Co_3O_4 nanoparticle modified N, P co-doping carbon paper as sodium carriers to construct stable anodes for Na-metal batteries

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Material Preparation

Materials. Diethylene glycol dimethyl ether (DEGME, 99.9 %), $NaCF_3SO_3$ (Aladdin Reagent, 98%) and pyrrole and 50 wt% phytic acid solution (w/w) in H_2O were purchased from Sigma-Aldrich. 0.1 M bis sodium trifluoromethanesulfonate salt ($NaCF_3SO_3$) is dissolved in 100 mL Diethylene glycol dimethyl ether (DEGME) to obtain 1M electrolyte. Ketjenblack (EC600JD) produced by Shanghai Tengmin Industry Co., Ltd. N-methyl-2-pyrrolidinone (C_5H_9NO, 99 %) was purchased from Aladdin Reagent. $LiClO_4$ (99.0 %), Na_2CO_3 (99.8 %) and $RuCl_3{\bullet}_XH_2O$ were purchased from Aladdin Reagent. Carbon paper was TGP-H-060 carbon paper. NVP powders was purchased from Kejing Company. Other chemicals were from Sinopharm Chemical Reagent Corp. All chemicals were used as received without further purification.

KB@Ru electrode preparation. The KB@Ru was synthesized by a reported method[9]. 50 mg of $RuCl_3{\bullet}XH_2O$ (40 % Ru content) was dissolved in 100 mL of ethylene glycol. 80 mg of KB carbon was added into the solution and was uniformly mixed through an ultrasonic bath. The suspension was refluxed for 3 h at 170 ^oC. After cooling down, the supernatant was removed and the remnant mixture was centrifuged with deionized water and ethanol several times. The resulting products were dried in a vacuum oven at 80 ^{o}C for 12 h. The preparation of KB@Ru-based air electrode, KB@Ru (80 wt%), KB (10 wt%) and polyvinylidene fluoride binder (PVDF, 10 wt%) in an N-methyl-2-pyrrolidone (NMP) solution was stirred to form homogeneous slurry. After that, the obtained slurry was spread on a 12mm diameter carbon paper via blade-coating to form the KB@Ru-based air electrode. Finally, the coated electrode was dried for 12 h at 100 ^{o}C under vacuum to remove residual solvent. The mass loading of active materials in the KB@Ru cathode was about 0.10 mg cm^{-2}.

NVP electrode preparation. The positive electrodes were made by mixing NVP, PVDF and super P with 8:1:1 in N-methyl-2-pyrrolidinone (NMP) solution, and then the obtained slurry was coated onto Al foil with doctor blade and subsequently dried at 80 ^{o}C for 12 h. Finally, the Al foil is cut into 12mm diameter sheets and the loading mass of NVP is about 3.0 mg cm^{-2}.

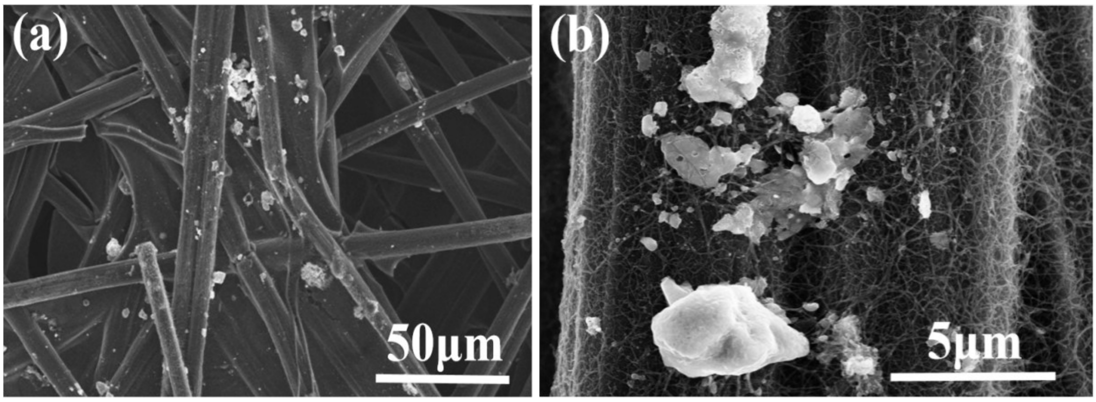

Fig. S1 SEM images of NP-CP precursor with different magnifications.

