

## Support Information

### **Hydrogen evolution reaction activity for facet-dependent electrocatalytic performance of NiCoP from first principles**

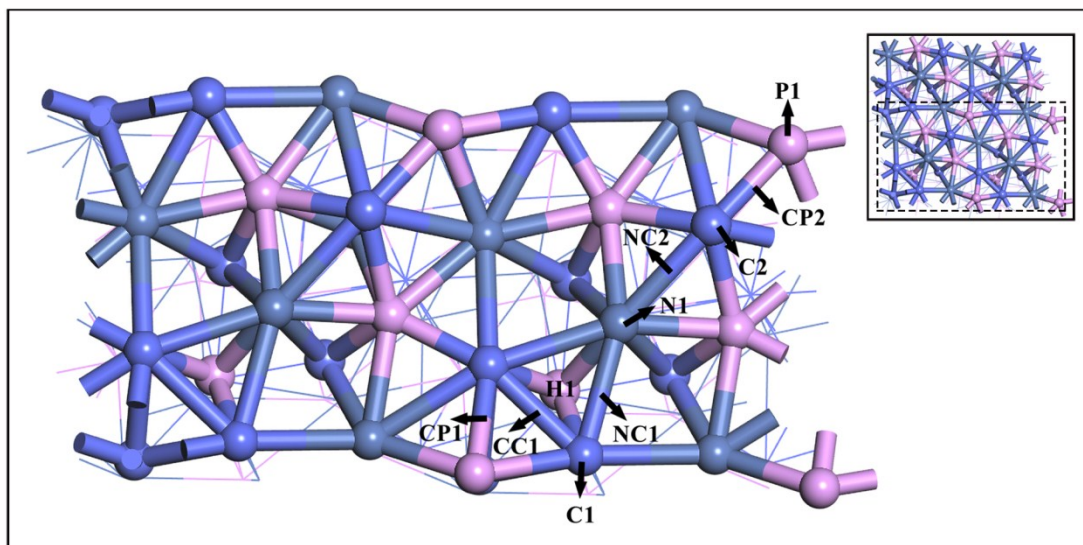
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**Table S1.** The vibrational frequencies of the facets with hydrogen adsorption (unit in  $\text{cm}^{-1}$ )

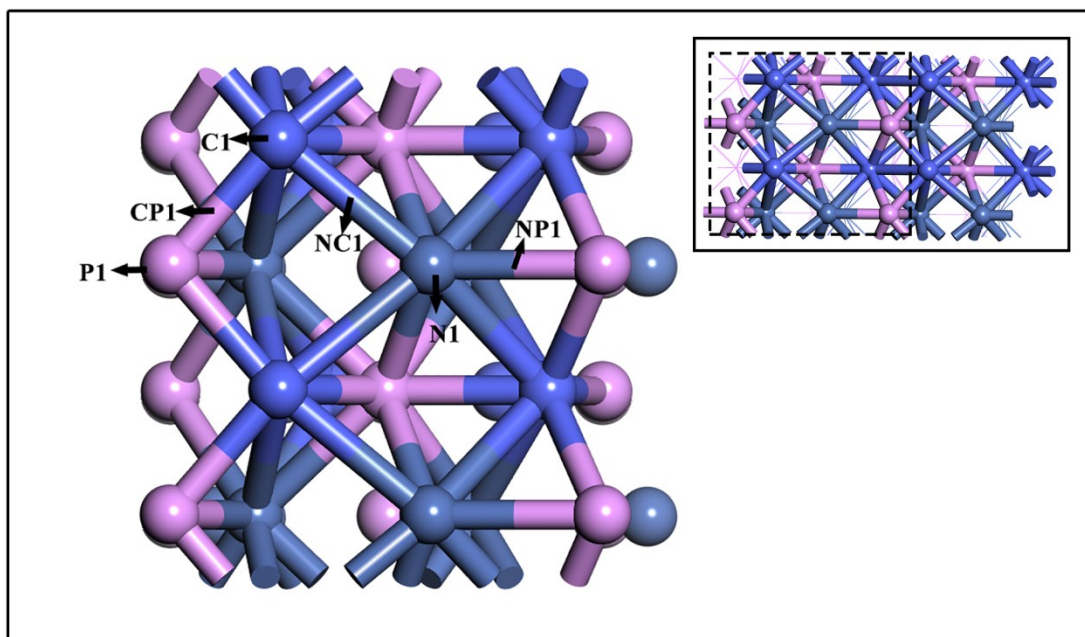
Surface type	$\nu_1$	$\nu_2$	$\nu_3$
(111)	1218	942	573
(100)	1281	933	600
(001)-NiP-t	1056	722	715
(001)-CoP-t	1138	768	764



**Figure S1.** All possible adsorption sites on (111) facet. Note that the color of gray, blue and pink stand for Ni, Co and P atoms, respectively.

