Supporting Information

Mechanistic Study of DETA-Modified CdS for Carbon Dioxide Reduction

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The adsorption energy (*E*ads) was defined as:

$$E_{ads} = E_{A\text{-}S} - E_S - E_A \quad (1)$$

where E_A, E_S and $E_{A\text{-}S}$ refer to the energies of isolated product (A),slab (S) with clean surface, and the adsorbed system after corrected by the solvation effect, respectively.[1]

The change of Gibbs free energy (ΔG) was computed as follows:

$$\Delta G = \Delta E + \Delta E_{ZPE} - T\Delta S \quad (2)$$

where ΔE is the electronic energy change from the total energy, and ΔE_{ZPE} and ΔS are the difference between the zero-point energy and entropy, respectively. T is the room temperature (298.15 K).[2]

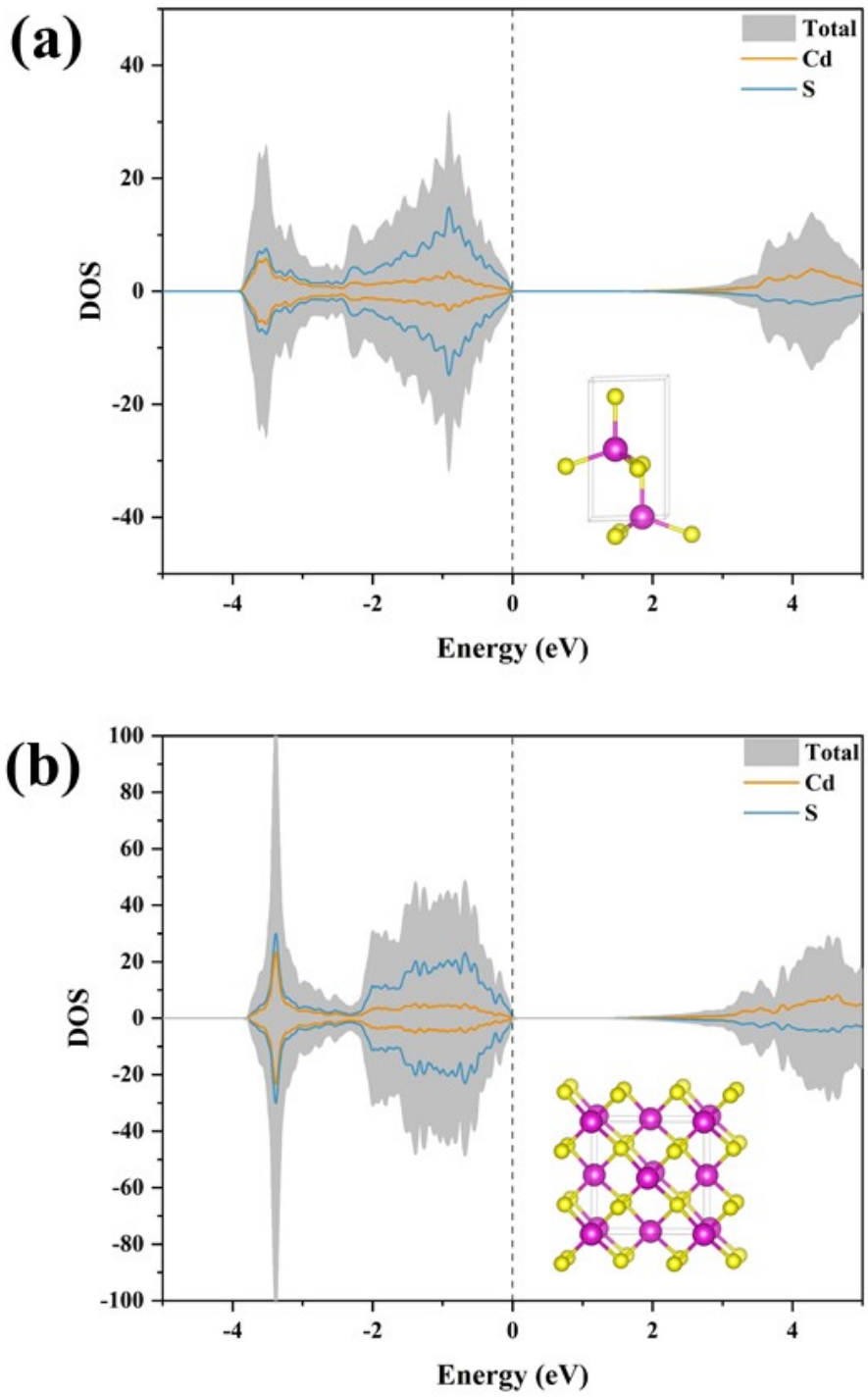


Fig. S1 The DOS of hexagonal (a) and cubic (b) CdS bulk. Atomic structures of CdS bulk were showed in insets. The magenta, and yellow balls represent Cd and S atoms, respectively.

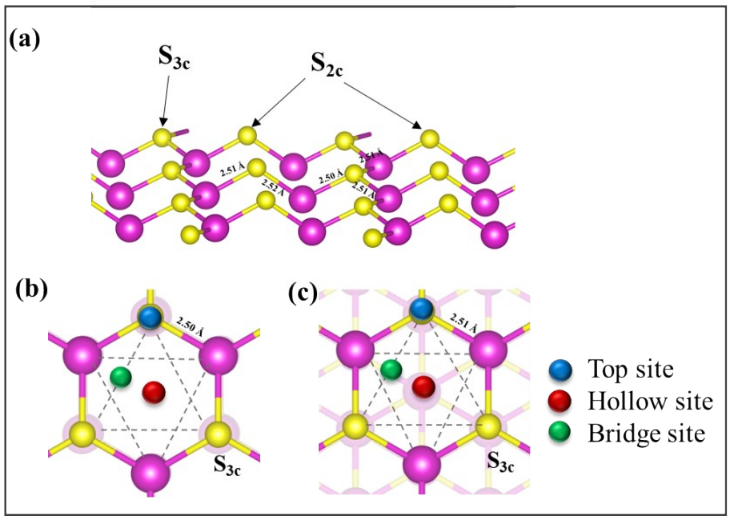


Fig. S2 Possible adsorption states on the (a)CdS (101), (b) CdS (001), and (c) CdS (111) of the sulfur terminations. The magenta, and yellow balls represent Cd and S atoms, respectively.

