Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting information for

Solar driven CO_2 hydrogenation to HCOOH on $(TiO_2)_n$ (n = 1–6) clusters

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Table S1. Key geometrical parameters of $(TiO_2)_n$ (n = 1 – 6) clusters including point group symmetry (sym.), average bond length ($d_{Ti–O}$), and the bond angle between Ti atoms and terminated O atoms ($\alpha_{<Ti–O–Ti>}$) calculated by VASP and Gaussian 09 program.

system	sym.		$d_{Ti–O}$ (Å)		$\alpha_{<Ti–O–Ti>}$ (°)	
	Gaussian 09	VASP	Gaussian 09	VASP	Gaussian 09	VASP
$(TiO_2)_1$	C_{2v}	C_{2v}	1.66	1.65	110.30	110.30
$(TiO_2)_2$	C_{2h}	C_{2h}	1.65	1.65	112.62	112.63
$(TiO_2)_3$	C_s	C_s	1.64	1.66	120.61	119.41
$(TiO_2)_4$	C_{2v}	C_{2v}	1.64	1.65	119.21	119.21
$(TiO_2)_5$	C_s	C_s	1.64	1.66	121.86	120.98
$(TiO_2)_6$	C_2	C_2	1.64	1.65	114.27	114.56

Table S2. The energy gap between HOMO and LUMO of $(TiO_2)_n$ (n = 1 – 6) clusters calculated by VASP and Gaussian 09 program based on PBE and HSE06 functional.

	VASP		Gaussian 09	
	PBE	HSE06	PBE	HSE06
$(TiO_2)_1$	2.07	3.64	2.26	3.78
$(TiO_2)_2$	2.89	4.79	3.12	4.84
$(TiO_2)_3$	1.58	3.32	1.83	3.56
$(TiO_2)_4$	2.95	4.87	2.78	4.92
$(TiO_2)_5$	2.67	4.52	2.72	4.63
$(TiO_2)_6$	2.48	4.36	2.50	4.48

Table S3. Gibbs free energy of CO_2 molecule on $(TiO_2)_n$ (n = 1 – 6) clusters calculated by VASP and Gaussian 09 program.

Method		$(TiO_2)_1$	$(TiO_2)_2$	$(TiO_2)_3$	$(TiO_2)_4$	$(TiO_2)_5$	$(TiO_2)_6$
VASP	PBE	–0.54	–0.23	0.18	0.21	0.47	0.86
	PBE-D2	–0.60	–0.34	–0.08	–0.02	0.25	0.65
	PBE-D3	–0.68	–0.36	–0.10	0.03	0.33	0.65
	HSE06	–0.52	–0.22	0.18	0.23	0.45	0.82
	HSE06-D2	–0.58	–0.32	–0.10	–0.05	0.23	0.58
	HSE06-D3	–0.68	–0.34	–0.11	0.05	0.36	0.62
Gaussian	PBE	–0.48	–0.25	0.20	0.24	0.52	0.93
	PBE-D3	–0.62	–0.34	–0.06	0.03	0.23	0.54
	HSE06	–0.50	–0.22	0.21	0.26	0.54	0.93

(Unit: eV)

Table S4. Zero-point energy (ZPE) and entropic correction (*TS*) at *T* =298.15 K for the molecules of H_2, H_2O, CO, CO_2, HCOOH, CH_2O, CH_3OH, and CH_4.

Species	ZPE (eV)	*TS* (eV)	ZPE–*TS* (eV)
H_2	0.29	0.41	–0.12
H_2O	0.60	0.59	0.01
CO	0.14	0.62	–0.48
CO_2	0.31	0.67	–0.45
HCOOH	0.92	1.02	–0.10
CH_2O	0.72	0.68	0.04
CH_3OH	1.39	0.79	0.60
CH_4	1.20	0.58	0.61

Table S5. Computational ZPE and *TS* at T =298.15 K for intermediate species involved in the CO_2 hydrogenation reaction on $(TiO_2)_4$ cluster, as a representative of $(TiO_2)_n$ (n = 1–6) clusters.

