Work Function Regulation of Nitrogen Doped Carbon Nanotubes Triggered by Metal Nanoparticles for Efficient Electrocatalytic Nitrogen Fixation

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SI. Experimental section

1. Materials

Nickel sulfate hexahydrate [NiSO₄·6H₂O, 99%], cobalt sulfate heptahydrate [CoSO₄·7H₂O, 99%], manganese sulfate monohydrate [MnSO₄·H₂O, 99%], melamine [C₃H₆N₆], dimethylglyoxime [C₄H₈N₂O₂, ACS], copper sulfate pentahydrate [CuSO₄·5H₂O, 99.99%], iron sulfate hydrate [Fe₂(SO₄)₃·xH₂O, 99.95%], chromium(III) sulfate hydrate [Cr₂(SO₄)₃·xH₂O, 99.999%], salicylic acid [C₇H₆O₃, \geq 99.0%], sodium citrate [C₆H₅Na₃O₇, 98%], sodium hypochlorite (NaClO), pdimethylaminobenzaldehyde [C₉H₁₁NO, 99.0%], sodium nitroferricyanide dihydrate [C₃FeN₆Na₂O·2H₂O, 99.0%], hydrazine standard solution, sodium hydroxide [NaOH, 98-100.5%], ammonium chloride [NH₄Cl, 99.5%] and Nafion membrane 211 were purchased from Sigma-Aldrich Chemical Reagent Co., Ltd. Ethanol (99.5%) were

2. Preparation of M@NCNTs

2 mmol metal salt reagent was dissolved 10 mL deionized water to form the homogeneous solution. After that, the above solution was added dropwise to a 25 mL aqueous solution containing 10 mmol of melamine under vigorous stirring and stirred for 1 h. The resulting solution was dried in a vacuum oven at 80 ° C for overnight. The as-prepared precursors were placed into a quartz boat and transferred into tube furnace and then increased to 800 ° C with 5 ° C min⁻¹ and maintained for 2 h under Ar atmosphere (or Ar/H₂ for Cr@NCNTs), denoted as M@NCNTs.

3. Preparation of NCNTs

The prepared Ni@NCNTs was immersed in aqua regia with the mixture of HCl : HNO₃ (3 : 1 vol) and stirred vigorously for 10h. The resulting powder was filtered and washed several times with deionized water to remove impurities. Then the product was named as NCNTs.

4. Characterization

X-ray diffraction (XRD, X'PERT PRO MPD diffractometer, Cu Ka radiation, λ =0.15418 nm, scanned range of 2-90°) was used to identify the crystal structure of all prepared catalysts. Scanning electron microscopy (SEM, JSM-7800F Prime) and transmission electron microscopy (TEM, JEM-2100F) were utilized to investigate the morphology of all samples. The Raman measurements were carried out on a Renishaw Raman Test system (λ =532 nm). Nitrogen adsorption-desorption isotherms were recorded on the nitrogen-adsorption apparatus (AUTOSORB-IQ-XR-C) and specific surface area was calculated based on the Brunauer-Emmett-Teller (BET) equation. X-ray photoelectron spectroscopy (XPS) data were collected by using Krato, AXIS-HS monochromatized Al Kα cathode source of 75-150 W under ultrahigh vacuum. Moreover, the UV-visible adsorption spectra were recorded on a spectrophotometer (UV-2550). H NMR spectra were collected on a superconductingmagnet NMR spectrometer (Bruker AVANCE III HD 700 MHz). Besides, dimethyl sulphoxide was utilized as an internal standard to calibrate the chemical shifts in the spectra. Fourier-transform infrared spectroscopy (FTIR) was performed on a Bruker Vertex 70.