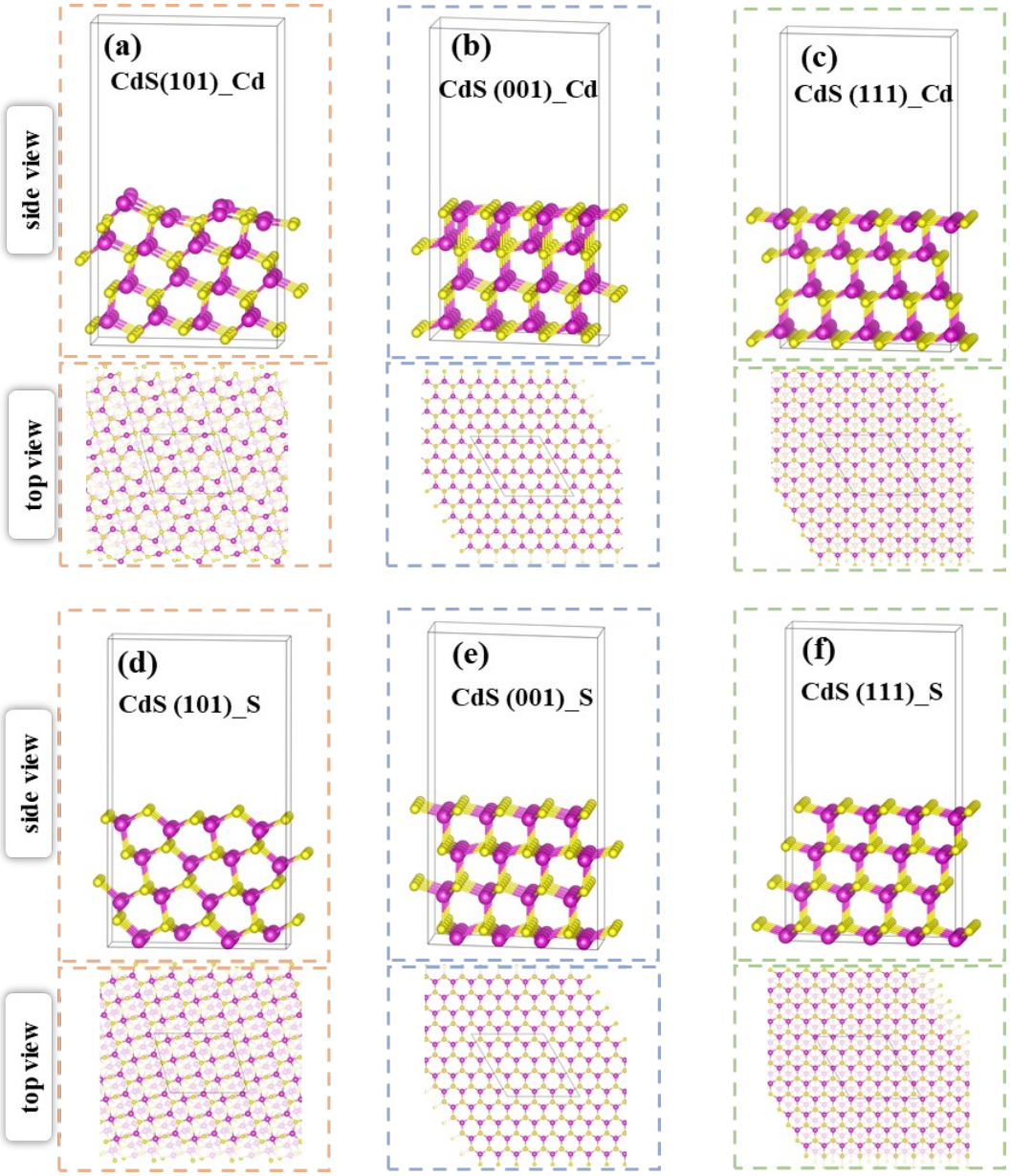


Fig. S3 Top and side views of the slab models of hexagonal (a-b、d-e) and cubic (c、f) CdS with different exposed facets. The magenta, and yellow balls represent Cd and S atoms, respectively.

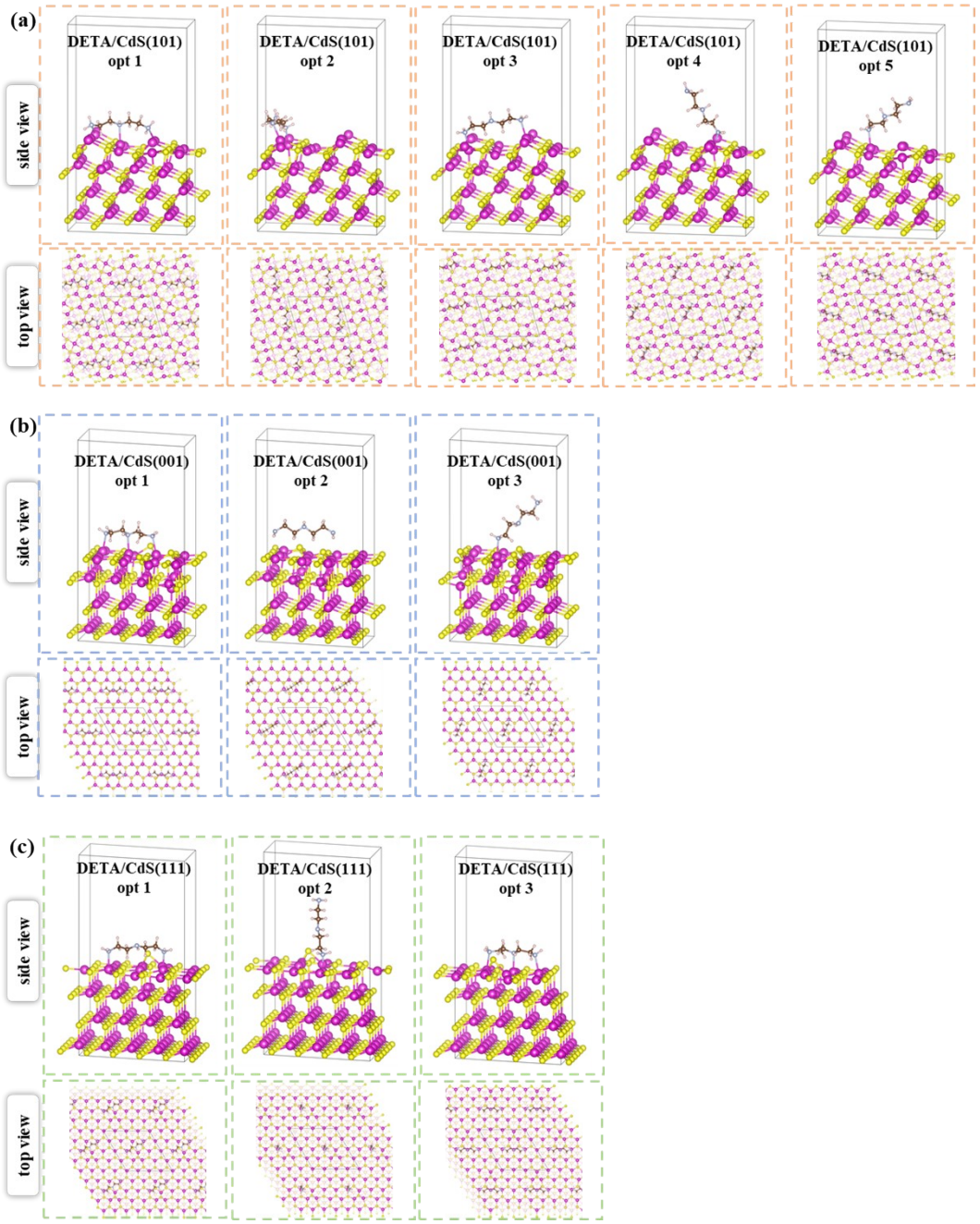


Fig. S4 Top and side views of chemisorption configuration of the (a)DETA/CdS (101), (b) DETA/CdS (001), and (c) DETA/CdS (111). The gray, brown, white, magenta, and yellow balls represent N, C, H, Cd and S atoms, respectively.

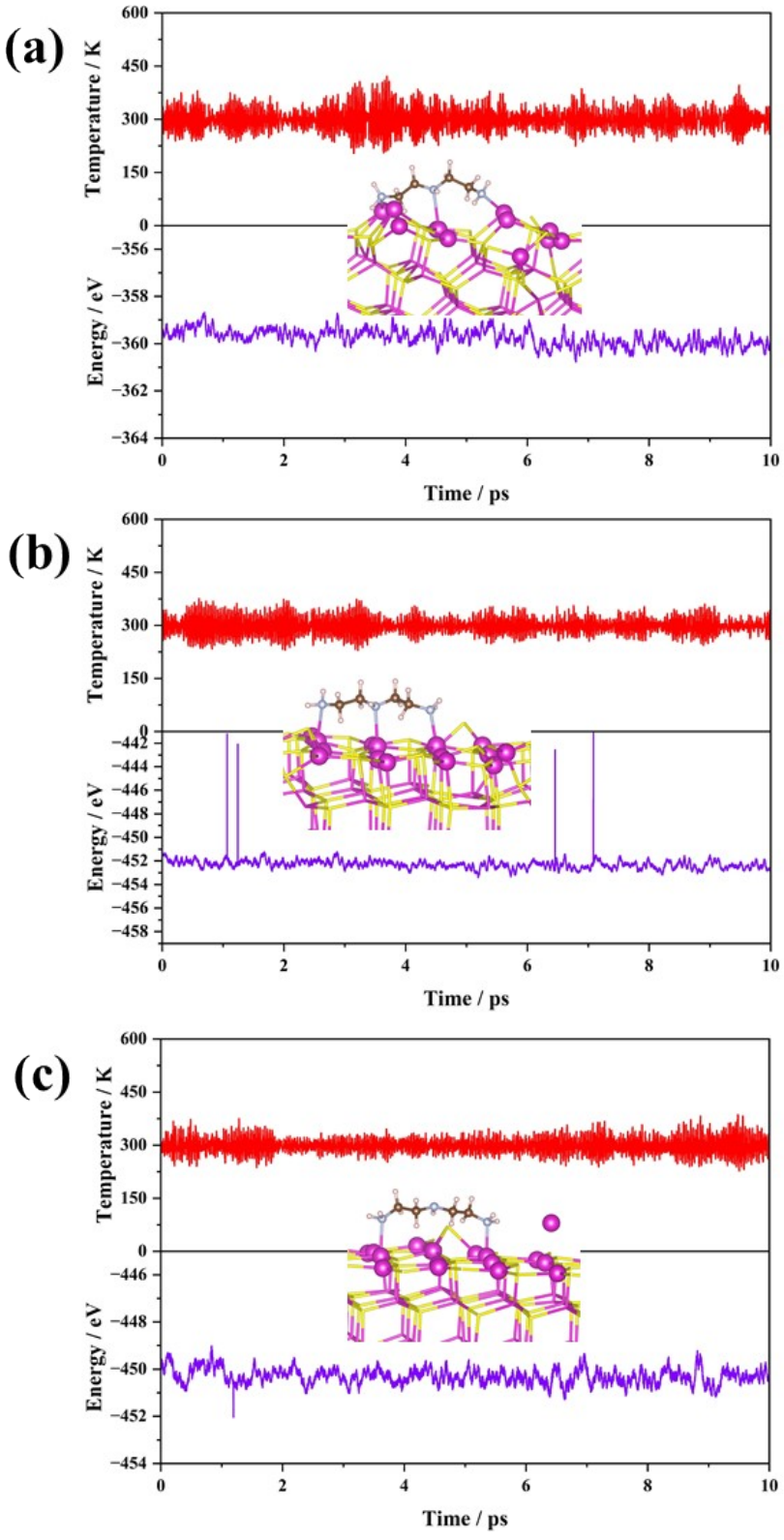


Fig. S5 Alteration of temperature and energy by AIMD simulations of the (a)DETA/CdS (101), (b)DETA/CdS (001), and (c)DETA/CdS (111); the simulation is going at 300 K for 10 ps with a time step of 1 fs. The gray, brown, white, magenta, and yellow balls represent N, C, H, Cd and S atoms, respectively.

