Supporting Information

Mechanism of CO_2 Photoreduced by Selenium-doped Carbon Nitride with Cobalt Cluster as Cocatalyst

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Table S1. The formation energy (E_{form}) of different N and C sites doping systems.

Site	E_{form} (eV)	Site	E_{form} (eV)
N1	-0.37	C1	3.64
N2	-0.54	C2	4.00
N3	-0.44	C3	3.43
N4	-0.25	C4	3.95
N5	-0.50	C5	3.56
N6	-0.33	C6	4.08
N7	0.25		

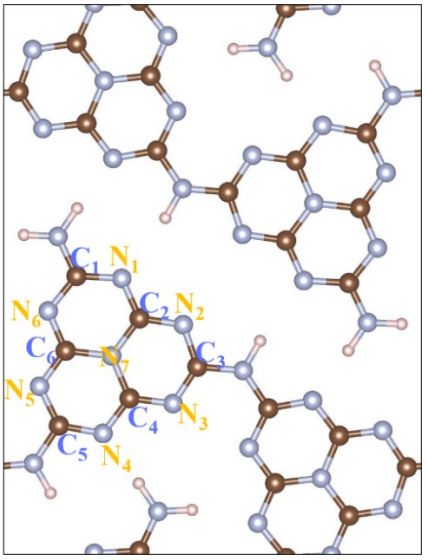

Fig. S1. The structural schematic diagrams of Se-decorated melon-based CN. The brown, grey, and light pink balls represent C, N, and H atoms, respectively.

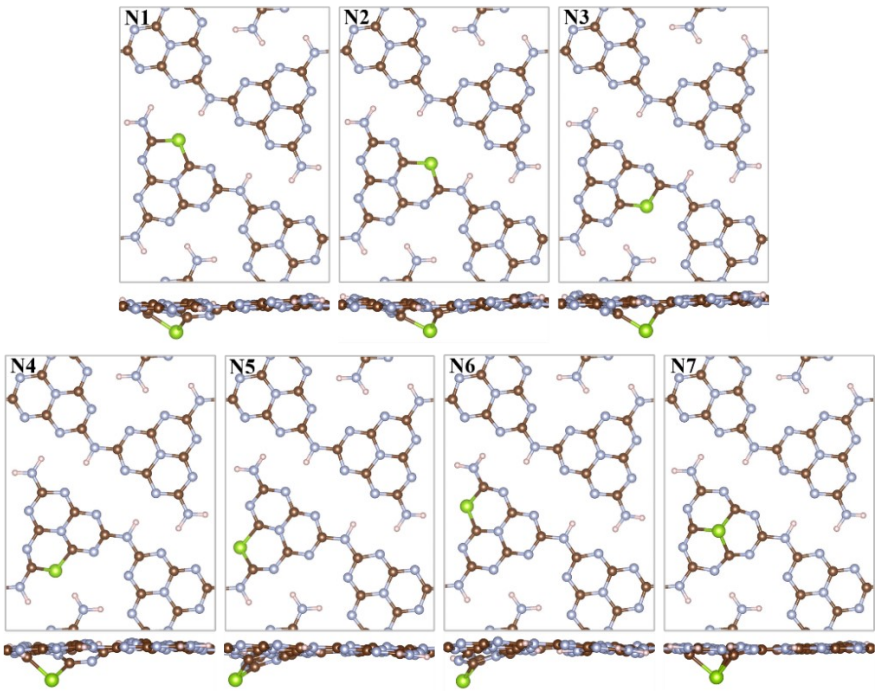

Fig. S2. Top and side views of geometric structure of Se-doped CN of the possible doping sites (N1, N2, N3, N4, N5, N6, N7). The brown, grey, light pink and green balls represent C, N, H and Se atoms, respectively.

