Ultrasmall Au nanocatalysts supported on nitrided carbon for electrocatalytic CO₂ reduction: the role of carbon support in high selectivity

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DFT calculation

All density functional theory (DFT) calculations are performed using DMol3^{1, 2} code. The generalized gradient approximation (GGA) and the revised Perdew-Burke-Ernzerhof (RPBE)³ functional are used in the calculation. Double- ζ numerical basis set with polarization d-function (DND)⁴ and Semi-core Pseudopot (DSPP) approximation are used to treat atomic orbitals and core electrons, respectively. The convergence criterion of the geometrical optimization was set to be 1.0×10^{-5} Hartree for energy change, 2.0×10^{-3} Hartree/Å for the gradient, and 5.0×10^{-3} Å for the displacement, respectively. The electron-rich and neutral Au₂₈ clusters were created by setting the charge q = -1 and q = 0, respectively. On the electron-rich and neutral Au₂₈ clusters, all the adsorbed species relevant to the reaction mechanism (COOH, CO, and H) are optimized. Zero point energy, heat capacity, and entropy are computed, and then used to convert the electronic energies into free energies at room temperature 298.15 K. The non-adsorbed species (CO₂, CO, H₂O and H₂) were analyzed using the same techniques as described above for the adsorbed species. The correction of +0.45 eV was applied to CO₂(g) in the RPBE functional.

The computational hydrogen electrode (CHE) was employed to determine free energies of reaction intermediates. In the CHE, the chemical potential of a proton-electron pair, $\mu_{H^+} + \mu_{e^-}$ is equivalent to a half of the chemical potential of hydrogen gas ($0.5\mu_{H2}$) at zero voltage, at all values of pH, at all temperatures, and at 101325 Pa of H₂. The chemical potential of the proton-electron pair is shifted by –eU when U is the applied potential:

$$\mu_{H^+} + \mu_{e^-} = \frac{1}{2}\mu_{H_2} - \mathrm{eU}$$

For every proton–electron pair transfer step, the potential U is contained within the free energy change (ΔG). For example, the free energy change of step (1) and step (2) are given as:

$$\Delta G(1) = G_{COOH^*} - G_* - G_{CO_2(g)} - (\frac{1}{2}G_{H_2} - eU)$$
(1)
$$\Delta G(2) = G_{CO^*} - G_{COOH^*} + \mu_{H_2O(l)} - (\frac{1}{2}G_{H_2} - eU)$$
(2)



Figure S1. Digital photo of the H-Cell used in the experiments. The height and diameter of both chamber are 85 mm, and 25 mm, respectively. The two chambers are connected by a frit bridge with a length of 25 mm and a diameter of 12 mm. 20 mL of electrolyte was added into both chambers, leaving 13 mL of head space in the chambers with working electrode and reference electrode.



Figure S2. HR-TEM (a), STEM-mapping (b-c), size distribution (d) and STEM-EDS spectroscopy (e) of Au-2@CN. The C, N, Au, and O are shown in red, green, yellow, and blue color in the mapping, respectively.



Figure S3. Thermogravimetric analysis (TGA) curves of Au-2@CN and nitrided carbon support. The loading mass of Au was estimated to be 2.5 wt%.



Figure S4. Gas products analysis from gas chromatograph (a) and liquid products analysis from NMR (b) using Au-2@CN at -0.35 V (*vs* RHE). The gas products are mainly CO and a small amount of H_2 . The liquid product is a trace amount of formate. The unsmoothed curve at 5.7 ppm is caused by the water suppression. DMSO was used as internal standard to calibrate the amount of products (the same for other NMR spectra below).



Figure S5. Gas products analysis from gas chromatograph (a) and liquid products analysis from NMR (b) using Au-2@CN at -0.43 V (vs RHE). The gas products are mainly CO and a small amount of H₂. The liquid product is a trace amount of formate. The unsmoothed curve at 5.7 ppm is caused by the water suppression.