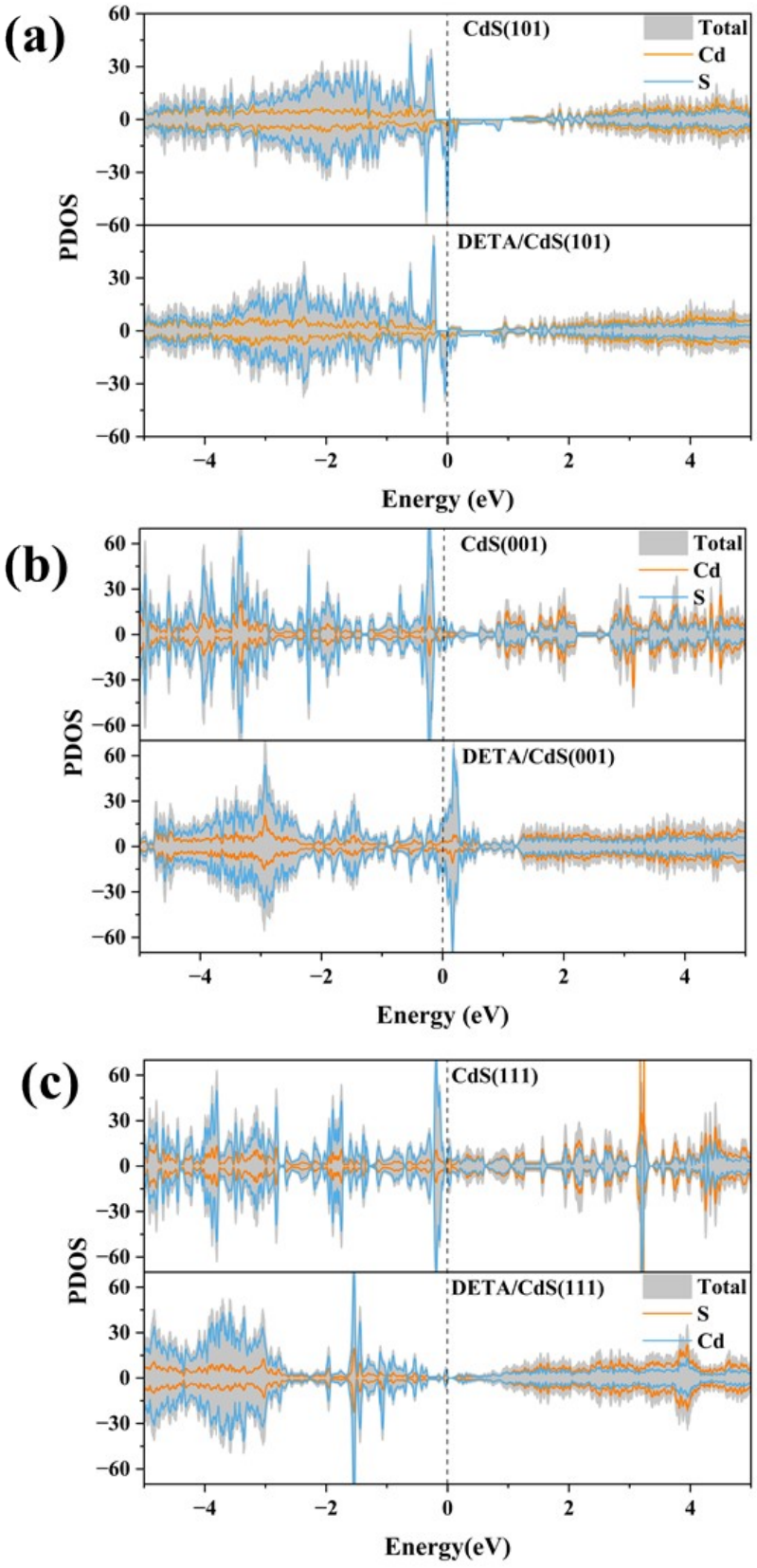


Fig. S6. PDOS of the conformation of DETA molecules before and after adsorption on the (a)CdS (101), (b) CdS (001), and (c)CdS (111) surface.

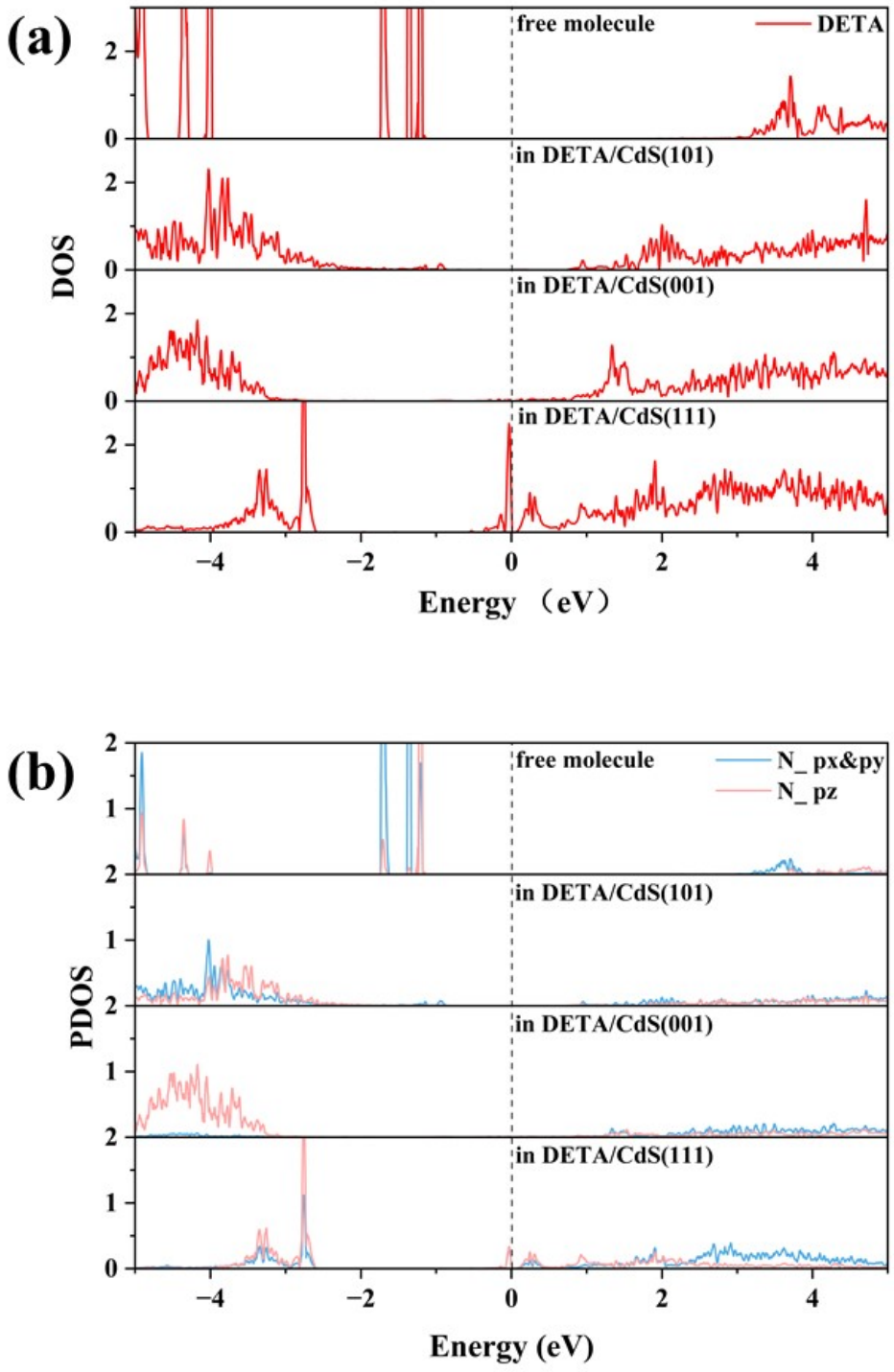


Fig. S7. (a) DOS of the adsorption configurations of DETA molecules on the CdS surface and (b) PDOS of N atoms.

