Helping Thy Neighbor: How Cobalt Doping Alters the Electrocatalytic Properties of Hematite

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ABSTRACT: We present analysis of the indirect role of Co doping on the electrocatalytic activity of α-Fe₂O₃. Upon substitution of one of the Fe atoms in the hematite surface, we observed a promoting effect of the substitution, upon which the overpotential required for the water-splitting reaction decreased in all substitution sites investigated. The cobalt site itself, however, does not exhibit the improved properties with respect to the undoped hematite. The promoting effect results purely from the altering of the properties of the nearest Fe atoms in the hematite surface. We conclude that the overpotential is reduced upon formation of the structure resembling the O₂ molecule strongly interacting with the surface between the Co and Fe sites, and this is consistent with the catalytic activity of the surface vacancies of the hematite.

Alongside nanosstructuralization, doping of semiconductors is one of the most frequently used methods to improve their catalytic properties in the water-splitting reaction.¹ Both of these methods are crucial in a photocatalytic process, because they alter the band structure of the semiconductor and as such influence the photophysical relaxation.² This is especially important for hematite, which despite its favorable characteristics such as band gap of 1.9–2.0 eV³–⁶ corresponding to visible light wavelengths⁷ and sufficient redox potential, still offers only moderate efficiency in the water-splitting reaction.⁸ This is due to the indirect band gap, which makes the optical excitation more difficult, and the flat shape of the bands, resulting in poor electron and hole conductivity.⁹

Although single-atom doping of hematite does not significantly improve its optical properties,⁹ those single atoms still can play an important role in altering the chemical properties of the system.¹⁰,¹¹ In this case, the dopant can act as the catalyst promoter, which leads to the differences in the interactions between the reactants and the catalyst, in this instance, a semiconductor.¹²

The promoting effect of a dopant would be possible only if the substitution at a particular site was influencing the properties of the surface in a nonlocal way.¹³ This work aims to explore the nature of a cocatalytic effect of cobalt substitution in the hematite(110) surface for the water-splitting reaction.

In a classical approach, a cocatalyst provides a cooperative effect, which enhances the activity of the main catalyst in the case of a multistep or a two-site reaction.¹⁴ There, a particular step of the reaction takes place on a different site provided by the cocatalyst rather than the catalyst itself, or a single-step reaction occurs more efficiently by making use of two different sites. In both cases, the cocatalyst improves properties with respect to the main catalyst. Similarly, a catalyst promoter is defined as a substance that by itself has no or little catalytic activity in the given reaction, but its influence on the catalyst leads to a significant boost of the activity.¹⁴ While in photocatalysis this effect is typically attributed to the stabilization of the exciton by preventing the recombination, here we present evidence for a different role of the cocatalyst/promoter that does not strictly fit to the classical definitions.

Our analysis is based on the calculations performed within the density functional theory (DFT) framework as implemented in the VASP code.¹⁵,¹⁶ We have used the Perdew–Burke–Ernzerhof functional¹⁷,¹⁸ with the energy cutoff of 500 eV and the electron–ion interactions described by the projector-augmented wave method.¹⁹,²⁰ The Brillouin zone (BZ) was sampled by 3 × 2 × 1 k-points grid according to the Monkhorst–Pack scheme.²⁰

The model of the slab used in this work consisted of 5 monolayers (MLs) of the 2 × 2 unit cell of the hematite (110) surface. This surface is not the same as the frequently investigated (0001) surface,²¹–²³ but rather it follows the choice of the Bieberle–Hütt group:²⁴ upon investigation of 11 different hematite surfaces, the (110) surface with an oxygen vacancy concentration of 1.26 vacancies/nm² was found to correspond to the lowest overpotential. The atoms of the central layer were fixed at their bulk positions. We have used Hubbard U corrections of 4.3 and 5.9 for Fe and Co, respectively.¹⁰ Importantly, we have disregarded the protonegation of the surface, as our approach considers the stabilization of the reactive intermediates at different surface
sites; the protonation would need to account for that, inevitably leading to a different configuration of protons at the surface, which in turn could affect the results.

The thermodynamics of the system has been calculated by taking into account the zero point energy (ZPE) contribution, which was calculated using the finite displacement method with the displacement of 0.015 Å. As the calculations have been performed in the constant-volume conditions and do not concern dynamic systems, the energies discussed in the Letter include ZPE contributions and have a meaning of Helmholtz free energies in 0 K.

