Supporting Information

Graphitic Carbon Nitride with the Pyridinic N Substituted by Al and Si as Efficient Photocatalysts for CO_2 Reduction

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Table S1 Optimized lattice constants of the B/O/P/S/As/Se/Si/Al/Ga/Ge-doped g-C_3N_4 supercell.

	lattice constant (Å)
pristine g-C_3N_4	14.24
B-doped g-C_3N_4	14.36
O-doped g-C_3N_4	14.25
Al-doped g-C_3N_4	14.53
Si-doped g-C_3N_4	14.48
P-doped g-C_3N_4	14.43
S-doped g-C_3N_4	14.42
Ga-doped g-C_3N_4	14.56
Ge-doped g-C_3N_4	14.52
As-doped g-C_3N_4	14.48
Se-doped g-C_3N_4	14.47

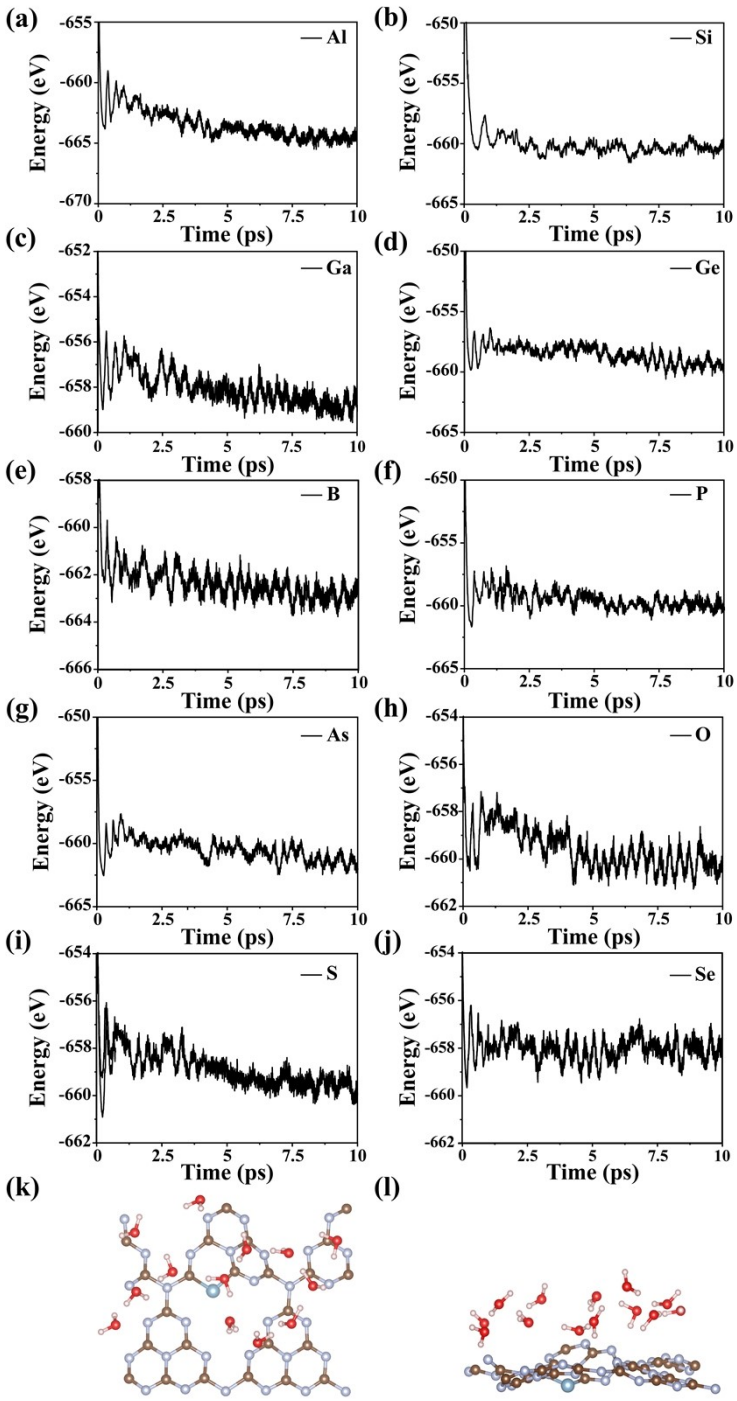


Figure S1 Potential energy variation of the Al- (a), Si- (b), Ga- (c), Ge- (d), B- (e), P- (f), As- (g), O- (h), S- (i), and Se-doped (j) g-C_3N_4 in aqueous