Species	ZPE (eV)	*TS* (eV)	ZPE–*TS* (eV)
$*CO_2$	0.31	0.14	0.15
*OOCH	0.58	0.22	0.36
*COOH	0.63	0.12	0.51
*CO	0.25	0.10	0.15
*HCOOH	0.89	0.25	0.64
*CHO	0.51	0.17	0.34
$*CH_2O$	0.79	0.15	0.64
$*CH_2OH$	1.13	0.28	0.85
$*CH_2$	0.72	0.16	0.58
$*CH_3$	0.98	0.14	0.84

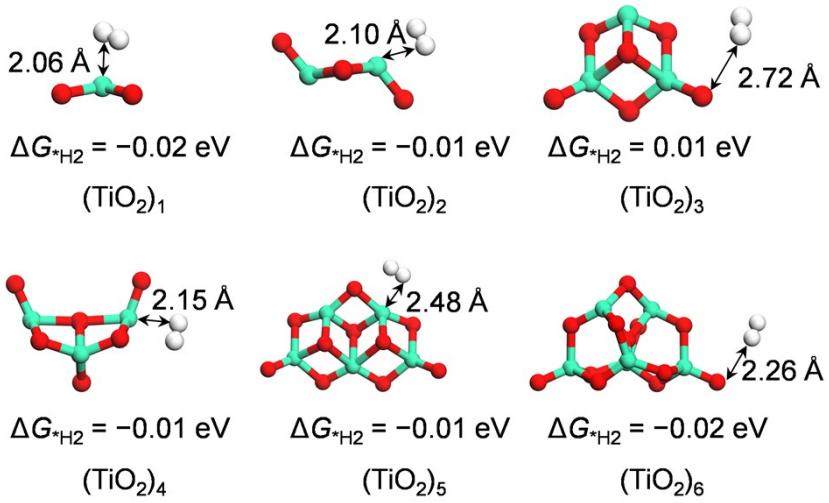
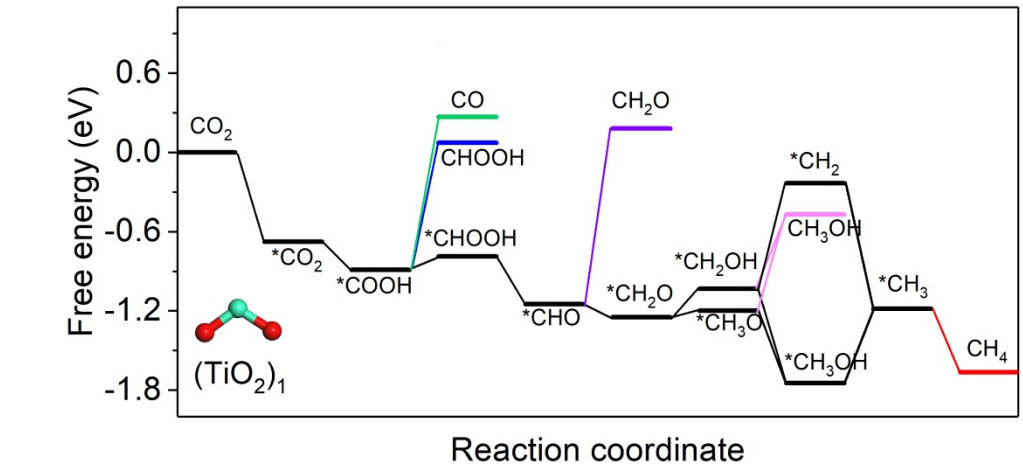


Fig. S1. The atomic configuration of a H_2 molecule on $(TiO_2)_n$ clusters. The minimum distance between H_2 and $(TiO_2)_n$ and corresponding Gibbs free energy of H_2 adsorption was shown.



