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

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Facet-dependent strain effects on hydrogen evolution reaction catalyzed by CoP are studied based on density functional theory methods. We show that both atomic and electronic effects need to be taken into consideration to understand the strain effects. For (111) surface tensile strain promotes hydrogen evolution at all hydrogen coverages. For (101) surface a moderate tensile strain of ~3% turns this facet to optimum performance.

The production of hydrogen fuel by economic water splitting methods provides an intriguing route towards sustainable clean energy¹. However, the hydrogen evolution reaction (HER) is mostly catalysed by Pt, a rare and expensive element, which impedes its massive utilization. Recently, transition metal phosphides (TMPs) have been intensively investigated to replace platinum, which show active catalytic properties for HER². Among the studied TMPs, CoP is especially promising due to its high performance, high stability and facile fabrication²⁻⁶.

Although being an active HER catalyst, performance of CoP is still significantly lower than that of Pt². Recent research efforts have established the strength of strain engineering in optimizing electrocatalytic properties of noble-metal-based catalysts⁷. Although TMPs are very promising HER catalysts, we note that strain effects on TMPs have rarely been studied. In the present work we study the possibility of utilizing surface straining to improve CoP performance towards more practical Pt replacement. In fact, fine tuning of surface strain towards catalyst optimization is under active research via, for example, core-shell structuring⁷, in situ transformation⁸ and substrate-catalyst interaction⁹. Interestingly, cobalt (II) oxide (CoO), which

was traditionally considered as HER-inactive, became highly active for HER when a tensile strain is applied to its surface¹⁰. In another work, nickel phosphide (NiP) showed an increased turnover frequency of 24 times for HER when a substantial compressive strain of 5.6% is induced⁸. We expect our contribution could serve as the solid theoretical guidance for experimental investigations to utilize strain effect to promote hydrogen evolution on CoP.

Rational improvement in catalysts performance requires solid understanding of catalysis mechanism. The high activity of TMPs has recently been correlated with the small hydrogen adsorption free energy (ΔG_H)². The as-synthesized CoP nanostructures are typically multi-faceted, with more than one crystal facets exposed which may function as the active sites⁴⁻⁶. As such, identifying the active surfaces is crucial. Density functional theory (DFT) methods^{11, 12} have shed light by calculating ΔG_H on CoP. It is found that TMPs follow the Sabatier principle, that is, materials with optimum performance exhibit close to zero ΔG_H ^{2, 13}. Kibsgaard et al. studied a series of TMPs and indicated that high performance of CoP originated from the (101) surface². For this surface, DFT calculations assigned a small ΔG_H of -0.085 eV, explaining the high performance. Hu et al. looked into hydrogen adsorption on various low-Miller-index surfaces of CoP via DFT calculations¹⁴. They concluded that (111) surface of CoP is thermodynamically stable with ΔG_H smaller than 0.1 eV in magnitude. Notably, most of the recent studies on CoP assigned the active facets to either the (101)¹⁵⁻¹⁸ or (111)^{19, 20} surface.

As shown in Figure 1, the CoP crystal has an orthorhombic unit cell. The present DFT study will focus on strain effects on both (111) and (101) surfaces. As mentioned above, these two are identified as the active facets for HER. Besides (111) and (101) surfaces, we have also calculated strain effects on other facets ((110), (100), and (011)) which were studied in reference¹⁴. The results are summarized from Fig. s2 to Fig. s4 in the Supporting Information. The detailed analysis for these facets is, however, beyond the scope of this work. For the (111) surface, previous study shows that hydrogen adsorption highly

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depends on coverage rate¹⁴. For low hydrogen coverage ($\leq 25\%$), ΔG_H is as low as -0.6 eV indicating too strong adsorption. For higher coverage ($>25\%$), magnitude of ΔG_H is around 0.1 eV, signalling good HER catalysis. Our model is similar to the reported one¹⁴. The adsorption of 1, 2, 3 and 4 hydrogen atoms to a simulation unit surface (Fig. 1) corresponds to an H coverage of 25%, 50%, 75% and 100%, respectively.