Figure S6. Gas products analysis from gas chromatograph (a) and liquid products analysis from NMR (b) using Au-2@CN at -0.50 V (*vs* RHE). The gas products are mainly CO and a small amount of H_2 . The liquid product is a trace amount of formate. The unsmoothed curve at 5.7 ppm is caused by the water suppression. The peaks labeled with asterisks in NMR are assigned to ethanol, which may be from the residual ethanol on the electrode from ink solution.



Figure S7. Gas products analysis from gas chromatograph (a) and liquid products analysis from NMR (b) using Au-2@CN at -0.58 V (*vs* RHE). The gas products are mainly CO and a small amount of H_2 . The liquid product is a trace amount of formate. The unsmoothed curve at 5.7 ppm is caused by the water suppression. The peaks labeled with asterisks in NMR are assigned to ethanol, which may be from the residual ethanol on the electrode from ink solution.



Figure S8. Gas products analysis from gas chromatograph (a) and liquid products analysis from NMR (b) using Au-2@CN at -0.65 V (vs RHE). The gas products are mainly CO and a small amount of H₂. The liquid product is a trace amount of formate. The unsmoothed curve at 5.7 ppm is caused by the water suppression. The peaks

labeled with asterisks in NMR are assigned to ethanol, which may be from the residual ethanol on the electrode from ink solution.



Figure S9. Gas products analysis from gas chromatograph (a) and liquid products analysis from NMR (b) using Au-2@CN at -0.73 V (*vs* RHE). The gas products are mainly CO and a small amount of H_2 . The liquid product is a trace amount of formate. The unsmoothed curve at 5.7 ppm is caused by the water suppression. The peaks labeled with asterisks in NMR are assigned to ethanol, which may be from the residual ethanol on the electrode from ink solution. The tiny peaks between 2-0 ppm are assigned to propanol, which may be introduced from the Nafion solution in the ink.



Figure S10. Gas products analysis from gas chromatograph (a) and liquid products analysis from NMR (b) using Au-2@CN at -0.80 V (*vs* RHE). The gas products are mainly CO and a small amount of H_2 . The liquid product is a trace amount of formate. The unsmoothed curve at 5.7 ppm is caused by the water suppression. The peaks labeled with asterisks in NMR are assigned to ethanol, which may be from the residual ethanol on the electrode from ink solution. The tiny peaks between 2-0 ppm are assigned to propanol, which may be introduced from the Nafion solution in the ink.



Figure S11. (a) LSV curves of CN and C in 0.5 M NaHCO₃ solution saturated by CO₂ at a scan rate of 10 mV s⁻¹. (b) Electrochemical impedance spectroscopy of CN and C. (c) Gas products analysis from gas chromatograph using CN and C at -0.73 V (vs RHE). (d) Gas products analysis from gas chromatograph using CN at different potentials. Both CN and C showed similar equivalent series resistance (R_s), similar activity, and H_2 is the only gas product with a Faradaic efficiency of ~100 %.



Figure S12. LSV scans of CN and Au-2@CN in the CO₂ saturated 0.5 M NaHCO₃ at scan rate of 10 mV s⁻¹. It can be seen that CN contributes less to the total activity.



Figure S13. (a, b) TEM images of Au-2@CN after CO2 reduction at -0.65 V (*vs* RHE) for 2 hr. CV scans of Au-2@CN (a) and Au-2@CN after CO₂ reduction at -0.65 V (*vs* RHE) for 2 h (b) in 0.1 M HClO₄ at the scan rate of 50 mV s⁻¹. The electrochemical chemical surface area decreased from 0.69 cm² to 0.16 cm², which is caused by the aggregation of small Au NPs on CN after 2 h of reaction.



Figure S14. (a) Reconstructed model and Hirshfeld charge analysis of neutral Au_{28} cluster (top) and electron-rich Au_{28} clusters. (b) Free energy diagrams for H_2 evolution using electron-rich and neutral Au_{28} clusters.