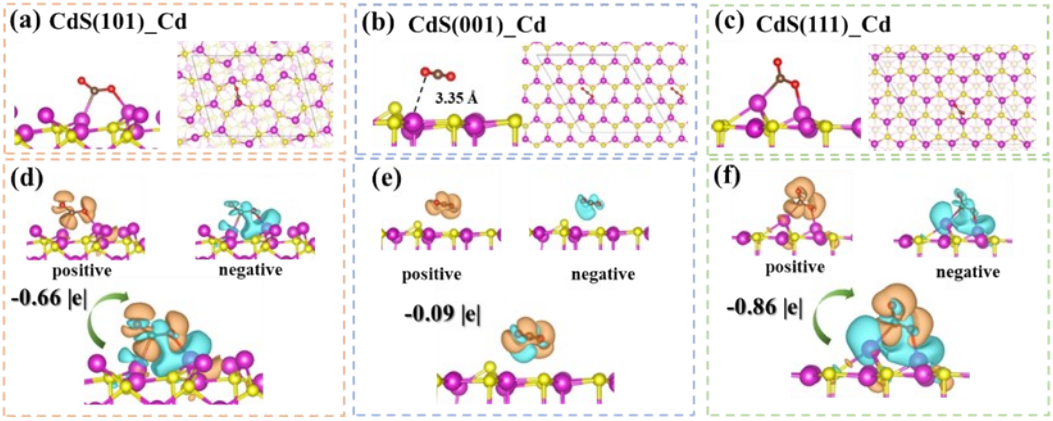


Fig. S8 The most stable adsorption configurations of CO_2 on CdS (a-c) and (d-f) charge density difference with the isovalues were set to 0.001 e $Å^{-3}$. Orange and cyan represent gaining and losing electrons, respectively. The red, gray, brown, white, magenta, and yellow balls represent O, N, C, H, Cd and S atoms, respectively.

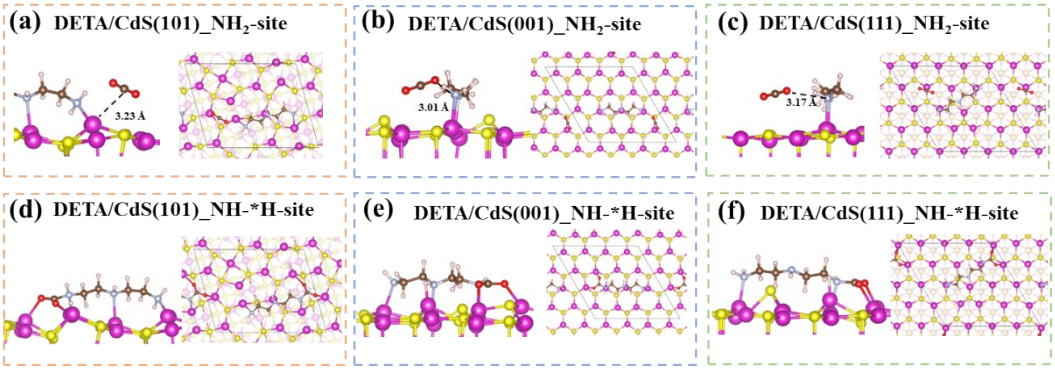


Fig. S9 The most stable adsorption configurations of CO_2 in DETA/CdS N site. The red, gray, brown, white, magenta, and yellow balls represent O, N, C, H, Cd and S atoms, respectively.

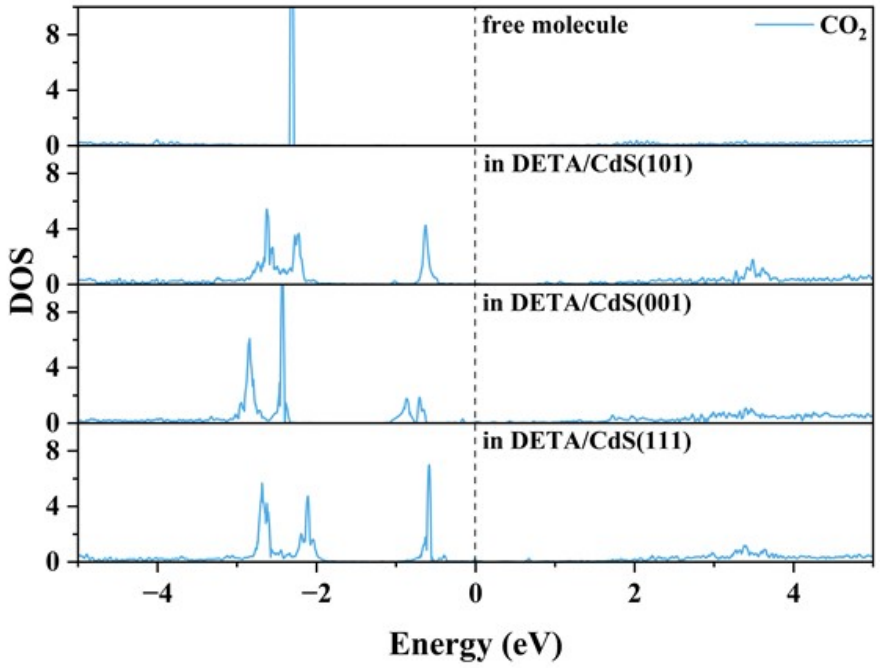


Fig. S10 DOS of the adsorption configurations of CO_2 molecules on the DETA/CdS surface.