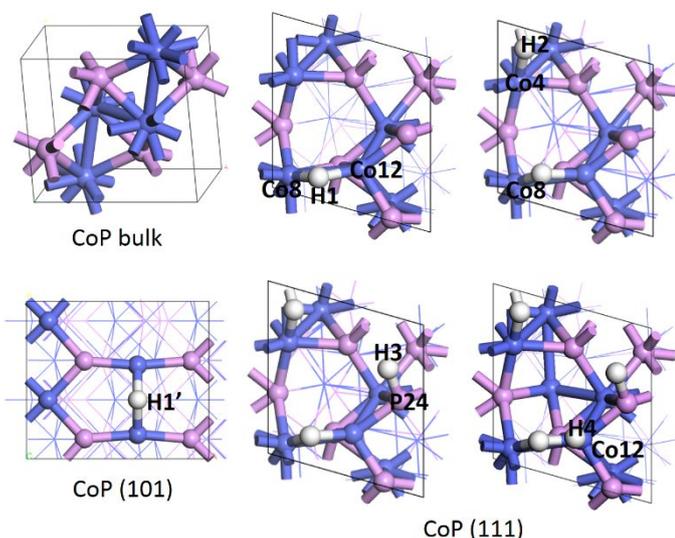


Fig. 1 Optimized structures of CoP bulk crystal as well as (111) and (101) surfaces at different H coverages. H1, H2, H3 and H4 represents hydrogen coverage of 25%, 50%, 75% and 100% on the (111) surface, respectively. H1' represents hydrogen coverage of 25% on the (101) surface. Colour scheme: H in grey, Co in blue and P in purple.

The first H atom (H1) binds with 2 Co atoms (Co8 and Co12) at the bridge site (Figure 1), exhibiting lowest ΔG_H among different adsorption sites on the (111) surface. After the adsorption of the first atom, the second H atom (H2) also binds with 2 Co atoms (Co4 and Co8) at the bridge site. Then the third H atom (H3) binds to 1 P atom (P24). Finally, the fourth H atom (H4) binds to 1 Co atom (Co12). The present results are in good agreement with the reported¹⁴, i.e., while H1 exhibits a low ΔG_H of -0.53 eV (without consideration of strain), H2 to H4 show ΔG_H with magnitude no greater than 0.2 eV (Fig. 2).

In reference¹⁴, the authors used a 2×2 supercell model for the (111) surface. In our calculation, we use a 1×1 unit cell model. We would like to point out that, although there is difference between our model and reference¹⁴, the calculated ΔG_H in general agrees well with reference¹⁴. As shown in Fig. 2, our calculation yields ΔG_H of -0.53 , 0.01 , -0.04 and 0.14 eV at coverage of 25%, 50%, 75% and 100% on the (111) surface, respectively. From Fig. 4 in reference¹⁴ one finds ΔG_H of -0.6 , -0.1 , -0.1 and 0.1 eV at these coverages. Thus, although our model is smaller, we get ΔG_H in line with reference¹⁴.

For CoP (101) surface we consider only one H atom adsorbed at Co bridge site to the surface unit cell (Fig. 1), which corresponds to an H coverage of 25%. This is the steady-state and most active H coverage². Since CoP (101) surface is likely to operate at this low hydrogen coverage rate, higher H coverage rate is expected to be irrelevant to HER².

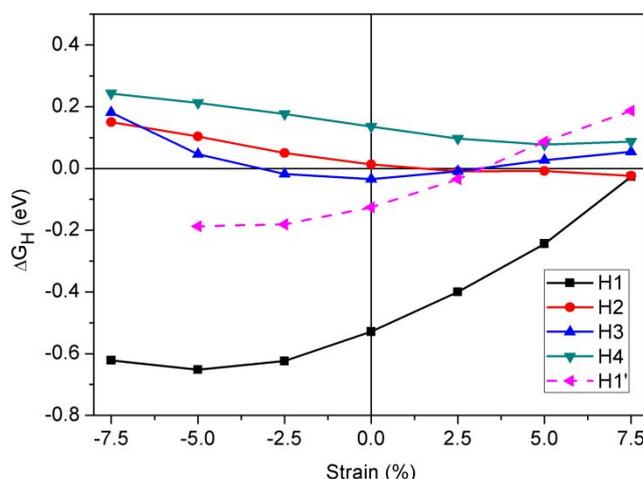


Fig. 2 Evolution of CoP surface hydrogen adsorption free energy as a function of applied strain. H1 to H4 corresponds to hydrogen on the (111) surface, while H1' corresponds to hydrogen on the (101) surface (see Fig. 1).

Figure 2 presents the variation of ΔG_H when strain is applied to CoP surfaces, showing interesting features. With low H coverage of 25% (H1 and H1'), ΔG_H increases (more positive) with expansive strains on both the (111) and (101) surfaces. For H1 on (111) surface, ΔG_H spans a considerable energy range of about 0.6 eV in the considered strain range (from -7.5% to 7.5%). Notably, ΔG_H is calculated to be -0.03 eV when a tensile strain (positive strain) of 7.5% is applied, signalling HER performance is close to optimum for this adsorption site (ΔG_H equals to zero). It is to be noted that without applying strain, H1 adsorption site is not expected to be HER-active due to low ΔG_H ¹⁴. When a compressive strain (negative strain) is applied, ΔG_H is even lower than the value at zero strain (-0.53 eV), indicating worse catalytic properties for this site. For H1' on (101) surface, unstained ΔG_H of -0.13 eV is also close to the reported (-0.09 eV²). Figure 2 indicates a positive strain of about $+3\%$ turns H adsorption to the energy-neutral point, i.e., ΔG_H equals to zero. This is very interesting since HER rate is proportional to the exponential of ΔG_H^2 , such that decrease of ΔG_H (in magnitude) indicates a notable promotion of HER. On the other hand, compressive strain renders more negative ΔG_H which negatively affects hydrogen evolution.