$(TiO_2)_1$	$*CO_2$	$*COOH$	$*CO$	$*HCOOH$	$*CHO$
$*CH_2O$	$*CH_2OH$	$*CH_3O$	$*CH_3OH$	$*CH_2$	$*CH_3$

Fig. S2. The free energy profiles of CO_2 hydrogenation reaction on $(TiO_2)_1$ cluster and corresponding atomic structures of reaction intermediates. The Ti, O, C, and H atoms are shown in cyan, red, gray, and white colors, respectively.

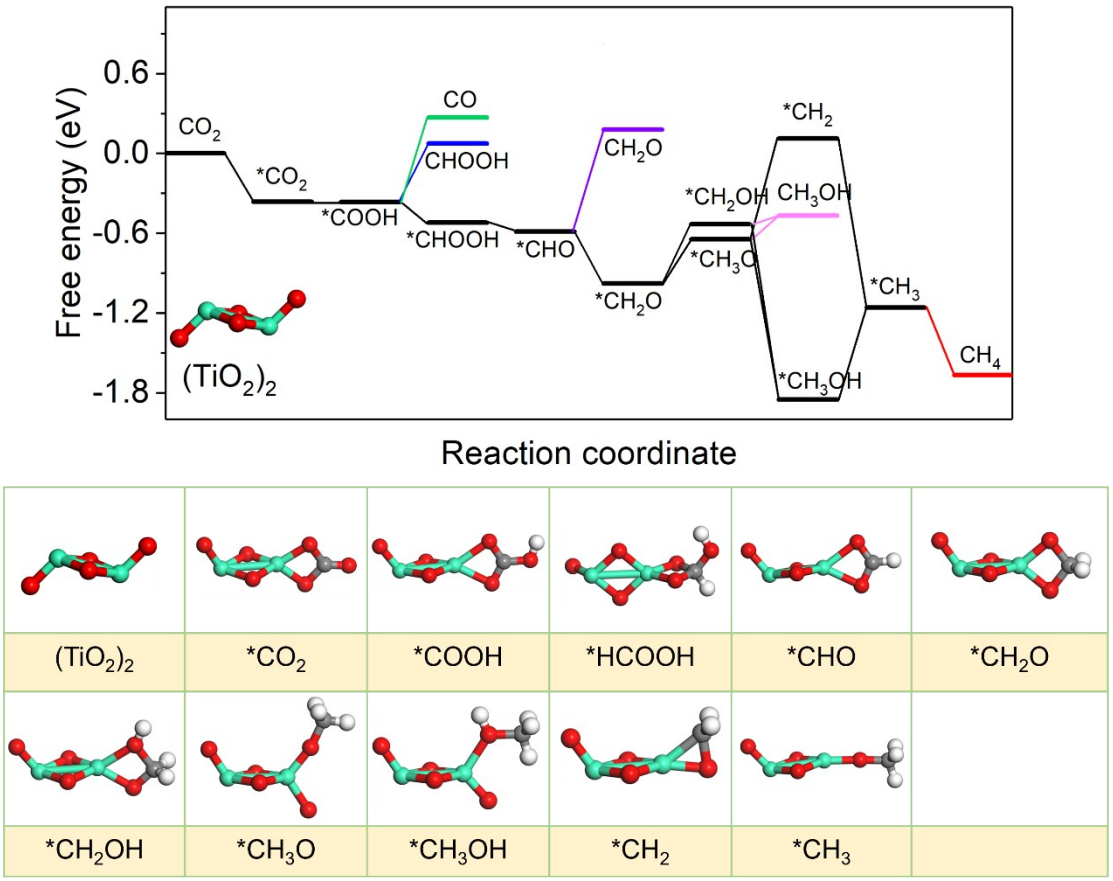
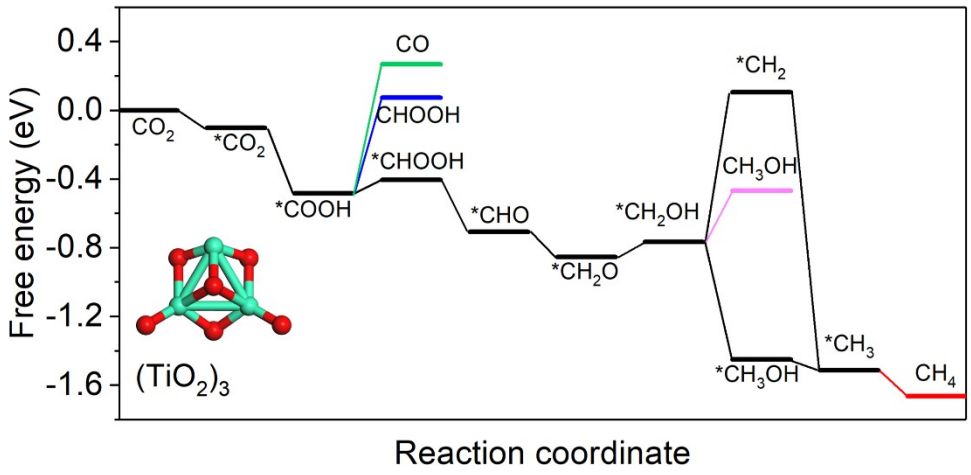