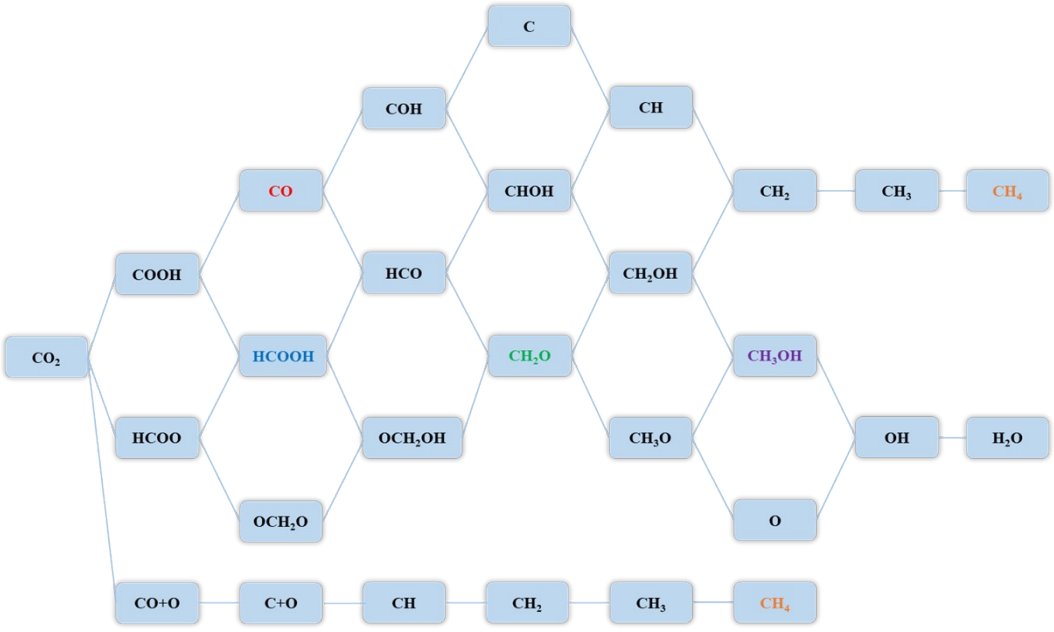
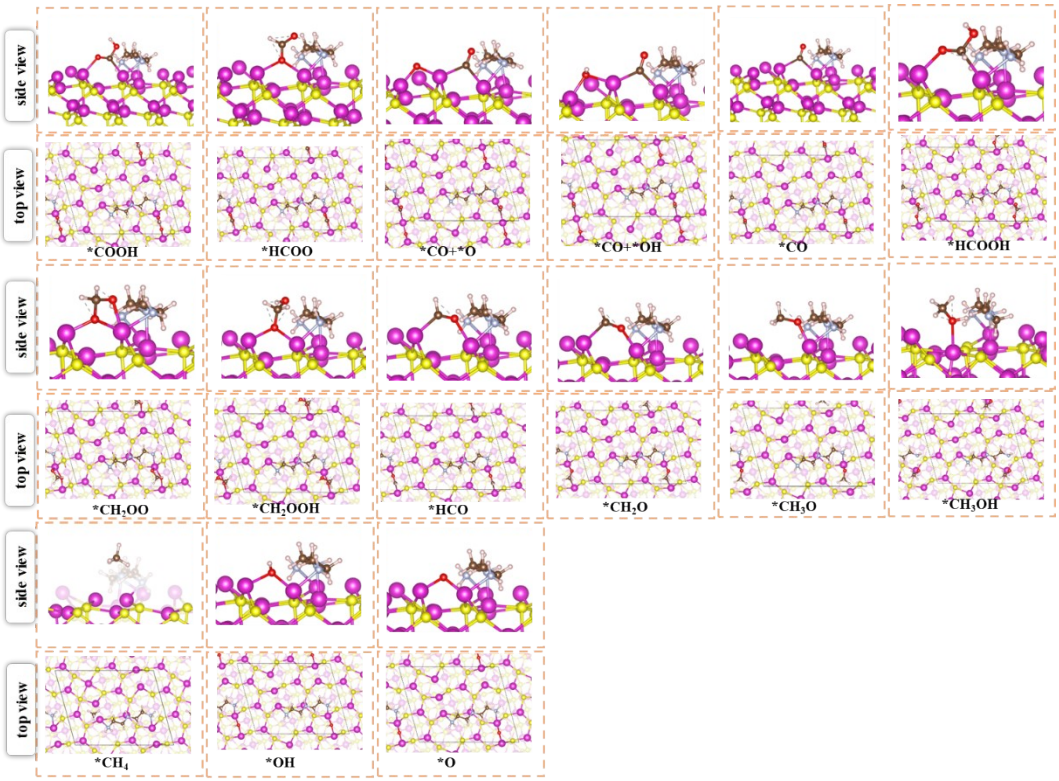
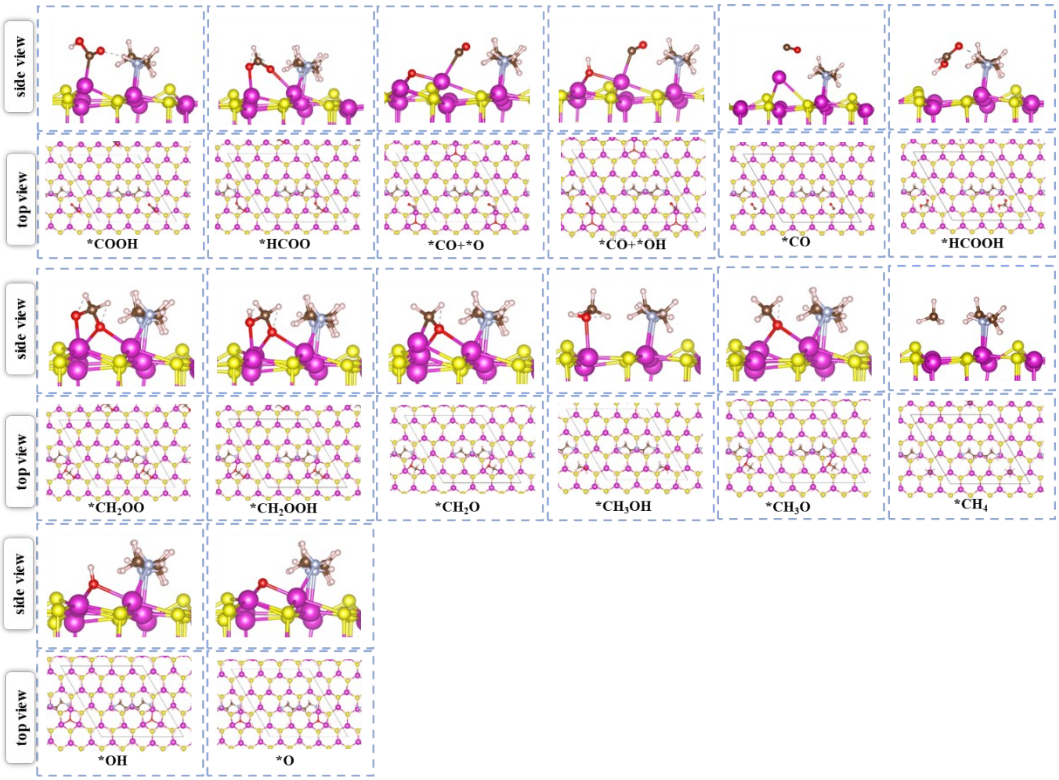


Fig. S11 Suggested reaction pathways for the CO_2RR. The initial CO_2 is shown at the center left. The final products are shown in color throughout the figure.


side view
top view
*COOH
*HCOO
*CO+*O
*CO+*OH
*CO
*HCOOH
side view
top view
*CH2OO
*CH2OOH
*HCO
*CH2O
*CH3O
*CH3OH
side view
top view
*CH4
*OH
*O


side view
top view
*COOH
*HCOO
*CO+*O
*CO+*OH
*CO
*HCOOH
side view
top view
*CH2OO
*CH2OOH
*CH2O
*CH3OH
*CH3O
*CH4
side view
top view
*OH
*O

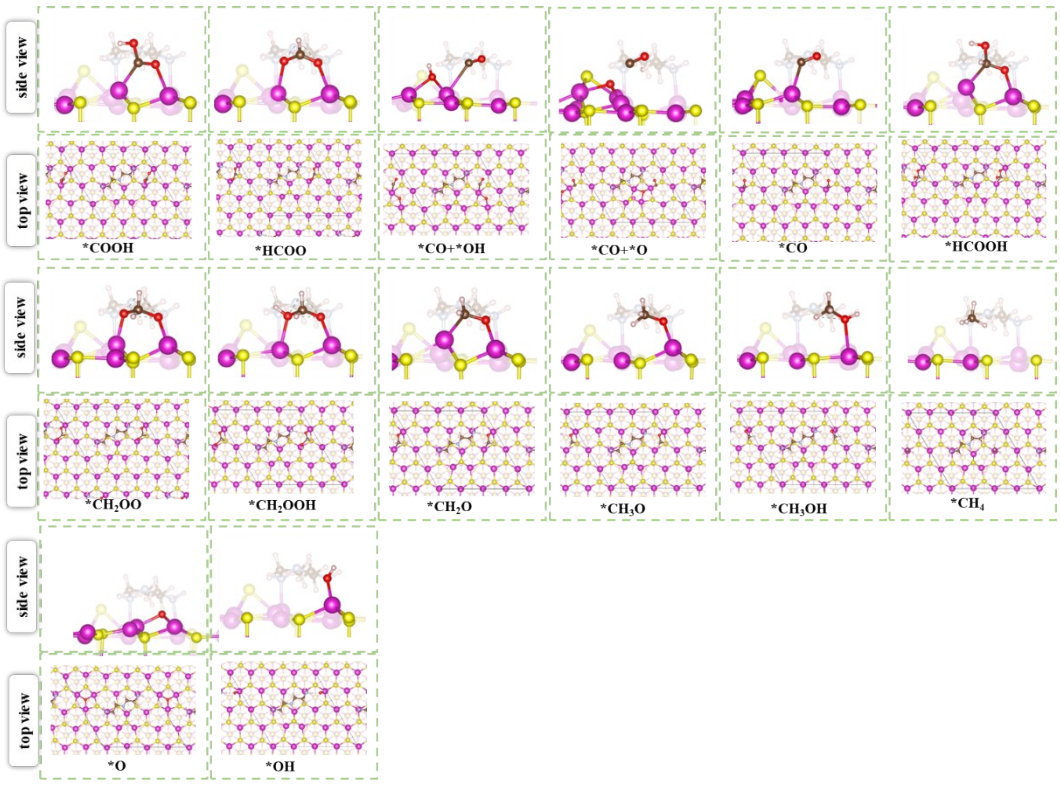


Fig. S12 Top and side views of the atomic configurations corresponding to different intermediates at each elementary step on the (a)DETA/CdS (101), (b) DETA/CdS (001), and (c) DETA/CdS (111) surface. The red, gray, brown, white, magenta, and yellow balls represent O, N, C, H, Cd and S atoms, respectively.

