Electronic Supplementary Material (ESI) for Inorganic Chemistry Frontiers.

Supporting Information

N-doped carbon nanotubes with Fe/Ni sites to stabilize lithium metal anodes

Guannan Xiao, Wenlong Cai, Linqin Zhu, Yuting Fang, Huaisheng Ao, Yongchun Zhu* and Yitai Qian

Hefei National Laboratory for Physical Science at Microscale and Department of Chemistry, University of Science and Technology of China, Hefei, Anhui 230026, P. R. China

Experimental

Materials: All chemicals and materials were used without further purification. Sodium hexacyanoferrate(Ⅱ)($Na_4Fe(CN)_6 \cdot 10H_2O$, AR, Sinopharm Chemical Regent Company, China), Nickel(Ⅱ) chloride hexahydrate ($NiCl_2 \cdot 6H_2O$, AR, Sinopharm Chemical Regent Company, China), Cobalt(Ⅱ) chloride hexahydrate ($CoCl_2 \cdot 6H_2O$, AR, Sinopharm Chemical Regent Company, China), Potassium ferricyanide;Potassium hexacyanoferrate(Ⅲ) ($K_3Fe(CN)_6$, AR, Sinopharm Chemical Regent Company, China), Trisodium citrate dihydrate（$C_6H_5Na_3O_7 \cdot 2H_2O$, AR, Sinopharm Chemical Regent Company, China）, Melamine($C_3H_6N_6$, CP, Sinopharm Chemical Regent Company, China), Polyvinylpyrrolidone K30($(C_6H_9NO)_n$, GR, SIGMA), Carbon nanotube(≥95%, Aladdin) and Nitric acid(HNO3, GR, Sinopharm Chemical Regent Company, China).

Synthesis of PB: In a typical synthesis process, polyvinylpyrrolidone(K30) (0.20 g) was dispersed in 100 mL of 0.4 M HCl solution by sonication to form clear solution A. In the meantime, of $Na_4[Fe(CN)_6] \cdot 10H_2O$ （0.480 g）was dissolved into 100 mL water to form clear solution B. Then, solutions A and B were mixed under magnetic stirring and sealed into a Teflon-lined autoclave at 80°C for 24 h. As-formed blue product was centrifuged and purified using deionized water， ethanol, and eventually dried at 60°C overnight.

Synthesis of PB analogue: Typically, nickel chloride (0.715 g) and sodium citrate (1.650 g) were dissolved in 100 mL deionized water to form clear solution A. In the meantime, $K_3[Fe(CN)_6]$ (0.660 g) was dissolved into 100 mL water to form clear solution B. Then, solutions A and B were mixed under magnetic stirring and aged at room temperature for 24 h. Fe-Ni PB analogue was harvested after being centrifuged and purified using deionized water， ethanol, and eventually dried at 60°C overnight. Similarly, the synthesis of Fe-Co PB analogue was conducted with cobalt chloride (0.389 g) and sodium citrate (1.985 g) as solution A.

Synthesis of Ms@N-CNTs(Fe/Ni@N-CNTs, Fe@N-CNTs and Fe/Co@N-CNTs)： PB or PB analogue (0.1 g) was dissolved into 4 mL deionized water. Then, melamine (2.0 g) was added under ultrasonic dispersing to get a homogeneous ink. After being dried in a vacuum chamber, the

precursor was further dispersed by ball-milling. The metal-modified N doped carbon nanotubes were prepared by calcining different amounts of melamine with a certain amount of dispersed precursor at the same time but in different porcelain boat (details see Fig. 1 and Table S1). The porcelain boats were placed in a tube furnace one after another and then heated to the desired temperature (950℃) for 120 min with a heating rate of 10°C min^{-1} in a stream of Ar.

Additional experiment： Acid leaching was carried out in 1.0 M HCl solution which sealed into a Teflon-lined autoclave at 120°C. The product was rinsed with deionized water until the solution became neutral. Then, repeated the above steps until the leaching liquor became colorless and finally dried at 60°C.

Characterization： Scanning electron microscopy (SEM, Zeiss Ultra55), transmission electron microscopy (TEM, Hitachi H7650) was used to characterize the morphology of materials. High resolution transmission electron microscopy (HRTEM), aberration-corrected high-angle annular darkfield scanning transmission electron microscope (HAADF-STEM) and element mapping images were recorded on a JEOL JEM-ARM200F TEM/STEM with a spherical aberration corrector. Inductive coupled plasma emission spectrometer-atomic emission spectrometer (ICP-AES) measurement was performed on Optima 7300 DV. X-ray diffraction (XRD) patterns was carried out on a Philips X' Pert Super diffractometer with Cu Kα radiation (λ=1.54178 Å). The X-ray photoelectron spectroscopy (XPS) was used to study the surface chemistry of the samples on the ESCALAB 250 spectrometer (Perkin-Elmer) (Al Kα radiation, hν = 1486.6 eV). Raman spectroscopy was performed on Lab-RAM HR Evolution.

