Supporting Information

Engineering $Ag-N_x$ Single-Atom Sites on Porous Concave N-doped Carbon for Boosting CO_2 Electroreduction

Rui Sui[†], Jiajing Pei[†], Jinjie Fang[†], Xuejiang Zhang[†], Yufeng Zhang[†], Feijun Wei[†], Wenxing Chen[‡], Zheng Hu[#], Shi Hu[#], Wei Zhu^{*†}, Zhongbin Zhuang^{*†,§}.

[†]State Key Lab of Organic-Inorganic Composites and Beijing Advanced Innovation Center for Soft Matter Science and Engineering, Beijing University of Chemical Technology, Beijing 100029, China.

*Beijing Key Laboratory of Construction Tailorable Advanced Functional Materials and Green Applications, School of Materials Science and Engineering, Beijing Institute of Technology, Beijing 100081, China.

^{*}Department of Chemistry, School of Science, Tianjin Key Laboratory of Molecular Optoelectronic Science, Tianjin University, Tianjin 300072, China.

[§]Beijing Key Laboratory of Energy Environmental Catalysis, Beijing University of Chemical Technology, Beijing 100029, China.

Additional experimental details

Synthesis of Ag NPs/C

The Ag NPs were prepared by similar approach reported in the literature. In a typical synthesis, silver trifluoroacetate (0.2 g), oleic acid (1.75 mL), and isoamyl ether (15 mL) were mixed in a 50 mL three-neck round-bottom flask, saturated with nitrogen, and heated to 160 °C in an oil bath with stirring, and kept for 0.5 h. When the temperature was raised from room temperature to 160 °C, the color of the solution gradually turned dark brown, indicating the formation of silver nanoparticles. After cooling to room temperature, it was centrifuged and washed twice with absolute ethanol, dispersed in cyclohexane (10 mL) and added dropwise to the carbon powder in cyclohexane solution (the ratio of solution to carbon powder was 1 mL: 1 mg). After stirring for 24 hours, it was filtered and dried under vacuum at 60 °C. Finally, the samples were annealed at 200 °C for 5 h under air atmosphere in a tube furnace for removing the surfactant.

XAFS Data Analysis

The EXAFS data were processed according to the standard procedures using the Athena and Artemis implemented in the IFEFFIT software packages. The acquired EXAFS data were processed according to the standard procedures using the ATHENA module implemented in the IFEFFIT software packages. The EXAFS spectra were obtained by subtracting the post-edge background from the overall absorption and then normalizing with respect to the edge-jump step. Subsequently, the $\chi(k)$ data of were Fourier transformed to real (R) space using a hanning windows (dk=1.0 Å⁻¹) to separate the EXAFS contributions from different coordination shells. To obtain the quantitative structural parameters around central atoms, least-squares parameter fitting was performed using the ARTEMIS module of IFEFFIT software packages.

The following EXAFS equation was employed:

$$\chi(k) = \sum_{j} \frac{N_{j} S_{o}^{2} F_{j}(k)}{k R_{j}^{2}} \exp[-2k^{2} \sigma_{j}^{2}] \exp[\frac{-2R_{j}}{\lambda(k)}] \sin[2k R_{j} + \phi_{j}(k)]$$

 S_0^2 is the amplitude reduction factor, $F_j(k)$ is the effective curved-wave backscattering amplitude, N_j is the number of neighbors in the j^{th} atomic shell, R_j is the distance

between the X-ray absorbing central atom and the atoms in the j^{th} atomic shell (backscatterer), λ is the mean free path in Å, $\phi_j(k)$ is the phase shift (including the phase shift for each shell and the total central atom phase shift), σ_j is the Debye-Waller parameter of the j^{th} atomic shell (variation of distances around the average R_j). The functions $F_j(k)$, λ and $\phi_j(k)$ were calculated with the ab initio code FEFF8.2. The coordination numbers of model samples were fixed as the nominal values. The obtained S_0^2 was fixed in the subsequent fitting. While the internal atomic distances R, Debye-Waller factor σ^2 , and the edge-energy shift ΔE_0 were allowed to run freely.

Supporting Figures and Tables



Figure S1. TEM images of a) ZIF-8 b) ZIF-8@SiO₂ and c) anneled-ZIF-8@SiO₂. The inset images in b) and c) show a SiO₂-coating layer formed on the surface of ZIF-8.



Figure S2. The a) TEM and b) SEM images of the $Ag_1-N_2/PCNC$ catalyst.



Figure S3. The High-resolution C 1s XPS spectra of (a) $Ag_1-N_3/PCNC$ and (b) $Ag_1-N_2/PCNC$.



Figure S4. XRD patterns of Ag₁-N₃/PCNC, Ag₁-N₂/PCNC and Ag NPs.



Figure S5. Raman spectra of Ag₁-N₃/PCNC and Ag₁-N₂/PCNC catalysts.



Figure S6. a) the N_2 sorption isotherms and b) the pore-size distributions of Ag_1 - N_3 /PCNC and Ag_1 - N_2 /PCNC catalysts.



Figure S7. The TEM images of a) Ag NPs and b) Ag NPs/C. The corresponding particle size distribution of c) Ag NPs and d) Ag NPs/C.