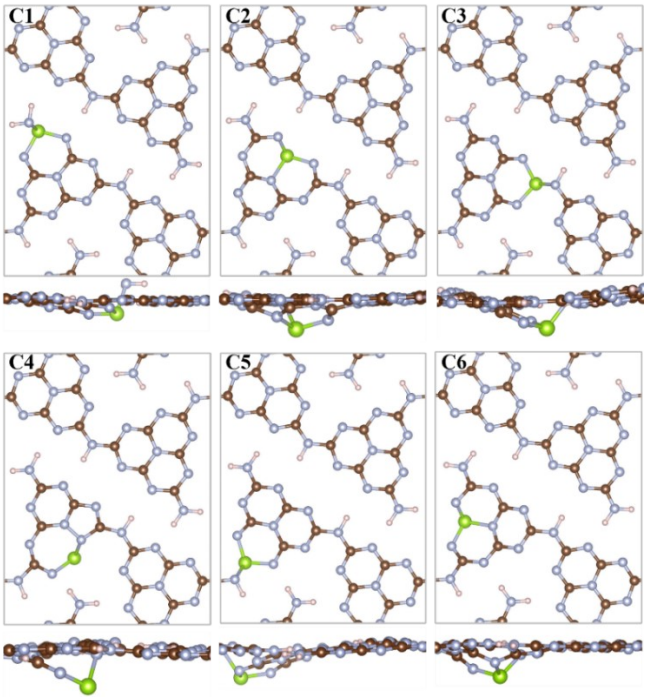

Fig. S3. Top and side views of geometric structure of Se-doped CN of the possible doping sites (C1, C2, C3, C4, C5, C6). The brown, grey, light pink and green balls represent C, N, H and Se atoms, respectively.

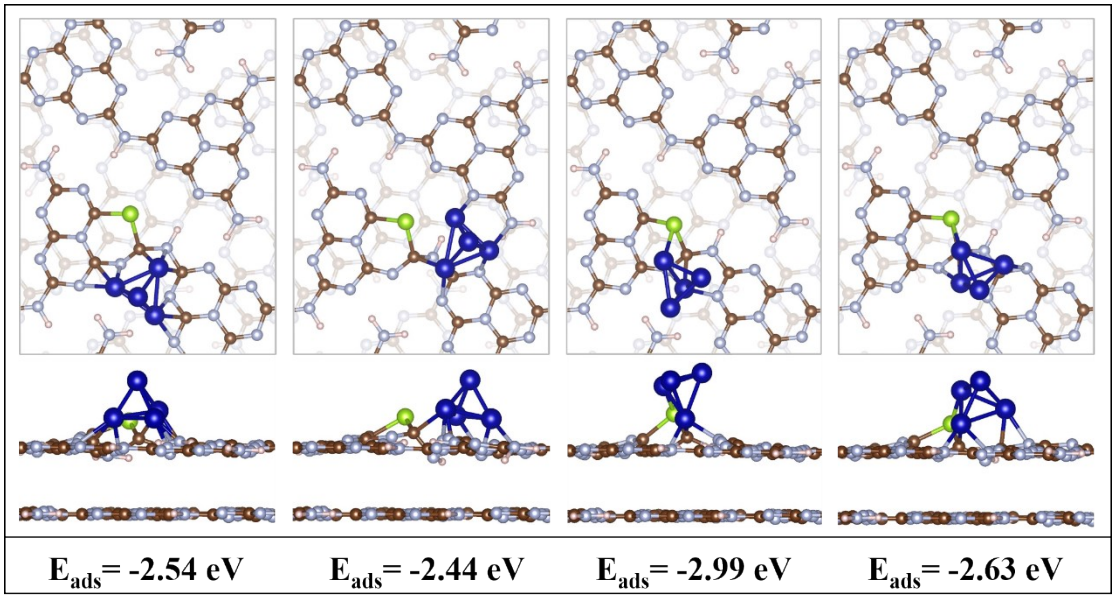

Fig. S4. Top and side views of geometric structure of Co_4@SeN_2. The brown, grey, light pink, green and blue balls represent C, N, H, Se and Co atoms, respectively.

