Supporting Information

Thin carbon layer covered Co_4N cubes encapsulated in N-doped porous carbon nanocages as tri-functional catalysts with enhanced charge-transfer efficiency for Zn-air battery and overall water-splitting

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Experimental Section

Synthesis of Co_4N/C

0.1g $Co(OH)_2$ and 5 mL above mixed solution were added into 25 mL of deionized water and stirred for 24 h. The obtained product $Co_3[Co(CN)_6]_2$/C-1 was washed with deionized water for several times, and dried at 60 °C for 3 h. Finally, 0.1 g $Co_3[Co(CN)_6]_2$/C was annealed at 700 °C for 2 h with a heating rate of 5 °C min^{-1} under N_2 atmosphere to obtain Co_4N/C.

Synthesis of CoNC

0.1g $Co(OH)_2$, 0.1 mmol citric acid and 0.2 mmol $K_3[Co(CN)_6]$ were added into 25 mL of deionized water and stirred for 24 h. The obtained product $Co_3[Co(CN)_6]_2$ was washed with deionized water for several times, and dried at 60 °C for 3 h. Finally, 0.1 g $Co_3[Co(CN)_6]_2$ was annealed at 700 °C for 2 h with a heating rate of 5 °C min^{-1} under N_2 atmosphere to obtain CoNC.

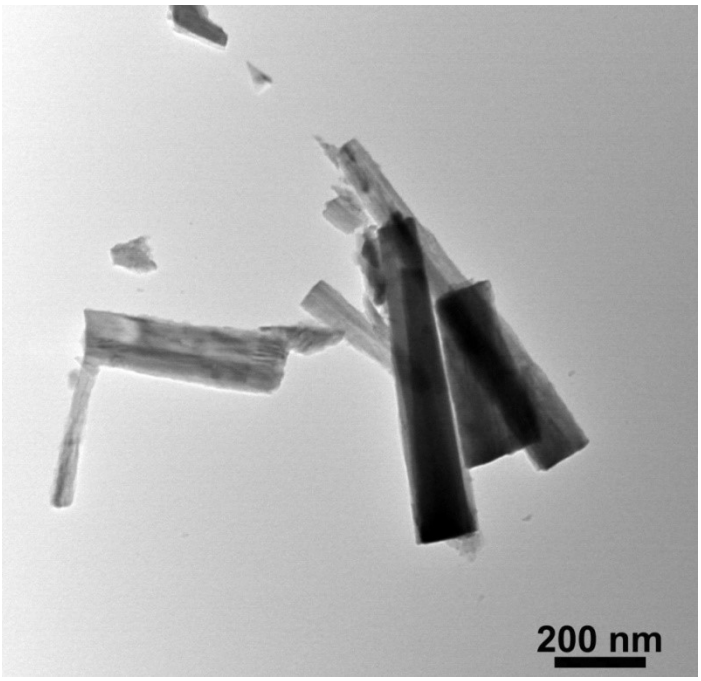

Fig. S1 A typical TEM image of the obtained $Co(OH)_2$.

