## **Supporting Information**

Lithiophilic Co/Co<sub>4</sub>N nanoparticles embedded in hollow N-doped carbon nanocubes stabilizing lithium metal anodes for Li–air batteries

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## **Material Preparation**

## Materials

dimethyl 99.9%) Tetraethylene glycol ether (TEGDME, and Li bis(trifluoromethanesulfonyl)imide (LiTFSI, 99.95%) were purchased from Sigma-Aldrich Corporation. Cobalt nitrate hexahydrate (CoNO<sub>3</sub>•6H<sub>2</sub>O, 99 %) were purchased from MACKLIN Reagent Corporation. 2-methylimidazole (99 %) were purchased from J&K Scientific Reagent Corporation. Cetyltrimethy lammonium bromide (CTAB) was purchased from Tianjin BODI Reagent Corporation. RuCl<sub>3</sub>•xH<sub>2</sub>O (35.0~42.0 % Ru basls), Citric acid monohydrate ( $C_6H_8O_7$ •H<sub>2</sub>O, 99.5 %), Potassium hydroxide (KOH, 90 %), Cobalt( II ) acetate tetrahydrate (Co(OAc)<sub>2</sub>•4H<sub>2</sub>O, 99.5 %) and Cobalt (Co, 99.5 %) were purchased from Aladdin Corporation. All chemicals were used as received without further purification.

*Synthesis of ZIF-67 nanocubes.* The cubic ZIF-67 was sythesized according to the previous report (ref. S1). In a typical synthesis, 2 mL of aqueous solution containing 58 mg of  $Co(NO_3)_2$ •  $6H_2O$  and 1 mg of cetyltrimethylammonium bromide (CTAB) is rapidly injected into 14 mL of aqueous solution with 908 mg of 2-methylimidazole and vigorously stirred at room temperature for 20 min. Then, the precipitate was collected by repeatedly washing with ethanol for at least 6 times before vacuum drying at room temperature overnight.

*Synthesis of Co/C*. For comparison with Co/Co<sub>4</sub>N-NC, the similar MOF (UTSA-16) was synthesized by using the ligand without nitrogen and then treated at the same conditions. For the detail, UTSA-16 was obtained by hydrothermal synthesis according to the previous report (ref. S2). Co(OAc)<sub>2</sub>•4H<sub>2</sub>O (0.249 g, 1 mmol), C<sub>6</sub>H<sub>8</sub>O<sub>7</sub>•H<sub>2</sub>O (0.21 g, 1 mmol), KOH (0.168 g, 3 mmol), H<sub>2</sub>O (2.5 ml) and C<sub>2</sub>H<sub>5</sub>OH (2.5 ml) in a molar ratio of 1 : 1 : 3 : 139 : 43 were put in a Teflon-lined 23 ml Parr acid digestion bomb. The bomb was then placed in a furnace that was heated from room temperature to 120 °C in half an hour, kept at 120 °C for 2 days, and then slowly cooled to room temperature at a rate of 4 °C h<sup>-1</sup>. The obtained sample is denoted as UTSA-16. The as-prepared UTSA-16 was then pyrolyzed by heating to

900 °C at a heating rate of 5 °C min<sup>-1</sup> under a  $N_2$  gas flow and further treated at 900 °C under  $N_2$  for 2 h. After cooling, the resulting sample is abbreviated as Co/ C.

