## **Supporting Information**

## Iron Clusters Boosted Performance in Electrocatalytic Carbon Dioxide Conversion

Dongchuang Wu,<sup>ab</sup> Xinyue Wang,<sup>c</sup> Linghao Shi,<sup>b</sup> Kaiyue Jiang,<sup>b</sup> Mengjia Wang,<sup>bd</sup> Chenbao Lu,<sup>b</sup> Zhenying Chen,<sup>be</sup> Pan Liu,<sup>d</sup> Jichao Zhang,<sup>f</sup> Diana Tranca,<sup>b</sup> Yang Hou,<sup>\*c</sup> Yu Chen,<sup>\*a</sup> Xiaodong Zhuang<sup>\*b</sup>

<sup>a.</sup> Key Laboratory for Advanced Materials and Joint International Research Laboratory of Precision Chemistry and Molecular Engineering, Feringa Nobel Prize Scientist Joint Research Center, School of Chemistry and Molecular Engineering, East China University of Science and Technology, Shanghai 200237, China. E-mail: chentangyu@yahoo.com

<sup>b.</sup> The meso-Entropy Matter Lab, State Key Laboratory of Metal Matrix Composites, Shanghai Key Laboratory of Electrical Insulation and Thermal Aging, School of Chemistry and Chemical Engineering, Frontiers Science Center for Transformative Molecules, Shanghai Jiao Tong University, Shanghai 200240, China. E-mail: zhuang@sjtu.edu.cn

<sup>c.</sup> Key Laboratory of Biomass Chemical Engineering of Ministry of Education, College of Chemical and Biological Engineering, Zhejiang University, Hangzhou, 310027, China. E-mail: yhou@zju.edu.cn

<sup>d.</sup> School of Materials Science and Engineering, Shanghai Jiao Tong University, 200240 Shanghai, China

<sup>e.</sup> College of Chemistry and Molecular Engineering, Zhengzhou University, 100 Science Avenue, Zhengzhou 450001, China

<sup>f.</sup> Shanghai Synchrotron Radiation Facility, Zhangjiang Laboratory, Shanghai Advanced Research Institute, Chinese Academy of Sciences, No. 239, Zhangheng Road, Shanghai 201204, China.

### **Supplementary Methods**

### Preparation of working electrodes

For preparation of working electrodes, typically, 5 mg of catalyst was blended with 500 $\mu$ L of Nafion solution (0.5 wt. %) and sonicated for 2 h to ensure uniform mixing catalyst ink. Then 100 $\mu$ L of catalyst ink was pipetted onto the carbon paper surface (1 cm<sup>-2</sup>), giving a catalyst loading of 1 mg cm<sup>-2</sup>.

## **Catalytic product analysis**

The gaseous products were monitored by an online gas chromatography (GC, Shimadzu GC-2014C), equipped with a thermal conductivity detector (TCD) detector for H<sub>2</sub> and a flame ionization detector (FID) detector for CO quantification. A GC run repeats every 18 minutes. The GC was calibrated with standard gas mixtures (Air Liquide, CO, H<sub>2</sub>, CH<sub>4</sub>, C<sub>2</sub>H<sub>4</sub> C<sub>2</sub>H<sub>6</sub>, C<sub>2</sub>H<sub>2</sub> in N<sub>2</sub>) before the product measurements. The liquid products in the KHCO3 solution was analyzed and quantified through a Bruker

500 MHZ (AVANCE III) NMR spectroscope with water suppression. After electrolysis,

KHCO3 electrolyte (0.5 mL) was collected and mixed with  $D_2O$  (0.1 mL) in an NMR tube and dimethyl sulfoxide (DMSO, 0.05  $\mu$ L) as an internal standard.

### Faradic efficiency (FE) calculation

Faradaic Efficiency (FE) of CO and  $H_2$  were calculated by using the concentration detected by GC based on the equation:

$$FE = \frac{Q_i}{Q_{total}} = \frac{2 \times P_o \times F \times v \times v_i}{R \times T \times I}$$

Where  $Q_i$  is the quantity of electric charge needed to produce product i.  $Q_{total}$  is the quantity of electric charge needed to produce all products. 2 is the number of electrons transferred per mole  $CO_2$  to CO or per mole  $H_2O$  to  $H_2$ .  $P_o$  is atmospheric pressure ( $1.01 \times 10^5$  Pa), F is the faradaic constant (96485 C mol<sup>-1</sup>). v is the gas flow rate measured by flow meter.  $v_i$  is the volume concentration of gas product in the exhaust gas from the cell determined by online GC. T is the reaction temperature (298.15 K), R is the idea gas constant (8.314 J mol<sup>-1</sup> K<sup>-1</sup>), and I is the current at each potential.

