*Electronic Supplementary Information*

# Surface Termination Dependent Carbon Dioxide Reduction Reaction on $Ti_3C_2$ MXene

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**Fig. S1** Top view of the $Ti_3C_2$ (0001) surface model, where brown spheres denote C atoms, and three different Ti layers are shown with different shades of blue, being the topmost one the darkest. High-symmetry sites are tagged, including top (T) and bridge (B) sites, and three-fold hollow carbon ($H_C$) and hollow metal ($H_M$) sites.

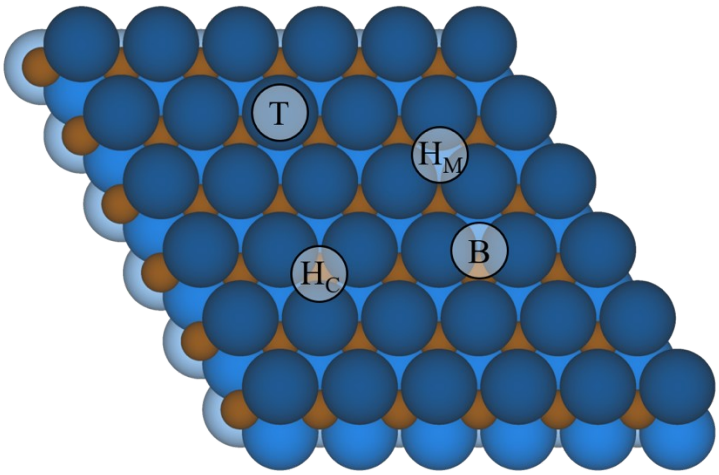

**Fig. S2** Predicted Pourbaix diagrams for $Ti_3C_2$ MXene (0001) surface regarding all single, binary, and ternary surface compositions including –O, –OH, –H, and –F terminations, as well as free sites. Left image corresponds to situations without any –F termination, while right image corresponds to situations when regarding–F termination. The black, dashed line indicates the HER equilibrium potential with respect RHE reference.

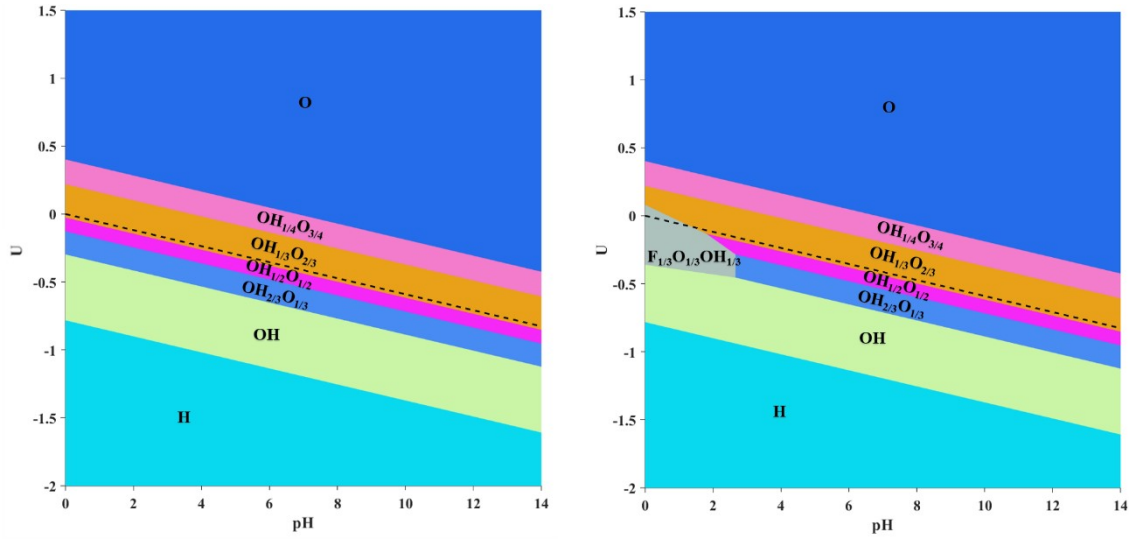

**Fig. S3** Total and projected density of states (PDOS) of the pristine $Ti_3C_2$ (0001) surface model, as well as of the fully –OH terminated model, and of the rest of binary and ternary models explored in the present work, derived from Pourbaix diagrams shown in Fig. 1 of the main text. Energy levels are referred to the Fermi energy, $E_F$, set to zero.

