Ab Initio Investigation of Water Adsorption and Hydrogen Evolution on Co\textsubscript{9}S\textsubscript{8} and Co\textsubscript{3}S\textsubscript{4} Low-Index Surfaces

Marco Fronzi,*\textsuperscript{a},† M. Hussein N. Assadi,*§ and Michael J. Ford*\textsuperscript{a},‡

\textsuperscript{a}International Research Centre for Renewable Energy, State Key Laboratory of Multiphase Flow in Power Engineering, Xi’an Jiaotong University, Xi’an 710049, Shaanxi, China
\textsuperscript{b}School of Mathematical and Physical Sciences, University of Technology, P.O. Box 123, Broadway, Sydney, New South Wales 2007, Australia
\textsuperscript{c}Center for Computational Sciences, University of Tsukuba, Tsukuba, Ibaraki 305-8577, Japan

\textbf{ABSTRACT:} We used density functional theory approach, with the inclusion of a semiempirical dispersion potential to take into account van der Waals interactions, to investigate the water adsorption and dissociation on cobalt sulfide Co\textsubscript{9}S\textsubscript{8} and Co\textsubscript{3}S\textsubscript{4}(100) surfaces. We first determined the nanocrystal shape and selected representative surfaces to analyze. We then calculated water adsorption and dissociation energies, as well as hydrogen and oxygen adsorption energies, and we found that sulfur vacancies on Co\textsubscript{9}S\textsubscript{8}(100) surface enhance the catalytic activity toward water dissociation by raising the energy level of unhybridized Co 3d states closer to the Fermi level. Sulfur vacancies, however, do not have a significant impact on the energetics of Co\textsubscript{3}S\textsubscript{4}(100) surface.

\section{INTRODUCTION}

Due to the depletion of carbon fossil fuel together with the environmental damage resulting from undesired emission from their combustion, finding new energy carriers is becoming a necessity.\textsuperscript{1,2} Hydrogen represents a clean and renewable alternative energy carrier and can be used to replace to conventional and less environmental friendly fuels.

The production of molecular hydrogen can be obtained through water splitting that currently represents the most energetically favorable process, which however consists of only 4% of the total production due to the inefficiency of the present catalysts.\textsuperscript{3–7} Another viable way is represented by thermal water splitting, where the necessary temperatures can be typically generated by either concentrating the sunlight or using waste heat from advanced nuclear reactors. However, this process suffers from a low efficiency due to the high temperatures, typically between 800 and 2500 K, necessary to obtain a complete reaction cycle.\textsuperscript{8}

Recent analysis reports transition-metal sulfides (TM–S) that have interesting catalytic properties for several chemical processes, showing a pronounced selectivity, which is a fundamental property of a good catalyst. At the moment, the main technological application of TM–S concerns the process of hydrogen desulfurization. However, the primary step of the reaction shares hydrogen as a surface intermediate with the hydrogen evolution reaction (HER) and thus has a common elementary step, suggesting that the same catalyst should, in principle, perform well for both hydrogenation and hydrogen evolution reaction (HER).\textsuperscript{9}

A particular class of interesting TM–S compounds are cobalt sulfides crystallized in pentlandite Co\textsubscript{9}S\textsubscript{8} and linnaeite Co\textsubscript{3}S\textsubscript{4} forms.\textsuperscript{10,11} Recent studies show that Co\textsubscript{9}S\textsubscript{8} and Co\textsubscript{3}S\textsubscript{4} have catalytic activity and can be used in hydrogen and oxygen evolution reactions, where Co is a catalytic center.\textsuperscript{12–15,17}

These works also suggest that a specific micro and nano-structuring of cobalt sulfide may significantly increase its catalytic performance, as also known for CoS\textsubscript{2}.\textsuperscript{18} Pan et al. analyzed Co\textsubscript{9}S\textsubscript{8} and Co\textsubscript{3}S\textsubscript{4} for HER, and they experimentally observed that spherelike Co\textsubscript{3}S\textsubscript{4} exhibits better electrocatalytic activity than the dandelion-like Co\textsubscript{9}S\textsubscript{8} for HER.\textsuperscript{15} Sidik et al. carried out theoretical investigations on (202) Co\textsubscript{9}S\textsubscript{8} surface to analyze oxygen evolution reaction. They calculated the strength of the interaction between the surfaces and water, molecular oxygen, and hydroxyl radical, and they predicted non-negligible activity for water oxidation, suggesting a possible use of this crystal surface for water splitting.\textsuperscript{12} However, although surface sulfur vacancies are often crucial in many catalytic processes and they may significantly affect the energetics for of many catalytic processes, their role in the catalytic activity of cobalt sulfides is not yet clear.\textsuperscript{19,20}

