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MOFs-Derived Nitrogen-Doped Nanoporous Carbon for Electroreduction of CO₂ to CO: the Calcining Temperature Effect and the Mechanism

Yonglong Zheng,^{‡a,b} Ping Cheng,^{‡a} Jiansheng Xu, ^c Jianyu Han, ^a Dawei Wang, ^a Changlong Hao, Hamideh Rezvani Alanagh, ^a Chang Long, ^a Xinghua Shi^{*a,b} and Zhiyong Tang, ^{a,b}

^aLaboratory of Theoretical and Computational Nanoscience, CAS Key Laboratory of Nanosystem

and Hierarchical Fabrication, CAS Center for Excellence in Nanoscience, National Center for

Nanoscience and Technology, Beijing 100190, China.

^bUniversity of Chinese Academy of Sciences, Beijing 100049, China.

^cInstitute of Electrical Engineering, Chinese Academy of Sciences, Beijing 100190, China.

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1. Materials and Methods

Chemicals:

Zinc nitrate hexahydrate (Zn(NO₃)₂•6H₂O,99%) was purchased from Tianjin Fuchen Chemical Reagent Factory). 2-Methylimidazole (97%), Nafion solution (5 wt%), Potassium bicarbonate (KHCO₃, 99%) were purchased from Alfa Aesar. Methanol (MeOH) was purchased from Beijing Chemical Works (Beijing, China). All the reagents were used without further purification.

Preparation of ZIF-8:

In a typical procedure, Zn(NO3)₂·6H₂O (1190 mg) was dissolved in 30 mL methanol, which was subsequently added into 15 mL methanol containing 1314 mg 2methylimidazole. Then the mixed solution was stored at room temperature with vigorous stir for 1 h. After that the mixed solution was transferred into a 100 ml teflonlined stainless-steel autoclave and heated at 120 °C for 4 h. The obtained product was washed with methanol for three times and dried at 60 °C under vacuum for overnight.

Preparation of NC:

The dried ZIF-8 was subjected to a thermal activation at a wide temperature range

from 800 to 1100 °C under Ar flow for 3 h in a tube furnace to obtain the NC800, NC900, NC1000 and NC1100.

Characterization: SEM, TEM, XRD, Raman, XPS

The morphology of the materials was characterized by scanning electron microscope (SEM, Hitachi S4800). TEM images were performed on Tecnai G2 F20 S-TWIN with an acceleration voltage of 200 kV. The crystallinity was measured by powder X-ray diffraction (XRD) collected by D/MAX-TTRIII (CBO) (Rigaku Corporation) with Cu K α radiation (λ =1.54 Å) at a scanning rate of 5°min⁻¹. The microstructure was studied by Raman spectra using Renishaw in Via Raman microscope with 514 nm laser excitation. X-ray photoelectron spectroscopy (XPS) survey was carried out using a Thermo Scientific ESCALAB 250 Xi XPS system, in which the analysis chamber pressure was 1.5×10⁻⁹ mbar and the size of the X-ray spot was 500 um.

Electrochemical measurements:

Electrode Preparation:

Cathode catalyst inks were prepared by mixing 10 mg sample and 10 μ L Nafion solutions (5wt %) in 0.99 mL ethanol solution. The inks were then sonicated for 1-2h to get a homogeneous solution. 100uL of the homogeneous ink was loaded onto the two sides of a carbon fiber paper electrode with 1×1 cm². The electrode was then dried overnight in a vacuum-oven at 60 °C.

Electrocatalytic Reduction of CO₂:

A customized airtight, two-compartment, three-electrode cell was utilized with

our samples as the working electrode, and Pt was isolated as the counter electrode. Ag/AgCl (saturated KCl) was used as the reference electrode. The CO₂ reduction was conducted in aqueous 0.5 M KHCO₃ saturated with CO₂ under high stirring by employing an electrochemical station (CHI760E). The electrolyte was saturated with CO₂ for at least 30 min before the start of each CO₂ reduction, and the flow rate of CO₂ was maintained at 5 mL min⁻¹ for all experiments.

