Supplementary Information:

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Figure S1: Electron energy levels relative to the band edges for different photoexcited electron models on the anatase (101) surface. Occupied orbitals are in black, while virtual orbitals are in green. Notations: BS0 – bare surface ground state; BS2 – bare surface excited triplet state; HS – hydrogen-compensated surface; "-U" indicates GGA+U calculations\*.

\*In the GGA+U calculations, the PBE functional was supplemented by the rotationally invariant "+U" description of Dudarev et al.<sup>1</sup> We adopted a value of U=4.5 eV in these calculations, which complies with the values of  $4\sim5$  eV used in previous theoretical studies.<sup>2</sup> The calculated band gap for the bulk is 2.9 eV, which is slightly below the observed band gap of anatase 3.2 eV. The band gap of the modeled surface slab broadens by 0.2 eV compared to that of the bulk, due to the quantum confinement effect. Similar effect was reported before.<sup>3</sup>



Figure S2: Spin density distributions for different photoexcited electron models. The isosurface values are written in the parentheses in the unit of e/Å<sup>3</sup>. Notations: BS2 – bare surface excited state; HS – hydrogen-compensated surface; "-U" indicates GGA+U calculations.



Figure S3: Effect of positive charge (hole or proton) distribution on the one-electron levels. All these results are from GGA+U calculations. Notation: BS2-U – bare surface excited state with largely delocalized hole; BS2-L – bare surface excited state with largely localized hole; BS2-R – bare surface excited state with delocalized hole (both surfaces of the slab model are relaxed); BS2-E – bare surface excited state with delocalized hole (extended surface model with 10 TiO<sub>2</sub> trilayers); HS – hydrogen-compensated surface.

BS2-U

BS2-L



BS2-R

**ВS2-**Е

Figure S4: Spin density distributions for photoexcited electron models with different electron and hole distributions. The isosurface value is set to 0.04 e/Å<sup>3</sup> for allthe cases. Notation: BS2-U – bare surface excited triplet state with largely delocalized hole; BS2-L – bare surface excited state with largely localized hole; BS2-R – bare surface excited triplet state with delocalized hole (both surfaces of the slab model are relaxed); BS2-E – bare surface excited triplet state with delocalized hole (extended surface model with 10 TiO<sub>2</sub> trilayers).



Figure S5: Comparison of results for the reaction path of 1e  $CO_2$  (A1) activation to  $CO_2^-$  (B1) using the current H<sup>+</sup>-compensation model at the GGA level HS (in red), at the GGA+U level HS-U (in green), and the model having bare surface in excited state at the GGA+U level BS2-U (in black). The reactant, transition state and product are labeled on the top and the bottom panel for the HS model and the BS model, respectively. The corresponding geometries are shown in the figure for the BS2-U case. Atoms: Ti in green, O in red, C in silver and H in white. The symbol notations are the same as in Fig. 3(b).



Figure S6: Comparison of results for the reaction path of forming HCOO<sup>-</sup> via the A1 configuration (concerted mechanism) with (in green) and without (in red) extra H<sup>+</sup>+OH<sup>-</sup> pair. The configurations of the reactant, transition state and product are shown for the frontier and latter case in the bottom and top panel, respectively. Atoms: Ti in green, O in red, C in silver and H in white. The symbol notations are the same as in Fig. 3(b).





Figure S7: Illustration of other reaction pathways from CO<sub>2</sub> to HCOOH: (a) Route III: via the A2 configuration to form carboxyl; (b) Route IV: via the B2 configuration to form formic acid. The sum of energies of the CO<sub>2</sub> and H<sub>2</sub> molecules is the zero reference for energy. The C-O bond lengths (Å) and the  $\angle$ OCO bond angle (degrees) of CO<sub>2</sub>, as well as the bond lengths between CO<sub>2</sub> and the interacting surface atoms of the TiO<sub>2</sub> surface are shown. Atoms: Ti in green, O in red, C in yellow and H in light blue. The hydrogen bond lengths are also labeled. The symbols in brackets label the states: g – gas phase; a – adsorbed species on the anatase (101) surface; A2, B2 – two adsorption configurations of CO<sub>2</sub>/CO<sub>2</sub><sup>-</sup> on surface; A2H, B2H - different adsorption configurations of COOH on surface; B1H2 - a adsorption configurations of HCOOH on surface. The sign of "+" indicates non-interacting species, while "..." indicates two species in proximity.