solution against time at 298 K calculated via *ab initio* molecular dynamics simulations. The aqueous solution was modelled by placing 13 water molecules around the dopant as shown in (k) and (l) for the top and the side views of one doped system as the example.

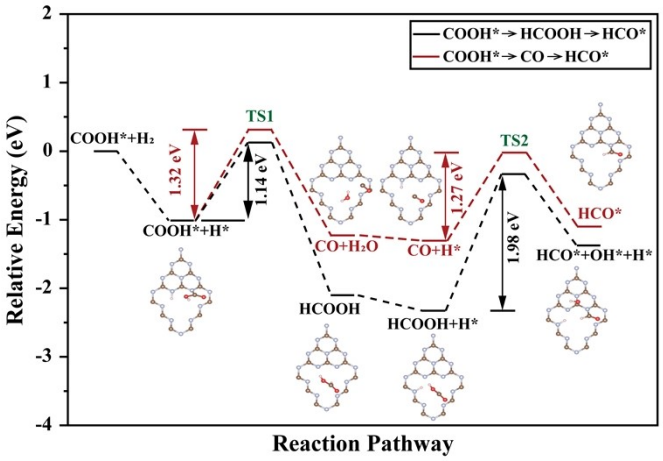


Figure S2 Potential energy diagram for COOH* reduction to HCO* through the intermediate HCOOH (black line) and that through the intermediate CO (red line) on the pristine g-C_3N_4. The reference energy (total energy of the catalyst, adsorbed COOH* and one H_2) is set to zero.

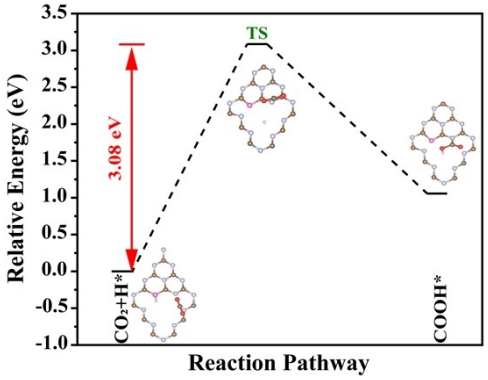


Figure S3 Potential energy diagram for CO_2 reduction to COOH* on the B-doped g-C_3N_4 with pyridinic N being the active site. Pink balls represent B atoms.

