

Supporting Information

1. Work function calculation

For modelling a charged interface for calculating the electrocatalytic reaction, H atoms were introduced into the water layer which could separate into protons and electrons. Thus, one may vary the surface charge and the potential by changing the concentration of protons. In the calculation of work function (Φ), a long time *ab initio* molecular simulation (20 ps) was performed. We calculated the work function of 20 structures from the last 5 ps MD simulation, and further averaged them as the representative value for the system. The calculated work functions of these 20 samples are listed in **Table S1** with the standard deviations. The electrode potential (U) was obtained by referring the work function of the system to the experimental work function of standard hydrogen electrode (SHE) according to the following equation, $U = \Phi/e - 4.44$. The electrostatic potential is plotted in **Fig. S1**. One can see that the work function is 2.40 ± 0.29 eV and the corresponding electrode potential is -2.04 V (vs SHE).

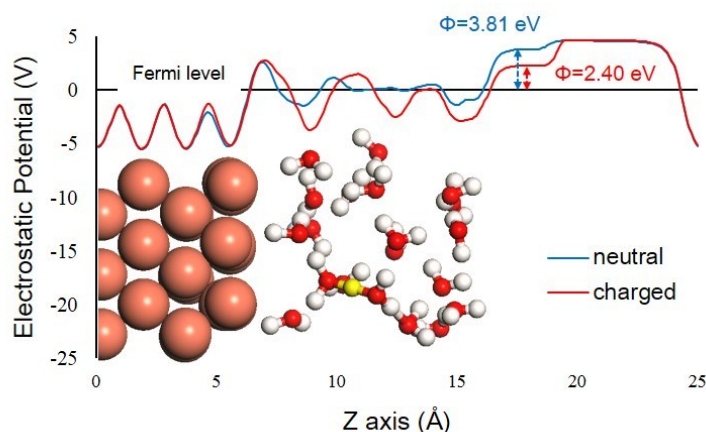


Fig. S1. Electrostatic potential profile averaged on the surface plane as a function of the z-axis. The blue line was calculated from the neutral system and the red line from

the charged system with H⁺ highlighted by yellow.

Table S1. Calculated work functions (Φ , in eV) of 20 structures from *ab initio* molecular dynamics simulations.

charged	Φ	$\bar{\Phi}$
	2.42,2.53,2.29,2.11,2.42,	2.40±0.29
	2.51,2.56,2.32,2.45,2.55,	
	2.46,2.34,2.2,2.41,2.42,	
	2.52,2.59,2.16,2.26,2.51,	

2. Free-energy gradient

For each state we performed *ab initio* MD simulation for 6 ps (1 fs per step, 6000 steps) at a constant room temperature ($T = 300$ K) until the interatomic forces were converged. We found that, the interatomic force starts usually to converge after a MD duration of at least 3 ps. To be accurate, we only selected the samples from the last 1 ps (1000 samples) of each MD simulation to do the average of the interatomic force, which was much longer than the oscillation period (~ 50 fs).

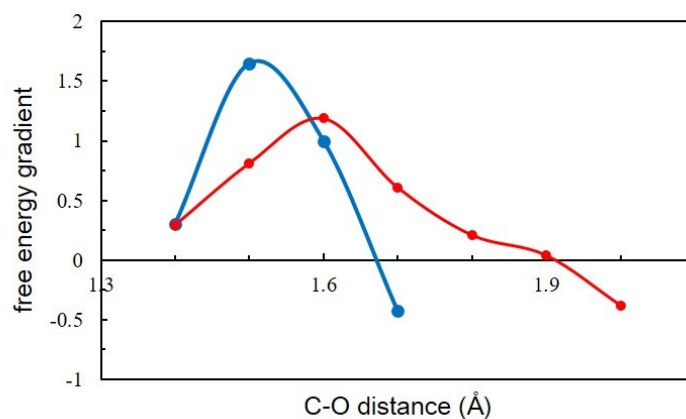


Fig. S2 Comparison of the free-energy gradients in the reactions (1) (in blue) and (2) (in red) from initial state to transition state.