

## Supporting Information

### **Mechanistic study on the competition between carbon dioxide reduction and hydrogen evolution reaction and selectivity tuning via single-atom catalyst loading on graphitic carbon nitride**

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## List of Abbreviations

<b>AIMD</b>	Ab initio molecular dynamics
<b>CBM</b>	Conduction band minimum
<b>CN</b>	g-C <sub>3</sub> N <sub>4</sub>
<b>CO<sub>2</sub>RR</b>	Carbon dioxide reduction reaction
<b>DFT</b>	Density functional theory
<b>DFT-D3</b>	Empirical correlation in Grimme's scheme
<b>GGA-PBE</b>	Generalized gradient approximation with Perdew-Burke-Ernzerhof exchange-correlation function
<b>HER</b>	Hydrogen evolution reaction
<b>M-SAC</b>	Metal single-atom catalyst
<b>PAW</b>	Projected augmented wave
<b>PDS</b>	Potential determining steps
<b>SAC</b>	Single-atom catalyst
<b>VASP</b>	Vienna Ab initio Simulation Package
<b>VBM</b>	Valence band maximum

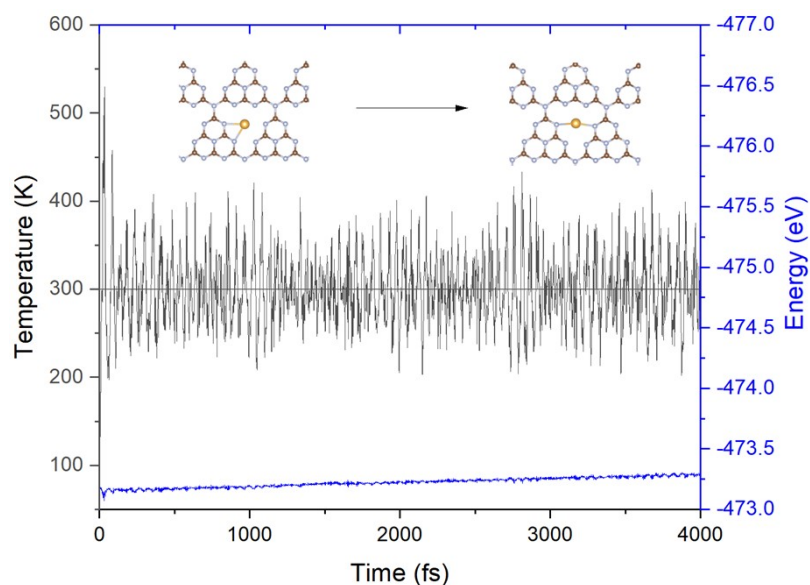


Fig. S1 AIMD evaluation of the AuCN system; Grey: temperature and Blue: energy evolution versus time, respectively. The AIMD simulation lasted 4000 fs at 300 K.

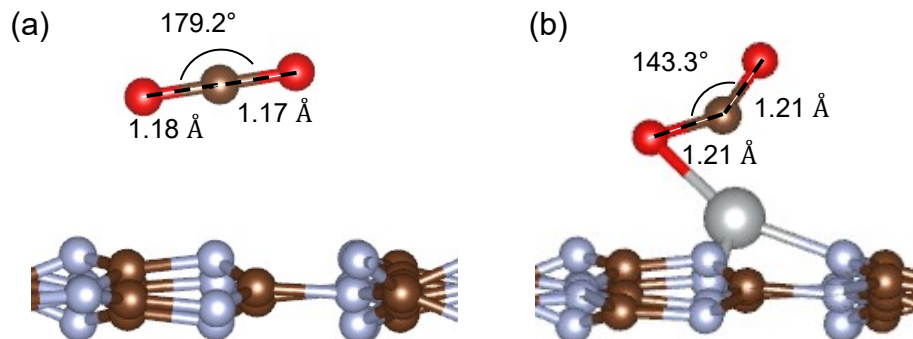


Fig. S2 The geometry-optimized model of the CO<sub>2</sub> adsorbed on the surface of the (a) CN and (b) NiCN system. The dashed line refers to the distance between the O and C molecules; the solid line refers to the angle of O-C-O.