Fig. S3. The free energy profiles of CO_2 hydrogenation reaction on $(TiO_2)_2$ cluster and corresponding atomic structures of reaction intermediates. The Ti, O, C, and H atoms are shown in cyan, red, gray, and white colors, respectively.



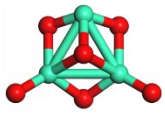
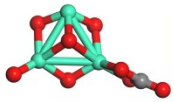
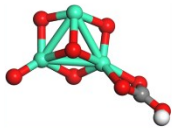
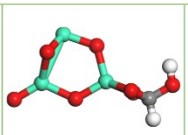
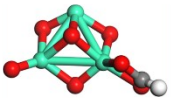
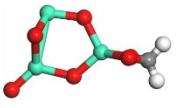
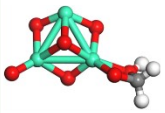
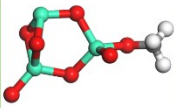
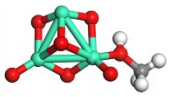
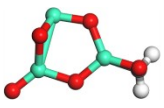
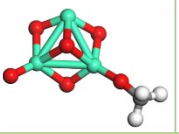
					
$(TiO_2)_3$	$*CO_2$	*COOH	*HCOOH	*CHO	$*CH_2O$
					
$*CH_2OH$	$*CH_3O$	$*CH_3OH$	$*CH_2$	$*CH_3$	

Fig. S4. The free energy profiles of CO_2 hydrogenation reaction on $(TiO_2)_3$ cluster and corresponding atomic structures of reaction intermediates. The Ti, O, C, and H atoms are shown in cyan, red, gray, and white colors, respectively.