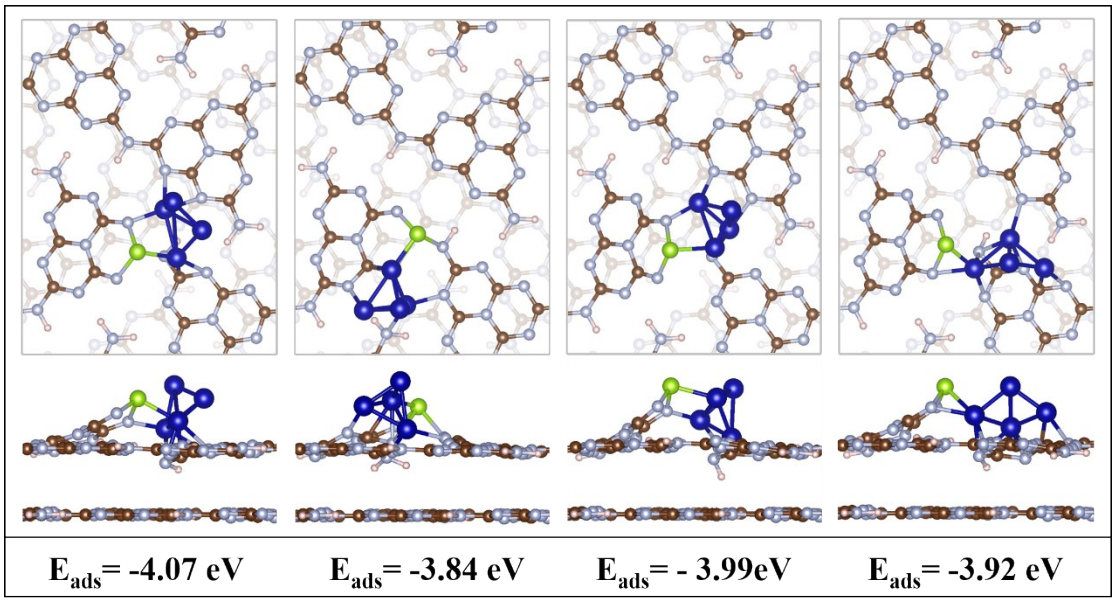

Fig. S5. Top and side views of geometric structure of Co_4@SeC_3. The brown, grey, light pink, green and blue balls represent C, N, H, Se and Co atoms, respectively.

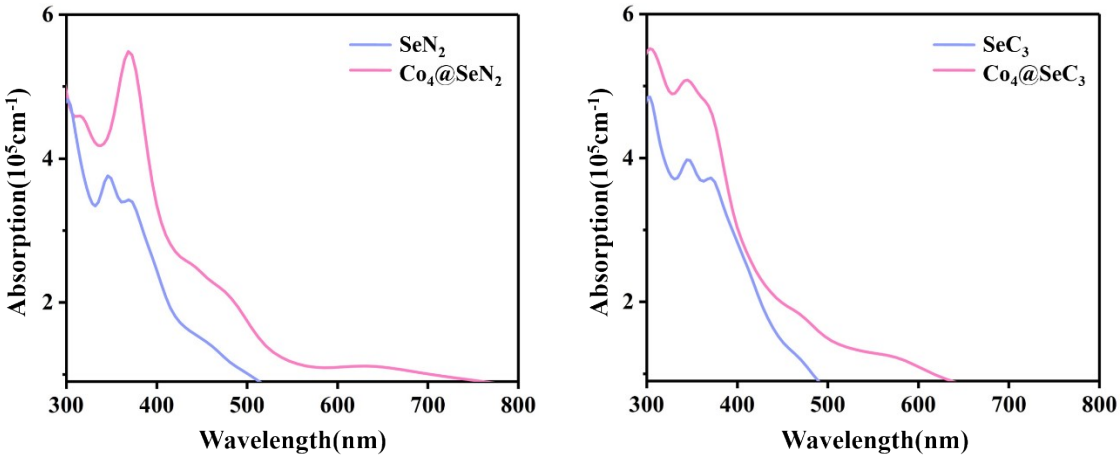

Fig. S6. Optical absorption behaviors of photocatalyst.