The mentioned works suggest a potential use of Co\textsubscript{9}S\textsubscript{8} and Co\textsubscript{3}S\textsubscript{4} in water splitting: however, an investigation of thermal driven processes toward H\textsubscript{2} production has not been carried out yet. Therefore, a study of the energetics of water...
adsorption and dissociation on stoichiometric and reduced cobalt sulfides, as well as hydrogen and oxygen adsorption, is crucial to understand the potential application of these crystals in technological applications. In particular, a detailed analysis of the adsorption energies of water and its fragments for a given surface is fundamental, since they provide excellent descriptors of the activation energy for water dissociation on that surface toward water splitting. Here, we present a comparative investigation of Co₉S₈ and Co₃S₄ with a focus on the role of sulfur vacancies in water dissociation and hydrogen evolution reaction. We apply density functional theory (DFT) calculations to analyze water, hydroxyl group, atomic oxygen, and atomic hydrogen adsorption energies in view of having a deeper understanding of the thermodynamics of the elementary processes that lead to HER. We compute electronic structure analysis and investigate the relation between stoichiometry of cobalt sulfides and catalytic properties for HER.

**CALCULATION METHODS**

The calculations presented in this work are performed by using a density functional theory approach, within the generalized gradient approximation (GGA) using the Perdew–Burke–Ernzerhof approach for the exchange−correlation term, and to describe correctly van der Waals interactions arising from the interaction of electric dipole moments, we include a correction as implemented in the method of Grimme. We use periodic boundary conditions and a plane wave basis set as implemented in VASP code, wherein the core−valence interaction is described by projector augmented wave and the convergence criteria for the energy and forces are 10−5 eV and 10−2 eV/Å, respectively. The energy barriers and transition states for water dissociation and hydrogen formation are located by using the climbing image nudged elastic band (NEB) method, which is an efficient method for searching the minimum energy path connecting the given initial and final states. Although we report both pure GGA and GGA + vdW results for readers’ reference, we develop our discussion on the basis of the GGA + vdW results as this functional encompasses more of the systems’ physics.

**RESULTS**

**Geometry and Energetics.** Among cobalt sulfide compounds, the Co₉S₈ and Co₃S₄ structure materials crystallize in a pentlandite Fm3m structure and linnaeite Fd3m, with lattice constants of 9.92 and 9.40 Å, respectively. Our calculated lattice constants and formation energies are 9.80 Å and −0.69 eV for Co₉S₈ and 9.29 Å and −0.75 eV for (Co₃S₄), in line with values reported in the literature. In both structures, Co atoms occupy octahedral (Co₉S₈) and tetrahedral (Co₃S₄) coordination, with a ratio of Co₉S₈/Co₃S₄ = 1:8 in Co₉S₈ and Co₉S₈/Co₃S₄ = 2:1 in Co₃S₄. Both crystals have Co−Co bonds with interatomic distances equal to or less than those in Co metal. The calculated Co₉S₈ and Co₃S₄ distances are 2.33 and 2.09−2.19 Å in Co₉S₈, whereas in Co₃S₄, Co₉S₈−S, 2.00 Å and Co₃S₄−S, 2.31 Å. Due to the symmetry of each surface, there is significant geometrical reconstruction of the three surfaces from the bulk cut, with a bond length change up to ∼0.1 Å, as reported in other works. On the basis of crystallographic planes, many different surface compositions are possible for the pentlandite structure so we analyze a number of terminations for each orientation and report here the energetics of representative ones (see Table 1).

### Table 1. Surface Energies of the Co₉S₈ and Co₃S₄(100), (110), and (111) Surfaces

| Surface | Energy (eV/Å²) |
|---------|---------------|
| (100)   | 0.20          |
| (110)   | 0.30          |
| (111)   | 0.19          |
| (100)   | 0.13          |
| (110)   | 0.16          |
| (111)   | 0.32          |

We calculate the surface energy for each surface termination, which corresponds to the energy required to create a surface from the bulk structure, as follows

\[ E_{surf} = \frac{1}{2A} \left( E_{slab} - \frac{M}{N} (E_{bulk}) \right) \]

where \( A \) is the surface area, \( E_{slab} \) is the free energy of the slab used in the calculations, and \( E_{bulk} \) is the free energy of the bulk. \( M \) and \( N \) are the number of atoms in each slab and in the bulk, respectively.