Figure S8. The ¹H-NMR spectra of liquid products after CO_2RR test using Ag₁-N₃/PCNC catalyst.



Figure S9. TOF of Ag_1 - N_3 /PCNC, Ag_1 - N_2 /PCNC and Ag NPs catalysts and other reported CO₂RR catalysts.

TOF for CO production was calculated as follow:

$$TOF = \frac{I_{product} / NF}{m_{cat} \times \omega / M_{metal}} \times 3600$$

Iproduct: partial current for CO, A;

N: the number of electrons transferred for CO, that is 2;

F: Faradaic constant, 96485 C/mol;

m_{cat}: catalyst mass on the electrode, g;

 ω : Ag loading in the catalyst;

M_{metal}: atomic mass of Ag (107.8 g/mol).



Figure S10. The LSV curves of Ag_1 - N_3 /PCNC before and after 40 h of stability test.



Figure S11. a) TEM image; b) HAADF-STEM image; c) EDS mappings; d) XRD pattern of Ag₁-N₃/PCNC after CO₂RR measurement.



Figure S12. The Tafel slopes of Ag₁-N₃/PCNC, Ag₁-N₂/PCNC and Ag NPs catalysts.



Figure S13. Schematic diagram of the reaction mechanism of CO_2 reduction to CO on $Ag_1-N_3/PCNC$ catalyst. Cyan for C, red for O, gray for H.

Sample	Scattering pair	CN	R(Å)	$\sigma^2(10^{-3}\text{\AA}^2)$	$\Delta E_0(eV)$	R factor
Ag ₁ -N ₃ /PCNC	Ag-N	3.1	1.96	6.1	1.5	0.006
Ag ₁ -N ₂ /PCNC	Ag-N	1.9	1.95	5.6	2.0	0.007

Table S1. Structural parameters extracted from the Ag K-edge EXAFS fitting. $(S_0^2=0.81)$

 S_0^2 is the amplitude reduction factor; CN is the coordination number; R is interatomic distance (the bond length between central atoms and surrounding coordination atoms); σ^2 is Debye-Waller factor (a measure of thermal and static disorder in absorber-scatterer distances); ΔE_0 is edge-energy shift (the difference between the zero kinetic energy value of the sample and that of the theoretical model). R factor is used to value the goodness of the fitting.

Error bounds that characterize the structural parameters obtained by EXAFS spectroscopy were estimated as N \pm 20%; R \pm 1%; $\sigma^2 \pm$ 20%; $\Delta E_0 \pm$ 20%.

Table S2. The atomic content of each elements in $Ag_1-N_3/PCNC$ and $Ag_1-N_2/PCNC$ catalysts

Sample	Ag (%)	C (%)	N (%)	O (%)
Ag ₁ -N ₃ /PCNC	0.09	86.7	9.1	4.1
Ag ₁ -N ₂ /PCNC	0.08	86.6	8.6	4.7

Catalysts	Pyridinic N	Pyrrolic N	Graphitic N	Ag-N	N _{total}
	(%)	(%)	(%)	(%)	(%)
Ag ₁ -N ₃ /PCNC	3.4	2.4	1.8	1.5	9.1
Ag ₁ -N ₂ /PCNC	3.2	2.6	1.6	1.2	8.6

Table S3. Each type N content in N_{total} of Ag_1 - N_3 /PCNC and Ag_1 - N_2 /PCNC.

Catalysts	Electrolyte	Potential	$J_{ m CO}$	FE _{CO}	Ref.	
	Electrolyte	(V vs. RHE)	$(mA cm^{-2})$	(%)		
Ag ₁ -N ₃ /PCNC	0.1 M KHCO ₃	-0.37	2.4	94.6	This	
		-0.49	5.9	87.5	work	
5 nm Ag	0.5 M KHCO ₃	-0.75	3.5	79.2	1	
OLA Ag/C	0.5 M KHCO ₃	-0.50	0.12	82	2	
OD-Ag	0.1 M KHCO ₃	-0.60	0.1	80	3	
Anodized		0.60	27	92.8	4	
treated Ag	0.1 M KHCO3	-0.00	5.7			
PON-Ag	0.5 M KHCO ₃	-0.69	4.4	96.7	5	
AE-Ag	0.1 M KHCO ₃	-0.40	0.1	92.0	6	
Tri-Ag-NPs	0.1 M KHCO ₃	-0.86	1.2	96.8	7	
Nanoporous Ag	0.5 M KHCO ₃	-0.41	3.0	65.0	8	
Ag nanosheets	0.5 M NaHCO ₃	-0.40	0.3	95.0	9	
Ag nanocoral	0.1 M KHCO ₃	-0.48	2.0	95.0	10	
Br-Ag	0.1 M KHCO3	-0.60	2.48	95.0	11	
I-Ag	0.1 M KHCO ₃	-0.60	0.864	75.0	11	
Ag_1/MnO_2	0.5 M KHCO ₃	-0.85	2.0	95.7	12	
Ag ₂ -G	0.5 M KHCO ₃	-0.50	2.5	85.0	13	
Electrodeposite d Ag	0.5 M KHCO ₃	-0.83	2.5	62.0	14	
Ag-IO	0.1 M KHCO ₃	-0.60	0.005	90.0	15	

Table S4. CO₂RR Performance comparison of various reported Ag-based catalysts.

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