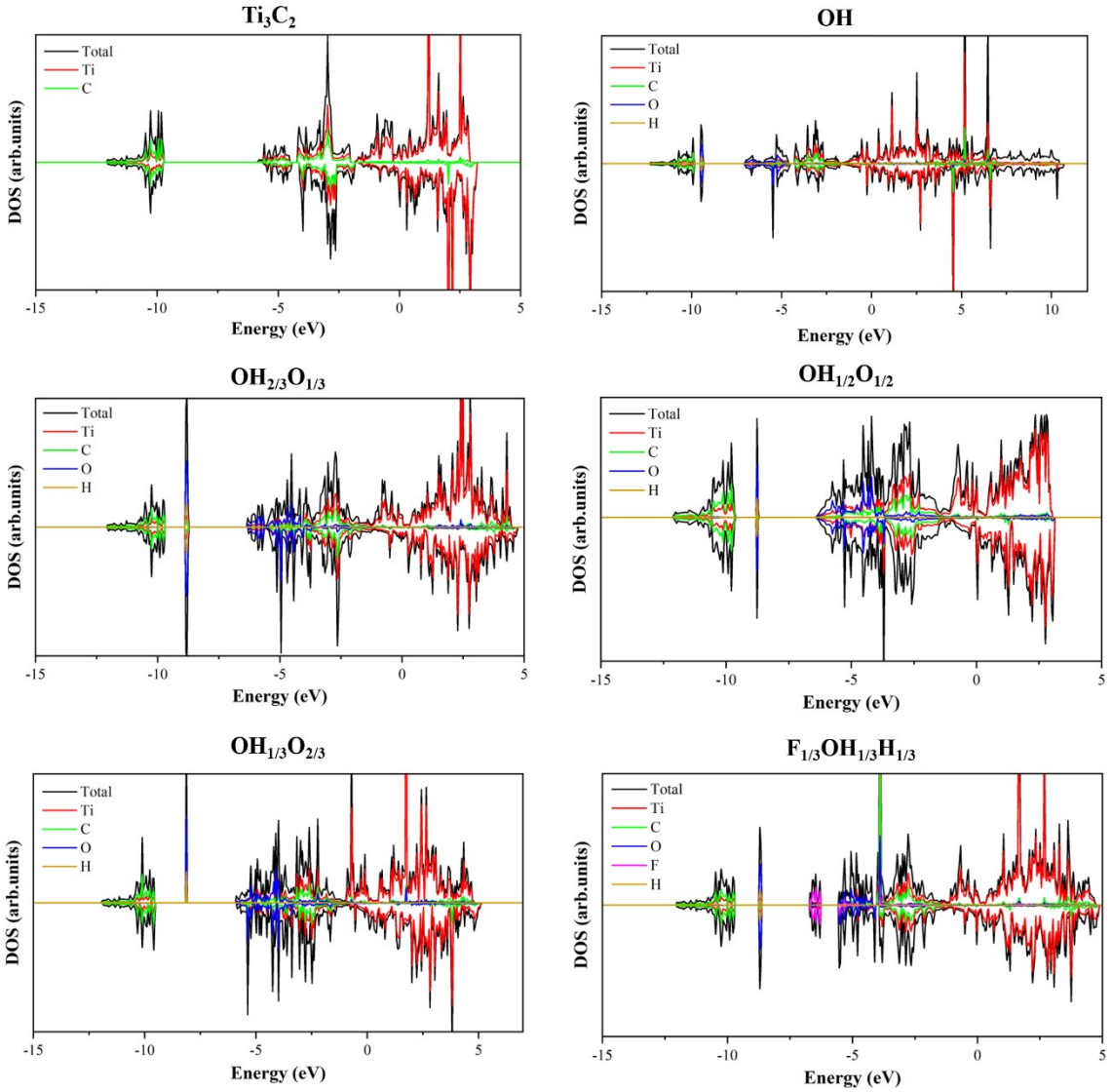

**Fig. S4** Details regarding the bonding modes of $CO_2$ adsorption on the $Ti_3C_2(0001)$ surface with $F_{1/3}OH_{1/3}O_{1/3}$ termination, encompassing (a) the exploration of various hexagonal centre configurations to elucidate distinct $CO_2$ adsorption environments, and (b) the investigation of different orientations for $CO_2$ adsorption.

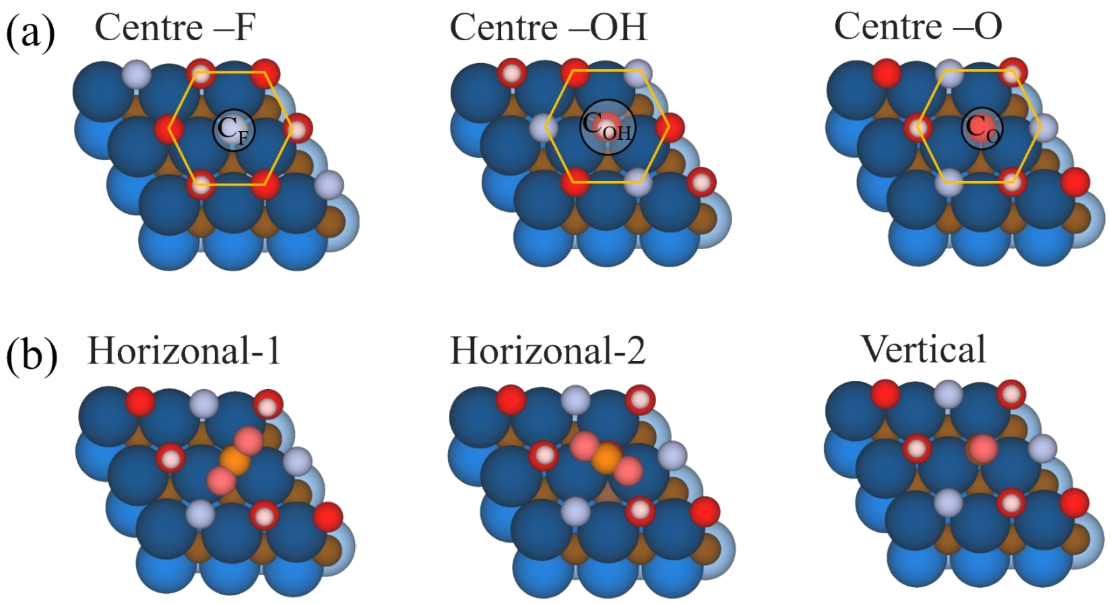

**Fig. S5** Top view of the charge density difference (CDD) plots of the studied $Ti_3C_2$ (0001) MXene models. Yellowish regions denote electron depletion, *i.e.* the formation of positively charged regions, while blueish regions denote electron accumulation, and the formation of negatively charged regions. The contour intervals range to 0.005 e·Å$^{-3}$ increments.

