Supplementary information for:

First-principles mechanistic insights into the hydrogen evolution reaction on Ni_2P electrocatalyst in alkaline medium

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This supporting information contains two figures and one table summarizing the results of the different co-adsorption geometries of OH and H explored on the (0001) and (10$\bar{1}$0) surface of Ni_2P.

Figure S1: The optimized structures of dissociated water configurations (C) on the Ni_3P_2- and Ni_3P-terminations of (0001) surface of Ni_2P.

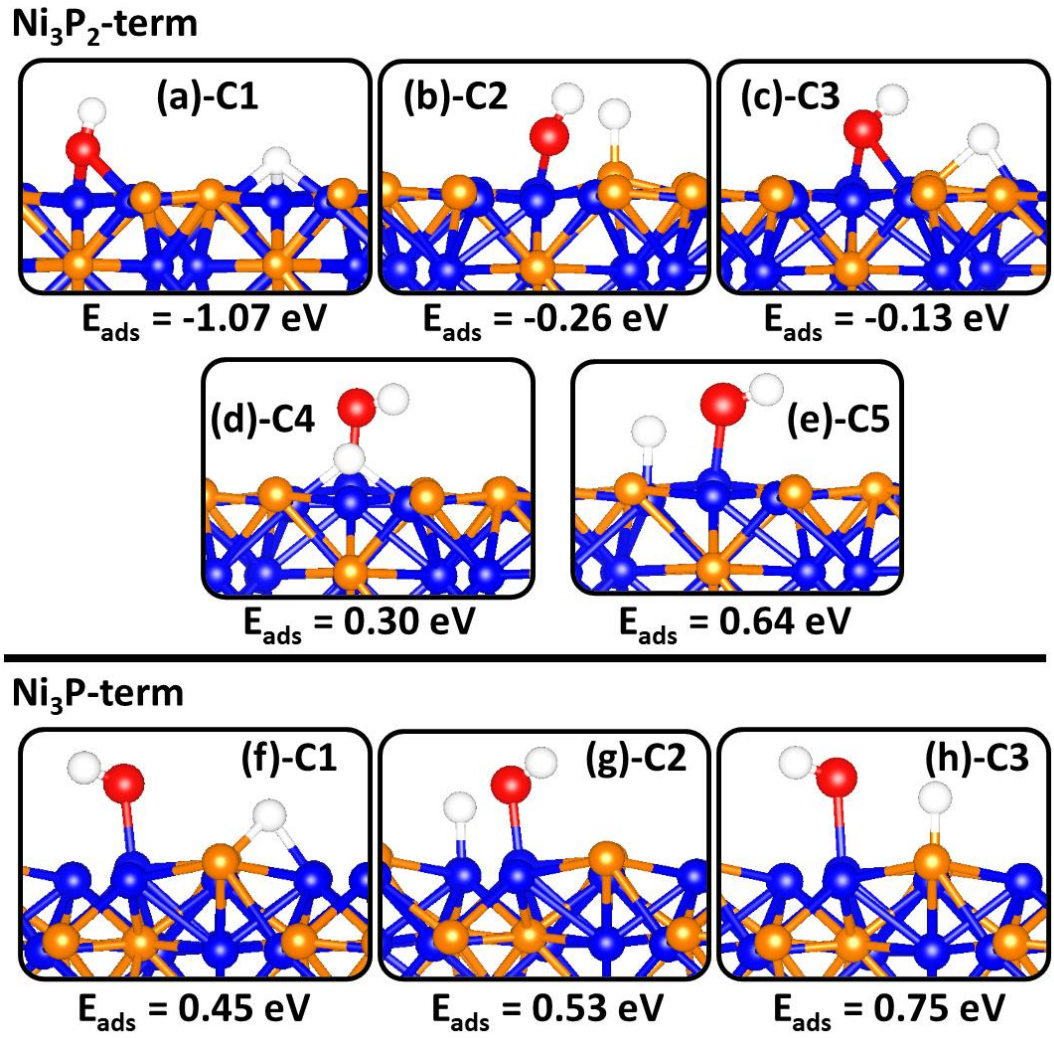

Figure S2: The optimized structures of dissociated water configurations (C) on the Ni_2P- and NiP-terminations of the $(10\bar{1}0)$ surface of Ni_2P.

