Electronic Supplementary Information

Synergistic catalysis between atomically dispersed Fe and a pyrrolic-N-C framework for CO₂ electroreduction

Chaochen Xu,^a Anthony Vasileff,^a Dan Wang,^b Bo Jin,^a Yao Zheng^{*a} and Shi-Zhang Qiao^{*a}

^a Centre for Materials in Energy and Catalysis, School of Chemical Engineering and Advanced

Materials, The University of Adelaide, Adelaide, SA 5005, Australia

^b Institute of Process Engineering, Chinese Academy of Sciences, Beijing, 100190, China.

* Email: s.qiao@adelaide.edu.au; yao.zheng01@adelaide.edu.au

Part I: Experimental Section

Chemicals. Dicyandiamide, glucose, and iron (III) chloride hexahydrate were purchased from Sigma-Aldrich and used without further purification. N₂ (99.999%) and CO₂ (99.995%) were supplied from BOC Gas.

Synthesis. Fe-SA samples were prepared using a modified method.¹ 2.0 g of dicyandiamide and 0.1 g of glucose were dissolved in 100 mL deionized water, followed by the dropwise addition of 1.0 mL of fresh 0.01 M iron (III) chloride solution. The solution was then mixed well and dried in a rotary vacuum evaporator. The resultant precursor was placed in a tube furnace and annealed at 700, 800, and 900°C for 2 h under N₂ atmosphere, respectively (heating rate of 5°C·min⁻¹). Once cooled to room temperature, the received powder was washed with deionized water several times and dried at 60°C overnight. For comparison, Fe-NP samples were prepared using the same method but 10.0 mL of the iron salt solution was added instead; NS samples were prepared using the same method but without the addition of the iron salt solution.

Material characterization. SEM images were taken using an FEI Quanta 450. TEM images and SAED patterns were acquired with a Philips CM200. HAADF-STEM images and EDS spectra were acquired with an FEI Titan Themis 80-200. XRD patterns were recorded on a Rigaku X-Ray Diffractometer (Cu K α). XPS measurements were performed on a Kratos AXIS Ultra (mono Al K α). Raman spectra were collected using a HORIBA Scientific Raman Spectroscopy (Laser excitation at 633 nm).

CO₂ **electroreduction measurements.** Experiments were performed on an electrochemical workstation (CH Instruments 760E) using a three-electrode H-cell separated by proton exchange membrane (Nafion 117). A glassy carbon electrode (\emptyset 5 mm), Ag/AgCl (3.5 M KCl), and RuO₂ coated titanium mesh served as the working, reference, and counter electrodes, respectively. To prepare the catalyst ink, 4 mg of catalyst was ultrasonically dispersed in 2 mL of 0.05 wt.% Nafion aqueous solution. Then, 40 µL of the ink was dropped onto the surface of the glassy carbon and dried in air (catalyst loading of 0.4 mg·cm⁻²). CO₂ electroreduction was carried out in CO₂-saturated 0.1 M KHCO₃ aqueous electrolyte. All *iR*-corrected potentials were converted to RHE at 25°C: *E* (*vs. RHE*) = *E* (*vs. Ag/AgCl*) + 0.059 × pH + 0.205, where pH is measured using a pH meter. For analysis of electrochemical kinetics, Tafel slopes were derived from the Tafel equation: $\eta = b \lg (j_{co} / j_0)$, where η [V] is the overpotential between the applied potential to the standard CO₂/CO reduction potential

(-0.11 V vs. RHE); b is the Tafel slope [mV·dec⁻¹]; j_{co} is the CO partial current density and j_0 is the CO exchange current density [mA·cm⁻²].

Reduction products were quantified using the same procedures as previous work.² Briefly, 100 μ L of headspace gas in the cathode compartment was manually injected into a GC (Agilent 7890B configured with TCD and Methanizer/FID) for gas product quantification; liquid products were determined using NMR (Agilent 500/600 MHz ¹H NMR) and quantified with internal standards (DMSO and phenol in D₂O).³ No liquid products were detected in this work. Faradaic efficiency of a certain product was calculated: $FE_i = n_i eF / Q_t \times 100\%$, where n_i is the total amount of a certain product i [mol]; e is the number of electrons transferred for product i formation, which is 2 for both CO and hydrogen; F is the Faradaic constant [C·mol⁻¹]; and Q_t is the total amount of passed charge [C].

Part II: Supplementary Results



Figure S1. Morphology characterization. (a) SEM image of Fe-SA-900 with some wrinkles. (b) HRTEM image of Fe-SA-900. (c) Raman spectra with D-to-G band intensity ratios for Fe-SA-900, Fe-NP-900, and NS-900. D band (~1350 cm⁻¹) and G band (~1580 cm⁻¹) are typical peaks assigned to carbon nanosheets.⁴ No sharp 2D peak (~2700 cm⁻¹) due to the stacking of carbon nanosheets was observed. (d) TEM image of Fe-SA-900 with a marked interplanar distance of 0.33 nm and inset of SAED pattern, which corresponds to the inter lattice spacing of the (002) plane in a hexagonal carbon structure.



Figure S2. Corresponding EDS spectra of (a) Fe-SA-900, (b) Fe-NP-900, and (c) NS-900.



Figure S3. High-resolution XPS Fe 2p spectra of Fe-NP-900.



Figure S4. High-resolution XPS N 1s spectra for (a) Fe-NP-900 and (b) NS-900. The deconvoluted peaks are attributed to graphitic, pyrrolic, pyridinic, and oxidized N species.⁵



Figure S5. (a) Nyquist diagrams and (b) Polarization plots for CO generation on NS-900, Fe-NP-900, and Fe-SA-900.



Figure S6. Amperometric *i*-*t* curves of (a) Fe-SA-900 and (b) Fe-NP-900 during CO₂ reduction.



Figure S7. Measured FEs of CO₂ reduction on (a) Fe-NP-900 and (b) NS-900.



Figure S8. High-resolution XPS N1s spectra for (a) Fe-SA-700, (b) Fe-SA-800, (c) Fe-NP-700, and (d) Fe-NP-800.



Figure S9. Raman spectra with D-to-G band intensity ratios for Fe-SA-900, Fe-SA-800, and Fe-SA-700.



Figure S10. Deconvoluted high-resolution XPS N 1s spectra for (a) Fe-SA-700, (b) Fe-SA-800, (c) Fe-NP-700, and (d) Fe-NP-800.



Figure S11. Fe 2p_{3/2} binding energy peak position for (a) Fe-SA and (b) Fe-NP group catalysts.

	Annealing T [°C]	Fe	С	0	Ν	Ng	N_{pyr}	N_{pyd}	N _{pyr} /N _{pyd}
Fe-SA Group	900	0.27	86.64	2.83	10.26	3.37	1.69	1.76	0.96
	800	0.28	80.11	2.93	16.67	5.26	2.37	5.27	0.45
	700	0.28	65.39	2.96	31.38	11.44	1.95	15.48	0.13
Fe-NP Group	900	0.90	88.42	5.08	5.60	1.37	1.03	1.38	0.74
	800	1.84	77.87	9.87	10.42	1.86	1.41	5.31	0.27
	700	1.88	75.24	4.98	17.91	4.16	2.58	9.82	0.26
NS Group	900	-	88.83	3.23	7.94	2.84	0.92	1.15	0.80

Table S1. XPS quantification of elemental composition and N species in at.%.

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