Synthesis of Co/NC. For comparison with Co/Co<sub>4</sub>N-NC, we used the ZIF-8 as precursor to obtained NC without Co<sub>4</sub>N species (the zinc metal in the ZIF-8 was easily removed under the high temperature and further acid treatment). The Co/NC without Co<sub>4</sub>N species was obtained by mixing the NC with Co particals. Specifically, ZIF-8 nanocubes were synthesized firstly according to the previous report (ref. S3). Typically, 1.81 g of zinc nitrate hexahydrate was dissolved in 8 mL of deionized water, and then 1.0 g of 2-methylimidazole was dissolved in 12.09 g of ammonium hydroxide solution; after that zinc nitrate and 2-methylimidazole were mixed together and then stirred for 10 min at room temperature to complete the crystallization. The product was collected by washing with ethanol for at least 6 times before vacuum drying at room temperature overnight. The as-prepared ZIF-8 nanocubes were then pyrolyzed by heating to 900°C for 2 h under a N<sub>2</sub> gas flow. After the temperature was cooled down to room temperature naturally, the black product was purified by 1.0 M hydrochloric acid at room temperature for 12.0 h to remove residual zinc species. The NC were collected by washing and filtered several times with deionized water. The SEM mapping investigation confirms that the elements N and C are uniformly distributed in this architecture, and there is no remaining zinc species (Fig. S2). To obtained the Co/NC, the NC was ball-milled with metallic Co in a molar ratio of 33 : 1 for 2 h.

*Synthesis of Co/Co<sub>4</sub>N-NC-800 and Co/Co<sub>4</sub>N-NC-1000.* For comparison with Co/Co<sub>4</sub>N-NC, Cubic ZIF-67 was also pyrolyzed at 800°C and 1000°C, respectively. All the synthesis procedures are similar to that of Co/Co<sub>4</sub>N-NC. The obtained ZIF-67-derived material pyrolyzed at 800°C and ZIF-67-derived material pyrolyzed at 1000°C were abbreviated as Co/Co<sub>4</sub>N-NC-800 and Co/Co<sub>4</sub>N-NC-1000, respectively.

*Synthesis of KB/Ru*. KB/Ru was obtained according to the previous report (ref. S4). 50 mg of RuCl<sub>3</sub>•xH<sub>2</sub>O (40% Ru content) was dissolved in 100 mL of ethylene glycol. 80 mg of Super P carbon was added into the solution and was uniformly mixed through an ultrasonic bath. The suspension was refluxed for 3 h at 170 °C. 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 °C for 12 h. The obtained sample is denoted as KB/Ru.

*Preparation of KB/Ru catalytic electrode.* In the preparation of KB/Ru catalytic electrode, KB/Ru (80 wt %), Super P (10 wt %) and a polyvinylidene fluoride binder (PVDF, 10 wt %) were intimately mixed in an N-methyl-2-pyrrolidone (NMP) solution, and the resulting slurry was coated on a carbon paper (TGP-H-060 carbon paper, Torray). The coated electrode was dried for 12 h at 100 °C under vacuum to remove residual solvent.

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## Characterization instrumentation.

XRD measurements were performed on a Bruker D8 Focus power X-ray diffractometer with Cu K□ radiation. Field emission scanning electron microscopy SEM investigations were conducted using a JSM-6390 microscope from JEOL. Transmission electron microscopy (TEM) experiments were conducted using a JEOL 2011 microscope (Japan) operated at 200 kV. The surface of as-prepared sample was characterized by Raman spectroscopy (LABRAM-1B). Specific surface areas were calculated by the Brunaure–Emmert–Teller method. Pore volumes and sizes were estimated from the pore-size distribution curves from the adsorption isotherms using the Barrett–Joyner–Halenda method. X-ray photoelectron spectroscopy (XPS) was conducted with a Thermo Escalab 250 equipped with a hemispherical analyzer and

using an aluminum anode as a source. Fourier transform-infrared spectroscopy (FT-IR) tests were performed on a Nicolet 6700 spectrometer. The surface of as-prepared sample was characterized by Raman spectroscopy (LABRAM-1B). LAND cycler (Wuhan Land Electronic Co. Ltd) was employed for electrochemical tests. Power electronic conductivity investigation with the pressure of 4 MPa was performed on a 4-pole conductivity instrument for powder materials (Powder Resistivity Meter, FZ-2010, Changbao Analysis Co., Ltd, Shanghai, China).



**Fig. S1** SEM and TEM images of the ZIF-67 precursor with different magnifications. It can be observed from Fig. S1a and b that the ZIF-67 precursor exhibits the nanocube morphology. In addition, the TEM images of the ZIF-67 precursor further reveal that the average particle size of ZIF-67 is ~400 nm (Fig. S1c and d).