### Evaluation of turnover frequency (TOF) (h<sup>-1</sup>)

The TOF (h<sup>-1</sup>) of product CO was evaluated as follows:

$$TOF = \frac{FE_{co} \times j_{total} \times A \times M_{Fe} \times t}{n \times F \times \omega_{Fe} \times m}$$

Where FE is the faradaic efficiency of CO, J is the total current density, A=1 cm<sup>2</sup> is the electrode geometric area,  $\omega_{Fe}$  is the mass fraction of iron on the catalyst (analyzed by ICP-AES), m is the mass of catalyst coated on working electrode, and M<sub>Fe</sub> is the atomic mass of Fe (55.84 g mol<sup>-1</sup>). F is the faradaic constant (96485.33289 C mol<sup>-1</sup>). t is the reaction time (1 h/3600 s); n is the number of electron transferred for product formation, which is 2 for CO.

**DFT calculations**. DFT calculations have been performed using the Vienna *ab* initio simulation package (VASP)<sup>1</sup> with the projector-augmented wave (PAW) method<sup>2</sup>. All calculations were based on the same generalized gradient approximation (GGA) method with Perdew-Burke-Ernzerhof (PBE)<sup>3</sup> functional for the exchange-correlation term. The plane wave cutoff was set to 400 eV.

Different surface models are proposed to assess the  $CO_2$  reduction reaction based on Fe/N-doped graphene, which contains different numbers of Fe atoms in the unit cell representing as single-Fe-atom site, dual-Fe-atom site and triple-Fe-atom site. Periodic boundary conditions were employed along x and y directions with a vacuum layer between graphene layers. We fully optimized isolated and adsorbed Fe sites and found the atomic interfaces have a different adsorption for the intermediates.

The free energy of each species is calculated by:  $G = E^{DFT} + ZPE - T\Delta S$ , where  $E^{DFT}$  is the DFT-optimized total energy, ZPE is the zero-point vibrational energy, T is the temperature, and  $\Delta S$  is the entropy).<sup>4</sup> The zero-point energies and entropies of the reaction species were calculated from the vibrational frequencies. During these frequency calculations, all atoms of substrate were rigidly constrained so that no additional degrees of freedom, due to the catalyst, are introduced in to the reacting system.



**Figure S1**. a) SEM images of Fe-NC; b) SEM images of Fe-NC-HS-40; c) SEM images of Fe-NC-TM-50. d) SEM images of Fe-NC-SBA-15. The Fe-NC, Fe-NC-HS-40, Fe-NC-TM-50 and Fe-NC-SBA-15 present bulk morphologies. Fe-NC-SBA-15 show the the typical rod-like morphology.



**Figure S2**. (a, b and c) TEM images of Fe-NC; (d, e and f) TEM images of Fe-NC-HS-40; (g, h and i) TEM images of Fe-NC-TM-50; (j, k and l) TEM images of Fe-NC-SBA -15. Due to no template involved in the preparation of Fe-NC, TEM images of Fe-NC show distinct tubular structures and graphitized fringe, which attributed to the catalytic results by the Fe elements at high temperatures. The TEM images of Fe-NC-HS-40, Fe-NC-TM-50 and Fe-NC-SBA-15 show the clear light and dark contrast structure, suggesting the porosity after the removal of the templates. Furthermore, no clear Fe nanoparticles can be observed in the TEM images.



Figure S3. The SAED pattern of Fe-NC-SBA-15.



Figure S4. XRD pattern of Fe-NC-SBA-15 before etching.



**Figure S5**. The N 1s spectra of Fe-NC (a), Fe-NC-HS-40 (b), Fe-NC-TM-50 (c) and Fe-NC-SBA-15 (d). The spectra can be divided into four peaks located at 398.1 eV, 399.9 eV, 401 eV and 404.3 eV, which are ascribed to pyridinic N, pyrrolic N, and graphitic N, N- $O_x$  species, respectively.



**Figure S6**. The C 1s spectra of Fe-NC (a), Fe-NC-HS-40 (b), Fe-NC-TM-50 (c) and Fe-NC-SBA-15 (d). The spectra can be divided into four peaks located at 284.6 eV, 285.7eV, and 289eV, which are ascribed to C=C, C–N, and O–C=O functional groups, respectively.  $^{5}$ 



Figure S7. N contents of as-prepared samples based on XPS analysis



Figure S8. XPS spectra of as-prepared samples.



