Electronic Supplementary Information for

The regulation of reaction processes and rate-limiting steps for efficient photocatalytic CO_2 reduction into methane over the tailored facets of TiO_2

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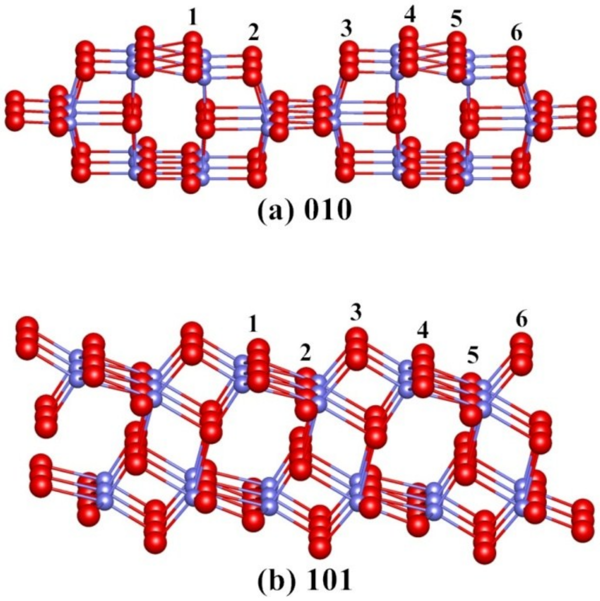

Figure S1. Relaxed structures of anatase TiO_2 models for {010} (a) and {101} (b) facets. The royal blue and red balls stand for titanium and oxygen atoms, respectively.

Table S1 Summary of charge transfer of adsorbed CO_2 on anatase TiO_2 {010} and {101} facets.

	Populated electrons/ Δq, e	
structures	{010}	{101}
Atom species		
C	2.09	2.11
O1	-0.99	-1.01
O2	-1.09	-1.08
Ti*	2.19	2.18

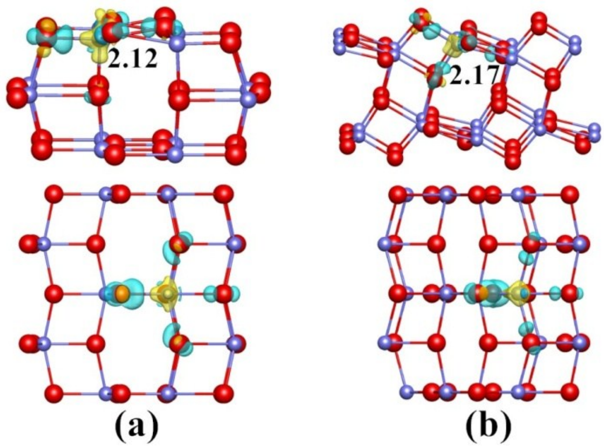

Figure S2. The charge difference density and Bader analysis for Ti atoms on anatase TiO_2 {010} facet (a) and {101} facet (b). The isosurfaces are set to 0.17 e Å^{-1}. All the Bader value are e, where a positive value denotes that it loses electrons. Yellow (blue) region means electron depletion (accumulation). The royal blue and red balls stand for titanium and oxygen atoms, respectively. It shows that more electrons can be transferred from the Ti atom to the other atoms for anatase {101} facet than {010} facet, which is agree with the result of CO_2 adsorption indicating electron transportation on the {101} facet is stronger than {010} facet.

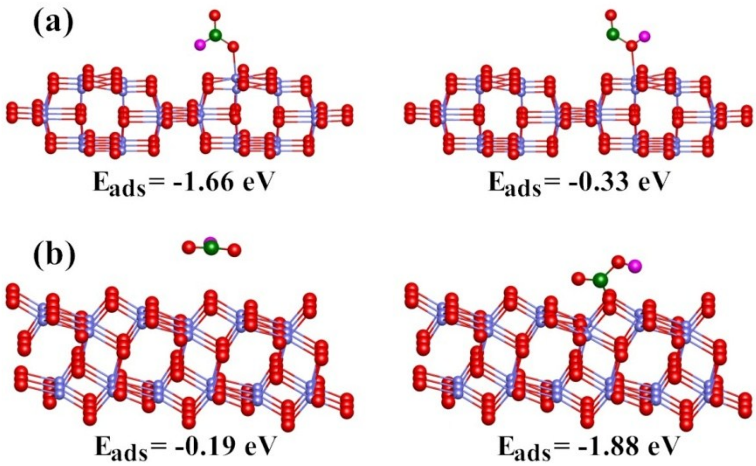

Figure S3. The most stable intermediate for the 1H step of CO_2 reduction to form CH_4 over anatase TiO_2 {010} (a) and {101} (b) facets.