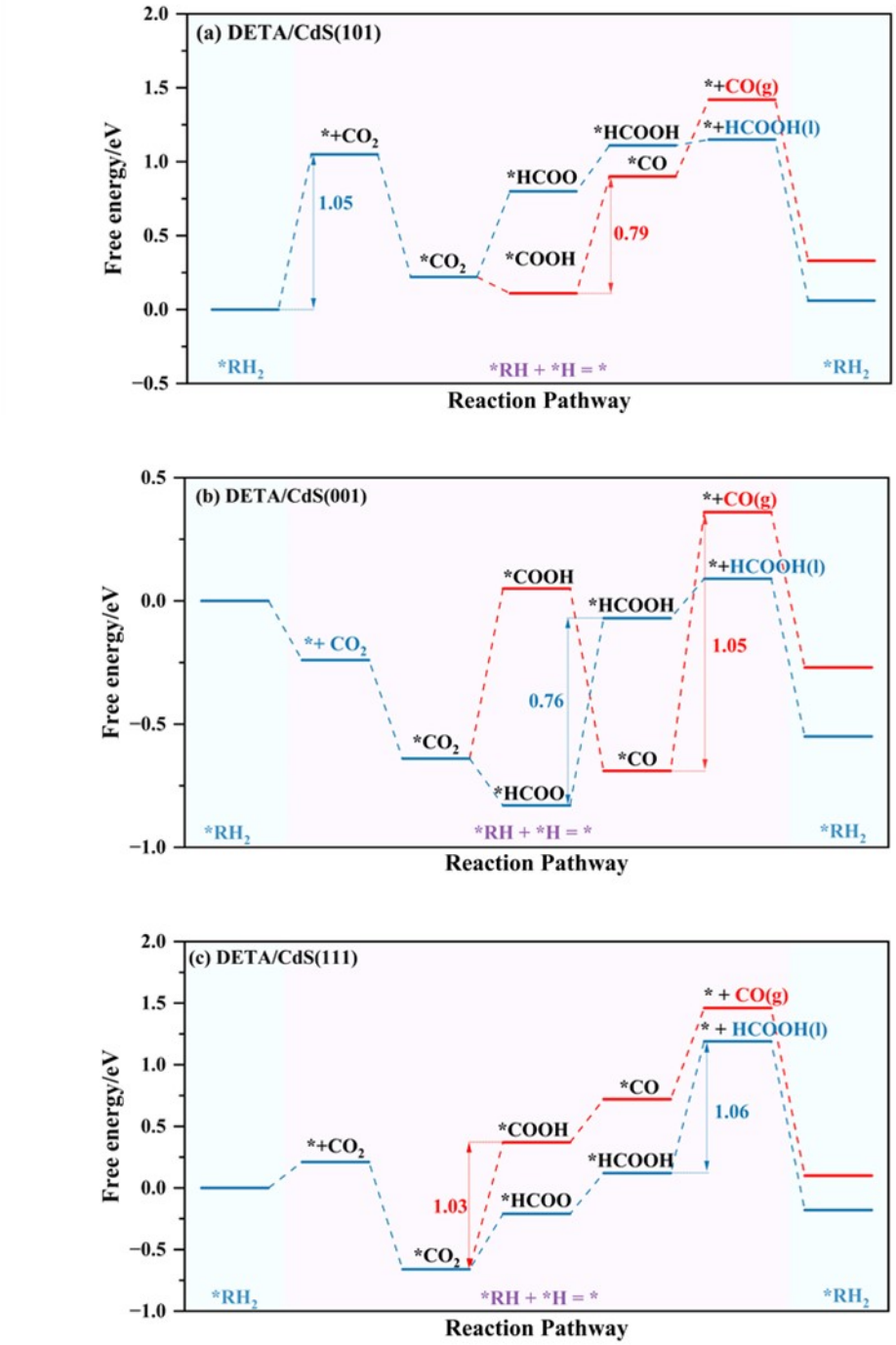


Fig. S13 Free energy diagrams for CO_2RR at the $*RH_2 \rightarrow *RH+*H$ sites on the (a)DETA/CdS (101), (b) DETA/CdS (001), and (c) DETA/CdS (111) surface.

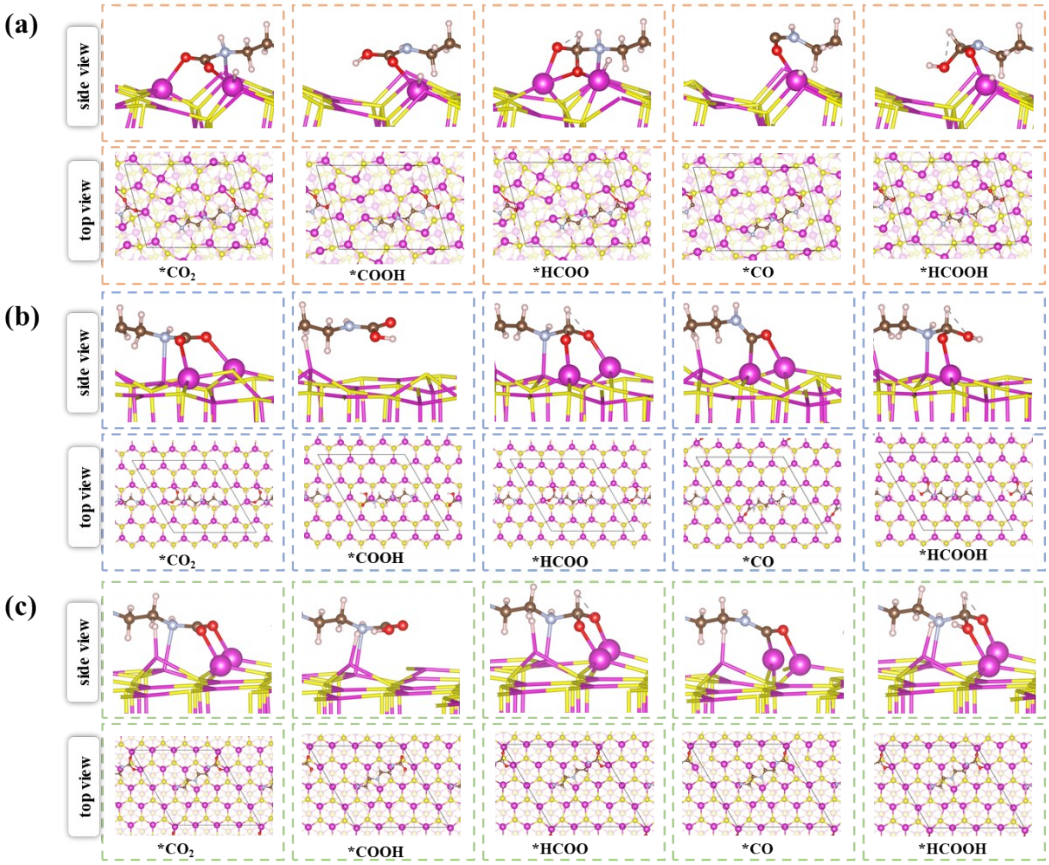


Fig. S14 Top and side views of the atomic configurations corresponding to different intermediates at each elementary step at the $*RH_2 \rightarrow *RH + *H$ sites on the (a)DETA/CdS(101), (b)DETA/CdS (001), and (c) DETA/CdS (111) surface. The red, gray, brown, white, magenta, and yellow balls represent O, N, C, H, Cd and S atoms, respectively.