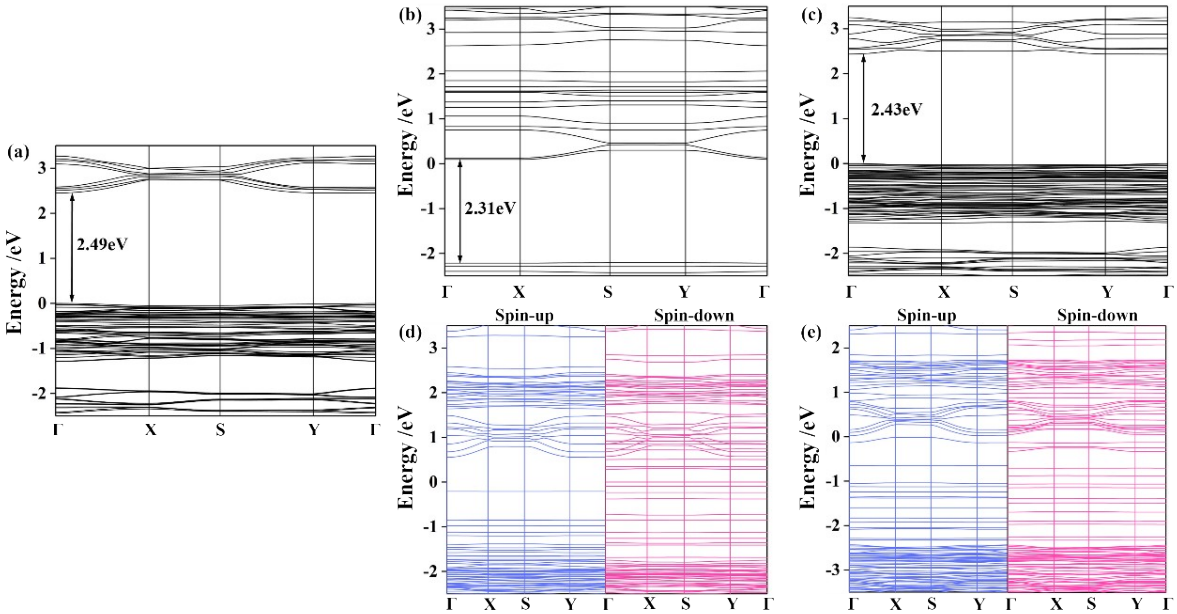

Fig. S7. Band structure of (a)pure melon (b)SeN_2 (c)SeC_3 (d)Co_4@SeN_2 and (e) Co_4@SeC_3.

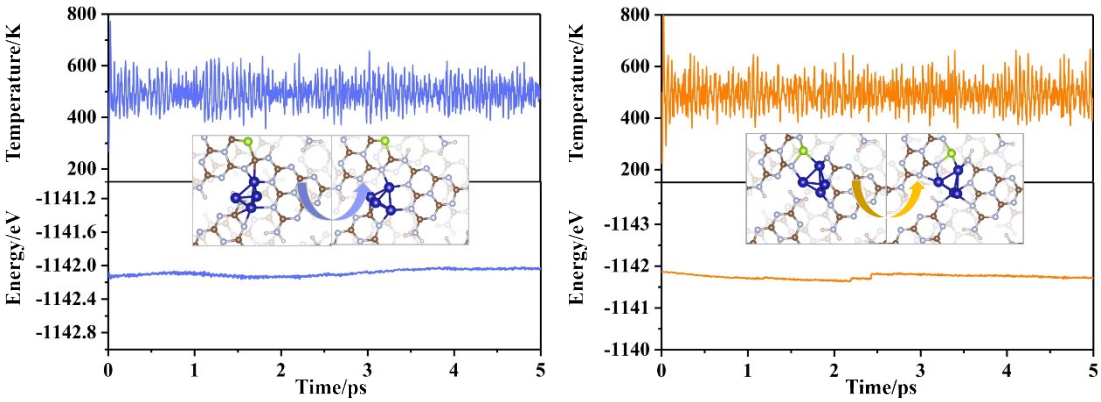

Fig. S8. Variations of temperature and energy as a function of (a) Co_4@SeN_2 (b) Co_4@SeC_3 the time for AIMD simulations of insert is top view of the snapshot of atomic configuration.