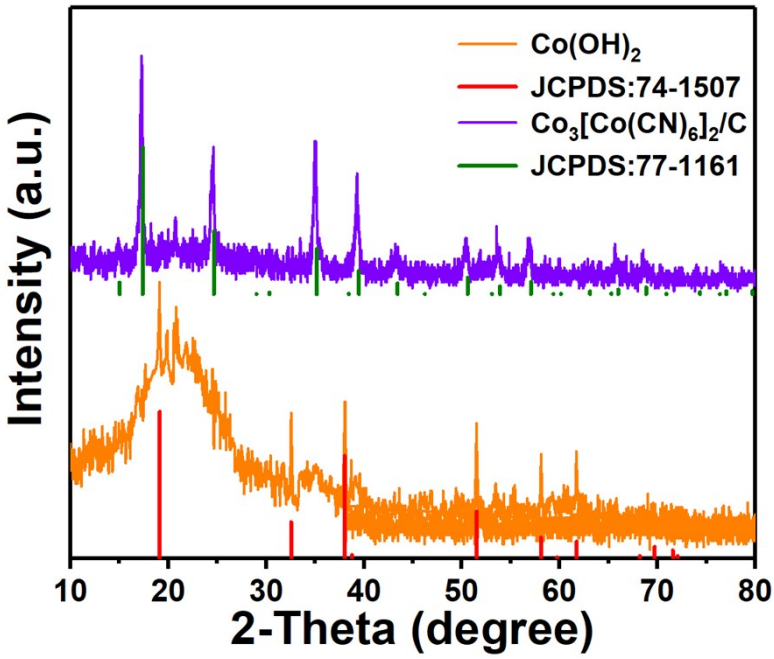

Fig. S2 XRD patterns of $Co(OH)_2$ and $Co_3[Co(CN)_6]_2$/C.

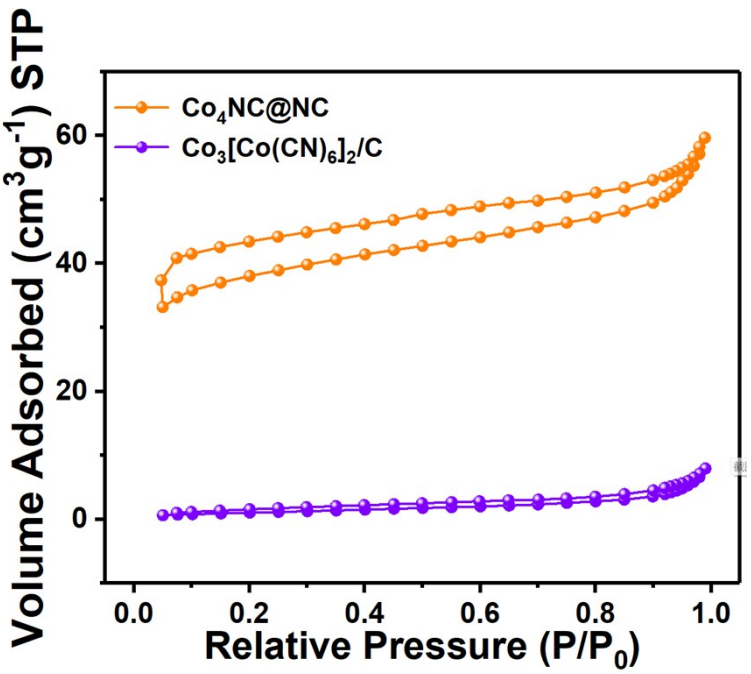

Fig. S3 The N_2 adsorption isotherm of the $Co_4NC@NC$ and $Co_3[Co(CN)_6]_2/C$.

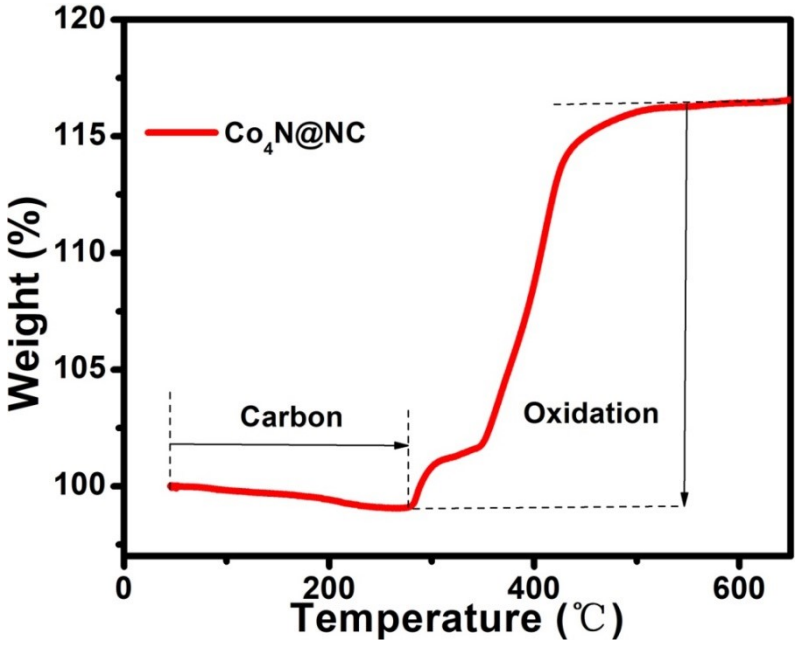

Fig. S4 TGA curve of the $Co_4NC@NC$.