By minimizing the total surface energy of a hypothetical particle of a given volume with respect to the energy of each calculated surface termination, we determine the nanoparticle geometry, as in the Wulff construction method, and show the predicted nanoparticles in Figure 1. The resulting particle shapes show that, in thermodynamic conditions, the surfaces exposed to the environment are (100) and (111) for Co₉S₈ and (100) and (110) for Co₃S₄. However, here, we focus our analysis of catalytic properties on the (100) surface, since it presents similar geometrical structure in both materials that enable us to highlight the intrinsic difference in the electronic structure and potential catalytic activity.

Both surfaces contain a mixture of Co and S sites; however, the main structural differences between Co₉S₈(100) and Co₃S₄(100) are the Co/S ratio, which is 1:4 in Co₉S₈ and 1:2 in Co₃S₄(100), and that, although Co₉S₈ only exposes...
Co\textsuperscript{oct}, Co\textsubscript{9}S\textsubscript{8} exposes a mixture of Co\textsuperscript{oct} and Co\textsuperscript{tetra} with dominance of Co\textsuperscript{tetra}, as shown in Figure 2.

Figure 2. Schematic representation of Co\textsubscript{9}S\textsubscript{8}(100) (top) and Co\textsubscript{3}S\textsubscript{4}(100) (bottom) terminations. Here, blue and yellow spheres represent cobalt and sulfur atoms, respectively. The outermost layers of the cleaved surfaces contain both Co and S ions. In the picture, Co\textsuperscript{oct} and Co\textsuperscript{tetra} indicate Co ions in tetrahedral and octahedral coordination, respectively. Unit cell is delimited by a black line.

Adsorption Energies and Geometries. Although in realistic conditions water splitting and HER can present several intermediate phases, we are interested in analyzing the fundamental steps of the following total reaction

\[
\text{H}_2\text{O} \rightarrow \text{H}_2 + \frac{1}{2}\text{O}_2
\]  

(2)

During thermal decomposition, the first step of eq 2 has been described in terms of water dissociation form adsorbed H (H\textsubscript{2}O \rightarrow H\textsubscript{ad} + OH\textsubscript{ad}). Then, eventually, two adsorbed surface hydrogens next to each other react to form H\textsubscript{2} (H\textsubscript{ad} + H\textsubscript{ad} \rightarrow H\textsubscript{2}).\textsuperscript{37–39} The direct thermal splitting of water will require temperatures of \(\sim 2500 \) K, which makes its practical application very challenging. The fundamental limitation of the thermal splitting of liquid water is the fact that the ground state of oxygen is in a triplet spin configuration, whereas the ground state of water is in a singlet spin configuration. Therefore, breaking a water molecule requires a substantial quantity of energy to excite the molecule to a higher spin state before the dissociation. However, by exploiting the catalytic properties of some surfaces, water dissociation and molecular hydrogen formation can be achieved at temperatures below \(\sim 1300 \) K.\textsuperscript{40}

In view of this, we can identify the required necessary characteristics of a good catalyst as follows: it must be able to dissociate water and attract protons and at the same time still be able to desorb H\textsubscript{2}. Experimentally, HER activity can be correlated to calculated hydrogen adsorption energies from density functional theory (DFT), where high activity corresponds to low Gibbs free energy of hydrogen adsorption (\(\Delta G_{\text{H}}\)).\textsuperscript{42,43} This is because a lower \(\Delta G_{\text{H}}\) results in a strong binding of the atomic hydrogen and prevents desorption of H\textsubscript{2}, whereas higher \(\Delta G_{\text{H}}\) prevents the binding of atomic hydrogen on the catalyst surfaces. Accordingly, \(\Delta G_{\text{H}}\) is considered as a good descriptor of HER activity and good catalysts are expected to have very small value of \(\Delta G_{\text{H}}\). On the other hand, to have an efficient reaction, water must be strongly adsorbed and easily split on the surface. Therefore, the total reaction should have a high water dissociation energy and at the same time, low hydrogen adsorption energy. We calculate the zero point energy upon adsorption to be \(\sim 0.4 \) eV H and \(\sim 0.1 \) eV for H\textsubscript{2}O, OH\textsubscript{ad}, and O\textsubscript{ad}, calculated considering the vibrational frequencies of the species in gas phase and those of the outermost surface atomic layer. Although this contribution to the total energy is significant, it is very similar in the two systems and therefore it will not give considerable additional information to this comparative analysis. Also, we adopt the approach used by Muhich et al. They suggest using a “benchmark” material to predict the H\textsubscript{2} production capacities of given materials,\textsuperscript{44} which is chosen as a standard against which to compare reduction enthalpies of candidate materials within a similar thermal water splitting class (i.e., a similar reaction mechanism). They assume that within a thermal water splitting reaction class, the reduction entropy of the benchmark materials is approximately the same. Therefore, when comparing the relative equilibrium extents of reduction between the two materials, the entropic terms cancel. According to these considerations, here, we approximate \(\Delta G \cong \Delta E\).