Table S1: Zero-point energy (*ZPE*) corrections and entropic contributions (-*TS*) to free energies  $(\Delta G=ZPE-TS)$  (in eV) at standard conditions along the reaction pathway to form HCOOH via the B1 configuration (Fig. 3(a)). We assume that there is no entropy change for surface bound species, while the entropy change for a gas molecule is given by the loss (adsorbed on surface) or gain (desorbed from surface) of its translational entropy.<sup>4</sup>

	ZPE	-TS	ΔG
$CO_2(g)+2H^+(a)+2e^-$	0.85	-0.48	0.37
$CO_2(A1)H^+(a)+H^+(a)+2e^-$	0.92	0	0.92
TS1	0.84	0	0.84
$CO_2^{-}(B1)H^{+}(a)+H^{+}(a)+e^{-}$	0.86	0	0.86
$CO_2^{-}(B1)H^{+}(a)H^{+}(a)+e^{-}$	0.85	0	0.85
TS2	0.85	0	0.85
HCOO <sup>-</sup> (B1H)H <sup>+</sup> (a)	0.93	0	0.93
TS3	0.90	0	0.9
HCOOH(B1H2)	0.89	0	0.89
HCOOH(g)	0.89	-0.48	0.41

Table S2: Zero-point energy (*ZPE*) corrections and entropic contributions (-*TS*) to free energies  $(\Delta G=ZPE-TS)$  (in eV) along the reaction pathway to form HCOOH via the A1 (Fig. 3(b): concerted mechanism). The estimation of change of entropy is the same as in Table S1.

	ZPE	- <i>TS</i>	$\Delta G$
$CO_2(g)+2H'(a)+2e^{-1}$	0.85	-0.48	0.37
$CO_2(A1)H^+(a)+H^+(a)+2e^-$	0.92	0	0.92
$CO_2(A1)2H^+(a)+2e^-$	0.92	0	0.92
TS1	0.85	0	0.85
$HCOO^{-}(A1H)H^{+}(a)$	0.89	0	0.89
TS2	0.92	0	0.92
HCOOH(A1H2)	0.91	0	0.91
HCOOH(g)	0.89	-0.48	0.41

Table S3: Free energies for the adsorption of gas phase molecules  $\Delta G_{ads} = E_{ads} + \Delta ZPE + \Delta TS + E_{vdW}$ , where the major corrections in zero-point energy difference ( $\Delta ZPE$ ), translational entropy contributions ( $\Delta TS$ ), and van der Waals energy correction  $E_{vdW}$  are included (all values reported in eV). The estimation of change of entropy is the same as in Table S1.

	$E_{\rm ads}$	$\Delta ZPE$	$\Delta TS$	$E_{ m vdW}$	$\Delta G_{ m ads}$
CO <sub>2</sub> (A1)	-0.21	0.07	0.48	-0.26	0.08
HCOOH(B1H2)	-1.00	0.00	0.48	-0.22	-0.74
HCOOH(A1H2)	-0.93	0.02	0.48	-0.22	-0.65
CO+H <sub>2</sub> O	-0.59	0.00	0.91	-0.30	0.02

Table S4. Summary of CO<sub>2</sub> adsorption on doped anatase (101) surfaces.

Calculated results	Doping elements
Form CO <sub>2</sub> <sup>-</sup> in B1 configuration, barrier reduced	Zr, Hf, Nb, Ta, Mo, Sn
Form CO <sub>2</sub> <sup>-</sup> in B1 configuration, barrier increased	W
Form $CO_2^-$ in B1 configuration, large distortion in lattice	Th
Do not form CO <sub>2</sub> <sup>-</sup> in B1 configuration	Mg, Sc, Y, La, V, Mn, Re, Cr, Fe, Ru, Os, Ir, Pt, Cu, Ag, Zn, Cd, B, Al, In, Tl, Si, Ge, Pb, Sb, Bi, Ce, Nd

TABLE S5: Calculated adsorption energies<sup>5</sup> (in eV) of  $CO_2$  on neutral anatase (101) surface using cluster and periodic models and on negatively charged anatase (101) surfaces using the cluster model (I)\* and the periodic model (II) with background charge compensation; and H reduced anatase (101) surface using the periodic model (III). Energies are relative to the sum of the energy of neutral or negatively charged or H reduced TiO<sub>2</sub> surface and the energy of a CO<sub>2</sub> molecule.

State	Neutral		Neutral Anion		
Model Config.	Cluster	Periodic	Ι	II	III
A1	-0.34	-0.20	-0.35	-0.07	-0.21
A2	-0.41	-0.14	-0.35	-0.23	-0.21
B1	-	-	0.33	0.72	0.50
B2	0.22	0.06	0.21	-0.03	-0.06

\* In Model I, a cluster of  $Ti_7O_{27}H_{26}$ , representing the anatase (101) surface, was adopted. An extra electron is introduced in the system to model the photoexcited electron whereas the hole is completely screened and not considered. The cluster calculations were performed with the B3LYP functional using the Gaussian03 program package. The 6-31+G(2df,p) basis set was used for the CO<sub>2</sub> molecule, and surface O atoms near the 5-fold-Ti reaction center, and the LanL2DZ basis set was used for Ti, the terminal H and the remaining O atoms.

## References:

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