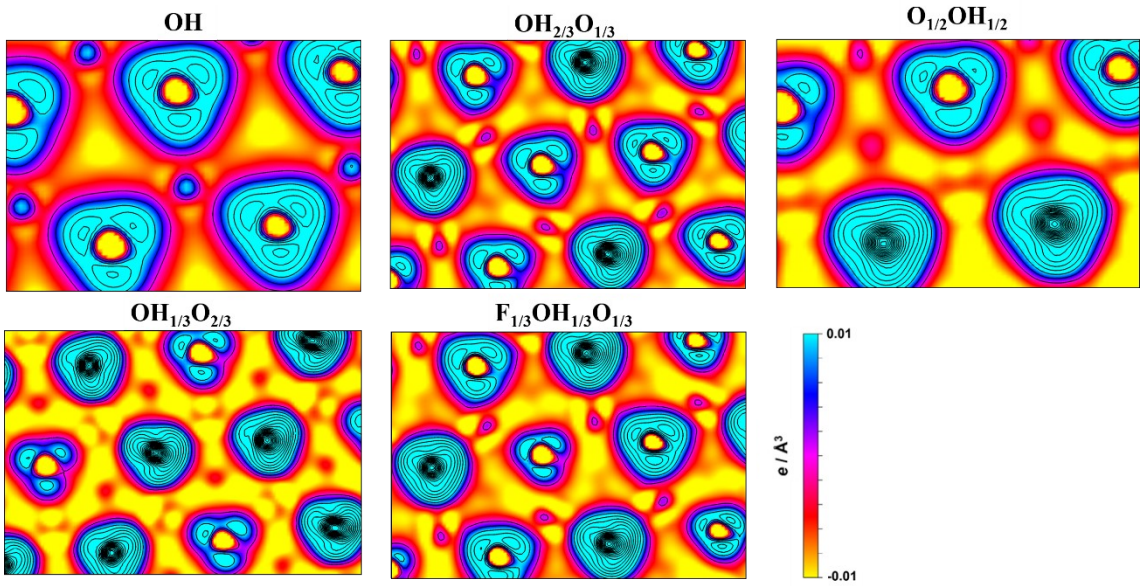

**Fig. S6** Calculated rates of adsorption, $r_{ads}$, and desorption, $r_{des}$, of $CO_2$ and $CH_4$ on (a) clean surface, (b) full –OH, (c) $–OH_{2/3}O_{1/3}$, (d) $–OH_{1/2}O_{1/2}$, (d) $–OH_{1/3}O_{2/3}$, (e) $–F_{1/3}OH_{1/3}O_{1/3}$ terminations, as a function of temperature, $T$, and the gas partial pressure, $p$, here shown for 1 bar.