We calculate adsorption energies values for H\textsubscript{2}O, OH, O, and H adsorption energies, as follows

\[
E_{\text{ads}} = \frac{1}{N}[E_{\text{surf+mol}} - (E_{\text{surf}} + E_{\text{mol}})]
\]  

(3)

where \(E_{\text{surf+mol}}\), \(E_{\text{surf}}\), and \(E_{\text{mol}}\) are the energies of the molecule–surface system, the surface, and molecule in gas phase, respectively whereas \(N\) is the number of molecules adsorbed per supercell.

We obtain a minimum energy configuration for stoichiometric surfaces when water adsorbs on the top of Co atom in a flat configuration with the hydrogen atoms stretched toward sulfur sites, whereas OH adsorbs at Co site in a planar configuration, as schematically depicted in Figure 3. Atomic oxygen and hydrogen adsorb favorably at cobalt and sulfur sites, respectively. Upon vacancy formation, water adsors on the top of the vacancy with the hydrogen pointing upward, whereas hydroxyl group and atomic oxygen fill the vacancy, as depicted in Figure 4. Representative atomic distances upon adsorption on stoichiometric and reduced surfaces are listed in Table 4.

Now let us examine how \(V_{\text{S}}\) alters the adsorption energies on these two surfaces based on adsorption energies reported in Tables 2 and 3. We calculated the energy gain from a single water molecule dissociation, from the difference between OH–H adsorption, schematically represented in Figure 5, and the water molecule in gas phase. We obtain energy values of \(\sim 1.02\) and \(\sim 0.98\) eV on Co\textsubscript{9}S\textsubscript{8} and Co\textsubscript{3}S\textsubscript{4}, respectively, indicating a very similar trend of the stoichiometric surfaces. On the other...
hand, when the same value is calculated for the reduced surfaces, we obtain an energy of $-0.91 \text{ eV}$ on Co$_9$S$_8$ and $-0.20 \text{ eV}$ on Co$_3$S$_4$, suggesting a significant difference of the energy trend of the reduced surfaces. The same conclusion can be reached also if we consider the energy balance of water dissociation reaction calculated from the separate H$_2$O, OH, and H adsorption energies, which gives an additional insight on the surface properties, since it takes into account the surface–adsorbate interaction strength of the individual species. The energy gain from splitting one H$_2$O molecule is 2.71 eV for stoichiometric Co$_9$S$_8$ and 2.44 eV for stoichiometric Co$_3$S$_4$. Since these values are comparable to each other, the overall performance is then determined by the H absorption energy; the smaller it is, the better an H generator the surface is. Consequently, stoichiometric Co$_3$S$_4$ with H adsorption energy 0.23 eV smaller than that of Co$_9$S$_8$ is predicted to have superior HER performance. This prediction is indeed in agreement with previous calculations done by Pan.

Figure 3. Schematic representation of water (a, c) and hydroxyl group (b, d) adsorption onto Co$_9$S$_8$(100) (top) and Co$_3$S$_4$(100) (bottom) surfaces. Here, blue, yellow, red, and white spheres represent, respectively, cobalt, sulfur, oxygen, and hydrogen atoms.

Figure 4. Schematic representation of water (a, c) and hydroxyl group (b, d) adsorption onto Co$_9$S$_8$(100) (top) and Co$_3$S$_4$(100) bottom surfaces upon sulfur vacancy formation. Here, blue, yellow, red, and white spheres represent, respectively, cobalt, sulfur, oxygen, and hydrogen atoms.
et al.\textsuperscript{15} The introduction of VS, on the other hand, significantly increases the energy gain from water dissociation on Co\textsubscript{9}S\textsubscript{8} surface compared to that on Co\textsubscript{3}S\textsubscript{4} surface. In this case, the energy gain is 6.25 eV for Co\textsubscript{9}S\textsubscript{8} and 4.94 eV for Co\textsubscript{3}S\textsubscript{4}. As a result, the energy gain upon water dissociation would be significantly higher on reduced Co\textsubscript{9}S\textsubscript{8} surface. Nonetheless, one should note that introduction of VS also strengthens the adsorption hydrogen by lowering the H adsorption energy from $-2.22$ eV on stoichiometric Co\textsubscript{9}S\textsubscript{8} surface to $-3.00$ eV on reduced Co\textsubscript{9}S\textsubscript{8} surface. However, the energy gain in the first step of the reaction, that is water dissociations, would probably offset the enhanced H adsorption. As a result, we expect that the introduction of V\textsubscript{s} makes Co\textsubscript{9}S\textsubscript{8} an efficient catalyst.