Electrochemical measurements： The electrodes for anode was prepared by mixing designated product with polyvinylidene difluoride binder (PVDF) at a weight ratio of 9:1 in N-methyl-2-pyrrolidone (NMP) solvent. Then, the slurry was *cast* onto a Cu foil and dried in a vacuum oven overnight.CR2016-type coin cells was assembled in an Ar-filled glove box (H_2O < 0.01 ppm and O_2 < 0.1 ppm) with the Cu foils, commercial CNTs, Fe/Ni@N-CNTs, Fe@N-CNTs, Fe@N-CNTs(acid) and Fe/Co@N-CNTs as the anode and commercial Li foils as counter cathode. 1 M LiTFSI in DME/DOL (1:1) with 1wt % lithium nitrate was used as the electrolyte. These cells were pre-cycled at 0-1 V (vs Li/Li^+) at 0.5 mA cm^{-2} for five cycles to remove contaminations and activate. Then, the LAND-CT2001A instruments was used to test the coulombic efficiency at a constant

current and the cycling stability.

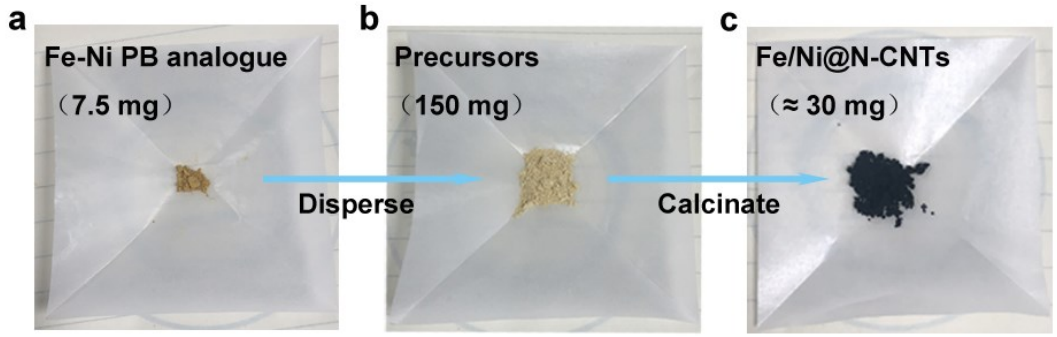

Fig. S1 Photo images of (a) Fe-Ni PB analogue, (b) Precursors and (c) Fe/Ni@N-CNTs. It shows high productivity of Fe/Ni @N-CNTs.