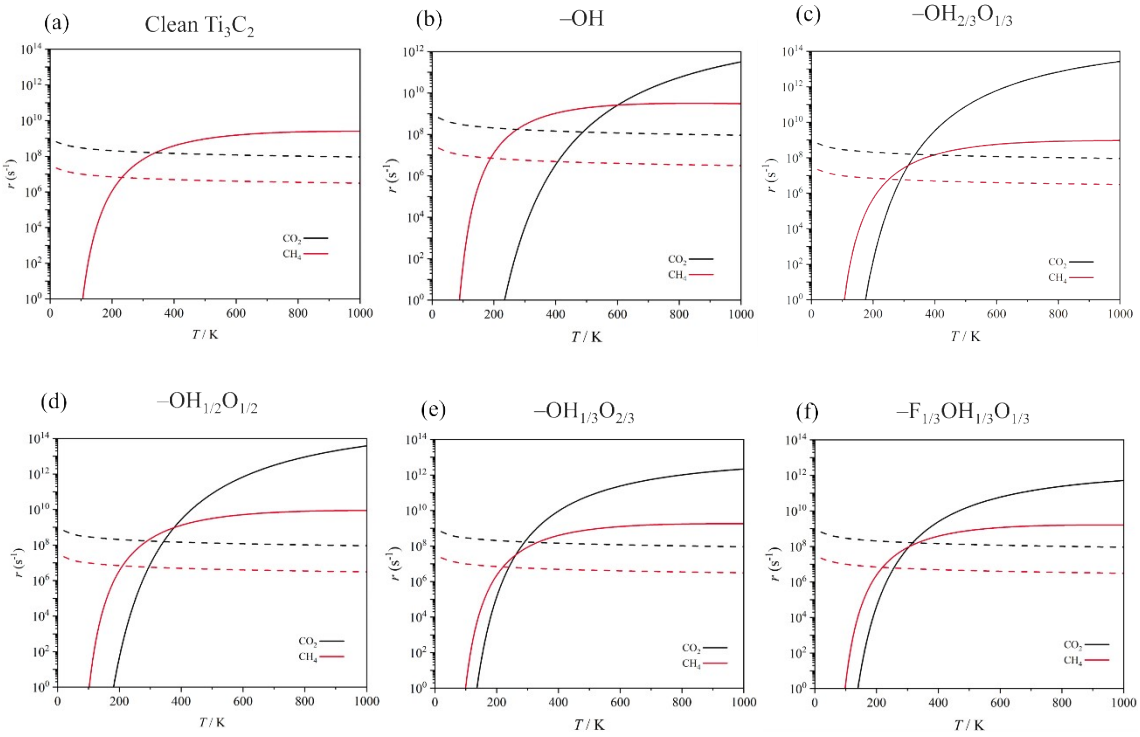

**Fig. S7** Complete Gibbs free energy, Δ*G*, diagram of $CO_2$RR on fully –OH terminated $Ti_3C_2$ MXene, under standard working conditions. Blue lines represent chemical steps of as-generated $H_2O$ or $CH_4$ desorptions, or $CO_2$ adsorption, while black and grey lines represent the electrochemical proton-coupled electron transfer (PCET) steps at zero potential *vs.* SHE. The –nH* symbols refer to how many H atoms have been transferred from surface –OH groups at the reaction stage.

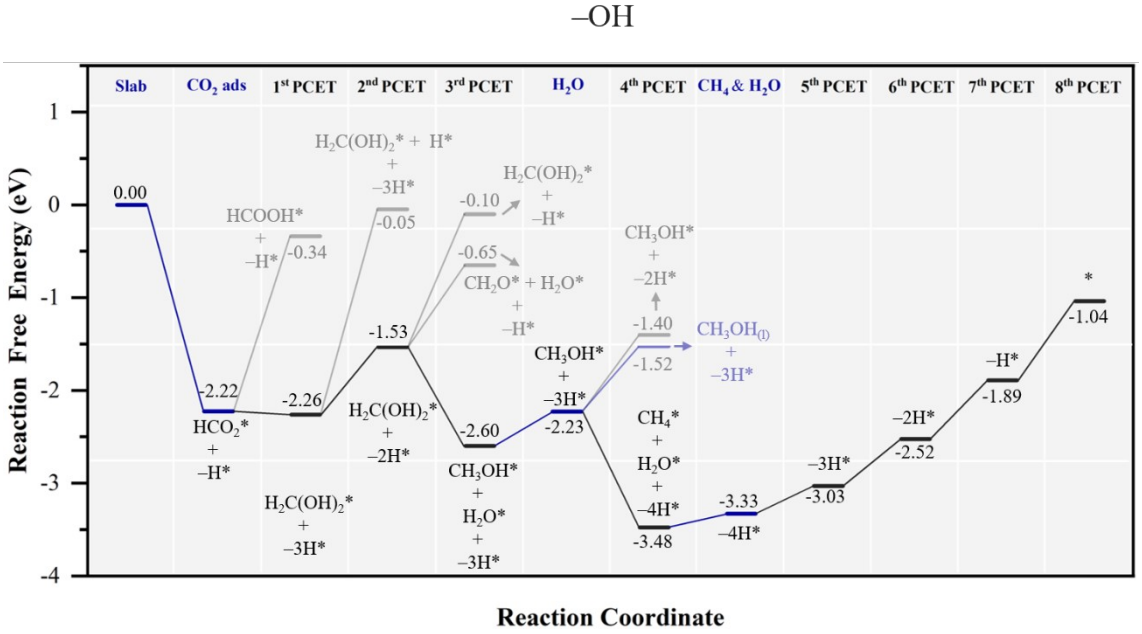

**Fig. S8** Complete Gibbs free energy, Δ*G*, diagram of $CO_2$RR on $–OH_{2/3}O_{1/3}$ $Ti_3C_2$ MXene model, under standard working conditions at zero potential *vs.* SHE. Colour code as in Figure S6. nH* symbols refer to how many H atoms have been reduced over surface –O groups at the given reaction stage.