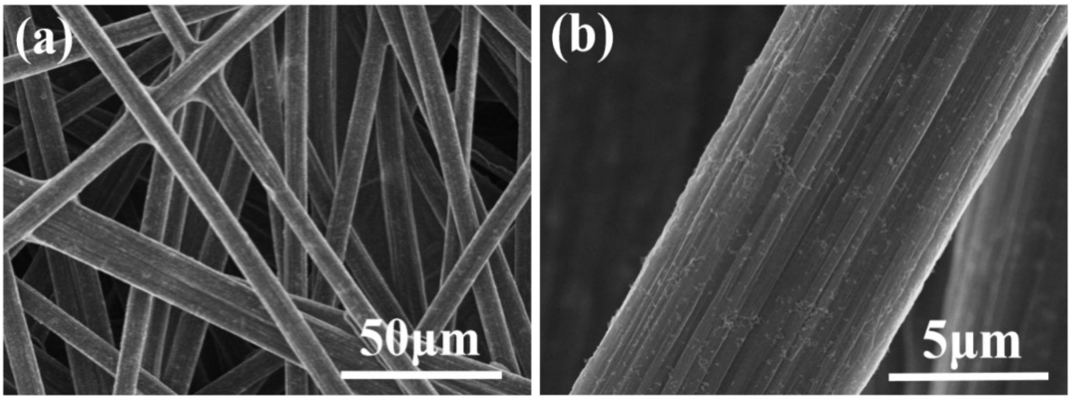

Fig. S2 SEM images of CP with different magnifications.

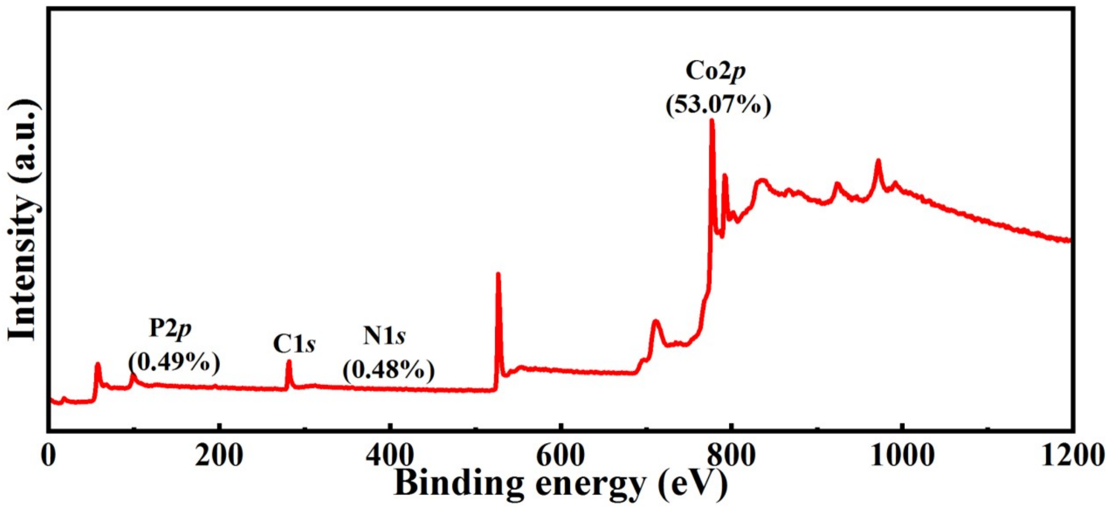

Fig. S3 Full XPS spectrum for Co_3O_4@NP-CP.

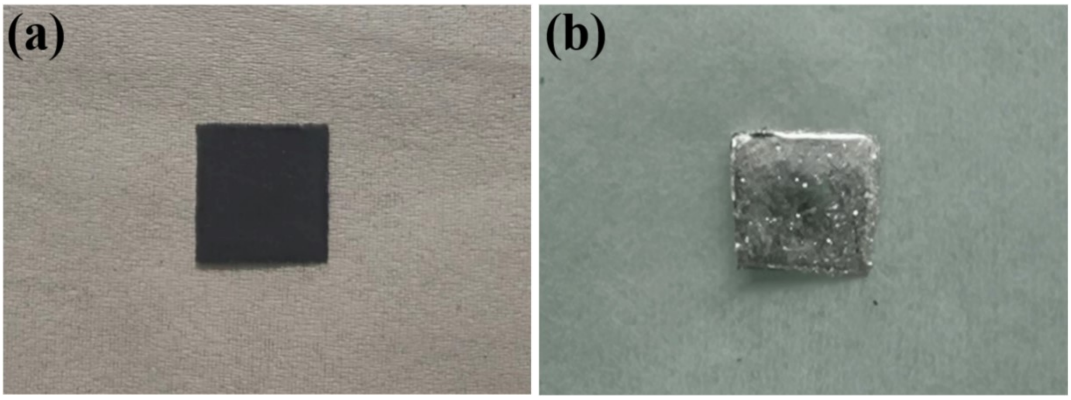

Fig. S4 Photos of (a) Co_3O_4@NP-CP and (b) Na-Co@NP-CP.