**Table S2.** Adsorption energy of the optimized hydrogen adsorption sites for (111) facet (unit in eV).

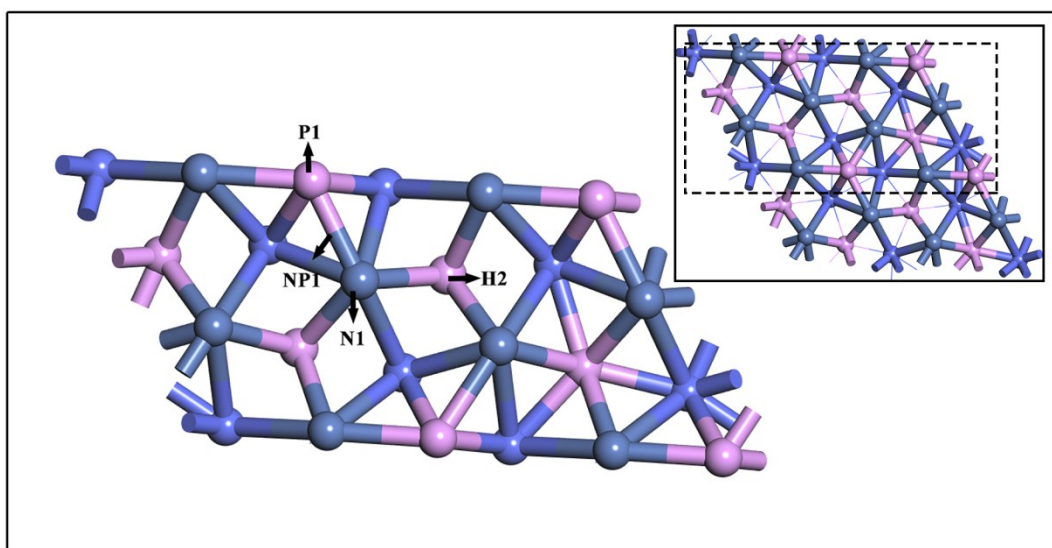
Adsorption sites	CP1	C1	CC1	NC1	H1	N1	NC2	C1	CP2	P1
(111) facet	move to H1	move to H1	move to H1	move to H1	-0.76	move to H1	-0.46	move to H1	move to NC2	0.43



**Figure S2.** All possible adsorption sites on (100) facet. Note that the color of gray, blue and pink stand for Ni, Co and P atoms, respectively.

**Table S3.** Adsorption energy of the optimized hydrogen adsorption sites for (100) facet (unit in eV).

Adsorption sites	P1	CP1	C1	NC1	N1	NP1
(100) facet	0.24	move to N1	move to N1	move to N1	-0.72	0.27

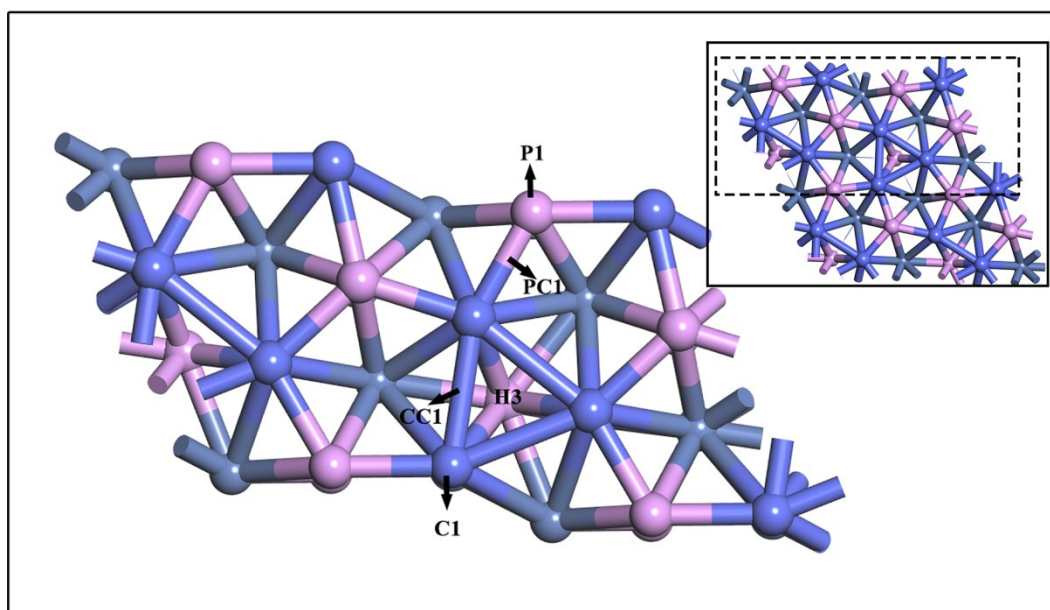


**Figure S3.** All possible adsorption sites on (001)-NiP-t facet. Note that the color of gray, blue and pink stand for Ni, Co and P atoms, respectively.