Formation of CH_4

On the TiO_2 {010} facet, the overall formula of formation of CH_4 on can be depicted

$$CO_2 + 8H^+ + 8e^- \rightarrow CH_4 + 2H_2O \quad (1)$$

The pathway following these eight elementary steps:

$$CO_2\ (CO\text{-}(Ti)^*O) + H^* \rightarrow CHO\text{-}(Ti)^*O \quad (2)$$

$$CHO\text{-}(Ti)^*O + H^* \rightarrow CHO\text{-}(Ti)^*OH \quad (3)$$

$$CHO\text{-}(Ti)^*OH + H^* \rightarrow (O)^*CH\text{-}O + H_2O \quad (4)$$

$$(O)^*CH\text{-}O + H^* \rightarrow (O)^*CH\text{-}OH \quad (5)$$

$$(O)^*CH\text{-}OH + H^* \rightarrow (O)^*CH_2\text{-}OH \quad (6)$$

$$(O)^*CH_2\text{-}OH + H^* \rightarrow (O)^*CH_2 + H_2O \quad (7)$$

$$(O)^*CH_2 + H^* \rightarrow (O)^*CH_3 \quad (8)$$

$$(O)^*CH_3 + H^* \rightarrow (O)^*CH_4 \quad (9)$$

On the anatase TiO_2 {010} facet, the overall formula of formation of CH_4 can be written

$$CO_2 + 8H^+ + 8e^- \rightarrow CH_4 + 2H_2O \quad (10)$$

The detailed reaction pathways of the generation of CH_4 through the eight elementary steps:

$$(O)^*CO\text{-}O + H^* \rightarrow (O)^*CO\text{-}OH \quad (11)$$

$$(O)^*CO\text{-}OH + H^* \rightarrow (Ti)^*OCH\text{-}OH \quad (12)$$

$$(Ti)^*OCH\text{-}OH + H^* \rightarrow CO + (O)^*H + H_2O \quad (13)$$

$$CO + (O)^*H \rightarrow (Ti)^*CH\text{-}O \quad (14)$$

$$(Ti)^*CH\text{-}O + H^* \rightarrow CH_2\text{-}(Ti)^*O \quad (15)$$

$$CH_2\text{-}(Ti)^*O + H^* \rightarrow CH_2\text{-}(Ti)^*OH \quad (16)$$

$$CH_2\text{-}(Ti)^*OH + H^* \rightarrow CH_3\text{-}(Ti)^*OH \quad (17)$$

$$CH_3\text{-}(Ti)^*OH + H^* \rightarrow {}^*CH_4 + (Ti)^*OH \quad (18)$$

$$(Ti)^*OH + H^* \rightarrow H_2O + (Ti)^* \quad (19)$$

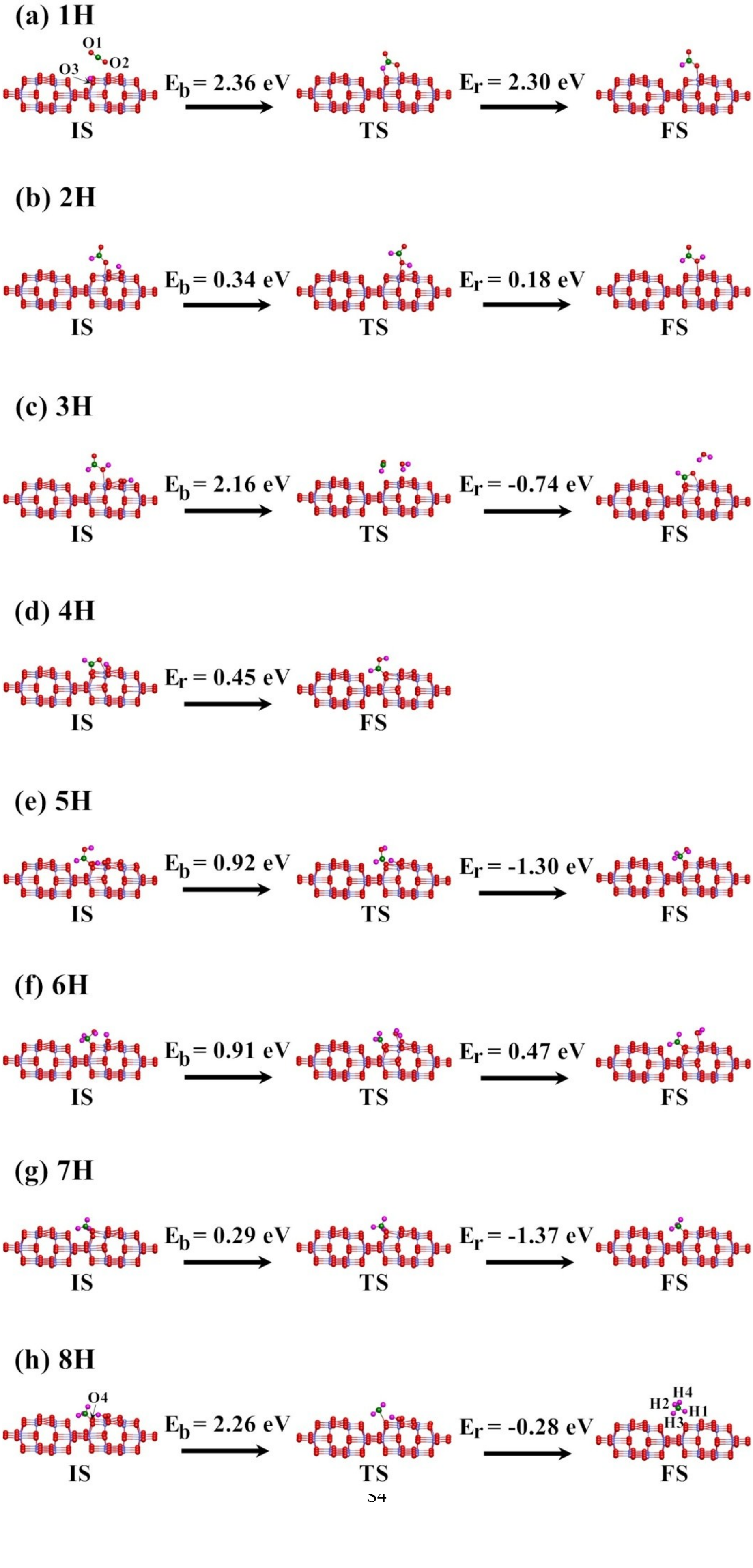
(a) 1H
O1
O2
O3
Eb = 2.36 eV
Er = 2.30 eV
IS
TS
FS
(b) 2H
Eb = 0.34 eV
Er = 0.18 eV
IS
TS
FS
(c) 3H
Eb = 2.16 eV
Er = -0.74 eV
IS
TS
FS
(d) 4H
Er = 0.45 eV
IS
FS
(e) 5H
Eb = 0.92 eV
Er = -1.30 eV
IS
TS
FS
(f) 6H
Eb = 0.91 eV
Er = 0.47 eV
IS
TS
FS
(g) 7H
Eb = 0.29 eV
Er = -1.37 eV
IS
TS
FS
(h) 8H
O4
H4
H2
H1
H3
Eb = 2.26 eV
Er = -0.28 eV
IS
TS
FS

Figure S4. Minimum energy pathway (MEP) of CO_2 reduction to CH_4 on anatase TiO_2 {010} facet and each steps are shown by a-h. E_b and E_r stand for the activation energy barrier and reaction energy, respectively. The red, royal blue, green and purple balls are behalf of oxygen, titanium, carbon and hydrogen atoms, respectively. All the lengths are given in Å. It needs to explain that the fourth step is just an endothermic process and requires energy 0.45 eV at least to overcome.