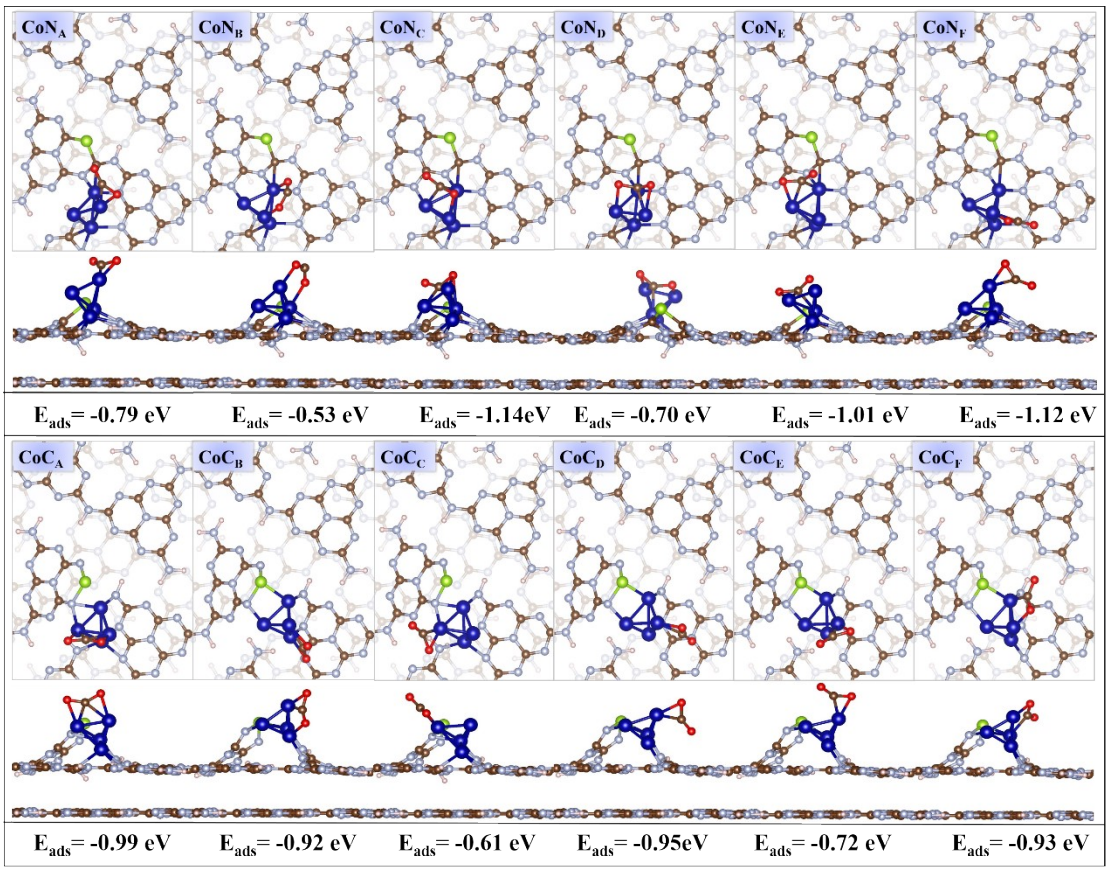

Fig. S9. The adsorption configuration of CO_2, where CoN_A-CoN_F are the adsorption situations on Co_4@SeN_2, and CoC_A-CoC_F are the adsorption results on Co_4@SeC_3.

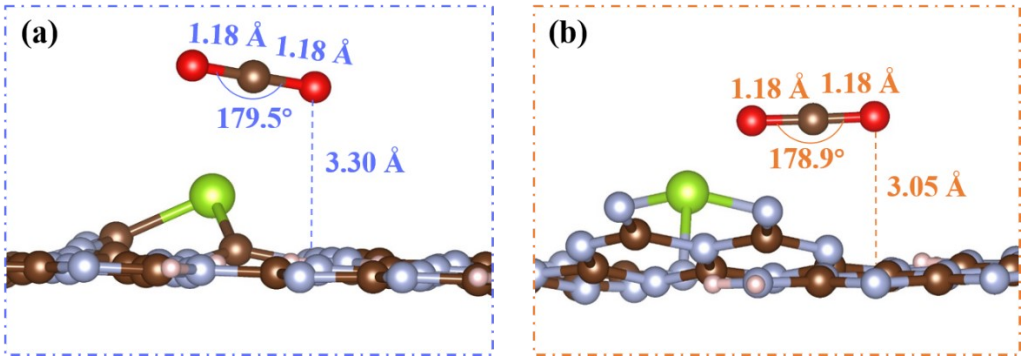

Fig. S10. The most stable adsorption configurations of CO_2 in (a) SeN_2 (b) SeC_3. The bluish violet frame indicates n-site doping, and the orange frame indicates C-site doping.