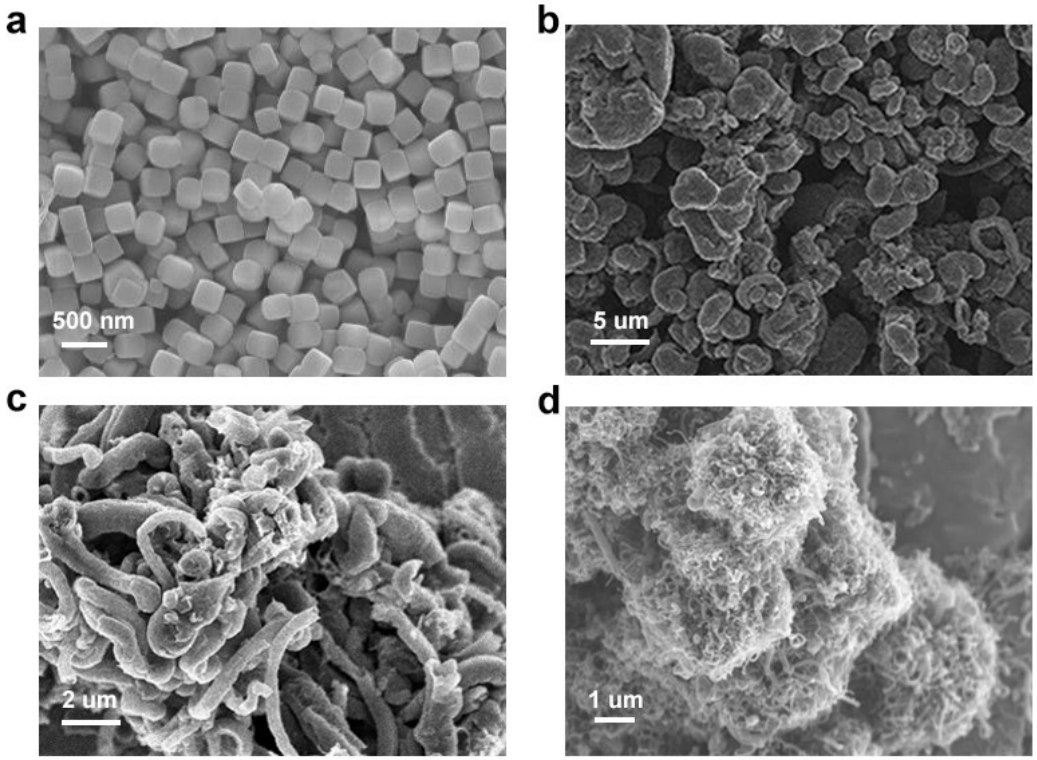

Fig. S2 SEM images (a) Fe-Ni PB analogue nanocubes. Products obtained with increasement of melamine, (b) carbon blocks, (c) carbon fiber and (d) masses of carbon nanotubes with a square shape.

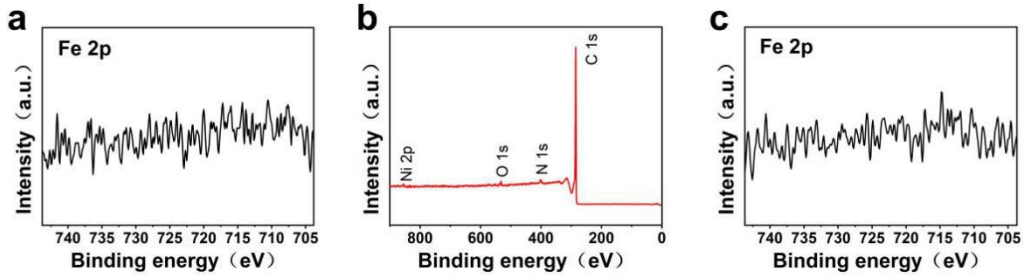

Fig. S3 (a) Fe 2p spectra of Fe/Ni@N-CNTs. (b) XPS element survey and (c) Fe 2p spectra of Fe/Ni@N-CNTs(acid).

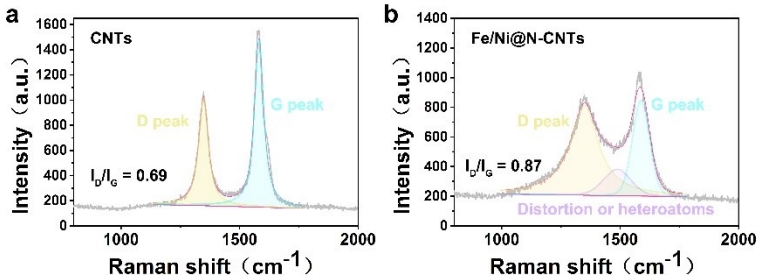

Fig. S4 Raman spectra of (a) commercial CNTs and (b) Fe/Ni@N-CNTs.