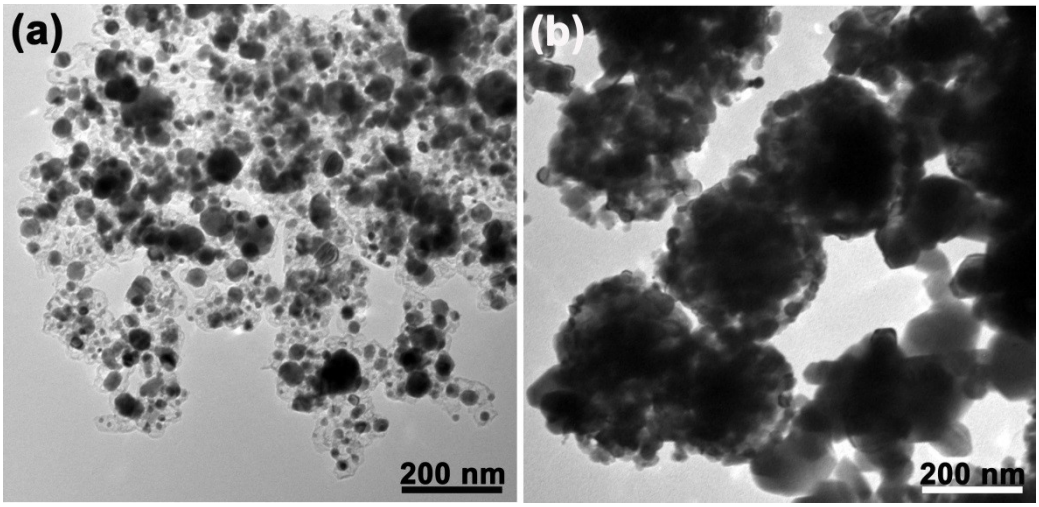

Fig. S5 TEM images of Co_4N/C and CoNC for (a) and (b).

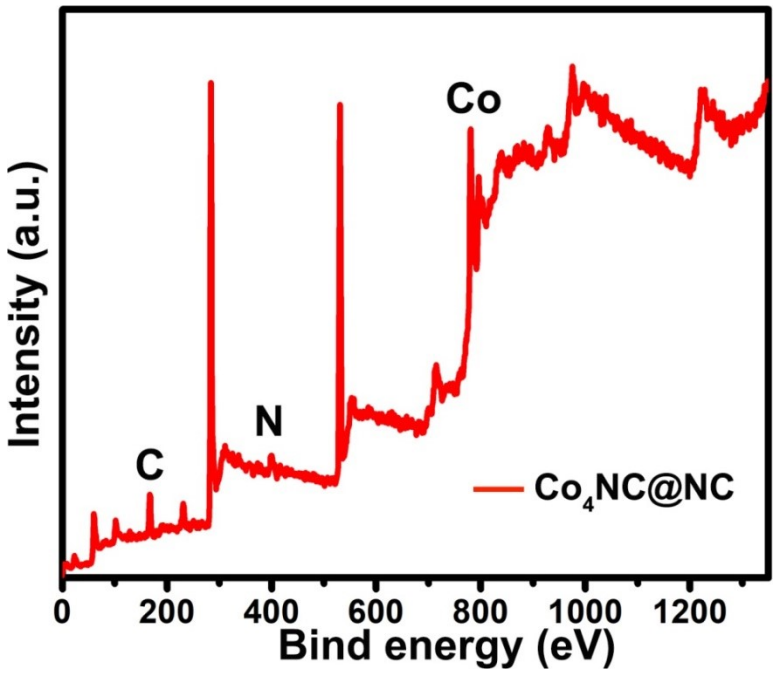

Fig. S6 Survey spectrum of the Co_4NC@NC.