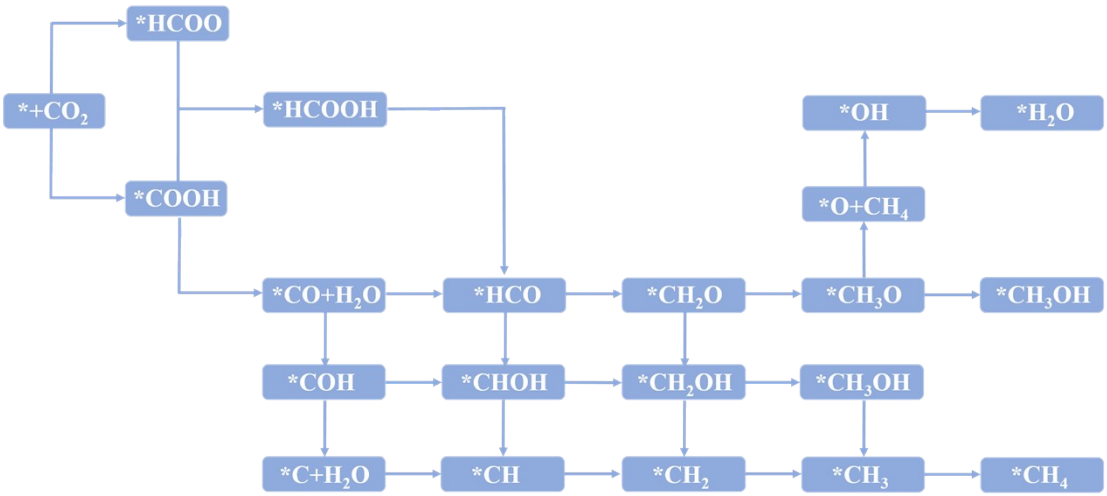

Fig. S11. All considered reaction pathways for CO_2 reduction.

Table S2. Calculated Gibbs free energies, T*S, EZPE (in eV) of intermediates in complicated paths

$Co_4@SeN_2$	Gibbs energies	$T*S$ (eV)	E_{ZPE} (eV)	$Co_4@SeC_3$	Gibbs energies	$T*S$ (eV)	E_{ZPE} (eV)
$*CO_2$	0.26	0.11	0.31	$*CO_2$	0.39	0.18	0.30
*COOH	0.53	0.15	0.60	*COOH	0.57	0.13	0.62
*HCOO	0.45	0.16	0.64	*HCOO	0.65	0.18	0.73
*HCOOH	0.84	0.16	0.91	*HCOOH	0.93	0.48	1.15
*CO	0.17	0.08	0.20	*CO	0.16	0.10	0.21
*COH	0.45	0.11	0.49	*COH	0.42	0.14	0.49
*CHO	0.41	0.09	0.44	*CHO	0.37	0.13	0.43
*C	0.10	0.02	0.11	*C	0.22	0.04	0.23
*CHOH	0.71	0.14	0.77	*CHOH	0.74	0.13	0.78
$*CH_2O$	0.71	0.15	0.78	$*CH_2O$	0.72	0.13	0.79
$*CH_2OH$	1.01	0.15	1.08	$*CH_2OH$	1.01	0.16	1.09
$*CH_3OH$	1.33	0.21	1.43	$*CH_3OH$	1.04	0.27	1.18
$*CH_3O$	0.96	0.18	1.06	$*CH_3O$	1.03	0.16	1.11
*CH	0.34	0.14	0.40	*CH	0.37	0.03	0.38
$*CH_2$	0.59	0.05	0.60	$*CH_2$	0.62	0.07	0.64
$*CH_3$	0.81	0.17	0.90	$*CH_3$	0.87	0.12	0.92
$*CH_4$	1.07	0.34	1.24	$*CH_4$	1.37	0.13	1.43
O	0.06	0.04	0.07	*O*	0.06	0.04	0.08
*OH	0.30	0.10	0.34	*OH	0.34	0.07	0.37
$*H_2O$	0.62	0.18	0.70	$*H_2O$	0.57	0.15	0.64