**Figure S9**. Nitrogen sorption isotherms for (a) Fe-NC, (b) Fe-NC-HS-40, (c) Fe-NC-TM-50 and (d) Fe-NC-SBA-15. Insets: pore size distributions calculated based on NLDFT method.



**Figure S10**. a) Surface energies and mean contact angle of water calculated from dynamic contact angle measurements. b) The representative images of water drops on the surface of the catalyst layers used for the determination of contact angles for Fe-NC and Fe-NC-SBA-15.



**Figure S11**. Raman spectra of as-prepared Fe-NC, Fe-NC-HS-40, Fe-NC-TM-50 and Fe-NC-SBA-15



**Figure S12**. TGA curves of as-prepared Fe-NC, Fe-NC-HS-40, Fe-NC-TM-50 and Fe-NC-SBA-15 from 50 to 900 under  $N_2$  gas flow with a temperature ramp of 5 min<sup>-1</sup>. They exhibit good thermal stability. TGA show the similar decomposition trend.



**Figure S13**. Fourier transformation EXAFS spectra of Fe-NC-SBA-15, FeO and Fe foil at k space.



**Figure S14**. a) Fe K-edge XANES spectra of Fe-NC-TM-50, FeO,  $Fe_2O_3$  and Fe foil. b) Fourier transformation EXAFS spectra of Fe-NC-TM-50, FeO and Fe foil at R space. Fourier transformation EXAFS spectra of Fe-NC-TM-50, FeO and Fe foil at k space.



**Figure S15**. a) Linear sweep voltammetry curves for Fe-NC-SBA-15 obtained in Ar- and  $CO_2$ -saturated 0.5M KHCO<sub>3</sub> solution. b) LSV comparison in  $CO_2$ -saturated KHCO<sub>3</sub> solution with different concentration.



**Figure S16**. <sup>1</sup>H nuclear magnetic resonance (NMR) spectroscopy for liquid products. No liquid products were detected.



**Figure S17**. Cyclic voltammetry measurements were then performed at scan rates varying. a) CV curves for Fe-NC. b) CV curves for Fe-NC-HS-40. c) CV curves for Fe-NC-TM-50. d) CV curves for Fe-NC-SBA-15; Capacitive current at -0.13V as a function of scan rate for Fe-NC, Fe-NC-HS-40, Fe-NC-TM-50 and Fe-NC-SBA-15. e) Linear fittings of the differences of current densities between anodic and cathodic scans with the scan rates to determine the double layer capacitance (C) and electrochemical surface area (ECSA).



**Figure S18**. The relationship between faradaic efficiency and BET specific surface area of as-synthesized catalysts.



**Figure S19**. a) Chronoamperometry curves of Fe-NC-SBA-15 in CO<sub>2</sub>-saturated 0.5M KHCO<sub>3</sub> solution. b) Chronoamperometry curves of Fe-NC-SBA-15 in CO<sub>2</sub>-saturated 0.1 KHCO<sub>3</sub> solution.



**Figure S20**. a) partial current density values ( $j_{CO}$ ). b) Nyquist plots of the samples. The inset of a is the enlarged EIS curves. Generally, materials that exhibit a larger semicircle will suffer from the slow transfer of charges. The Nyquist plots in Figure S20b demonstrate that Fe-NC-SBA-15, Fe-NC-TM-50 and Fe-NC-HS-40 share similar charge-transfer process during the CO<sub>2</sub> reduction process, which is faster than Fe-NC.



**Figure S21**. a) Faradaic efficiency of Fe-NC-SBA-15-T (T refer to the temperature of pyrolysis). b). Raman spectra of Fe-NC-SBA-15-T



Figure S22. The relationship between faradaic efficiency and the intensity ratio between the D and G peaks  $(I_D/I_G)$  of as-synthesized catalysts.



**Figure S23.** a) Linear sweep voltammetry curves for Fe-NC-SBA-15 before applying voltage and after applying voltage. b) Fe 2p XPS results before applying voltage and after applying voltage.



Figure S24. The DFT-calculated representative models from Top-view and side-view



Figure S25. The calculated free energy diagrams for HER.

**Table S1**. Contents of Fe element quantified by inductively coupled plasma opticalemission spectroscopy

Sample	Content of Fe	
	element (wt.%)	
Fe-NC	0.85%	
Fe-NC-HS-40	0.49%	
Fe-NC-TM-50	0.46%	
Fe-NC-SBA-15	0.32%	

Table S2. N<sub>2</sub> physisorption results of as-prepared materials.