Figure S15. (a) TEM image of Au-2@QCN1. (b) LSV curves of Au-2@QCN1 in 0.5 M NaHCO₃ solution saturated by CO₂ at a scan rate of 10 mV s⁻¹. (c) CV curve of Au-2@QCN1 in 0.1 M HClO₄ at a scan rate of 50 mV/s. The ECSA was calculated to be 0.513 cm². (d) The FE of products at different potentials produced using Au-2@QCN1.



Figure S16. (a) TEM image of Au-2@QCN2. (b) LSV curves of Au-2@QCN2 in 0.5 M NaHCO₃ solution saturated by CO_2 at a scan rate of 10 mV s⁻¹. (c) CV curve of Au-2@QCN2 in 0.1 M HClO₄ at a scan rate of 50 mV/s. The ECSA was calculated to be 0.482 cm². (d) The FE of products at different potentials produced using Au-2@QCN2.



Figure S17. N K-edge XAS spectra of (a-b) Au-2@CN, Au-2@QCN1 and Au-2@QCN2; and (c-d) CN, QCN1 and QCN2. There are two absorption edges around 400 eV and 407 eV assigning to $1s \rightarrow \pi^*$ and $1s \rightarrow \sigma^*$ transitions, respectively.⁵ The $1s \rightarrow \pi^*$ edge consists of three main absorption peaks at 398.9 eV, 400.2 eV and 401.4 eV designating as pyridinic N (N1), ureido (or amide) (N2), and graphitic N (N3), respectively.^{6, 7} The broad peak at ~407.5 eV was attributed to the $1s \rightarrow \sigma^*$ excitation of C-N bonds. Note that, a shoulder peak at ~399.2 eV is obvious for Au-2@CN compared to the two quenched samples, as indicated by the arrow in (b). We interpret this shoulder peak as the metal-N (or Au-N) binding, similar to those reported in Fe-N interaction. The disappearance of the shoulder peak after quenching N sites is evidential to the weakened metal-N interaction.

The change in N sites before and after quenching is obvious from the intensity ratio of various states of N sites. Given that ureido (or amide) sites (N2) were not reacted in our quenching experiments, the ratios of N1/N2 and N3/N2 represent the changes in pyridinic N sites and graphitic N sites. For Au-2@CN, N1/N2 decreased gradually from 2.78, 2.68 (Au-2@QCN1) to 1.72 (Au-2@QCN2); and N3/N2 decreased from 0.54, 0.45 (Au-2@QCN1) to 0.37 (Au-2@QCN2), respectively. Those results suggest that pyridinic N sites and graphitic N sites decreased relative to the N sites from ureido (or amide) groups. This is consistent with our XPS analysis (see Figure 3). Similar trends are seen when using carbon as controlled experiments. Therefore, the reduced Au-N interaction is responsible for the depression in CO₂ reduction performance.



Figure S18. XPS survey of Au-2@CN, Au-2@QCN1, and Au-2@QCN2. The percentage of N was decreased after quenching process.



Figure S19. TGA-mass spectroscopy of CN (a), and C (b). CN showed a strong CO₂ desorption peak at around 380 °C, while C did not show the CO₂ desorption peak.



Figure S20. TEM images and size distribution of Au-5@CN (a-b), and Au-8@CN (c-d).



Figure S21. CV scans of Au-5@CN (a) and Au-8@CN (b) in 0.1 M HClO₄ at the scan rate of 50 mV s⁻¹. The electrochemical chemical surface area was calculated to be 0.115 cm^2 for Au-5@CN and 0.096 cm^2 for Au-8@CN. (c) LSV scans of Au-2@CN, Au-5@CN, and Au-8@CN in the CO₂ saturated 0.5 M NaHCO₃ at scan rate of 10 mV s⁻¹.



Figure S22. TEM images and size distribution of Au-2.4 nm (a), 2.7 nm (b), Au-3.3 nm (c), Au-3.9 nm (d), and Au-4.7 nm (e).