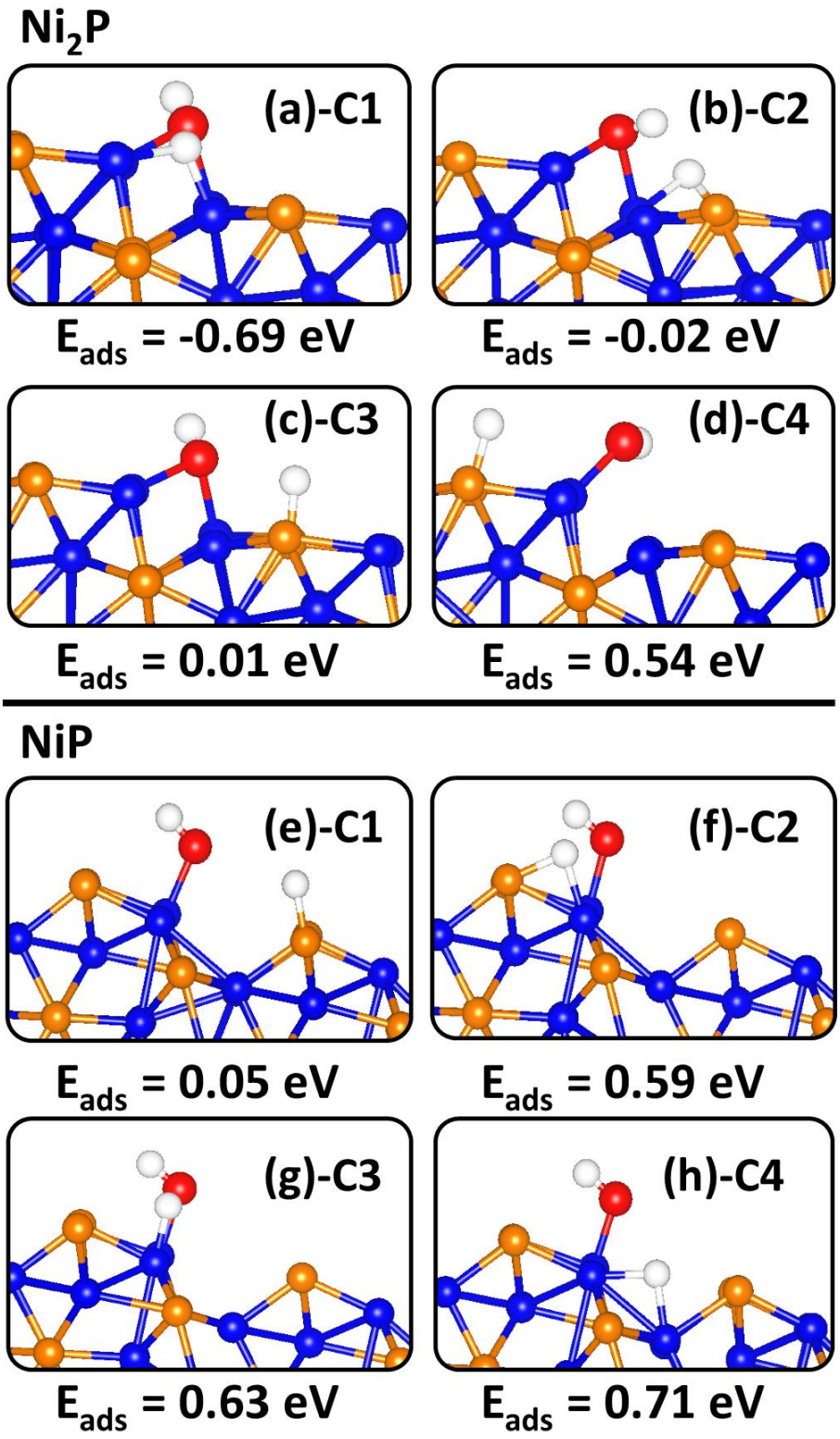

Table S1: Dissociative adsorption energies (E_{ads}) and bond lengths (d) for water on Ni_2P (0001) and (10$\bar{1}$0) surfaces. H-P bond distances are denoted as d(P). Sites Ni, P, Ni-Ni and Ni-P denote top-Ni, top-P, bridge-Ni-Ni and bridge-Ni-P.

Surface	**Term/Config**	**H-Site**	E_{ads}**(OH + H) (eV)**	**avg.** d**(Ni−O) (Å)**	d**(O−H) (Å)**	d**(Ni−H) (Å)**
(0001)	Ni_3P_2/C1	Ni	-1.07	2.034	0.978	1.761
	Ni_3P_2/C2	P	-0.26	2.051	0.976	1.439
	Ni_3P_2/C3	Ni-P	-0.13	1.998	0.987	1.633 /1.646(P)
	Ni_3P_2/C4	Ni-Ni	0.30	1.848	0.982	1.635
	Ni_3P_2/C5	Ni	0.64	1.861	0.978	1.480
	Ni_3P/C1	Ni-P	0.45	1.860	0.977	1.746, 1.547 (P)
	Ni_3P/C2	Ni	0.53	1.838	0.973	1.493
	Ni_3P/C3	P	0.75	2.064	0.999	1.506 (P)
(10$\bar{1}$0)	Ni_2P/C1	Ni-Ni	-0.69	1.969	0.975	1.582
	Ni_2P/C2	Ni-P	-0.02	1.995	0.980	1.757, 1.499 (P)
	Ni_2P/C3	P	0.01	1.979	0.977	1.435 (P)
	Ni_2P/C4	P	0.54	1.826	0.983	1.436 (P)
	NiP/C1	P	0.05	1.841	0.980	1.427 (P)
	NiP/C2	Ni-P	0.59	1.849	0.993	1.673 /1.584 (P)
	NiP/C3	Ni	0.63	1.830	0.982	1.495
	NiP/C4	Ni-Ni	0.71	1.836	0.984	1.662