5. Electrochemical measurements

In order to eliminate any ammonia and other contaminants, all components of the electrochemical cell were firstly soaked in 0.05 M H₂SO₄ solution for 24 h and then washed copiously with fresh ultrapure water before NRR tests. Besides, all labware (needles, vials, pipet tips, containers, etc.) utilized in this work were also treated by 0.1 M H₂SO₄ solution and water. All electrochemical characterizations were performed using a CHI 660E workstation coupled with a three-electrode system in a two-compartment cell separated by Nafion membrane. And the Nafion membrane was treated by boiling in ultrapure water for 1 h and heating in H_2O_2 (5%) aqueous solution at 80°C for another 1 h, respectively. Carbon cloth utilized in this work was purchased from CeTech (W1S1009 type) and treated with the mixture of H₂SO₄:H₂O₂ (1:3 vol.) for 12 h to remove surface impurities. To avoid excessive oxidation by oxygen and contamination with ambient ammonia or other nitrogen-containing species in air, electrodes were used either immediately after preparation or kept in vacuum before being used in electrochemical experiments. The prepared catalyst loaded on a piece of pretreated carbon cloth $(1 \times 3 \text{ cm}^2)$ was used as the working electrode, a graphite rod and Ag/AgCl (saturated KCl electrolyte) were employed as counter electrode and reference electrode, respectively. Potential without iRcompensated were converted to RHE scale via the following equation: E (vs. RHE) = E (vs. Ag/AgCl) + 0.269. The catalyst ink for working electrode was prepared by dispersing 3.23 mg of catalyst in a mixed solution of 30 µL Nafion (0.5 wt%), 500 µL ethanol and 470 µL water followed by sonication for 30 minutes. Mass loading of 0.3 mg cm⁻² was used for electrochemical study. All experiments were carried out at room temperature (25°C). To remove the impurities in the inlet gas, such as NH₃ and NO_X, the prepurification of high-purity N₂ (purity 99.999%) and Ar (purity 99.99%) by passing through a saturator filled with 0.05 M NaOH and a saturator filled with 0.05 M H₂SO₄ solution to remove any possible contaminants. Before carrying out all the electrochemical characterizations, the 0.1 M HCl electrolyte solution was purged with N₂ for 30 minutes. Cyclic voltammetry (CV) test was carried out on at a scan rate of 50 mV s⁻¹ ranging from -0.8-0.1 V (vs. RHE). Linear sweep voltammetry (LSV) was also conducted at a scan rate of 5 mV s⁻¹. Chronoamperometric test were then conducted at different potentials and pure N2 was continuously fed into the cathodic cell during the experiments. The recycle test was to perform five consecutive cycles of chronoamperometric runs without changing the electrolyte at -0.1 V. Electrochemical impedance spectroscopy (EIS) was conducted at a frequency range from 100 kHz to 1 Hz with a 10 mV AC signal amplitude at -0.1 V vs. RHE on a PAR-STAT 2273 test system.

6. Calculation of Faradaic efficiency (FE) and NH₃ formation rate

The FE for NRR was defined as the amount of electric charge used for producing NH₃ divided the total charge passed through the electrodes during the electrolysis. Assuming three electrons were needed to produce one NH₃ molecule, the FE was calculated according to the following equation:

$$FE=3 \times 0.318 \times F \times C_{NH4Cl} \times V / (17 \times Q)$$

The rate of formation of NH₃ was calculated using the following equation:

NH₃ yield rate =
$$0.318 \times C_{\text{NH4Cl}} \times \text{V} / (\text{m}_{\text{cat}} \times \text{t})$$

Where F is Faraday constant (96485 C mol⁻¹), C_{NH4C1} is the measured mass concentration of NH₄Cl; V is the volume of the cathodic reaction electrolyte; Q is the quantity of applied charge/electricity; t is the time for which the potential was applied; m_{cat} is the mass of catalyst loaded at the carbon cloth.

7. DFT calculations

DFT calculations were performed using the Vienna ab initio Simulation Package (VASP) [Phys. Rev. B., 1996, 54, 11169], the core electrons is treated by the projector-augmented-wave pseudopotential [Phys. Rev. B., 1994, 50, 17953], while the Perdew-Burke-Ernzerhof [Phys. Rev. Lett., 1996, 77, 3865.] exchange-correlation functional of the generalized gradient approximation is used for describing the electron interactions. A 400 eV plane-wave kinetic energy cutoff was chosen. The Brillouin zone was sampled with $2 \times 2 \times 1$ Monkhorst–Pack grids, respectively, for surface calculations. The atomic positions were fully relaxed until a maximum energy difference and residual force on atoms, respectively, converged to 10⁻⁵ eV and 0.03 Å⁻¹ eV and a 20 Å thick vacuum layer was used to avoid the interaction between top and bottom surfaces. The free energy of the electrochemical steps of the reaction were calculated based on the computational hydrogen electrode (CHE) model. The free energies of species were calculated as: $G = E_{DFT} + E_{ZPE}$ - T ΔS , where E_{DFT} was obtained from DFT energy, E_{ZPE} and T ΔS of adsorbed species were calculated by vibration analysis, whereas the thermodynamic corrections for gas molecules were from standard database.