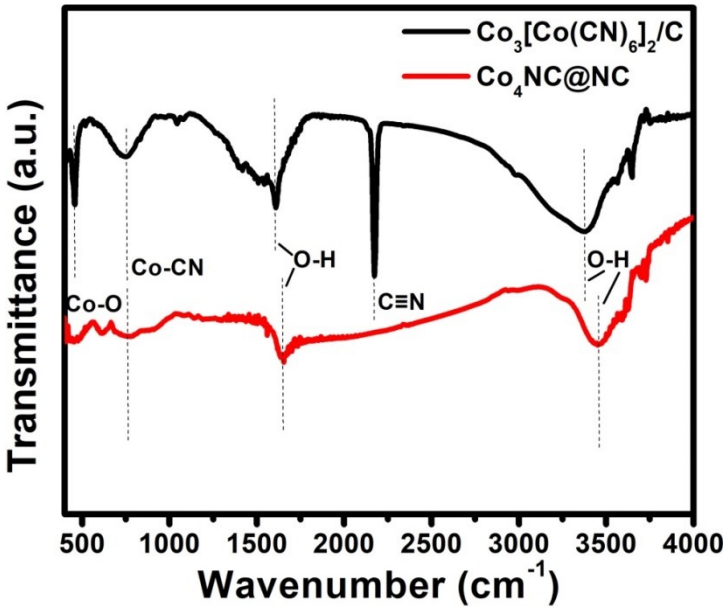

Fig. S7 FTIR spectra of $Co_4NC@NC$ and $Co_3[Co(CN)_6]_2/C$.