**Table S4.** Adsorption energy of the optimized hydrogen adsorption sites for (001)-NiP-t facet (unit in eV).

Adsorption sites	P1	PN1	N1	H2
(001)-NiP-t facet	move to H2	move to H2	move to H2	-0.42

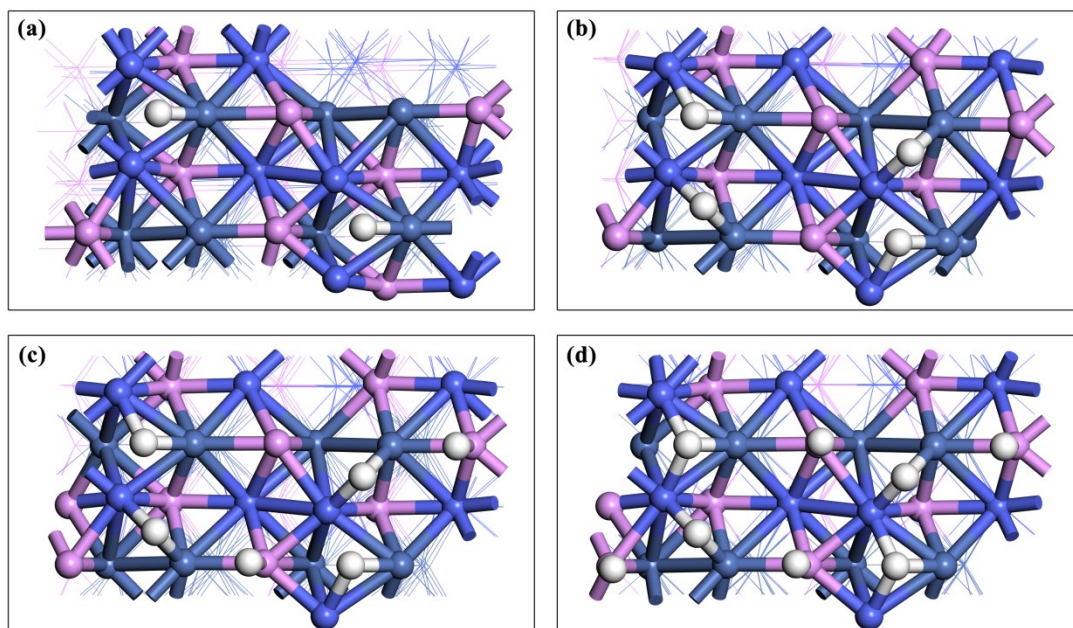




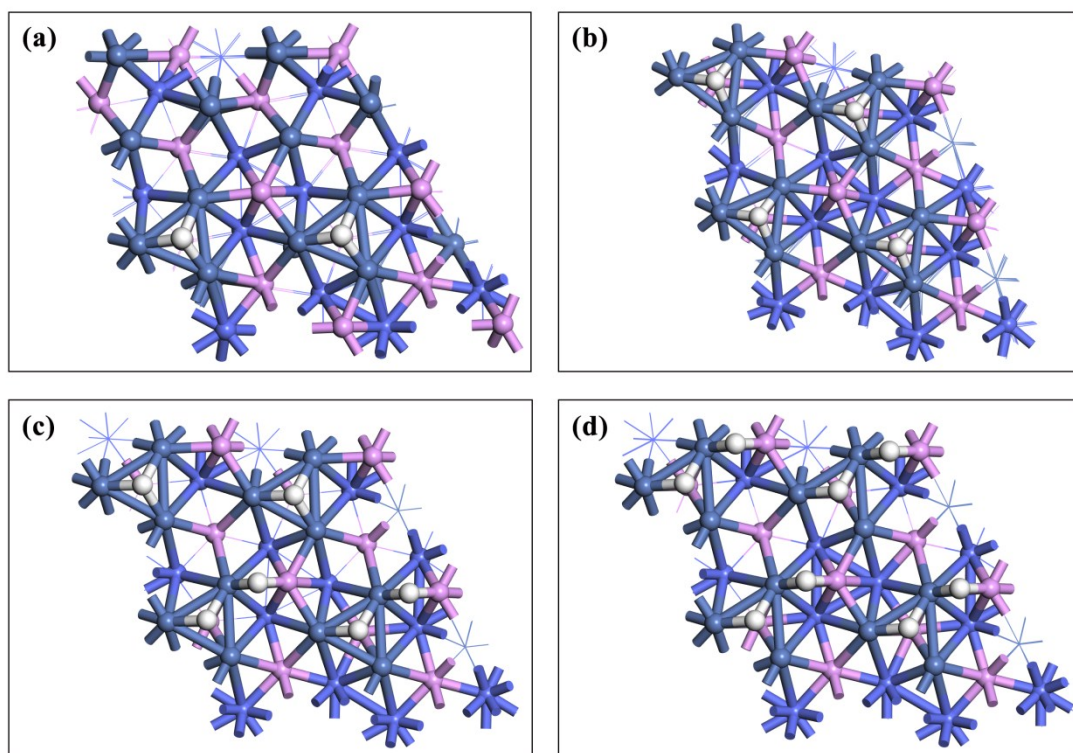
**Figure S4.** All possible adsorption sites on (001)-CoP-t facet. Note that the color of gray, blue and pink stand for Ni, Co and P atoms, respectively.

