Supplementary Information for "Enhancing Electrocatalysis for Hydrogen Production over CoP Catalyst by Strain: a Density Functional Theory Study"

Fanghan Liu, Cong Liu and Xiaoliang Zhong *
* Correspondence: xzhong@hust.edu.cn

1. DFT Calculation methods

DFT calculations were performed using the plane-wave technique implemented in the Vienna ab initio Simulation package (VASP)[1]. The electron-ion interactions were described by the projector augmented plane wave (PAW) pseudopotentials[2]. Perde-Burke-Ernzerhof (PBE) functional[3] was used to express the generalized gradient approximation (GGA). Plane-wave cutoff energy was set to 400 eV in all computations. The convergences of energy and force were set as 10^{-4} eV and 0.03 eV/Å, respectively. 1x1 and 1x2 supercell models of (111) and (101) facets were built for the calculation of ΔG_H, with a slab thickness about 10Å. A vacuum about 10Å along the c direction was added to avoid the interaction between periodic images. A 6x6x1 Monkhorst–Pack k-point mesh were set for the structure optimization. Denser k-points were set as 12x12x1 for the calculation of energy and DOS.

2. The Gibbs Free Energy of Absorbed H

The binding energy of hydrogen atoms on the surface is calculated by the following formula:

$$\Delta E_H = E(CoP + nH) - E[CoP + (n-1)H] - \frac{1}{2}E(H_2)$$

where $E(CoP+nH)$ and $E[CoP+(n-1)H]$ represent the total energy of the CoP system with n and n-1 adsorbed hydrogen atoms on the surface, respectively. The total energy of a gas phase H_2 molecule is represented by $E(H_2)$. The differential Gibbs free energy of adsorption ΔG_H can be calculated as below:

$$\Delta G_H = \Delta E_H + \Delta E_{ZPE} - T\Delta S_H$$

The ΔE_H, ΔE_{ZPE}, and ΔS_H are the binding energy, zero-point-energy change and entropy change of H adsorption, respectively. This formula can be further simplified to the following[4] :

$$\Delta G_H = \Delta E_H + 0.24\mathrm{e}V$$

3. CoP (101) surface adsorption site electronic structure

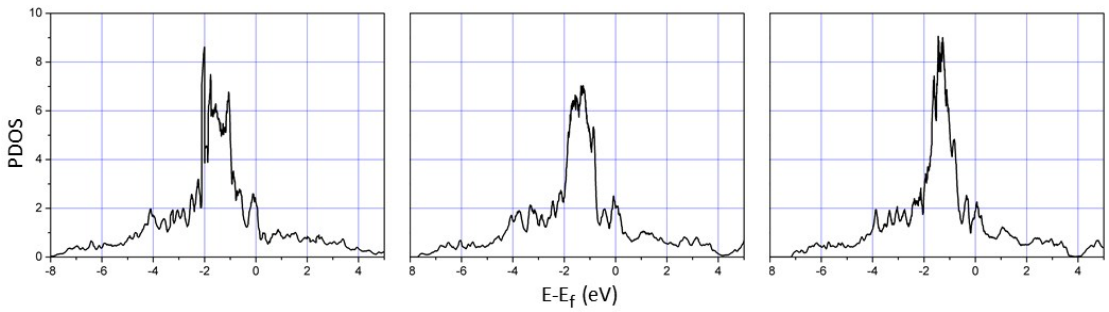

Fig. s1 Evolution of d-band PDOS with arbitrary unit for hydrogen adsorption site.

4.

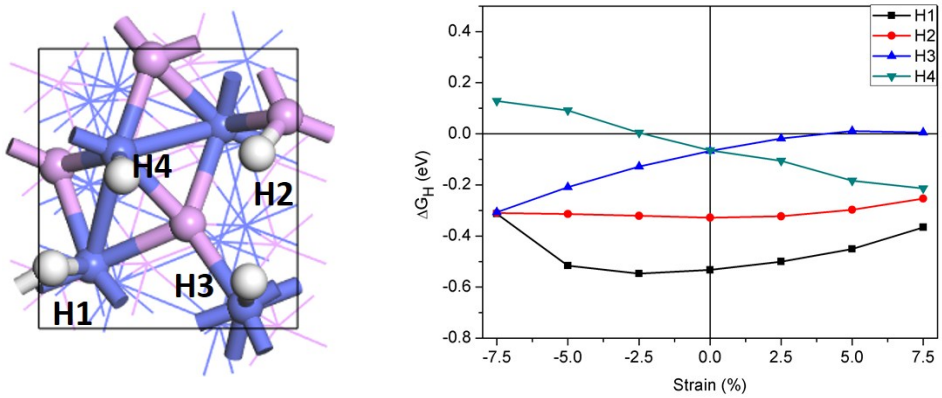

Fig. s2 Structure of CoP (110) surface with hydrogen adsorption (left) and evolution of ΔG_H under strain (right).