On the other hand, upon water dissociation, OH group is adsorbed favorably at VS, filling the gap left from sulfur atom, with a strong adsorption energy of $-4.24$ and $-3.34$ eV at the vacancy site. The high adsorption energies suggest a possible poisoning mechanism that will cancel the effect of the vacancy on the reaction energy balance. However, we calculated that hydrogen dissociation from OH will leave an oxygen atom trapped at the sulfur site with energies of $-2.81$ and $-2.16$ eV on Co\textsubscript{9}S\textsubscript{8} and Co\textsubscript{3}S\textsubscript{4}, respectively. As summarized in eq 2, we expect oxygen atoms to react to form molecular oxygen. Upon O\textsubscript{2} formation, we calculated a reduction of $\sim 1$ eV when the trapped oxygen reacts to form O\textsubscript{2}. Considering that this is a natural path of the total reaction under operating conditions, the energy values calculated for O\textsubscript{2} desorption from V\textsubscript{s} suggest

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure5.png}
\caption{Schematic representation of hydrogen and hydroxyl group adsorption upon H\textsubscript{2}O splitting, onto (a) stoichiometric and (b) reduced Co\textsubscript{9}S\textsubscript{8}(100) and (c) stoichiometric and (d) reduced Co\textsubscript{3}S\textsubscript{4}(100) surfaces. Here, blue, yellow, red, and white spheres represent respectively cobalt, sulfur, oxygen, and hydrogen atoms.
}
\end{figure}

\begin{table}[h]
\centering
\small
\begin{tabular}{|c|c|c|}
\hline
surface--adsorbate & GGA & vdW \\
\hline
(100)--H & $-2.16$ & $-2.22$ \\
(100)--O & $-0.95$ & $-1.08$ \\
(100)--OH & $-2.04$ & $-2.15$ \\
(100)--O--H & $-1.24$ & $-1.35$ \\
(100)--H\textsubscript{2}O & $-0.32$ & $-0.52$ \\
(100)--OH--H & $-0.99$ & $-1.02$ \\
(100)--V\textsubscript{s}--H & $-2.92$ & $-3.00$ \\
(100)--V\textsubscript{s}--O & $-2.78$ & $-2.81$ \\
(100)--V\textsubscript{s}--OH & $-4.12$ & $-4.24$ \\
(100)--V\textsubscript{s}--OH & $-3.32$ & $-3.40$ \\
(100)--V\textsubscript{s}--H\textsubscript{2}O & $-0.51$ & $-0.80$ \\
(100)--V\textsubscript{s}--OH--H & $-0.80$ & $-0.91$ \\
\hline
\end{tabular}
\caption{H\textsubscript{2}O, OH, O, and H Adsorption Energies Calculated for Stoichiometric and Reduced Co\textsubscript{9}S\textsubscript{8}(100) Surfaces\textsuperscript{a}
}
\end{table}

\begin{table}[h]
\centering
\small
\begin{tabular}{|c|c|c|}
\hline
surface--adsorbate & GGA & vdW \\
\hline
(100)--H & $-1.92$ & $-1.99$ \\
(100)--O & $-0.89$ & $-0.95$ \\
(100)--OH & $-2.18$ & $-2.29$ \\
(100)--O--H & $-0.70$ & $-1.03$ \\
(100)--H\textsubscript{2}O & $-0.34$ & $-0.50$ \\
(100)--OH--H & $-0.96$ & $-0.98$ \\
(100)--V\textsubscript{s}--H & $-1.68$ & $-1.74$ \\
(100)--V\textsubscript{s}--O & $-2.07$ & $-2.16$ \\
(100)--V\textsubscript{s}--OH & $-3.25$ & $-3.34$ \\
(100)--V\textsubscript{s}--OH & $-1.85$ & $-1.90$ \\
(100)--V\textsubscript{s}--H\textsubscript{2}O & $-0.38$ & $-0.56$ \\
(100)--V\textsubscript{s}--OH--H & $-0.14$ & $-0.20$ \\
\hline
\end{tabular}
\caption{H\textsubscript{2}O, OH, O, and H Adsorption Energies Calculated for Stoichiometric and Reduced Co\textsubscript{3}S\textsubscript{4}(100) Surfaces\textsuperscript{a}
}
\end{table}

\textsuperscript{a}Energies are calculated with respect to the species in gas phase.
that the possible poisoning effect strongly depends on the operating temperature of the catalyst, which should ideally allow molecular oxygen desorption from the sulfur vacancy site.