**Fig. S2** SEM image of NC (left) and the corresponding EDX mapping images of C and N elements.

SEM image of NC (Fig. S2a) also shows the typical nanocube structure, which is similar to the morphology of  $Co/Co_4N$ -NC (Fig. 2a). Energy-dispersive X-ray (EDX) mapping was further used to investigate the elemental distribution and composition of NC composite. As shown in Fig. S2b and c, the co-existence of C and N species can be found on the surface of NC. Moreover, C and N species are uniformly distributed in NC.



**Fig. S3** SEM image of Co/NC (left) and the corresponding EDX mapping images of C, Co, and N elements.

Energy-dispersive X-ray (EDX) mapping was further used to investigate the elemental distribution and composition of Co/NC composite. As shown in Fig. S3, the co-existence of C, Co and N species can be found on the surface of Co/NC. Moreover, Co, C and N species are uniformly distributed in Co/NC.



**Fig. S4** The high-resolution (f) Co  $2p_{3/2}$  and (g) N 1s XPS spectra of Co/NC. As shown in Fig. S4a, the detailed XPS N1s spectra for the Co/ NC sample can be deconvoluted into three different bands at ~399, 400.9, and 402.2 eV, which correspond to pyridinic N (N-6), pyrrolic N (N-5) and graphitic N (N-Q), respectively. This result indicates the successful N-doping in Co/NC. In addition, there are only two deconvoluted peaks in the high-resolution Co  $2p_{3/2}$  XPS spectrum (Fig. S4b): a metallic Co peak (~778.5 eV), and a broad peak attributed to Co<sup>2+</sup> (~780.0 eV), further demonstrating the absence of Co<sub>4</sub>N species in the Co/NC sample.



**Fig. S5** SEM image of Co/C (left) and the corresponding EDX mapping images of C and Co elements.

Energy-dispersive X-ray (EDX) mapping was further used to investigate the distribution and composition of Co/C composite. As shown in Fig. S5, the co-existence of C and Co species can be found on the surface of Co/C. Moreover, Co and C species are uniformly distributed in Co/C.



**Fig. S6** (a) Full XPS spectra and the high-resolution Co  $2p_{3/2}$  of Co/C. As shown in Fig. S6a, full XPS spectra of Co/C also revealed the presence of C, Co and O species. In addition, the detailed Co  $2p_{3/2}$  spectra for the Co/C sample can be deconvoluted into two different bands at ~778.5 and 780.0 eV, which correspond to metallic Co and Co<sup>2+</sup>, respectively (Fig. S6b). This result further indicates there are not N atoms in the Co/C sample.



Fig. S7 XRD pattern of as-synthesized ZIF-67.

As shown in Fig. S7, all of the main XRD diffraction peaks are attributed to ZIF-67, indicating the successful synthesis of ZIF-67.



Fig. S8 Raman spectra of as-synthesized ZIF-67 and Co/Co<sub>4</sub>N-NC.

As shown in Fig. S8, the G band at 1590 cm<sup>-1</sup> and D band at 1330 cm<sup>-1</sup> can be found in Co/Co<sub>4</sub>N-NC, but cannot be observed in ZIF-67 precursor, suggesting that there is the formation of graphitized carbon in Co/Co<sub>4</sub>N-NC.



Fig. S9 Full XPS spectra of as-synthesized ZIF-67 and Co/Co<sub>4</sub>N-NC.

As shown in Fig. S9, full XPS spectra of ZIF-67 also revealed the presence of C, N, O, and Co species. The C 1s peak centered at 284.7 eV is the typical graphitic carbon peak. The intensity of O 1s peak in ZIF-67 is much higher than that of Co/Co<sub>4</sub>N-NC, confirming the reduction of Co<sup>2+</sup> to metallic Co by carbon during the pyrolysis process.

**Tab. S1** The relative surface content of C, Co, N and O elements for ZIF-67 and  $Co/Co_4N$ -NC measured by XPS analysis.