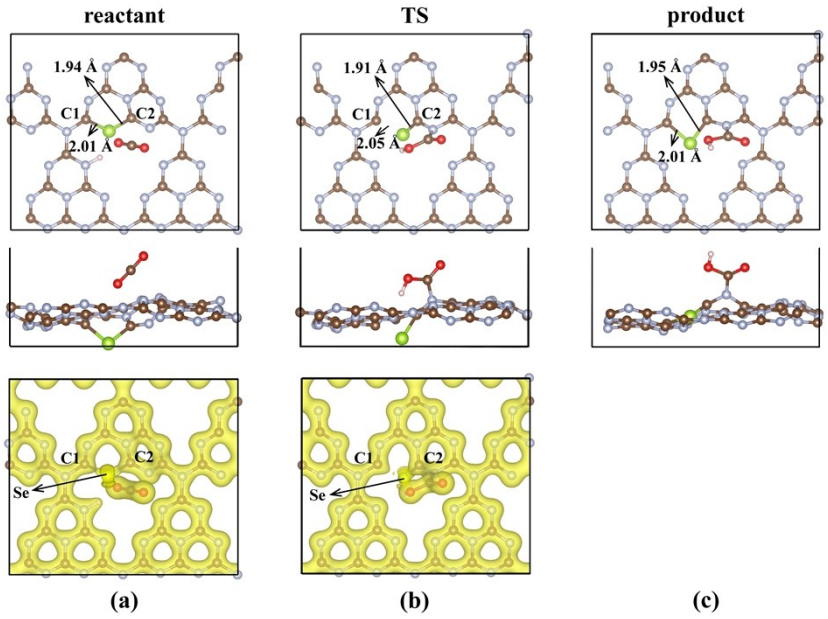


Figure S4 Geometries of the reactant (a), transition state (b) and product (c) in the CO_2 reduction to COOH* on the Se-doped g-C_3N_4. The first row shows top views of the geometries. The second row shows side views of the geometries. The third row shows electron distributions of the reactant and the transition state at the density of 0.125 e/Å^3. Green balls represent Se atoms.

Table S2 Bond lengths between the dopant and its two adjacent carbon atoms (C1 and C2 as marked in Fig. S4) in the reactant and the transition state in the CO_2 reduction to COOH* on the Se/O/S/P/As doped g-C_3N_4.

	Bond length (Å)			
	Reactant		Transition state	
	C1-dopant	C2-dopant	C1-dopant	C2-dopant
Se-doped g-C_3N_4	2.01	1.94	2.05	1.91
O-doped g-C_3N_4	1.48	1.40	1.46	1.39
S-doped g-C_3N_4	1.84	1.79	1.83	1.77
P-doped g-C_3N_4	1.81	1.80	1.80	1.78
As-doped g-C_3N_4	1.96	1.94	1.96	1.92

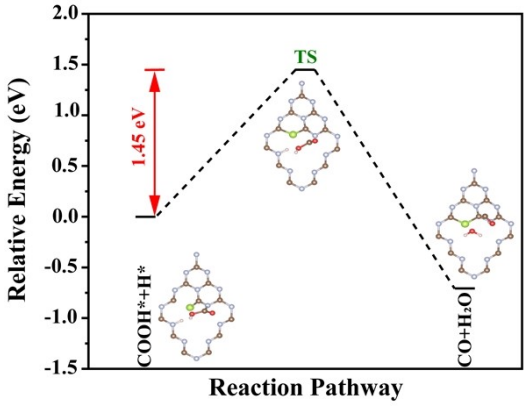


Figure S5 Potential energy diagram for COOH* reduction to CO on the Se-doped g-C_3N_4. Green balls represent Se atoms.

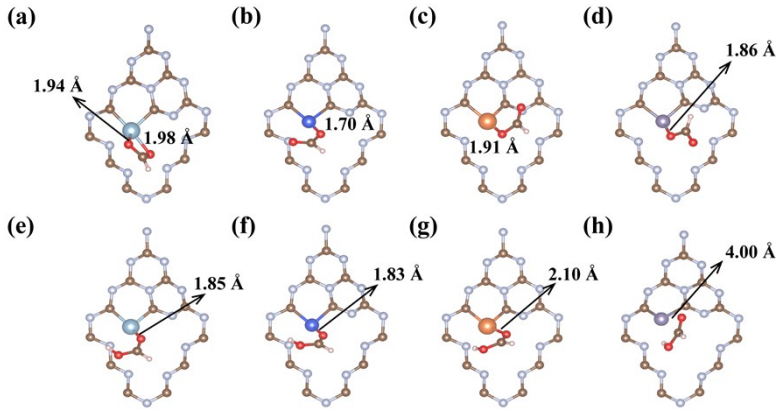
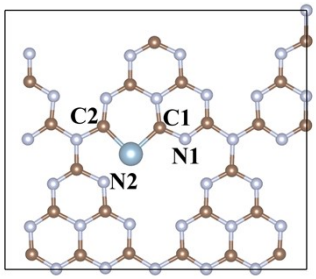


Figure S6 Geometries of HCOO (a-d) and HCOOH (e-h) on the Al-, Si-, Ga- and Ge-doped g-C_3N_4. Al: (a) and (e). Si: (b) and (f). Ga: (c) and (g). Ge: (d) and (h). Distances between the dopants and the O atoms in HCOO* and HCOOH are shown. Sky blue, blue, orange and grayish purple balls represent Al, Si, Ga and Ge atoms, respectively.