The (110) surface of hematite contains four nonequivalent Fe atoms in the unit cell, differing in the geometric position at the surface (named here “hill” and “valley” because of a change in the z-coordinate) and magnetic moment direction (”up” and “down”). These factors make them different in terms of their properties, which allows us to expect differences of the characteristics if the atoms in these positions are substituted by a heteroatom. Hence, we have calculated the properties and the reaction profiles for all these substitutions. In addition, along with the nonlocal character of the substitution effect,10 three surface Fe atoms in the second coordination sphere were also taken into consideration as the potential active sites. The models with substitution sites and Fe neighbors named FeA, FeB, and FeC are shown in Figure 1.

Figure 1. Top view of the models used in the simulations. Co sites are marked with green. Red spheres represent oxygen atoms; dark and light blue spheres are iron atoms with magnetic moment pointing up and down, respectively. The specific neighboring Fe atoms for each Co substitution are marked with letters A, B, and C.

It is generally accepted that the water splitting occurs according to the following reactions:

\[
\begin{align*}
H_2O & \rightarrow (OH^*) + H^+ + e^- \\
(OH^*) & \rightarrow (O^*) + H^+ + e^- \\
(O^*) + H_2O & \rightarrow (OOH^*) + H^+ + e^- \\
( OO H^* ) & \rightarrow O_2 + H^+ + e^- 
\end{align*}
\]

where * represents a surface site, where the reaction takes place. The determination of the overpotential of this reaction in the case when a single type of site is available at the surface is a straightforward procedure, where the transfer of 4 protons and 4 electrons is related to the \( \Delta G \) of the 2H2O \( \rightarrow \) 2H2 + O2 reaction, which amounts to 4.92 eV.25 Thus, each transfer of the proton/electron pair needs a potential of \( U = 1.23 \) V, and the overpotential is the biggest value of the \( \Delta G \) of the particular reaction step reduced by 1.23 V.

In this work, we assume a cocatalytic effect of a dopant, which means that these reactions do not necessarily need to occur on a single site and the overpotential of the overall reaction needs to be calculated differently. Thus, we have taken into account the differences in the chemical properties of particular sites, i.e., the interaction energy of the particular intermediate with those sites. The second assumption is the intermediates might easily “migrate” between the sites, and the barriers for such migrations are negligible. To justify this, it is necessary to state that the migration does not need to occur via the surface diffusion mechanism, but rather via Grotthuss mechanism of proton transfers in liquid water,26 for instance, at a particular potential the (OH*) and (O*) intermediates may coexist at different surface sites. We assume that a proton can be transferred from a distant site from (OH*) to (O*) via the Grotthuss mechanism, provided this process is thermodynamically favorable. This assumption is similar to the one made in our other work.27

This approach required all possible intermediates to be optimized at all available surface sites. Then, the cooperation between the sites was accounted for by considering the most thermodynamically stable intermediate for the calculation of the overpotential, analogous to the minimum-energy pathway. The energy profiles for those systems are shown in Figure 2.

The substitution of Co in the valley-down position yields a similarly stable (OH*) intermediate on each of the available sites. Differences vary within 0.26–0.37 eV, with the most stable site being FeC; however, the difference between the second most stable Co site is negligible (0.04 eV). The (O*) intermediate at the FeB site is characterized by a significantly lower energy (\( \Delta G = 0.76 \) eV lower than at the second most stable FeC site), and this is the only system that significantly differs in stability from others. In the next step, the most favorable site changes again, and this time the FeA site becomes the most stable, contrary to its lesser stability in previous steps. It is worth noting that if sites of only one type were available at the surface, the reaction would occur most efficiently at the FeC site, with the overpotential of \( \eta = 0.80 \) V, and as such, the multisite mechanism is slightly more beneficial for this system, reducing the overpotential to \( \eta = 0.63 \) V (see Table 1).

We have observed a similar behavior for other substitution sites. For the valley-up substitution it is the FeA site that provides the most favorable interaction with the (OH*) intermediate, and similarly to the valley-down, the optimal site for the (O*) intermediate is significantly more stable at FeB (0.97 eV more stable than at the FeA). This changes again in the next step, and the FeA becomes the favored site for the (OOH*) intermediate. In total, the overpotential required for the reaction taking place in this configuration is only \( \eta = 0.47 \) V. This configuration is characterized by the smallest overpotential among all the investigated systems; interestingly, however, the overpotential for the single-site mechanism at the FeB site amounts to \( \eta = 0.66 \) V, which is comparable to multisite mechanisms at the other substitution sites.