Sample	OxygenCarboncontentcontent(at%)(at%)	Cobalt content (at%)					Nitrogen content (at%)				
		(at%)	Total	Co	Co <sup>2+</sup>	Co-N	Total	N-5	N-6	N-Q	Co-N
ZIF-67	10.31	66.52	5.07	-	-	-	18.1	-	-	-	-
Co/Co <sub>4</sub> N-NC	3.19	87.1	2.76	0.60	0.38	1.78	6.95	2.31	3.19	0.31	1.14

As listed in Tab. S1, the atom percentage of the O phase in Co/Co<sub>4</sub>N-NC (3.19 %) is also found to be obviously smaller compared with that in ZIF-67 (10.31 %), indicating the reduction of the oxygen-containing functional groups during the pyrolysis process. In addition, the relative surface concentrations of Co, Co<sup>2+</sup> and Co<sub>4</sub>N species are 0.60, 0.38 and 1.78 % for Co/Co<sub>4</sub>N-NC, respectively, which suggests the co-existence of metallic Co, Co<sup>2+</sup> and Co<sub>4</sub>N in Co/Co<sub>4</sub>N-NC. Moreover, N-5, N-6 and Co<sub>4</sub>N atoms are overwhelmingly dominant (95.4%) among these nitrogen species in Co/Co<sub>4</sub>N-NC.

Materials	Nitrogen content (atom%)	References
NG	3.14	Ref. S1
Co/NC	3.3	Ref. S2
NCNTFs	2.4	Ref. S3
N-CG–CoO	5	Ref. S4
N/Co-doped PCP//NRGO	3.5	Ref. S5
NGSH	0.58	Ref. S6
CoNC-1000	1.36	Ref. S7
MOFs-800	3.5	Ref. S8
HS-N-OMC	5	Ref. S9
Co/Co <sub>4</sub> N-NC	6.95	This Work

Tab. S2 Summary of Nitrogen content in various materials

As listed in Tab. S2, the content of N species in  $Co/Co_4N$ -NC is much higher than other recently reported materials.

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**Fig. S10** (a) Nitrogen adsorption-desorption isotherms and (b) pore-size distribution of as-synthesized ZIF-67.

As shown in Fig. S10a, a distinctly increased sorption at low relative pressure  $(P/P_0 < 0.05)$  is observed, suggesting that there are lots of microporous channels in ZIF-67. Moreover, it can be seen from the pore size distribution in Fig. S10b that the micropore sizes of ZIF-67 are mainly centered at 1.0-2.0 nm.



Fig. S11 (a) Nitrogen adsorption-desorption isotherms and (b) pore-size distribution of as-synthesized  $Co/Co_4N$ -NC.

As shown in Fig. S11a, a distinctly increased sorption at low relative pressure  $(P/P_0 < 0.05)$  and a slight hysteresis in a wide relative pressure  $(P/P_0)$  range from 0.5-0.8 are observed, suggesting that there are microporous and mesoporous channels in Co/Co<sub>4</sub>N-NC. Moreover, it can be detected from Fig. S11b that there are three kinds of pores in pore-size distribution curves: micropores (0.5-1.8 nm), mesopores (2.0–4.0 nm) and macropores (80–150 nm), which is slightly different from that of ZIF-67 (Fig. S10). This result indicates the typical hierarchical porous nature of Co/Co<sub>4</sub>N-NC.



Figure S12 TEM images of (a, b)  $Co/Co_4N$ -NC-800 and (c, d)  $Co/Co_4N$ -NC-1000 with different magnifications.

As shown in Fig. S12a and b, the TEM images of the Co/Co<sub>4</sub>N-NC-800 after pyrolysis at 800 °C reveal that Co nanoparticles are uniformly dispersed in the carbon framework. In contrast, when being pyrolyzed at 1000°C, many Co particles agglomerate together in the carbon framework of Co/Co<sub>4</sub>N-NC-1000 (Fig. S12c and d). Moreover, it can be found that the average size of Co particles of Co/Co<sub>4</sub>N-NC (pyrolyzed at 900°C) in the manuscript (Fig. 2d and e) is slightly larger than that of Co/Co<sub>4</sub>N-NC-800 (Fig. S12a and b), but is much smaller than that of Co/Co<sub>4</sub>N-NC-1000 (Fig. S12c and d). This result demonstrates that the rise of pyrolysis temperature can distinctly accelerate the aggregation of Co species.