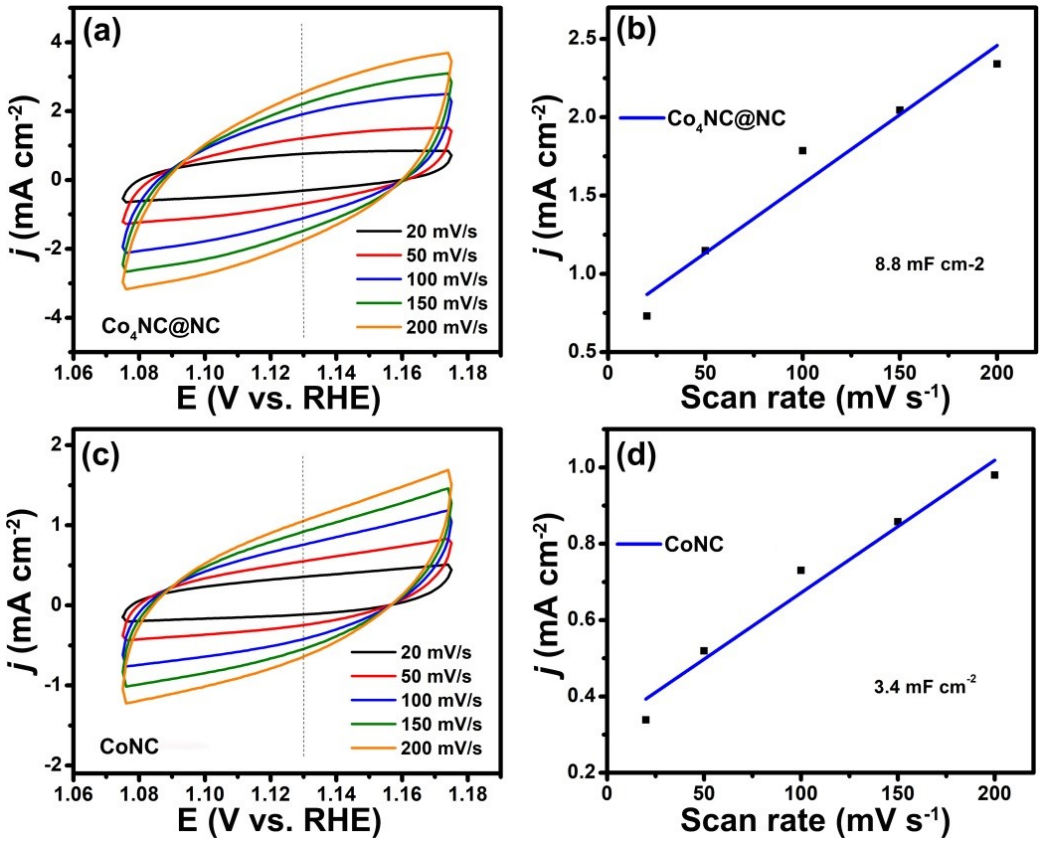

Fig. S8 (a) CV curves of $Co_4NC@NC$ measured in a potential window with a non-Faradaic region at different scan rates: 20, 50, 100, 150 and 200 mV s^{-1}. (b) ECSA curve of the $Co_4NC@NC$ material. (c) CVs of CoNC was measured in a potential window with a non-Faradaic region at different scan rates: 20, 50, 100, 150 and 200 mV s^{-1}. (d) ECSA was measured to evaluate the exposed catalytically active sites in CoNC material.

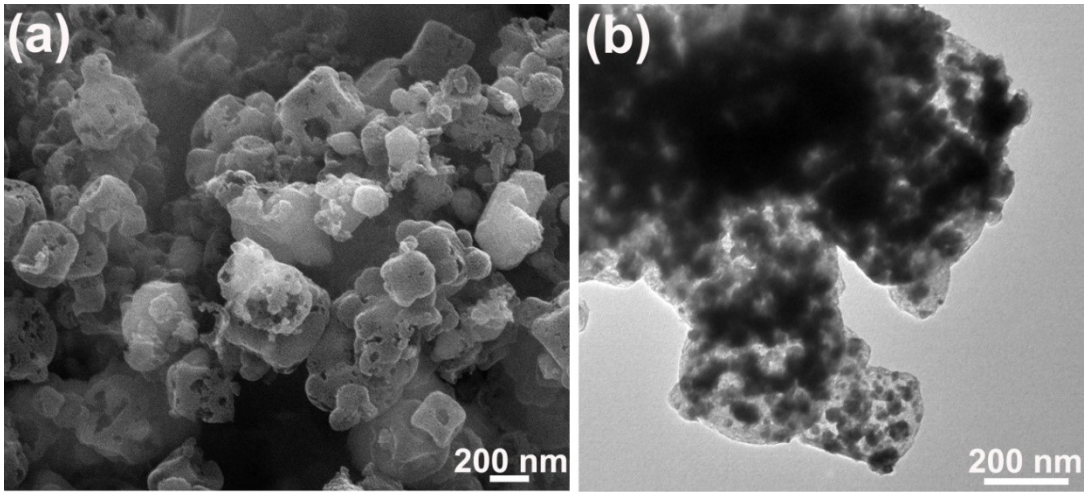

Fig. S9 SEM and TEM images of Co_4NC@NC after 10000 s of OER test.