As shown in Fig. S4, the color of Co_3O_4@NP-CP is black and Co_3O_4@NP-CP was cut into 1cm square. After deposition of metal Na, the obtained Na-Co@NP-CP shows metallic luster.

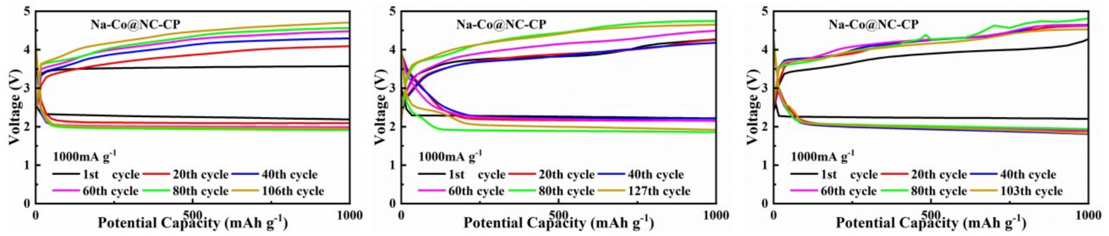

Fig. S5 The voltage curve of Na-CO_2 battery with Na-Co@NP-CP anode was tested multiple times at the current density of 1000 mA g^{-1} and the limited capacity of 1000 mAh g^{-1}.

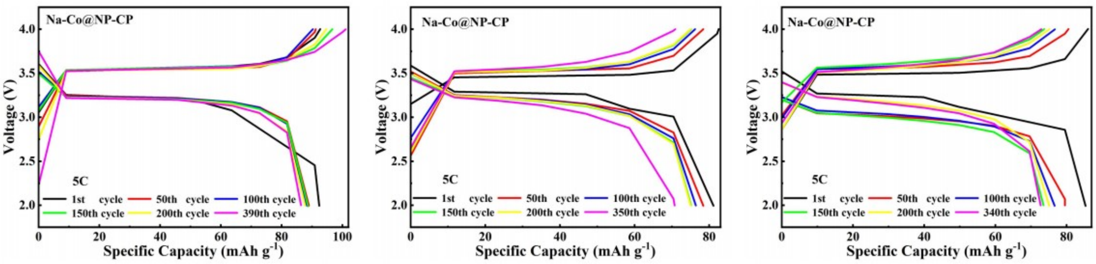

Fig. S6 The voltage curve of Na-Co@NP-CP||NVP full battery was tested multiple times at the current density of 5C.

Sample	Pyridinic N	Pyrrolic N	Graphitic N
Co_3O_4@NP-CP	46.5 %	32.9 %	20.6 %

Table. S1 Distribution of each N species are obtained from fitting the N1s XPS spectra results.

	Current density	Specific capacity	Cycle number
Na-Co@NP-CP (This work)	**500 mA g^{-1}** **1000 mA g^{-1}**	**500 mAh g^{-1}** **1000 mAh g^{-1}**	**165** **125**
NaF-rich[10]	500 mA g^{-1}	1000 mAh g^{-1}	100
rGO-Na[11]	200 mA g^{-1}	1000 mAh g^{-1}	50
Na@In[12]	1 mA cm^{-2}	1 mAh cm^{-2}	30

Table. S2 Comparison of the current density, specific capacity and cycling performance of Na-CO_2 battery in this work with previous reports.

	Current density	Capacity retention (%)	Cycle number
Na-Co@NP-CP (This work)	**1C** **5C**	**92.4** **89.6**	**346** **330**
NaF-rich[10]	1C	80	200
CuS NWs@NC[13]	0.2 A g^{-1}	54.2	200
CC@Bi@C/Na[14]	5C	82	350
Na@CC[15]	100 mA g^{-1}	79	100

Table. S3 Comparison of the current density, capacity retention and cycling performance of Na-Co@NP-CP||NVP full battery in this work with previous reports.

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