**Tab. S3** Electronic conductivities of the as-prepared Co/Co<sub>4</sub>N-NC-800, Co/Co<sub>4</sub>N-NC and Co/Co<sub>4</sub>N-NC-1000 powders.

Sample	Co/Co <sub>4</sub> N-NC-800	Co/Co <sub>4</sub> N-NC	Co/Co <sub>4</sub> N-NC-1000
Conductivity (S cm <sup>-1</sup> )	0.10	0.92	1.03

As shown in Tab. S3, the electronic conductivity of  $Co/Co_4N$ -NC powder is close to that of  $Co/Co_4N$ -NC-1000 powder, and is much higher than that of  $Co/Co_4N$ -NC-800 powder. This result further demonstrates that the rise of pyrolysis temperature can lead to the increase of the electrical conductivity.



Fig. S13 The typical high resolution XPS spectra of N 1s for  $Co/Co_4N-NC-800$ ,  $Co/Co_4N-NC$  and  $Co/Co_4N-NC-1000$ , respectively.

**Tab. S4** The relative surface content of N and other elements for  $Co/Co_4N-NC-800$ ,  $Co/Co_4N-NC$  and  $Co/Co_4N-NC-1000$  measured by XPS analysis.

Sample	Nitrogen content (at%)	Other elements content (at%)
Co/Co <sub>4</sub> N-NC-800	7.23	92.77
Co/Co <sub>4</sub> N-NC	6.95	93.05
Co/Co <sub>4</sub> N-NC-1000	2.43	97.57

As shown in Fig. S13, the N1s peak intensity of Co/Co<sub>4</sub>N-NC is slightly lower than that of Co/Co<sub>4</sub>N-NC-800, but much higher than that of Co/Co<sub>4</sub>N-NC-1000. It can be clearly observed that the N content of Co/Co<sub>4</sub>N-NC is similar to that of Co/Co<sub>4</sub>N-NC-800, but obviously larger than that of Co/Co<sub>4</sub>N-NC-1000 (Tab. S4). This phenomenon confirms that the increase of pyrolysis temperature can lead to the decrease of N species. Based on these above results (Fig. S12, 13 and Tab. S3, 4), we can conclude that Co/Co<sub>4</sub>N-NC has the appropriate electrical conductivity, N content and Co particle size.



**Fig. S14** (a) The voltage curves of Li plating on the Co/Co<sub>4</sub>N-NC-800 and Co/Co<sub>4</sub>N-NC-1000 electrodes at 0.01 mA cm<sup>-2</sup> and a duration of 20 h and (b) Comparison of coulombic efficiencies of Li plating/stripping on the Co/Co<sub>4</sub>N-NC-800 and Co/Co<sub>4</sub>N-NC-1000 electrodes at 0.5 mA cm<sup>-2</sup> with a limited capacity of 0.5 mAh cm<sup>-2</sup>.