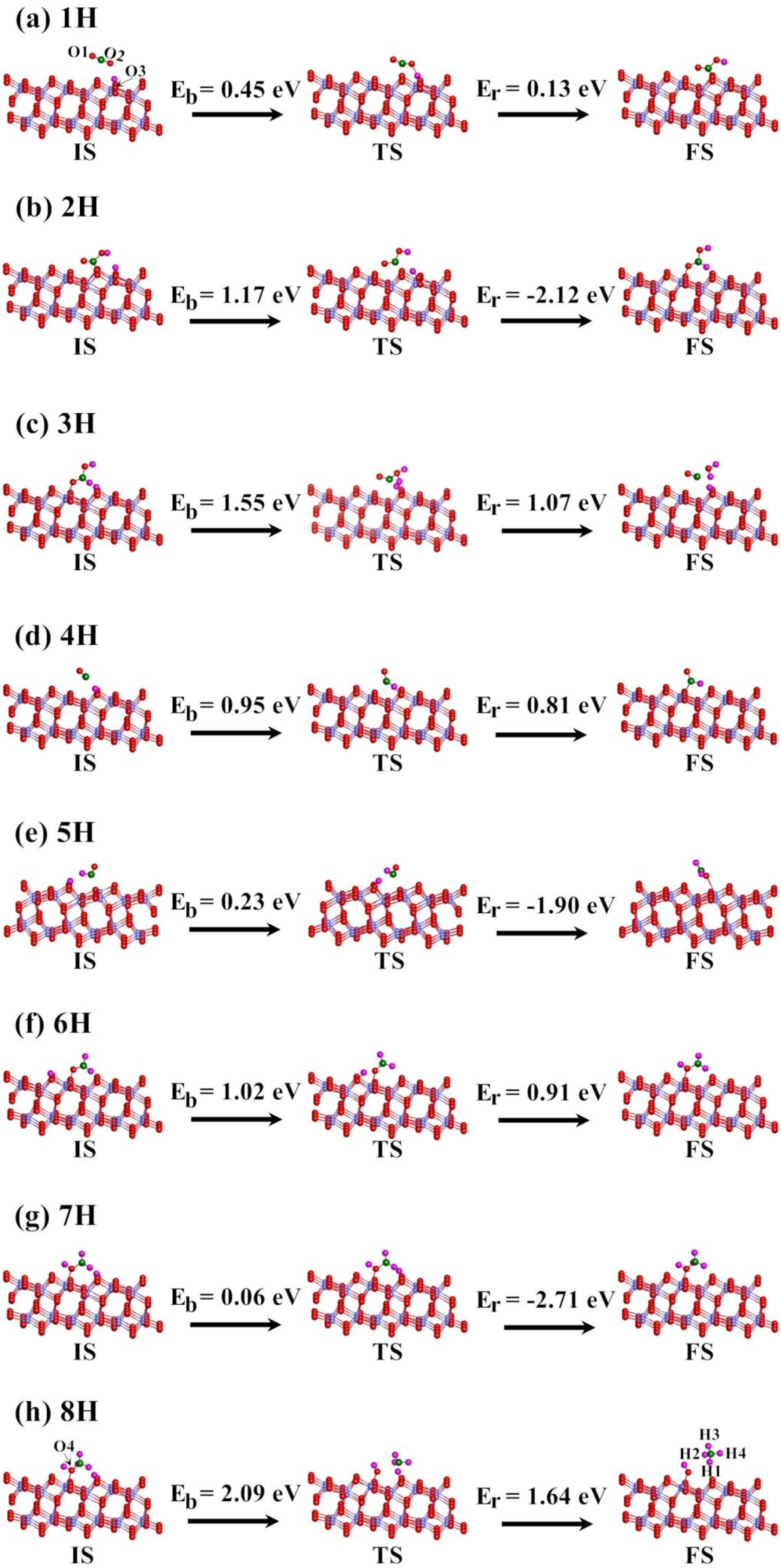
(a) 1H
O1
O2
O3
Eb = 0.45 eV
Er = 0.13 eV
IS
TS
FS
(b) 2H
Eb = 1.17 eV
Er = -2.12 eV
IS
TS
FS
(c) 3H
Eb = 1.55 eV
Er = 1.07 eV
IS
TS
FS
(d) 4H
Eb = 0.95 eV
Er = 0.81 eV
IS
TS
FS
(e) 5H
Eb = 0.23 eV
Er = -1.90 eV
IS
TS
FS
(f) 6H
Eb = 1.02 eV
Er = 0.91 eV
IS
TS
FS
(g) 7H
Eb = 0.06 eV
Er = -2.71 eV
IS
TS
FS
(h) 8H
O4
Eb = 2.09 eV
Er = 1.64 eV
H3
H2
H4
H1
IS
TS
FS

Figure S5. Minimum energy pathway (MEP) of CO_2 reduction to CH_4 on anatase TiO_2 {101} facet and each steps are shown by a-h. E_b and E_r stand for the activation energy barrier and reaction energy, respectively. The red, royal blue, green and purple balls are behalf of oxygen, titanium, carbon and hydrogen atoms, respectively. All the lengths are given in Å.

Table S2 Summary of charge transfer of IS and TS for the 1H step on anatase TiO_2 {010} and {101} photocatalysts.

Populated electrons/ Δq, e				
structures	{010}		{101}	
Config. / Atom species	IS	TS	IS	TS
H	0.68	0.21	0.73	0.66
C	2.07	1.52	2.11	2.07
O1	-1.01	-0.95	-1.01	-1.03
O2	-1.05	-1.08	-1.08	-1.10
O3	-1.23	-0.95	-1.37	-1.30

Table S3 Summary of charge transfer of IS and TS for the 8H step on anatase TiO_2 {010} and {101} facets.

Populated electrons/ Δq, e				
structures	{010}		{101}	
Config. / Atom species	IS	TS	IS	TS
H1	0.62	0.61	0.72	0.20
H2	0.12	0.17	0.06	0.12
H3	0.16	0.17	0.10	0.06
H4	0.08	0.07	0.10	0.01
C	0.24	-0.28	0.31	-0.18
O4	-1.11	-1.01	-1.19	-1.03