Cyclic voltammetry (CV) was performed with a scan rate of 5 mV s⁻¹ from -0.72 to -1.92 V vs. Ag/AgCl (0 to -1.2 V vs. RHE) in Ar saturated 0.5 M KHCO₃ (pH=8.8) and -0.62 to -1.82 V vs. Ag/AgCl (0 to -1.2 V vs. RHE) in CO₂ saturated 0.5 M KHCO₃ (pH=7.2) electrolyte. All potentials in this study were measured against the Ag/AgCl reference electrode and converted to the RHE reference scale using E (vs. RHE) = E (vs. Ag/AgCl) + 0.1989 V + 0.059 × pH.

Product Quantification:

Gas products from the outlet of the cathodic compartment were vented directly into the gas sampling loop of the gas chromatograph (GC, Shimadzu GC-2014C). A GC run was initiated every 15 min. The gas concentration was averaged over three measurements. Liquid products were identified using ¹H-NMR spectroscopy (Bruker AVANCE III HD 400) using a pre-saturation sequence. The dimethyl sulfoxide (DMSO) was used as the internal standard to quantify the liquid product concentration.

DFT Calculations:

First-principle density functional theory (DFT) calculations were performed using the Vienna ab initio simulation package (VASP) ¹⁻³ and the projector augmented wave

(PAW) method. ⁴ The exchange-correlation effects were treated in generalized gradient approximation (GGA) with the Perdew-Burke-Ernzerhof (PBE) potential. ⁵The kinetic energy cutoff was chosen to be 550 eV. Brillouin zone integration was sampled with 3×3×1 Monkhorst-Pack mesh K-points for all the calculations. Gaussian smearing method ⁶ was employed to determine electron occupancies with a width of 0.2 eV. A vacuum region of 15 Å was used to eliminate the interaction of periodic images of the systems. The 5×6 graphene with 60 carbon atoms were used as the initial model. Two carbon atoms of the graphene model were removed to build a defect, since the porous catalysts were pyrolyzed from ZIF-8. Then the N doping is carried out to build the N doped graphene. All N-doped graphene are relaxed before attaching any molecules. For COOH and CO adsorption on the different NCs, all possible sites were considered. We found that both COOH and CO prefer the defect atom sites that the coordination is unsaturated. No atom was fixed during the relaxation. The energy and fore convergence criteria were set as 10⁻⁵ eV and 0.01 eV/Å, respectively. For N4 and pyrrolic systems, the active site is the N atom. For the other systems, the active site is carbon atom.

The Gibbs free energy diagrams were calculated using the computational hydrogen electrode (CHE). In the CHE, the chemical potential of a proton-electron pair was defined as $G(H^+ + e^-) = \frac{1}{2}G(H_2) - eU$, where U is the electrochemical potential relative to RHE. The Gibbs free energy of a species is calculated according to

$$G = E_{DFT} + E_{ZPE} + \int C_p dT - TS$$

where E_{DFT} is the electronic energy calculated by DFT, E_{ZPE} is the zero point energy obtained from the vibrational frequencies of adsorbates or molecules as calculated within DFT. For an adsorbate, the changes in $\int C_p dt$ and TS are much smaller compared to the variations in E_{DFT} and E_{ZPE} . Therefore, $\int C_p dt$ and TS were assumed constant for COOH* and CO*. The $\int C_p dt$ and TS for COOH* were used as 0.096 and -0.178 eV.⁷ For chemical adsorbed CO, the $\int C_p dt$ and TS were used as 0.076 and -0.153 eV,⁷ and for physical adsorbed CO, they were used as the value of gas-phase CO, since the properties of physical adsorbed CO is more closer to those of gas-phase CO. For gas-phase molecules, the $\int C_p dt$ and TS at 298.15K were used. To account for the gas-phase errors encountered with PBE exchange-correlation functionals, -0.51, +0.13, -0.08 eV correction are added to the CO, CO₂, and H₂ electronic energy, respectively. The solvation effect has been considered for COOH* and chemical adsorbed CO* by stabilizing 0.25 eV and 0.1 eV, respectively.⁷ 2. Supplementary Figures and Tables



Figure S1. (a) SEM image of ZIF-8 (b) TEM image of ZIF-8.