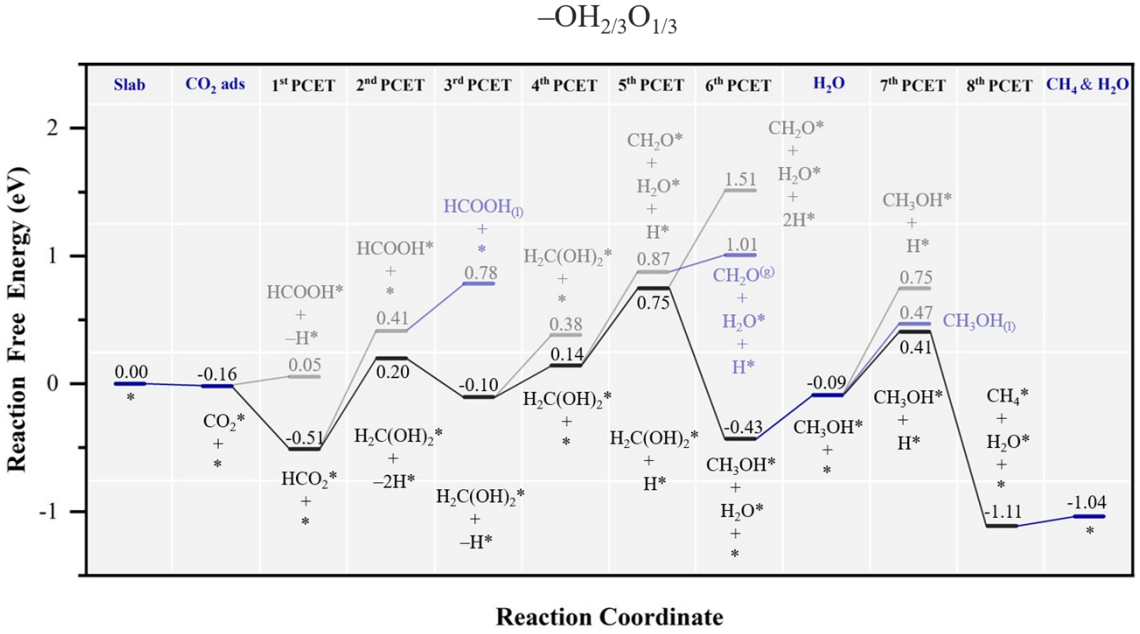

**Fig. S9** Complete Gibbs free energy, Δ*G*, diagram of $CO_2$RR on $–OH_{1/2}O_{1/2}$ $Ti_3C_2$ MXene model, under standard working conditions at zero potential *vs.* SHE. Colour code and notation as in Figures S6 and S7.