Table S3 Bader charges at the atoms (C1, C2, N1 and N2 as marked in the figure below) adjacent to the dopant in the Al-, Ga-, Si- and Ge-doped g-C_3N_4 and the corresponding data in the pristine g-C_3N_4.



	Bader charge				
	C1	C2	N1	N2	dopant
pristine g-C_3N_4	2.35	2.46	6.14	6.17	
Al-doped g-C_3N_4	3.59	3.73	6.27	6.37	0.03
Ga-doped g-C_3N_4	3.18	3.39	6.35	6.22	1.93
Si-doped g-C_3N_4	3.49	3.77	6.31	6.36	2.19
Ge-doped g-C_3N_4	3.18	3.41	6.33	6.21	3.02

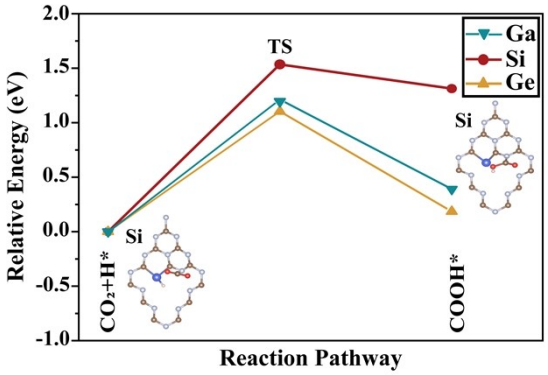


Figure S7 Potential energy diagrams for CO_2 reduction to COOH* at pyridinic N on the g-C_3N_4 doped with Si, Ga and Ge. Geometries of the reactant and the product on the Si-doped g-C_3N_4 are shown as the examples. Blue balls represent Si atoms.

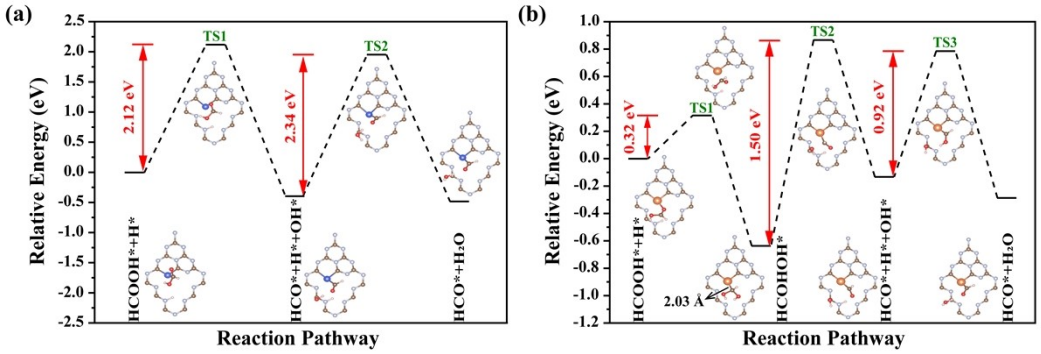


Figure S8 Potential energy diagrams for HCOOH reduction to HCO* on the Si-doped (a) and the Ga-doped (b) g-C_3N_4. Blue and orange balls represent Si and Ga atoms, respectively.