To estimate the vacancy concentration and real stoichiometry of the surface in thermodynamic conditions, we calculated the vacancy formation energy as follows

$$E_{\text{vac}} = (E_{\text{surf-vac}} + E_{\text{atom}}) - E_{\text{surf}}$$  (4)

If calculated with respect to the atomic sulfur atom, the cost to create a vacancy is $E_{\text{Co}_9\text{S}_8} = 5.07$ eV and in $E_{\text{Co}_3\text{S}_4}$ is 4.43 eV, whereas the same value calculated with respect to the sulfur $S_8$ drops to 2.65 eV in $E_{\text{Co}_9\text{S}_8}$ and 2.01 eV in $E_{\text{Co}_3\text{S}_4}$, suggesting that in sulfur-rich conditions at operating temperature, the concentration of vacancies is relatively low.

However, the chemical potential of sulfur, controlled through temperature and partial pressure during synthesis, determines the abundance of sulfur vacancy at the surface. To have an insight into the sulfur vacancy formation and stability, we use the energy values calculated using DFT within the ab initio atomistic thermodynamics framework, as reported in the literature.

$$\gamma(p, T) = \frac{1}{2A} \left[ G - \sum_i N \mu_i(p, T) \right]$$  (5)

where $G$ is the surface energy of the slab with surface area $A$ and the factor $\frac{1}{2}$ is due to the presence of two surfaces, one on each side of the slab. $\mu_i(p, T)$ is the pressure and temperature-dependent chemical potential of the various species $i$ present in the system; in this case, $i = \text{Co}$ and $\text{S}$. $N_i$ is the total number of atoms in the component $i$ of the system. Figure 6 shows the surface energies of reduced and stoichiometric $E_{\text{Co}_9\text{S}_8}$ and $E_{\text{Co}_3\text{S}_4}$. We find that for values of $\mu_S \leq -6.78$ and $-9.64$ eV, the reduced surfaces of $E_{\text{Co}_9\text{S}_8}$ and $E_{\text{Co}_3\text{S}_4}$ become stable if compared with the stoichiometric ones, suggesting a possible viable way to create conditions for the fabrication of reduced structures for both crystals. Using the definition of universal chemical potential for sulfur vapor formulated by Jackson et al., we converted, for a given partial pressure of sulfur in gas conditions, our energy values into temperature, and we found the transition between the stoichiometric and reduced surface to occur at $\sim 360$ and $\sim 410$ K at $p = 1$ atm, for $E_{\text{Co}_9\text{S}_8}$ and $E_{\text{Co}_3\text{S}_4}$, respectively, as shown in Figure 6.

Table 4. Atomic Distances (in Å) upon Molecular and Atomic Adsorption on the Co$_9$S$_8$(100) and Co$_3$S$_4$(100) Surfaces

| surf.       | H$_2$O–Co | OH–Co | O–Co | H–S |
|-------------|-----------|-------|------|-----|
| Co$_9$S$_8$ | 2.23      | 1.90  | 1.68 | 1.36|
| Co$_9$S$_8$–V$\_S$ | 2.13      | 2.02  | 1.83 | 1.64|
| Co$_3$S$_4$ | 2.16      | 1.87  | 1.56 | 1.41|
| Co$_3$S$_4$–V$\_S$ | 2.18      | 2.13  | 1.91 | 1.82|

*a For water and hydroxyl group, we report the distance from oxygen to surface cobalt atoms.

Figure 6. Calculated surface free energy of stoichiometric and reduced Co$_9$S$_8$(100) and Co$_3$S$_4$(100) surfaces as a function of the sulfur chemical potential $\mu_S$. In the additional bars, the chemical potential of sulfur has been converted to temperature at two different partial pressures of the sulfur, 1 and 0.01 atm, respectively.

Figure 7. Calculated activation energies for H$_2$O dissociation into OH and H onto (a) pristine and defective Co$_9$S$_8$, (b) pristine and defective Co$_3$S$_4$, and (c) H$_2$ formation from H–H onto Co$_9$S$_8$ and Co$_3$S$_4$. 