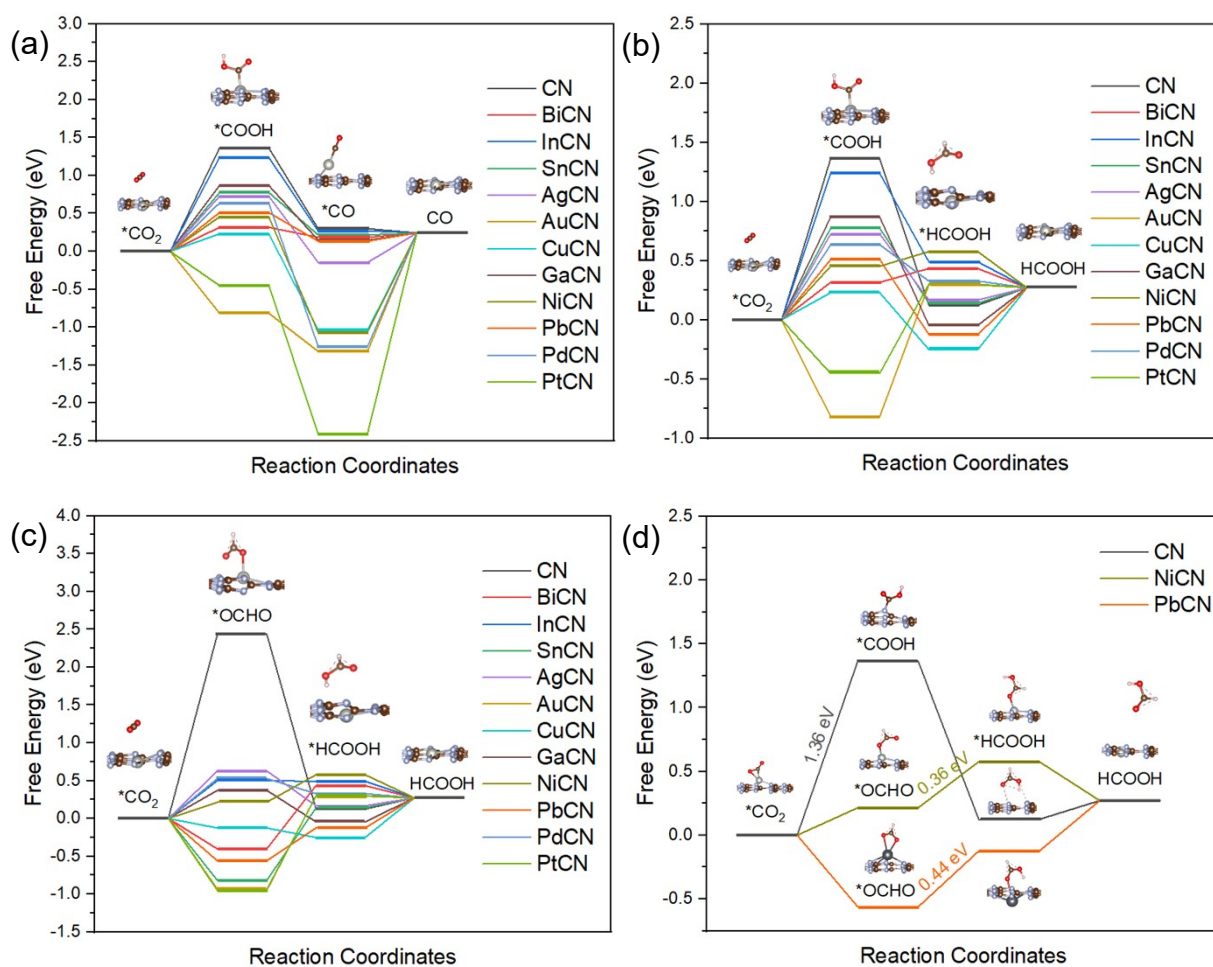


Fig. S3 Gibbs free energy of the CO<sub>2</sub>RR to (a) CO via Pathway 1 and HCOOH via (b) Pathway 2 and (c) Pathway 3 with different M-SACs loaded carbon nitride catalyst systems. (d) The comparison between Gibbs free energy of the pristine (Pathway 2) and the best performance MCN (M = Ni and Pb) (Pathway 3) to the formation of HCOOH.

Table S1 The distance between the M-SAC and the unsaturated N atoms.