Figure S23. (a) Specific activities of Au-2@CN, Au-5@CN and Au-8@CN at different potentials; (b) Specific activities of AuNCs synthesized via seed-mediated growth using Au-2@CN as seeds.



Figure S24. TEM images and size distribution of Au-6/CN (a-b), and Au-6/CN (c-d).



Figure S25. LSV scans of Au-6/CN (a), and Au-6/C (b) in the CO₂ saturated 0.5 M NaHCO₃ at scan rate of 10 mV s⁻¹. CV curve of Au-6/CN (c) and Au-6/C (d) in 0.1 M HClO₄ at a scan rate of 50 mV/s. The electrochemical surface area was calculated to be 0.106 cm² for Au-6/CN and 0.077 cm² for Au-6/C.

	Flectrolyte	Onset Potential	COFE	<i>i</i>	i i	
Catalysts	(nH)	(vs. RHE)	(V)	(A/g_{Au})	(mA/cm^2)	Ref
	0.5 M NaHCO ₃ /CO ₂	(*3. 1412)	89%	721.06	1.06	
Au-2@CN	(7.2)	-0.28	(-0.65V)	(-0.65 V)	(-0.65 V)	This work
Au-2@CN	0.5 M NaHCO ₃ /CO ₂	-0.28	33.9%	11.30	0.03	This work
	(7.2)		(-0.35 V)	(-0.35 V)	(-0.35 V)	
4 nm Au NPs	0.5 M NaHCO ₃ /CO ₂	-0.37	14%	0.33 (-0.35 V)		8
	(7.2)		(-0.37 V)		N/A	
8 nm Au NPs	0.5 M NaHCO ₃ /CO ₂	-0.37	22%	0.14 (-0.35 V)	N/A	8
	(7.2)		(-0.37 V)		IN/A	
500 nm Au NWs	0.5 M NaHCO ₃ /CO ₂	-0.20	94%	1.84	8.16	9
	(7.2)		(-0.35 V)	(-0.35 V)	(-0.35 V)	
100 nm Au NWs	0.5 M NaHCO ₃ /CO ₂	-0.30	45%	0.77	3.28	9
	(7.2)		(-0.35 V)	(-0.35 V)	(-0.35 V)	
Au ₂₅ cluster	0.1 M NaHCO ₃ /CO ₂	-0.193	9.3%	N/Λ	N/Δ	10
	(7.0)		(-0.499 V)	11/21	11/21	
Au _{2 nm}	0.1 M NaHCO ₃ /CO ₂	-0.499	8±1%	N/A	~7.99*	10
	(7.0)		(-0.499 V)		(-1.0 V)	
Au _{5 nm}	0.1 M NaHCO ₃ /CO ₂	-0.551	$11\pm2\%$	N/A	~0.32*	10
	(7.0)		(-0.551 V)		(-1.0 V)	
Oxide-derived Au	0.5 M NaHCO ₃ /CO ₂	-0.20	96%	N/A	<3.84*	11
	(7.2)		(-0.35 V)		(-0.35 V)	
Au-CeO _v /C	0.1 M KHCO ₃ /CO ₂	-0.50	89.1%	32.4	12.9	12
	(6.8)	0.00	(-0.89 V)	(-0.89 V)	(-0.89 V)	
Au-CNTs	$0.5 \text{ M NaHCO}_3/\text{CO}_2$	-0.15	70%	N/A	10	13
	(7.2)		(-0.55 V)		(-0.55V)	
Au/CNT	$0.5 \text{ M NaHCO}_3/\text{CO}_2$	N/A	~94%	~15*	~0.095*	14
	(7.2)	1.0.1.1	(-0.5 V)	(-0.5 V)	(-0.5 V)	
Au-Cb NPs	0.1 M KHCO ₃ /CO ₂	-0.26	83%	N/A	~2.00	15
	(6.8)		(-0.57 V)		(~-0.55 V)	
Concave Au	$0.5 \text{ M KHCO}_3/\text{CO}_2$	-0.23	92%	~5.2*	~2.6*	16
	(7.3)		(-0.67 V)	(-0.7 V)	(-0.7 V)	
AuNP-GNR	0.5 M KHCO ₃ /CO ₂	-0.14	~82%	36.8	8.00	17
	(7.3)	0.11	(-0.87 V)	(-0.87 V)	(-0.87 V)	
Au3Cu	0.1 M KHCO ₃ /CO ₂	N/A	~65%	240 N/A (-0.73 V)	N/A	18
	(6.8)		(-0.73 V)			
AuCu	0.1 M KHCO ₃ /CO ₂	N/A	80%	830	1.4	19
	(6.8)		(-0.77 V)	(-0.77 V)	(-0.77 V)	
AuCu-1.4 nm	$0.1 \text{ M KHCO}_3/\text{CO}_2$	/CO ₂ N/A	12%*	N/A	6.24*	20
	(6.8)		(-1.2 V)		(-1.2 V)	
Cu/Au core-shell	$0.5 \text{ M KHCO}_3/\text{CO}_2$	N/A	33%	N/A	4.45*	21
arrays	(7.3)		(-0.65 V)		(-0.65 V)	