Sample	S <sub>BET</sub>	S <sub>micro</sub>	V <sub>Tot</sub>	V <sub>micro</sub>	D <sub>av</sub>
	(m²/g) <sup>a)</sup>	(m²/g) <sup>b)</sup>	(cm <sup>3</sup> g <sup>-1</sup> ) <sup>c)</sup>	(cm <sup>3</sup> g <sup>-1</sup> ) <sup>d)</sup>	(nm) <sup>e)</sup>
Fe-NC	116	0	0.24	0	8.4
Fe-NC-HS-40	436	85	1.16	0.04	10.5
Fe-NC-TM-50	194	54	0.74	0.03	15
Fe-NC-SBA-15	148	42	0.26	0.02	7

a) Specific surface area measured by BET model; b) The microporous surface area analyzed by t-plot method; c) The total pore volume measured at  $P/P_0 = 0.99$ ; d) The microporous volume analyzed by t-plot method; e) Average pore size.

**Table S3.** The free energy for the formation of different intermediates on different sites.

	*COOH(eV)	*CO(eV)	*H(eV)
FeN <sub>4</sub> site	0.74	-0.35	0.32
Fe <sub>2</sub> N <sub>6</sub> site	0.15	-0.85	-0.29
Fe <sub>3</sub> N <sub>6</sub> site	-0.87	-1.48	-1.01

Catalysts	Test condition CO <sub>2</sub> RR			Reference		
	electrolyte	Onset	Overpotential	FE <sub>co</sub>	Stability	
		potential	(V, vs RHE)	(%)		
		(V, vs RHE)				
Fe-NC-SBA-15	0.5M KHCO <sub>3</sub>	-0.32	0.38	98.2	> 50h	This work
	0.1M KHCO <sub>3</sub>	-0.44	0.49	98.6	> 50h	This work
Fe <sup>3+</sup> -N-C	0.5M KHCO <sub>3</sub>	-0.19	0.34	>90	12h	6
H-M-G	0.1M KHCO <sub>3</sub>	-0.26	0.35	97	24h	7
FePGF	0.1M KCl	-0.44	0.48	93	24	8
Fe <sub>0.5</sub> d	0.5M NaHCO <sub>3</sub>	-0.3	0.39	80	6h	9
	0.5M NaHCO <sub>3</sub>	/	0.49	91	/	-
Fe/NG	0.1 M KHCO <sub>3</sub>	-0.3	0.49	80	10	10
C-AFC©	0.5M KHCO <sub>3</sub>	/	0.42	89.6%	/	11
21F-8	1M KHCO <sub>3</sub>	-0.33	0.32	93%	/	-
C-FePc(CN) <sub>8</sub> / ZIF-8	0.5M KHCO <sub>3</sub>	-0.31	0.35	94%	10	12
FeNPCN	0.1 M KHCO <sub>3</sub>	-0.2	0.39	94%	12	13
Fe-PB	0.5M KHCO <sub>3</sub>	-0.48	0.51	100±2 %	24	14
Ni/Fe-N-C	0.5 M KHCO <sub>3</sub>	-0.4	0.59	98%	30	15
NiPor-CTF	0.5 M KHCO <sub>3</sub>	-0.44	0.79	97%	20	16
Ni-N <sub>3</sub> -V	0.5 M KHCO <sub>3</sub>	/	0.69	94%	14	17
NC-CNTs(Ni)	0.1M KHCO <sub>3</sub>	-0.6	0.69	>90%	10	18
A-Ni-NSG	0.5 M KHCO <sub>3</sub>	-0.18	0.39	97%	100	19
NapCo@SNG	0.1M KHCO <sub>3</sub>	-0.4	0.69	97%	2.5	20
Co-N <sub>2</sub>	0.5 M KHCO <sub>3</sub>	-0.22	0.57	95%	60	21
Ni–NG	0.5 M KHCO <sub>3</sub>	-0.31	0.55	95%	20	22
Ni–N <sub>4</sub> –C	0.5 M KHCO <sub>3</sub>	/	0.7	99%	/	23
ZnN <sub>x</sub> /C	0.5 M KHCO <sub>3</sub>	-0.13	0.32	95%	75	24
F-CPC	0.5 M KHCO <sub>3</sub>	-0.6	0.9	93.1%	12	25

**Table S4**. Comparison of  $CO_2RR$  performance with reported electrocatalysts.

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