Each step of photochemistry is treated as the simultaneous transfer of proton-electron pairs. For

example, the reaction mechanism for CO_2 reduction to CO is illustrated below,

$$CO_2(g) \rightarrow *CO_2 \quad (1)$$

$$*CO_2 + H^+ + e^- \rightarrow *COOH \quad (2)$$

$$*COOH + H^+ + e^- \rightarrow *CO + H_2O_{(l)} \quad (3)$$

$$*CO \rightarrow * + CO_{(g)} \quad (4)$$

where * stands for the adsorption site. Using the state of gaseous CO_2 which is unbound above surface as a reference, the Gibbs free energy is represented as,

$\Delta G[*CO_2] = G[*CO_2] - (G[*] + G[CO2])$

$\Delta G[*COOH] = G[*COOH] - (G[*] + G[CO2] + G[H])$

$\Delta G[*CO] = G[*CO] + G[H2O] - (G[*] + G[CO2] + 2G[H])$

$\Delta G[CO] = G[CO] + G[H2O] - (G[CO2] + 2G[H])$

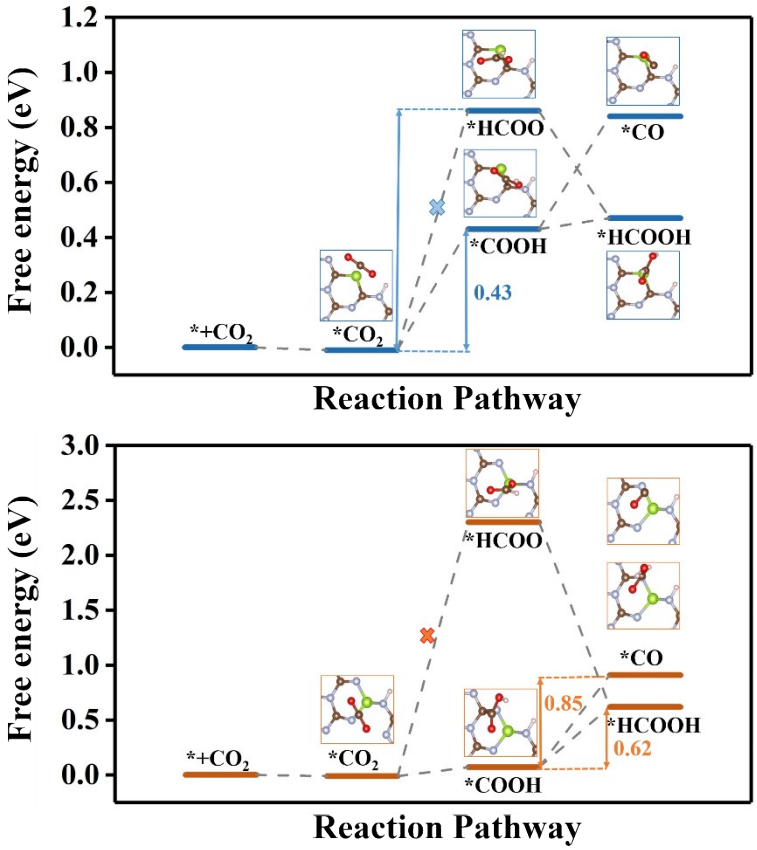

Fig. S12. Free energy diagrams for CO_2 reducing to CO and HCOOH via a 2-ele process on (a) SeN_2 (b) SeC_3.