Figure S1. The Fermi level (E_F), valence band maximum (E_V) and onset level (Eonset) of the UPS spectra of (a) NCNTs; (b) Cr@NCNTs; (c) Cu@NCNTs; (d) Mn@NCNTs; (e) Co@NCNTs; (f) Fe@NCNTs and (g) Ni@NCNTs; (h) energy band diagrams of NCNTs; Cr@NCNTs; Cu@NCNTs; Mn@NCNTs; Co@NCNTs; Fe@NCNTs and Ni@NCNTs determined from the UPS data in panels (a-g).

The work function values can be calculated using the formula Φ =hv-E_{onset}, where hv represents the energy of incident photons (20.2 eV) and E_{onset} represents the onset level connected to the secondary edge.



Figure S2. TEM images and the size distribution of (a) Cr@NCNTs; (b) Cu@NCNTs; (c) Mn@NCNTs; (d) Co@NCNTs; (e) Fe@NCNTs and (f) Ni@NCNTs.



Figure S3. (a) SEM image; (b) XPS survey spectrum; (c) Co 2p and (d) XRD patterns of Co@NCNTs; (e) SEM image; (f) XPS survey spectrum; (g) XPS spectrum of Mn 2p and (h) XRD patterns of Mn@NCNTs; (i) SEM image; (j) XRD patterns and (k) XPS survey spectrum of Cr@NCNTs; (l) SEM image; (m) XRD patterns and (n) XPS survey spectrum of Cu@NCNTs; (o) SEM image; (p) XRD patterns and (q) XPS survey spectrum of Fe@NCNTs.



Figure S4. N_2 adsorption isotherms and the corresponding pore size of (a) Cr@NCNTs, (b) Cu@NCNTs, (c) Mn@NCNTs, (d) Co@NCNTs, (e) Fe@NCNTs; pore size of (f) Ni@NCNTs and (g) NCNTs.



Figure S5. CV curves and ΔJ of catalysts plotted against scan rate at the potential of 0.05 V vs. RHE for (a) Ni@NCNTs; (b) Fe@NCNTs; (c) Co@NCNTs; (d) Mn@NCNTs; (e) Cu@NCNTs; (f) Cr@NCNTs and (g) NCNTs.

The electrochemical active surface area (ECSA) was estimated based on the C_{dl} according to the following equation [*Energy Environ. Sci.*, 2016, 9, 1771; *Nanoscale*, 2018, 10, 5163]:

$ECSA=C_{dl}/0.040$

it is clear that the C_{dl} of Ni@NCNTs, Fe@NCNTs, Co@NCNTs, Mn@NCNTs, Cu@NCNTs, Cr@NCNTs and NCNTs are 40.42 mF cm⁻², 40.45 mF cm⁻², 40.40 mF cm⁻², 40.43 mF cm⁻², 40.42 mF cm⁻², 40.44 mF cm⁻² and 40.44 mF cm⁻², respectively. And the ECSA of Ni@NCNTs, Fe@NCNTs, Co@NCNTs, Mn@NCNTs, Cu@NCNTs, Cr@NCNTs and NCNTs can be calculated as 1010.5 cm², 1011.3 cm², 1010.0 cm², 1010.7 cm², 1010.5 cm², 1011.0 cm² and 1011.0 cm², respectively.



Figure S6. Raman spectra of (a) Cr@NCNTs; (b) Cu@NCNTs; (c) Mn@NCNTs; (d) Co@NCNTs and (e) Fe@NCNTs.



Figure S7. XPS spectrum of N 1s for Cr@NCNTs; Cu@NCNTs; Mn@NCNTs; Co@NCNTs, Fe@NCNTs and NCNTs.