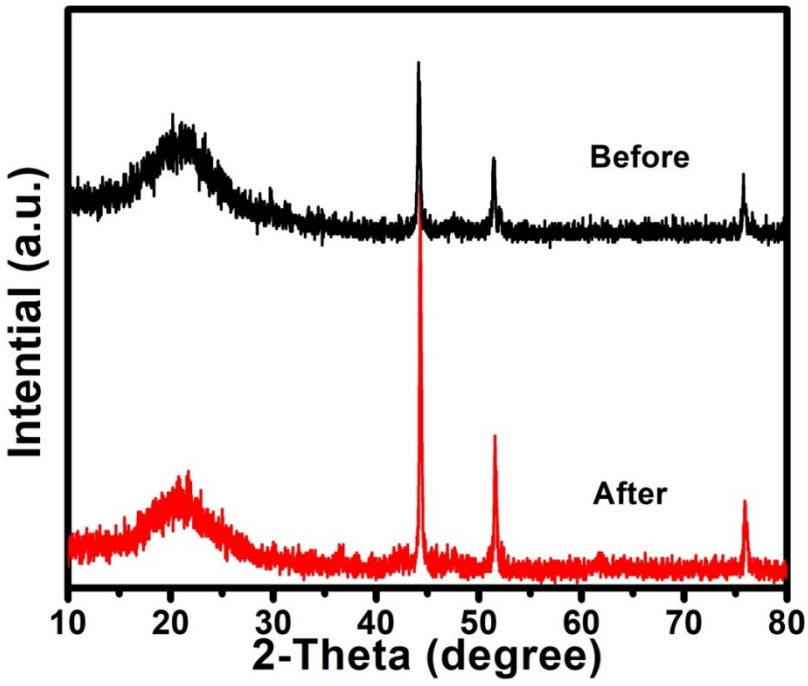

Fig. S10 XRD patterns of the obtained Co_4NC@NC before and after 10000 s of OER test.

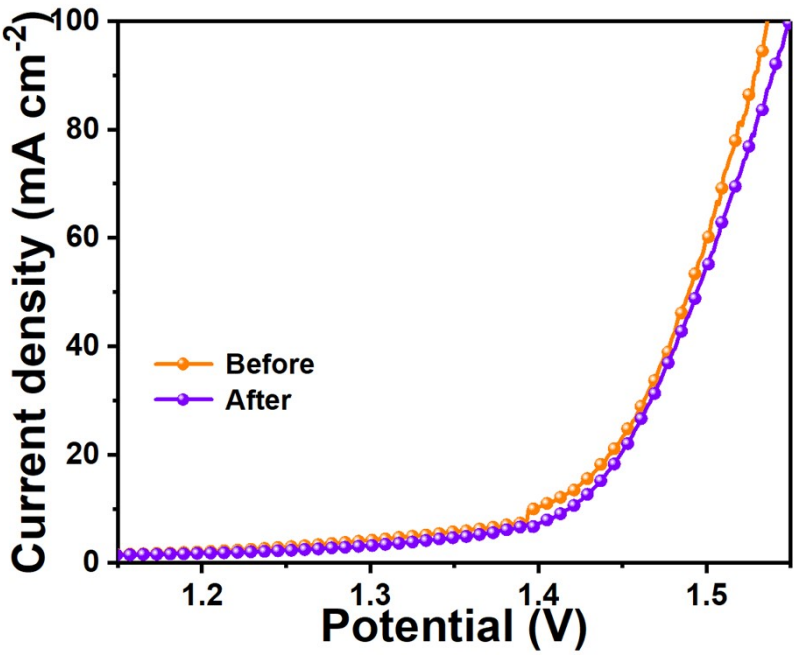

Fig. 11 The LSV of the Co_4NC@NC before and after the 10000 s of OER test.

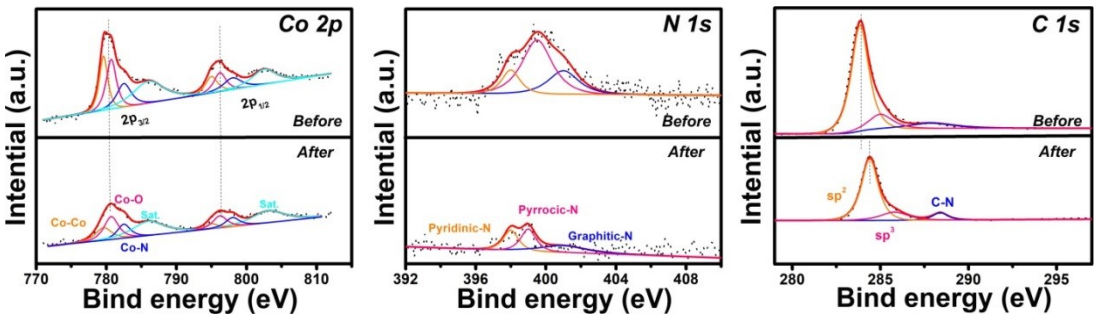

Fig. S12 XPS spectra of the Co 2p, N 1s and C 1s for Co_4NC@NC before and after 10000 s of OER test.