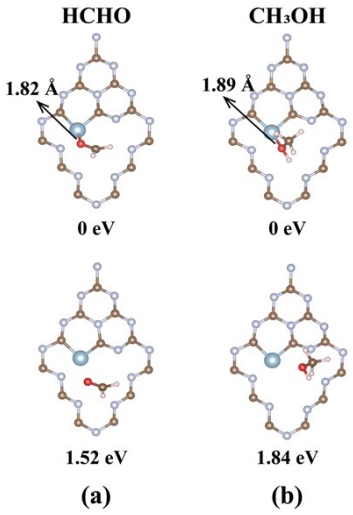


Figure S9 Geometries and potential energies of HCHO (a) and CH_3OH (b) on the Al doped g-C_3N_4. Top panels: O atoms in HCHO and CH_3OH form bonds with Al. Bottom panels: HCHO and CH_3OH are desorbed from the catalyst. Potential energies of the geometries in top panels are set to zero.

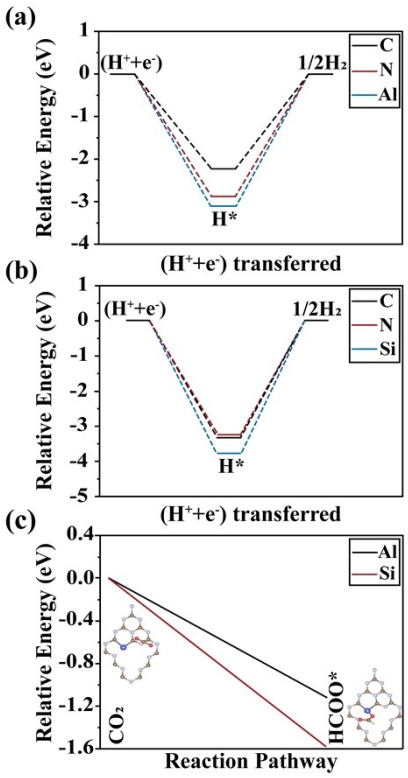


Figure S10 Gibbs free energy profiles for hydrogen evolution reactions (HER) on the Al-doped g-C_3N_4 (a), HER on the Si-doped g-C_3N_4 (b), and CO_2 reduction to HCOO* on the Al- and Si-doped g-C_3N_4 (c).