Table S1. Electrochemical CO₂ reduction of Au-2@CN and other reported Au catalysts.

* The values were read from figures or calculated from the given data.

Loading	Electrolyte	CO FE	$j_{ m co}$
(mg cm ⁻²)	(pH)	(V)	(A/g_{Au})
0.2	0.5 M NaHCO ₃ /CO ₂	72.2%	1145
0.2	(7.2)	(-0.80 V)	(-0.80 V)
0.2	0.5 M NaHCO ₃ /CO ₂	83.3%	967
0.2	(7.2)	(-0.73 V)	(-0.73 V)
0.2	0.5 M NaHCO ₃ /CO ₂	89.0%	721
0.2	(7.2)	(-0.65 V)	(-0.65 V)
0.2	0.5 M NaHCO ₃ /CO ₂	87.0%	498
0.2	(7.2)	(-0.58 V)	(-0.58 V)
0.2	0.5 M NaHCO ₃ /CO ₂	73.7%	270
0.2	(7.2)	(-0.50 V)	(-0.50 V)
0.2	0.5 M NaHCO ₃ /CO ₂	79.2%	220
0.2	(7.2)	(-0.46 V)	(-0.46 V)
0.2	0.5 M NaHCO ₃ /CO ₂	68.7%	148
0.2	(7.2)	(-0.43 V)	(-0.43 V)
0.2	0.5 M NaHCO ₃ /CO ₂	63.7%	91.1
0.2	(7.2)	(-0.39 V)	(-0.39 V)
0.2	0.5 M NaHCO ₃ /CO ₂	33.9%	30.1
0.2	(7.2)	(-0.35 V)	(-0.35 V)
0.2	0.5 M NaHCO ₃ /CO ₂	21.1%	14.7
0.2	(7.2)	(-0.33 V)	(-0.33 V)
0.2	0.5 M NaHCO ₃ /CO ₂	8.78%	4.3
0.2	(7.2)	(-0.31 V)	(-0.31 V)
0.2	0.5 M NaHCO ₃ /CO ₂	3.53%	1.3
0.2	(7.2)	(-0.28 V)	(-0.28 V)
0.2	0.1 M NaHCO ₃ /CO ₂	86.4	437.1
0.2	(7.0)	(-0.65 V)	(-0.65 V)
0.1	0.5 M NaHCO ₃ /CO ₂	77.4%	914.2
0.1	(7.2)	(-0.65 V)	(-0.65 V)
0.4	0.5 M NaHCO ₃ /CO ₂	83.5%	584.5
0.4	(7.2)	(-0.65V)	(-0.65V)
0.0	0.5 M NaHCO ₃ /CO ₂	86.4%	437.1
0.8	(7.2)	(-0.65V)	(-0.65V)
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Table S2. Electrochemical CO2 reduction of Au-2@CN at different conditions.

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