Figure S2. SEM image of NC samples (a) NC800 (b) NC900 and (c) NC1000 (d) NC1100.



Figure S3. TEM image of NC samples (a) NC800 (b) NC900 and (c) NC1000 (d) NC1100.



Figure S4. XPS survey spectra of ZIF-8, NC800, NC900, NC1000 and NC1100.







Figure S6. Dependence of FE toward H₂ on applied potential for NC samples.



Figure S7. I-t curves on applied potential for NC samples.



Figure S8. Dependence of FE of CO on applied potential for NC sample synthesized at 1200 °C.



Figure S9. Nyquist plots for NC samples.



Figure S10. I-t curve for NC1100 in CO₂ saturate KHCO₃ at -0.8 V vs. RHE. 10 mM SCN⁻ ions were added to the solution to check the effects of SCN⁻ ions on CO₂ reduction activity.



Figure S11. (a) N_2 adsorption/desorption isotherm of NC800, NC900, NC1000 and NC1100 (b) Pore size distribution of NC800, NC900, NC1000 and NC1100.





Figure S12. Cyclic voltammograms of different catalysts studied in 0.1 M Na₂SO₄ (degassed with Ar) at various scan rates for the estimation of double layer capacitances (a) NC800 (b) NC900 (c) NC1000 and (d) NC1100. The geometric area of all electrodes is 1 cm^{-2} and the loading of catalysts is 1mg.



Figure S13. Double layer capacitances of NC800, NC900, NC1000 and NC1100.



Figure S14. Free energy diagram of CRR on N1 at the sites of "2" and "3".



Figure S15. Free energy diagram of HER at pH=0 on NGs.

The active sites for HER are identical to CRR. At pH=0, the graphitic N shows an energetic uphill for H* while other NGs (N1-N4, pyrrolic N) show a downhill for H* but require energy to release the H* into H₂. It means that N1-N4 and pyrrolic N would be very easily passivated by H* at pH=0. The pH affects the free energy of H⁺ ions by $G(pH) = kTln \ 10 \times pH$. The base environment near the electrode surface would suppress the passivation of H* and simultaneously enhance the CRR. In our work, the CRR was conducted in the aqueous of CO₂ saturated 0.5M KHCO₃ (pH=7.2) to suppress the passivation of H*.

Sample	C (at%)	N (at%)	O (at%)	Zn (at%)
ZIF-8	74.616	12.416	9.306	3.662
NC800	77.633	8.875	11.756	1.735
NC900	83.101	6.608	8.934	1.359
NC1000	87.964	4.096	7.592	0.348
NC1100	89.336	1.055	9.55	0.059

Table S1. Content of elements in ZIF-8, NC800, NC900, NC1000 and NC1100obtained from XPS analysis.

Table S2. Electrocatalytic performance of recently reported nitrogen-doped carbon

Catalyst	CO-FE (%)	Potential of highest	Floctrolyto	Referenc	
		FE	Liectioiyte	e	
ZIF-CNT-FA-	100	0.96 (mg DUE)	0.1 M	8	
р	100	-0.80 (VS. KHE)	NaHCO ₃		
N-CNF	98	-0.573 (vs. SHE)	EMIM-BF ₄	9	
N-CNT	80	-0.78 (vs. SHE)	0.1M KHCO ₃	10	
N-CNT	80	-1.05 (vs. SHE)	0.1M KHCO ₃	11	
N-CNT	90	-0.90 (vs. RHE)	0.5M	12	
			NaHCO ₃		
Graphene foam	85	-0.58 (vs. RHE)	0.1M KHCO ₃	13	
g-C3N4/CNT	60	-0.75 (vs. RHE)	0.1M KHCO ₃	14	
N-GRW	87.6	-0.40 (vs. RHE)	0.5M KHCO ₃	15	
NC1100	95.4	-0.50 (vs. RHE)	0.5M KHCO ₃	This work	

catalysts for CO₂ reduction to CO.

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