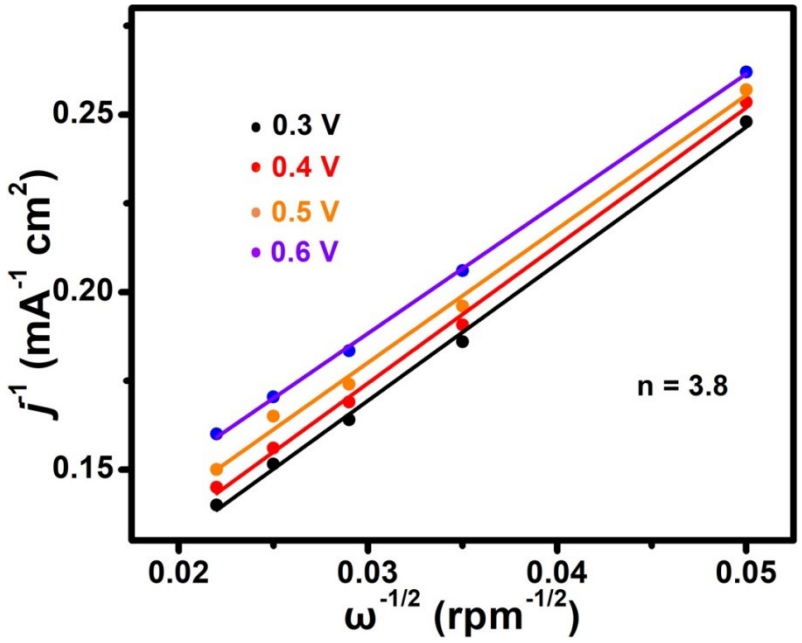

Fig. S13 K-L plots of the $Co_4NC@NC$ catalysts.

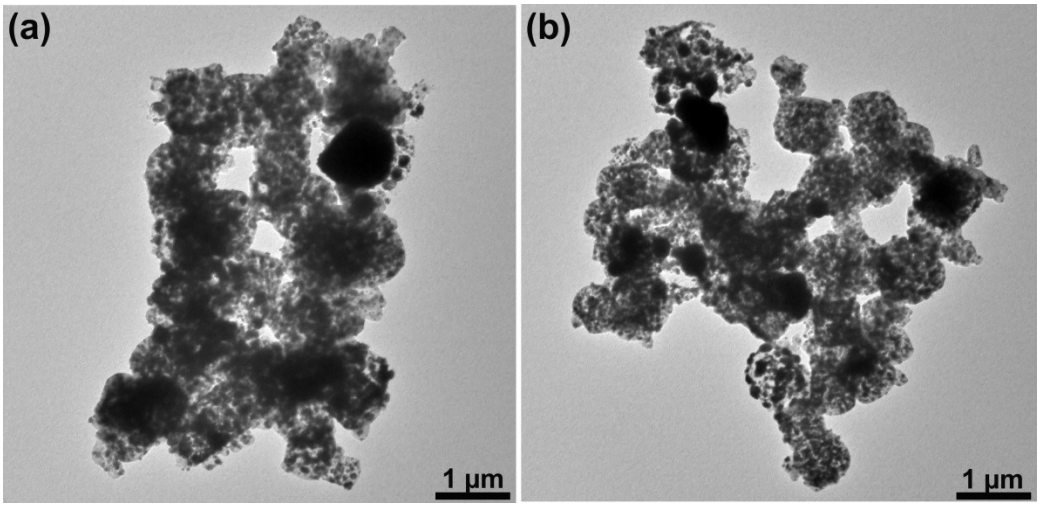

Fig. 14 The TEM of $Co_4NC@NC$ before and after charging and discharging test.