The hill-down substitution is characterized by the overpotential comparable to the valley-down system, which amounts to \( \eta = 0.74 \) V; however, the differences in the stability of the intermediates at different sites are much larger than in the case of the valley-down system. This suggests stronger influence of the substituting Co on the neighboring surface...
with the FeA site is very small and amounts to 0.08 eV. The step, the (OOH*) intermediate is the most stable, which was the most stable in the earlier stages, turns into the (OH*) intermediate being the most stable at the FeA site, and the (O*) intermediate is comparable to the FeB and Co sites. In contrast, the (O*) intermediate at the FeA site is significantly more stable than FeC (ΔG = 0.84 eV), FeB (ΔG = 1.11 eV), and Co (ΔG = 1.86 eV). For the (OOH*) intermediate, the FeA site, which was the most stable in the earlier stages, turns into the least stable one. The FeB site is the most stable, and the ΔG difference with the FeA site is as much as 0.96 eV. Similar to other substitutions, the multisite mechanism is beneficial with respect to the single-site one, to even a greater extent; at the optimal FeB site, the overpotential is as high as η = 0.67 V. For this reason, this configuration would also benefit from the multisite mechanism.

The most important observation, however, is the fact that the Co site is never the most favorable site in the reaction pathways—with the only exception of (OH.*) in the hill-up substitution, where the difference with respect to the Fe site is negligible. Hence, the Co substitution site does not allow for the formation of the stable intermediate at itself, which could lead to a reduction of the overpotential. This holds for all the investigated configurations, regardless of the geometrical position or magnetic moment. This allows for a conclusion that the Co site by itself should not be considered a cocatalyst in the strict sense, as it does not play a direct role in the reaction—neither by facilitation of a particular step of the reaction, nor by providing a single cooperative site to stabilize the intermediate. The cobalt substituent should rather be considered a promoter; however, this is not in the strict sense in which the promoter has little or no catalytic activity by itself. Bajdich et al.28 determined the most active surface of β-CoOOH to be able to reduce the overpotential to η = 0.48 V, which suggests that it should be considered even more active than undoped hematite.29

Instead, the doping influences the electronic structure of the Fe atoms to a varying degree, depending on the distance and orientation with respect to the substitution site. This allows many sites having different characteristics, exhibiting potentially different effect in the investigated reaction; some of them are stabilizing, some are destabilizing. This can be discussed in the example of the hill-up system. At zero potential, the system is at its initial state, with no surface intermediates present. Gradual increase of the potential leads to the formation of the (OOH*) intermediate at the Co site and then at the FeA site. Only further increase of the potential allows for the formation of that intermediate at the FeC and FeB sites, as these sites are characterized by a lesser binding energy with the intermediates.

Table 1. Overpotential Calculated with Respect to a Single-Site Mechanism at Co Site and Each Neighboring Fe Site
d

|       | Co       | FeA      | FeB      | FeC      | MEP(c) | MEP(d) |
|-------|----------|----------|----------|----------|--------|--------|
| valley down | 0.88     | 0.97     | 0.85     | 0.80     | 0.70   | 0.63   |
| valley up   | 1.16     | 1.14     | 0.66     | 1.05     | 0.47   | 0.47   |
| hill up     | 2.11     | 1.70     | 1.22     | 1.55     | 0.74   | 0.62   |
| hill up     | 1.82     | 1.15     | 1.18     | 1.00     | 0.67   | 0.67   |

“MEP values represent the multisite reaction mechanism considering the most stable intermediates for each path, analogously to minimum energy pathways. MEP(c) takes into account only closely located sites (Co substitution and neighboring Fe sites); MEP(d) considers also distant Fe sites, unaffected by the Co substitution.

![Figure 2. Energy profiles for Co substitutions at hill and valley sites with magnetic moment up and down.](https://dx.doi.org/10.1021/acs.jpclett.0c00900)
Even further increase of the potential moves the system to the state where the \((\text{O}^*)\) intermediate is formed at the \(\text{Fe}_A\) site (see Figure 3) and subsequently \(\text{Fe}_C\) at approximately 4 V.

Interestingly, at this point even a slight increase of the potential leads to the coexistence of the \((\text{O}^*)\) intermediate at the \(\text{Fe}_C\) site, \((\text{O}^*)\) intermediate at the \(\text{Fe}_A\) site, and \((\text{O}^*)\) at the \(\text{Co}\) and \(\text{Fe}_B\) site. The reaction can proceed without involving the \((\text{OOH}^*)\) intermediate at the \(\text{Fe}_A\) site, because the potential needed to form this intermediate is higher than the one needed to release the \(\text{O}_2\).

The overpotential limiting step for most of the calculated single-site pathways is the formation of \((\text{O}^*)\) intermediate. This is consistent with the observation of Zhang et al., where the same step was determined to be a limiting one for all hematite surfaces, with the exception of the \((100)\) surface. Thus, this seems to be the crucial step of the reaction, where the hematite can benefit from the optimization of the interaction with this particular intermediate.