Figure S8. FTIR spectrum of Cr@NCNTs; Cu@NCNTs; Mn@NCNTs; Co@NCNTs, Fe@NCNTs; Ni@NCNTs and NCNTs.



Figure S9. XPS spectrum of C 1s for (a) NCNTs; (b) Cr@NCNTs; (c) Cu@NCNTs; (d) Mn@NCNTs; (e) Co@NCNTs; (f) Fe@NCNTs and (g) Ni@NCNTs.



Figure S10. Contact angle of (a) NCNTs; (b) Cr@NCNTs; (c) Cu@NCNTs; (d) Mn@NCNTs; (e) Co@NCNTs; (f) Fe@NCNTs and (g) Ni@NCNTs.



Figure S11. (a) UV-vis curves and (b) concentration-absorbance of NH₄Cl solution with a series of standard concentration (0-3.5 μ g mL⁻¹) in 0.1 M HCl. The absorbance at 655 nm was measured by UV-vis spectrophotometer. The standard curve showed good linear relation of absorbance with NH₄Cl concentration (y=0.1238x+0.0704, R²=0.9999).



Figure S12. (a) UV-vis curves and (b) concentration-absorbance of N_2H_4 solution with a series of standard concentration. The absorbance at 455 nm was measured by UV-vis spectrophotometer. The standard curve showed good linear relation of absorbance with N_2H_4 concentration (y=1.0852x+0.0339, R²=0.9999).



Figure S13. UV-Vis spectra of electrolytes colored with Watt-Chrisp method before and after 2h electrocatalytic reduction.



Figure S14. NH₃ yield rate and Faradaic efficiency of Ni@NCNTs in different electrolyte at -0.3 V vs. RHE.



Figure S15. NH₃ yield rate of NCNTs; Cr@NCNTs; Cu@NCNTs; Mn@NCNTs; Co@NCNTs; Fe@NCNTs and Ni@NCNTs.



Figure S16. The chronoamperometric curves of Ni@NCNTs in N₂-saturated 0.1 M HCl electrolyte at -0.3 V vs. RHE for 24 h.



Figure S17. The NH₃ yield rate and FE of Ni@NCNTs during recycling tests for 5 times (5h for every time).



Figure S18. (a) Experimental XRD patterns; (b) XPS survey spectrum; (c) XPS spectrum of Ni 2p; (d) SEM image; (e) FTIR spectrum of Ni@NCNTs after NRR testing.



Figure S19. (a) UV-Vis spectra of the electrolyte stained with indophenol indicator for the work electrode at different conditions; (b) and (c) represent the FE and NH₃ yield rate of Ni@NCNTs tested in Ar-or N₂-bubbled electrolyte (0.1 M HCl) with no electro-chemistry (represent by Ar and N₂, respectively) and then Ar- or N₂-bubbled electrolyte under applied potential (represent by Ar+E_{chem} and N₂+E_{chem}, respectively).



Figure S20. ¹H NMR spectra (700 MHz) for ¹⁴NH₄⁺ and ¹⁵NH₄⁺ produced from N_2 electrochemical reduction using N_2 and ¹⁵N₂ as the feeding gas, respectively.



Figure S21. Free energy diagrams for N_2 and N_2H adsorbed on (a) NCNTs; (b) Cr@NCNTs; (c) Cu@NCNTs; (d) Mn@NCNTs; (e) Co@NCNTs; (f) Fe@NCNTs and (g) Ni@NCNTs.



Figure S22. TEM images of Ni@NCNTs treating by (a) SCN⁻ and (b) HF acid.



Figure S23. Schematic depiction of distal and alternating mechanisms for N_2 electroreduction to NH_3 on active sites (*).

The pyridinic-N-C act as the active sites to firstly facilitate N₂ adsorption. Then, the adsorbed N₂ can react with H⁺ and electron following the alternating mechanism and distal mechanism. As for alternating pathway (Figure 5g), the (H⁺ + e⁻) alternately attacks the two N atoms and release the first NH₃ at the sixth step. Next, the (H⁺ + e⁻) reacts with adsorbed *NH₂ intermediates to relase the second NH₃. When the NRR pursues the distal route (Figure 5f), the coupled proton-electron pair consecutively reacts with the distal N atoms and prodeces the first NH₃ at fourth step. After that, the (H⁺ + e⁻) continuous attacks *N intermediates until generating the second NH₃.