**Table S5.** Adsorption energy of the optimized hydrogen adsorption sites for (001)-CoP-t facet (unit in eV).

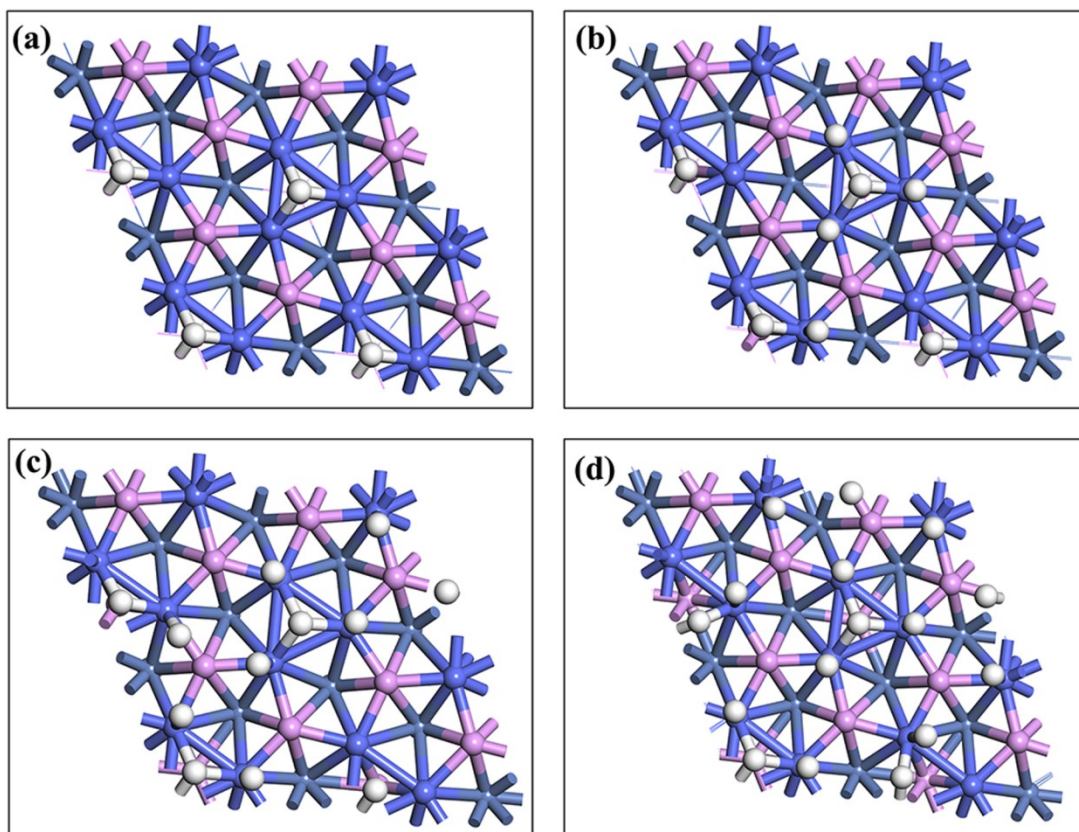
Adsorption sites	P1	C1	PC1	CC1	H3
(001)-CoP-t facet	move to H3	move to H3	move to H3	move to H3	-0.80



**Figure S5.** Optimized structures of (100) facet at typical hydrogen coverage: (a) 25%, (b) 50%, (c) 75% and (d) 100%. Note that the color of gray, blue, pink and white stand for Ni, Co, P and H atoms, respectively.



**Figure S6.** Optimized structures of (001)-NiP-t facet at typical hydrogen coverage: (a) 25%, (b) 50%, (c) 75% and (d) 100%. Note that the color of gray, blue, pink and white stand for Ni, Co, P and H atoms, respectively.



**Figure S7.** Optimized structures of (001)-CoP-t facet at typical hydrogen coverage: (a) 25%, (b) 50% (c) 75% and (d) 100%. Note that the color of gray, blue, pink and white stand for Ni, Co, P and H atoms, respectively.