Figure 3 shows the geometry of the \((\text{O}^*)\) intermediate at the \(\text{Fe}_A\) which is optimal for the hill-up substituted system. A strong interaction can be seen with the oxygen atom bridging the \(\text{Co}\) and \(\text{Fe}_B\) sites. The \(\text{O}−\text{O}\) bond length is \(1.36\) Å, compared to \(r = 1.21\) Å for the gas-phase \(\text{O}_2\) molecule. Additionally the \(\text{Co}−\text{O}\) and \(\text{Fe}_B−\text{O}\) distances increase to \(r = 2.01\) Å and \(r = 2.10\) Å from \(r = 1.75\) and \(1.84\) Å, respectively. The system stability increases because of the formation of the structure resembling the \(\text{O}_2\) molecule strongly interacting with the surface and is consistent with the catalytic activity of the surface vacancies of the hematite.

This observation calls for the comparison with the unsubstituted \(\text{Fe}_2\text{O}_3\) system so as to compare the stability of the particular intermediates on the \(\text{Fe}_A\), \(\text{Fe}_B\), and \(\text{Fe}_C\) sites neighboring \(\text{Co}\) substitution, as discussed above, and similar neighbors of an unsubstituted \(\text{Fe}\) atom. The mechanisms taking into account the undoped systems are shown in Figure 4 on the example of hill-down and valley-down systems. These two systems show additional stabilization of the \((\text{O}^*)\) intermediate at the \(\text{Fe}_A\) and \(\text{Fe}_B\) site neighboring the \(\text{Co}\) substitution at valley-down and hill-down, respectively.

This analysis assumes that not every valley-down or hill-down site is substituted with \(\text{Co}\), and the Grotthuss mechanism described before can also involve distant \(\text{Fe}\) sites, which are not affected by the \(\text{Co}\) substitution. All the profiles show the \(\text{Co}\) site is the least stable site for any of the involved intermediates, and undoped systems provide the most stable sites for \((\text{OH}^*)\) and \((\text{OOH}^*)\) intermediates. Both these systems show the \(\text{Fe}\) site affected by the \(\text{Co}\) substitution lead to additional stabilization of the \((\text{O}^*)\) intermediate, lowering the overpotential further, from \(\eta = 0.74\) V to \(\eta = 0.62\) V and from \(\eta = 0.70\) V to \(\eta = 0.63\) V for hill-down and valley-down substituted systems, respectively.

The lowest calculated overpotential value in this study is for the valley-up substituted system \((\eta = 0.47\text{V})\); however, it has to be noted that systems substituted in the hill and valley positions significantly differ in the binding energy of the dopant. That suggests that hill substitution would be more likely to be obtained experimentally, rather than the valley substitution. The strongest binding energy of the dopant does not coincide with the lowest overpotential, in which case the valley-up substitution would be the most preferred. This leads to the conclusion that the binding energy of the dopant, although playing an important role, cannot be the only factor responsible for altering the properties of the \(\text{Fe}\) site.

In conclusion, we have shown that the role of \(\text{Co}\) doping in decreasing the overpotential is to alter the stability of the particular intermediate at the neighboring \(\text{Fe}\) site. Although the optimal pathway never leads through the \(\text{Co}\) site, the overpotentials calculated for the systems are lower with respect to pure hematite. This effect has some characteristics of the cocatalytic or promoting effect; however, it does not strictly fit the classical definitions, where the cocatalyst enables additional active site or a promoter has little or no catalytic effect by itself. In the investigated cases, the \(\text{Co}\) substitution...
causes a modification of the neighboring sites to a varying degree, creating many sites influencing the stability of the intermediates to a different extent. This allows for making use of many sites, with reaction occurring according to the minimum-energy path.

**ASSOCIATED CONTENT**

### Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.jpcl.0c00900.

Optimized geometries of the intermediates (ZIP)

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**Notes**

The authors declare no competing financial interest.

**ACKNOWLEDGMENTS**

This work has been carried out within the M.ERANET-2 project “Multiscale Modeling and Design of Photo-Electrochemical interfaces” Grant No. 4089, for which authors gratefully acknowledge the financial support from National Centre of Science Grant nr. 2016/23/Z/ST4/04376. The simulations have been performed at Poznań Supercomputing and Networking Center, Academic Computer Centre Cyfronet in Kraków and Interdisciplinary Centre for Mathematical and Computational Modeling in Warsaw. We acknowledge PRACE for awarding us access to Beskow hosted by the PDC Centre for High Performance Computing, KTH Royal Institute of Technology, Sweden. This research was supported in part by PL-Grid Infrastructure. This article is based upon work from COST Action 18234, supported by COST (European Cooperation in Science and Technology).

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