Figure S24. Nyquist plots of electrochemical impedance spectra (EIS) for (a) Ni@NCNTs; (b) Fe@NCNTs; (c) Co@NCNTs; (d) Mn@NCNTs; (e) Cu@NCNTs; (f) Cr@NCNTs and (g) NCNTs.

The charge transfer resistance (Rct), regarded as essential factor, was utilized to explore NRR at triple-phase boundary regions. Nyquist plots of the EIS response for all catalysts were showed in Figure S24. Clearly, all electrocatalysts showed the similar semicircle and slope. The results demonstrate that all catalysts have the similar electron transfer impedance and ion diffusion / transfer resistance [*ACS Appl. Mater. Interfaces*, 2018, 10, 19258–19270; *Colloids Surf. A*, 2018, 538, 748–756]

Table S1. Comparison of the electrocatalytic activity of Ni@NCNTs to produce NH_3 through NRR with previously reported NRR electrocatalysts.

Catalysts	Potent ial (V vs. RHE)	Faradaic efficiency (%)	NH3 yield rate	Reference		
Ni@NCN Ts	-0.3 -0.5	7.33	53.88 μg h ⁻¹ mg _{cat} ⁻¹	This work		
NiCo@Ni CoO 2 Core@She ll Nanoparti cles NiCo@Ni CoO 2 Core@She ll Nanoparti cles SA- Mo/NPC	-0.25	6.8±0.3 %	31.5±1.2 μg h ⁻¹ mg _{cat} ⁻¹	Angew Chem Int Ed., 2019, 58, 2321-2325		
B ₄ C	-0.75	15.95	26.57 μg h ⁻¹ mg _{cat} ⁻¹	Nat. Commun., 2018, 9, 3485		
Bi ₄ V ₂ O ₁₁ / CeO ₂	-0.2	10.16	23.21 μg h ⁻¹ mg _{cat} ⁻¹	Angew Chem. Int. Ed. 2018, 57, 6073		
Boron- doped graphene	-0.5	10.8	9.8 µg h ⁻¹ cm ⁻²	Joule 2018, 2, 1610		
PCN	-0.2	11.59	8.09 μg h ⁻¹ mg _{cat} ⁻¹	Angew Chem. Int. Ed. 2018, 57, 10246		

	I			
MoS ₂	-0.5	0.096	8.48×10 ⁻¹¹ mol s ⁻¹ cm ⁻²	Adv. Mater., 2018, 30, 1800191
NPC	-0.9	1.42	27.2 μg h ⁻¹ mg _{cat} ⁻¹	ACS Catal., 2018, 8, 1186
Nb ₂ O ₅ nanofiber	-0.55	9.26	43.6 μg h ⁻¹ mg _{cat} ⁻¹	Nano Energy., 2018, 52, 264
ZIF- derived carbon	-0.3	10.20	23.8 μg h ⁻¹ mg _{cat} ⁻¹	Nano Energy., 2018, 48, 217
a- Au/CeO _x - RGO	-0.2	10.1	8.3 μg h ⁻¹ mg _{cat} ⁻¹	Adv. Mater., 2017, 29, 1700001
Au cluster/Ti O ₂	-0.2	8.11	21.4 μg h ⁻¹ mg _{cat} ⁻¹	Adv. Mater., 2017, 29, 1606550
MoO ₃	-0.3	1.9	29.43 μg h ⁻¹ mg _{cat} ⁻¹	J. Mater. Chem. A., 2018, 6, 12974
MoN	-0.3	1.15	3.01×10 ⁻¹⁰ mol s ⁻¹ cm ⁻²	ACS Sustainable Chem Eng., 10.1039/C8CC03 627F
Pd/C	0.1	8.2	4.5 μg h ⁻¹ mg ⁻¹ cat	Nat. Commun., 2018, 9, 1795
Fe ₂ O ₃ - CNT	-2 V vs. Ag/A gCl	4.9	2.2×10 ⁻³ g h ⁻¹ cm ⁻²	Angew Chem. Int. Ed. 2017, 56, 2699
PdՐո				Adv. Energy