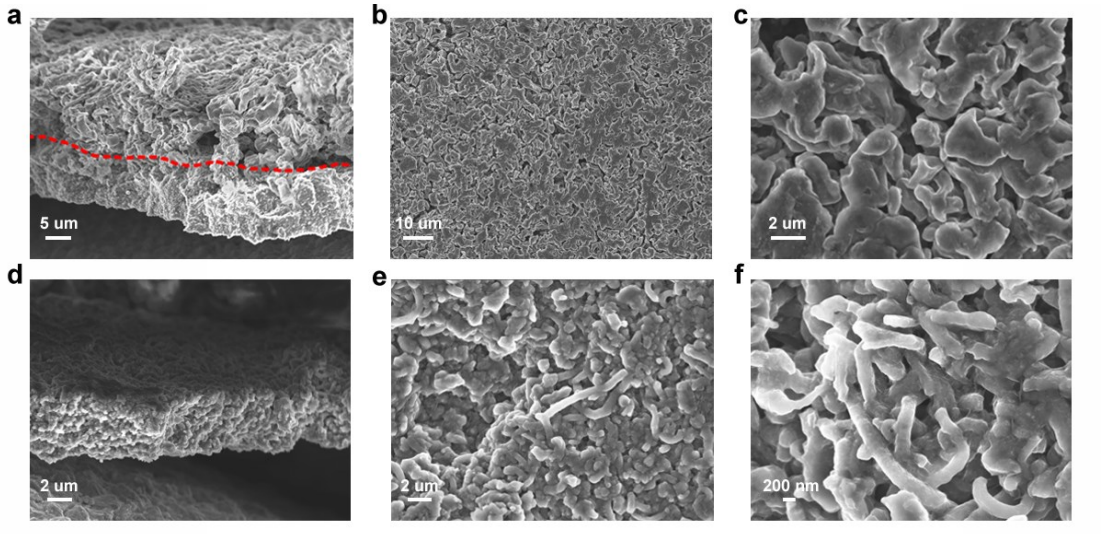

Fig. S5 SEM images of 1 mAh cm^{-2} Li plating on CNTs: (a) cross section, (b) and (c) top view. SEM images of 1 mAh cm^{-2} Li plating on Fe/Ni@N-CNTs: (a) cross section, (b) and (c) top view

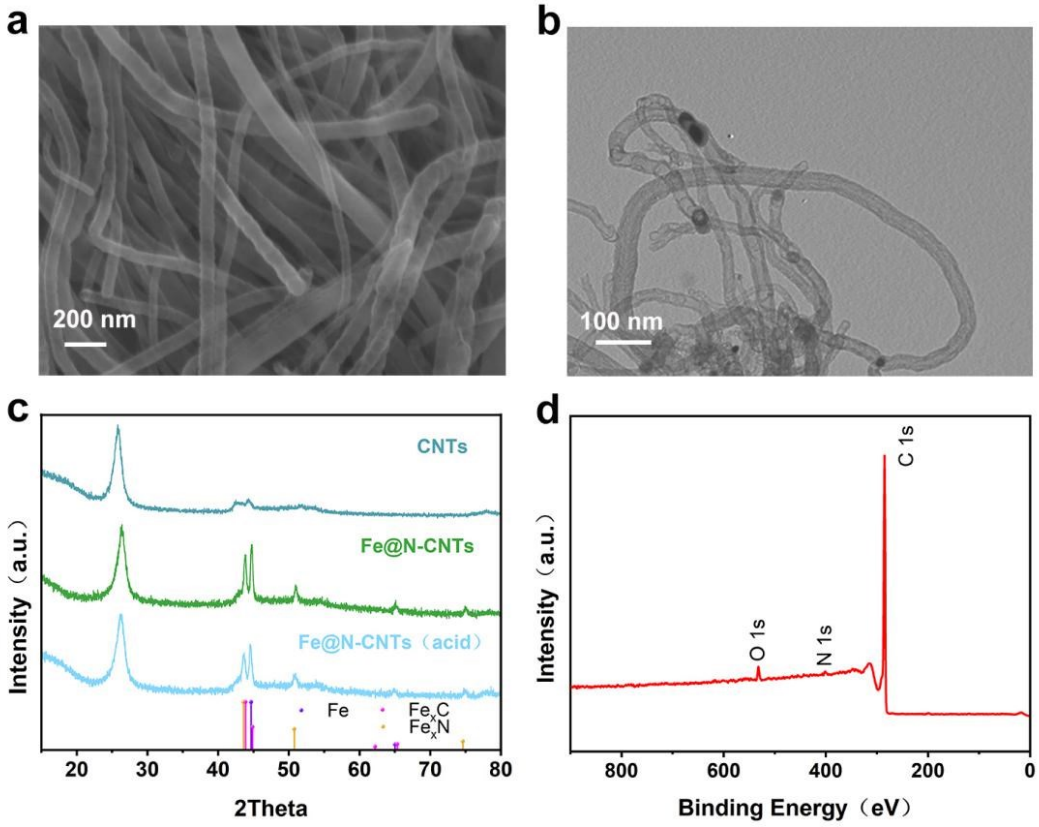

Fig. S6 Characterizations of Fe@N-CNTs. (a) SEM image, (b) TEM image, (c) XRD profile, (d) XPS element survey of Fe@N-CNTs.