Table 4. Atomic Distances (in Å) upon Molecular and Atomic Adsorption on the Co$_9$S$_8$(100) and Co$_3$S$_4$(100) Surfaces

| surf.       | H$_2$O–Co | OH–Co | O–Co | H–S |
|-------------|-----------|-------|------|-----|
| Co$_9$S$_8$ | 2.23      | 1.90  | 1.68 | 1.36|
| Co$_9$S$_8$–V$\_S$ | 2.13      | 2.02  | 1.83 | 1.64|
| Co$_3$S$_4$ | 2.16      | 1.87  | 1.56 | 1.41|
| Co$_3$S$_4$–V$\_S$ | 2.18      | 2.13  | 1.91 | 1.82|

*a For water and hydroxyl group, we report the distance from oxygen to surface cobalt atoms.
To have an insight into the reaction kinetics, we calculate the activation energies of water dissociation and molecular hydrogen formation by employing NEB method and schematically report the results in Figure 2. Interestingly, we found that the formation of molecular hydrogen is exothermic and that its activation energy is lower at Co$_9$S$_8$(100) than at Co$_3$S$_4$(100). The energy reaction profile shows how both water splitting and hydrogen formation are exothermic reaction, with the exception of water dissociation onto...
defective \( \text{Co}_3\text{S}_4 \)\((100)\). However, since the total reaction indicated in eq 2 is endothermic, an intermediate step is supposed to be highly endothermic. We found one possible endothermic step to be OH dissociation, with an energy value of \( \sim0.80\) eV in Co\(\!\!\!\!\!\!\!\!\_\text{p} \) and \( \sim1.80\) eV in Co\(\!\!\!\!\!\!\!\!\_\text{d} \), as indicated by the energy values reported in Tables 2 and 3. Our results indicates that vacancy assists the reactions by decreasing the barriers in both crystals; however, hydrogen formation is kinetically favored on Co\(\!\!\!\!\!\!\!\!\_\text{d} \) (Table 4).

Figure 9. (a, b) pDOS of the Co\(\!\!\!\!\!\!\!\!\_\text{d} \) stoichiometric surfaces. (c) COOP analysis of the surface Co–S bond.
Electronic Structure. Here, we report the analysis of the electronic structure of the two surfaces in their stoichiometric and reduced form (Figure 7). Figures 8 and 9 show the projected density of states (pDOS) of surface cobalt and sulfur atoms in the stoichiometric slabs, together with the crystal orbital overlap population (COOP) analysis. Our electronic structure calculations

Figure 10. (a, b) pDOS of the Co₉S₈(100) surfaces upon sulfur vacancy formation. In (a), low-coordinated cobalt located next to sulfur vacancy is indicated. (c) COOP analysis of the surface Co–S bond, with Co atom being low coordinated near sulfur vacancy.
show that Co₉S₈ and Co₃S₄ have similar density of state function around the Fermi level, in line with the ability of the sulfide to conduct electronic currents. Both surfaces show a pronounced Co 3d peak right below the Fermi energy and an evident hybridization with the S 3p in a broad range. COOP analysis suggests the formation of bonding states below the Fermi energy at ∼−2 eV.

Figure 11. (a, b) pDOS of the Co₃S₄(100) surfaces upon sulfur vacancy formation. In (a), low-coordinated cobalt located next to sulfur vacancy is indicated. (c) COOP analysis of the surface Co–S bond, with Co atom being low-coordinated near sulfur vacancy.
Interestingly, upon sulfur vacancy formation, \( \text{Co}_9\text{S}_8 \) and \( \text{Co}_3\text{S}_4 \) show different features (see Figures 10 and 11). We calculated the site-projected pDOS for low-coordinated cobalt atoms adjacent to the sulfur vacancy and high-coordinated cobalt atoms distant from the vacancy for both surfaces. In reduced \( \text{Co}_3\text{S}_4 \), there is no significant difference between the two on site pDOS. However, reduced \( \text{Co}_9\text{S}_8 \) shows a significant difference in the intensity of the two peaks at the Fermi energy, with the 3d states of the cobalt atoms adjacent to the vacancy showing an intensity significantly higher than that by the ones distant from the vacancy, which suggests a relation with the higher catalytic activity for water dissociation in reduced \( \text{Co}_9\text{S}_8 \).