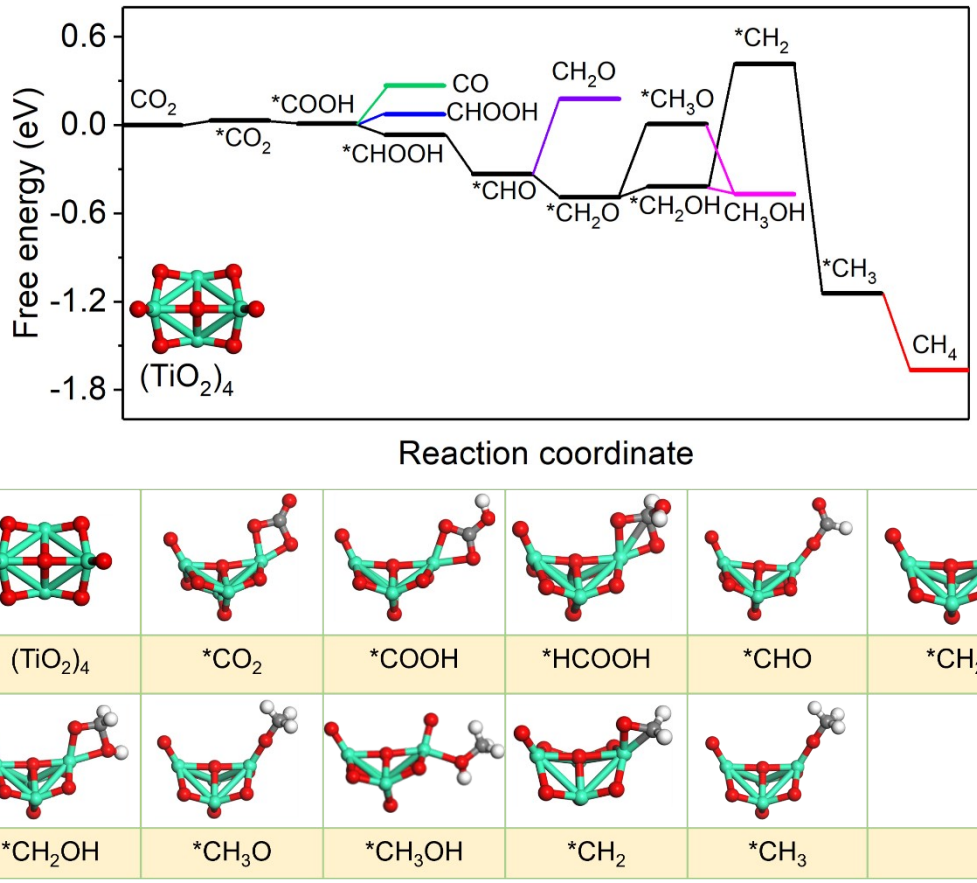
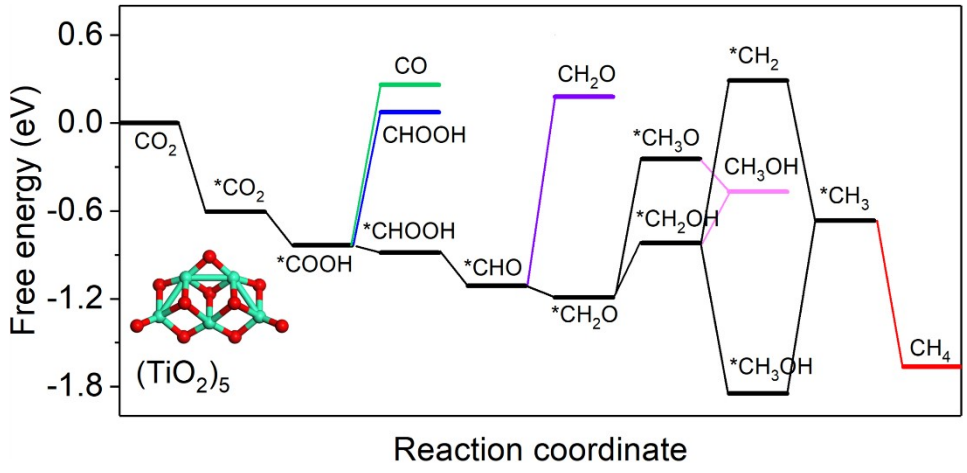


Fig. S5. The free energy profiles of CO_2 hydrogenation reaction on $(TiO_2)_4$ cluster and corresponding atomic structures of reaction intermediates. The Ti, O, C, and H atoms are shown in cyan, red, gray, and white colors, respectively.



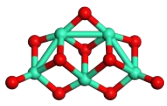
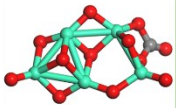
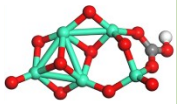
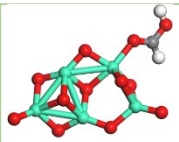
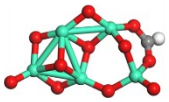
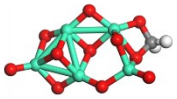
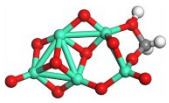
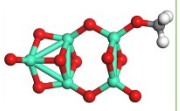
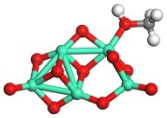
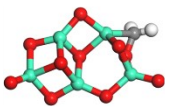
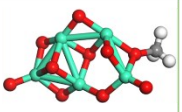
					