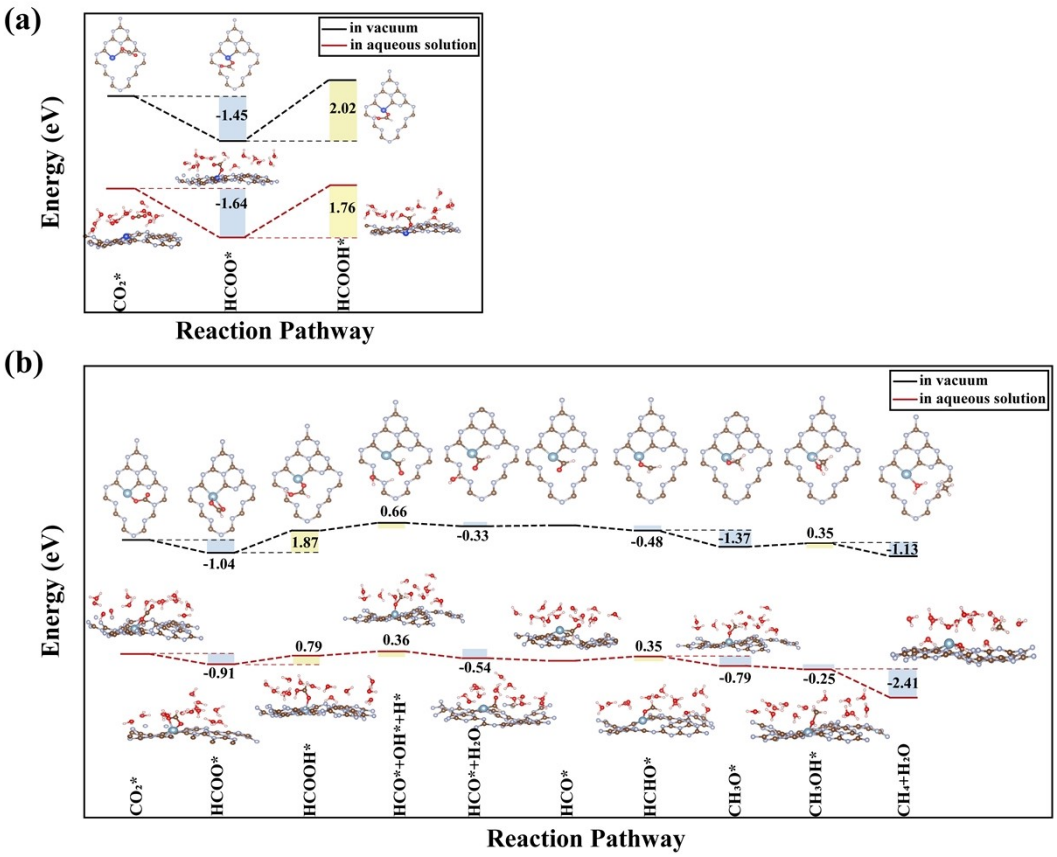


Figure S11 Gibbs free energy diagrams for CO_2RR on the Si- (a) and Al-doped (b) g-C_3N_4 in vacuum and in aqueous solution.

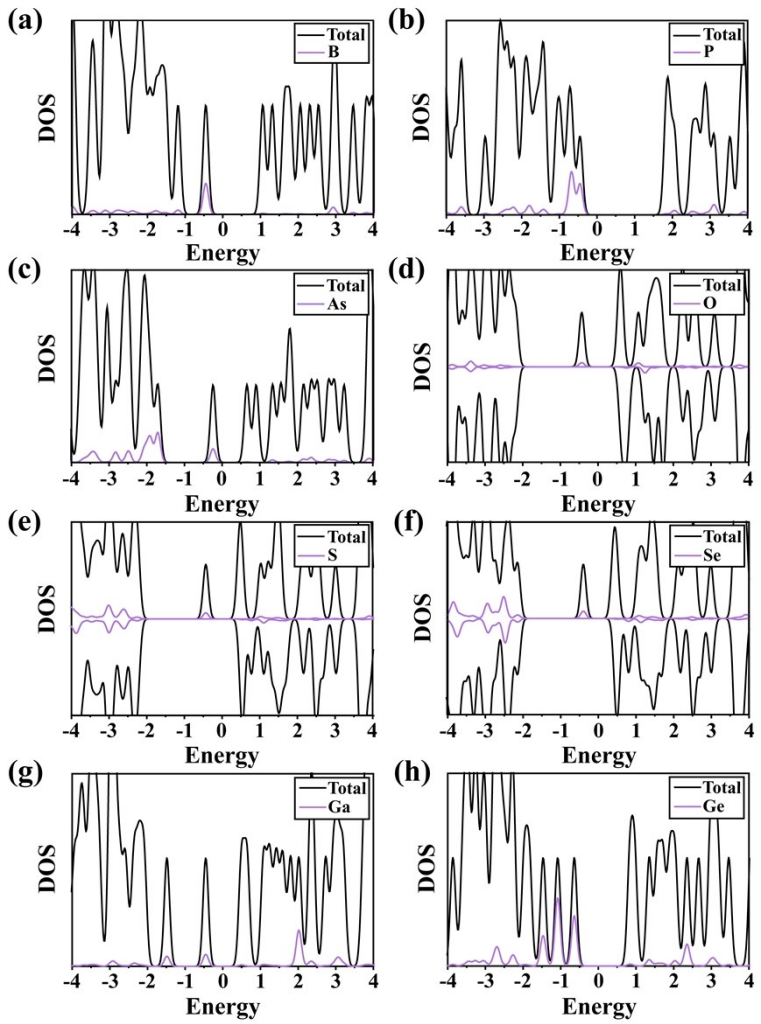


Figure S12 Total and projected density of states (DOS) of the B- (a), P- (b), As- (c), O- (d), S- (e), Se- (f), Ga- (g) and Ge-doped (h) g-C_3N_4. Energy zero corresponds to the Fermi level. Spin polarization is considered in the O-, S- and Se-doped g-C_3N_4. For clarity, magnitude of the projected DOS in all panels are enlarged by three times.