To clarify the role of the nitrogen content and Co nanoparticle size on the battery performance, we also studied the Li growing/stripping performance of Co/Co<sub>4</sub>N-NC-800 and Co/Co<sub>4</sub>N-NC-1000 electrodes compared with Co/Co<sub>4</sub>N-NC electrode. It can be calculated from Fig. S14a that the nucleation  $\mu_n$  at 0.01 mA cm<sup>-2</sup> of the Co/Co<sub>4</sub>N-NC-800 electrode and the Co/Co<sub>4</sub>N-NC-1000 electrode are 0.0151 V and 0.0162 V, respectively, which are obviously higher than the Co/Co<sub>4</sub>N-NC electrode (Fig. 4a). In addition, the CEs of the Co/Co<sub>4</sub>N-NC-800, Co/Co<sub>4</sub>N-NC and Co/Co<sub>4</sub>N-NC-1000 electrodes are also analyzed by the galvanostatic charge/discharge profiles at 0.5 mA cm<sup>-2</sup> with a limited areal capacity of 0.5 mAh cm<sup>-2</sup> (Fig. S14b). As shown in Fig. S14b, the CE of the Co/Co<sub>4</sub>N-NC-800 and Co/Co<sub>4</sub>N-NC-1000 electrodes remained 97.5% and 97.1% after 100 cycles, which are also smaller than the Co/Co<sub>4</sub>N-NC electrode (Fig. 4c). These results further demonstrate that the appropriate N content, electrical conductivity and Co particle size in the Co/Co<sub>4</sub>N-NC can enhance the surface lithiophilicity and thus is beneficial to the uniform Li deposition. Hence, Co/Co<sub>4</sub>N-NC is the optimized material for Li plating in this work.



**Fig. S15** The typical discharge/charge voltage profile of the Co/Co<sub>4</sub>N-NC electrode at a constant current of 0.2 mA cm<sup>-2</sup> between 0.05 and 3.0 V.

As shown in Fig. S15, the first cycle discharge capacity was ~0.3 mAh and the first cycle charge capacity was ~0.1 mAh. The irreversible specific capacity could be explained by SEI formation and irreversible  $Li^+$  ion trapping. The reversible capacity (~0.1 mAh) can be mainly attributed to the intercalation reaction of graphited carbon in the Co/Co<sub>4</sub>N-NC electrode. In addition, the conversion reaction of CoO and Co<sub>4</sub>N can also contribute the part capacity for the Co/Co<sub>4</sub>N-NC electrode.



**Fig. S16** The voltage curves of Li planting on the Co/Co<sub>4</sub>N-NC, Co/NC, Co/C and Cu foil electrodes at 0.05 mA cm<sup>-2</sup> with a limited time of 10 h.



**Fig. S17** The voltage curves of Li planting on the Co/Co<sub>4</sub>N-NC, Co/NC, Co/C and Cu foil electrodes at 0.5 mA cm<sup>-2</sup> with a limited time of 2.0 h.



Fig. S18 The voltage curves of Li planting on the Co/Co<sub>4</sub>N-NC, Co/NC, Co/C and Cu foil electrodes at 1 mA cm<sup>-2</sup> with a limited time of 1.0 h.



**Fig. S19** Surface composition on Co/Co<sub>4</sub>N-NC electrode after (a, b, c) 5th and after (d, e, f) 10th Li stripping cycles. (a, d) C 1s, (b, e) N 1s and (c, f) F 1s XPS spectra of SEI layer on the surface of Co/Co<sub>4</sub>N-NC electrode.

Fig. S19 shows XPS specta of the Co/Co<sub>4</sub>N-NC electrode after diferent Li stripping cycles. As shown in Fig. S19, there are many ROLi, ROCOOLi,  $LiN_xO_y$ , and LiF species formed on the surface of the Co/Co<sub>4</sub>N-NC electrode diferent Li stripping cycles. Furthermore, XPS specta spectra of the Co/Co<sub>4</sub>N-NC electrode after 5th and 10th Li stripping cycles are very similar, which indicates the formation of a stable SEI layer on the Co/Co<sub>4</sub>N-NC electrode.



**Fig. S20** The FT-IR spectra of the Co/Co<sub>4</sub>N-NC electrode (a) after 5th and (b) 10th Li stripping. The peaks of  $v_{S=O}$ ,  $v_{N-S}$  and  $v_{C-F}$  may result from the residual LiTFSI. As shown in Fig. S20, the measured spectra contain features of ROLi (around 2900 and 1090 cm<sup>-1</sup>), ROCOOLi (around 2900, 1650, 1435, and 1090 cm<sup>-1</sup>), and LiN<sub>x</sub>O<sub>y</sub> (around 1385 cm<sup>-1</sup>), which indicates that a SEI layer is formed on the surface of the Co/Co<sub>4</sub>N-NC electrode. Furthermore, the FT-IR spectra of the Co/Co<sub>4</sub>N-NC electrode after 5th and 10th Li stripping are very similar, indicating that the formation of a SEI

layer on the Co/Co<sub>4</sub>N-NC electrode is very stable during Li plating/stripping process.