<b>Systems</b>	<b>M-N Distance (Å)</b>
BiCN	2.49 – 2.53
InCN	-
SnCN	2.47 – 2.57
AgCN	-
AuCN	2.26 – 2.27
CdCN	2.41 – 2.52
CuCN	2.08 – 2.09
GaCN	-
NiCN	1.89 – 1.90
PbCN	2.56 – 2.76
ZnCN	2.22 – 2.23
PbCN	2.20 – 2.23
PtCN	2.09 – 2.31

Table S2. Relative Gibbs free energy of the CN and MCN system for CO<sub>2</sub> conversion to CO via pathway 1 through the \*COOH intermediate. (Red font indicates the potential determining step for each of the system)

System	Relative Gibbs Free Energy (eV)			PDS (eV)
	*CO <sub>2</sub> → *COOH	*COOH → CO	*CO → CO	
CN	1.3635	-1.0655	-0.056	1.3635
BiCN	0.3175	-0.1325	0.057	0.3175
InCN	1.2385	-0.9705	-0.026	1.2385
SnCN	0.7745	-0.5585	0.026	0.7745
AgCN	0.7255	-0.8725	0.389	0.7255
AuCN	-0.8165	-0.5035	1.562	1.562
CdCN	0.3155	-0.1045	0.031	0.3155
CuCN	0.2305	-1.2695	1.281	1.281
GaCN	0.8675	-0.7195	0.094	0.8675
NiCN	0.4535	-1.5255	1.314	1.314
PbCN	0.5105	-0.3765	0.108	0.5105
ZnCN	-0.3415	0.1335	0.45	0.45
PdCN	0.6355	-1.8915	1.498	1.498
PtCN	-0.4525	-1.9535	2.648	2.648

\*PDS = Potential-determining step (the highest potential required for the transition state in the entire reaction path)

Table S3. Relative Gibbs free energy of the CN and MCN system for CO<sub>2</sub> conversion to HCOOH via pathway 2 through the \*COOH intermediate. (Red font indicates the potential-determining step for each of the system)

System	Relative Gibbs Free Energy (eV)			PDS (eV)
	*CO <sub>2</sub> → *COOH	*COOH → CO	*CO → CO	
CN	1.3635	-1.2385	0.147	1.3635
BiCN	0.3175	0.1165	-0.162	0.3175
InCN	1.2385	-0.7475	-0.219	1.2385
SnCN	0.7745	-0.6325	0.13	0.7745
AgCN	0.7255	-0.5565	0.103	0.7255
AuCN	-0.8165	1.1115	-0.023	1.1115
CdCN	0.3155	-0.4005	0.357	0.357
CuCN	0.2305	-0.4805	0.522	0.522
GaCN	0.8675	-0.9125	0.317	0.8675
NiCN	0.4535	0.1235	-0.305	0.4535
PbCN	0.5105	-0.6345	0.396	0.5105
ZnCN	-0.3415	-0.3625	0.976	0.976
PdCN	0.6355	-0.3075	-0.056	0.6355
PtCN	-0.4525	0.7535	-0.029	0.7535

\*PDS = Potential-determining step (the highest potential required for the transition state in the entire reaction path)

Table S4. Relative Gibbs free energy of the CN and MCN system for CO<sub>2</sub> conversion to HCOOH via pathway 3 through the \*OCHO intermediate. (Red font indicates the potential-determining step for each of the system)

System	Relative Gibbs Free Energy (eV)			PDS (eV)
	*CO <sub>2</sub> →	*OCHO →	*HCOOH →	
	*OCHO	HCOOH	HCOOH	
CN	2.4385	-2.3135	0.147	2.4385
BiCN	-0.4025	0.8365	-0.162	0.8365
InCN	0.5015	-0.0105	-0.219	0.5015
SnCN	-0.8195	0.9615	0.13	0.9615
AgCN	0.6285	-0.4595	0.103	0.6285
AuCN	-0.9345	1.2295	-0.023	1.2295
CdCN	-0.6455	0.5605	0.357	0.5605
CuCN	-0.1255	-0.1245	0.522	0.522
GaCN	0.3725	-0.4175	0.317	0.3725
NiCN	0.2155	0.3615	-0.305	0.3615
PbCN	-0.5605	0.4365	0.396	0.4365
ZnCN	-1.3135	0.6095	0.976	0.976
PdCN	0.5275	-0.1995	-0.056	0.5275
PtCN	-0.9525	1.2535	-0.029	1.2535

\*PDS = Potential-determining step (the highest potential required for the transition state in the entire reaction path)