On the other hand, for higher H coverages (H2 to H4) on (111) surface, ΔG_H shows significantly less variation of about 0.2 eV in the whole strain range. For H2 and H4, the variation of ΔG_H is monotonic with applied strain and decreases when surface is expanded. For H3, a lowest ΔG_H appears around zero strain and either tensile or compressive strain shifts up ΔG_H . Interestingly, at tensile strain of about 7.5% all H coverages from H1 to H4 exhibit ΔG_H smaller than 0.1 eV in magnitude. This implies considerably improved HER catalysis with all hydrogen adsorption sites close to highest performance.

We note that both the atomic and electronic effects need to be taken into account, to explain the change of hydrogen adsorption strength under strain. Atomically, H atoms adsorbed at Co bridge sites (H1, H2 and H1') undergo H-Co bond length change on surface straining (Table 1). These H atoms bind with 2 Co atoms. When the 2 Co atoms get apart/closer as a result of

strain applying, the corresponding H-Co bond length increases/decreases. To better understand the trend of ΔG_H variation as shown in Fig. 2, we plot in Fig. 3(a) the percentage change of bond length between adsorbed hydrogen and CoP surface atoms (either Co or P, Table 1) with which hydrogen bind.

Table 1. Bond length in Å at H adsorption under strain for both (111) and (101) surfaces. H1 to H4 are hydrogen atoms on (111) while H1' is on (101).

Strain		-5%	0	+5%
Bond length	H1(Co8, Co12)	1.643, 1.641	1.674, 1.682	1.709, 1.740
	H2(Co4, Co8)	1.646, 1.622	1.646, 1.639	1.663, 1.658
	H3(P24)	1.456	1.448	1.444
	H4(Co12)	1.481	1.480	1.480
	H1'(Co12', Co24')	1.684	1.720	1.754

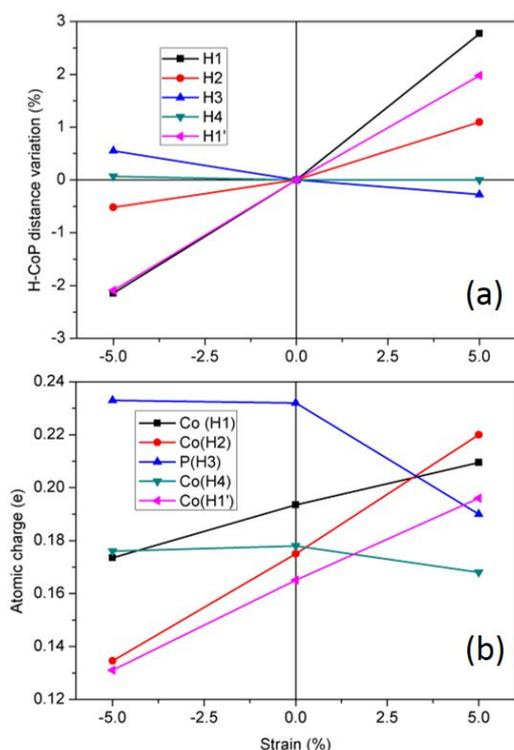


Fig 3. (a) Percentage change of H-CoP surface bond length at -5%, 0 and +5% strain (see text). (b) Atomic charge variation of CoP surface atoms with hydrogen adsorption under strain. The corresponding adsorbed hydrogen atoms are shown in parentheses.

As expected, hydrogen adsorbed at Co bridge sites (H1, H2 and H1') has the largest variation of bond length under strain (Fig. 3. (a)). On the other hand, for H3 and H4 on the (111) surface, these H atoms only form chemical bonds with 1 surface atom, with much less change of bond length between H and surface atoms under strain (Fig. 3(a)). One would expect decreased H binding strength for increased H-Co bond lengths. This is indeed the case for H1 and H1', for which the corresponding H-Co bond lengths are significantly affected by strain (Fig. 3(a)). These H atoms exhibit increased ΔG_H at expansive strain (Fig. 2). However, although H-Co bond lengths for H2 also increase

when surface expands (Fig. 3(a)), ΔG_H decreases for positive strains (Fig. 2). Thus, atomic effects alone are not able to cover the strain effects on hydrogen adsorption for all hydrogen coverages.