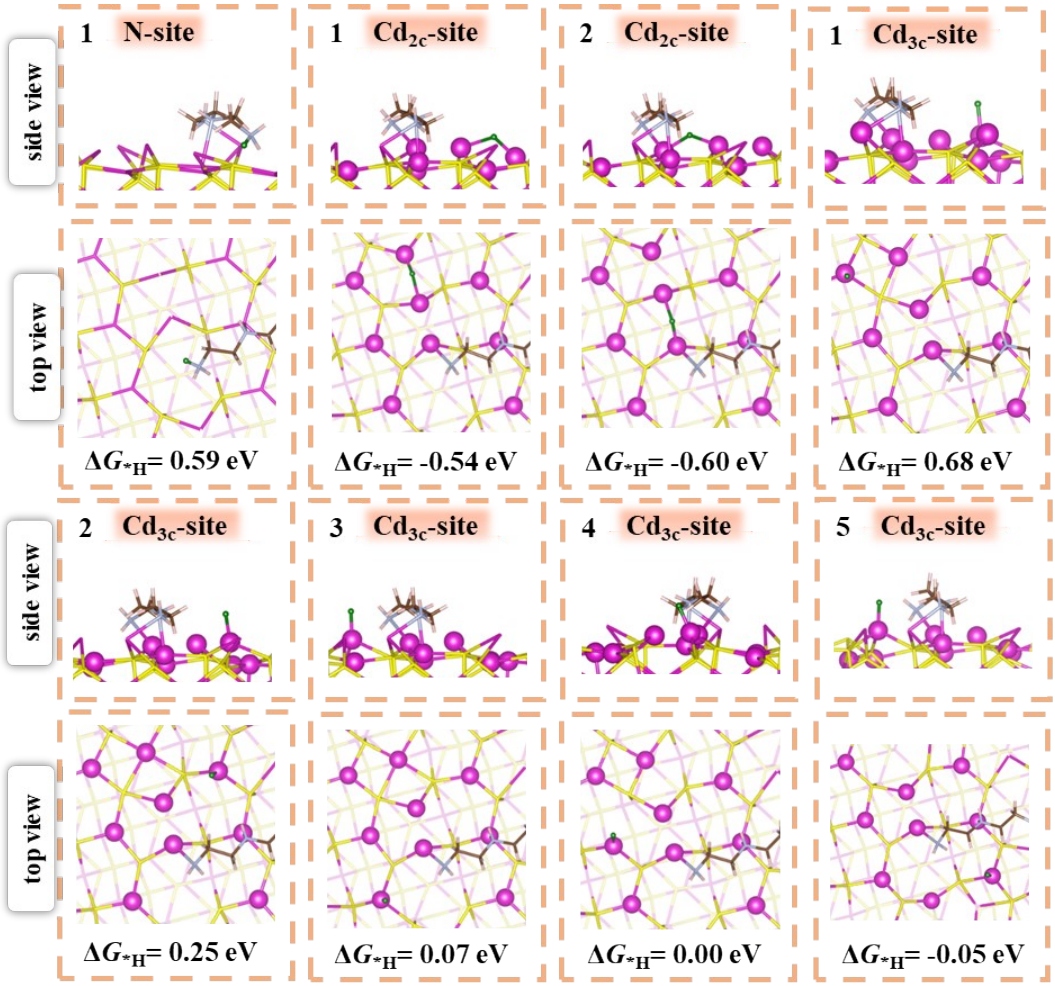


Fig. S15. Top and side views of the H adsorption structures and ΔG_{*H} at different sites of DETA/CdS(101), respectively. Green ball represents adsorbed H atom.

Table S1 Energy and structural information of DETA/CdS, where $E_{relative}$ (eV) represents the relative energy compared to opt1 and bond length(Å) of DETA absorbed on CdS.

Surfaces		$E_{relative}$ **(eV)**	**N-Cd/Å**
DETA/CdS(101)	opt1	0.00	2.45, 2.55, 2.39
	opt2	0.13	2.40, - , 2.33
	opt3	0.43	2.35, - ,2.45
	opt4	0.85	2.34
	opt5	0.98	2.38
DETA/CdS(001)	opt1	0.00	2.44, 2.48, 2.44
	opt2	1.13	-
	opt3	0.68	2.37
DETA/CdS(111)	opt1	0.00	2.37, - , 2.37
	opt2	1.56	2.28
	opt3	0.02	2.43, 2.46, 2.44

Table S2 Adsorption energy of (E_{ads}) of CO_2, C-O bond lengths (Å), ∠O-C-O (°) , bond angles(Å), and adsorption bond lengths (Å) of CO_2 absorbed on the DETA/CdS surface.

Surfaces	E_{ads} **(eV)**	**C-O$_a$**	**C-O$_b$**	**∠O-C-O**	**Cd-C**	**Cd-O$_a$**	**Cd-O$_b$**	**N-C**
CdS(101)	-0.30	1.26	1.22	136.14	2.34	2.24	-	-
CdS(001)	-0.69	1.18	1.17	178.98	-	-	-	-
CdS(111)	-1.41	1.29	1.22	128.88	2.30	2.18	-	-
DETA/CdS(101) _Cd-site	-0.82	1.29	1.25	124.18	2.26	2.14	-	-
DETA/CdS(001) _Cd-site	-1.80	1.30	1.23	127.07	2.25	2.28	-	-

DETA/CdS(111) _Cd-site	-1.49	1.32	1.24	122.57	2.26	2.19	-	-
DETA/CdS(101) _NH_2-site	0.20	1.18	1.18	177.47	-	-	-	-
DETA/CdS(001) _NH_2-site	-0.18	1.18	1.18	178.51	-	-	-	-
DETA/CdS(111) _NH_2-site	-0.15	1.17	1.18	179.18	-	-	-	
DETA/CdS(101) _NH-*H-site	-1.29	1.26	1.27	128.66	-	2.47	2.35	1.46
DETA/CdS(001) _ NH-*H-site	-0.98	1.26	1.27	129.30	-	2.43	2.35	1.45
DETA/CdS(111) _ NH-*H-site	-1.47	1.28	1.27	127.91	-	2.32	2.30	1.43

Table S3 Bader charge of CO_2, C, O_a and O_b atoms after CO_2 adsorption on CdS and DETA/CdS surfaces.

Surfaces	**CO_2**	**C**	**O_a**	**O_b**
CdS(101)	-0.66	+0.65	-0.67	-0.64
CdS(001)	-0.09	+1.35	-0.68	-0.76
CdS(111)	-0.86	+1.00	-0.99	-0.87
DETA/CdS(101)	-0.93	+1.33	-1.13	-1.13
DETA/CdS(001)	-0.90	+1.39	-1.17	-1.12
DETA/CdS(111)	-0.97	+1.31	-1.14	1.14

Table S4 Energy corrections of free molecules to the free energies. *E*, E_{sol}, *ZPE*, *TS*, and *G* are the total electronic energy(eV), the solvation energy correction(eV), the zero-point energy(eV), the entropy correction(eV), and free energy (eV) at 298.15 K, respectively.

Free molecules	***E* (eV)**	**E_{sol} (eV)**	***ZPE* (eV)**	***TS* (eV)**	***G* (eV)**
$H_{2(g)}$	-6.67	-6.75	0.27	0.40	-6.80
$CO_{2(g)}$	-22.99	-23.08	0.21	0.73	-23.49
$CO_{(g)}$	-14.80	-14.80	0.13	0.61	-15.19
$CH_2O_{(g)}$	-22.16	-22.30	0.7	0.68	-22.17
$CH_{4(g)}$	-24.05	-24.03	1.17	0.58	-23.33
$H_2O_{(l)}$	-14.22	-14.49	0.56	0.67	-14.50
$HCOOH_{(l)}$	-29.77	-30.18	0.88	0.77	-29.96
$CH_3OH_{(l)}$	-30.25	-30.42	1.35	0.79	-29.73
$DETA_{(l)}$	-108.98	-108.89	4.88	1.22	104.96

Table S5 Electronic energies (*E*), free energy (*G*), and corresponding thermodynamic energy corrections for the intermediate states where the * refers to adsorption on the surface. *E*, E_{sol}, *ZPE*, *TS*, and *G* are the total electronic energy(eV), the solvation energy correction(eV), the zero-point energy(eV), the entropy correction(eV), and free energy (eV) at 298.15 K, respectively.

Surfaces	**Intermediate state**	***E* (eV)**	**E_{sol} (eV)**	***ZPE* (eV)**	***TS* (eV)**	***G* (eV)**
CdS(101)	clean surface	-251.98	-252.15	-	-	-
	$*CO_2$	-275.02	-275.52	-	-	-
	*H	-256.02	-256.21	0.16	0.01	-256.05
DETA/CdS(101)	clean surface	-362.92	-362.94	-	-	-
	$*CO_2$(Cd-site)	-386.02	-386.84	029	021	-386.66
	$*CO_2$(N-site)	-385.65	-385.82	0.20	0.32	-385.60

Surfaces	Intermediate state	*E* (eV)	E_{sol} (eV)	*ZPE* (eV)	*TS* (eV)	*G* (eV)
	*COOH	-390.21	-390.05	0.59	0.189	-389.55
	*OCHO	-390.98	-390.93	0.61	0.21	-390.42
	*CO+*O	-384.81	-385.41	0.24	0.23	-385.29
	*HCOOH	-393.11	-393.16	0.89	0.24	-392.39
	*OCH_2O	-393.47	-393.89	0.88	0.21	-393.11
	*CO+*OH	-389.39	-389.66	0.54	0.23	-389.23
	*CO	-377.81	-377.96	0.21	0.10	-377.80
	*CHO	-381.87	-382.7	0.46	0.14	-381.78
	*$HOCH_2O$	-397.94	-398.15	1.24	0.23	-397.02
	*CH_2O	-386.04	-385.49	0.74	0.18	-384.84
	*CH_2OH	-389.56	-389.40	1.10	0.17	-388.38
	*CH_3O	-390.22	-390.48	1.05	0.21	-389.54
	*CH_3OH	-393.40	-393.77	1.40	0.21	-392.47
	*O + CH_4	-369.67	-370.18	0.06	0.06	-370.15
	*OH	-374.96	-375.17	0.36	0.09	-374.85
DETA/CdS(101)_NH-*H	*NH+*H(*)	361.77	-362.04	0.15	0.02	-361.90
	*CO_2	-386.22	-386.40	0.32	0.22	-386.21
	*COOH	-390.13	390.32	0.67	0.15	-389.72
	*OCHO	-389.03	-389.62	0.64	0.12	-389.04
	*HCOOH	-392.56	-392.99	0.94	0.17	-392.12
	*CO	-377.01	-377.83	0.21	0.10	-377.83
CdS(001)	clean surface	-343.52	-343.25	-	-	-
	*CO_2	-367.14		-	-	-
	*H	-347.48	-347.43	0.13	0.04	-347.31
DETA/CdS(001)	clean surface	-454.93	-454.76	-	-	-
	*CO_2(Cd-site)	-478.85	-479.64	0.28	0.16	-479.43