This result is in line with some hypothesis reported in the literature that suggests a relation between high HOMO occupancy at Fermi and catalytic activity.\(^{47-49}\) Harris et al. correlated the \( t_{2g}\)-HOMO occupation, the TM–S bond covalence and the TM–S bond strength with the catalytic activity.\(^{50}\) The more electrons in a \( t_{2g}\)-HOMO, at comparable bond strength, the better is the catalytic activity. Furthermore, Smit et al. performed DFT calculations on octahedral TM–S clusters, confirming the suggested trend between the strength of interaction between the metal 3d and the S 3p electrons and the catalytic activity.\(^{51}\)

To analyze the bonding nature of Co–S, we determined the COOP by multiplying the sign of two overlapping atomic wavefunctions by the corresponding DOS, providing additional information regarding the bonding character: positive and negative values indicate bonding and antibonding interactions, respectively. Our COOP analysis suggests that for both surfaces in their stoichiometric forms, Co 3d S 3p bonding state below the Fermi energy reaches \( \sim -2 \) eV. Upon vacancy formation, we notice the presence of a nonbonding state around \( \sim -1.5 \) eV in \( \text{Co}_9\text{S}_8 \), whereas there is no significant change in \( \text{Co}_3\text{S}_4 \). The formation of a nonbonding state may suggest the presence of unhybridized d orbitals in reduced \( \text{Co}_9\text{S}_8 \) that enhance catalytic activity. This is also supported by the geometric features of the two surfaces that, upon vacancy formation, presents surface III and IV coordinate Co atoms in \( \text{Co}_9\text{S}_8 \) and IV and V coordinated Co atoms in \( \text{Co}_3\text{S}_4 \).

This result, being in line with the pDOS assumption of Smit et al. and Harris et al., suggests a possible enhanced catalytic activity of reduced \( \text{Co}_9\text{S}_8 \) with respect to its stoichiometric form, whereas the same trend is not predicted for \( \text{Co}_3\text{S}_4 \), confirming our conclusions presented in the previous section.
predict that nanostructured nonstoichiometric Co$_9$S$_8$ will show particularly active for water dissociation. Furthermore, we only in Co$_9$S$_8$. The increased water adsorption energies upon Fermi energy for the low-coordinated tetragonal Co centers. The projected density of states shows intense peaks around the Fermi level. The inclusion of dispersion potentials to the conventional Kohn–Sham DFT energy results in a decrease of the adsorption energies of ~15%. However, this effect is relatively larger in water, identifying the vdW character of the interaction. Our results suggest that nanostructured nonstoichiometric Co$_9$S$_8$ could in principle act as a low-temperature catalyst or co-catalyst for HER and that a test on nanoengineered surfaces is worthwhile.

■ APPENDIX A

In the previous section, we show the projected density of states of the two systems, comparing them. However, DFT calculations are not able to catch the d–d splitting into $e_g$ and $t_{2g}$ states, resulting in an overlap of degenerate 3d states. To have a correct description of the electronic structure, Hubbard correction should be introduced. However, at the moment, there is no unique choice of $U$ that gives a satisfactory description of both the electronic structure and the energetics of the system for molecular adsorption. Also, it is not clear if the the Hubbard correction provides a systematic improvement of molecular adsorption energies if compared to DFT. Also, self-consistent methods to determine $U$ cannot find a good agreement with experimental values. As pointed out by Da Silva et al., for similar systems, there is no unique choice of $U$ that at the same time gives a reasonable description of structural parameters, relative energies, and spectroscopic properties. However, in this section, we report the projected density of states by using DFT + $U$ ($U$(Co 3d) = 5 eV) to test if vacancy formation has the same effect on HOMO at the Fermi level.

Figure 12 shows pDOS of stoichiometric and reduced Co$_9$S$_8$ and Co$_3$S$_4$. We obtain a d–d splitting for Co$^{tet}$ of ~2 eV, in line with the experimental value. Here, HOMO occupancy at Fermi is higher in reduced than stoichiometric Co$_9$S$_8$. This effect is not seen in Co$_3$S$_4$ confirming that our conclusions drawn in Electronic Structure by using by using pure GGA–DFT are adequate and correct.

■ APPENDIX B

We performed convergence tests for the cutoff and the k-point set, as shown in Figure 13. It can be seen that convergence to within 0.1 eV is obtained for a k-point sampling in the Brillouin zone of $2 \times 2 \times 1$ compared with the $4 \times 4 \times 1$ k-point set. With regard to the plane wave cutoff energy of 500 eV, employed in all our calculations, Figure 13 shows that compared with a cut–cut of 600 eV, the total energy is converged within 0.005 eV. This setup leads to an error on the adsorption energies within 0.01 eV.

■ AUTHOR INFORMATION

Corresponding Authors
*E-mail: marco.fronzi@mail.xjtu.edu.cn (M.F.).
*E-mail: Mike.Ford@uts.edu.au (M.J.F.).

ORCID
Marco Fronzi: 0000-0001-7855-9216

Notes
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