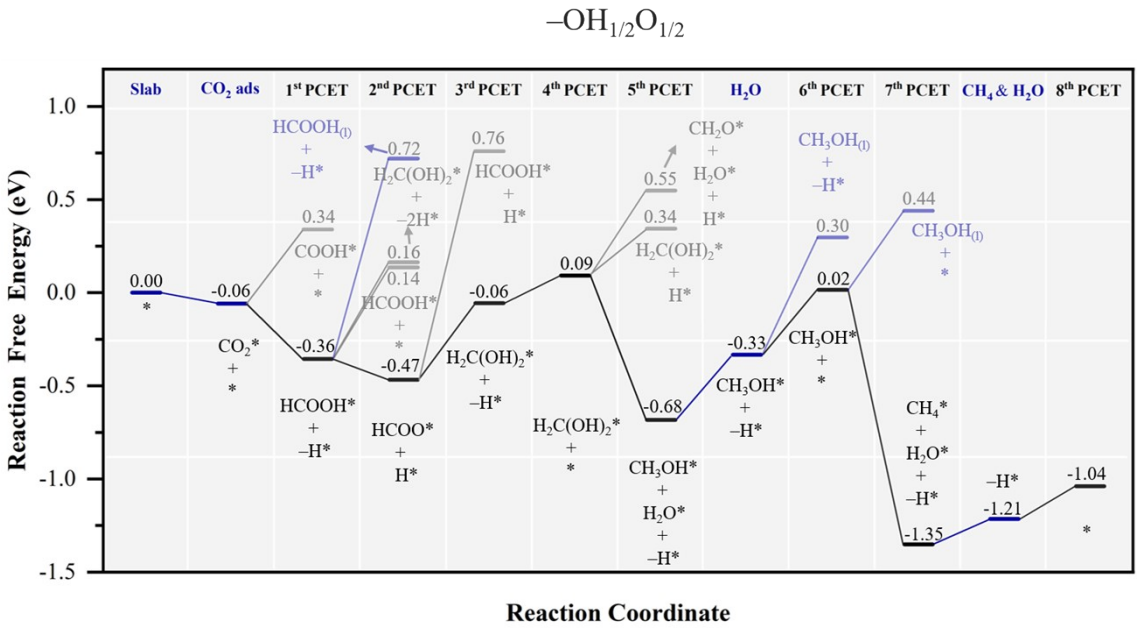

**Fig. S10** Complete Gibbs free energy, Δ*G*, diagram of $CO_2$RR on $–OH_{1/3}O_{2/3}$ $Ti_3C_2$ MXene model, under standard working conditions at zero potential *vs.* SHE. Colour code and notation as in Figures S6 and S7.

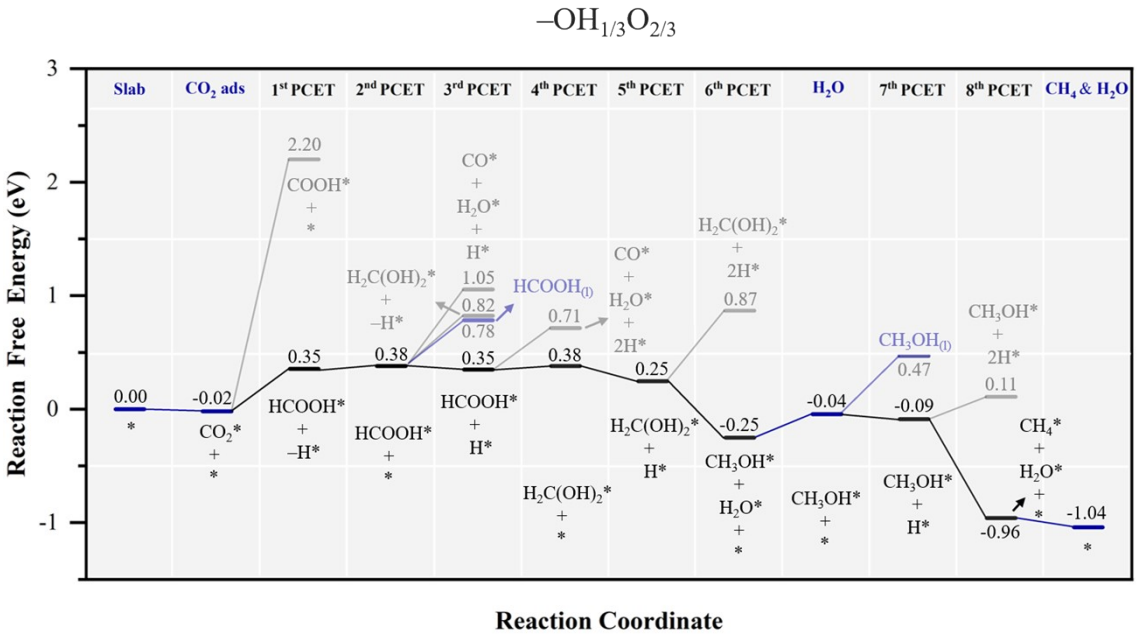

**Fig. S11** Complete Gibbs free energy, Δ*G*, diagram of $CO_2$RR on $–F_{1/3}OH_{1/3}O_{1/3}$ $Ti_3C_2$ MXene model, under standard working conditions at zero potential *vs.* SHE. Colour code and notation as in Figures S6 and S7.