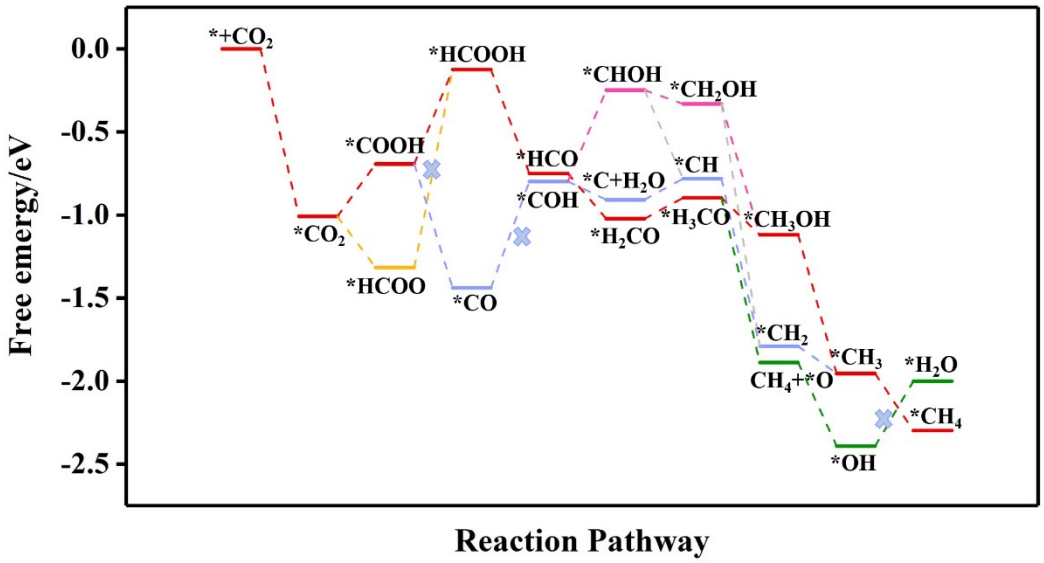

Fig. S13. Free-energy profile for CH_3OH and CH_4 production of CRR on $Co_4@SeN_2$.

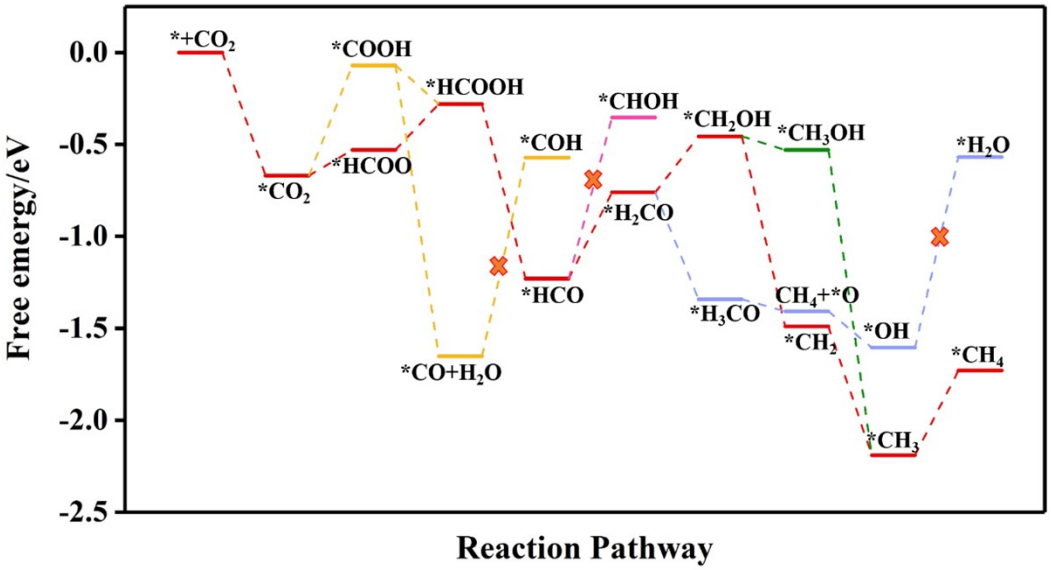

Fig. S14. Free-energy profile for CH_3OH and CH_4 production of CRR on $Co_4@SeC_3$.