Electronically, surface straining also leads to variation of surface Co-P bond lengths, which in turn, results in variation of charge transfer between Co and P atoms. As Fig. 3(b) shows, Co atoms (Co4 and Co8) at H2 adsorption are most prone to applied strain. The (averaged) Co atom charge increases by almost 0.1 e from -5% to +5% strain. This indicates Co4 and Co8 become significantly more positively charged on surface expansion. Compared with H1 and H1', H-Co bond lengths of H2 changes less under strain (Fig. 3(a)). On the other hand, Co atom charge at H2 adsorption changes more under strain (Fig. 3(b)). Consequently, the electronic effects surpass the atomic effects for H2. Under expansive strain, more positively charged Co4 and Co8 interact with adsorbed H2 more strongly, leading to decreased ΔG_H (Fig. 2). For H3 and H4, both the atomic effects (Fig. 3(a)) and electronic effects (Fig. 3(b)) are in general small, leading to small change of ΔG_H under strain (Fig. 2).

The d-band model has been widely used to understand strain effects on noble-metal-based catalysts, where the variation of ΔG_H is correlated with the shift of the center of metal d bands¹⁵. To compare with strain effects on metal, we have studied electronic structure of CoP (111) surface under strain denoted by the d-band projected density of states (PDOS) of the adsorption sites (Fig. 3). For both H1 and H2, d-band PDOS appears to shift up when surface is expanded (more positive strain). Quantitatively, d-band centre for H1 adsorption site is calculated to be -2.28, -2.16 and -2.03 eV at a strain of -5%, 0 and +5%, respectively. For H2 adsorption site, d-band centre is -2.54, -2.42 and -2.26 eV at these strains. Comparing Fig. 3 (b) and Fig. 4 one notes that charge transfer between Co and P determines the location of d-band center. At positive strain, Co atoms become more positively charged. The reduction of electron occupation causes a up-shift of d-band (Fig. 4). However, the d-band center model only manifests the electronic effects. As discussed above, the atomic effects may surpass the electronic effects. As such, the d-band center model can't be used alone to explain the strain effects.

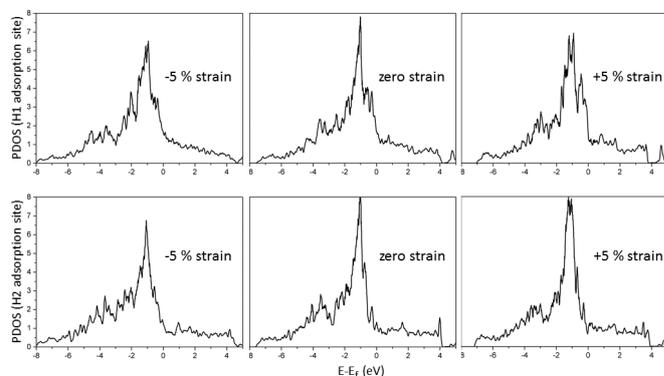


Fig. 4 Evolution of d-band PDOS (arbitrary unit) under strain for both H1 adsorption site (Co8 and Co12, the upper part) and H2 adsorption site (Co4 and Co8, the lower part) of CoP (111) surface.

In summary, we have investigated the possibility of enhancing hydrogen evolution over CoP by means of surface straining. CoP is intrinsically highly active for HER as a result of the small ΔG_H . Based on DFT calculations we show that applying surface strain is very promising to further improve CoP's catalytic properties by tuning ΔG_H . For both the already active (111) and (101) surfaces, tensile strain appears to bring ΔG_H even closer to zero. Especially, for the (101) surface a moderate tensile strain of about 3% is predicted to render a zero ΔG_H . We disclose that both atomic variation and electronic variation affect ΔG_H under strain. For H1 on (111) surface and H1' on (101) surface, variation of hydrogen adsorption energy is majorly caused by enlarged Co-Co bond lengths under tensile strain, which in turn results in an increase of H-Co bond lengths. For H2 on (111) surface, the electronic effects surpass the atomic effects. The interplay between atomic and electronic effects yields complex variation of ΔG_H under strain, for different hydrogen coverages as shown in Fig. 2. It is to be noted that the details of DFT calculation such as unit cell size and used functional may slightly change calculated value of ΔG_H . However, we think the disclosed trend in ΔG_H variation under strain should be robust, as we have disclosed the atomic and electronic origins for ΔG_H changes. Considering the active research efforts being conducted for catalysts strain engineering and the recent success on CoO¹⁰ and NiP⁸, we expect the present work to serve as a solid theoretical guidance for future experimental strain manipulation on CoP.

Conflicts of interest

There are no conflicts to declare.

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