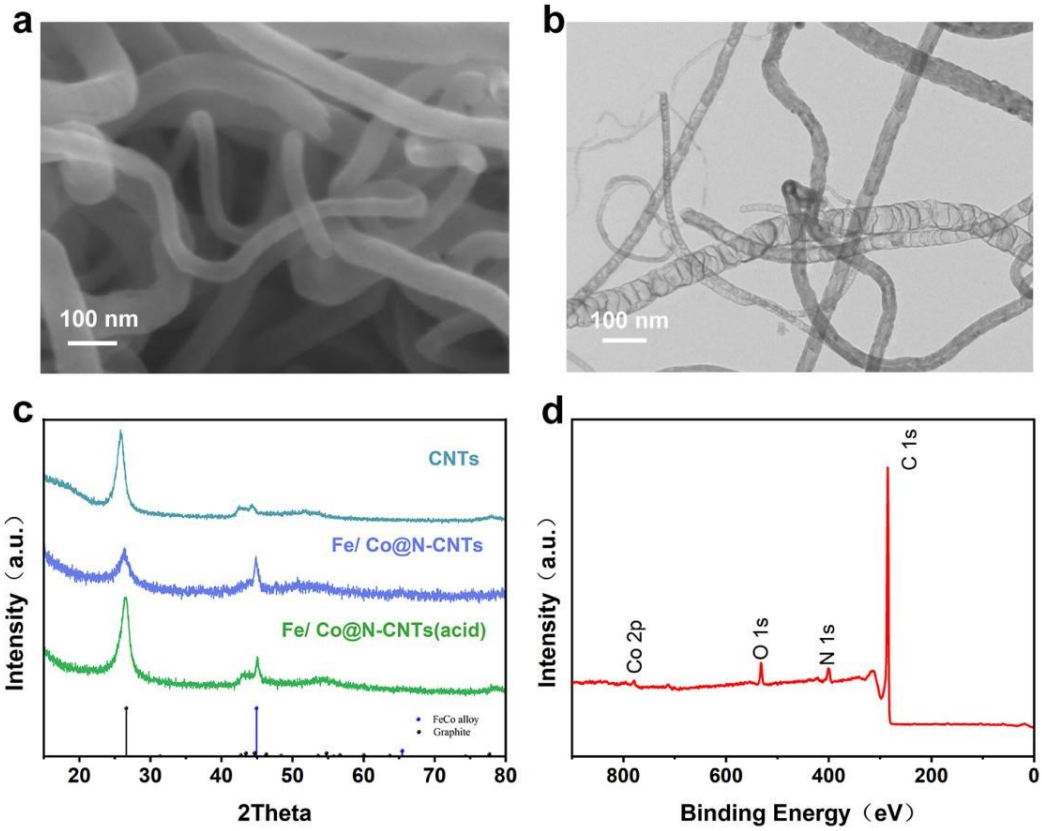

Fig. S7 Characterizations of Fe/Co@N-CNTs. (a) SEM image, (b) TEM image, (c) XRD profile, (d) XPS element survey of Fe/Co@N-CNTs.

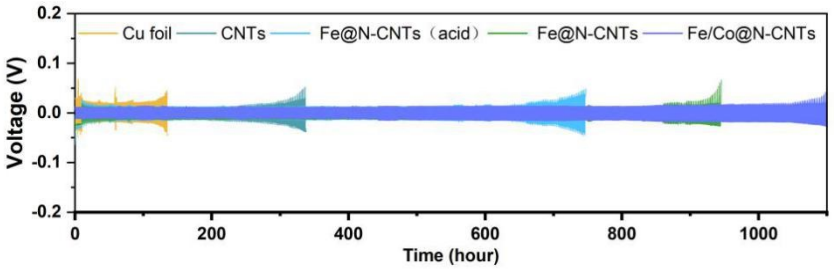

Fig. S8 The voltage-time curves of Li plating/stripping in Cu foil, CNTs, Fe@N-CNTs,Fe@N-CNTs(acid) and Fe/Co@N-CNTs electrode symmetrical cell at a current density of 1.0 mA cm^{-2}.

Table S1 consumption of raw material

Raw material weight / Sample	Dispersed precursor	Melamine（ in different porcelain
Fe@N-CNTs	200 mg	3000 mg
Fe/Ni@N-CNTs	150 mg	2000 mg
Fe/Co@N-CNTs	100 mg	2500 mg

Table S2 The survey of ICP data.

Element wt % / Sample	Fe	Ni	Co
Fe@N-CNTs	26.04	-	-
Fe@N-CNTs(acid)	8.39	-	-
Fe/Ni@N-CNTs	4.63	5.21	-
Fe/Ni@N-CNTs(acid)	3.4	2.5	-
Fe/Co@N-CNTs	3.7	-	3.8
Fe/Co@N-CNTs(acid)	1.15	-	1.15