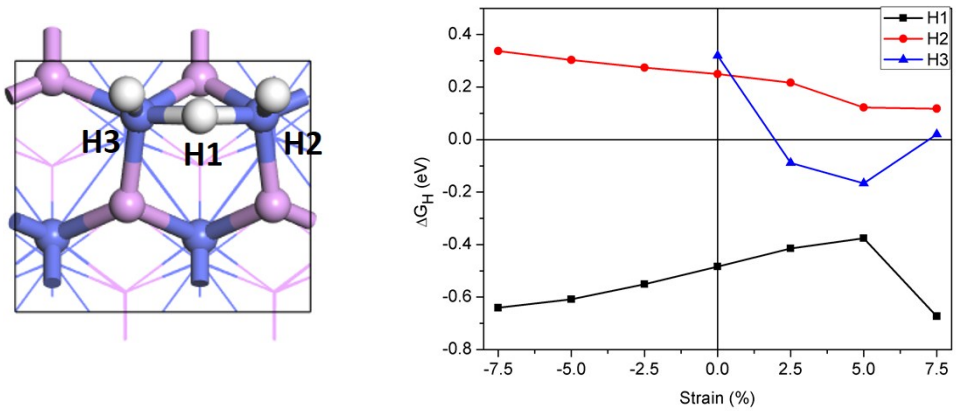

Fig. s3 Structure of CoP (100) surface with hydrogen adsorption (left) and evolution of ΔG_H under strain (right).

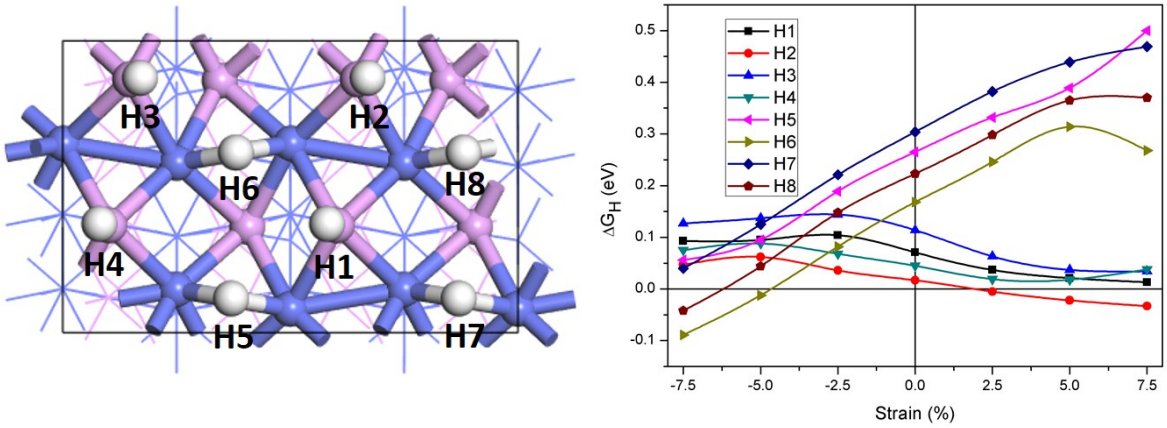

Fig. s4 Structure of CoP (011) surface with hydrogen adsorption (left) and evolution of ΔG_H under strain (right).

1. G. Kresse and J. Hafner, *Physical Review B*, 1993, **47**, 558-561.
2. G. Kresse and D. Joubert, *Physical Review B*, 1999, **59**, 1758-1775.
3. J. P. Perdew, K. Burke and M. Ernzerhof, *Physical Review Letters*, 1996, **77**, 3865-3868.
4. J. K. Nørskov, T. Bligaard, A. Logadottir, J. R. Kitchin, J. G. Chen, S. Pandelov and U. Stimming, *Journal of The Electrochemical Society*, 2005, **152**, J23-J26.