Tab. S5 Comparison of Coulombic efficiency, cycle numbers, areal capacity and
current density of various anode substrates.

Materials	Coulombic Efficiency (%)	Cycle numbers	Current density (mA cm <sup>-2</sup> )	Specific Capacity (mAh cm <sup>-2</sup> )	References
Cu-MOFs	98.5	200	0.5	1	Ref. S14
copper mesh	93.8	100	0.5	1	Ref. S15
LiF-rich Cu	98.7	120	0.5	1	Ref. S16
5% FEC electrolyte	95	100	0.5	0.5	Ref. S17
3D Ni@Cu	96	300	1	0.5	Ref. S18
Graphene@Ni foam	98	100	0.5	1	Ref. S19
CuO-NC/Cu	96.7	150	0.5	1	Ref. S20
graphene	93	50	0.5	0.5	Ref. S21
Co/Co <sub>4</sub> N-NC	98.5	300	0.5	1	This work

As listed in Tab. S5, the Co/Co<sub>4</sub>N-NC electrode displays a Coulombic efficiency of 98.5% over 300 cycles at a limited capacity of 1.0 mAh cm<sup>-2</sup>, which outperform most of the reported anode substrates in the recent literatures (ref. S14-21), further confirming the superior Li plating/stripping behavior of the Co/Co<sub>4</sub>N-NC electrode.

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**Fig. S21** Comparison of the coulombic efficiencies of the Co/C and Co/NC electrodes at various current densities of (a)  $0.5 \text{ mA cm}^{-2}$ , (b) 1 mA cm<sup>-2</sup> and (c) 2 mA cm<sup>-2</sup> with the same areal capacity of 1.0 mAh cm<sup>-2</sup>.

As shown in Fig. S21a, the Co/NC and Co/C electrodes only exhibit the CE of 90 % after 200 cycles and 88% after 170 cycles at 0.5 mA cm<sup>-2</sup>, respectively, which is much lower than that of the Co/Co<sub>4</sub>N-NC electrode (98.5 % after 300 cycles) (Fig. 5a). When the current density increases to 1 mA cm<sup>-2</sup>, the Co/Co<sub>4</sub>N-NC electrode still displays CE of 97.5% over 95 cycles (Fig. 5b), while the CEs of the Co/NC and Co/C electrodes are only 88.1% and 81.3% after 95 cycles, respectively (Fig. S21b). Moreover, even at relatively higher current densities of 2 mA cm<sup>-2</sup>, the CE of the Co/Co<sub>4</sub>N-NC electrode over 95 cycles can maintain 96.9 % (Fig. 5c), whereas the CEs of the Co/NC and Co/C electrodes rapidly decrease to 80 % after 76 and 55 cycles, respectively (Fig. S21c). These results indicate that the Co/Co<sub>4</sub>N-NC electrode has longer cycle life and higher CE compared with the Co/NC and Co/C electrodes, which may be attributed to the plentiful lithiophilic N-containing groups and typical porous structure in Co/Co<sub>4</sub>N-NC.



Fig. S22 The variation of CE of the Co/Co<sub>4</sub>N-NC electrode at different current densities with the limited capacity of 1.0 mAh cm<sup>-2</sup>. Stage 1: at 2 mA cm<sup>-2</sup> for 50 cycles; Stage 2: at 0.5 mA cm<sup>-2</sup> for 20 cycles.

As shown in Fig. 22, the average CE of the Co/Co<sub>4</sub>N-NC electrode at 2 mA cm<sup>-2</sup> is ~96.5% for 50 cycles (Stage 1). After Stage 1, the Co/Co<sub>4</sub>N-NC electrode still exhibits a superior CE of ~98.2% after 20 cycles at 0.5 mA cm<sup>-2</sup> (Stage 2), which is similar to the CE (98.5%) of Co/Co<sub>4</sub>N-NC electrode before application of the higher rate (Fig. 5a). This result further demonstrates the good rate performance of the Co/Co<sub>4</sub>N-NC electrode.



