_3)</td>
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<td>500</td>
<td>80</td>
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<tr>
<td>S4</td>
<td>LaNiO(_3) nanocubes</td>
<td>0.08 mA cm(^{-2})</td>
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<td>76</td>
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<tr>
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<td>1000</td>
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<tr>
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<td>CoO-Ni</td>
<td>100 mA g(^{-1})</td>
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<td>50</td>
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<td>NiCo(_2)O(_4) nanosheets</td>
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<td>Carbon embedded α-MnO(_2)@Graphene nanosheets</td>
<td>100 mA g(^{-1})</td>
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**References:**