/rGO				Mater. 2018, 8, 1800124
Au film	-0.5	<1	$\begin{array}{c} {\rm 3.84\times 10^{-12}\ mol}\\ {\rm cm^{-2}\ s^{-1}} \end{array}$	J. Am. Chem. Soc. 2018, 140, 1496
Au nanorods	-0.2	4.02	1.648 µg h ⁻¹ cm ⁻²	Adv. Mater. 2017, 29, 1604799

Table S2. Comparison of all catalyst parameters to verify the rationality of work function theory.

		Elec	trocata						
Parameter	Cr	Cu	Mn	Co	Fe	Ni	NC	Location	Conclusion
							NTs		
composition	C,N,O, Cr	C,N,O, Cu	C,N,O, Mn	C,N,O, Co	C,N,O, Fe	C,N,O, Ni	C,N,O	Figure 3; S3	same element except for embedded metal
	Pd-N;	Pd-N;	Pd-N;	Pd-N;	Pd-N;	Pd-N;	Pd-N;		
N-type	G-N;	G-N;	G-N;	G-N;	G-N;	G-N;	G-N;	Figure 3;	same
	Ox-N	Ox-N	Ox-N	Ox-N	Ox-N	Ox-N	Ox-N	57	
N-content	4.76	4.76	4.74	4.74	4.75	4.76	4.75	Table S2	similar
(wt /0)									
content (molar ratios of M to NCNT)	0.03 59	0.03 58	0.03 59	0.03 56	0.03 56	0.03 58		Table S2	similar
funtional	C=C;	C=C;	C=C;	C=C;	C=C;	C=C;	C=C;	Figure	same

group	C-	C-	C-	C-	C-	C-	C-	S8; S9	
	N;C=	N;C=	N;C=	N;C=	N;C=	N;C=	N;C=		
	N;C=	N;C=	N;C=	N;C=	N;C=	N;C=	N;C=		
	O; C-	O; C-	O; C-	O; C-	O; C-	O; C-	O; C-		
	C=O	C=O	C=O	C=O	C=O	C=O	C=O		
morphology	homi	no liko N	ICNTa or	Figure 2,	60 m 0				
morphology	Damu	oo-like r	NCIN I S EI	S2, S3	same				
gurfago argo								Eiguro 2	similar surface
$(m^2 \sigma^{-1})$	72.31	72.44	72.49	72.47	72.23	72.38	35.89	rigule 5,	area expect for
(m²g²)								54	NCNT
ECSA	1010	1011	1010	1010	1010.	1011	1011.	Figure	
(cm ²)	.5	.3	.0	.7	5	.0	0	S5	similar
	1.96	1.98	1.92	1.98	1.99	1.95	1.99	Figure	
pore size	nm	nm	nm	nm	nm	nm	nm	S4	similar
L-S-G								Figure	
contact	90.7°	91.2°	90.9°	91.2°	91.1°	91.0°	91.0°	S10	similar
EIS	sir	similar electron transfer and ion diffusion resistance						S24	similar
surface									
defects	1.29	1.29	1.30	1.29	1.31	1.29	1.25	Figure	similar
(I_D/I_G)								S6	
crystallinity	20.1		25.1		21 -	20.0			
(average	30.1	33.6	35.1	33.4	31.7	30.8		Figure	similar
size)	nm	nm	nm	nm	nm	nm		S2	
work	5.72	5.64	5.53	5.35	5.30	5.20	5.73	Figure	completely
function	eV	eV	eV	eV	eV	eV	eV	S 1	different

Notably, although the specific surface area (SSA) of M@NCNTs is about twice that of NCNTs, not all the surface are catalytically active [*Adv Funct Mater.*, DOI:

10.1002/adfm.202004208; *J Colloid Interf Sci.*, 2019, 533, 503-512]. Therefore, electrochemical active surface area (ECSA) can better correlate the electrocatalytic activity than SSA. In addition, similar ECSA values indicate that all catalysts are exposed to the same electrochemically active site.