Fig. S23 Comparison of the coulombic efficiencies of Cu foil and Co/Co<sub>4</sub>N-NC electrodes at  $1.5 \text{ mA cm}^{-2}$  with a limited capacity of  $3.0 \text{ mAh cm}^{-2}$ .

As shown in Fig. S23, even at a higher limited capacity of 3.0 mAh cm<sup>-2</sup>, the CE of Co/Co<sub>4</sub>N-NC electrode can maintain at ~91.1% more than 90 cycles while the CE of Cu electrodes would be sharply oscillation after 5 cycles.



**Fig. S24** Nyquist plots obtained from the symmetric cells using (a) the Co/Co<sub>4</sub>N-NC electrode or (b) bare Cu foil electrode/Li anode at different Li plating/stripping cycles: before electrochemical cycling, and after 5 cycles and 10 cycles at current density of 1 mA cm<sup>-2</sup> with a cycling capacity of 1 mAh cm<sup>-2</sup>.

Fig. S24 gives the Nyquist plots of symmetrical cells which are used to compare the internal resistances of the Co/Co<sub>4</sub>N-NC and bare Cu foil electrodes at different cycles. The interfacial resistance between electrolyte/electrode and the charge transfer resistance at the anode surface are associated with the semi-circle in high frequency region. Before cycling, the Co/Co<sub>4</sub>N-NC anode shows a large interfacial resistance of about 33  $\Omega$ , which could be due to the formation of passivation films on the electrode. The interfacial resistance drops to 20  $\Omega$  after five cycles and decreases to 10  $\Omega$  after 10 cycles (Fig. S24a). This could be related to the decomposition of the passivation film and the gradually increased surface area from the formation of Li dendrites. In comparison, cells with bare Cu foil electrode shows high interfacial resistances of 65  $\Omega$  before cycling, 68  $\Omega$  after 5 cycles, and 71  $\Omega$  after 10 cycles (Fig. S24b). It suggests that the Co/Co<sub>4</sub>N-NC electrodes can enlarge the Li/electrolyte interface, favor the redox reactions and reduce the charge transfer resistance due to the high electroactive area, enough lithiophilic sites and typical porous structure of Co/Co<sub>4</sub>N-NC. Hence, the Co/Co<sub>4</sub>N-NC electrode shows the lower voltage hysteresis compared with the bare Cu foil electrode (Fig. 5d).



Fig. S25 (a) SEM and (b) TEM images, (c) XRD pattern of KB/Ru nanoparticles.

As shown in Fig. S25a and b, KB was uniformly covered by Ru nanoparticles. The HR-TEM image indicates that the lattice fringe of the inner Ru nanoparticles shows an interspacing of ~0.235 nm which corresponds to the (100) plane of Ru crystal structure (Fig. S25b inset). Moreover, the XRD of KB/Ru nanoparticles exhibits the typical peaks at around 38, 42, 44 and 58° (Fig. S25c), respectively. These peaks could be identified as metallic Ru according to the standard powder diffraction file of Ru (JCPDS No.06-663), further demonstrating the successful synthesis of KB/Ru nanoparticles.



**Fig. S26** (a) *Ex-situ* XRD pattern and (b) *Ex-situ* FTIR spectra analyses for KB/Ru electrodes of Li–air batteries with the lithiated  $Co/Co_4N$ -NC anodes in ambient air before discharge, after discharge and at the end of full recharge.

In the *ex situ* XRD pattern and FT-IR spectra of the KB/Ru based air electrode after discharge, it can be observed that crystalline Li<sub>2</sub>O<sub>2</sub>, LiOH and Li<sub>2</sub>CO<sub>3</sub> are formed in discharged electrode, and then they are decomposed during the full recharge process.