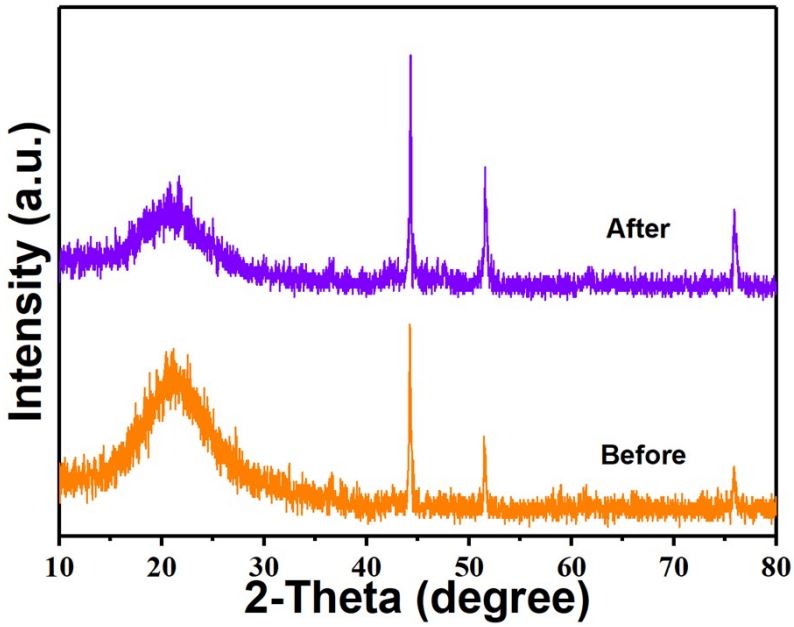

Fig. 15 The XRD of Co_4NC@NC before and after charging and discharging test.

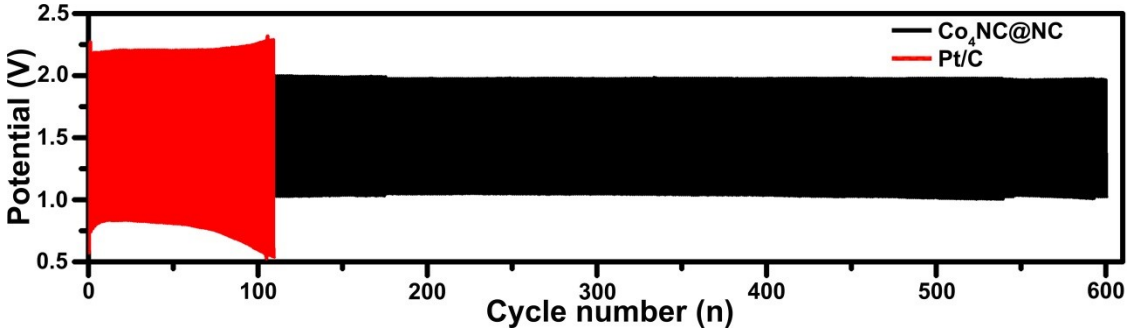

Fig. S16 Cycling stability of Co_4NC@NC and Pt/C at discharge/charge current densities of 10.0 mA cm^{-2}.

Fig. S17 Flexible soft-pack ZABs of open-circuit voltage.

Table S1 The battery performance comparisons of the present with previously reported similar materials.

Catalysts	Cycling condition	Stability	Flexible	Ref.
Co/$ZnCo_2O_4$@NC-CNTs	5 mA cm^{-2}	103 h	Yes	Nano Energy 82 (2021) 105710.
Co-N-C	2 mA cm^{-2}	140 h	No	Small 16 (2020) 2001171
P-CoO@PWC-2	10 mA cm^{-2}	232 h	Yes	Adv. Sci. (2021) 2101314
Ni_3Fe/Co-N-C	10 mA cm^{-2}	65 h	No	Chem. Eng. J. 395 (2020) 125151
Co-Fe-S@NSRPC	10 mA cm^{-2}	52 h	No	Nanoscale 12 (2020) 11746-11758
Co-MOF/LC-0.5	5 mA cm^{-2}	120 h	No	J. Power Sources 468 (2020) 228377
Co-MOF-800	1 mA cm^{-2}	85 h	No	Journal of Energy Chemistry 56 (2020) 290-298
KNiFe$(CN)_6$/C	5 mA cm^{-2}	333 h	Yes	Electrochim. Acta 397 (2021) 139278
Co/CoFe@NC	5 mA cm^{-2}	183 h	Yes	Nano-Micro Lett. (2021) 13 126
Co_4NC@NC	5 mA cm^{-2} 10 mA cm-2	350 h 200 h	Yes	This Work