$(TiO_2)_5$	$*CO_2$	*COOH	*HCOOH	*CHO	$*CH_2O$
					
$*CH_2OH$	$*CH_3O$	$*CH_3OH$	$*CH_2$	$*CH_3$	

Fig. S6. The free energy profiles of CO_2 hydrogenation reaction on $(TiO_2)_5$ cluster and corresponding atomic structures of reaction intermediates. The Ti, O, C, and H atoms are shown in cyan, red, gray, and white colors, respectively.

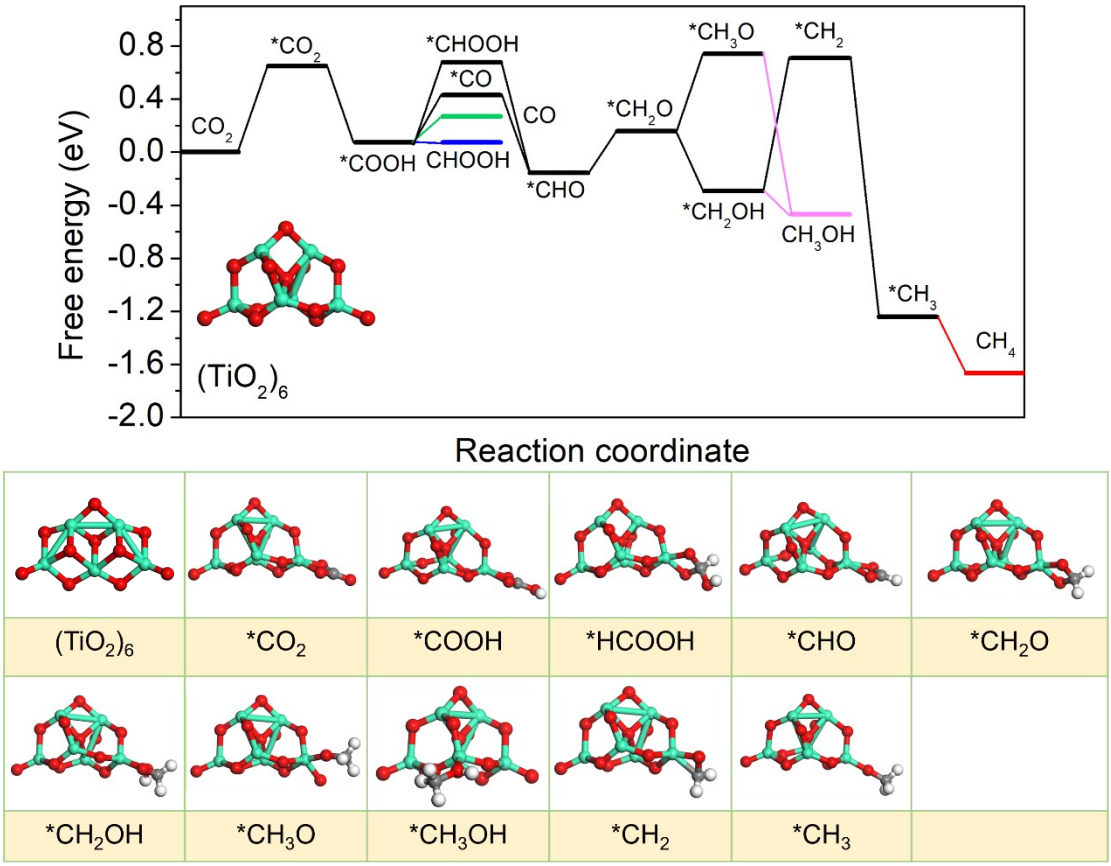


Fig. S7. The free energy profiles of CO_2 hydrogenation reaction on $(TiO_2)_6$ cluster and corresponding atomic structures of reaction intermediates. The Ti, O, C, and H atoms are shown in cyan, red, gray, and white colors, respectively.