Surfaces	**Intermediate state**	***E*** **(eV)**	E_{sol} **(eV)**	***ZPE*** **(eV)**	***TS*** **(eV)**	***G*** **(eV)**
	*CO_2(N-site)	-478.18	-478.01	0.32	0.22	-477.82
	*COOH	-482.18	-482.37	0.59	0.13	-481.84
	*OCHO	-483.25	-483.17	0.60	0.23	-482.69
	*CO+*O	-477.65	-477.75	0.21	0.20	0.11
	*HCOOH	-485.69	-486.69	0.90	0.28	-484.95
	*OCH_2O	-486.50	-486.72	0.89	0.19	-485.92
	*CO+*OH	-481.79	-481.57	0.47	0.26	-481.23
	*CO	-470.54	-470.59	0.14	0.20	-470.56
	*OH	-466.50	-466.27	0.33	0.09	-465.98
	*$HOCH_2O$	-489.80	-489.63	1.19	0.26	-488.56
	*CH_2O	-478.78	-478.67	0.76	0.13	-477.96
	*CH_2OH	-482.21	-482.07	1.08	0.2	-481.09
	*CH_3O	-482.73	-482.54	1.06	0.22	-481.59
	*CH_3OH	-485.88	-485.78	1.41	0.27	-484.51
	*O + CH_4	-462.61	-462.63	0.07	0.05	-462.59
	*OH	-466.61	-466.45	0.33	0.09	-466.16
DETA/CdS(001)_NH-*H	*NH+*H(*)	-454.92	-455.13	0.14	0.03	-455.00
	*CO_2	-478.99	-479.19	0.36	0.13	-478.88
	*COOH	-482.04	-482.18	0.67	0.18	-481.60
	*OCHO	-482.57	-482.96	0.57	0.18	-482.48
	*HCOOH	-485.94	-485.97	0.93	0.18	-485.11
	*CO	-471.49	-471.44	0.24	0.08	-471.23
CdS(111)	clean surface	-341.21	-340.93	-	-	-
	*CO_2	-365.41	-366.18	-	-	-
	*H	-345.43	-345.37	0.13	0.04	-345.26
DETA/Cd	clean surface	-453.58	-453.60	5.01	0.51	-453.60

Surfaces	Intermediate state	*E* (eV)	E_{sol} (eV)	*ZPE* (eV)	*TS* (eV)	*G* (eV)
S(111)	*CO_2(Cd-site)	-477.39	-478.17	0.29	0.19	-477.97
	*CO_2(N-site)	-476.80	-476.83	0.32	0.27	-476.66
	*COOH	-480.76	-481.01	0.61	0.22	-480.51
	*OCHO	-482.00	-482.13	0.60	0.23	-481.65
	*CO+*O	-475.25	-475.62	0.21	0.25	-475.54
	*HCOOH	-484.07	-484.45	0.88	0.21	-483.66
	*OCH_2O	-485.06	-485.63	0.90	0.18	-484.81
	*CO+*OH	-480.13	-480.13	0.49	0.29	-479.79
	*CO	-468.52	-458.53	0.15	0.21	-468.50
	*OH	-465.14	-465.26	0.34	0.10	-464.97
	*$HOCH_2O$	-488.82	-488.91	1.21	0.23	-487.81
	*CH_2O	-477.24	-477.47	0.77	0.13	-476.76
	*CH_2OH	-480.64	-480.67	1.08	0.18	-479.68
	*CH_3O	-481.50	-481.66	1.06	0.22	-480.71
	*CH_3OH	-484.34	-484.33	1.40	0.29	-483.10
	*O + CH_4	-461.08	-461.41	0.07	0.04	-461.36
	*OH	-465.20	-465.28	0.33	0.09	-464.98
DETA/CdS(111)_NH-*H	*NH+*H(*)	-452.90	-453.51	0.14	0.04	-453.39
	*CO_2	-477.58	-478.06	0.36	0.12	-477.75
	*COOH	-480.44	-480.71	0.65	0.14	-480.12
	*OCHO	-480.40	-481.27	0.63	0.13	-480.70
	*HCOOH	-484.36	-484.65	0.94	0.14	-483.77
	*CO	-468.57	-468.88	0.24	0.07	-468.67

Table S6 Adsorption energy of (E_{ads}) of CO, HCOOH, CH_2O, CH_3OH and CH_4 products.

Surfaces	E_{ads} **(eV)**				
	CO	**HCOOH**	**CH_2O**	**CH_3OH**	**CH_4**
DETA/CdS(101)	-0.22	-0.04	-0.25	-0.41	-0.11
DETA/CdS(001)	-0.14	-0.75	-1.61	-0.60	-0.14
DETA/CdS(111)	-0.13	-0.67	-1.57	-0.31	-0.20

Table S7 ΔG in the unit of eV of all intermedia states of the DETA/CdS surfaces compared to CO_2(g).

ΔG (eV)	**Cd-site**			**NH-*H-site**		
	(101)	**(001)**	**(111)**	**(101)**	**(001)**	**(111)**
$*+ H^+ + e^-$ → *H	-0.60	-0.54	-0.58	-	-	-
$*+ CO_2 + e^-$ → *CO +*O	1.14	0.61	1.55	-	-	-
$*+ CO_2 + H^+ + e^-$ → *COOH	0.28	-0.19	-0.02	0.11	0.05	0.37
$*+ CO_2 + H^+ + e^-$ → *OCHO	-0.59	-1.14	-1.17	0.80	-0.83	-0.21
$*+ CO_2 + H^+ + e^-$ → *CO+*OH	0.60	0.42	0.70	-	-	-
$*+ CO_2 + 2H^+ + e^-$ → $*+CO_{(g)} + *OH$	-	0.96	1.03	-	-	-
$*OH + H^+ + e^-$ → $* + H_2O_{(l)}$	-	0.61	0.58	-	-	-
$*+ CO_2 + 2H^+ + e^-$ → $*CO_{(g)} + H_2O_{(l)}$	0.93	-	-	0.90	-0.69	0.72
$*CO_{(g)}$ → $* + CO_{(g)}$	0.59	-	-	0.52	1.05	0.74
$*+ CO_2 + 2H^+ + e^-$ → $*HCOOH_{(g)}$	0.84	0.10	0.22	1.11	-0.07	0.12
$*HCOOH_{(g)}$ → $* + HCOOH_{(l)}$	1.50	0.24	0.08	0.04	0.15	1.06
$*+ CO_2 + 2H^+ + e^-$ → $*OCH_2O$	0.12	-0.88	-0.93	-	-	-
$*+ CO_2 + 3H^+ + e^-$ → $*CHO + H_2O_{(l)}$	0.35	-	-	-	-	-
$*+ CO_2 + 3H^+ + e^-$ → $*HOCH_2O$	-0.39	-0.12	-0.52	-	-	-

$*+ CO_2+ 4H^+ + e^- \rightarrow *CH_2O_{(g)} + H_2O_{(l)}$	0.69	-0.62	-0.58	-	-	-
$*CH_2O_{(g)} \rightarrow * + CH_2O_{(g)}$	1.51	1.04	0.96	-	-	-
$*+ CO_2+ 5H^+ + e^- \rightarrow *CH_2OH + H_2O_{(l)}$	0.54	-0.36	-0.10	-	-	-
$*+ CO_2+ 5H^+ + e^- \rightarrow *CH_3O + H_2O_{(l)}$	-0.61	-0.86	-1.13	-	-	-
$*+ CO_2+ 6H^+ + e^- \rightarrow *CH_3OH_{(g)} + H_2O_{(l)}$	-0.15	-0.38	-0.12	-	-	-
$*CH_3OH_{(g)} \rightarrow * + CH_3OH_{(l)}$	0.98	0.56	0.55	-	-	-
$*+ CO_2+ 6H^+ + e^- \rightarrow *O + CH_{4(g)} + H_2O_{(l)}$	-1.16	-1.78	-1.71	-	-	-
$*+ CO_2+ 7H^+ + e^- \rightarrow *OH + CH_{4(g)} + H_2O_{(l)}$	-2.46	-1.95	-1.93	-	-	-
$*OH + H^+ + e^- \rightarrow * + H_2O_{(l)}$	-1.66	-1.65	-1.68	-	-	-

Table S8 ΔG of the first protonation step for the HER and CO_2RR.

Surfaces	ΔG_{*H} (eV)	ΔG_{*OCHO} (eV)	ΔG_{*COOH} (eV)
DETA/CdS(101)	-0.60	-0.37	0.51
DETA/CdS(001)	-0.54	0.14	1.00
DETA/CdS(111)	-0.58	-0.29	0.86

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